10

Ionic Equilibrium

QUICK LOOK

Most of the chemical reactions occur in solutions. When a given substance is dissolved in the solvents like water. In an ionic solution the substance splits up into ions whereas in molecular solution, the substance remains as sluch. Both the solutions can be represented as

 $XY(s) + aq \xrightarrow{} XY(aq) \xrightarrow{} X^{+}(aq) + Y^{-}(aq)$ (for ionic solution) $XY(s) + aq \longrightarrow XY(aq)$ (for molecular solution)

Electrolyte (Conducting): Those substance whose aqueous solution or molten form can conduct electricity. They are further classified into:

Strong electrolyte: Those substance whose aqueous solution or molten form conduct electricity to a greater extent. They almost completely ionised in water.

e.g., NaCl, H₂SO₄, HCl, NaOH, NH₄Cl

Since strong electrolyte completely ionised in aqueous solution so their ionisation is represented as, $HCl + aq \longrightarrow H^{+}(aq) + Cl^{-}(aq)$

Weak electrolyte: Those substance whose aqueous solution or molten form conducts electricity to a lesser extent. They do not completely ionised in water i.e. partly ionised. They behaves as poor conductor of electricity.

e.g. when CH₃COOH is dissolved in water, it is ionised partly and an equilibrium is setup between the ions and the unionised electrolyte.

 $CH_3COOH + aq \implies CH_3COO^{-}(aq) + H^{+}(aq)$

Non-electrolyte Non-conducting: Those sub-stance whose aqueous solution or molten form does not conduct electricity to any extent. They are bad conductor of electricity. e.g. aqueous solution of sugar, urea, etc. do not conduct electricity.

Degree of ionisation ' α ' it may be defined as "fraction of total number of molecules which dissociates into ion". It is represented by α.

 $\alpha = \frac{\text{Number of molecules dissociated as ions}}{\text{Total number of molecules dissolved}}$

Number of moles dissociated

Total number of moles dissolved

Ostwald Dilution Law (Ionisation of Weak Electrolytes): It is the law of mass action as applied to weak electrolytes like CH₂COOH, NH₄OH, HCN, etc. Consider a binary electrolyte AB which dissociates into its ions, there exist a dynamic equilibrium between ions and unionised molecule of the electrolyte as

$$AB + aq \rightleftharpoons A^{+}(aq) + B^{-}(aq)$$
Initial conc.
when t = 0 C 0 0 ...(i)
Conc. at
equilibrium C-C\alpha C\alpha C\alpha

Apply the law of mass action to equilibrium (i)

$$K = \frac{[A^{+}(aq)][B^{-}(aq)]}{[AB]}$$
$$= \frac{C\alpha \times C\alpha}{[C - C\alpha]} = \frac{C\alpha^{2}}{1 - \alpha}$$

For weak electrolyte, $\alpha \ll 1$, $\Rightarrow 1 - \alpha \approx 1$ *i.e.* $\alpha < 5\%$

$$K = C\alpha^{2}$$

or $\alpha = \sqrt{\frac{K}{C}}$...(*ii*)

If one mole of electrolyte is dissolved in V litre of solution

i.e.
$$C = \frac{1}{V}$$

 $\alpha = \sqrt{KV}$ (*iii*)

Thus "degree of dissociation of a weak electrolyte is proportional to the square root of dilution". This is called Ostwald law.

Note

If $\alpha > 5\%$ then we cannot neglect α from denominator $C\alpha^2$

$$K = \frac{c \alpha}{(1 - \alpha)}$$

 α can be calculate by quadratic equation (ax² + bx + c = 0)

$$C\alpha^{2} - (1 - \alpha)K = \alpha = \frac{-b \pm \sqrt{b^{2} - 4ac}}{2a}$$

Here b = -(1-\alpha), a = C and c = 0

Relative Strength of Weak Acids and Bases: The relative strength of weak acids and bases are generally determined by their dissociation constant K_a and K_b respectively.

