CHAPTER 7

Equilibrium

Section-A JEE Advanced/ IIT-JEE

A Fill in the Blanks

1. The conjugate base of HSO_4^- in aqueous solution is .... *(1982 - 1 Mark)*

2. An element which can exist as a positive ion in acidic solution and also as a negative ion in basic solution is said to be .... *(1984 - 1 Mark)*

3. For a given reversible reaction at a fixed temperature, equilibrium constants K_p and K_c are related by........ *(1994 - 1 Mark)*

4. A ten-fold increase in pressure on the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at equilibrium results in .... in K_P. *(1996 - 1 Mark)*

5. In the reaction $I^- + I_2 \rightarrow I_3^-$, the Lewis acid is .... *(1997 - 1 Mark)*

B True / False

1. Aluminium chloride ($AlCl_3$) is a Lewis acid because it can donate electrons. *(1982 - 1 Mark)*

2. If equilibrium constant for the reaction $A_2 + B_2 \rightleftharpoons 2AB$, is K, then for the backward reaction $AB \rightleftharpoons ½A_2 + ½B_2$, the equilibrium constant is 1/K. *(1984 - 1 Mark)*

3. When a liquid and its vapour are at equilibrium and the pressure is suddenly decreased, cooling occurs. *(1984 - 1 Mark)*

4. Solubility of sodium hydroxide increases with increase in temperature. *(1985 - ½ Mark)*

C MCQs with One Correct Answer

1. Molten sodium chloride conducts electricitry due to the presence of *(1981 - 1 Mark)*
   - (a) free electrons
   - (b) free ions
   - (c) free molecules
   - (d) atoms of sodium and chlorine

2. An acidic buffer solution can be prepared by mixing the solutions of *(1981 - 1 Mark)*
   - (a) ammonium acetate and acetic acid
   - (b) ammonium chloride and ammonioum hydroxide
   - (c) sulphuric acid and sodium sulphate
   - (d) sodium chloride and sodium hydroxide.

3. The pH of a 10^{-8} molar solution of HCl in water is *(1981 - 1 Mark)*
   - (a) 8
   - (b) –8
   - (c) between 7 and 8
   - (d) between 6 and 7

4. The oxidation of SO_2 by O_2 to SO_3 is an exothermic reaction. The yield of SO_3 will be maximum if *(1981 - 1 Mark)*
   - (a) temperature is increased and pressure is kept constant
   - (b) temperature is reduced and pressure is increased
   - (c) both temperature and pressure are increased
   - (d) both temperature and pressure are reduced

5. For the reaction : *(1981 - 1 Mark)*

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

   the equilibrium constant K_p changes with
   - (a) total pressure
   - (b) catalyst
   - (c) the amounts of H_2 and I_2 present
   - (d) temperature

6. Of the given anions, the strongest Bronsted base is *(1981 - 1 Mark)*
   - (a) ClO^-
   - (b) ClO_2^-
   - (c) ClO_3^-
   - (d) ClO_4^-

7. At 90°C, pure water has $[H_3O^+]$ 10^{-6} mole litre^{-1}. What is the value of K_w at 90°C? *(1981 - 1 Mark)*
   - (a) 10^{-6}
   - (b) 10^{-12}
   - (c) 10^{-14}
   - (d) 10^{-8}

8. The precipitate of *(1982 - 1 Mark)*

$$CaF_2(K_{sp} = 1.7 \times 10^{-10})$$

   is obtained when equal volumes of the following are mixed
   - (a) $10^{-4}M\ Ca^{2+} + 10^{-4}M\ F^-$
   - (b) $10^{-2}M\ Ca^{2+} + 10^{-3}M\ F^-$
   - (c) $10^{-5}M\ Ca^{2+} + 10^{-3}M\ F^-$
   - (d) $10^{-3}M\ Ca^{2+} + 10^{-5}M\ F^-$

9. A liquid is in equilibrium with its vapour at its boiling point. On the average, the molecules in the two phases have equal : *(1984 - 1 Mark)*
   - (a) inter-molecular forces
   - (b) potential energy
   - (c) total energy
   - (d) kinetic energy

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10. Pure ammonia is placed in a vessel at a temperature where its dissociation constant (a) is appreciable. At equilibrium : *(1984 - 1 Mark)*

(a) K_p does not change significantly with pressure.
(b) does not change with pressure.
(c) concentration of NH_3 does not change with pressure.
(d) concentration of hydrogen is less than that of nitrogen.

11. A certain buffer solution contains equal concentration of X^- and HX. The K_b for X^- is 10^{-10}. The pH of the buffer is :

(a) 4 (b) 7 *(1984 - 1 Mark)*
(c) 10 (d) 14

12. A certain weak acid has a dissociation constant of 1.0×10^{-4}. The equilibrium constant for its reaction with a strong base is : *(1984 - 1 Mark)*

(a) 1.0×10^{-4} (b) 1.0×10^{-10}
(c) 1.0×10^{10} (d) 1.0×10^{14}

13. An example of a reversible reaction is : *(1985 - 1 Mark)*

(a) $Pb(NO_3)_2aq + 2NaI(aq) \rightarrow PbI_2(s) + 2NaNO_3(aq)$
(b) $AgNO_3(aq) + HCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$
(c) $2Na(s) + H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$
(d) $KNO_3(aq) + NaCl(aq) \rightarrow KCl(aq) + NaNO_3(aq)$

14. The best indicator for detection of end point in titration of a weak acid and a strong base is : *(1985 - 1 Mark)*

(a) methyl orange (3 to 4)
(b) methyl red (5 to 6)
(c) bromothymol blue (6 to 7.5)
(d) phenolphthalein (8 to 9.6)

15. The conjugate acid of NH_2^- is : *(1985 - 1 Mark)*

(a) NH_3 (b) NH_2OH
(c) NH_4^+ (d) N_2H_4

16. The compound that is not a Lewis acid is : *(1985 - 1 Mark)*

(a) BF_3 (b) $AlCl_3$
(c) $BeCl_2$ (d) $SnCl_4$

17. The compound insoluble in acetic acid is : *(1986 - 1 Mark)*

(a) calcium oxide (b) calcium carbonate
(c) calcium oxalate (d) calcium hydroxide

18. The compound whose 0.1 M solution is basic is : *(1986 - 1 Mark)*

(a) ammonium acetate (b) ammonium chloride
(c) ammonium sulphate (d) sodium acetate

19. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with

(a) 10^{-4} M (Ag^+) and 10^{-4} M (Cl^-) *(1988 - 1 Mark)*
(b) 10^{-5} M (Ag^+) and 10^{-5} M (Cl^-)
(c) 10^{-6} M (Ag^+) and 10^{-6} M (Cl^-)
(d) 10^{-10} M (Ag^+) and 10^{-10} M (Cl^-)

20. The pK_a of acetylsalicyclic and (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2-3 and the pH in the small intestine is about 8. Aspirin will be *(1988 - 1 Mark)*

(a) unionised in the small intestine and in the stomach
(b) completely ionised in the small intestine and in the stomach
(c) ionised in the stomach and almost unionised in the small intestine
(d) ionised in the small intestine and almost unionised in the stomach.

21. Which one of the following is the strongest acid? *(1989 - 1 Mark)*

(a) $ClO_3(OH)$ (b) $ClO_2(OH)$
(c) $SO(OH)_2$ (d) $SO_2(OH)_2$

22. Amongst the following hydroxides, the one which has the lowest value of K_{sp} at ordinary temperature (about 25°C) is *(1990 - 1 Mark)*

(a) $Mg(OH)_2$ (b) $Ca(OH)_2$
(c) $Ba(OH)_2$ (d) $Be(OH)_2$

23. The reaction which proceeds in the forward direction is *(1991 - 1 Mark)*

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

24. The following equilibrium in established when hydrogen chloride is dissolved in acetic acid.

$$HCl + CH_3COOH \rightleftharpoons Cl^- + CH_3COOH_2^+$$

The set that characterises the conjugate acid-base pairs is *(1992 - 1 Mark)*

(a) (HCl, CH_3COOH) and ($CH_2COOH_2^+$, Cl^-)
(b) (HCl, $CH_3COOH_2^+$) and (CH_3COOH, Cl^-)
(c) ($CH_3COOH_2^+$, HCl) and (Cl^-, CH_3COOH)
(d) (HCl, Cl^-) and ($CH_3COOH_2^+$, CH_3COOH)

25. Which of the following solutions will have pH close to 1.0? *(1992 - 1 Mark)*

(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

26. The degree of dissociation of water at 25°C is 1.9×10^{-7}% and density is 1.0 g cm^{-3}. The ionic constant for water is : *(1995S)*

(a) 1.0×10^{-10} (b) 1.0×10^{-14}
(c) 1.0×10^{-16} (d) 1.0×10^{-8}

27. Which one is more acidic in aqueous solution. *(1995S)*

(a) $NiCl_2$ (b) $FeCl_3$
(c) $AlCl_3$ (d) $BeCl_2$

28. The following acids have been arranged in the order of decreasing acid strength. Identify the correct order.

ClOH (I), BrOH(II), IOH(III) *(1996 - 1 Mark)*

(a) I > II > III (b) II > I > III
(c) III > II > I (d) I > III > II

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29. The pH of 0.1 M solution of the following salts increases in the order. *(1999 - 2 Marks)*

(a) $NaCl < NH_4Cl < NaCN < HCl$
(b) $HCl < NH_4Cl < NaCl < NaCN$
(c) $NaCN < NH_4Cl < NaCl < HCl$
(d) $HCl < NaCl < NaCN < NH_4Cl$

30. For the chemical reaction $3X(g) + Y(g) \rightleftharpoons X_3Y(g)$, the amount of X_3Y at equilibrium is affected by *(1999 - 2 Marks)*

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

31. For the reversible reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500°C, the value of K_p is 1.44×10^{-5} when partial pressure is measured in atmospheres. The corresponding value of K_c, with concentration in mole litre^{-1}, is *(2000S)*

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

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

32. When two reactants, A & B are mixed to give products C & D, the reaction quotient Q, at the initial stages of the reaction *(2000S)*

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

33. The set with correct order of acidity is *(2001S)*

(a) $HClO < HClO_2 < HClO_3 < HClO_4$
(b) $HClO_4 < HClO_3 < HClO_2 < HClO$
(c) $HClO < HClO_4 < HClO_3 < HClO_2$
(d) $HClO_4 < HClO_2 < HClO_3 < HClO$

34. For a sparingly soluble salt A_pB_q, the relationship of its solubility product (L_S) with its solubility (S) is *(2001S)*

(a) $L_S = S^{p+q}.p^p.q^q$ (b) $L_S = S^{p+q}.p^q.q^p$
(c) $L_S = S^{pq}.p^p.q^q$ (d) $L_S = S^{pq}.(pq)^{p+q}$

35. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction $N_2O_4 \rightleftharpoons 2NO_2$ is expressed by $K_p = (4x^2P)/(1-x^2)$, where P = pressure, x = extent of decomposition. Which one of the following statements is true? *(2001S)*

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

36. Consider the following equilibrium in a closed container *(2002S)*

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

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

(a) neither K_p nor α changes
(b) both K_p and α change
(c) K_p changes, but α does not change
(d) K_p does not change, but α changes

37. A weak acid HX has the dissociation constant 1×10^{-5} M. It forms a salt NaX on reaction with alkali. The percentage hydrolysis of 0.1 M solution of NaX is *(2004S)*

(a) 0.0001% (b) 0.01%
(c) 0.1% (d) 0.15%

38. A 0.004 M solution of Na_2SO_4 is isotonic with 0.010 M solution of glucose at same temperature. The percentage dissociation of Na_2SO_4 is *(2004S)*

(a) 25% (b) 50%
(c) 75% (d) 85%

39. 0.1 mole of CH_3NH_2 ($K_b = 5 \times 10^{-4}$) is mixed with 0.08 mole of HCl and diluted to one litre. What will be the H^+ concentration in the solution? *(2005S)*

(a) 8×10^{-2} M (b) 8×10^{-11} M
(c) 1.6×10^{-11} M (d) 8×10^{-5} M

40. The Haber's process for the formation of NH_3 at 298K is $N_2 + 3H_2 \rightleftharpoons 2NH_3$; $\Delta H = -46.0$ kJ; Which of the following is the correct statement *(2006 - 3M, –1)*

(a) The condition for equilibrium is

$$G_{N_2} + 3G_{H_2} = 2G_{NH_3}$$

where G is Gibb's free energy per mole of the gaseous species measured at that partial pressure.

(b) On adding N_2, the equilibrium will shift to forward direction because according to IInd law of thermodynamics the entropy must increase in the direction of spontaneous reaction

(c) The catalyst will increase the rate of forward reaction by 2 times and that of backward reaction by 1.5 times

(d) None of these

41. 2.5 ml of (2/5) M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°) is titrated (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) *(2008S)*

(a) 3.7×10^{-14} M (b) 3.2×10^{-7} M
(c) 3.2×10^{-2} M (d) 2.7×10^{-2} M

42. Solubility product constant (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature T are 4.0×10^{-8}, 3.2×10^{-14} & 2.7×10^{-15}, respectively. Solubilities (mol dm^{-3}) of the salts at temperature 'T' are in the order – *(2008S)*

(a) $MX > MX_2 > M_3X$ (b) $M_3X > MX_2 > MX$
(c) $MX_2 > M_3X > MX$ (d) $MX > M_3X > MX_2$

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D MCQs with One or More Than One Correct

1. For the gas phase reaction : *(1984 - 1 Mark)*

$$C_2H_4 + H_2 \rightleftharpoons C_2H_6 \ (\Delta H = -32.7 \text{ kcal})$$

carried out in a vessel, the equilibrium concentration of C_2H_4 can be increased by :

(a) increasing the temperature
(b) decreasing the pressure
(c) removing some H_2
(d) adding some C_2H_6

2. When $NaNO_3$ is heated in a closed vessel, oxygen is liberated and $NaNO_2$ is left behind. At equilibrium. *(1986 - 1 Mark)*

(a) addition of $NaNO_2$ favours reverse reaction
(b) addition of $NaNO_3$ favours forward reaction
(c) increasing temperature favours forward reaction
(d) increasing pressure favours reverse reaction

3. The equilibrium : *(1989 - 1 Mark)*

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

is attained at 25°C in a closed container and an inert gas, helium is introduced. Which of the following statements are correct?

(a) Concentration of SO_2, Cl_2 and SO_2Cl_2 do not change
(b) More chlorine is formed
(c) Concentration of SO_2 is reduced
(d) More SO_2Cl_2 is formed.

4. For the reaction : *(1991 - 1 Mark)*

$$PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$$

The forward reaction at constant temperature is favoured by

(a) introducing an inert gas at constant volume
(b) introducing chlorine gas at constant volume
(c) introducing an inert gas at constant pressure
(d) increasing the volume of the container
(e) introducing PCl_5 at constant volume

5. For the reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ at a given temperature the equilibrium amount of $CO_2(g)$ can be increased by *(1998 - 2 Marks)*

(a) adding a suitable catalyst
(b) adding an inert gas
(c) decreasing the volume of the container
(d) increasing the amount of CO(g).

6. Which of the following statements(s) is (are) correct? *(1998 - 2 Marks)*

(a) The pH of 1.0×10^{-8} M solution of HCl is 8
(b) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}
(c) Autoprotolysis constant of water increases with temperature
(d) When a solution of a weak monoprotic acid is titrated against a strong base, at half-neutralisation point $pH = (1/2)\, pK_a$.

7. A buffer solution can be prepared from a mixture of *(1999 - 3 Marks)*

(a) sodium acetate and acetic acid in water
(b) sodium acetate and hydrochloric acid in water
(c) ammonia and ammonium chloride in water
(d) ammonia and sodium hydroxide in water

8. Aqueous solutions of HNO_3, KOH, CH_3COOH and CH_3COONa of identical concentrations are provided. The pair(s) of solutions which form a buffer upon mixing is(are) *(2010)*

(a) HNO_3 and CH_3COOH
(b) KOH and CH_3COONa
(c) HNO_3 and CH_3COONa
(d) CH_3COOH and CH_3COONa

9. The initial rate of hydrolysis of methyl acetate (1M) by a weak acid (HA, 1M) is 1/100th of that of a strong acid (HX, 1M), at 25°C. The K_a of HA is *(JEE Adv. 2013)*

(a) 1×10^{-4} (b) 1×10^{-5}
(c) 1×10^{-6} (d) 1×10^{-3}

10. The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M $AgNO_3$ solution is *(JEE Adv. 2013)*

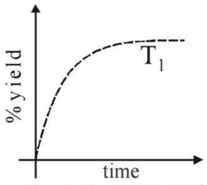
(a) 1.1×10^{-11} (b) 1.1×10^{-10}
(c) 1.1×10^{-12} (d) 1.1×10^{-9}

11. The thermal dissociation equilibrium of $CaCO_3(s)$ is studied under different conditions *(JEE Adv. 2013)*

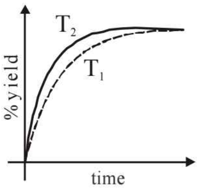
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$. For this equilibrium, the correct statement(s) is(are)

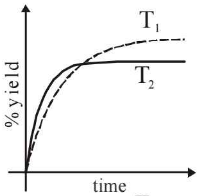
(a) ΔH is dependent on T
(b) K is independent of the initial amount of $CaCO_3$
(c) K is dependent on the pressure of CO_2 at a given T
(d) ΔH is independent of catalyst, if any

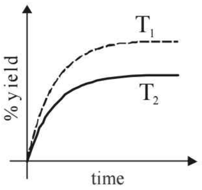
12. The %yield of ammonia as a function of time in the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H < 0$ at (P, T_1) is given below

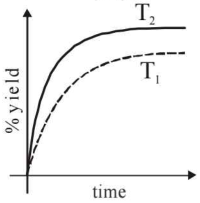


If this reaction is conducted at (P, T_2), with $T_2 > T_1$, the %yield of ammonia as a function of time is represented by *(JEE Adv. 2015)*

(a)


(b)


(c)


(d)


E Subjective Problems

1. A solution contains Na_2CO_3 and $NaHCO_3$. 10 ml of solution requires 2.5 ml of 0.1 M H_2SO_4 for neutralisation using phenolphthalein as an indicator. Methyl orange is then added when a further 2.5ml of 0.2M H_2SO_4 was required. Calculate the amount of Na_2CO_3 and $NaHCO_3$ in one litre of the solution. *(1979)*

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2. How many moles of sodium propionate should be added to one litre of an aqueous solution containing 0.020 mole of propionic acid to obtain a buffer solution of pH 4.75? What will be pH if 0.010 mole of hydrogen chloride is dissolved in the above buffer solution. Compare the last pH value with the pH of 0.010 molar HCl solution. Dissociation constant of propionic acid, K_a at 25°C = 1.34×10^{-5}.
(1981 - 4 Marks)

3. One mole of nitrogen is mixed with three moles of hydrogen in a 4 litre container. If 0.25 per cent of nitrogen is converted to ammonia by the following reaction *(1981 - 4 Marks)*
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g),$$
calculate the equilibrium constant (K_c) in concentration units. What will be the value of K_c for the following equilibrium ?
$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(ag)$$

4. Twenty ml. of 0.2 M sodium hydroxide is added to 50 ml. of 0.2 M acetic acid to give 70 ml of the solution. What is the pH of this solution? Calculate the additional volume of 0.2 M NaOH required to make the pH of the solution 4.74. The ionization constant of acetic acid is 1.8×10^{-5}.
(1982 - 3 Marks)

5. The dissociation constant of a weak acid HA is 4.9×10^{-8}. After making the necessary approximations, calculate (i) percentage ionization, (ii) pH and (iii) OH^- concentration in a decimolar solution of the acid. Water has a pH of 7.
(1983 - 2 Marks)

6. A solution contains a mixture of Ag (0.10 M) and Hg_2^{++} (0.10 M) which are to be separated by selective precipitation. Calculate the maximum concentration of iodide ion at which one of them gets precipitated almost completely. What percentage of that metal ion is precipitated?
[K_{sp} : $AgI = 8.5 \times 10^{-17}$; $Hg_2I_2 = 2.5 \times 10^{-26}$]
(1984 - 4 Marks)

7. One mole of Cl_2 and 3 moles of PCl_5 are placed in a 100 litre vessel heated to 227°C. The equilibrium pressure is 2.05 atmosphere. Assuming ideal behaviour, calculate the degree of dissociation for PCl_5 and K_p for the reaction :
$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. *(1984 - 6 Marks)*

8. Arrange the following in :
   (*i*) increasing bond length : F_2, N_2, Cl_2, O_2
   (1985 - 1 Mark)
   (*ii*) increasing acid strength : $HClO_3$, $HClO_4$, $HClO_2$, $HClO$
   (1986 - 1 Mark)
   (*iii*) increasing basicity : H_2O, OH^-, CH_3OH, CH_3O^-
   (1992 - 1 Mark)
   (*iv*) Arrange the following oxides in the decreasing order of Bronsted basicity :
   $BaO, SO_3, CO_2, Cl_2O_7, B_2O_3$
   (2004 - 2 Marks)

9. The [H^+] in 0.2 M solution of formic acid is 6.4×10^{-3} mole litre^{-1}. To this solution sodium formate is added so as to adjust the concentration of sodium formate to one mole litre^{-1}. What wil be pH of this solution? K_a for HCOOH is 2.4×10^{-4} and degree of dissociation of HCOONa is 0.75.
(1985 - 3 Marks)

10. The equilibrium constant of the reaction
$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$
at 100°C is 50. If a one litre flask containing one mole of A_2 is connected to a two litre flask containing two mole of B_2, how many mole of AB will be formed at 373°C?
(1985 - 4 Marks)

11. The solubility of $Mg(OH)_2$ in pure water is 9.57×10^{-3} g/litre. Calculate its solubility (in g/litre) in 0.02 M $Mg(NO_3)_2$ solution. *(1986 - 5 Marks)*

12. What is the pH of the solution when 0.20 mole of hydrochloric acid is added to one litre of a solution containing.
(1987 - 5 Marks)
   (i) 1 M each of acetic acid and acetate ion?
   (ii) 0.1 M each of acetic acid and acetate ion?
   Assume the total volume is one litre.
   K_a for acetic acid = 1.8×10^{-5}.

