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

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

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 25°C. 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, 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. 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. 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 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 follows: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. 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 place at 250°C in order to obtain 75% conversion of PCl_3 into PCl_5? Given: $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$; $K_P = 2\ atm^{-1}$

(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

(a) $\frac{3P.\sqrt{3.K_P}}{8}$
(b) $\frac{8P}{3\sqrt{3.K_P}}$
(c) $\frac{3\sqrt{3.K_P}}{8P}$
(d) $\frac{8}{P}.\sqrt{\frac{K_P}{3}}$

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, concentration of 'XY' is 0.7 M. 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 K_P for the 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 $\frac{w(N_2)}{w(H_2)} = \frac{14}{3}$ at $t = \frac{t_1}{3}$ and $t = \frac{t_1}{2}$. 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 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. 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 CH_3COOH and 46 g CH_3CH_2OH reacts in 5 L flask to form 44 g $CH_3COOC_2H_5$ at equilibrium. On taking 120 g CH_3COOH and 46 g 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) 0.75

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, K_P for the reaction is

(a) $\frac{13}{36}$ (b) $\frac{13}{256}$
(c) $\frac{13}{512}$ (d) $\frac{13}{128}$

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 K_P of the reaction is

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

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

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

At a pressure of 730 mm and with an initial mixture containing 8% HCl and 92% 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 $K_P = 8 \times 10^8$ atm^{-1}. If 'A' atoms are taken at 1 atm pressure, 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, 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, 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, as

(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. Reaction: $A(g) + B(g) \rightleftharpoons C(g) + D(g)$, occurs in a single step. The rate constant of forward reaction is 2.0×10^{-3} mol^{-1} 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) 5.0×10^{-4} mol^{-1} L s^{-1}
(b) 8.0×10^{-3} mol^{-1} L s^{-1}
(c) 1.25×10^{2} mol^{-1} L s^{-1}
(d) 2.0×10^{3} mol^{-1} 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) 2.5×10^{-3} 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) $\frac{100RT}{3PV}\%$ (b) $\frac{RT}{3PV}\%$

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

31. For the equilibrium: $SrCl_2 \cdot 6H_2O(s) \rightleftharpoons SrCl_2 \cdot 2H_2O(s) + 4H_2O(g)$, $K_P = 8.1 \times 10^{-7}$ atm^4 at 27°C. If 1.642L of air saturated with water vapour at 27°C is exposed to a large quantity of $SrCl_2 \cdot 2H_2O(s)$, 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 increase
(b) PCl_5 remain unchanged
(c) PCl_5 decrease
(d) Cl_2 increase

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 of that 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 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, 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: 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) $\dfrac{K_1}{K_1 + K_2 + K_3}$

(b) $\dfrac{1}{1 + K_1 + K_2}$

(c) $\dfrac{1}{K_1 + K_2 + K_3}$

(d) $\dfrac{1}{K_1 + K_2}$

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 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 1L container. Simultaneously the following two equilibria are established:

$A \rightleftharpoons B + C$; $K_C = 10^6\ M^2$ 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) $\dfrac{K_1 a - K_2 b}{K_1 + K_2}$

(b) $\dfrac{K_1 a - K_2 b}{K_1 - K_2}$

(c) $\dfrac{K_1 a - K_2 b}{K_1 K_2}$

(d) $\dfrac{K_1 a + K_2 b}{K_1 + K_2}$

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 equation:

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

The temperature at which the equilibrium constant (K_P°) becomes 1.0, is

(a) 4.8 K (b) 4800 K
(c) 480 K (d) Impossible

44. $\Delta_f G^\circ$ 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, 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, called mutarotation, stops when 64.0% of the glucose is in the β-form. Assuming that equilibrium has been attained, what is ΔG° 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

$$-\frac{d[A]}{dt} = (2.0\times10^{-3}\,s^{-1})[A] - (5.0\times10^{-4}\,s^{-1})[B] \text{ (at 27°C)}$$

$$-\frac{d[A]}{dt} = (8.0\times10^{-2}\,s^{-1})[A] - (4.0\times10^{-3}\,s^{-1})[B] \text{ (at 127°C)}$$

The enthalpy of reaction in the given temperature range is

(a) $-\dfrac{2.303\times8.314\times300\times400}{100}\cdot\log(50)\,\text{J/mol}$
(b) $-\dfrac{2.303\times8.314\times300\times400}{100}\cdot\log(5)\,\text{J/mol}$
(c) $\dfrac{2.303\times8.314\times300\times400}{100}\cdot\log(50)\,\text{J/mol}$
(d) $\dfrac{2.303\times8.314\times300\times400}{100}\cdot\log(5)\,\text{J/mol}$

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 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:

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

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) $\frac{a}{1-a} \alpha P$

(b) $\frac{a}{(1-a)^2} \alpha P$

(c) $\frac{a}{(1+a)^2} \alpha P$

(d) $\frac{a}{1+a} \alpha P$

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 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:

$A(g) + B(g) \rightleftharpoons C(g) + D(g) + E(g)$; $\Delta E^\circ = -30$ 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* and *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 20°C, 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 20°C, 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 presence of $NH_3(g)$, the extent of dissociation of $NH_4HS(s)$ 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 25°C. Which operation results in a decrease in the equilibrium vapour pressure?

(a) moving the piston downward 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. 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 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. Decreases of pressure at constant temperature or increases 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 the 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) $\log \dfrac{K_{P_2}}{K_{P_1}} = \dfrac{\Delta H}{2.303R}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$

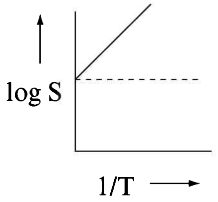
(c) $\log \dfrac{K_{C_2}}{K_{C_1}} = \dfrac{\Delta U}{2.303R}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$

(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 temperature as given by $S = A.e^{-\Delta H/RT}$, where ΔH is 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:

(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 2.0×10^{-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 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 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: $\Delta_f G^\circ[N_2O_4(g)] = 100$ kJ/mol; $\Delta_f G^\circ[NO_2(g)] = 50$ kJ/mol.

(a) K_P for the reaction is 1.0 bar.
(b) ΔG° 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 per cent of AB(g) at final equilibrium is nearly 27%.
(b) The volume per cent 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, 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 $\Delta G^\circ = -1743$ 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 1L 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:

$A(g) \rightleftharpoons B(g);\ K_1 = ?$

$B(g) \rightleftharpoons C(g);\ K_2 = 0.4$

$C(g) \rightleftharpoons A(g);\ K_3 = 0.6$

If one mole of A is taken in a closed vessel of volume 1L, 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 27°C.

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

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

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

The vapour pressure of water at 27°C is 0.04 atm.

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

(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 27°C?

(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 27°C?

(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°C 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°C, 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°C, 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. K_P for the reaction: $NH_3(g) + H_2S(g) \rightleftharpoons NH_4HS(s)$, is

(a) 6.25×10^4 atm^2

(b) 1.6×10^{-5} atm^{-2}

(c) 1.6×10^{-3} atm^{-2}

(d) 4.53×10^5 atm^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 2:3. Assume that the pre-exponential factor is the same for the forward and backward reactions.

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?

(a) e^4 (b) e^{-4}

(c) e^{10} (d) e^{-10}

19. Identify the correct statement?

(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. 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, 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

(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 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, 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 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 following

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 following

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 Column I with Column II

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

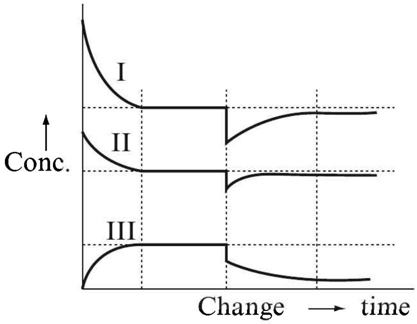
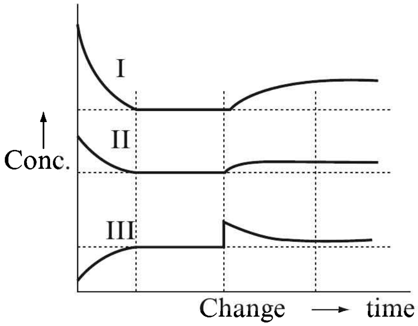
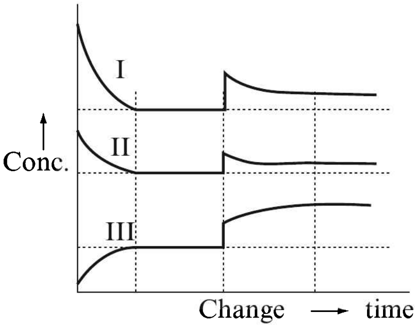
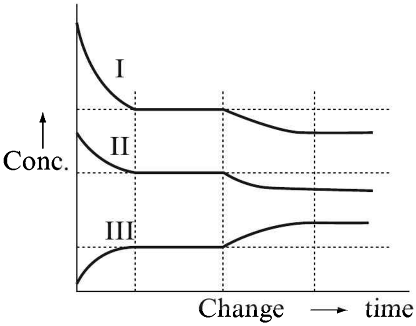
4. Match Column I with Column II

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 Column I with Column II

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 following

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: $2A(g) \rightleftharpoons 3B(g) + C(s);\ \Delta H = -\text{ve}$

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 increase in moles of $CO_2(g)$

10. Match the following

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 per cent 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 5 atm at 200°C. What pressure (in atm) will be developed when 2.085 g of this substance is vaporized at 200°C in 448 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-$N_2S_2O_3$ 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 480 ml. If the amount of ester at equilibrium is 0.6 mole in the second experiment, 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 per cent 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. Following equilibria are established on mixing two gases A_2 and C:

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

    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

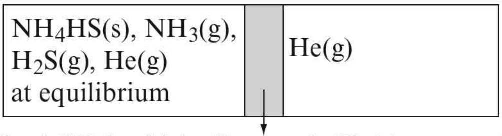
12. A 8.28 g sample of IBr(g) is placed in a container of capacity 164.2 ml and heated to 500 K. The equilibrium pressure of $Br_2(g)$ in the system is 4.0 atm. The value of K_P for the reaction:

    $2IBr(g) \rightleftharpoons I_2(g) + Br_2(g)$ is (Given: Atomic masses: 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.