For weak acid CH₃COOH:

 $CH_{3}COOH + aq \underbrace{\overset{K_{a}}{\longleftarrow}} CH_{3}COO^{-}(aq) + H^{+}(aq)$ Initially C 0 0 At equilibrium C - C α C α C α $K_{a} = \frac{C\alpha \times C\alpha}{C - C\alpha} = \frac{C\alpha^{2}}{1 - \alpha} (1 - \alpha \approx 1 \text{ assuming } \alpha \text{ is very small}).$ $\therefore K_{a} = C\alpha^{2}$

Where K_a is equilibrium constant of weak acid which depends on temperature. Greater the value of K_a , more is the strength of an acid. Similarly for base NH_4OH

$$K_{b} = C\alpha^{2}$$

Where K_b is the equilibrium constant for weak base. For two acids having equi-molar concentrations

 $\frac{\text{Strength of acid I}}{\text{Strength of acid II}} = \sqrt{\frac{K_{a_1}}{K_{a_2}}},$

Similarly for two base $\frac{\text{Strength of base I}}{\text{Strength of base II}} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$

Self Ionization of Water (Ionic Product of Water): Pure

water is a weak electrolyte and itself ionises as $H O + H O \implies H O^+ + OH^-$ or simply

$$H_2O + H_2O = H_3O + OH \text{ of sim}$$

$$H_2O = H^+ + OH^-$$

Applying law of mass action

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

or $K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$

Where K is called dissociation constant.

Since the ionisation of water is very small it means very few H_2O molecule are dissociated into H and OH ions *i.e.*,



pH Scale: Sorenson gave the best way of expressing the acidic or basic nature of solution. This is a logarithmic scale in which

hydrogen ion concentration ranges from 10^{-14} to 1 mole/litre. pH may be defined as logarithm of reciprocal of [H₃O⁺].

or negative logarithm of hydronium ion concentration. $pH = -\log[H O^{+}]$

$$pH = -\log[H_3O^+]$$

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

The pH range is taken from 0 to 14. The acidity or alkalinity of a solution can be represented on pH scale as



In similar manner, we can define pOH scale as

$$pOH = -log[OH^{-}]$$

Both pH and pOH scale are related as

$$[H^+][OH^-] = 10^{-14} at 25^{\circ}C - log[H^+] - log[OH^-] = 14$$

pH + pOH = 14

Limitations of pH Scale

- pH value of solutions do not give immediate idea of their relative strength.
- pH value can be negative too.
- A 10⁻⁸ M solution of acid cannot have pH = 8. Since the value of pH of acid may close to 7 but < 7.

Buffer Solutions

A buffer solution is a solution which resists a change in its pH when such a change is caused by the addition of a small amount of acid or base. This does not mean that the pH of the buffer solution does not change (we make this assumption while doing numerical problems). It only means that the change in pH would be less than the pH that would have changed for a solution that is not a buffer.

Acid-base Indicators

Some common acid-base indicators, the pH ranges in which they show colour change and the colours exhibited in acidic and basic medium are given below:

Indicator	pH range	Colour in acidic medium	Colour in basic medium
Methyl orange	3.1 – 4.5	Pink	Yellow
Methyl red	4.2 - 6.3	Red	Yellow
Phenolphthalein	8.0 - 9.8	Colourless	Pink

Two theories have been proposed to explain the change of colour of these acid-base indicators. These therories are Ostwald's theory and Quinonoid theory

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Type of titration	Indicator used
Strong acid with strong base	Phenolphthalein, methyl orange
	or methyl red
Weak acid with strong base	Phenolphthalein
Strong acid with weak base	Methyl orange or Methyl red

Note

Phenolphthalein is not suitable if the base is weak, methyl orange is not suitable if the acid is weak.

Ostwald Theory of Indicators: An indicator generally a weak organic acid or weak organic bases is a substance which is used to determine the end point in a titration. They change their colours within a certain pH range generally the colour change is due to shifting of indicator equilibrium, *eg*, for phenolphthalein (HPh).