13. At a certain temperature equilibrium constant (K_c) is 16 for the reaction. *(1987 - 5 Marks)*
$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$
If we take one mole each of all the four gases in a one litre container, what would be the equilibrium concentrations of NO(g) and NO_2(g)?

14. N_2O_4 is 25% dissociated at 37°C and one atmosphere pressure. Calculate (i) K_p and (ii) the percentage dissociation at 0.1 atmosphere and 37°C. *(1988 - 4 Marks)*

15. How many gram-mole of HCl will be required to prepare one litre of buffer solution (containing NaCN and HCl) of pH 8.5 using 0.01 gram formula weight of NaCN?
K dissociation (HCN) = 4.1×10^{-10}. *(1988 - 4 Marks)*

16. The equilibrium constant K_p of the reaction :
$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
is 900 atm. at 800 K. A mixture containing SO_3 and O_2 having initial partial pressure of 1 and 2 atm. respectively is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at 800 K. *(1989 - 3 Marks)*

17. Freshly precipitated aluminium and magnesium hydroxides are stirred vigorously in a buffer solution containing 0.25 mole/*l* of ammonium chloride and 0.05 mole/*l* of ammonium hydroxide. Calculate the concentration of aluminium and magnesium ions in solution: *(1989- 3 Marks)*
$$K_b[NH_4OH] = 1.80 \times 10^{-5}$$
$$K_{sp}\,[Mg(OH)_2] = 6 \times 10^{-10}$$
$$K_{sp}\,[Al(OH)_3] = 6 \times 10^{-32}$$

18. For the reaction : $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$
hydrogen gas is introduced into a five litre flask at 327°C, containing 0.2 mole of CO(g) and a catalyst, until the pressure is 4.92 atm. At this point 0.1 mole of CH_3OH(g) is formed. Calculate the equilibrium constant, K_p and K_c.
(1990 - 5 Marks)

19. What is the pH of 1.0 M solution of acetic acid? To what volume must one liter of this solution be diluted so that the pH of the resulting solution will be twice the original value? Given : $K_a = 1.8 \times 10^{-5}$. *(1990 - 4 Marks)*

20. The solubility product of $Ag_2C_2O_4$ at 25°C is 1.29×10^{-11} mol^3 l^{-3}. A solution of $K_2C_2O_4$ containing 0.1520 mole in 500 ml water is shaken at 25°C with excess of Ag_2CO_3 till the following equilibrium is reached : *(1991 - 4 Marks)*
$$Ag_2CO_3 + K_2C_2O_4 \rightleftharpoons Ag_2C_2O_4 + K_2CO_3$$
At equilibrium the solution contains 0.0358 mole of K_2CO_3. Assuming the degree of dissociation of $K_2C_2O_4$ and K_2CO_3 to be equal, calculate the solubility product of Ag_2CO_3.

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21. A 40.0 ml solution of weak base, BOH is titrated with 0.1N HCl solution. The pH of the solution is found to be 10.04 and 9.14 after adding 5.0 ml and 20.0 ml of the acid respectively. Find out the dissociation constant of the base. ***(1991 - 6 Marks)***

22. The solubility product (K_{sp}) of $Ca(OH)_2$ at 25°C is 4.42×10^{-5}. A 500 ml. of saturated solution of $Ca(OH)_2$ is mixed with equal volume of 0.4 M NaOH. How much $Ca(OH)_2$ in milligrams is precipitated? ***(1992 - 4 Marks)***

23. 0.15 mole of CO taken in a 2.5 *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 8.5 atmosphere at equilibrium and 0.08 mole of methanol is formed. Calculate (i) K_p and K_c and (ii) the final pressure if the same amount of CO and H_2 as before are used, but with no catalyst so that the reaction does not take place. ***(1993 - 5 Marks)***

24. The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5M $NaHCO_3$ solution should be mixed with a 10 ml sample of blood which is 2M in H_2CO_3 in order to maintain a pH of 7.4 ? K_a for H_2CO_3 in blood is 7.8×10^{-7}. ***(1993 - 2 Marks)***

25. An aqueous solution of a metal bromide MBr_2 (0.05M) is saturated with H_2S. What is the minimum pH at which MS will precipitate? ***(1993 - 3 Marks)***

K_{sp} for $MS = 6.0 \times 10^{-21}$; concentration of saturated $H_2S = 0.1$ M

$K_1 = 10^{-7}$ and $K_2 = 1.3 \times 10^{-13}$, for H_2S.

26. At temperature *T*, a compound AB_2 (g) dissociates according to the reaction ***(1994 - 4 Marks)***

$$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$$

with a degree of dissociation x which is small compared with unity. Deduce the expression for x in terms of the equilibrium constant K_p and the total pressure, *P*.

27. For the reaction

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

the equilibrium constant, at 25°C , is 4.0×10^{-19}. Calculate the silver ion concentration in a solution which was originally 0.10 molar in KCN and 0.03 molar in $AgNO_3$. ***(1994 - 3 Marks)***

28. Calculate the pH of an aqueous solution of 1.0 M ammonium formate assuming complete dissociation.

(pK_a of formic acid = 3.8 and pK_b of ammonia = 4.8.) ***(1995 - 2 Marks)***

29. What is the pH of a 0.50 M aqueous NaCN solution? pK_b of CN^- is 4.70. ***(1996 - 2 Marks)***

30. A sample of AgCl was treated with 5.00 mL of 1.5 M Na_2CO_3 solution to give Ag_2CO_3. The remaining solution contained 0.0026 g of Cl^- per litre. Calculate the solubility product of AgCl ($K_{sp}(Ag_2CO_3) = 8.2 \times 10^{-12}$). ***(1997 - 5 Marks)***

31. An acid type indicator, HIn differs in colour from its conjugate base (In^-). The human eye is sensitive to colour differences only when the ratio$[In^-]/[HIn]$ is greater than 10 or smaller than. 0.1. What should be the minimum change in the pH of the solution to observe a complete colour change ($K_a = 1.0 \times 10^{-5}$)? ***(1997 - 2 Marks)***

32. Given : $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$, $K_c = 6.2 \times 10^{-8}$ and K_{sp} of AgCl $= 1.8 \times 10^{-10}$ at 298 K. If ammonia is added to a water solution containing excess of AgCl(s) only, calculate the concentration of the complex in 1.0 M aqueous ammonia. ***(1998 - 5 Marks)***

33. What will be the resultant pH when 200mL of an aqueous solution of HCl (pH = 2.0) is mixed with 300 mL of an aqueous solution of NaOH (pH = 12.0) ? ***(1998 - 2 Marks)***

34. When 3.06 g of solid NH_4HS is introduced into a two litre evacuated flask at 27° C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide. (i) Calculate K_c and K_p for the reaction at 27°C. (ii) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask ? ***(1999 - 7 Marks)***

35. The solubility of $Pb(OH)_2$ in water is 6.7×10^{-6} M. Calculate the solubility of $Pb(OH)_2$ in a buffer solution of pH = 8. ***(1999 - 4 Marks)***

36. 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 1.3653 moles $litre^{-1}$ and the pK_a of H_2SO_3 is 1.92, estimate the pH of rain on that day. ***(2000 - 5 Marks)***

37. 500 mL of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25°C.

(i) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.

(ii) If 6 g of NaOH is added to the above solution, determine the final pH.
[Assume there is no change in volume on mixing; K_a of acetic acid is 1.75×10^{-5} mol L^{-1}]. ***(2002 - 5 Marks)***

38. Match the following if the molecular weights of *X*, *Y* and *Z* are same. ***(2003 - 2 Marks)***

	Boiling Point	K_b
x	100	0.63
y	27	0.53
z	253	0.98

G Comprehension Based Questions

PARAGRAPH 1

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7 °C was measured for the beaker and its contents (Expt. 1). Because the enthalpy of neutralization of a strong acid with a strong base is a constant (–57.0 kJ mol^{-1}), this experiment could be used to measure the calorimeter constant. In a second experiment (Expt. 2), 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to Expt. 1) where a temperature rise of 5.6 °C was measured. (Consider heat capacity of all solutions as 4.2 J g^{-1} K^{-1} and density of all solutions as 1.0 g mL^{-1}) ***(JEE Adv. 2015)***

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1. Enthalpy of dissociation (in kJ mol^{-1}) of acetic acid obtained from the Expt.2 is
   (a) 1.0 (b) 10.0 (c) 24.5 (d) 51.4
2. The pH of the solution after Expt. 2 is
   (a) 2.8 (b) 4.7
   (c) 5.0 (d) 7.0

PARAGRAPH 2

Thermal decomposition of gaseous X_2 to gaseous X at 298 K takes place according to the following equation:

$$X_2(g) \rightleftharpoons 2X(g)$$

The standard reaction Gibbs energy, $\Delta_r G^\circ$, of this reaction is positive. At the start of the reaction, there is one mole of X_2 and no X. As the reaction proceeds, the number of moles of X formed is given by β. Thus, $\beta_{equilibrium}$ is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally.

(Given R = 0.083 L bar K^{-1} mol^{-1}) *(JEE Adv. 2016)*

3. The equilibrium constant K_p for this reaction at 298 K, in terms of $\beta_{equilibrium}$, is
   (a) $\dfrac{8\beta^2_{equilibrium}}{2-\beta_{equilibrium}}$ (b) $\dfrac{8\beta^2_{equilibrium}}{4-\beta^2_{equilibrium}}$
   (c) $\dfrac{4\beta^2_{equilibrium}}{2-\beta_{equilibrium}}$ (d) $\dfrac{4\beta^2_{equilibrium}}{4-\beta^2_{equilibrium}}$
4. The INCORRECT statement among the following, for this reaction, is
   (a) Decrease in the total pressure will result in formation of more moles of gaseous X
   (b) At the start of the reaction, dissociation of gaseous X_2 takes place spontaneously
   (c) $\beta_{equilibrium} = 0.7$
   (d) $K_C < 1$

H Assertion & Reason Type Questions

1. **Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 5 choices (a), (b), (c) and (d) out of which ONLY ONE is correct. Mark your answer as**
   (a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -2.
   (b) If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement -1.
   (c) If Statement -1 is correct but Statement -2 is incorrect.
   (d) If Statement -1 is incorrect but Statement -2 is correct.

   Statement -1 The endothermic reactions are favoured at lower temperature and the exothermic reactions are favoured at higher temperature.

   Statement -2 When a system in equilibrium is disturbed by changing the temperature, it will tend to adjust itself so as to overcome the effect of change. *(1991 - 2 Marks)*
2. Read the following statement and explanation and answer as per the options given below :

   Statement -1 HNO_3 is a stronger acid than HNO_2

   Statement -2 In HNO_3 there are two nitrogen-to-oxygen bonds whereas in HNO_2 there is only one. *(1998 - 2 Marks)*
3. **Statement -1** For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.

   Statement -2 At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy. *(2008)*

I Integer Value Correct Type

1. 0.1 M NaOH is titrated with 0.1 M HA till the end point; K_a for HA is 5.6×10^{-6} and degree of hydrolysis is less compared to 1. Calculate pH of the resulting solution at the end point. *(2004 - 2 Marks)*
2. The dissociation constant of a substituted benzoic acid at 25°C is 1.0×10^{-4}. The pH of a 0.01 M solution of its sodium salt is *(2009 - 2 Marks)*
3. Amongst the following, the total number of compounds whose aqueous solution turns red litmus paper blue is
   KCN, K_2SO_4, $(NH_4)_2C_2O_4$, NaCl, $Zn(NO_3)_2$, $FeCl_3$, K_2CO_3, NH_4NO_3 and LiCN *(2010)*
4. The total number of diprotic acids among the following is:
   H_3PO_4, H_2SO_4, H_3PO_3, H_2CO_3, $H_2S_2O_7$, H_3BO_3, H_3PO_2, H_2CrO_4 and H_2SO_3. *(2010)*
5. In 1 L saturated solution of AgCl [$K_{sp}(AgCl) = 1.6 \times 10^{-10}$], 0.1 mol of CuCl [$K_{sp}(CuCl) = 1.0 \times 10^{-6}$] is added. The resultant concentration of Ag^+ in the solution is 1.6×10^{-x}. The value of "x" is *(2011)*

Section-B JEE Main / AIEEE

1. 1 M NaCl and 1 M HCl are present in an aqueous solution. The solution is **[2002]**
   (a) not a buffer solution with pH < 7
   (b) not a buffer solution with pH > 7
   (c) a buffer solution with pH < 7
   (d) a buffer solution with pH > 7.
2. Species acting as both Bronsted acid and base is
   (a) $(HSO_4)^{-1}$ (b) Na_2CO_3 **[2002]**
   (c) NH_3 (d) OH^{-1}.
3. Let the solubility of an aqueous solution of $Mg(OH)_2$ be x then its K_{sp} is **[2002]**
   (a) $4x^3$ (b) $108x^5$
   (c) $27x^4$ (d) $9x$.
4. Change in volume of the system does not alter which of the following equilibria? **[2002]**

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(a) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
(b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
(c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
(d) $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$.

5. For the reaction $CO(g) + (1/2)O_2(g) = CO_2(g)$, K_p/K_c is **[2002]**
(a) RT (b) $(RT)^{-1}$
(c) $(RT)^{-1/2}$ (d) $(RT)^{1/2}$

6. Which one of the following statements is not true? **[2003]**
(a) pH + pOH = 14 for all aqueous solutions
(b) The pH of 1×10^{-8} M HCl is 8
(c) 96,500 coulombs of electricity when passed through a $CuSO_4$ solution deposits 1 gram equivalent of copper at the cathode
(d) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}

7. The solubility in water of a sparingly soluble salt AB_2 is 1.0×10^{-5} mol L^{-1}. Its solubility product number will be **[2003]**
(a) 4×10^{-10} (b) 1×10^{-15}
(c) 1×10^{-10} (d) 4×10^{-15}

8. For the reaction equilibrium **[2003]**
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$
the concentrations of N_2O_4 and NO_2 at equilibrium are 4.8×10^{-2} and 1.2×10^{-2} mol L^{-1} respectively. The value of K_c for the reaction is
(a) 3×10^{-1} mol L^{-1} (b) 3×10^{-3} mol L^{-1}
(c) 3×10^{3} mol L^{-1} (d) 3.3×10^{2} mol L^{-1}

9. Consider the reaction equilibrium **[2003]**
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g); \Delta H° = -198$ kJ
On the basis of Le Chatelier's principle, the condition favourable for the forward reaction is
(a) increasing temperature as well as pressure
(b) lowering the temperature and increasing the pressure
(c) any value of temperature and pressure
(d) lowering of temperature as well as pressure

10. When rain is accompanied by a thunderstorm, the collected rain water will have a pH value **[2003]**
(a) slightly higher than that when the thunderstorm is not there
(b) uninfluenced by occurrence of thunderstorm
(c) which depends on the amount of dust in air
(d) slightly lower than that of rain water without thunderstorm.