Fixed SPM, which allows only He(g) to cross it

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

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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 $6.4 \times 10^{19}\ M^{-5}$. 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° and ΔS° 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. $\Delta_f G^\circ$ 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: $NiO(s) + CO(g) \rightleftharpoons Ni(s) + CO_2(g)$, $\Delta G^\circ(\text{cal/mol}^{-1}) = -5320 - 5.6T(\text{K})$. The temperature (in Kelvin) at which the gaseous mixture at equilibrium contains 400 ppm of CO, by mole, is [$\ln 10 = 2.3$, $\ln 2 = 0.7$)

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

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 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 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 following equilibrium is established:

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

At equilibrium, 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:

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

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 of 'A', 'B' and 'D' is added to a 1.0 L container.

$A(g) + B(g) \rightleftharpoons C(g);\ K_C = 2 \times 10^{10}\ M^{-1}$

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

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 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:

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

$B_2(g) \rightleftharpoons 2B(g),\ K_P = y$ 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, the value of $y{:}x$ is

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Answer Keys – Exercise II

Section A (Only one Correct)

1. (a) 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. (b)
21. (b) 22. (b) 23. (d) 24. (b) 25. (b) 26. (c) 27. (a) 28. (b) 29. (b) 30. (a)
31. (a) 32. (c) 33. (b) 34. (c) 35. (d) 36. (b) 37. (a) 38. (b) 39. (c) 40. (a)

41. (a) 42. (d) 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. (c) 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), (b), (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. (b) 3. (b) 4. (a) 5. (a) 6. (a) 7. (a) 8. (a) 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, S
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 → Q, R, T
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. (4) 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)

EXERCISE II (JEE ADVANCED)

Section A (Only one Correct)

1. Liquid ammonia ionizes to slight extent. At −50°C, its self-ionization constant, $K = [NH_4^+][NH_2^-] = 10^{-30}\ M^2$. How many amide ions are present per ml of pure liquid ammonia? ($N_A = 6 \times 10^{23}$)

(a) 10^{-15}
(b) 10^{-18}
(c) 6×10^5
(d) 6×10^8

2. For a sample of pure water,

(a) pH increases and pOH decreases with increase in temperature.
(b) pH decreases and pOH increases with increase in temperature.
(c) both pH and pOH increases with increase in temperature.
(d) both pH and pOH decrease with increase in temperature.

3. The pH at which water is maximum dissociated at 25°C, is

(a) 2
(b) 7
(c) 10
(d) 14

4. What will be the resultant pH when 200 ml of an aqueous solution of HCl (pH = 2.0) is mixed with 300 ml of an aqueous solution of NaOH (pH = 12.0)?

(a) 2.7
(b) 11.3
(c) 3.7
(d) 10.3

5. When 20 ml of 0.2 M – DCl solution is mixed with 80 ml of 0.1 M – NaOD solution, pD of the resulting solution becomes 13.6. The ionic product of heavy water, D_2O, is

(a) 10^{-15}
(b) 10^{-16}
(c) 4×10^{-15}
(d) 4×10^{-16}

6. Equilibrium constant of T_2O (Tritium is an isotope of H) differ from those of H_2O at 298 K. Let at 298 K, pure T_2O has pT (like pH) 7.60. What is the pT of a solution prepared by adding 100 ml of 0.4 M – TCl to 400 ml of 0.2 M – NaOT? (log 2 = 0.3)

(a) 1.1
(b) 0.08
(c) 6.5
(d) 14.1

7. The acid ionization constant of Zn^{2+} is 2.0×10^{-10}. What is the basic dissociation constant of $Zn(OH)^+$?

(a) 5×10^{-5}
(b) 2.0×10^4
(c) 2×10^{-10}
(d) 5×10^9

8. The dissociation constant of NH_3 at 27°C from the following data:

$NH_3 + H^+ \rightleftharpoons NH_4^+$; $\Delta H° = -52.21$ kJ/mol; $\Delta S° = +1.6\ JK^{-1}\ mol^{-1}$

$H_2O \rightleftharpoons H^+ + OH^-$; $\Delta H° = 54.70$ kJ/mol; $\Delta S° = -76.3\ JK^{-1}\ mol^{-1}$

Given: R = 8.3 J/K-mol

(a) e^{10}
(b) e^{-10}
(c) e^{-8}
(d) e^{-9}

9. How many moles of acetic acid should be added to 100 ml of 0.6 M formic acid solution such that the percentage dissociation of formic acid remains unchanged? K_a for acetic acid = 1.8×10^{-5} and K_a for formic acid = 2.4×10^{-4}.

(a) 0.8
(b) 0.08
(c) 8.0
(d) 0.6

10. The dissociation constant of a weak monoprotic acid is numerically equal to the dissociation constant of its conjugate base. What is pH of 0.1M solution of this acid?

(a) 7.0
(b) 6.0
(c) 8.0
(d) 4.0

11. The ionization constant of NH_4^+ in water is 5.6×10^{-10} mol L^{-1} s^{-1} at 25°C. The rate constant for the reaction of NH_4^+ and OH^- to form NH_3 and H_2O at 25°C is 3.4×10^{10} L mol^{-1} s^{-1}. The rate constant for proton transfer from water to NH_3 at 25°C is

(a) $6.07 \times 10^{5}\ s^{-1}$
(b) $6.07 \times 10^{-18}\ s^{-1}$
(c) $1.65 \times 10^{-6}\ s^{-1}$
(d) $1.65 \times 10^{-19}\ s^{-1}$

12. A solution is prepared in which 0.1 mole each of HCl, CH_3COOH and $CHCl_2COOH$ is present in a litre. If the ionization constant of CH_3COOH is 10^{-5} and that of $Cl_2CHCOOH$ is 0.15, the pH of solution is (log 2 = 0.3, log 3 = 0.48)

(a) 1.18 (b) 0.82
(c) 1.0 (d) 0.95

13. A solution contains 4.25 g ammonia per 250.0 ml of solution. Electrical conductivity measurement at 25°C show that 0.40% of the ammonia has reacted with water. The pH of the solution is (log 2 = 0.3)

(a) 11.6 (b) 2.4
(c) 12.6 (d) 10.6

14. Morphine, $C_{17}H_{19}NO_3$, is administered medically to relieve pain. It is a naturally occurring base, or alkaloid. What is the pH of a 0.0025 M solution of morphine at 25°C? The base-ionization constant, K_b, is 1.6×10^{-6} at 25°C. (log 2 = 0.3)

(a) 4.2 (b) 9.8
(c) 3.7 (d) 10.3

15. Saccharin ($K_a = 2 \times 10^{-12}$) is a weak acid represented by formula, HSac. A 4×10^{-4} mole amount of saccharin is dissolved in 200 ml water of pH, 3.0. Assuming no change in volume, the concentration of Sac^- ions in the resulting solution at equilibrium is

(a) 4×10^{-12} M
(b) 2×10^{-12} M
(c) 8×10^{-13} M
(d) 6.32×10^{-8} M

16. Dissociation constants of acids HA and HB are 2.0×10^{-4} and 5×10^{-5}, respectively. The $[H^+]$ in the resulting solution obtained by mixing 20 ml of 0.5 M – HA solution and 30 ml of 0.2 M – HB solution is

(a) 1.05×10^{-2} M (b) 6.78×10^{-3} M
(c) 1.05×10^{-3} M (d) 6.78×10^{-2} M

17. At 25°C, the dissociation constants of acid HA and base BOH in aqueous solution is same. The pH of 0.01 M solution of HA is 5.0. The pH of 0.1 M solution of BOH is

(a) 5.0 (b) 9.0
(c) 9.5 (d) 8.5

18. An aqueous solution initially contains 0.01 M – RNH_2 ($K_b = 2.0 \times 10^{-6}$) and 10^{-4} M – NaOH. The final concentration of OH^- in the solution is about

(a) 10^{-4} M (b) 2.0×10^{-4} M
(c) 3.0×10^{-4} M (d) 1.414×10^{-4} M

19. What will be the effect of adding 100 ml of 0.001 M – HCl solution to 100 ml of a solution having 0.1 M – HA? The acid dissociation constant of HA is 10^{-5}.

(a) The degree of dissociation of HA will decrease but the pH of solution remains unchanged.
(b) The degree of dissociation of HA remains unchanged but the pH of solution decreases.
(c) Neither degree of dissociation nor pH of solution will change.
(d) The degree of dissociation as well as pH of solution will decrease.

20. Fear or excitement, generally cause one to breathe rapidly and it results in the decrease of concentration of CO_2 in blood. In what way, it will change pH of blood?

(a) pH will increase
(b) pH will decrease
(c) no change
(d) pH becomes 7.0

21. An amount of 0.16 g of N_2H_4 is dissolved in water and the total volume made up to 500 ml. What is the percentage of N_2H_4 that has reacted with water in this solution? K_b for $N_2H_4 = 4.0 \times 10^{-6}$.

(a) 0.02%
(b) 0.014%
(c) 2%
(d) 2.82%

22. Water in equilibrium with air contains 4.4×10^{-5}% CO_2. The resulting carbonic acid, H_2CO_3, gives the solution a hydronium ion concentration of 2.0×10^{-6} M, about 20 times greater than that of pure water. What is the pH of the solution at 298 K? (log 4.4 = 0.64, log 2 = 0.3)

(a) 5.36
(b) 5.70
(c) 8.30
(d) 5.64

23. What is the pH of 6.67×10^{-3} M aqueous solution of $Al(OH)_3$ if its first dissociation is 100%, second dissociation is 50% and the third dissociation is negligible.

(a) 2 (b) 12
(c) 11 (d) 3

24. The only incorrect information related with 0.09 M solution of $NH_2CH_2CH_2NH_2$, ethylenediamine (en) is ($K_{b1} = 8.1 \times 10^{-5}$, $K_{b2} = 7.0 \times 10^{-8}$, log 3 = 0.48, log 7 = 0.85)

(a) pH = 11.44
(b) $[enH^+] = 2.7 \times 10^{-3}$ M
(c) $[enH_2^{2+}] = 7.0 \times 10^{-8}$ M
(d) $[H^+] = 2.7 \times 10^{-3}$ M

25. Calculate $[S^{2-}]$ in a solution originally having 0.1 M – HCl and 0.2 M – H_2S. For H_2S, $K_{a1} = 1.4 \times 10^{-7}$ and $K_{a2} = 1.0 \times 10^{-14}$.