 $HPh = H^+ + Ph^-$

Colourless pink

and shifting of this equilibrium from left to right produces pink colours

$$K_{In} = \frac{\left[H^{+}\right] \left[Ph^{-}\right]}{\left[HPh\right]} \text{ and } pH = pK_{In} + \frac{\left[Ph^{-}\right]}{\left[HPh\right]}$$

At equilibrium point [Ph⁻] = [HPh]

 \therefore pH = pK_{In}. also K_{In} = [H⁺]

Where K_{In} is the ionization constant of the indicator

Solubility Product: Consider a binary electrolyte A_xB_y it solubility S mole/litre.

$$A_{x}B_{y} \xrightarrow{xA^{+y}} yB^{-x} K_{eq} = \frac{[x^{+y}]^{x}[B^{-x}]^{y}}{[A_{x}B_{y}]}$$
$$K_{eq}[A_{x}B_{y}] = [x^{+y}]^{x}[B^{-x}]^{y}$$
$$K_{sp} = [x^{+y}]^{x}[B^{-x}]^{y} = x^{x}y^{y}S^{(x+y)}$$

 K_{sp} is called solubility product. Solubility product may be defines as "the product of the concentration of ions in a saturated solution of an electrolyte at a given temperature". From solubility product, we may conclude that;

- Case (i): If, [ionic product] < K_{sp}. Then, the solution is unsaturated *i.e.* more solute go into the solution.
- Case (ii): If, [ionic product] = K_{sp}. The solution is just saturated *i.e.* no more solute can be dissolved.
- Case (iii): If, [ionic product] > K_{sp}. The solution is supersaturated *i.e.*, precipitation takes place. Knowing the values of K_{sp} and K_a, solubility of the salt can be calculated.

Calculation of Solubilities of Salts: We shall now discuss the solubilities of different types of salts under various conditions.

 Solubilities of AgCl (salt of a strong acid and strong base) in water: AgCl would dissolve in water as,

 $AgCl(s) \longrightarrow Ag^{+}(aq) + Cl^{-}(aq)$

At saturation point, $AgCl(s) \Longrightarrow Ag^+(aq) + Cl^-(aq)$

If the solubility of the salt is x moles /l

- \therefore [Ag⁺] = xM,[Cl⁻] = xM \Rightarrow x² = K_{sp} or x = $\sqrt{K_{sp}}$
- Solubility of CH₃COOAg (salt of weak acid and strong base) in water: CH₃COOAg dissolves and reaches saturation. Since it is a salt of weak acid and strong base, it would hydrolyse. If the solubility of the salt is *x* moles/*l* then
 CH COOAg(s) CH COO⁻(ag) + Ag⁺(ag)

At eqb:
$$x - y$$
 x

$$CH_{3}COO^{-}(aq) + H_{2}O \Longrightarrow CH_{3}COOH(aq) + H^{+}(aq)$$

Where y is the amount of CH₃COO⁻ ion that is hydrolysed.

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$$\therefore = \frac{C\alpha \times C\alpha}{[C - C\alpha]} \frac{y^2}{(x - y)} = \frac{K_w}{K_a}$$

Knowing the values of K_{sp} and K_a , solubility of the salt can be calculated.

Solubility of CH_3COOAg (salt of a weak acid and strong base) in an acid buffer of pH = 4 (assuming that the buffer does not have any common ion by CH_3COOAg) CH_3COOAg would dissolve and reach equilibrium. It would then be hydrolysed. If the solubility of the salt is x'M in this solution, then

At eq;
$$CH_3COOAg(s) \rightleftharpoons CH_3COO^-(aq) + Ag^+(aq)$$

 $x' - y'$
 x'
 $CH_3COO^-(aq) + H^+ \rightleftharpoons CH_3COOH(aq)$
 $x' - y'$
 10^{-4}
 y'

Since the solution is a buffer, the pH will be maintained.

$$\therefore (x'-y')x' = K_{sp}$$

$$y' = 1$$

$$\Rightarrow \frac{y}{10^{-4} \times (x' - y')} = \frac{1}{K_a}$$

Since in presence of basic buffer, the degree of hydrolysis will be suppressed by already existing ⁻OH ions, therefore the approximated formula which can be used is

$$x'^{2} = K_{sp}^{"}(CH_{3}COOAg)$$
 (neglecting y'')

Knowing K_{sp} and K_{a} , the solubility can be calculated.