11. The conjugate base of $H_2PO_4^-$ is **[2004]**
(a) H_3PO_4 (b) P_2O_5
(c) PO_4^{3-} (d) HPO_4^{2-}

12. What is the equilibrium expression for the reaction
$P_4(s) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)$? **[2004]**
(a) $K_c = [O_2]^5$
(b) $K_c = [P_4O_{10}]/5[P_4][O_2]$
(c) $K_c = [P_4O_{10}]/[P_4][O_2]^5$
(d) $K_c = 1/[O_2]^5$

13. For the reaction, $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$ the K_p/K_c is equal to **[2004]**
(a) $\sqrt{RT}$ (b) RT
(c) $1/RT$ (d) 1.0

14. The equilibrium constant for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ at temperature T is 4×10^{-4}. The value of K_c for the reaction
$NO_2(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$ at the same temperature is
(a) 4×10^{-4} (b) 50 **[2004]**
(c) 2.5×10^2 (d) 0.02

15. The molar solubility (in mol L^{-1}) of a sparingly soluble salt MX_4 is 's'. The corresponding solubility product is K_{sp}. 's' is given in term of K_{sp} by the relation : **[2004]**
(a) $s = (256K_{sp})^{1/5}$ (b) $s = (128K_{sp})^{1/4}$
(c) $s = (K_{sp}/128)^{1/4}$ (d) $s = (K_{sp}/256)^{1/5}$

16. If α is the degree of dissociation of Na_2SO_4, the Vant Hoff's factor (i) used for calculating the molecular mass is **[2005]**
(a) $1 - 2\alpha$ (b) $1 + 2\alpha$
(c) $1 - \alpha$ (d) $1 + \alpha$

17. The solubility product of a salt having general formula MX_2, in water is : 4×10^{-12}. The concentration of M^{2+} ions in the aqueous solution of the salt is **[2005]**
(a) 4.0×10^{-10} M (b) 1.6×10^{-4} M
(c) 1.0×10^{-4} M (d) 2.0×10^{-6} M

18. The exothermic formation of ClF_3 is represented by the equation :
$Cl_2(g) + 3F_2(g) \rightleftharpoons 2ClF_3(g)$; $\Delta H = -329$ kJ
Which of the following will increase the quantity of ClF_3 in an equilibrium mixture of Cl_2, F_2 and ClF_3? **[2005]**
(a) Adding F_2
(b) Increasing the volume of the container
(c) Removing Cl_2
(d) Increasing the temperature

19. For the reaction : $2NO_{2(g)} \rightleftharpoons 2NO_{(g)} + O_{2(g)}$,
($K_c = 1.8 \times 10^{-6}$ at 184°C) (R = 0.0831 kJ/(mol. K))

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When K_p and K_c are compared at 184°C, it is found that **[2005]**

(a) Whether K_p is greater than, less than or equal to K_c depends upon the total gas pressure

(b) $K_p = K_c$

(c) K_p is less than K_c

(d) K_p is greater than K_c

20. Hydrogen ion concentration in mol/L in a solution of pH = 5.4 will be : **[2005]**

(a) 3.98×10^{-6} (b) 3.68×10^{-6}

(c) 3.88×10^{6} (d) 3.98×10^{8}

21. What is the conjugate base of OH^- ? **[2005]**

(a) O^{2-} (b) O^-

(c) H_2O (d) O_2

22. An amount of solid NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. Ammonium hydrogen sulphide decomposes to yield NH_3 and H_2S gases in the flask. When the decomposition reaction reaches equilibrium, the total pressure in the flask rises to 0.84 atm? The equilibrium constant for NH_4HS decomposition at this temperature is

(a) 0.11 (b) 0.17 **[2005]**

(c) 0.18 (d) 0.30

23. Phosphorus pentachloride dissociates as follows, in a closed reaction vessel **[2006]**

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

If total pressure at equilibrium of the reaction mixture is P and degree of dissociation of PCl_5 is x, the partial pressure of PCl_3 will be

(a) $\left(\frac{x}{x-1}\right)P$ (b) $\left(\frac{x}{1-x}\right)P$

(c) $\left(\frac{x}{x+1}\right)P$ (d) $\left(\frac{2x}{1-x}\right)P$

24. The equilibrium constant for the reaction

$$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$$

is $K_c = 4.9 \times 10^{-2}$. The value of K_c for the reaction

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

will be **[2006]**

(a) 9.8×10^{-2} (b) 4.9×10^{-2}

(c) 416 (c) 2.40×10^{-3}

25. Given the data at 25°C

$$Ag + I^- \longrightarrow AgI + e^- \quad E° = 0.152\ V$$

$$Ag \longrightarrow Ag^+ + e^- \quad E° = -0.800\ V$$

What is the value of $\log K_{sp}$ for AgI? ($2.303\ RT/F = 0.059$ V)

(a) –37.83 (b) –16.13 **[2006]**

(c) –8.12 (d) +8.612

26. The first and second dissociation constants of an acid H_2A are 1.0×10^{-5} and 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be **[2007]**

(a) 0.2×10^{5} (b) 5.0×10^{-5}

(c) 5.0×10^{15} (d) 5.0×10^{-15}.

27. The pK_a of a weak acid (HA) is 4.5. The pOH of an aqueous buffer solution of HA in which 50% of the acid is ionized is

(a) 7.0 (b) 4.5 **[2007]**

(c) 2.5 (d) 9.5

28. In a saturated solution of the sparingly soluble strong electrolyte $AgIO_3$ (molecular mass = 283) the equilibrium which sets in is $AgIO_{3\,(s)} \rightleftharpoons Ag^+_{(aq)} + IO^-_{3(aq)}$. If the solubility product constant K_{sp} of $AgIO_3$ at a given temperature is 1.0×10^{-8}, what is the mass of $AgIO_3$ contained in 100 ml of its saturated saolution? **[2007]**

(a) 1.0×10^{-4} g (b) 28.3×10^{-2} g

(c) 2.83×10^{-3} g (d) 1.0×10^{-7} g.

29. The equilibrium constants K_{p_1} and K_{p_2} for the reactions $X \rightleftharpoons 2Y$ and $Z \rightleftharpoons P + Q$, respectively are in the ratio of 1 : 9. If the degree of dissociation of X and Z be equal then the ratio of total pressures at these equilibria is **[2008]**

(a) 1:36 (b) 1 : 1

(c) 1 : 3 (d) 1 : 9

30. For the following three reactions a, b and c, equilibrium constants are given: **[2008]**

(i) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g); K_1$

(ii) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g); K_2$

(iii) $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g); K_3$

(a) $K_1\sqrt{K_2} = K_3$ (b) $K_2K_3 = K_1$

(c) $K_3 = K_1K_2$ (d) $K_3.K_2^3 = K_1^2$

31. Four species are listed below: **[2008]**

i. HCO_3^- ii. H_3O^+

iii. HSO_4^- iv. HSO_3F

Which one of the following is the correct sequence of their acid strength?

(a) iv < ii < iii < i (b) ii < iii < i < iv

(c) i < iii < ii < iv (v) iii < i < iv < ii

32. The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the correspondng salt, BA, will be **[2008]**

(a) 9.58 (b) 4.79

(c) 7.01 (d) 9.22

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33. Solid $Ba(NO_3)_2$ is gradually dissolved in a 1.0×10^{-4} M Na_2CO_3 solution. At what concentration of Ba^{2+} will a precipitate begin to form? (K_{SP} for for $BaCO_3 = 5.1 \times 10^{-9}$) **[2009]**

(a) 5.1×10^{-5} M
(b) 8.1×10^{-8} M
(c) 8.1×10^{-7} M
(d) 4.1×10^{-5} M

34. Three reactions involving $H_2PO_4^-$ are given below :

(i) $H_3PO_4 + H_2O \rightarrow H_3O^+ + H_2PO_4^-$
(ii) $H_2PO_4^- + H_2O \rightarrow HPO_4^{2-} + H_3O^+$
(iii) $H_2PO_4^- + OH^- \rightarrow H_3PO_4 + O^{2-}$

In which of the above does $H_2PO_4^-$ act as an acid ? **[2010]**

(a) (ii) only
(b) (i) and (ii)
(c) (iii) only
(d) (i) only

35. In aqueous solution the ionization constants for carbonic acid are

$K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$.

Select the correct statement for a saturated 0.034 M solution of the carbonic acid. **[2010]**

(a) The concentration of CO_3^{2-} is 0.034 M.
(b) The concentration of CO_3^{2-} is greater than that of HCO_3^-.
(c) The concentrations of H^+ and HCO_3^- are approximately equal.
(d) The concentration of H^+ is double that of CO_3^{2-}.

36. Solubility product of silver bromide is 5.0×10^{-13}. The quantity of potassium bromide (molar mass taken as 120 g mol^{-1}) to be added to 1 litre of 0.05 M solution of silver nitrate to start the precipitation of AgBr is **[2010]**

(a) 1.2×10^{-10} g
(b) 1.2×10^{-9} g
(c) 6.2×10^{-5} g
(d) 5.0×10^{-8} g

37. At 25°C, the solubility product of $Mg(OH)_2$ is 1.0×10^{-11}. At which pH, will Mg^{2+} ions start precipitating in the form of $Mg(OH)_2$ from a solution of 0.001 M Mg^{2+} ions? **[2010]**

(a) 9
(b) 10
(c) 11
(d) 8

38. A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm. Some of the CO_2 is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K is : **[2011]**

(a) 1.8 atm
(b) 3 atm
(c) 0.3 atm
(d) 0.18 atm

39. The equilibrium constant (K_c) for the reaction $N_2(g) + O_2(g) \rightarrow 2NO(g)$ at temperature T is 4×10^{-4}. The value of K_c for the reaction **[2012]**

$NO(g) \rightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$ at the same temperature is:

(a) 0.02
(b) 2.5×10^2
(c) 4×10^{-4}
(d) 50.0

40. The pH of a 0.1 molar solution of the acid HQ is 3. The value of the ionization constant, K_a of the acid is : **[2012]**

(a) 3×10^{-1}
(b) 1×10^{-3}
(c) 1×10^{-5}
(d) 1×10^{-7}

41. How many litres of water must be added to 1 litre an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2 ? **[JEE M 2013]**

(a) 0.1 L
(b) 0.9 L
(c) 2.0 L
(d) 9.0 L

42. For the reaction $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$, if $K_P = K_C(RT)^x$ where the symbols have usual meaning then the value of x is (assuming ideality): **[JEE M 2014]**

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

43. The standard Gibbs energy change at 300 K for the reaction $2A \rightleftharpoons B + C$ is 2494.2 J. At a given time, the composition of the reaction mixture is $[A] = \frac{1}{2}$, $[B] = 2$ and $[C] = \frac{1}{2}$. The reaction proceeds in the : [$R = 8.314$ J/K/mol, $e = 2.718$] **[JEE M 2015]**

(a) forward direction because $Q < K_c$
(b) reverse direction because $Q < K_c$
(c) forward direction because $Q > K_c$
(d) reverse direction because $Q > K_c$

44. The following reaction is performed at 298 K.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

The standard free energy of formation of NO(g) is 86.6 kj/mol at 298 K. What is the standard free energy of formation of $NO_2(g)$ at 298 K? ($K_p = 1.6 \times 10^{12}$) **[JEE M 2015]**

(a) $86600 - \frac{\ln(1.6 \times 10^{12})}{R(298)}$
(b) $0.5[2 \times 86{,}600 - R(298)\ln(1.6 \times 10^{12})]$
(c) $R(298)\ln(1.6 \times 10^{12}) - 86600$
(d) $86600 + R(298)\ln(1.6 \times 10^{12})$

45. The equilibrium constant at 298 K for a reaction $A + B \rightleftharpoons C + D$ is 100. If the initial concentration of all the four species were 1 M each, then equilibrium concentration of D (in mol L^{-1}) will be : **[JEE M 2016]**

(a) 1.818
(b) 1.182
(c) 0.182
(d) 0.818

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7

Equilibrium

Section-A : JEE Advanced/ IIT-JEE

A **1.** SO_4^{2-} **2.** amphoteric **3.** $K_p = K_c(RT)^{\Delta n}$ **4.** no change **5.** I_2

B **1.** F **2.** F **3.** T **4.** F

C

1. (b)	**2.** (a)	**3.** (d)	**4.** (b)	**5.** (d)	**6.** (a)	**7.** (b)
8. (b)	**9.** (c)	**10.** (a)	**11.** (a)	**12.** (c)	**13.** (d)	**14.** (d)
15. (a)	**16.** (d)	**17.** (c)	**18.** (d)	**19.** (a)	**20.** (d)	**21.** (a)
22. (d)	**23.** (a)	**24.** (d)	**25.** (d)	**26.** (b)	**27.** (c)	**28.** (a)
29. (b)	**30.** (a)	**31.** (b)	**32.** (d)	**33.** (a)	**34.** (a)	**35.** (d)
36. (d)	**37.** (b)	**38.** (c)	**39.** (b)	**40.** (a)	**41.** (d)	**42.** (d)

D

1. (a, b, c, d)	**2.** (c, d)	**3.** (a)	**4.** (c, d, e)	**5.** (d)	**6.** (b, c)	**7.** (a, c)
8. (c, d)	**9.** (a)	**10.** (b)	**11.** (a, b, d)	**12.** (b)		

E

1. 5.3 g/l; 4.2 g/l; **2.** 1.5072×10^{-2} mol, 4.09, 2 **3.** $1.48 \times 10^{-5}\ l^2\ mol^{-2}$, 3.82×10^{-3} litre mol^{-1}

4. 4.5686, 4.86 ml **5.** (i) 7×10^{-2}%, (ii) 4.1549, (iii) 1.43×10^{-10} mol/*l*

6. 5.0×10^{-13} M, 99.83% **7.** 33.3%, 0.41

8. (i) $N_2 < O_2 < F_2 < Cl_2$, (ii) $HClO < HClO_2 < HClO_3 < HClO_4$ (iii) $H_2O < CH_3OH < OH^- < CH_3O^-$
(iv) $BaO > B_2O_3 > CO_2 > SO_3 > Cl_2O_7$

9. 4.19 **10.** 1.886 **11.** 8.7×10^{-4} g/litre **12.** 4.5686, 1

13. 1.6 moles, 0.4 moles **14.** 0.266 atm, 64% **15.** 8.85×10^{-3} M

16. $p_{SO_2} = 0.0236$ atm, $p_{O_2} = 2.0118$ atm, $p_{SO_3} = 0.9764$ atm **17.** 46.29 mol ion/*l*, 1.286×10^{-15} mol ion/*l*

18. 277.78 $mol^{-2}\ l^2$, 0.1144 atm^{-2} **19.** 2.3724, 2.78×10^4 litres

20. $3.794 \times 10^{-12}\ mol^3\ l^{-3}$ **21.** 1.828×10^{-5} **22.** 743.3 mg

23. (i) 0.05 atm^{-2}, 187.85 $mol^{-2}\ l^2$, (ii) 12.438 atm **24.** 78.36 ml **25.** 0.983

26. $\left[\frac{2K_p}{P}\right]^{1/3}$ **27.** 7.5×10^{-18} M **28.** 6.5 **29.** 11.5

30. 1.71×10^{-10} **31.** 2 **32.** 0.0538 M **33.** 11.3010

34. $8.1 \times 10^{-5}\ mol^2\ l^{-2}$, $4.90 \times 10^{-2}\ atm^2$ **35.** 1.203×10^{-3} mol $litre^{-1}$

36. 4.865 **37.** 1.75×10^{-4}, 1, 4.75 **38.** $x = 0.63, y = 0.53, z = 0.98$

G **1.** (a) **2.** (b) **3.** (b) **4.** (c)

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

I **1.** 9 **2.** 8 **3.** 3 **4.** 6 **5.** 7

Section-B : JEE Main/ AIEEE

1. (a)	**2.** (a)	**3.** (a)	**4.** (a)	**5.** (c)	**6.** (b)	**7.** (d)
8. (b)	**9.** (b)	**10.** (d)	**11.** (d)	**12.** (d)	**13.** (c)	**14.** (b)
15. (d)	**16.** (b)	**17.** (c)	**18.** (a)	**19.** (d)	**20.** (a)	**21.** (a)
22. (a)	**23.** (c)	**24.** (c)	**25.** (b)	**26.** (d)	**27.** (d)	**28.** (c)
29. (a)	**30.** (c)	**31.** (c)	**32.** (c)	**33.** (a)	**34.** (a)	**35.** (c)
36. (b)	**37.** (b)	**38.** (a)	**39.** (d)	**40.** (c)	**41.** (d)	**42.** (b)
43. (d)	**44.** (b)	**45.** (a)				

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Section-A JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. SO_4^{2-} ; Conjugate base = Acid – H^+

$\therefore$ Conjugate base of HSO_4^- is SO_4^{2-}

2. **amphoteric;** because amphoteric substances show properties of both acids and basic.

3. $k_p = k_c\,(RT)^{\Delta n}$;
Here Δn = No. of moles of gaseous products
– no. of moles of gaseous reactants
R = gas constant, and T = absolute temperature.

4. **no change;** (K_p of an equilibrium reaction is independent of the pressure of the system.)

5. I_2. $\because$ electron acceptors are Lewis acids.

B. True/False

1. **False :** $AlCl_3$ is a Lewis acid (although they do not have a proton, aprotic) because it accepts electrons (octet being incomplete).

2. **False :** K for $A_2 + B_2 \rightleftharpoons 2AB$ is $\dfrac{[AB]^2}{[A_2][B_2]}$

K' for $AB \rightleftharpoons \tfrac{1}{2}A_2 + \tfrac{1}{2}B_2$ is $\dfrac{[A_2]^{1/2}[B_2]^{1/2}}{[AB]}$

or $(K')^2 = \dfrac{[A_2][B_2]}{[AB]^2} = \dfrac{1}{K}$ $\therefore$ $K' = \sqrt{\dfrac{1}{K}}$

3. **True :** Lower the pressure, lower will be boiling point. More liquid will vapourise and temperature decreases.

4. **TIPS/Formulae :**

Dissolution of NaOH is exothermic.

False : When a solute like NaOH is added to a solvent exothermic dissolution takes place. An increase in temperature always favour endothermic process. So solutes having exothermic dissolution shows a decrease in their solubility with temperature.

C. MCQs with One Correct Answer

1. **(b)** In molten state the cations and anions become free and flow of current is due to migration of these ions in opposite directions in the electric field.

2. **(a)** **NOTE :** Acidic buffer is mixture of weak acid and its salt with common anion.
   (a) $CH_3COOH + CH_3COONH_4$ is acidic buffer.
   (b) $NH_4Cl + NH_4OH$ is basic buffer.
   (c) $H_2SO_4 + Na_2SO_4$ is not buffer because both the compounds are strong electrolytes.
   (d) $NaCl + NaOH$ is not buffer solution because both compounds are strong electrolytes.

3 **(d)** **TIPS/Formulae :**
(i) pH of acid cannot be more than 7.
(ii) While calculating pH in such case, consider contribution $[H^+]$ from water also.

Molar conc. of HCl = 10^{-8}. (given)

$\therefore$ pH = 8. But this cannot be possible as pH of an acidic solution can not be more than 7. So we have to consider $[H^+]$ coming from H_2O.

Total $[H^+] = [H^+]_{HCl} + [H^+]_{H_2O}$

Ionisation of H_2O : $H_2O \rightleftharpoons H^+ + OH^-$
$K_w = 10^{-14} = [H^+][OH^-]$
Let x be the conc. of $[H^+]$ from H_2O
or $[H^+] = x = [OH^-]$ $[\because [H^+] = [OH]^-$ in water$]$
$\therefore 10^{-14} = (x + 10^{-8})(x)$ or $x = 9.5 \times 10^{-8}$ M

[For quadratic equation $x = \dfrac{-b \pm \sqrt{4ac}}{2a}$]

$\therefore$ Total $[H^+] = 10^{-8} + 9.5 \times 10^{-8} = 10.5 \times 10^{-8}$ or pH $= -\log(10.5 \times 10^{-8}) = \mathbf{6.98}$

It is between 6 and 7.

4. **(b)** **TIPS/Formulae :**
(i) According is Le-Chateliers principle, exothermic, reactions are favoured at low temperature.
(ii) According to Le-Chateliers principle, the reaction in which $n < 0$, are favoured at high pressure.

Given $2SO_2 + O_2 \rightleftharpoons 2SO_3 + \text{Heat}$
$\because$ It is exothermic reaction
$\therefore$ Yield of SO_3 is maximum at low temperature
$n = 2 - 3 = -1$ or $n < 0$
$\therefore$ Yield of SO_3 is maximum at high pressure.

5. **(d)** Only temperature affects the equilibrium constant. Since here $\Delta H = 2 - 2 = 0$, so there is no change in K_p when total pressure changes.

6. **(a)** **TIPS/Formulae :**
(i) Lower the oxidation state of central atom, weaker will be oxy acid.
(ii) Weaker the acid, stronger will be its conjugate base.

Oxidation state of Cl in HClO is + 1, in $HClO_2$ is + 3, in $HClO_3$ is + 5, and in $HClO_4$ is + 7
$\therefore$ HClO is the weakest acid and so its conjugate base ClO^- is the strongest Bronsted base.