(a) 0.1 M
(b) 2.8×10^{-20} M
(c) 2.8×10^{-22} M
(d) 1.4×10^{-20} M

26. For a tribasic acid, H_3A, $K_{a1} = 2 \times 10^{-5}$, $K_{a2} = 5 \times 10^{-9}$ and $K_{a3} = 4 \times 10^{-12}$. The value of $\frac{[A^{3-}]}{[H_3A]}$ at equilibrium in an aqueous solution originally having 0.2 M – H_3A is

(a) 5×10^{-17} (b) 5×10^{-9}
(c) 1×10^{-17} (d) 2×10^{-22}

27. H_3A is a weak tribasic acid with $K_{a1} = 10^{-5}$, $K_{a2} = 10^{-9}$ and $K_{a3} = 10^{-13}$. The value of pX of 0.1 M – H_3A solution, where $pX = -\log_{10}X$ and $X = \frac{[A^{3-}]}{[HA^{2-}]}$, is

(a) 5.0 (b) 4.0
(c) 9.0 (d) 10.0

28. To 20 ml of 0.1 M – NaOH solution, 3 ml of 1 M acetic acid solution is added. Is the solution now neutral, acidic or alkaline? How much more of the acetic acid solution we add to produce a change of pH = 0.3 unit? (pK_a for CH_3COOH = 4.74, log 2 = 0.3)

(a) acidic, 2 ml
(b) alkaline, 1 ml
(c) acidic, 1 ml
(d) neutral, 2 ml

29. A volume of 18 ml of mixture of acetic acid and sodium acetate required 6 ml of 0.1 M – NaOH for neutralization of the acid and 12 ml of 0.1 M – HCl reaction with salt separately. If pK_a of acetic acid is 4.75, what is the pH of the mixture? (log 2 = 0.3)

(a) 5.05 (b) 4.45
(c) 4.15 (d) 5.35

30. What is the ratio of pH of a solution containing 1 mole of CH_3COONa and 1 mole of HCl per litre and the other solution containing 1 mole of CH_3COONa and 1 mole of CH_3COOH per litre?

(a) 1:2 (b) 2:1
(c) pK_a:2 (d) zero

31. To a solution of acetic acid, solid sodium acetate is gradually added. When 'x g' of the salt has been added, the pH has a certain value. When total 'y g' of the salt has been added, the pH has been further raised by 0.6 units. What is the ratio of $x{:}y$? ($\log 3.98 = 0.6$)

(a) 3.98:1 (b) 1:3.98
(c) 2:3.98 (d) 3.98:2

32. Two buffers, X and Y of pH 4.0 and 6.0 respectively are prepared from acid HA and the salt NaA. Both the buffers are 0.50 M in HA. What would be the pH of the solution obtained by mixing equal volumes of the two buffers? K_a of HA $= 1.0 \times 10^{-5}$. ($\log 5.05 = 0.7$)

(a) 5.0 (b) 4.3
(c) 4.7 (d) 5.7

33. The buffer capacity (β) for a weak acid (A) – conjugate base (B) buffer is defined as the number of moles of strong acid or base needed to change the pH of 1 L of solution by 1 pH unit, where $\beta = \dfrac{2.303(C_A + C_B)K_a[H^+]}{([H^+]+K_a)^2}$. Under what condition will a buffer best resist a change in pH?

(a) pH = 3 p*K*a (b) 2 pH = p*K*a
(c) pH = p*K*a (d) pH = 2 p*K*a

34. A 40.0 ml solution of weak base, BOH is titrated with 0.1 N – HCl solution. The pH of the solution is found to be 10.0 and 9.0 after adding 5.0 ml and 20.0 ml of the acid, respectively. The dissociation constant of the base is ($\log 2 = 0.3$)

(a) 2×10^{-5} (b) 1×10^{-5}
(c) 4×10^{-5} (d) 5×10^{-5}

35. How many grams of NaOH should be added in 500 ml of 2 M acetic acid solution to get a buffer solution of maximum buffer capacity?

(a) 20.0 (b) 10.0
(c) 40.0 (d) 30.0

36. A 0.28 g sample of an unknown monoprotic organic acid is dissolved in water and titrated with a 0.1 M sodium hydroxide solution. After the addition of 17.5 ml of base, a pH of 5.0 is recorded. The equivalence point is reached when a total of 35.0 ml of NaOH is added. The molar mass of the organic acid is

(a) 160
(b) 80
(c) 40
(d) 120

37. Equilibrium constant for the acid ionization of Fe^{3+} to $Fe(OH)^{2+}$ and H^+ is 9.0×10^{-3}. What is the maximum pH, which could be used so that at least 90% of the total Fe^{3+} in a dilute solution exists as Fe^{3+}? ($\log 3 = 0.48$)

(a) 3.0
(b) 1.08
(c) 1.92
(d) 2.04

38. A student was given 0.01 mole of a weak organic acid and told to determine the K_a of the acid. He prepared 100 ml of an aqueous solution containing the sample. The volume of 50 ml of this solution was then titrated with NaOH to the equivalence point. The titrated solution was then mixed with the other 50 ml of the solution and the pH determined. A value of 4.80 was obtained for the mixed solution. What is the approximate value of pK_a for the acid?

(a) 5.10 (b) 4.50
(c) 4.80 (d) 4.20

39. What is the aqueous ammonia concentration of a solution prepared by dissolving 0.15 mole of $NH_4^+CH_3COO^-$ in 1 L of water? Given: K_a (CH_3COOH) $= 1.8 \times 10^{-5}$; K_b (NH_4OH) $= 1.8 \times 10^{-5}$.

(a) 8.3×10^{-4} M
(b) 0.15 M
(c) 5.52×10^{-3} M
(d) 3.8×10^{-4} M

40. A volume of 2.5 ml of $\frac{2}{5}$ M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with $\frac{2}{15}$ M – HCl in water at 25°C. The concentration of H^+ at equivalence point is ($K_w = 1 \times 10^{-14}$ at 25°C)

(a) 3.7×10^{-13} M
(b) 3.2×10^{-7} M
(c) 3.2×10^{-2} M
(d) 2.7×10^{-2} M

41. A volume of 10 ml of 0.1 M tribasic acid, H_3A is titrated with 0.1 M – NaOH solution. What is the ratio (approximate value) of $\frac{[H_3A]}{[A^{3-}]}$ at the second equivalent point? Given: $K_1 = 7.5 \times 10^{-4}$; $K_2 = 10^{-8}$; $K_3 = 10^{-12}$

(a) 10^{-4}
(b) 10^{-3}
(c) 10^{-7}
(d) 10^{-6}

42. The equilibrium carbonate ion concentration after equal volumes of 0.7 M – Na_2CO_3 and 0.7 M – HCl solutions are mixed, is (K_{a1} and K_{a2} for H_2CO_3 are 4.9×10^{-6} and 4.0×10^{-11}, respectively)

(a) 0.7 M
(b) 0.35 M
(c) 0.002 M
(d) 0.001 M

43. Calcium Lactate is a salt of weak acid and represented as $Ca(Lac)_2$. A saturated solution of $Ca(Lac)_2$ contains 0.125 mole of salt in 0.50 L solution. The pOH of this is 5.60. Assuming complete dissociation of salt, calculate K_a of lactate acid. (log 2.5 = 0.4)

(a) 1.25×10^{-11}
(b) 8.0×10^{-4}
(c) 3.2×10^{-17}
(d) 4×10^{-5}

44. A volume of 50 ml of a solution which is 0.05 M in the acid HA ($pK_a = 3.80$) and 0.08 M in HB ($pK_a = 8.20$) is titrated with 0.2 M – NaOH solution. The pH of solution at the first equivalent point is (log 2 = 0.3, log 1.6 = 0.2)

(a) 6.0
(b) 9.2
(c) 4.8
(d) 5.9

45. What is the concentration of aqueous ammonia in the solution prepared by dissolving 1.8 moles of ammonium acetate in 10 L water? (K_a of CH_3COOH = K_b of $NH_4OH = 1.8 \times 10^{-5}$)

(a) 1.0×10^{-3} M
(b) 0.01 M
(c) 3.24×10^{-3} M
(d) 3.09×10^{-4} M

46. When glycinium hydrochloride ($NH_2CH_2COOH.HCl$) is titrated against NaOH, pH at the first half equivalence point is 2.40 and the pH at second half equivalence point is 9.60. The pH at first equivalence point is

(a) 2.40
(b) 9.60
(c) 6.00
(d) 7.20

47. An acid–base indicator has $K_a = 3.0 \times 10^{-5}$. The acid form of the indicator is red and the basic form is blue. The $[H^+]$ required to change the indicator from 75% blue to 75% red is

(a) 8×10^{-5} M
(b) 9×10^{-5} M
(c) 1×10^{-5} M
(d) 3.33×10^{-5} M

48. An acid base indicator which is a weak acid has a pK_a value = 5.5. At what concentration ratio of sodium acetate to acetic acid would the indicator show a colour half way between those of its acid and conjugate base forms? pK_a of acetic acid = 4.75. [Antilog (0.75) = 5.62, Antilog (0.79) = 6.3, Antilog (0.69) = 4.93]

(a) 4.93:1
(b) 6.3:1
(c) 5.62:1
(d) 2.37:1

49. A volume of 224 ml of $CO_2(g)$ at 1 atm and 0°C was passed in 1 L of NaOH solution of unknown molarity. The resulting solution when titrated with 1.0 M – HCl solution, requires 30 ml for the phenolphthalein end point. The molarity of NaOH solution used is

(a) 0.04 M
(b) 0.02 M
(c) 0.03 M
(d) 0.08 M

50. The correct increasing order of solubility of the following substances in g/100 ml is $PbSO_4$ ($K_{sp} = 2 \times 10^{-9}$), ZnS ($K_{sp} = 1 \times 10^{-22}$), AgBr ($K_{sp} = 4 \times 10^{-13}$), $CuCO_3$ ($K_{sp} = 1 \times 10^{-8}$). (Atomic masses: Pb = 208, Zn = 65, Ag = 108, Br = 80, Cu = 63)

(a) $PbSO_4 < ZnS < AgBr < CuCO_3$
(b) $PbSO_4 < CuCO_3 < AgBr < ZnS$
(c) $ZnS < AgBr < CuCO_3 < PbSO_4$
(d) $ZnS < AgBr < PbSO_4 < CuCO_3$

51. Calculate K_{form} for $HgCl_4^{2-}$ if the concentration of Hg^{2+} is 1.6×10^{-17} M in a solution prepared by dissolving 0.10 mole of $Hg(NO_3)_2$ in 1 L of solution containing 0.9 mole of NaCl.