MULTIPLE CHOICE QUESTIONS

Oswald Dilution Law (Ionisation of Weak Electrolytes)

- 1. Degree of dissociation of 0.1 N CH₃COOH is: (Dissociation constant = 1×10^{-5})
- **a.** 10^{-5} **b.** 10^{-4} **c.** 10^{-3} **d.** 10^{-2} **2.** In weak electrolytic solution, degree of ionization:

a. Will be proportional to dilution

b. Will be proportional to concentration of electrolyte

c. Will be proportional to the square root of dilution

- d. Will be reciprocal to the dilution
- **3.** 0.2 molar solution of formic acid is ionized 3.2%. Its ionization constant is:

a.	1×10^{-12}	b.	2.1×10^{-4}
c.	1.25×10^{-6}	d.	1×10^{-14}

 A monoprotic acid in 1.00 M solution is 0.01% ionised. The dissociation constant of this acid is:

a.	1×10^{-8}	b.	1×10^{-4}
c.	1×10^{-6}	d.	10^{-5}

5. If α is the degree of ionization, C the concentration of a weak electrolyte and Ka the acid ionization constant, then the correct relationship between α , C and K_a is:

a.
$$\alpha^2 = \sqrt{\frac{K_a}{C}}$$

b. $\alpha^2 = \sqrt{\frac{C}{K_a}}$
c. $\alpha = \sqrt{\frac{K_a}{C}}$
d. $\alpha = \sqrt{\frac{C}{K_a}}$

 Vant hoff factor of BaCl₂ of conc. 0.01M is 1.98. Percentage dissociation of BaCl₂ on this conc. Will be:

a. 49 **b.** 69 **c.** 89 **d.** 98

7. The addition of a polar solvent to a solid electrolyte results in:

a. Polarization	b. Association
c. Ionization	d. Electron transfer

8. The values of dissociation constants of some acids (at 25°C) are as follows. Indicate which is the strongest acid in water?

a.	1.4×10^{-2}	b.	1.6×10^{-4}
c.	4.4×10^{-10}	d.	4.3×10^{-7}

9. At infinite dilution, the percentage ionisation for both strong and weak electrolytes is:

a. 1% **b.** 20% **c.** 50% **d.** 100%

10. Electrolytes when dissolved in water dissociate into their constituent ions. The degree of dissociation of an electrolyte increases with:

- a. Increasing concentration of the electrolyte b. Decreasing concentration of the electrolyte c. Decreasing temperature d. Presence of a substance yielding a common ion 11. Which of the following substance is an electrolyte? a. Chloroform **b.** Benzene c. Toluene d. Magnesium chloride 12. An example for a strong electrolyte is: a. Urea **b.** Ammonium hydroxide c. Sugar d. Sodium acetate **Relative Strength of Weak Acids and Bases 13.** The conjugate acid of HPO_3^{2-} is: a. H₃PO₄ **b.** H₃PO₃ \mathbf{c} . $\mathrm{H}_{2}\mathrm{PO}_{3}^{-}$ **d.** PO_4^{3-}
- 14. The pKa for acid A is greater than pKa for acid B. The strong acid is:
 a. Acid B
 b. Acid A
 - c. Both A and B d. Neither A nor B
- **15.** Which of the following can act both as Bronsted acid and Bronsted base?

a. Cl^- **b.** HCO_3^- **c.** H_3O^+ **d.** OH^-

16. Which one of the following can be classified as a Bronsted base?

a. NO_3	b. H ₃ O ⁺
c. NH ⁺	d. CH ₂ COOH

- 17. The strength of an acid depends on its tendency to:
 a. Accept protons
 b. Donate protons
 c. Accept electrons
 d. Donate electrons
- **18.** Dissociation of H_3PO_4 takes place in following steps: **a.** 1 **b.** 2 **c.** 3 **d.**4
- 19. 100ml of 0.2 M H_2SO_4 is added to 100ml of 0.2 M NaOH. The resulting solution will be:

a. Acidic	b. Basic
c. Neutral	d. Slightly basic

- 20. When 100 ml of 1M NaOH solution is mixed with 10 ml of 10 M H₂SO₄, the resulting mixture will be?
- a. Acidic
 b. Alkaline
 c. Neutral
 d. Strongly alkaline