7. **(b)** For pure water, $[H_3O^+] = [OH^-]$
$\Rightarrow K_w = 10^{-6} \times 10^{-6} = 10^{-12}$

8. **(b)** **TIPS/Formulae :**
For precipitation to occur ionic product > solubility products

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Given, $K_{sp}CaF_2 = 1.7 \times 10^{-10}$

$$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$$

Ionic product of $CaF_2 = [Ca^{2+}]\,[F^-]^2$

Calculate I.P. in each case

(a) I.P. of $CaF_2 = (10^{-4}) \times (10^{-4})^2 = 10^{-12}$

(b) I.P. of $CaF_2 = (10^{-2}) \times (10^{-3})^2 = 10^{-8}$

(c) I.P. of $CaF_2 = (10^{-5}) \times (10^{-3})^2 = 10^{-11}$

(d) I.P. of $CaF_2 = (10^{-3}) \times (10^{-5})^2 = 10^{-13}$

$\because$ I.P > solubility in choice (b) only.

$\therefore$ ppt of CaF_2 is obtained in case of choice (b) only.

9. **(c)** Vapours and liquid are at the same temperature.

10. **(a)** Statement (a) is correct and the rest statements are wrong. K_p depends only on temperature hence at constant temp. K_p will not change.

11. **(a)** For a basic buffer, $\text{pH} = 14 - pK_b - \log\dfrac{[\text{salt}]}{[\text{base}]}$

$$\text{pH} = 14 - pK_b - \log\frac{[\text{salt}]}{[\text{base}]} = 14 - (-\log 10^{-10}) - \log 1$$

$\Rightarrow \text{pH} = 4$

12. **(c)** **TIPS/Formulae :**

The equilibrium constant for the nuetralization of a weak acid with a strong base is given by

$$K = K_a / K_w = \frac{1.0 \times 10^{-4}}{1.0 \times 10^{-14}} = 1.0 \times 10^{10}$$

13. **(d)** As all the reactants and products are present in aqueous form in (d) so it is a reversible reaction. In others either solid or gas is generated which is insoluble or volatile and hence makes the reaction unidirectional.

14. **(d)** **TIPS/Formulae :**

The pH of the solution at the equivalence point will be greater than 7 due to salt hydrolysis. So an indicator giving colour in basic medium will be suitable.

Phenolphthalein is a good indicator if the base is strong because strong base immediately changes the pH at end point.

15. **(a)** Base + $H^+ \rightarrow$ (conjugate acid)

$$NH_2^- \text{ (base)} + H^+ \rightarrow NH_3 \text{ (conjugate acid)}$$

16. **(d)** **NOTE :** Electron acceptors or elements having incomplete octet are Lewis acids.

(i) BF_3 (B has 6 e^- in valance shell), $AlCl_3$ (Al has 6 electrons in valance shell), $BeCl_2$ (Be has 4 e^- in valance shell) are electron defecient compounds and hence Lewis acids.

(ii) $SnCl_4$ has complete octet so it is Lewis base.

17. **(c)** CaO, $CaCO_3$ and $Ca(OH)_2$ dissolve in CH_3COOH due to formation of $(CH_3COO)_2Ca$. But CaC_2O_4 does not dissolve as CH_3COO^- is a stronger conjugate base than $C_2O_4^{2-}$.

18. **(d)** (a) is a neutral solution due to both cationic and anionic hydrolysis ($K_a = K_b = 1.8 \times 10^{-5}$); (b) is acidic solution due to cationic hydrolysis; (c) is acidic solution due to cationic hydrolysis; (d) is basic solution due to anionic hydrolysis.

Alternate solution. Step-1.

19. **(a)** For a precipitation to occur

Solubility product < Ionic product

Given $K_{sp} = 1.8 \times 10^{-10}$

Calculating ionic products in each

$$\text{Ionic product} = [Ag^+]\,[Cl^-] = \frac{10^{-4}}{2} \times \frac{10^{-4}}{2}$$

$$= 2.5 \times 10^{-9}$$

which is greater than K_{sp} (1.8×10^{-10}).

$$\left(\begin{array}{l}\because \text{equal volumes are mixed,} \\ \text{so } [Ag^+] = \dfrac{10^{-4}}{2} \text{ and } [Cl^-] = \dfrac{10^{-4}}{2}\end{array}\right)$$

Step-2

20. **(d)** **TIPS/Formulae :**

In acidic medium weak acids are unionized due to common ion effect and they are completely ionised in alkaline medium.

Aspirin (or acetyl salicylic acid) is unionised in stomach (where pH is 2-3) and is completely ionised in small intestine (when pH is 8).

21. **(a)** **TIPS/Formulae :**

(i) Higher the electronegatively of central atom higher will be the acidic strength.

(ii) In case of same atom higher the value of oxidation state of the metal, higher will be its acidic strength.

The electronegativity of Cl > S.

Oxidation no. of Cl in $ClO_3(OH) = +7$

Oxidation no. of Cl in $ClO_2(OH) = +5$

Oxidation no. of S in $SO(OH)_2 = +4$

Oxidation no. of S in $SO_2(OH)_2 = +6$

$\therefore$ $ClO_3(OH)$ is the strongest acid.

22. **(d)** **NOTE :** In case of alkaline earth hydroxides solubility increases on moving down the group.

$Be(OH)_2$ has lowest solubility and hence lowest solubility product. [Be at tip of the group]

23. **(a)** Due to absence of hydrolysation of $FeCl_3$ backward reaction will not take place.

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24. **(d)** Since HCl is stronger than CH_3COOH hence acts as acid. On the other hand Cl^- is a stronger base than $CH_3COOH_2^+$ and is the conjugate base of HCl.

$$\underset{\text{acid}_1}{HCl} + \underset{\text{base}_2}{CH_3COOH} \rightleftharpoons \underset{\text{base}_1}{Cl^-} + \underset{\text{acid}_2}{CH_3COOH_2^+}$$

25. **(d)** (a) It is not correct answer because 100 ml M/10 HCl will completely neutralise 100 ml M/10 NaOH and the solution will be neutral.

(b) After neutralisation resultant solution will be acidic due to presence of excess of HCl.

(c) After netralisation resultant solution will be basic due to presence of excess of NaOH.

(d) M. eq. of HCl = 75 N/5 = 15 Meq

$$\text{M.eq. of NaOH} = 25 \times \frac{1}{5} = 5\ \text{Meq}$$

$$\therefore \text{M. eq. of HCl left} = 10 \ \therefore\ [HCl] = \frac{10}{100} = M/10$$

$$\therefore pH = -\log[H^+] = -\log\left[\frac{1}{10}\right] = 1$$

26. **(b)** **TIPS/Formulae :**

$$\underset{(1-\alpha)\,c}{H_2O} \rightleftharpoons \underset{\alpha\,c}{H^+} + \underset{\alpha\,c}{OH^-}$$

$$\alpha = 1.9 \times 10^{-7};\ \text{Density of water} = \frac{1.0\ \text{gm}}{\text{cm}^3}$$

$$\therefore c = \frac{1}{18} \times 1000 = 55.56\ \text{moles/l}$$

$$\therefore [H^+] = 55.56 \times 1.9 \times 10^{-9} = 1.055 \times 10^{-7}$$

$$[\because\ 1.9 \times 10^{-}\% = 1.9 \times 10^{-9}]$$

$$\therefore K_w = [H^+][OH^-] = (1.055 \times 10^{-7})^2 = 1.0 \times 10^{-14}$$

27. **(c)** Salts of weak base and strong acid get hydrolysed in aqueous solution forming an acidic solution.

$$\underset{\text{(weak)}}{AlCl_3} + 3H_2O \longrightarrow \underset{\text{(strong)}}{Al(OH)_3} + \underset{\text{(acidic)}}{3HCl}$$

28. **(a)** Among oxyacids of the same type formed by different elements, acidic nature increases with increasing electronegativity. In general, the strength of oxyacids decreases as we go down the family in the periodic table.

HOCl (I) > HOBr (II) > HOI (III)

[In halogen groups Cl is above Br and I]

29. **(b)** The characteristics of the given solutions are:

NaCl – neutral solution

NH_4Cl – slightly acidic due to the following reaction

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

NaCN – slightly alkaline due to the following reaction

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

HCl – highly acidic

The pH of the solution will follow the order highly acidic < slightly acidic < neutral < slightly alkaline *i.e.* HCl < NH_4Cl < NaCl < NaCN

30. **(a)** The given reaction will be exothermic in nature due to the formation of three X - Y bonds from the gaseous atoms. The reaction is also accompanied with the decrease in the gaseous species (i.e. Δn is negative). Hence, the reaction will be affected by both temperature and pressure. The use of catalyst does not affect the equilibrium concentrations of the species in the chemical reaction.

31. **(b)** $K_b = K_c.(RT)^{\Delta n}$

$$\Delta n = 2 - 4 = -2 \quad K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}},$$

(R in L.atm.K^{-1} $mole^{-1}$).

32. **(d)** At initial stage of reaction, concentration of each product will increase and hence Q will increase.

33. **(a)** **TIPS/Formulae :**

For oxyacids containing similar central atom, the acid strength increases with the increase in the number of oxygen atom attached to the central atom and not attached to any other atom.

TIPS/Formulae :

Higher the oxidation number of the central atom, higher is the acidity of the species. Thus acidity follows the order

$$\text{Oxi. No. of Cl} \quad \underset{+1}{HClO} < \underset{+3}{HClO_2} < \underset{+5}{HClO_3} < \underset{+7}{HClO_4}$$

34. **(a)** $A_pB_q(s) \rightleftharpoons \underset{pS}{pA^{+q}} + \underset{qS}{qB^{-p}}$

$$\boldsymbol{L_S} = (pS)^p.(qS)^q = p^p.q^q.S^{(p+q)}$$

35. **(d)** At constant temperature K_p pressure constant. With change of pressure, x will change in such a way that K_p remains a constant.

36. **(d)** **TIPS/Formulae :**

At constant temperature K_p or K_c remains constant.

For the equilibria :

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

NOTE : $K_P = K_C$ because here $\Delta n = 1$

$[K_P = K_C \times (RT)^{\Delta n}]$ Since temperature is constant so K_c or K_p will remain constant. Further since volume is halved, the pressure will be doubled so α will decrease so as to maintain the constancy of K_c or K_p.

	N_2O_4	$\rightleftharpoons$	$2NO_2$
initial	1		0
at equilibrium	$(1-\alpha)$		2α

$\therefore$ Total mole $= 1 - \alpha + 2\alpha = 1 + \alpha$

Let total pressure = P

$$\therefore pN_2O_4 = \frac{1-\alpha}{1+\alpha}.p\ ;\ pNO_2 = \frac{2\alpha}{1-\alpha}p$$

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$$K_p = \frac{(pNO_2)^2}{pN_2O_4} = \frac{4\alpha^2 \times p}{(1-\alpha)(1+\alpha)} = \frac{4\alpha^2 p}{1-\alpha^2}$$

Since K_p = constant, so $\alpha \propto \frac{1}{\sqrt{p}}$

So when volume is halved, pressure gets doubled and thus α will decrease.

37. **(b)** $h = \sqrt{\frac{K_w}{K_a \times c}} = \sqrt{\frac{10^{-14}}{10^{-5} \times 0.1}} = 10^{-4}$;

Hence, % hydrolysis $= 10^{-4} \times 100 = 0.01$

38. **(c)** **NOTE :** For isotonic solutions, osmotic pressure is same.

$$\underset{(0.004-x)}{Na_2SO_4} \rightleftharpoons \underset{2x}{2Na^+} + \underset{x}{SO_4^{2-}}$$

Since both solutions are isotonic,
therefore, $0.004 + 2x = 0.01$; $x = 3 \times 10^{-3}$

$$\therefore \ \% \text{ Dissociation } = \frac{3 \times 10^{-3}}{0.004} \times 100 = 75\%$$

Alternate eqn. Total no. of moles $= 0.004 \times x + 2x + x$

39. **(b)** **NOTE:**

For basic buffer pH is more than 7.

$$CH_3NH_2 + HCl \longrightarrow CH_3NH_3^+Cl^-$$

	CH_3NH_2	HCl	$CH_3NH_3^+Cl^-$
Initial moles	0.1	0.08	0
Moles after mixing	0.02	0	0.08

As it is a basic buffer solution.

$$pOH = pK_b + \log \frac{0.08}{0.02} = -\log 5 \times 10^{-4} + \log 4$$

$$= 3.30 + 0.602 = 3.902$$

$pH = 14 - 3.902 = 10.09$; $[H^+] = 7.99 \times 10^{-11} \approx 8 \times 10^{-11}$ M

40. **(a)** In a reversible reaction, catalyst speeds up both the forward and backward reactions to the same extent, so (c) is wrong. At equilibrium,

$$\Delta G = G_{products} - G_{reactants} = 0$$

$$\Rightarrow 2G_{NH_3} - (G_{N_2} + 3G_{H_2}) = 0$$

$$\text{or } 2G_{NH_3} = G_{N_2} + 3G_{H_2}$$

41. **(d)** Let the weak manoacidic base be BOH, then the reaction that occurs during titration is

$BOH + HCl \rightarrow BCl + H_2O$

$$\text{Equilibrium : } \underset{C(1-h)}{B^+} + H_2O \rightleftharpoons \underset{C.h}{BOH} + \underset{C.h}{H^+}$$

Using the normality equation, $\underset{(acid)}{N_1V_1} = \underset{(base)}{N_2V_2}$

Substituting various given values, we get

$$\frac{2}{15} \times V_1 = 2.5 \times \frac{2}{5}$$

$$\text{or } V_1 = 2.5 \times \frac{2}{5} \times \frac{15}{2} = 2.5 \times 3 = 7.5 \text{ ml}$$

Then the concentration of BCl in resulting solution is given by

$$[BCl] = \frac{\frac{2}{15} \times 2.5}{10} = \frac{2}{10} \text{ or } 0.1 \text{ M}$$

$$\text{Since } K_h = \frac{K_w}{K_b} \quad \therefore K_h = \frac{1 \times 10^{-14}}{1 \times 10^{-12}} = 10^{-2}$$

$$\text{Thus } K_h = \frac{0.1h^2}{(1-h)} \quad \text{or} \quad 10^{-2} = \frac{0.1h^2}{(1-h)}$$

or $10^{-2} - 10^{-2}h = 0.1h^2$ or $0.1h^2 + 10^{-2}h - 10^{-2} = 0$

(Solving this quadratic equation for h, we get)

$$h = \frac{-10^{-2} \pm \sqrt{(10^{-2})^2 + 4 \times 10^{-1} \times 10^{-2}}}{2 \times 0.1}$$

$$\left[x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}\right] = \frac{-10^{-2} \pm \sqrt{10^{-4} + 4 \times 10^{-3}}}{2 \times 0.1}$$

$$= \frac{-0.01 \pm \sqrt{.0001 + 0.004}}{0.2} = \frac{-0.01 \pm \sqrt{0.0041}}{0.2}$$

$$= \frac{-0.01 \pm 0.64}{0.2} = \frac{0.54}{0.2} \text{ [Neglecting the negative term]}$$

$= 0.27$

$\therefore [H^+] = C.h = 0.1 \times 0.27 = 2.7 \times 10^{-2}$ M

Thus the correct answer is [d].

42. **(d)** $MX \longrightarrow \underset{s}{M^+} + \underset{s}{X^-}$ (Where s is the solubility)

$$\text{Then } K_{sp} = s^2 \quad \text{or} \quad s = \sqrt{K_{sp}}$$

Similarly for $MX_2 \longrightarrow M^{2+} + 2X^-$

$$K_{sp} = s \times (2s)^2 = 4s^3 \quad \text{or} \quad s = \left[\frac{K_{sp}}{4}\right]^{\frac{1}{3}}$$

and for $M_3X \longrightarrow \underset{3s}{3M^+} + \underset{s}{X^{-3}}$

$$K_{sp} = (3s)^3 \times s = 27s^4 \quad \text{or} \quad s = \left[\frac{K_{sp}}{27}\right]^{\frac{1}{4}}$$

From the given values of K_{sp} for MX, MX_2 and M_3X, we can find the solubilities of those salts at temperature, T.

Solubility of $MX = \sqrt{4 \times 10^{-8}} = 2 \times 10^{-4}$

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$$\text{Solubility of } MX_2 = \left[\frac{3.2\times10^{-14}}{4}\right]^{\frac{1}{3}} \text{ or } \left[\frac{32}{4}\times10^{-15}\right]^{\frac{1}{3}}$$

$$= \left[8\times10^{-15}\right]^{\frac{1}{3}} \quad \text{or} \quad 2\times10^{-15}$$

$$\text{Solubility of } M_3X = \left[\frac{2.7\times10^{-15}}{27}\right]^{\frac{1}{4}}$$

$$= \left[10^{-16}\right]^{\frac{1}{4}} \text{ or } 10^{-4}$$

Thus the solubilities are in the order $MX > M_3X > MX_2$

i.e the correct anser is (d).

D. MCQs with One or More Than One Correct

1. **(a, b, c, d)** The reaction is exothermic, hence increasing temperature will favour backward reaction (i.e. conc. of C_2H_4 increases) removing H_2 and adding C_2H_6 favours backward reaction.

2. **(c, d)** $2NaNO_3 \rightleftharpoons 2NaNO_2 + O_2$
According to Le-chatelier principle an increase in pressure always favours the reaction, where volume or moles decrease (i.e. reverse direction). As heat is added, i.e. reaction is endothermic and is supported in forward direction with increase in temperature.

3. **(a)** At constant volume, concentrations do not change.

4. **(c, d, e)** Introduction of an inert gas at constant pressure causes the equilibrium to shift in a direction in which number of moles increases. The forward reaction is further accelerated by increase in the quantity of substrate, *i.e.*, PCl_5 and by the increase of space, *i.e.*, volume of container.

5. **(d)** $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$

$$K_C = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

A catalyst simply helps in attaining the equilibrium earlier.
Addition of inert gas has no effect on a reaction because in it $\Delta n = 0$.
This equilibrium is not based upon volume because in it $\Delta n = 0$.
On increasing the amount of CO, K_C will decrease but it is constant at constant temperature, so for maintaining the constant value of K_C, the amount of CO_2 increases.

6. **(b, c)** *pH* of 1×10^{-8} M is below 7 because it is an acid.
$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$
$H_2O + H_2O \rightleftharpoons OH^- + H_3O^+$
K (Auto protolysis constant of water i.e. ionic product of water) increases with temperature. For half neutralisation of a weak acid by a weak base,

$$pH = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$[\text{Salt}] = [\text{Acid}]$, $\therefore\ pH = pK_a$

7. **(a,c)** A buffer solution is prepared by mixing a weak acid/base with salt of its conjugate base/acid.

8. **(c,d)** Any solution of a weak acid and its salt with strong base acts as an acidic buffer solution.
If volume of HNO_3 solution added is less as compared to that of CH_3COONa solution, it results in the formation of an acidic buffer solution.

$$\begin{array}{llll} CH_3COONa\ + & HNO_3 & \longrightarrow CH_3COOH & +\ NaNO_3 \\ \text{Excess} & \text{limiting reagent} & & \\ MV & MV' & - & - \\ M(V-V') & 0 & MV' & MV' \quad (V' < V) \end{array}$$

9. **(a)** As ester hydrolysis is first order with respect $[H^+]$.
$R_{HA} = K[H^+]_{HA}\,[\text{ester}]$
$R_{HX} = K[H^+]_{HX}\,[\text{ester}]$

$$\therefore \frac{R_{HA}}{R_{HX}} = \frac{[H^+]_{HA}}{[H^+]_{HX}};\ \frac{1}{100} = [H^+]_{HA} = 0.01$$

$$\begin{array}{cccc} HA & \rightleftharpoons & H^+ & + \quad A^- \\ 1-0.01 & & 0.01 & \quad 0.01 \\ \approx 1 & & & \end{array}$$

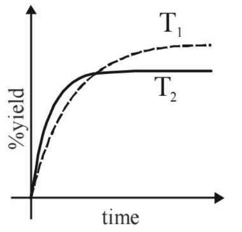
$$K_a = \frac{0.01\times0.01}{1} = 10^{-4}$$

10. **(b)** $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

$K_{sp} = 1.1\times10^{-12} = [Ag^+]^2\,[CrO_4^{-2}]$
$1.1\times10^{-12} = [0.1]^2\,[s]$; $s = 1.1\times10^{-10}$

11. **(a, b, d)**
(A) $\Delta H = C_{P(rxn)}\,\Delta T$
Hence enthalpy depends on temperature.
(B) $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)} \quad K_p = P_{CO_2}$
(C) K_{eq} depends only on temperature and not on Pressure.
(D) Enthalpy of reaction is independent of the catalyst. Catalyst generaly changes activation energy.