(a) 10^{17} (b) 10^{16}
(c) 10^{18} (d) 6.25×10^{16}

52. Unexposed silver halides are removed from photographic film when they react with sodium thiosulphate to form the complex ion $Ag(S_2O_3)_2^{3-}$. What amount of $Na_2S_2O_3$ is needed to prepare 1 L of a solution that dissolves 0.1 moles of AgBr by the formation of $Ag(S_2O_3)_2^{3-}$? K_{sp} of AgBr = 4.0×10^{-13} and K_f of $Ag(S_2O_3)_2^{3-}$ = 1.6×10^{12}.

(a) 3.25 g
(b) 3.25 moles
(c) 0.325 moles
(d) 6.5 moles

53. A saturated solution of silver benzoate, $AgOCOC_6H_5$, has pH of 8.6. K_a for benzoic acid is 5.0×10^{-5}. The value of K_{sp} for silver benzoate is (log 2 = 0.3)

(a) 8.0×10^{-2}
(b) 6.4×10^{-3}
(c) 6.4×10^{-4}
(d) 0.282

54. The solubility product of $Co(OH)_3$ is 2.7×10^{-43}. The pH of saturated solution of $Co(OH)_3$ is about

(a) 7.0 (b) 11.0
(c) 3.0 (d) 3.48

55. In an attempted determination of the solubility product constant of Tl_2S, the solubility of this compound in pure CO_2 free water was determined as 2.0×10^{-6} M. Assume that the dissolved sulphide hydrolyses almost completely to HS^- and that the further hydrolysis to H_2S can be neglected, what is the computed K_{sp}? For H_2S, $K_{a1} = 1.4 \times 10^{-7}$, $K_{a2} = 1.0 \times 10^{-14}$

(a) 6.4×10^{-23} (b) 1.6×10^{-23}
(c) 3.2×10^{-17} (d) 3.2×10^{-24}

56. Calculate the formation constant for the reaction of a tripositive metal ion with thiocyanate ions to form the monocomplex if the total metal concentration in the solution is 2×10^{-3} M, the total SCN^- concentration is 1.51×10^{-3} M and the free SCN^- concentration is 1.0×10^{-5} M.

(a) 7.55×10^4 (b) 3×10^5
(c) 3.33×10^{-6} (d) 1.5×10^5

57. After solid $SrCO_3$ was equilibrated with a buffer at pH 8.6, the solution was found to have $[Sr^{2+}] = 2.0 \times 10^{-4}$ M, what is K_{sp} of $SrCO_3$? (K_{a2} for $H_2CO_3 = 5.0 \times 10^{-11}$, log 2 = 0.3, $5.1 \times 0.196 = 1.0$)

(a) 4.0×10^{-8} (b) 8.0×10^{-8}
(c) 8.0×10^{-10} (d) 3.38×10^{-8}

58. What is the solubility of MnS in pure water, assuming hydrolysis of S^{2-} ions? K_{sp} of MnS = 2.5×10^{-10}, $K_{a1} = 1 \times 10^{-7}$ and $K_{a2} = 1 \times 10^{-14}$ for H_2S. ($0.63^3 = 0.25$)

(a) 6.3×10^{-4} M
(b) 2.5×10^{-4} M
(c) 6.3×10^{-3} M
(d) 1.58×10^{-5} M

59. An amount of 0.10 moles of AgCl(s) is added to one litre of water. Next, the crystals of NaBr are added until 75% of the AgCl is converted to AgBr(s), the less soluble silver halide. What is Br^- at this point? K_{sp} of AgCl = 2×10^{-10} and K_{sp} of AgBr = 4×10^{-13}.

(a) 0.075 M (b) 0.025 M
(c) 1.5×10^{-4} M (d) 0.027 M

60. An amount of 0.01 moles of solid AgCN is rendered soluble in 1 l by adding just sufficient excess cyanide ion to form $Ag(CN)_2^-$ and the concentration of free cyanide ion is 2.5×10^{-7} M. Determine $[Ag^+]$ in the solution neglecting hydrolysis of cyanide ion. K_{diss} for $Ag(CN)_2^-$ $= 1.0 \times 10^{-20}$.

(a) 6.25×10^{-9} M
(b) 1.6×10^{-9} M
(c) 1.6×10^{-7} M
(d) 6.25×10^{-7} M

61. An amount of 2.0 M solution of Na_2CO_3 is boiled in a closed container with excess of CaF_2. Very little amount of $CaCO_3$ and NaF are formed. If the solubility product of $CaCO_3$ is 'x' and molar solubility of CaF_2 is 'y', the molar concentration of F^- in the resulting solution after equilibrium is attained is

(a) $\sqrt{\dfrac{2y}{x}}$
(b) $\dfrac{8y^3}{x}$
(c) $\sqrt{\dfrac{8y^3}{x}}$
(d) $\sqrt{\dfrac{4y^3}{x}}$

62. Solid BaF_2 is added to a solution containing 0.1 mole of $Na_2C_2O_4$ solution (1 L) until equilibrium is reached. If the K_{sp} of BaF_2 and BaC_2O_4 is 10^{-6} mol^3 L^{-3} and 10^{-10} mol^2 L^{-2}, respectively, find the equilibrium concentration of Ba^{2+} in the solution. Assume addition of BaF_2 does not cause any change in volume.

(a) 0.2 M
(b) 4×10^{-6} M
(c) 2.5×10^{-5} M
(d) 2.5×10^{-6} M

63. What is the solubility of solid zinc hydroxide at a pH of 13? Given that

$Zn(OH)_2(g) \rightleftharpoons Zn(OH)_2(aq)$; $K_1 = 10^{-6}$ M

$Zn(OH)_2(aq) \rightleftharpoons Zn(OH)^+ + OH^-$; $K_2 = 10^{-7}$ M

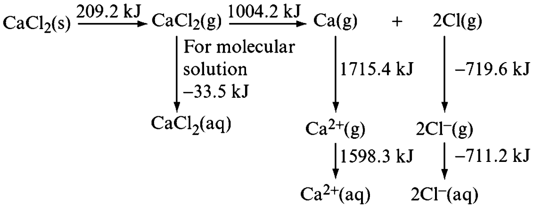
$Zn(OH)^+ \rightleftharpoons Zn^{2+} + OH^-$; $K_3 = 10^{-4}$ M

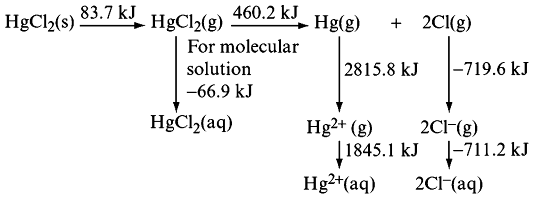
$Zn(OH)_2(aq) + OH^- \rightleftharpoons Zn(OH)_3^-$; $K_4 = 10^3$ M^{-1}

$Zn(OH)_3^- + OH^- \rightleftharpoons Zn(OH)_4^{2-}$; $K_5 = 10$ M^{-1}

(a) 10^{-17} M
(b) 10^{-6} M
(c) 10^{-4} M
(d) 2×10^{-4} M

64. On dissolving a substance in water, it can produce either an ionic or molecular solution. From the following data, predict what type of solution is likely to be formed by $CaCl_2$ and $HgCl_2$ at 25°C.





The maximum contribution of $T\Delta S$ in dissolution process is 30 kJ at 25°C

(a) both ionic
(b) both molecular
(c) $CaCl_2$ ionic but $HgCl_2$ molecular
(d) $CaCl_2$ molecular but $HgCl_2$

65. A volume of 250 ml of saturated clear solution of $CaC_2O_4(aq)$ requires 6.0 ml of 0.001 M – $KMnO_4$ in acid medium for complete oxidation of $C_2O_4^{2-}$ ions. What is K_{sp} of CaC_2O_4?

(a) 3.6×10^{-9}
(b) 6×10^{-5}
(c) 5.76×10^{-10}
(d) 1.44×10^{-8}

66. Sr^{2+} forms a very unstable complex with NO_3^-. A solution that was 0.001 M – $Sr(ClO_4)_2$ and 0.05 M – KNO_3 was found to have only 75% of its strontium in the uncomplexed Sr^{2+} form, the balance being $Sr(NO_3)^+$. What is K_f for complexation?

(a) 6.67
(b) 0.15
(c) 60
(d) 26.67

67. The concentration of CH_3COO^- ion in a solution prepared by adding 0.1 mole of $CH_3COOAg(s)$ in 1 L of 0.1 M – HCl solution is [Given: $K_a(CH_3COOH) = 10^{-5}$; $K_{sp}(AgCl) = 10^{-10}$; $K_{sp}(CH_3COOAg) = 10^{-8}$]

(a) 10^{-3} M
(b) 10^{-2} M
(c) 10^{-1} M
(d) 1 M

68. Among different types of salts have nearly same solubility product constant, K_{sp} but much smaller than one, the most soluble salt is that which

(a) produces maximum number of ions
(b) produces minimum number of ions
(c) produces high charge on ions
(d) produces low charges on ions

69. When excess oxalic acid is added to $CaCl_2$ solution, CaC_2O_4 is precipitated and the solution still contains some unprecipitated Ca^{2+}. The reason is

(a) CaC_2O_4 is a soluble salt.
(b) Oxalic acid does not ionize at all.
(c) Solution becomes acidic and hence ionization of $H_2C_2O_4$ is suppressed.
(d) Solution becomes basic and hence ionization of $H_2C_2O_4$ increases.