 21. When FeCl₃ gets soluble in water, then its solution represents which of the characteristics?

 a. Amphoteric
 b. Acidic
 - c. Basic d. Neutral

22. For the reaction in aqueous solution $Zn^{2+} + X^{-} = ZnX^{+}$, the K_{eq} is greatest when X is:

d. I⁻

a. F⁻ **b.** $NO_2^$ c. ClO_4^-

- 23. In the equilibrium:
 - $CH_{3}COOH + HF \implies CH_{3}COOH_{2}^{+} + F^{-}$
 - **a.** F⁻ is the conjugate acid of CH₂COOH
 - **b.** F⁻ is the conjugate base of HF
 - **c.** CH₃COOH is the conjugate acid of CH₃COOH₂⁺
- 24. With reference to protonic acids, which of the following statements is correct?
 - **a.** PH_3 is more basic than NH_3
 - **b.** PH_3 is less basic than NH_3
 - c. PH_3 is equally basic as NH_3
 - **d.** PH_3 is amphoteric while NH_3 is basic

25.	Orthoboric acid in aqueous medium is:		
	a. Monobasic	b. Dibasic	
	c. Tribasic	d. All are correct	

pH Scale and Buffer Solutions

26. Which of the anhydrous salts when come in contact with water turns blue?

- a. Ferrous sulphate **b.** Copper sulphate d. Cobalt sulphate c. Zinc sulphate
- 27. The species among the following, which can act as an acid and a base, is?

a.	HSO_4^-	b. SO_4^{2-}	c. H ₃ O ⁺	d .	C1 ⁻
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28. Which one is Lewis acid?

a.	Cl	b. Ag ⁺	c. C_2H_5OH	d. S^2
		U U	2 3	

29. Let the solubility of an aqueous solution of $Mg(OH)_2$ be then its k_{sp} is:

a. $4x^{3}$ **b.** 108x⁵ **c.** $27x^4$ **d.** 9x

- **30.** The solubility product of $BaSO_4$ at 25°C is 1.0×10^{-9} . What would be the concentration of H₂SO₄ necessary to precipitate BaSO₄ from a solution of 0.01M Ba²⁺ ions? **a.** 10⁻⁹ **b.** 10⁻⁸ **c.** 10^{-7} **d.** 10^{-6}
- **31.** The solubility of CaF_2 is a moles/litre. Then its solubility product is:

a. s² **b.** $4s^{3}$ **c.** $3s^2$ **d.** s^3

32. In which of the following salt hydrolysis takes place? a. KCl **b.** NaNO₃ c. CH₃COOK d. K_2SO_4

- 33. Which of the following 0.1M solution will contain the largest concentration of hydronium ions?
 - a. NaHCO₃ **b.** NH₄Cl
 - c. HCl d. NH₃
- 34. Given pH of a solution A is 3 and it is mixed with another solution B having pH 2. If both mixed then resultant pH of the solution will be:
 - **a.**3.2 **d.**3.5 **b.**1.9 **c.**3.4
- 35. On adding solid potassium cyanide to water: a. pH will increase
 - **b.** pH will decrease

a. 3

- c. pH will not change
- d. Electrical conductance will not change
- **36.** The pH of a 0.001M NaOH will be **b.** 2
- 37. When solid potassium cyanide is added in water then

c. 11

d. 12

- a. pH will increase
- **b.** pH will decrease
- c. pH will remain the same
- d. Electrical conductivity will not change
- **38.** The pH of water at 25°C is nearly
 - **a.** 2 **b.** 7 **c.** 10 **d.** 12
- **39.** Which will have maximum pH?
 - **a.** Distilled water
 - **b.** 1M NH₃
 - c. 1M NaOH
 - d. Water saturated by chlorine
- **40.** The dissociation constant of an acid HA is 1×10^{-5} . The pH of 0.1 molar solution of the acid will be
 - a. Five **b**. Four c. Three d. One
- **41.** What will be the pH of a 10^{-8} M HCl Solution? **a.** 8.0 **b.** 7.0 **c.** 6.98 **d.** 14.0
- 42. 20ml of 0.5 N HCl and 35ml of 0.1N NaOH are mixed. The resulting solution will
 - **a.** Be neutral
 - **b.** Be basic
 - c. Turn phenolphthalein solution pink
 - d. Turn methyl orange red
- 43. An acidic buffer solution can be prepared by mixing solution of
 - a. Ammonium acetate and acetic acid
 - b. Ammonium chloride and hydrochloric acid
 - c. Sulphuric acid and sodium sulphate
 - d. Acetic acid and sulphuric acid