12. **(b)** Initially on increasing temperature rate of reaction will increase, so % yield will also increase with time. But at equilibrium % yield at high temperature (T_2) would be less than at T_1 as reaction is exothermic so the graph is



E. Subjective Problems

1. Phenolphthalein indicates half neutralization.

$$Na_2CO_3 + H^+ \longrightarrow NaHCO_3 + Na^+ \quad \text{...(i)}$$

Methyl orange indicates complete neutralisation

$$NaHCO_3 + H^+ \longrightarrow Na^+ + H_2O + CO_2 \quad \text{...(ii)}$$

$\therefore$ Volume of 0.1 M H_2SO_4 required for complete neutralisation $= 2 \times 2.5 = 5.0$ ml

0.1 M $H_2SO_4 \equiv 0.2$ N H_2SO_4

[For H_2SO_4 molarity $= 2 \times$ normality]

($\because$ Mol. wt. of $H_2SO_4 = 98$, and eq. wt. of $H_2SO_4 = 49$)

$\therefore$ 0.2 M $H_2SO_4 \equiv 0.4$ N H_2SO_4

N_1 = normality of Na_2CO_3, V_1 = volume of $Na_2CO_3 = 10$ ml,

N_2 = normality of $H_2SO_4 = 0.2$, V_2 = volume of $H_2SO_4 = 5.0$ ml

$\therefore N_1V_1 = N_2V_2 \Rightarrow N_1 \times 10 = 0.2 \times 5$

$$\therefore N_1 = \frac{0.2\times5}{10} = 0.1\text{ N}$$

$$\therefore \text{Eq. wt. of } Na_2CO_3 = \frac{1}{2} \times \text{molecular weight} = \frac{106}{2} = 53$$

Strength of $Na_2CO_3 = 53 \times 0.1 =$ **5.3 g/l**

[$\because$ strength = normality × Eq. wt]

For neutralization with methyl orange, volume of 0.2 M H_2SO_4 used = 2.5 ml = 2.5 ml of 0.4 N H_2SO_4

= 5 ml of 0.2 N H_2SO_4 $\quad [\because N_1V_1 = N_2V_2]$

From 5 ml of 0.2 N H_2SO_4, 2.5 ml is used for neutralising $NaHCO_3$ formed during first half neutralization Na_2CO_3

$\therefore$ Volume of 0.2N H_2SO_4 used for neutralisation of $NaHCO_3$ present in original solution $= 5.0 - 2.5 = 2.5$ ml

$\therefore N_1V_1 = N_2V_2$

where N_1 = Normality of $NaHCO_3$,

N_2 = Normality of $H_2SO_4 = 0.2$,

V_1 = Volume of $NaHCO_3 = 10$ ml, V_2 = Volume of $H_2SO_4 = 2.5$ ml

$N_1V_1 = N_2V_2 \Rightarrow N_1 \times 10 = 0.2 \times 2.5$

$$N_1 = \frac{0.2\times2.5}{10} = 0.05\text{ N}$$

Eq. wt. of $NaHCO_3 = 84$

$\therefore$ Strength of $NaHCO_3 = 84 \times 0.05 =$ **4.2 g/l**

2. Suppose the number of moles of sodium propionate $= x$

$$\text{Then } pH = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$4.75 = -\log(1.34 \times 10^{-5}) + \log\left(\frac{x}{0.02}\right)$$

$$\text{or } 4.75 = 5 - 0.1271 + \log\frac{x}{0.02}$$

$$\text{or } 4.75 = 4.8729 + \log\frac{x}{0.02}$$

$$\log\frac{x}{0.02} = -0.1229$$

$$\text{or } \frac{x}{0.02} = \text{Antilog}[-0.1229] \quad \text{or} \quad \frac{x}{0.02} = 0.7536$$

$x = 0.7536 \times 0.02 = \mathbf{1.5072 \times 10^{-2}}$ **mol**

$$\underset{0.01\text{ mole}}{HCl} \rightleftharpoons \underset{0.01\text{ mole}}{H^+} + Cl^-$$

When 0.01 mole of HCl is added, there is (0.01 + 0.02) M of propionic acid and (0.015 – 0.010) M of propionate. Therefore

$$pH = -\log(1.34 \times 10^{-5}) + \log\frac{0.005}{0.03} = \mathbf{4.09}$$

The pH of a 0.010 molar HCl solution $= -\log 10^{-2} =$ **2**

3.

	$N_2(g)$	+ $3H_2(g)$	$\rightleftharpoons$ $2NH_3(g)$
Initial moles	1	3	0
Eq. moles	1 – 0.0025	3 – 0.0075	2 × 0.0025
Eq. conc.	$\frac{1-0.0025}{4}$	$\frac{3-0.0075}{4}$	$\frac{2\times0.0025}{4}$

$$\text{Now we know that } K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Since 0.0025 and 0.0075 are very small, 1–0.0025 and 3–0.0075 may be taken as 1 and 3 respectively.

Substitute the various values

$$K_c = \frac{\left(\frac{2\times0.0025}{4}\right)^2}{\left[\frac{1}{4}\right]\left[\frac{3}{4}\right]^3} = \frac{0.0025\times0.0025}{4} \times \frac{4\times4\times4\times4}{3\times3\times3}$$

$= \mathbf{1.48 \times 10^{-5}}$ **litre² mol⁻²**

For the equilibrium,

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$

$$K_c' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = \sqrt{K_c}$$

$$= \sqrt{(1.48\times10^{-5}\text{ litre}^2\text{ mol}^{-2})}$$

$= \mathbf{3.82 \times 10^{-3}}$ **litre mol⁻¹**

4. **TIPS/Formulae :**

(i) Find the moles of each species after reaction.

(ii) $pH = -\log K_a + \log\left[\frac{\text{salt}}{\text{Acid}}\right]$

Given, NaOH 0.2 M, 20 ml; CH_3COOH 0.2 M, 50 ml

$K_a = 1.8 \times 10^{-5}$

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V of 0.2M NaOH required to make $pH = 4.74 = ?$

From the chemical reaction

$$\underset{50\text{ ml}}{CH_3COOH} + \underset{20\text{ ml}}{NaOH} \longrightarrow \underbrace{CH_3COONa + H_2O}_{20\text{ ml}}$$

It is evident that 70 ml of the product will contain

(i) 30 ml of 0.2 M unused CH_3COOH
[unused $CH_3COOH = 50 - 20 = 30$ ml]

(ii) 20 ml of CH_3COONa.

∴ No. of moles of CH_3COOH in solution

$$= \frac{0.2}{1000} \times 30 = 0.006 \text{ mole}$$

Similarly, No. of moles of CH_3COONa solution

$$= \frac{0.2}{1000} \times 20 = 0.004 \text{ moles}$$

$$pH = -\log K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

Substituting the values of the various values

$$pH = -\log 1.8 \times 10^{-5} + \log\frac{0.004}{0.006}$$

$$= 4.7447 - 0.1761 = \mathbf{4.5686}$$

Calculation of the additional volume of 0.2 M NaOH required to make pH of solution 4.74.

$$pH = -\log K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{or } 4.74 = -\log 1.8 \times 10^{-5} + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{or } 4.74 = 4.7447 + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\therefore \log\frac{[\text{Salt}]}{[\text{Acid}]} = 0.0047 \quad \text{or} \quad \frac{[\text{Salt}]}{[\text{Acid}]} = \frac{1}{1.011}$$

NOTE THIS STEP: Let x ml. be the volume of additional 0.2 M NaOH added to make the pH of the solution 4.74. This will further neutralise x ml. of 0.2 M CH_3COOH and produce x ml. of 0.2 M sodium acetate. The resulting solution $(70 + x)$ will now contain

(i) $(30 - x)$ ml of 0.2 M acetic acid.

(ii) $(20 + x)$ ml of 0.2 M sodium acetate.

Number of moles of acetic acid in $(70 + x)$ ml. solution

$$= \frac{0.2}{1000} \times (30 - x) = 2 \times 10^{-4}(30 - x)$$

Number of moles of CH_3COONa in $(70 + x)$ ml. solution

$$= \frac{0.2}{1000} \times (20 + x) = 2 \times 10^{-4}(20 + x)$$

$$\text{Therefore, } \frac{[\text{Salt}]}{[\text{Acid}]} = \frac{2 \times 10^{-4}(20 + x)}{2 \times 10^{-4}(30 - x)} = \frac{20 + x}{30 - x}$$

$$\frac{1}{1.011} = \frac{20 + x}{30 - x} \quad \text{or} \quad 20.22 + 1.011x = 30 - x$$

or $1.001x + x = 30 - 20.22$; $2.011x = 9.78$ or $x = 4.86$

Therefore, the additional volume of 0.2 M NaOH required to make the pH of the solution 4.74 is **4.86 ml**.

5. (i) From the dissociation of weak acid HA,

$$HA \rightleftharpoons H^+ + A^-$$

It α is the degree of ionization of the acid HA,

then $[H^+] = 0.1\,\alpha$ [∵ the acid is decimolar]

$[A^-] = 0.1\,\alpha$; $[HA] = 0.1(1 - \alpha)$

Therefore,

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{0.1\alpha \times 0.1\alpha}{0.1(1-\alpha)}$$

$$= \frac{0.1\alpha \times 0.1\alpha}{0.1} \quad \text{(since acid is weak, } 1 - \alpha = 1)$$

$K_a = 0.1\,\alpha^2$ or $4.9 \times 10^{-8} = 0.1\,\alpha^2$

$$\text{or } \alpha^2 = \frac{4.9 \times 10^{-8}}{0.1} \text{ or } \alpha = 7 \times 10^{-4}$$

∴ Percentage ionization $= 100 \times 7 \times 10^{-4} = \mathbf{7 \times 10^{-2}\%}$

(*ii*) Calculation of pH

$[H^+] = 0.1\alpha = 0.1 \times 7 \times 10^{-4}$ mole/litre $[\because \lambda = 7 \times 10^{-4}]$

$= 7 \times 10^{-5}$ mole/litre

Now since $pH = -\log[H^+] = -\log[7 \times 10^{-5}]$

$= 5 - \log 7 = 5 - 0.8451 = \mathbf{4.1549}$

(*iii*) Concentration of OH^- in decimolar solution

$[H^+] = 7 \times 10^{-5}$ mole per litre

Now, $K_w = [H^+][OH^-]$ or $1.0 \times 10^{-14} = 7 \times 10^{-5} \times [OH^-]$

$$\therefore [OH^-] = \frac{1 \times 10^{-14}}{7 \times 10^{-5}} = \mathbf{1.43 \times 10^{-10}} \textbf{ mole per litre}$$

6. **TIPS/Formulae :**

For precipitation to occur ionic product > K_{sp}.

Mixture solution contains 0.1 M Ag^+ and 0.1 Mg Hg_2^{2+}.

K_{sp} of $Hg_2I_2 = 2.5 \times 10^{-26}$ is much smaller than K_{sp} of AgI which is 8.5×10^{-17}.

$[I^-]$ concentration needed to precipitate Hg_2I_2 is calculated as :

$$Hg_2I_2 \rightleftharpoons Hg_2^{2+} + 2I^-$$

$$[I^-] = \sqrt{\frac{K_{sp}}{[Hg_2^{2+}]}} = \sqrt{\frac{2.5 \times 10^{-26}}{0.1}} = \mathbf{5.0 \times 10^{-13}\ M}$$

Similarly, $[I^-]$ concentration needed to precipitate AgI is :

$$AgI \rightleftharpoons Ag^- + I^-$$

$$[I^-] = \frac{K_{sp}}{[Ag^+]} = \frac{8.5 \times 10^{-17}}{0.1} = 8.5 \times 10^{-16}\ M$$

NOTE : Since [I^-] concentration needed to ppt. AgI is smaller than that needed to ppt. Hg_2I_2, AgI is completely precipitated first. AgI starts precipitation with [I^-] = 8.5×10^{-16} M. However, Hg_2I_2 starts precipitating with AgI only when molar concentration of I^- reaches **5.0×10^{-13} M**.

[Ag^+] left when Hg_2I_2 begins to ppt. is given by

$$\frac{K_{sp} \text{ of AgI}}{[I^-]_{Hg_2I_2}} = \frac{8.5\times10^{-17}}{5.0\times10^{-13}} = 1.7\times10^{-4}\text{ M}$$

$$\text{Thus \% [Ag}^+\text{] left unprecipitated} = \frac{1.7\times10^{-4}}{0.1}\times100$$

$$= 0.17\%$$

Hence % Ag^+ precipitated = **99.83%**

7. Let x be the degree of dissociation of $PCl_5(g)$, then

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

Initial	3	0	1
At equilibrium	$3(1-x)$	$3x$	$1+3x$

$\therefore$ Total number of moles at equilibrium

$= 3(1-x) + 3x + 1 + 3x = 3(1+x) + 1$

Using the gas equation : $PV = nRT$

$$\therefore n = \frac{PV}{RT}$$

Here, $P = 2.05$ atm., $V = 100$ litres, $R = 0.082$ atm/deg.,

$T = 273 + 227 = 500$ K

$$\therefore \quad n = \frac{2.05\times100}{0.082\times500} = 5 \quad \therefore 3(1+x)+1 = 5$$

$$\text{or} \quad 3+3x+1 = 5 \quad \text{or} \quad 3x = 5-4 \quad \text{or} \quad x = \frac{1}{3} = 0.333$$

Hence perecentage dissociation of PCl_5 = 0.333 × 100 = **33.3%**

Calculation of K_p for the reaction :

$$K_p = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\left[\frac{3xP}{3(1+x)+1}\right]\left[\frac{(1+3x)P}{3(1+x)+1}\right]}{\left[\frac{3(1-x)}{3(1+x)+1}P\right]}$$

$$= \frac{3x\,(3x+1)}{4+3x}\times\frac{1P}{3(1-x)}$$

$$= \frac{(3x^2+x)\times P}{(4+3x)\,(1-x)} = \frac{x\,(3x+1)\times P}{(4+3x)\,(1-x)}$$

Substituting, $x = 1/3$ and $P = 2.05$ atm., we get

$$K_p = \frac{\frac{1}{3}\left(3\times\frac{1}{3}+1\right)\times2.05}{\left(4+3\times\frac{1}{3}\right)\left(1-\frac{1}{3}\right)} = \frac{4.1}{10} = \mathbf{0.41}$$

8. (*i*) $N_2 < O_2 < F_2 < Cl_2$

i.e., $N\equiv N < O=O < F-F < Cl-Cl$

NOTE :

As the number of bonds increases the bond length decreases.

So $N_2 < O_2 <$ halogens. Among F_2 and Cl_2 bond length of Cl_2 will be higher because of higher atomic radii.

(*ii*) Among oxyacids of the same element, acidic nature increases with its oxidation number, *e.g.*,

$$\begin{array}{lcccc} & HOCl & < HOClO & < HOClO_2 & < HOClO_3 \\ \text{O.N. of Cl} & +1 & +3 & +5 & +7 \end{array}$$

(*iii*) $H_2O < CH_3-\ddot{\underset{\cdot}{O}}H < {}^-OH < {}^-OCH_3$

Weaker the base stronger is its conjugate acids

$H_3O^+ > CH_3\overset{+}{O}H_2 > H_2O > CH_3OH$ (Decreasing acidic order of the conjugate bases.)

(*iv*) $BaO > B_2O_3 > CO_2 > SO_3 > Cl_2O_7$

Basicity increases with increase in oxidation state ($Ba = +2, B = +3, C = +4, S = +6, Cl = +7$).

9. **TIPS/Formulae :**

For acidic buffer $pH = -\log K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$

Calculation of concentration of HCOOH.

Here, $c = 0.2$ M; [H^+] = 6.4×10^{-3}

$$[H^+] = c\alpha \text{ or } \alpha = \frac{[H^+]}{c} \Rightarrow \alpha = \frac{6.4\times10^{-3}}{0.2} = 3.2\times10^{-2}$$

NOTE : Thus the degree of dissociation of HCOOH is very low which on addition of sodium formate is further suppressed due to common ion effect.

Since the degree of dissociation is very low (3.2×10^{-2}), it can be neglected and hence [HCOOH] can be taken as 0.2 M.

Calculation of concentration of $HCOO^-$, [$HCOO^-$]

It can be obtained in the following manner :

$$HCOONa \rightleftharpoons HCOO^- + Na^+$$

At start	1	0	0
At equb.	0.25	0.75	0.75

$\therefore$ [$HCOO^-$] = 0.75

$$\text{For acidic buffer } pH = -\log K_a + \log\frac{[\text{Salt}]}{[\text{acid}]}$$

$$= -\log 2.4\times10^{-4} + \log\frac{0.75}{0.20} = \mathbf{4.19}$$

10.

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

At start	1	2	0
At equ.	$1-x$	$2-x$	$2x$

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

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

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On solving we get, $23x^2 - 75x + 50 = 0; x = 2.317$ or 0.943

The value 2.317 is inadmissable because initial concentration of reactants is 2 moles and so $x = 0.943$

$\therefore$ Moles of AB formed $= 2 \times 0.943 = \mathbf{1.886}$

11. Solubility of $Mg(OH)_2$ in water

$$S = 9.57 \times 10^{-3} \text{ g/litre} = \frac{9.57 \times 10^{-3}}{58} = 1.65 \times 10^{-4} \text{ mole/litre}$$

[$\because$ M for $Mg(OH)_2 = 58$]

$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

$K_{sp} = (S)(2S)^2 = 4S^3 = 4(1.65 \times 10^{-4})^3 = 1.8 \times 10^{-11}$ approx.

Calculation of solubility of $Mg(OH)_2$, say, x, in $Mg(NO_3)_2$

or $[Mg^{2+}] = x + 0.02; [OH^-] = x$

$K_{sp} = [Mg^{2+}][2OH^-]^2$ or $1.8 \times 10^{-11} = (x + 0.02)(2x)^2$

Neglecting x in comparison to 0.02 (common ion effect)

$$\Rightarrow 4x^2 = \frac{1.8 \times 10^{-11}}{0.02} = 9 \times 10^{-10} \quad \text{or } 2x = 3 \times 10^{-5}$$

$x = 1.5 \times 10^{-5}$ moles/litres

$= 1.5 \times 58 \times 10^{-5} = \mathbf{8.7 \times 10^{-4}}$ **g/litre.**

12. (i) Amount of HCl added = 0.20 mole

$[H^+] = 0.2$ g litre^{-1}

NOTE : Added H^+ ions will combine with the acetate ions forming acetic acid with the result concentration of acetate ions will decrease while that of acetic acid will increase.

$$\begin{array}{lcccc} & CH_3COO^- + & HCl \longrightarrow & CH_3COOH + & Cl^- \\ \text{before reaction} & 1 & 0.2 & 1 & 0 \\ \text{after reaction} & 0.8 & 0 & 1.2 & 0.2 \end{array}$$

$\therefore$ Concentration of acetate ions after adding 0.20 mole of HCl.