70. At what pH, is the solubility of $Zn(OH)_2$, minimum? What is the minimum solubility?

$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq)$; $K_{sp} = 1.2 \times 10^{-17}$

$Zn(OH)_2(s) + 2OH^-(aq) \rightleftharpoons Zn(OH)_4^{2-}(aq)$; $K_f = 0.12$

(a) 10.0, 2.4×10^{-9} M
(b) 4.0, 2.4×10^{-9} M
(c) 10.0, 1.2×10^{-9} M
(d) 10.0, 1.32×10^{-9} M

71. At what minimum pH will 10^{-3} M – $Al(OH)_3$ go into solution (V = 1 L) as $Al(OH)_4^-$ and at what maximum pH, it will dissolved as Al^{3+}? Given: log 2 = 0.3

$Al(OH)_4^- \rightleftharpoons Al^{3+} + 4OH^-$; $K_{eq} = 1.6 \times 10^{-34}$

$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$; $K_{eq} = 8.0 \times 10^{-33}$

(a) 9.3, 9.7
(b) 9.7, 9.3
(c) 4.3, 9.3
(d) 4.7, 9.3

72. A 0.1 M solution of $[Cu(NH_3)_4]^+$ is stirred with an excess of potassium cyanide sufficient to convert all the ammonium complex to the corresponding cuprocyanide complex $[Cu(CN)_4]^{-3}$ and in addition to provide the solution with an excess of CN^- equal to 0.2 M. Calculate the maximum pH of the solution when the final solution is treated with hydrogen sulphide to maintain $[H_2S]$ = 0.1 M and the precipitation of cuprous sulphide is prevented. The instability constant for $[Cu(CN)_4]^{-3}$ is 5×10^{-28}, $K_{a,overall}$ of $H_2S = 1.6 \times 10^{-21}$.

(a) 4.0
(b) 10.0
(c) 10.8
(d) 3.2

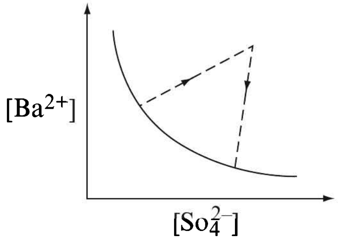
73. A particular water sample has 136 ppm $CaSO_4$. What percentage of water, by mass, must be evaporated in a container before solid $CaSO_4$ begins to deposit. Assume that the solubility of $CaSO_4$ does not change with temperature in the range 0°C to 100°C. K_{sp} of $CaSO_4 = 1.6 \times 10^{-5}$.

(a) 80% (b) 50%
(c) 75% (d) 60%

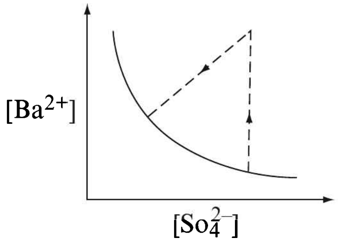
74. There exist an equilibrium between solid $BaSO_4$, Ba^{2+} and SO_4^{2-} ions in aqueous medium. Now, if equilibrium is disturbed by addition of (a) $BaNO_3$ and (b) K_2SO_4 in different experiments and the equilibrium is re-achieved, then match the columns given below. (Thick line represents the initial equilibrium and the dotted line represents the approach of system towards equilibrium.)

(a) Addition of $BaNO_3$
(b) Addition of K_2SO_4

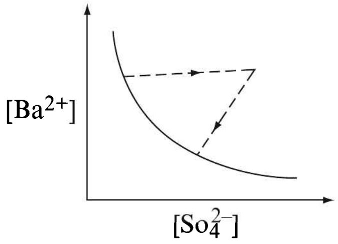
(c)



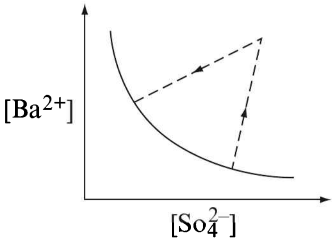
(d)



(e)



(f)



(a) ac, bd (b) ad, be
(c) af, be (d) ad, be

75. A volume of 1.0 L of solution which was in equilibrium with solid mixture of AgCl and Ag_2CrO_4 was found to contain 1×10^{-4} moles of Ag^+ ions, 1.0×10^{-6} moles of Cl^- ions and 8.0×10^{-4} moles of CrO_4^{2-} ions. Ag^+ ions are added slowly to the above mixture (keeping the volume constant) till 8.0×10^{-7} moles of AgCl got precipitated. How many moles of Ag_2CrO_4 were precipitated simultaneously?

(a) 7.68×10^{-4} (b) 4.8×10^{-4}
(c) 8.0×10^{-4} (d) 7.68×10^{-5}

76. What concentration of free CN^- must be maintained in a solution that is 1.8 M – $AgNO_3$ and 0.16 M – NaCl to prevent AgCl from precipitating? K_f for $Ag(CN)_2^- = 6.4 \times 10^{17}$ and K_{sp} for AgCl $= 1.8 \times 10^{-10}$.

(a) 2.5×10^{-9} M (b) 5×10^{-5} M
(c) 2.5×10^{-5} M (d) 1×10^{-4} M

77. A solution contains 0.1 M – Mg^{2+} and 0.1 M – Sr^{2+}. The concentration of H_2CO_3 in solution is adjusted to 0.05 M. Determine the pH range which would permit the precipitation of $SrCO_3$ without any precipitation of $MgCO_3$. H^+ ion concentration is controlled by external factors. Given: $K_{sp}(MgCO_3) = 4 \times 10^{-8}\ M^2$; $K_{sp}(SrCO_3) = 9 \times 10^{-10}\ M^2$; $K_{a,overall}(H_2CO_3) = 5 \times 10^{-17}$; log 2 = 0.3; log 3 = 0.48.

(a) 4.78 to 5.6 (b) 4.6 to 5.78
(c) 5.78 to 6.4 (d) 5.22 to 5.4

78. A buffer solution is 0.25 M – CH_3COOH + 0.15 M – CH_3COONa, saturated in H_2S (0.1 M) and has $[Mn^{2+}]$ = 0.04 M, $K_a(CH_3COOH) = 2.0 \times 10^{-5}$, $K_a(H_2S) = 1.0 \times 10^{-21}$ and $K_{sp}(MnS) = 2.5 \times 10^{-13}$. Which buffer component should be increased in concentration and to which minimum value to just start precipitation of MnS?

(a) CH_3COOH, 1.25 M
(b) CH_3COONa, 0.25 M
(b) CH_3COONa, 1.25 M
(d) CH_3COONa, 0.50 M

79. To 0.35 l of 0.1 M – NH_3 is added 0.15 L of 0.1 M – $MgCl_2$. What mass of $(NH_4)_2SO_4$ should be added to cause the $Mg(OH)_2$ to re-dissolve? K_{sp} for $Mg(OH)_2 = 1.2 \times 10^{-11}$, K_b for $NH_3 = 2.0 \times 10^{-5}$.

(a) 4.62 g
(b) 2.31 g
(c) 9.24 g
(d) 1.155 g

80. A volume of 500 ml of 0.01 M – $AgNO_3$ solution, 250 ml of 0.02 M – NaCl solution and 250 ml of 0.02 M – NaBr solution are mixed. The final concentration of bromide ion in the solution is (K_{sp} of AgCl and AgBr are 10^{-10} and 5×10^{-13}, respectively.)

(a) 0.01 M
(b) 0.02 M
(c) 0.005 M
(d) 2.5×10^{-5} M

Section B (One or More than one Correct)

1. Which of the following solutions will have pH close to 1.0?

(a) 100 ml of (M/10) HCl + 100 ml of (M/10) NaOH
(b) 55 ml of (M/10) HCl + 45 ml of (M/10) NaOH
(c) 10 ml of (M/10) HCl + 90 ml of (M/10) NaOH
(d) 75 ml of (M/5) HCl + 25 ml of (M/5) NaOH

2. Which of the following relation(s) is/are true for alkaline solution?

(a) $pH > \frac{pK_w}{2}$
(b) pH > pOH
(c) $pOH < \frac{pK_w}{2}$
(d) pH < pOH

3. Which of the following expression(s) for the degree of dissociation of weak monobasic acid in aqueous solution is/are incorrect?

(a) $\sqrt{\frac{K_a}{C}}$
(b) $\frac{K_a}{K_a + [H^+]}$
(c) $\frac{[H^+]}{K_a + [H^+]}$
(d) $\frac{1}{1 + 10^{(pK_a - pH)}}$

4. Which of the following will occur if a 0.1 M solution of a weak acid is diluted to 0.01 M at constant temperature?

(a) $[H^+]$ will decrease
(b) pH will increase
(c) Percentage ionization will increase
(d) K_a will increase

5. The relation $pK_a = 14 - pK_b$ is true for which of the following pair(s)?

(a) $MeNH_3^+$, CH_3NH_2
(b) CH_3COOH, CH_3COO^-
(c) H_3O^+, OH^-
(c) Na^+, NaOH

6. Which would decrease the pH of 25 ml of a 0.01 M solution of hydrochloric acid? The addition of

(a) magnesium metal
(b) 25 ml 0.02 M HCl
(c) 25 ml 0.005 M HCl
(d) 50 ml water

7. Which of the following result(s) is/are correct for the equilibrium state in a solution originally having 0.1 M – CH_3COOH and 0.1 M – HCl? K_a of $CH_3COOH = 1.8 \times 10^{-5}$.

(a) $[H^+] = 0.1$ M
(b) $[CH_3COO^-] = 1.8 \times 10^{-5}$ M
(c) degree of dissociation of acetic acid $= 1.8 \times 10^{-4}$
(d) $[H^+]$ from water $= 10^{-13}$ M

8. The equilibrium constant for the ionization of $RNH_2(g)$ in water as

$RNH_2(g) + H_2O(l) \rightleftharpoons RNH_3^+(aq) + OH^-(aq)$

is 10^{-6} at 25°C. Which of the following is/are correct?