44.	If pOH of a	solution	is 6.0,	then i	its pH y	will
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a. 6	b. 10
c. 8	d. 14

- 45. 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
 c. 10
 d. 14
- **46.** A physician wishes to prepare a buffer solution at pH = 3.58 that efficiently resists changes in pH yet contains only small concentration of the buffering agents. Which of the following weak acids together with its sodium salt would be best to use
 - **a.** m-chlorobenzoic acid $(pK_a = 3.98)$
 - **b.** p-chlorocinnamic acid $(pK_a = 4.41)$
 - **c.** 2, 5– dihydroxy benzoic acid $(pK_a = 2.97)$
 - **d.** Acetoacetic acid $(pK_a = 3.58)$
- 47. What will be the pH of a solution formed by mixing 40 ml of 0.10 M HCl with 10 ml of 0.45 M 0.45 NaOH
 a. 12
 b. 10

c. 8	d. 6

- **48.** As the temperature increases, the pH of a KOH solution **a.** Will decreases
 - **b.** Will increases
 - **c.** Remains constant
 - **d.** Depends upon concentration of KOH solution
- 49. pH value of N/10 NaOH solution is

a. 10	b. 11
c. 12	d. 13

Solubility Product

- **50.** An aqueous solution of sodium carbnate has a pH greater than 7 because:
 - a. It contains more carbonate ions than H₂O molecules
 - **b.** Contains more hydroxide ions than carbonate ions
 - **c.** Na^+ ions react with water
 - **d.** Carbonate ions react with H_2O
- **51.** Assuming complete dissociation, which of the following aqueous solutions will have the same pH value?
 - a. 100ml of 0.01 M HCl
 - **b.** 100ml of 0.01 M H₂SO₄
 - **c.** 50 ml of 0.01 M HCl
 - d. Mixture of 50 ml of 0.02 M $\rm H_2SO_4$ and 50 ml of 0.02 M NaOH

52. The expression for the solubility product of $Al_2 (SO_4)_3$ is

a.	$K_{sp} = [Al^{3+}] (SO_4^{2-}]$	b. $K_{sp} = [Al^{3+}]^2 (SO_4^{2-}]^3$
c.	$K_{sp} = [Al^{3+}]^3 (SO_4^{2-}]^2$	d. $K_{sp} = [Al^{3+}]^2 (SO_4^{2-})^2$

53. 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

a.
$$2.0 \times 10^{-6}$$
 M **b.** 1.0×10^{-4} M **c.** 1.6×10^{-4} M **d.** 4.0×10^{-10} M

54. If the solubility product K_{sp} of a sparingly soluble salt MX_2 at 25°C is 1.0×10^{-11} , the solubility of the salt in *mole litre*⁻¹ at this temperature will be

a. 2.46×10^{14}	b. 1.36×10 ⁻⁴
c. 2.60×10^{-7}	d. 1.20×10^{-10}

- 55. Solubility product of a sulphide MS is 3×10⁻²⁵ and that of another sulphide NS is 4×10⁻⁴⁰. In ammoniacal solution
 a. Only *NS* gets precipitated
 b. Only *MS* gets precipitated
 c. No sulphide precipitates
 d. Both sulphides precipitate
- **56.** At 298 K, the solubility product of $PbCl_2 is 1.0 \times 10^{-6}$.. What will be the solubility of $PbCl_2$ in moles/litre