$[CH_3COO^-] = 1.0 - 0.2 = 0.8$ mole

Similarly, concentration of acetic acid,

$[CH_3COOH] = 1.0 + 0.2 = 1.2$ mole

$$\text{Now, } pH = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= -\log 1.8 \times 10^{-5} + \log \frac{0.8}{1.2}$$

$pH = 4.7447 + 0.3010 - 0.4771 = \mathbf{4.5686}$

(ii) Amount of HCl added = 0.20 mole

Out of 0.2 mole of $[H^+]$ added, 0.1 mole will combine with 0.1 mole of CH_3COO^- forming 0 mole of CH_3COOH.

$$\begin{array}{lcccc} & CH_3COO^- + & H^+ \rightarrow & CH_3COOH + & Cl^- \\ \text{before reaction} & 0.1 & 0.2 & 0.1 & 0 \\ \text{after reaction} & 0 & 0.1 & 0.2 & 0.1 \end{array}$$

$\therefore$ Total concentration of acetic acid $[CH_3COOH]$

$= 0.1 + 0.1 = 0.2$ mole

In presence of $[H^+]$, CH_3COOH will not ionize. Therefore, pH of the solution will be due to the presence of H^+ of HCl, *i.e.* $0.2 - 0.1 = 0.1$ mole HCl

$pH = -\log [H^+] = -\log [0.1] = \mathbf{1}$

13. Initial concentration of each gas = 1 mole

Let the No. of moles of NO_2 reacted at equilibrium = x

$$\begin{array}{lcccc} \text{Then,} & SO_2(g) + & NO_2(g) \rightleftharpoons & SO_3(g) + & NO_2(g) \\ \text{At equilibrium} & (1-x) & (1-x) & (1+x) & (1+x) \end{array}$$

$$\text{Now we know that, } \frac{[SO_3][NO]}{[SO_2][NO_2]} = K_c$$

$$\text{or } \frac{(1 + x/V)(1 + x/V)}{(1 - x/V)(1 - x/V)} = 16 \quad \text{or } \frac{(1+x)^2}{(1-x)^2} = 16 \ (\because V = 1L)$$

$$\text{or } \frac{1+x}{1-x} = 4 \quad \text{or } 1 + x = 4 - 4x \quad \text{or } 5x = 3$$

$$x = \frac{3}{5} = 0.6$$

$\therefore$ Thus the concentration of NO at equilibrium

$= 1 + x = 1 + 0.6 = \mathbf{1.6}$ **moles**

Concentration of NO_2 at equilibrium

$= 1 - x = 1 - 0.6 = \mathbf{0.4}$ **moles**

14. (i)

$$\begin{array}{lcc} & N_2O_4 \rightleftharpoons & 2NO_2 \\ \text{Before dissociation} & 1 & 0 \\ \text{After dissociation} & 1-\alpha & 2\alpha \end{array}$$

$\therefore$ Total moles $= 1 - \alpha + 2\alpha = 1 + \alpha$

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

where P is total pressure

$$K_p = \frac{\left(\frac{2 \times 0.25 \times 1}{1 + 0.25}\right)^2}{\left(\frac{1 - 0.25}{1 + 0.25} \times 1\right)} = \mathbf{0.266 \text{ atm}} \qquad [\because \alpha = 0.25]$$

$$\text{(ii)} \quad K_p = \frac{4\alpha^2 P^2 \times (1 + \alpha)}{(1+\alpha)^2 (1-\alpha) \times P} = \frac{4\alpha^2 P}{(1+\alpha)(1-\alpha)}$$

$$0.266 = \frac{4\alpha^2 \times 0.1}{1 - \alpha^2} \Rightarrow \alpha = 0.64$$

$\therefore$ Percentage dissociation = **63 %**

15. TIPS/Formulae :

$$pH = pK_a + \log\left(\frac{\text{Salt}}{\text{Acid}}\right)$$

If x moles of HCl are added then they will combine with NaCN to form x moles of very weak acid HCN.

$$\begin{array}{lcccc} & NaCN + & HCl \rightarrow & NaCl + & HCN \\ \text{At equilibrium :} & (0.01-x) & x & x & x \end{array}$$

For an acidic buffer,

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$$pH = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\therefore\ 8.5 = -\log 4.1\times 10^{-10} + \log\left(\frac{0.01-x}{x}\right)$$

or $$8.5 = (10-\log 4.1) + \log\left(\frac{0.01-x}{x}\right)$$

$$\log\left(\frac{0.01-x}{x}\right) = -0.8872 \qquad [\log 4.1 = 0.6128]$$

$$\frac{0.01-x}{x} = 0.1296$$

$x = 8.85 \times 10^{-3}$ M $=$ **8.85×10^{-3} moles of HCl**

16. **NOTE :** Since the reaction is carried out at constant volume, change in partial pressure of a species will be directly proportional to the change in its amount. Hence, we can write

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

	$2SO_2(g)$	$O_2(g)$	$2SO_3(g)$
Initial pressure	0	2 atm	1 atm
Equb. pressure	$2x$	2 atm + x	1 atm − $2x$

Where $2x$ is the change in partial pressure of SO_3 at equilibrium.

Substituting the expression of partial pressure in the expression. For K_b, we get

$$K_p = \frac{(p_{SO_3})^2}{(p_{SO_2})^2\,(p_{O_2})}$$

or $$900\ \text{atm}^{-1} = \frac{(1\ \text{atm} - 2x)^2}{(2x)^2\,(2\ \text{atm} + x)}$$

Assuming x is very small as compared to 1

$$900\ \text{atm}^{-1} = \frac{1\ \text{atm}^2}{(4x^2)\,(2\ \text{atm})}$$

On usual calculations, $x = 0.0118$ atm

Thus $p_{SO_2} = 2x = 2 \times 0.0118$ atm $=$ **0.0236 atm**

$p_{O_2} = 2$ atm $+ x = 2 + 0.0118 =$ **2.0118 atm**

$p_{SO_3} = 1$ atm $- 2x = 1 - 0.0236 =$ **0.9764 atm**

17. **TIPS/Formulae :**

$$\text{p(OH) for basic buffer} = pK_b + \log\left(\frac{\text{Salt}}{\text{Base}}\right)$$

We know that

$$\text{pOH} = pK_b + \log\frac{[\text{Salt}]}{[\text{Base}]} \quad \text{or} \quad -\log 1.8\times10^{-5} + \log\frac{0.25}{0.05}$$

$\text{pOH} = 5 - \log 1.8 + \log 5 = 5.6989 - 0.2552$

$-\log[\text{OH}^-] = 5.4437;\quad \log[\text{OH}^-] = -5.4437$

$[\text{OH}^-] = 3.5999 \times 10^{-6}$ [Taking antilog]

K_{sp} for $Mg(OH)_2 = [Mg^{2+}][OH^-]^2$

$6 \times 10^{-10} = [Mg^{2+}][3.5999 \times 10^{-6}]^2$

$$[Mg^{2+}] = \frac{6\times10^{-10}}{12.9598\times10^{-12}} = 0.4629\times10^2$$

$=$ **46.29 mole ion per litre**

K_{sp} for $Al(OH)_3 = [Al^{3+}][OH^-]^3$

$6 \times 10^{-32} = [Al^{3+}](3.5999 \times 10^{-6})^3$

$$[Al^{3+}] = \frac{6\times10^{-32}}{(3.5999\times10^{-6})^3} = \mathbf{1.286\times10^{-15}\ \text{mol ion}/l}$$

18. Let the total number of moles of all gases at equilibrium point $= n$

$P = 4.92$ atm. $V = 5l$

$R = 0.0821$ atm. $l\,\text{mol}^{-1}\,\text{K}^{-1}$ $T = 273 + 327 = 600\text{K}$

By applying the formula $PV = nRT$

$$n = \frac{PV}{RT} = \frac{4.92\times5}{0.0821\times600} = 0.5\ \text{moles}$$

(i) *Calculation of the number of moles of the individual gases at equilibrium point.*

No. of moles of CH_3OH formed $= 0.1$ (Given)

$\therefore$ No. of moles of CO (also) $= 0.1$

[$\because$ moles of CO $=$ moles of CH_3OH formed]

Hence No. of moles of $H_2 = 0.5 - (0.1 + 0.1) = 0.3$

$\therefore$ Molar concentration of various species will be

$$[CH_3OH] = [CO] = \frac{0.1}{5} = 0.02;\ [H_2] = \frac{0.3}{5} = 0.06$$

$$\therefore K_c = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{0.02}{0.02\times(0.06)^2} = \mathbf{277.78\ \text{mol}^{-2}\,l^2}$$

(ii) *Calculation of K_p.* We know that

$K_p = K_c \times (RT)^{\Delta n} = 277.78 \times (0.0821 \times 600)^{-2}$

($\Delta n = 1 - 3 = -2$)

$$= \frac{277.78}{2426.54} = \mathbf{0.1144\ \text{atm}^{-2}}$$

19. **Case I.** $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

	CH_3COOH	CH_3COO^-	H^+
At start	1	0	0
At equib.	$1-\alpha$	α	α

$$[H^+] = c\alpha = c\sqrt{\frac{K_a}{c}} = \sqrt{K_a c}$$

$$\therefore [H^+] = \sqrt{1.8\times10^{-5}\times1} = 4.24\times10^{-3}\ \text{M}$$

Thus $pH = -\log H^+ = -\log 4.24 \times 10^{-3} =$ **2.3724**

Case II. pH after dilution $= 2 \times$ original pH

$= 2 \times 2.3724 = 4.7448$

Let conc. after dilution $= c_1$

and degree of dissociation $= \alpha_1$

Since $pH = -\log[H^+]$

$4.7448 = -\log[H^+]$

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$[H^+] = 1.8 \times 10^{-5} = c_1\alpha_1 \ \therefore c_1\alpha_1 = 1.8 \times 10^{-5}$

Dissociation constant

Since $K_a = \dfrac{[CH_3COO^-][H^+]}{[CH_3COOH]}$

$$= \frac{(c_1\alpha_1)(c_1\alpha_1)}{c_1[1-\alpha_1]} = \frac{c_1\alpha^2}{(1-\alpha_1)}$$

$$1.8 \times 10^{-5} = \frac{1.8 \times 10^{-5} \times \alpha_1}{1-\alpha_1} \quad \therefore \alpha_1 = 0.5$$

Substituting the value of α_1 in the following relation

$c_1\alpha_1 = [H^+]; c_1 \times 0.5 = 1.8 \times 10^{-5}$

$$c_1 = \frac{1.8 \times 10^{-5}}{0.5} = 3.6 \times 10^{-5} \text{ M}$$

Since the number of moles of CH_3COOH before and after dilution will be same

$\therefore$ Mole of CH_3COOH before dilution = Mole of CH_3COOH after dilute

$(\because \text{Mole} = M \times V_{\text{in litre}})$

$1 \times 1 = 3.6 \times 10^{-5} \times V \Rightarrow$ $V = \mathbf{2.78 \times 10^4}$ **litres**

20.

	Ag_2CO_3 +	$K_2C_2O_4$ →	$Ag_2C_2O_4$ +	K_2CO_3
Moles at start	Excess	0.1520	0	0
Moles after reaction		0.1520–0.0358 = 0.1162	0.0358	0.0358

Molar concentration of $K_2C_2O_4$ or $C_2O_4^{2-}$ left unreacted

$$= \frac{0.1162}{0.5} = 0.2324 \text{ moles } l^{-1} \qquad [\because 500 \text{ ml} = 0.5 \text{ L}]$$

$[K_2CO_3] = [CO_3^{2-}]$ at equilibrium

$$= \frac{0.0358}{0.5} = 0.07156 \text{ moles } l^{-1}$$

Given that K_{sp} for $Ag_2C_2O_4 = 1.29 \times 10^{-11}$ mol^3 l^{-3} at 25°C

So, $[Ag^+]^2 [C_2O_4^{2-}] = 1.29 \times 10^{-11}$

or $[Ag^+]^2 \times 0.2324 = 1.29 \times 10^{-11}$

Hence $[Ag^+]^2 = \dfrac{1.29}{0.2324} \times 10^{-11}$

Then K_{sp} for Ag_2CO_3

$$= [Ag^+]^2 [CO_3^{2-}] = \frac{1.29 \times 10^{-11}}{0.2324} \times 0.0716$$

$= \mathbf{3.974 \times 10^{-12}}$ **mol^3 l^{-3}**

21. **Case I.** Write the concerned chemical reaction

	BOH +	HCl ⟶	BCl +	H_2O
Moles before reaction	x	0.1 × 5 = 0.5	0	0
Moles after reaction	$(x - 0.5)$	0	0.5	0.5
∴ Molar concentration	$\frac{x-0.5}{V}$		$\frac{0.5}{V}$	$\frac{0.5}{V}$

Since the solution represents a basic buffer, following Hendersen equation can be applied.

$$pOH = -\log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$14 - 10.04 = -\log K_b + \log \frac{0.5}{(x-0.5)} \qquad ...(i)$$

Case II.

	BOH +	HCl ⟶	BCl +	H_2O
Moles at start	x	0.1 × 20 = 2	0	0
Moles after adding 20 ml. of 0.1N HCl	$(x - 2)$	0	2	2
∴ Molar concentration	$\frac{x-2}{V_1}$	0	$\frac{2}{V_1}$	$\frac{2}{V_1}$

Again the solution is acting as basic buffer

$$\therefore pOH = -\log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$14 - 9.14 = -\log K_b + \log \frac{2}{(x-2)} \qquad ...(ii)$$

Divide (*i*) by (*ii*),

$$\frac{3.96}{4.86} = \frac{0.5}{(x-0.5)} \times \frac{(x-2)}{2} \Rightarrow x = 0.088 \text{ mol } l^{-1}$$

Substituting x in (*i*) and solving for K_b

$$3.96 = -\log K_b + \log \frac{0.5}{0.088 - 0.5}$$

$K_b = \mathbf{1.828 \times 10^{-5}}$

22. Let the solubility of $Ca(OH)_2$ in pure water = S moles/litre

$$Ca(OH)_2 \rightleftharpoons \underset{S}{Ca^{2+}} + \underset{2S}{2OH^-}$$

Then $K_{sp} = [Ca^{2+}][OH^-]^2$

$4.42 \times 10^{-5} = S \times (2S)^2; \ 4.42 \times 10^{-5} = 4S^3$

$S = 2.224 \times 10^{-2} = 0.0223$ moles litre^{-1}

$\therefore$ No. of moles of Ca^{2+} ions in 500 ml. of solution = λ

$$= \frac{0.0223 \times 500}{4000} = 0.01115$$

NOTE THIS STEP : Now when 500 ml. of saturated solution is mixed with 500 ml of 0.4M NaOH, the resultant volume is 1000 ml. The molarity of OH^- ions in the resultant solution would therefore be 0.2 M.

$$\therefore [Ca^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{4.42 \times 10^{-5}}{(0.2)^2} = 0.001105 \text{ M}$$

Thus, No. of moles of Ca^{2+} or $Ca(OH)_2$ precipitated

$= 0.01115 - 0.001105 = 0.010045$

Mass of $Ca(OH)_2$ precipitated

$= 0.010045 \times 74 = \mathbf{0.7433\ g = 743.3\ mg}$

[mole wt. of $Ca(OH)_2 = 74$]

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23. (i)

	$CO(g)$	$+\ 2H_2(g)$	$\rightleftharpoons\ CH_3OH$
Moles at start	0.15	a	0
Moles at equb.	$(0.15 - x)$	$(a - 2x)$	0.08
or	$(0.15 - 0.08)$	$(a - 0.16)$	0.08

$\therefore$ Total moles at equb. $= 0.15 - 0.08 + a - 0.16 + 0.08$

$= a - 0.01$

Total moles at equilibrium can also be calculated from the following relation

$$n = \frac{PV}{RT} = \frac{8.5 \times 2.5}{0.0821 \times 750} = 0.345$$

$\therefore 0.345 = a - 0.01$ [Comparing (i) and (ii)]

or $a = 0.355$

Thus, Moles of CO at equilibrium $= 0.15 - 0.08 = 0.07$

Moles of H_2 at equilibrium $= 0.355 - 0.16 = 0.195$

Moles of CH_3OH at equilibrium $= 0.08$

Substituting the values in the relation,

$$K_c = \frac{[CH_3OH]}{[H_2]^2\,[CO]} = \frac{0.08/2.5}{(0.195/2.5)^2 \times (0.07/2.5)}$$

$= \mathbf{187.85\ mole^{-2}\ litre^{2}}$ [$\because V = 2.5$ L]

Calculation of K_p

$K_p = K_c(RT)^{\Delta n} = 187.85 \times (0.0821 \times 750)^{-2} = \mathbf{0.05\ atm^{-2}}$

[$\because \Delta n = -2$]

(ii) *Calculation of final pressure when there is no reaction*

Moles of CO $= 0.15$; Moles of $H_2 = 0.355$

$\therefore$ Total moles $= 0.15 + 0.355 = 0.505$

$PV = nRT$

$P \times 2.5 = 0.505 \times 0.0821 \times 750 \Rightarrow P = \mathbf{12.438\ atm.}$

24. Volume of blood = 10 ml. (given)

$[H_2CO_3]$ in blood = 2 M (given)

$[NaHCO_3]$ to be added = 5 M (given)

Let volume of $NaHCO_3$ added in 10 ml blood = V ml

$$\therefore [H_2CO_3] \text{ in blood mixture} = \frac{2 \times 10}{(V + 10)}$$

$$[NaHCO_3] \text{ in blood mixture} = \frac{5 \times V}{(V + 10)}$$

$$\therefore pH = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{or } 7.4 = -\log 7.8 \times 10^{-7} + \log\frac{5V/(V+10)}{20/(V+10)} \quad \therefore V = \mathbf{78.36\ ml}$$

25. $H_2S \rightleftharpoons H^+ + HS^- \quad \therefore K_1 = \dfrac{[H^+][HS^-]}{[H_2S]}$

Further, $HS^- \rightleftharpoons H^+ + S^{2-} \quad \therefore K_2 = \dfrac{[H^+][S^{2-}]}{[HS^-]}$

Dissociation constant of H_2S, $K = K_1 \times K_2$

i.e. $K = 1 \times 10^{-7} \times 1.3 \times 10^{-13} = 1.3 \times 10^{-20}$

Now we know that

$K_{sp} = [M^{2+}][S^{2-}] \Rightarrow 6 \times 10^{-21} = 0.05 \times [S^{2-}]$

$$[S^{2-}] = \frac{6 \times 10^{-21}}{0.05} = 1.2 \times 10^{-19}$$

Substituting the various values in the following relation

$$K = \frac{[H^+]^2\,[S^{2-}]}{[H_2S]}$$

$$1.3 \times 10^{-20} = \frac{[H^+]^2[1.2 \times 10^{-19}]}{0.1} \quad \because [H_2S] = 0.1\text{ M}$$

$$[H^+]^2 = \frac{1.3 \times 10^{-20} \times 0.1}{1.2 \times 10^{-19}}$$

$$[H^+] = \sqrt{\frac{1.3 \times 10^{-20} \times 0.1}{1.2 \times 10^{-19}}} = 1.04 \times 10^{-1}$$

$pH = -\log[H^+]$; $pH = -\log(1.04 \times 10^{-1})$

$= 1.0 - \log 1.04 = 1.0 - 0.017 = \mathbf{0.983}$

26.