(a) pH of the solution is 11.0 at partial pressure of $RNH_2(g) = 1$ bar.
(b) Forward reaction is favoured by the addition of HCl(aq).
(c) Forward reaction is favoured by the addition of $H_2O(l)$.
(d) Forward reaction is favoured by the addition of $RNH_2(g)$.

9. Which of the following processes will increase $[OH^-]$ in NH_4OH solution?

(a) Addition of HCl solution.
(b) Addition of water.
(c) Addition of NH_4Cl solution.
(d) Addition of solid NH_4OH.

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

(a) The pH of 10^{-8} M – HCl solution is 8.
(b) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}.
(c) Autoprotolysis constant of water increases with the increase in temperature.
(d) When a solution of a weak monoprotic acid is titrated against a strong base, at half neutralization point, $pH = pK_a/2$.

11. If K_1 and K_2 are the first and second ionization constants of H_2CO_3 and $K_1 >> K_2$, the incorrect relation(s) is/are

(a) $[H^+] = [HCO_3^-]$
(b) $[H^+] = \sqrt{K_1.[H_2CO_3]}$
(c) $K_2 = [CO_3^{2-}]$
(d) $[H^+] = 2.\ [CO_3^{2-}]$

12. Which of the following may act as buffer in aqueous solution?

(a) $NH_4Cl + NH_4OH$
(b) $CH_3COOH + CH_3COONa$
(c) $CH_3COONa + NaCl$
(d) Borax + Boric acid

13. A buffer solution can be prepared from a mixture of

(a) NH_4Cl and NaOH in 2:1 mole ratio
(b) CH_3COONa and HCl in 1:1 mole ratio
(c) CH_3COONa and HCl in 2:1 mole ratio
(d) CH_3COONa and HCl in 1:2 mole ratio

14. Which of the following statements is/are correct?

(a) A buffer solution may contain a weak acid and its conjugate base.
(b) A buffer solution shows little change in pH on the addition of a small amount of acid or base.
(c) A buffer solution can be prepared by mixing a solution of ammonium acetate and acetic acid.
(d) The addition of solid potassium cyanide to water increases the pH of water.

15. A 2.5 g impure sample containing weak monoacidic base (Molecular weight = 45) is dissolved in 100 ml water and titrated with 0.5 – M HCl at 25°C. When 1/5th of the base was neutralized, the pH was found to be 9 and at equivalent point, pH of solution is 4.5.

(a) K_b of base is less than 10^{-6}.
(b) Concentration of salt at equivalent point is 0.25 M.
(c) Volume of HCl used at equivalent point is 100 ml.
(d) Mass percentage of base in given sample is 80%.

16. H_2CO_3 ionizes as:

$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$; $K_1 = 4.0 \times 10^{-6}$
$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$; $K_2 = 5.0 \times 10^{-11}$

The correct information(s) related with 0.5 M – Na_2CO_3 solution is/are

(a) The degree of hydrolysis of Na_2CO_3 is 0.02.
(b) pH of solution is 2.0.
(c) pOH of solution is 2.0.
(d) $[H_2CO_3] = 2.5 \times 10^{-9}$ M

17. The amino acid glycine, NH_2CH_2COOH, is basic because of its $-NH_2$ group and acidic because of its –COOH group. By a process equivalent to base dissociation, glycine can acquire an additional proton to form $\overset{\oplus}{N}H_3CH_2COOH$. The resulting cation may be considered to be a diprotic acid, since one proton from the –COOH group and one from the $-\overset{\oplus}{N}H_3$ group may be lost. The pK_a values for these processes are 2.22 and 9.78, respectively. For a 0.01 M solution of neutral glycine (log 1.7 = 0.22, log 6 = 0.78),

(a) the pH is 6.0.
(b) percentage of the glycine in the cationic form is 0.0017%.
(c) the pOH is 6.0.
(d) percentage of the glycine in the anionic form is 0.0017%.

18. A certain indicator (an organic dye) has pK_a = 5. For which of the following titrations may it be suitable?

(a) Acetic acid against NaOH
(b) Aniline hydrochloride against NaOH
(c) Sodium carbonate against HCl
(d) Barium hydroxide against oxalic acid

19. Which of the following statement(s) is/are incorrect?

(a) When water is added to KCN, a reaction occurs because the CN^- ion is a strong proton acceptor.
(b) No reaction occurs when KCl is dissolved in water because neither K^+ nor Cl^- can remove or accept proton from water.
(c) When water is added to sodium acetate, an acidic solution is produced because of the formation of free acetic acid from the action of water on CH_3COO^-.
(d) $(NH_4)_2CO_3$ smells strongly of NH_3 because the strong base CO_3^{2-} is able to remove protons from NH_4^+ ion.

20. An aqueous solution contains 0.02 M – $FeCl_2$ and 0.05 M – $FeCl_3$. The solubility products are 8×10^{-16} for $Fe(OH)_2$ and 4×10^{-28} for $Fe(OH)_3$. Identify the correct option(s) among the following regarding the precipitation of metal hydroxides?

(a) At pH = 9.0, neither $Fe(OH)_2$ nor $Fe(OH)_3$ will precipitate.
(b) At pH = 6.0, neither $Fe(OH)_2$ nor $Fe(OH)_3$ will precipitate.
(c) If the pH of solution is in between 6.7 and 8.7, only $Fe(OH)_3$ will precipitate but not $Fe(OH)_2$.
(d) If the pH of solution is in between 6.7 and 8.7, only $Fe(OH)_2$ will precipitate but not $Fe(OH)_3$.

Section C (Comprehensions)

Comprehension I

Acetic acid tends to form dimer due to formation of intermolecular hydrogen bonding.

$$2\,CH_3COOH \rightleftharpoons (CH_3COOH)_2$$

The equilibrium constant for this reaction is 1.5×10^2 M^{-1} in benzene solution and 3.6×10^{-2} M^{-1} in water. In benzene, monomer does not dissociate but in water, monomer dissociates simultaneously with acid dissociation constant 2.0×10^{-5} M. Dimer does not dissociate in benzene as well as water.

1. The molar ratio of dimer to monomer for 0.1 M acetic acid in benzene is equal to

(a) 150:1 (b) 1:150
(c) 5:2 (d) 2:5

2. The molar ratio of dimer to monomer for 0.1 M acetic acid in water (neglecting the dissociation of acetic acid in water) is equal to

(a) 250:1 (b) 1:250
(c) 9:2500 (d) 2500:9

3. The pH of 0.1 M acetic acid solution in water, considering the simultaneous dimerization of acid is

(a) 1
(b) 2.85
(c) 5.7
(d) 3.42

Comprehension II

The dissociation constant of acetic acid is 2.0×10^{-5}. An aqueous solution of acetic acid is prepared by dissolving 0.7 millimole acetic acid in sufficient water to get 10 m^3 of solution at 25°C.

4. What is the pH of solution? ($\log 2 = 0.3$, $\log 7 = 0.85$, $\log 17 = 1.23$, $\sqrt{4.49} = 2.1$)

(a) 7.15
(b) 6.77
(c) 6.85
(d) 7.0

5. What is the concentration of unionized acetic acid in the solution?

(a) 0
(b) 4.9×10^{-10} M
(c) 7×10^{-8} M
(d) 2.45×10^{-10} M

Comprehension III

The concentration of hydrogen ion in a 0.2 M solution of formic acid is 8.0×10^{-3} M. To this solution is added formate so as to adjust the concentration of sodium formate to 1.0 M. The degree of dissociation of sodium formate is 0.8. ($\log 2 = 0.3$)

6. What will be the pH of the final solution?

(a) 4.1 (b) 2.1
(c) 2.9 (d) 4.9

7. The dissociation constant of formic acid is

(a) 2.4×10^{-4} (b) 3.2×10^{-4}
(c) 3.2×10^{-5} (d) 1.6×10^{-4}

Comprehension IV

A buffer solution of contains 0.8 M – NH_4OH and 0.2 M – NH_4Cl. K_a of $NH_4^+ = 5.0 \times 10^{-10}$. (log 2 = 0.3, log 3 = 0.48)

8. The pH of the solution is
(a) 9.9 (b) 8.7
(c) 9.6 (d) 4.1

9. The pH of the resulting solution on adding 0.15 mole HCl in 500 ml of the buffer solution
(a) 9.3 (b) 0.48
(c) 0.52 (d) 9.9

10. The pH of the resulting solution on adding 0.5 mole HCl in 500 ml of the buffer solution
(a) 9.3
(b) 0.30
(c) 0.70
(d) 9.9

Comprehension V

Potash alum is $KAl(SO_4)_2 \cdot 12H_2O$. As a strong electrolyte it is considered to be 100% dissociated into K^+, Al^{3+} and SO_4^{2-}. The solution is acidic because of the hydrolysis of Al^{3+}, but not so acidic as might be expected, because the SO_4^{2-} can sponge up some of the H_3O^+ by forming HSO_4^-. Given a solution made by dissolving 11.85 g of $KAl(SO_4)_2 \cdot 12H_2O$ in enough water to make 100 cm^3 of solution. What is $[H_3O^+]$ of the solution if (K = 39, Al = 27)

11. None of the ion is hydrolysing.
(a) 10^{-7} M
(b) less than 10^{-7} M
(c) more than 10^{-7} M
(d) 0.0

12. Only Al^{3+} is hydrolysing and its first hydrolysis constant is 1.4×10^{-5} M.
(a) 1.87×10^{-3} M
(b) 6.24×10^{-4} M
(c) 0.09 M
(d) 6.32×10^{-7} M

13. Only SO_4^{2-} is hydrolysing and acid dissociation constant of HSO_4^- in water is 1.25×10^{-2}.
(a) 1.26×10^{-13} M
(b) 6.32×10^{-7} M
(c) 4.47×10^{-7} M
(d) 1.58×10^{-8} M

14. Both, Al^{3+} and SO_4^{2-} are hydrolysing.
(a) 2.93×10^{-4} M
(b) 0.0114 M
(c) 5.43×10^{-6} M
(d) 9.35×10^{-4} M

Comprehension VI

A 0.010 M solution of $PuO_2(NO_3)_2$ was found to have a pH of 3.80. [Antilog (–3.8) = 1.6×10^{-4}]

15. What is the hydrolysis constant, K_b, for PuO_2^{2+}?
(a) 2.6×10^{-6}
(b) 3.2×10^{-8}
(c) 5.2×10^{-4}
(d) 2.6×10^{-8}

16. What is K_b for $PuO_2 \cdot OH^+$?
(a) 1.0×10^{-6}
(b) 3.8×10^{-8}
(c) 3.8×10^{-9}
(d) 3.8×10^{-10}

Comprehension VII

A volume of 100 ml of 0.1 M – H_3PO_4 solution is titrated with 0.5 M – NaOH solution till the second equivalence point. Then 10 ml of 0.5 M – HCl solution is mixed in the resulting solution. The dissociation constants of H_3PO_4 are 10^{-3}, 10^{-8} and 10^{-13}.