	$2AB_2(g)$	$\rightleftharpoons\ 2AB(g)$	$+\ B_2(g)$
Initial mole	1	0	0
Moles at equb	$1 - x$	x	$\frac{x}{2}$

Total moles at equb. $= 1 - x + x + \dfrac{x}{2} = 1 + \dfrac{x}{2} = \dfrac{2 + x}{2}$

$$p_{AB_2} = \frac{(1 - x)}{2 + x/2}P = \frac{2(1 - x)}{2 + x}P$$

$$p_{AB} = \frac{x}{2 + x/2}P = \frac{2x}{2 + x}P$$

$$p_{B_2} = \frac{x/2}{2 + x/2}P = \frac{x}{2 + x}P$$

$$\therefore K_p = \frac{(p_{AB})^2\,(p_{B_2})}{(p_{AB_2})^2} = \frac{\left(\frac{2x}{2 + x}P\right)^2\left(\frac{x}{2 + x}P\right)}{\left[\frac{2(1 - x)}{(2 + x)}P\right]^2}$$

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

$$K_p \approx \frac{x^3}{2}P \quad \text{or} \quad x = \left[\frac{\mathbf{2K_p}}{\mathbf{P}}\right]^{1/3}$$

27. **TIPS/Formulae :**

Consider common ion effect

Conc. of Ag^+ ions = Conc. of $AgNO_3 = 0.03$ M

Most of these Ag^+ ions will be present in the form of $[Ag(CN)_2]^-$.

0.03 M $AgNO_3$ requires 2×0.03 M

$= 0.06$ M CN^- to form $[Ag(CN)_2]^-$

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$\therefore$ Conc. of free CN^- at equilibrium will be $0.1 - 0.06 = 0.04$ M

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

$$\therefore K = \frac{[Ag^+][CN^-]^2}{[Ag(CN)_2]}; 4.0\times 10^{-9} = \frac{[Ag^+][0.04]^2}{0.03}$$

$$[Ag^+] = \frac{4.0\times 10^{-19}\times 0.03}{(0.04)^2} = \mathbf{7.5\times 10^{-18}\ M}$$

28. For ammonium formate which is a salt of weak acid with weak base, we know that

$$pH = \frac{1}{2}[pK_w + pK_a - pK_b] = \frac{1}{2}[14 + 3.8 - 4.8] = \mathbf{6.5}$$

29. $pK_b = 4.70$, $\therefore K_b = 10^{-4.7}$

Now we know that

$$[OH^-] = \sqrt{K_b \times c}$$

$$\therefore [OH^-] = \sqrt{10^{-4.7}\times 0.5} = 3.158\times 10^{-3}\,M$$

Now we know that

$pOH = -\log[OH^-]$

$pOH = -\log 3.158\times 10^{-3} = 2.5$

or, $pH = 14 - 2.5 = \mathbf{11.5}$

30. The concerned chemical reaction is

$$2AgCl + Na_2CO_3 \longrightarrow Ag_2CO_3 + 2NaCl$$

Calculation of $[Ag^+]$ left in the solution :

$K_{sp}(Ag_2CO_3) = [Ag^+]^2\,[CO_3^{2-}]$

$$[Ag^+] = \sqrt{\frac{8.2\times 10^{-12}}{1.5}} = 2.34\times 10^{-6}\,M$$

Concentration of Cl^- left $= 0.0026$ g/l

$$= \frac{0.0026}{35.5}\,mol/l = 7.33\times 10^{-5}\,M$$

$\therefore K_{sp}(AgCl) = [Ag^+][Cl^-] = (2.34\times 10^{-6})(7.33\times 10^{-5})$

$= \mathbf{1.71\times 10^{-10}}$

31. Given $K_a = 1\times 10^{-5}$

$\therefore pK_a = 5$

The two conditions when colour indicator will be visible are derived by

$$pH = pK_a + \log\frac{[In^-]}{[HIn]}$$

(i) $pH = 5 + \log 10 = 6$

(ii) $pH = 5 + \log 0.1 = 4$

Thus minimum change in pH = **2**

32. For AgCl; $AgCl \rightleftharpoons Ag^+ + Cl^-$

$\therefore K_{sp} = [Ag^+][Cl^-]$ .....(i)

Again it is given that

$[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3$; $K_c = 6.2\times 10^{-8}$

or $Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$;

$$K_f = \frac{1}{6.2\times 10^{-8}} = \frac{10^8}{6.2}$$

$$\therefore K_f = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2} \text{ or } [Ag^+] = \frac{[Ag(NH_3)_2]^+}{K_f[(NH_3)_2]}$$

NOTE THIS STEP : Since the formation constant of the complex is very high, most of the $[Ag^+]$ which dissolves must be converted into complex and each Ag^+ dissolved also requires dissolution of Cl^-.

$\therefore [Cl^-] = [Ag(NH_3)_2]^+$ and let it be c M

Equation (i) becomes

$$K_{sp} = \frac{[Ag(NH_3)_2]^+}{K_f[NH_3]^2}\times c \Rightarrow K_{sp} = \frac{c}{K_f[1]^2}\times c$$

$$c^2 = K_{sp}\times K_f[1]^2 = 1.8\times 10^{-10}\times\frac{10^8}{6.2}\times(1)^2$$

$$c^2 = \frac{1.8\times 10^{-2}}{6.2} = 0.2903\times 10^{-2}$$

or $c = 0.538\times 10^{-1} = \mathbf{0.0538\ M}$

33.

	HCl	$+ NaOH$	$\longrightarrow NaCl$	$+ H_2O$
Meq. before reaction	200×10^{-2}	300×10^{-2}		
Meq. after reaction	0	100×10^{-2}	200×10^{-2}	200×10^{-2}

pH of HCl = 2, pH of NaOH = 12

$\therefore [HCl] = 10^{-2}$ M, $\therefore [NaOH] = 10^{-2}$ M

$$\therefore [OH^-] = \frac{100\times 10^{-2}}{500} = 2\times 10^{-3} \text{ or } p[OH] = -\log(2\times 10^{-1})$$

$\therefore pOH = 2.6989$; $\therefore pH = \mathbf{11.3010}$ $[pH = 14 - p(OH)]$

34.

	$NH_4HS_{(s)}$	$\rightleftharpoons NH_{3(g)}$	$+ H_2S_{(g)}$
Initial moles	$\frac{3.06}{51}$	0	0
Moles at eq.	$\frac{3.06}{51}\times\frac{70}{100}$	$\frac{3.06}{51}\times\frac{30}{100}$	$\frac{3.06}{51}\times\frac{30}{100}$

Given $V = 2$ litre, $T = 300$K, $\Delta n = 2 - 0 = 2$

$$\therefore K_c = [NH_3][H_2S] = \frac{3.06\times 30}{51\times 100\times 2}\times\frac{3.06\times 30}{51\times 100\times 2}$$

$= \mathbf{8.1\times 10^{-5}\ mol^2\ litre^{-2}}$

Also $K_p = K_c(RT)^{\Delta n} = 8.1\times 10^{-5}(0.082\times 300)^2$

$= \mathbf{4.90\times 10^{-2}\ atm^2}$

NOTE : Addition of more NH_4HS on this equilibrium will cause no effect because concentration of NH_4HS is not involved in formula of K_p or K_c.

35.

	$Pb(OH)_2$	$\rightleftharpoons Pb^{2+}$	$+ 2OH^-$
(given)	6.7×10^{-6}M	6.7×10^{-6}M	$2\times 6.7\times 10^{-6}$M

$\therefore K_{sp} = [Pb^{2+}][OH^-]^2 = (6.7\times 10^{-6})(2\times 6.7\times 10^{-6})^2$

$= 1.203\times 10^{-15}$

The buffer solution pH = 8 (given)

$\therefore pOH = 6$ or $[OH^-] = 10^{-6}$

Thus in this buffer we have, $[Pb^{2+}][OH^-]^2 = 1.203\times 10^{-15}$

or $[Pb^{2+}]\times[10^{-6}]^2 = 1.203\times 10^{-15}$

$\therefore [Pb^{2+}] = \mathbf{1.203\times 10^{-3}\ mol\ litre^{-1}}$

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36. Amount of SO_2 in atmosphere $= \dfrac{10}{10^6} = 10 \times 10^{-6}$

Molar concentration of SO_2 present in water

$=$ Amount of $SO_2 \times$ Solubility of SO_2 in water

$= 10 \times 10^{-6} \times 1.3653 \text{ mole L}^{-1} = 1.3653 \times 10^{-5}$ M

Writing the concerned chemical equation

$$H_2SO_3 \longrightarrow H^+ + HSO_3^-$$

	H_2SO_3	H^+	HSO_3^-
Initial conc.	1.3653×10^{-5}	0	0
Molar conc. at equb.	$1.3653 \times 10^{-5} - x$	x	x

Therefore $K_a = \dfrac{x^2}{(1.3653 \times 10^{-5} - x)}$

$$\Rightarrow \quad 10^{-1.92} = \frac{x^2}{(1.3653 \times 10^{-5} - x)}$$

$(pK_a = 1.92, \therefore K_a = 10^{-1.92})$

$$\Rightarrow 1.2 \times 10^{-2} = \frac{x^2}{(1.3653 \times 10^{-5} - x)}$$

$x^2 = 1.2 \times 10^{-2}(1.3653 \times 10^{-5} - x)$ On solving, $x = 1.364 \times 10^{-5}$

Therefore, $pH = -\log(1.364 \times 10^{-5}) = \mathbf{4.865}$

37. (*i*) The volume being doubled by mixing the two solutions, the molarity of each component will be halved i.e. $[CH_3COOH] = 0.1$ M, $[HCl] = 0.1$ M.

NOTE :

HCl being a strong acid will remain completely ionised and hence H^+ ion concentration furnished by it will be 0.1 M. This would exert common ion effect on the dissociation of acetic acid, (a weak acid.)

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

	CH_3COOH	CH_3COO^-	H^+
At start	C	0	0
At equilibrium	$C(1 - \alpha)$	$C\alpha$	$C\alpha + 0.1$

$$K_a = \frac{C\alpha(C\alpha + 0.1)}{C(1-\alpha)} = \frac{C\alpha^2 + 0.1\alpha}{(1-\alpha)}$$

Since α is very very small, $C\alpha^2$ can be neglected and $1 - \alpha$ can be taken as unity

$\therefore K_a = 0.1\,\alpha$

or $\alpha = \dfrac{K_a}{0.1} = \dfrac{1.75 \times 10^{-5}}{0.1} = \mathbf{1.75 \times 10^{-4}}$

$[H^+]_{Total} = 0.1 + C\alpha,$

$C\alpha$ is negligible as compared to 0.1.

$\therefore [H^+]_{Total} = 0.1 \qquad \therefore \; pH = \mathbf{1}$

(*ii*) $6\text{g NaOH} = \dfrac{6}{40} = 0.15\text{mol}$

0.1 mole of NaOH will be consumed by 0.1 mole of HCl. Thus, 0.05 mole of NaOH will react with acetic acid according to the equation.

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

	CH_3COOH	$NaOH$	CH_3COONa	H_2O
Initial moles	0.1 mol	0.05 mol	0	0
At equilibrium	0.05 mol	0 mol	0.05 mol	0.05mol

Thus, solution of acetic acid and sodium acetate will become acidic buffer. So pH of the buffer will be

$$pH = pK_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$

$$= -\log\left(1.75 \times 10^{-5}\right) + \log 1 = \mathbf{4.75}$$

38. **TIPS/Formulae :**

Higher the value of dipole-dipole interaction higher is b.p. Higher value of K_b of a solvent suggests larger polarity of solvent molecules which in turn leads to higher dipole – dipole interaction implies higher boiling point due to dipole – dipole interaction. Therefore, the correct order of K_b values of the three given solvents is

Mathematically $K_b = \dfrac{M_A R T_b^2}{\Delta H_{vap} \times 1000}$

or $K_b \propto T_b$ (b.pt.)

Solvents	***Boiling point***	***K_b values***
X	100°C	0.63
Y	27°C	0.53
Z	283°C	0.98

G. Comprehension Based Questions

1. **(a)** Let the heat capacity of insulated beaker be C.

Mass of aqueous content in expt. $1 = (100 + 100) \times 1 = 200$ g

$\Rightarrow$ ± Total heat capacity $= (C + 200 \times 4.2)$ J/K

Moles of acid, base neutralised in expt. $1 = 0.1 \times 1 = 0.1$

$\Rightarrow$ Heat released in expt. $1 = 0.1 \times 57 = 5.7$ KJ $= 5.7 \times 1000$ J

$\Rightarrow$ $5.7 \times 1000 = (C + 200 \times 4.2) \times \Delta'T.$

$5.7 \times 1000 = (C + 200 + 4.2) \times 5.7$

$\Rightarrow$ $(C + 200 \times 4.2) = 1000$

In second experiment,

$n_{CH_3COOH} = 0.2, \; n_{NaOH} = -0.1$

Total mass of aqueous content $= 200$ g

$\Rightarrow$ Total heat capacity $= (C + 200 \times 4.2) = 1000$

$\Rightarrow$ Heat released $= 1000 \times 5.6 = 5600$ J.

Overall, only 0.1 mol of CH_3COOH undergo neutralization.

$\Rightarrow$ $\Delta H_{\text{neutralization}}$ of $CH_3COOH = \dfrac{-5600}{0.1}$

$= -56000$ J/mol

$= -56$ KJ/mol.

$\Rightarrow$ $\Delta H_{\text{neutralization}}$ of $CH_3COOH = 57 - 56 = 1$ KJ/mol

2. **(b)** Final solution contain 0.1 mole of CH_3COOH^2 and CH_3COONa each.

Hence it is a buffer solution.

$$pH = pK_a \; \log\frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$= 5 - \log 2 + \log\frac{0.1}{0.1} = 4.7$$

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3. **(b)**

$$\begin{array}{llcl} & X_2(g) & \rightleftharpoons & 2X(g) \\ \text{Initial mole :} & 1 & & 0 \\ \text{moles at equilibrium :} & \left(1-\dfrac{\beta_{eqbm}}{2}\right) & & \beta_{eqbm} \\ \text{Partial pressure :} & \dfrac{1-\dfrac{\beta_{eqbm}}{2}}{\left(1+\dfrac{\beta_{eqbm}}{2}\right)}\times P & & \dfrac{\beta_{eqbm}}{\left(1+\dfrac{\beta_{eqbm}}{2}\right)}P \end{array}$$

$$\therefore \quad K_p = \frac{(P_x)^2}{P_{x_2}} = \frac{\beta^2_{eqbm}P}{\left(1-\dfrac{\beta^2_{eqbm}}{4}\right)}$$

$$\therefore \quad K_p = \frac{4\beta^2_{eqbm}P}{\left(4-\beta^2_{eqbm}\right)}$$

Since $P = 2$ bar

So, $\boxed{K_p = \dfrac{8\beta^2_{eqbm}}{\left(4-\beta^2_{eqbm}\right)}}$

4. **(c)**

(A) Correct statement.

As on decrease in pressure reaction move indirection where no. of gaseous molecules increase.

(B) Correct statement

At the start of reaction $Q_P < K_P$ so dissociation of X_2 take place spontaneously.

(C) Incorrect statement as

$$K_P = \frac{8\beta^2_{eq}}{4-\beta^2_{eq}} = \frac{8\times(0.7)^2}{4-(0.7)^2} > 1$$

H. Assertion & Reason Type Questions

1. **(d)** The statement-1 is clearly wrong in context to Le-Chateliers principle, which states that "increase in temperature shifts the equilibrium in the forward direction of those reactions which proceed with absorption of heat (**endothermic reactions**), and in the backward direction of those reactions which proceed with the evolution of heat (**exothermic reactions**)."

Statement -2 is clearly true again according to Le-chatelier principle.

2. **(c)** **TIPS/Formulae :**

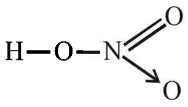
Among oxyacids, the acidic character increases with increase in oxidation state of the central atom.

O.S. of N in $HNO_3 = +5$

O.S.of N in $HNO_2 = +3$

thus HNO_3 stronger than HNO_2. Hence assertion is correct.

Structure of HNO_2 : $O—H—N=O$;

Structure of HNO_3 : 

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

3. **(d)** We know that for every chemical reaction at equilibrium, Gibb's free energy ($\Delta G = 0$) is zero. However standard Gibb's free energy ($\Delta G°$) may or may not be zero. Thus statement 1 is False.

For a spontaneous reaction, at constant temperature and pressure, the reaction proceeds in the direction in which ΔG is < 0 i.e. in the direction of decreasing Gibb's energy (G) so the statement 2 is True.

Thus the only such option is (d) which is correct answer.

I. Integer Value Correct Type

1. $HA + NaOH \longrightarrow NaA + H_2O$

At the end point, the solution contains only NaA whose concentration is $0.1/2 = 0.05$ M

Since the salt NaA is formed by strong alkali (NaOH) and weak acid HA (indicated by its low K_a value), its pH can be evaluated by the following relation.

$$pH = \frac{1}{2}(pK_w + pK_a + \log C)$$

$$= \frac{1}{2}(14 + 5.3010 + (-1.3010)] = \mathbf{9}$$

2. pH of sodium salt of weak acid

$$= \frac{1}{2}(pK_w + pK_a + \log C) = \frac{1}{2}(14 + 4 - 2) = 8$$

3. KCN, K_2CO_3 and LiCN are the salts of weak acid and strong base. So, their aqueous solutions turns red litmus paper blue.

4. Diprotic acids are H_2SO_4, H_3PO_3, H_2CO_3, $H_2S_2O_7$, H_2CrO_4 and H_2SO_3.

5. 7

Let the solubility of AgCl is x mol litre^{-1} and that of CuCl is y mol litre^{-1}

$$\begin{array}{l} AgCl \rightleftharpoons \underset{x}{Ag^+} + \underset{x}{Cl^-} \\ CuCl \rightleftharpoons \underset{y}{Cu^+} + \underset{y}{Cl^-} \end{array}$$

$\therefore$ K_{sp} of AgCl $= [Ag^+][Cl^-]$

$1.6 \times 10^{-10} = x(x+y)$ ....(i)

Similarly, K_{sp} of CuCl $= [Cu^+][Cl^-]$

$1.6 \times 10^{-6} = y(x+y)$ ... (ii)

On solving, (i) and (ii)

$[Ag^+] = 1.6 \times 10^{-7} \therefore x = 7$

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Section-B JEE Main/ AIEEE

1. **(a)** **NOTE :** A buffer is a solution of weak acid and its salt with strong base and vice versa.
HCl is strong acid and NaCl is its salt with strong base. pH is less than 7 due to HCl.

2. **(a)** $(HSO_4)^-$ can accept and donate a proton
$(HSO_4)^- + H^+ \rightarrow H_2SO_4$ (acting as base)
$(HSO_4)^- - H^+ \rightarrow SO_4^{2-}$. (acting as acid)

3. **(a)** $Mg(OH)_2 \rightarrow \underset{x}{[Mg^{2+}]} + \underset{2x}{2[OH^-]}$
$K_{sp} = [Mg][OH]^2 = [x][2x]^2 = x.4x^2 = 4x^3$.

4. **(a)** In this reaction the ratio of number of moles of reactants to products is same i.e. 2 : 2, hence change in volume will not alter the number of moles.