17. pH at the second equivalence point is

(a) 13.0 (b) 8.0

(c) 5.5 (d) 10.5

18. pH of the solution after adding HCl is

(a) 8.0 (b) 1.0

(c) 6.0 (d) 10.5

19. The solubility product of base $A(OH)_2$ is 4.0×10^{-30}. Its solubility in the final solution is

(a) 10^{-10} M

(b) 4.0×10^{-16} M

(c) 4.0×10^{-18} M

(d) 4.0×10^{-22} M

Comprehension VIII

Human blood has a narrow pH range of 7.3–7.4, which must be maintained for metabolic processes to function properly. To keep the pH in this range, requires a delicate balance between the concentrations of the conjugate acid–base pairs, making up to the buffer system. The main buffer is a carbonic acid-hydrogen carbonate system, which involves the following equilibria:

$$CO_2(g) \rightleftharpoons CO_2(aq)$$
$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$
$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$

At the body temperature, the pK_a for carbonic acid is 6.40. However, the normal concentration of $CO_2(g)$ in the lungs maintains a ratio of $HCO_3^-(aq)$ and $H_2CO_3(aq)$ in blood plasma at about 8:1. H_2CO_3 concentration in the blood is largely controlled by breathing and respiration and HCO_3^- concentration is largely controlled by excretion in urine.

If blood pH rises above 7.4, a potentially life-threatening condition called alkalosis can result. It normally occurs in climbers suffering from oxygen deficiency at high altitude or in patients who are hyperventilating from severe anxiety. (log 2 = 0.3)

20. The pH of blood at body temperature is

(a) 6.4

(b) 7.4

(c) 7.3

(d) 7.2

21. The maximum permissible value of $\frac{[H_2CO_3]}{[HCO_3^-]}$ in human blood to just prevent alkalosis is

(a) 0.1

(b) 10

(c) 8.0

(d) 0.125

22. The only correct statement among the following is

(a) One way to treat alkalosis can be to get the patient to breathe more quickly so that the amount of CO_2 exhaled increases and the blood becomes deficient in CO_2.

(b) One way to treat alkalosis is to get the patient breathe into a bag so that the exhaled CO_2 is re-inhaled.

(c) pH of blood is independent of concentration of CO_2.

(d) Alkalosis cannot be controlled by breathing and respiration.

Comprehension IX

The first and second dissociation constants of H_2CO_3 are 4.0×10^{-6} and 2.5×10^{-11}, respectively. In a particular titration, 50 ml of 1.0 M – Na_2CO_3 is taken in a flask and 1.0 M – HCl solution is added drop by drop. Determine the pH of the resulting solution on adding the following volume of HCl solution. Assume volume is additive. (log 2 = 0.3, log 3 = 0.48)

23. 0 ml?

(a) 1.7 (b) 12.3
(c) 3.7 (d) 10.3

24. 25 ml?

(a) 10.6 (b) 10.3
(c) 10.9 (d) 3.4

25. 50 ml?

(a) 10.6 (b) 5.4 (c) 8.0 (d) 6.0

26. 75 ml?

(a) 10.6 (b) 8.6
(c) 8.0 (d) 5.4

27. 100 ml?

(a) 2.94
(b) 11.06
(c) 5.4
(d) 5.88

Comprehension X

Amino acid glycine (NH_2–CH_2–COOH) exists as a zwitterion in aqueous solution. The K_a and K_b values of glycine are 1.6×10^{-10} ($pK_a = 9.8$) and 2.5×10^{-12} ($pK_b = 11.6$) respectively. The K_a and K_b values are for zwitterion of amino acid with the following structure $[\overset{+}{N}H_3 - CH_2 - COO^-]$.

28. What is the K_b for $-NH_2$ group in glycine?

(a) 4×10^{-3}
(b) 1.6×10^{-10}
(c) 6.25×10^{-5}
(d) 2.5×10^{-12}

29. An aqueous solution of glycine has pH

(a) nearly 7
(b) nearly 7.9
(c) nearly 6.1
(d) nearly 11.5

Comprehension XI

To find the K_{sp} of $AgBrO_3$, a student prepared 1 L of a just saturated solution by adding $AgBrO_3$ in water at 27°C. He found that a copper wire left in the solution overnight became covered with silver and Cu^{2+} ions were also formed in the solution. The wire was cleaned, dried and found to weigh 6.35 mg less that its original weight. Given:

$$Cu(s) + 2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s);\ \Delta G^\circ = -115.15\ kJ$$

(R = 8.0 J/K-mol; Cu = 63.5)

30. The number of moles of Cu reacted was

(a) 1.0×10^{-4} (b) 1.0
(c) 0.10 (d) 1.0×10^{-3}

31. The concentration of Ag^+ in the original saturated solution was

(a) 1.0×10^{-2} (b) 1.0×10^{-4}
(c) 2.0×10^{-4} (d) 5.0×10^{-5}

32. The K_{sp} for $AgBrO_3$ is

(a) 1.0×10^{-8}
(b) 3.0×10^{-9}
(c) 1.6×10^{-4}
(d) 4.0×10^{-8}

Comprehension XII

The solubility product of AgCN is 1.0×10^{-16} and the formation constant of $Ag(CN)_2^-$ is 1.5×10^{17}.

33. The solubility of AgCN in 0.02 M – KCN solution, assuming no complex formation, is

(a) 1.0×10^{-8} M (b) 5.0×10^{-15} M
(c) 0.02 M (d) 5.0×10^{-14} M

34. The solubility of AgCN in 0.02 M – KCN solution, assuming complex formation, is

(a) 0.3 M (b) 0.02 M
(c) 1.33×10^{-19} M (d) 3.0×10^{-6} M

35. At what [CN⁻] in the solution, the solubility of AgCN will be minimum?

(a) 3.65×10^{-9} M
(b) 1.33×10^{-17} M
(c) 2.58×10^{-9} M
(d) 5.48×10^{-8} M

Section D (Assertion–Reason)

The following questions consist of two statements. Mark

(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:** An aqueous solution having pH 6.8 must be acidic.

   Statement II: An aqueous solution having $[H^+] > \sqrt{K_w}$ must be acidic.

2. **Statement I:** pH of 10^{-7} M – NaOH solution is in between 7.0 to 7.3 at 25°C.

   Statement II: Due to common ion effect, ionization of water is reduced.

3. **Statement I:** 10^{-4} M – HCl solution is more acidic compared to 1 M – HCOOH solution ($K_a = 10^{-3}$ M).

   Statement II: HCl is stronger acid compared to HCOOH.

4. **Statement I:** When an aqueous solution of weak base, BOH, is diluted, [OH⁻] increases.

   Statement II: On dilution, the degree of dissociation of weak electrolytes increases.

5. **Statement I:** pH of acidic buffer solution always increases on dilution.

   Statement II: pH of any aqueous solution of acid always increases on dilution.

6. **Statement I:** An aqueous solution containing a weak base (HA) and its conjugate base (A⁻) may behave as buffer solution.

   Statement II: At 25°C, pH of such buffer solution must be less than 7.0.

7. **Statement I:** Aqueous solutions of NaCl and CH_3COONH_4 are neutral (pH = 7.0 at 25°C).

   Statement II: Both the salts do not undergo hydrolysis.

8. **Statement I:** In general, phenolphthalein is used as an indicator for the titration of weak acid against strong base.

Statement II: At equivalent point, solution is basic and pH range of phenolphthalein is about 8.0 to 10.0.

9. **Statement I:** Phenolphthalein does not show any change in colour during the titration of $NaHCO_3$ with HCl.

   Statement II: In the presence of phenolphthalein, HCl does not react with $NaHCO_3$.

10. **Statement I:** Moles of Sr^{2+} furnished by sparingly soluble substance $Sr(OH)_2$ decreases due to dilution.

    Statement II: Solubility product of $Sr(OH)_2$ is not affected by dilution.

Section E (Column Match)

1. Match the column

Column I	Column II
(A) NaCl	(P) True electrolyte
(B) HCl	(Q) Strong electrolyte in water
(C) CH_3COOH	(R) Potential electrolyte
(D) $CrCl_3 \cdot 3NH_3$	(S) Weak electrolyte in water
	(T) Non-electrolyte in water

2. Match the column

Column I (pH value)	Column II (solution)
(A) 5.0	(P) pH at which $Mg(OH)_2$ just start precipitating from 2.0×10^{-3} M – Mg^{2+} solution (K_{sp} of $Mg(OH)_2 = 2 \times 10^{-6}\ M^3$)
(B) 9.0	(Q) Maximum pH at which 0.1 mole of $Al(OH)_3$ dissolves completely as Al^{3+} in 1 L solution (K_{sp} of $Al(OH)_3 = 1 \times 10^{-28}\ M^4$)
(C) 12.5	(R) pH at which 0.1 M – CH_3COOH dissociates 1000/11% (K_a of $CH_3COOH = 1.0 \times 10^{-5}$ M)
(D) 6.0	(S) pH of 0.001 M – HA (weak acid) solution (pK_a of HA = pK_b of A^-)
	(T) pH of 3×10^{-5} M – CaA_2 solution (CaA_2 dissociates completely in water; K_a of HA = 5×10^{-9})

3. Match the column

Column I	Column II
(A) NaCl	(P) Cationic hydrolysis
(B) Na_2CO_3	(Q) Anionic hydrolysis
(C) NH_4Cl	(R) pH = 7.0 at 25°C
(D) CH_3COONH_4	(S) pH < 7.0 at 25°C
	(T) pH > 7.0 at 25°C

4. For a tribasic acid, H_3A, $K_{a1} = 10^{-4}$, $K_{a2} = 10^{-8}$ and $K_{a3} = 10^{-12}$. Match the pH (Column II) of the resulting solution (Column I), at 25°C.