5. **(c)** $K_p = K_c(RT)^{\Delta n}$;

$$\Delta n = 1 - \left(1 + \frac{1}{2}\right) = 1 - \frac{3}{2} = -\frac{1}{2}. \therefore \frac{K_p}{K_c} = (RT)^{-1/2}$$

6. **(b)** pH of an acidic solution should be less than 7. The reason is that from H_2O. $[H^+] = 10^{-7}M$ which cannot be neglected in comparison to $10^{-8}M$. The pH can be calculated as.
from acid, $[H^+] = 10^{-8}M$.
from H_2O, $[H^+] = 10^{-7}M$
$\therefore$ Total $[H^+] = 10^{-8} + 10^{-7} = 10^{-8}(1 + 10) = 11 \times 10^{-8}$
$\therefore pH = -\log[H^+] = -\log 11 \times 10^{-8} = -[\log 11 + 8 \log 10]$
$= -[1.0414 - 8] = 6.9586$

7. **(d)** $AB_2 \rightleftharpoons A^{+2} + 2B^-$
$[A] = 1.0 \times 10^{-5}$, $[B] = [2.0 \times 10^{-5}]$,
$K_{sp} = [B]^2[A] = [2 \times 10^{-5}]^2[1.0 \times 10^{-5}] = 4 \times 10^{-15}$

8. **(b)** $K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{[1.2 \times 10^{-2}]^2}{[4.8 \times 10^{-2}]} = 3 \times 10^{-3}$ mol/L

9. **(b)** Due to exothermicity of reaction low or optimum temperature will be required. Since 3 moles are changing to 2 moles.
$\therefore$ High pressure will be required.

10. **(d)** The rain water after thunderstorm contains dissolved acid and therefore the pH is less than rain water without thunderstorm.

11. **(d)** **NOTE :** Conjugate acid-base differ by H^+

$$\underset{\text{Acid}}{H_2PO_4^-} \xrightarrow{-H^+} \underset{\text{conjugate base}}{HPO_4^{--}}$$

12. **(d)** For $P_4(s) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)$

$K_c = \frac{1}{(O_2)^5}$. The solids have concentration unity

13. **(c)** $K_p = K_c(RT)^{\Delta n}$; Here $\Delta n = 1 - 2 = -1$

$$\therefore \frac{K_p}{K_c} = \frac{1}{RT}$$

14. **(b)** $K_c = \frac{[NO]^2}{[N_2][O_2]} = 4 \times 10^{-4}$

$$K'_c = \frac{[N_2]^{1/2}[O_2]^{1/2}}{[NO]} = \frac{1}{\sqrt{K_c}} = \frac{1}{\sqrt{4 \times 10^{-4}}} = 50$$

15. **(d)** $MX_4 \rightleftharpoons \underset{S}{M^{4+}} + \underset{4S}{4X^-}$

$$K_{sp} = [s][4s]^4 = 256 s^5 \quad \therefore s = \left(\frac{K_{sp}}{256}\right)^{1/5}$$

16. **(b)** $\underset{1-\alpha}{Na_2SO_4} \rightleftharpoons \underset{2\alpha}{2Na^+} + \underset{\alpha}{SO_4^{--}}$

Vant. Hoff's factor $i = \frac{1 - \alpha + 2\alpha + \alpha}{1} = 1 + 2\alpha$

17. **(c)** $MX_2 \rightleftharpoons \underset{s}{M^{++}} + \underset{2s}{2X^-}$
Where s is the solubility of MX_2
then $K_{sp} = 4s^3$; $s \times (2s)^2 = 4 \times 10^{-12} = 4s^3$; $s = 1 \times 10^{-4}$
$\therefore [M^{++}] = s = 1[M^{++}] = 10 \times 10^{-4}$

18. **(a)** The reaction given is an exothermic reaction thus accordingly to Lechatalier's principle lowering of temperature, addition of F_2 and or Cl_2 favour the for ward direction and hence the production of ClF_3.

19. **(d)** For the reaction:- $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$

Given $K_c = 1.8 \times 10^{-6}$ at 184 °C
$R = 0.0831$ kj/mol. k
$K_p = 1.8 \times 10^{-6} \times 0.0831 \times 457 = 6.836 \times 10^{-6}$
$[\because 184°C = (273 + 184) = 457 k, \Delta n = (2 + 1, -1) = 1]$
Hence it is clear that $K_p > K_c$

20. **(a)** $pH = -\log[H^+] = \log\frac{1}{[H^+]}$; $5.4 = \log\frac{1}{[H^+]}$
On solving, $[H^+] = 3.98 \times 10^{-6}$

21. **(a)** Conjugate acid-base pair differ by only one proton.

$OH^- \longrightarrow H^+ + O^{2-}$ Conjugate base of OH^- is O^{2-}

22. **(a)** $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

start	0.5 atm	0 atm
At equib.	0.5 + x atm	x atm.

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Then $0.5 + x + x = 2x + 0.5 = 0.84$ (given)

$\Rightarrow x = 0.17$ atm.

$p_{NH_3} = 0.5 + 0.17 = 0.67$ atm ; $p_{H_2S} = 0.17$ atm

$K = p_{NH_3} \times p_{H_2S} = 0.67 \times 0.17\ \text{atm}^2 = 0.1139 = 0.11$

23. **(c)** $\underset{1-x}{PCl_5(g)} \rightleftharpoons \underset{x}{PCl_3(g)} + \underset{x}{Cl_2(g)}$

Total moles after dissociation $1 - x + x + x = 1 + x$

p_{PCl_3} = mole fraction of PCl_3 × Total pressure

$$= \left(\frac{x}{1+x}\right)P$$

24. **(c)** $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$

$$K_c = \frac{[SO_2][O_2]^{1/2}}{[SO_3]} = 4.9 \times 10^{-2};$$

On taking the square of the above reaction

$$\frac{[SO_2]^2[O_2]}{[SO_3]^2} = 24.01 \times 10^{-4}$$

now K'_C for $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3$

$$= \frac{[SO_3]^2}{[SO_2]^2\,[O_2]} = \frac{1}{24.01 \times 10^{-4}} = 416$$

25. **(b)** (i) $Ag \longrightarrow Ag^+ + e^-$ $E° = -0.800$ V

(ii) $Ag + I^- \longrightarrow AgI + e^-$ $E° = 0.152$ V

From (i) and (ii) we have,

$AgI \longrightarrow Ag^+ + I^-$ $E° = -0.952$ V

$$E^o_{cell} = \frac{0.059}{n}\log K$$

$$\therefore\ -0.952 = \frac{0.059}{1}\log[Ag^+][I^-]\ \ [\because k = [Ag^+][I^-]]$$

$$\text{or } -\frac{0.952}{0.059} = \log K_{sp} \ \text{ or } -16.13 = \log K_{sp}$$

26. **(d)** $H_2A \rightleftharpoons H^+ + HA^-$

$$\therefore K_1 = 1.0 \times 10^{-5} = \frac{[H^+][HA^-]}{[H_2A]} \qquad \text{(Given)}$$

$HA^- \longrightarrow H^+ + A^{--}$

$$\therefore K_2 = 5.0 \times 10^{-10} = \frac{[H^+][A^{--}]}{[HA^-]}\text{(Given)}$$

$$K = \frac{[H^+]^2[A^{2-}]}{[H_2A]} = K_1 \times K_2$$

$$= (1.0 \times 10^{-5}) \times (5 \times 10^{-10}) = 5 \times 10^{-15}$$

27. **(d)** For acidic buffer $pH = pK_a + \log\left[\frac{\text{salt}}{\text{acid}}\right]$

$$\text{or } pH = pK_a + \log\frac{[A^-]}{[HA]}$$

Given $pK_a = 4.5$ and acid is 50% ionised.

$[HA] = [A^-]$ (when acid is 50% ionised)

$\therefore pH = pK_a + \log 1$ $\therefore pH = pK_a = 4.5$

$pOH = 14 - pH = 14 - 4.5 = 9.5$

28. **(c)** Let s = solubility

$AgIO_3 \rightleftharpoons \underset{s}{Ag^+} + \underset{s}{IO_3^-}$

$K_{sp} = [Ag^+][IO_3^-] = s \times s = s^2$

Given $K_{sp} = 1 \times 10^{-8}$

$$\therefore\ s = \sqrt{K_{sp}} = \sqrt{1 \times 10^{-8}}$$

$= 1.0 \times 10^{-4}$ mol/lit $= 1.0 \times 10^{-4} \times 283$ g/lit

($\because$ Molecular mass of $AgIO_3 = 283$)

$$= \frac{1.0 \times 10^{-4} \times 283 \times 100}{1000}\ \text{gm/100ml}$$

$= 2.83 \times 10^{-3}$ gm/ 100 ml

29. **(a)** Let the initial moles of X be ‘a’ and that of Z be ‘b’ then for the given reactions, we have

	X	$\rightleftharpoons$	2Y
Initial	a moles		0
At equi. (moles)	$a(1-\alpha)$		$2a\alpha$

Total no. of moles $= a(1-\alpha) + 2a\alpha$

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

$$\text{Now, } K_{P_1} = \frac{(n_y)^2}{n_x} \times \left(\frac{P_{T_1}}{\Sigma n}\right)^{\Delta n}$$

$$\text{or, } K_{P_1} = \frac{(2a\alpha)^2 . P_{T_1}}{[a(1-\alpha)][a(1+\alpha)]}$$

	Z	$\rightleftharpoons$	P	+	Q
Initial	b moles		0		0
At equi. (moles)	$b(1-\alpha)$		$b\alpha$		$b\alpha$

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$$\text{Total no. of moles} = b(1-\alpha)+b\alpha+b\alpha$$
$$= b - b\alpha + b\alpha + b\alpha = b(1+\alpha)$$

$$\text{Now } K_{P_2} = \frac{n_Q \times n_P}{n_z} \times \left[\frac{P_{T_2}}{\Sigma_n}\right]^{\Delta_n}$$

$$\text{or} \quad K_{P_2} = \frac{(b\alpha)(b\alpha).P_{T_2}}{[b(1-\alpha)][b(1+\alpha)]}$$

$$\text{or} \quad \frac{K_{P_1}}{K_{P_2}} = \frac{4\alpha^2.P_{T_1}}{(1-\alpha^2)} \times \frac{(1-\alpha)^2}{P_{T_2}.\alpha^2} = \frac{4P_{T_1}}{P_{T_2}}$$

$$\text{or} \quad \frac{P_{T_1}}{P_{T_2}} = \frac{1}{9} \quad \left[\because \frac{K_{P_1}}{K_{P_2}} = \frac{1}{9} \text{ given}\right]$$

$$\text{or} \quad \frac{P_{T_1}}{P_{T_2}} = \frac{1}{36} \quad \text{or} \quad 1 : 36$$

i.e., (a) is the correct answer.

30. (c) Reaction (c) can be obtained by adding reactions (a) and (b) therefore $K_3 = K_1 . K_2$

Hence (c) is the correct answer.

31. (c) The correct order of acidic strength of the given species

$$\text{in} \quad \underset{(iv)}{HSO_3F} > \underset{(ii)}{H_3O^+} > \underset{(iii)}{HSO_4^-} > \underset{(i)}{HCO_3^-}$$

or (i) < (iii) < (ii) < (iv)

It corresponds to choice (c) which is correct answer.

32. (c) In aqueous solution BA(salt) hydrolyses to give

$$BA + H_2O \rightleftharpoons \underset{\text{Base}}{BOH} + \underset{\text{acid}}{HA}$$

Now pH is given by

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pKa - \frac{1}{2}pK_b$$

Substituting given values, we get

$$pH = \frac{1}{2}(14 + 4.80 - 4.78) = 7.01$$

33. (a) $$\underset{1\times10^{-4}M}{Na_2CO_3} \longrightarrow \underset{1\times10^{-4}M}{2Na^+} + \underset{1\times10^{-4}M}{CO_3^{2-}}$$

$$K_{SP(BaCO_3)} = [Ba^{2+}][CO_3^{2-}]$$

$$[Ba^{2+}] = \frac{5.1\times10^{-9}}{1\times10^{-4}} = 5.1\times10^{-5}\,M$$

34. (a) (i) $$\underset{acid_1}{H_3PO_4} + \underset{base_2}{H_2O_4} \longrightarrow \underset{acid_2}{H_3O^+} + \underset{base_1}{H_2PO_4^-}$$

(ii) $$\underset{acid_1}{H_2PO_4^-} + \underset{base_2}{H_2O} \longrightarrow \underset{base_1}{HPO_4^{--}} + \underset{acid_2}{H_3O^+}$$

(iii) $$\underset{base_1}{H_2PO_4^-} + \underset{acid_2}{OH^-} \longrightarrow \underset{acid_1}{H_3PO_4} + \underset{base_2}{O^{--}}$$

Hence only in (ii) reaction $H_2PO_4^-$ is acting as an acid.

35. (c) $$\underset{0.034-x}{H_2CO_3(aq)} + H_2O(l) \rightleftharpoons \underset{x}{HCO_3^-(aq)} + \underset{x}{H_3O^+(aq)}$$

$$K_1 = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]} = \frac{x \times x}{0.034 - x}$$

$$\Rightarrow 4.2\times10^{-7} \simeq \frac{x^2}{0.034} \Rightarrow x = 1.195\times10^{-4}$$

As H_2CO_3 is a weak acid so the concentration of H_2CO_3 will remain 0.034 as $0.034 >> x$.

$x = [H^+] = [HCO_3^-] = 1.195 \times 10^{-4}$

$$\text{Now, } \underset{x-y}{HCO_3^-(aq)} + H_2O(l) \rightleftharpoons \underset{y}{CO_3^{2-}(aq)} + \underset{y}{H_3O^+(aq)}$$

As HCO_3^- is again a weak acid (weaker than H_2CO_3) with $x >> y$.

$$K_2 = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]} = \frac{y \times (x+y)}{(x-y)}$$

Note : $[H_3O^+] = H^+$ from first step (x) and from second step (y) = $(x + y)$

[As $x >> y$ so $x + y \simeq x$ and $x - y \simeq x$]

$$\text{So, } K_2 \simeq \frac{y \times x}{x} = y$$

$$\Rightarrow K_2 = 4.8\times10^{-11} = y = [CO_3^{2-}]$$

So the concentration of $[H^+] \simeq [HCO_3^-]$ = concentrations obtained from the first step. As the dissociation will be very low in second step so there will be no change in these concentrations.

Thus the final concentrations are

$[H^+] = [HCO_3^-] = 1.195 \times 10^{-4}$ & $[CO_3^{2-}] = 4.8\times10^{-11}$

36. (b) $AgBr \rightleftharpoons Ag^+ + Br^-$

$K_{sp} = [Ag^+][Br^-]$

For precipitation to occur

Ionic product > Solubility product

$$[Br^-] = \frac{K_{sp}}{[Ag^+]} = \frac{5\times10^{-13}}{0.05} = 10^{-11}$$

i.e., precipitation just starts when 10^{-11} moles of KBr is added to 1ℓ $AgNO_3$ solution

$\therefore$ Number of moles of Br^- needed from KBr = 10^{-11}

$\therefore$ Mass of KBr = $10^{-11} \times 120 = 1.2 \times 10^{-9}$ g

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37. **(b)** $Mg(OH)_2 \rightleftharpoons Mg^{++} + 2OH^-$

$K_{sp} = [Mg^{++}][OH^-]^2$

$1.0 \times 10^{-11} = 10^{-3} \times [OH^-]^2$

$$[OH^-] = \sqrt{\frac{10^{-11}}{10^{-3}}} = 10^{-4}$$

$\therefore$ pOH = 4 $\therefore$ pH + pOH = 14 $\therefore$ pH = 10

38. **(a)** $CO_2 + C_{(grapnite)} \rightleftharpoons 2CO$

$P_{initial}$ 0.5atm 0

P_{final} (0.5 – x)atm 2x atm

Total P at equilibrium $= 0.5 - x + 2x = 0.5 + x$ atm

$0.8 = 0.5 + x$

$\therefore$ $x = 0.8 - 0.5 = 0.3$ atm

$$\text{Now } k_p = (P_{CO})^2 / P_{CO_2} = \frac{(2 \times 0.3)^2}{(0.5 - 0.3)} = \frac{(0.6)^2}{(0.2)}$$

= 1.8 atm

39. **(d)** For the reaction

$N_2 + O_2 \longrightarrow 2NO$ $K = 4 \times 10^{-4}$

Hence for the reaction

$$NO \longrightarrow \frac{1}{2}N_2 + \frac{1}{2}O_2 \quad K' = \frac{1}{\sqrt{K}} = \frac{1}{\sqrt{4 \times 10^{-4}}} = 50$$

40. **(c)** $H^+ = C\alpha ; \alpha = \dfrac{[H^+]}{C}$ or $\alpha = \dfrac{10^{-3}}{0.1} = 10^{-2}$

$Ka = C\alpha^2 = 0.1 \times 10^{-2} \times 10^{-2} = 10^{-5}$

41. **(d)** $\because$ pH = 1 ; $H^+ = 10^{-1} = 0.1$ M

pH = 2 ; $H^+ = 10^{-2} = 0.01$ M

$\therefore M_1 = 0.1 \ \ V_1 = 1; M_2 = 0.01 \ \ V_2 = ?$

From

$M_1V_1 = M_2V_2; 0.1 \times 1 = 0.01 \times V_2$

$V_2 = 10$ litre

$\therefore$ volume of water added = 10 – 1 = 9 litre.

42. **(b)** $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$

$K_P = K_C(RT)^x$

where $x = \Delta n_g$ = number of gaseous moles in product – number of gaseous moles in reactant

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

43. **(d)** $\Delta G° = 2494.2J$

$2A \rightleftharpoons B + C.$

R = 8.314 J/K/mol.

e = 2.718

$$[A] = \frac{1}{2}, [B] = 2, [C] = \frac{1}{2}; Q = \frac{[B][C]}{[A]^2} = \frac{2 \times 1/2}{\left(\frac{1}{2}\right)^2} = 4$$

$\Delta G° = -2.303\ RT \log K_C.$

$2494.2\ J = -2.303 \times (8.314\ J/K/mol) \times (300K) \log K_C$

$$\Rightarrow \log K_C = -\frac{2494.2\ J}{2.303 \times 8.314\ J/K/mol \times 300\ K}$$

$\Rightarrow \log K_C = -0.4341 ; K_C = 0.37 ; Q > K_C.$

44. **(b)** $\Delta G°_{NO(g)} = 86.6k\ J/mol = 86600\ J/mol;\ G°_{NO_2(g)} = x\ J/mol$

$T = 298, K_p = 1.6 \times 10^{12}$

$\Delta G° = -RT \ln K_p$

Given equation,

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

$\therefore$ $2\Delta G°_{NO_2} - 2\Delta G°_{NO} = -R(298) \ln (1.6 \times 10^{12})$

$2\Delta G°_{NO_2} - 2 \times 86600 = -R(298) \ln (1.6 \times 10^{12})$

$2\Delta G°_{NO_2} = 2 \times 86600 - R(298) \ln (1.6 \times 10^{12})$

$$\Delta G°_{NO_2} = \frac{1}{2}[2 \times 86600 - R(298) \ln (1.6 \times 10^{12})]$$

$= 0.5\ [2 \times 86600 - R(298) \ln (1.6 \times 10^{12})]$

45. **(a)** Given,

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

	A	B	C	D
No. of moles initially	1	1	1	1
At equilibrium	1–a	1–a	1+a	1+a

$$\therefore K_c = \left(\frac{1+a}{1-a}\right)^2 = 100$$

$$\therefore \frac{1+a}{1-a} = 10$$

On solving

a = 0.81

$[D]_{At\ eq} = 1 + a = 1 + 0.81 = 1.81$

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