Column I	Column II
(A) Equimolar mixture of H_3A and NaH_2A	(P) 12.0
(B) Equimolar mixture of NaH_2A and Na_2HA	(Q) 8.0
(C) Equimolar mixture of Na_2HA and Na_3A	(R) 4.0
(D) Equimolar mixture of H_3A and NaOH	(S) 6.0
(E) Equimolar mixture of NaH_2A and NaOH	(T) 10.0

5. Match the column

Column I	Column II
(A) $\frac{pK_{a,H_2O} + pK_{b,H_2O}}{2}$ at 25°C ($d_{water} = 1.0$ g/ml)	(P) $\frac{pK_w}{2}$
(B) pH of CH_3COONH_4(aq) ($K_{a,CH_3COOH} = K_{b,NH_4OH}$)	(Q) $16 - \log 1.8$
(C) pH of pure water at 320 K	(R) $-\log K_{a,H_2O}$
	(S) < 7.0

Section F (Subjective)

Single-digit Integer Type

1. The ionic product of heavy water, D_2O, is 1.0×10^{-16} at 7°C. The PD value of pure heavy water at 7°C is

2. The self-ionization constant for pure formic acid, $K = [HCOOH_2^+][HCOO^-]$ has been estimated as 10^{-6} M^2 and the density of formic acid is 1.15 g/cm^3 at room temperature. If 'x %' of formic acid molecules in pure formic acid is converted to formate ions, then the value of '1000x' is

3. An aqueous solution contains 10% ammonia by mass and has a density of 0.85 g/ml. If $[H_3O^+]$ in this solution is 'xM', then the value of '$x \times 10^{12}$' is (K_a for $NH_4^+ = 5.0 \times 10^{-10}$ M)

4. Boric acid, $B(OH)_3$ is used as a mild antiseptic. What is the pH of a 0.0025 M aqueous solution of boric acid? The hydrogen ion arises principally from the reaction:

   $B(OH)_3(aq) + H_2O(l) \rightleftharpoons B(OH)_4^-(aq) + H^+(aq)$; $K = 4.0 \times 10^{-10}$.

5. The average concentration of SO_2 in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of SO_2 in water at 298 K is 1.28 moles litre^{-1} and the pK_a of H_2SO_3 is 2.0, estimate the pH of rain on that day.

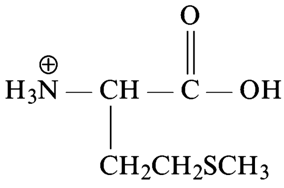
6. An artificial fruit beverage contains 30.0 g of tartaric acid, $H_2C_4H_4O_6$, and 18.8 g of its salt, potassium hydrogen tartrate, per

litre. What is pH of the beverage? For tartaric acid, $K_{a1} = 5.0 \times 10^{-4}$, $K_{a2} = 4 \times 10^{-9}$.

7. When 0.05 mole of HCl is added in 200 ml of a buffer solution, pH of the solution decreases by 0.05 unit. What is the buffer capacity of the solution?

8. A solution of weak acid was titrated with base NaOH. The equivalence point was reached when 36.12 ml of 0.1 M – NaOH have been added. Now, 18.06 ml 0.1 M – HCl was added to the titrated solution, the pH was found to be 5.0. The pK_a of acid is

9. A volume of 30 ml of 0.06 M solution of the protonated form of an amino acid, methionine (H_2A^+) is titrated with 0.09 M – NaOH. The pH of the resulting solution after addition of 20 ml of base, is (pK_{a1} = 2.28, pK_{a2} = 9.72)



$H_3\overset{\oplus}{N}-\underset{CH_2CH_2SCH_3}{CH}-\overset{O}{\overset{\|}{C}}-OH$

(methionine cation)

10. The pH range of a basic indicator (InOH) is 3.4 – 4.6. Determine the ratio $[In^+]/[InOH]$, above which the solution appears only in the colour of In^+?

Four-digit Integer Type

1. An aqueous solution of aniline of concentration 0.2 M is prepared. How many milligrams of NaOH should be added in 500 ml of this solution so that anilinium ion concentration in the solution becomes 10^{-8} M? K_b of $C_6H_5NH_2$ = 4.0×10^{-10}.

2. How many milligram of sodium acetate should be added in 500 ml of 0.2 M acetic acid solution in order to make the $[H^+]$ in the solution, 4×10^{-4} M. K_a of $CH_3COOH = 1.8 \times 10^{-5}$.

3. For H_2SO_4, K_{a1} = infinite and $K_{a2} = 1.2 \times 10^{-2}$. The molarity of H_2SO_4 solution of pH 2.0 is 'xM'. The value of '1000000x' is

4. The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5 M – $NaHCO_3$ solution should be mixed with a 10 ml sample of blood which is 2 M in H_2CO_3 in order to maintain a pH of 7.4? K_a for H_2CO_3 in blood is 8.0×10^{-7}. (log 2 = 0.3)

5. The hydronium ion concentration (in millimole per litre) in a solution containing 1.8 g $NaHSO_4$ per 100 ml is (K_a for HSO_4^- is 4.0×10^{-2})

6. The acid ionization of hydrated aluminium ion is

$Al(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons Al(H_2O)_5OH^{2+}(aq) + H_3O^+(aq)$; $K_a = 1.0 \times 10^{-5}$

How many milligrams of $AlCl_3$ should be dissolved in sufficient water to get 400 ml of solution of pH, 3.0?

7. A weak acid-type indicator was found to be 60% dissociated at pH = 9.18. What will be the percentage dissociation at pH = 9.0? (log 2 = 0.3, log 3 = 0.48)

8. A saturated solution of iodine in water contains 0.254 g of I_2 in 1 L. More than this can dissolve in a KI solution because of the following equilibrium:

$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$

A 0.1 M – KI solution actually dissolved 12.7 g of iodine per litre, most of which is converted to I_3^-. Assuming that the concentration of I_2 in all saturated solutions is the same, calculate the equilibrium constant for the above reaction. (Take: 9.6 × 5.1 = 4.9, Atomic mass of iodine = 127)

9. The solubility product (K_{sp}) of $Ca(OH)_2$ at 25°C is 3.2×10^{-5}. A 500 ml of saturated solution of $Ca(OH)_2$ is mixed with equal volume of 0.36 M – NaOH. How much $Ca(OH)_2$ (in milligrams) is precipitated?

10. Most ordinary soaps are sodium salt of long chain fatty acids and are soluble in water. Soaps of divalent cations such as Ca^{2+} are only slightly soluble and are often seen in the common soap is calcium palmitate, $Ca[CH_3(CH_2)_{14}COO]_2$. A handbook of chemistry lists the solubility of this soap as 0.0055 g per 100 ml at 25°C. If sufficient sodium soap is used to produce a final concentration of palmitate ion equal to 0.10 M in a water sample having 40 ppm Ca^{2+} initially, how many milligrams of calcium palmitate would precipitate in a bowl containing 10 l of this water sample?

Answer Keys – Exercise II

Section A (Only one Correct)

1. (c) 2. (d) 3. (b) 4. (b) 5. (a) 6. (d) 7. (a) 8. (b) 9. (a) 10. (d)
11. (a) 12. (b) 13. (a) 14. (b) 15. (a) 16. (b) 17. (c) 18. (b) 19. (c) 20. (a)
21. (c) 22. (b) 23. (b) 24. (d) 25. (b) 26. (a) 27. (d) 28. (c) 29. (a) 30. (a)
31. (b) 32. (d) 33. (c) 34. (a) 35. (a) 36. (b) 37. (b) 38. (c) 39. (a) 40. (d)
41. (c) 42. (d) 43. (b) 44. (d) 45. (a) 46. (c) 47. (a) 48. (c) 49. (a) 50. (c)
51. (c) 52. (b) 53. (b) 54. (a) 55. (a) 56. (b) 57. (c) 58. (a) 59. (c) 60. (b)
61. (c) 62. (c) 63. (d) 64. (c) 65. (a) 66. (a) 67. (b) 68. (a) 69. (c) 70. (a)
71. (c) 72. (b) 73. (c) 74. (b) 75. (a) 76. (b) 77. (a) 78. (b) 79. (b) 80. (d)

Section B (One or More than one Correct)

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

Section C

Comprehension I

1. (c) 2. (c) 3. (b)

Comprehension II

4. (c) 5. (b)

Comprehension III

6. (a) 7. (b)

Comprehension IV

8. (a) 9. (a) 10. (c)

Comprehension V

11. (a) 12. (a) 3. (d) 14. (a)

Comprehension VI

15. (a) 16. (c)

Comprehension VII

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

Comprehension VIII

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

Comprehension IX

23. (b) 24. (a) 25. (c)
26. (d) 27. (a)

Comprehension X

28. (c) 29. (c)

Comprehension XI

30. (a) 31. (c) 32. (d)

Comprehension XII

33. (b) 34. (a) 35. (a)

Section D (Assertion – Reason)

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

Section E (Column Match)

1. A → P, Q; B → Q, R; C → R, S; D → T
2. A → Q, S; B → T; C → P; D → R
3. A → R; B → Q, T; C → P, S; D → P, Q, R
4. A → R; B → Q; C → P; D → S; E → T
5. A → Q, R; B → P; C → P, S

Section F (Subjective)

Single-digit Integer Type

1. (8) 2. (4) 3. (1) 4. (6) 5. (2) 6. (3) 7. (5) 8. (5) 9. (6) 10. (4)

Four-digit Integer Type

1. (0160) 2. (0369) 3. (6470) 4. (0080) 5. (0060)
6. (5340) 7. (0050) 8. (0960) 9. (0681) 10. (5500)