a. 6.3×10^{-3}	b. 1.0×10^{-3}
c. 3.0×10^{-3}	d. 4.6×10^{-14}

- **57.** The solubility of $BaSO_4$ in water is 2.33×10^{-3} gm/litre. Its solubility product will be (molecular weight of $BaSO_4=233$)
 - **a.** 1×10^{-5} **b.** 1×10^{-10} **c.** 1×10^{-15} **d.** 1×10^{-20}
- 58. The addition of HCl will not suppress the ionization ofa. Acetic acidb. Benzoic acid
 - **c.** H_2S **d.** Sulphuric acid
- **59.** Why pure NaCl is precipitated when HCl gas is passed in a saturated solution of NaCl:
 - a. Impurities dissolves in HCl
 - **b.** The value of $[Na^+]$ and $[Cl^-]$ becomes smaller than K_{sp} of NaCl
 - **c.** The value of $[Na^+]$ and $[Cl^-]$ becomes greater than K_{sp} of NaCl
 - **d.** HCl dissolves in the water
- **60.** Which one of the following is most soluble?
 - **a.** $\text{CuS}(\text{K}_{\text{sp}} = 8 \times 10^{-37})$ **b.** $\text{MnS}(\text{K}_{\text{sp}} = 7 \times 10^{-16})$ **c.** $\text{Bi}_2\text{S}_3(\text{K}_{\text{sp}} = 1 \times 10^{-70})$ **d.** $\text{Ag}_2\text{S}(\text{K}_{\text{sp}} = 6 \times 10^{-51})$

NCERT EXEMPLAR PROBLEMS

More than One Answer

- 61. Assuming complete dissociation, which of the following aqueous solutions will have the same pH value:
 a. 100ml of 0.01 M HCl
 b. 100ml of 0.01 M H₂SO₄
 - **c.** 50ml of 0.01 M HCl

d. Mixture of 50ml of 0.02 M $\rm H_2SO_4$ and 50ml of 0.02 M NaOH

- 62. Which of the following will not function as a buffer solution?
 a. NaCl and NaOH
 b. NaOH and NH₄OH
 c. CH₃COONH₄ and HCl
 d. Borax and boric acid
- **63.** An acid-base indicator has the acid form of the indicator is red and the form is blue. Then:
 - **a.** pH is 4.04 when indicator is 75% red
 - **b.** pH is 5.00 when indicator is 75% blue.
 - **c.** pH is 5.00 when indicator is 75% red.
 - **d.** pH is 4.05 when indicator is 75% blue.
- 64. The colour of an electrolyte solution depends on:
 - **a.** The nature of the anion
 - **b.** The nature of the cation
 - **c.** The nature of both the ions
 - **d.** The nature of the solvent
- **65.** Correct statement is:
 - **a.** NH₄Cl gives alkaline solution in water
 - **b.** CH₃COONa gives acidic solution in water
 - **c.** CH₃COOH is a weak acid
 - **d.** NH_4OH is a strong base
- 66. At 90°C pure water has $[H_3O^+] = 10^{-6}$ M, the value of K_w at this temperature will be:

a.	10 ⁻⁶	b.	10^{-12}
c.	10^{-14}	d.	10^{-8}

67. K_{sp} value of Al(OH)₃ and Zn(OH)₂ are 8.5×10^{-23} and 1.8×10^{-14} respectively. If NH₄ OH is added in a solution of Al³⁺ and Zn²⁺, which will precipitate earlier:

a. Al(OH) ₃	b. $\operatorname{Zn}(\operatorname{OH})_2$
c. Both together	d. None

- 68. The compound whose 0.1M solution is basic is:a. Ammonium acetateb. Calcium carbonatec. Ammonium sulphated. Sodium acetate
- 69. The following reaction is known to occur in the body CO₂ + H₂O → H₂CO₃ → H⁺ + HCO₃⁻. If CO₂ escapes from the system:

- a. pH will decrease
- b. Hydrogen ion concentration will decrease
- **c.** H₂CO₃ concentration will be unaltered
- **d.** The forward reaction will be promoted
- **70.** The K_{sp} of Mg(OH)₂ is 1×10^{-12} , 0.01 M Mg (OH₂) will precipitate at the limiting pH:

a. 3	b. 9
c. 5	d. 8

Assertion and Reason

Note: Read the Assertion (A) and Reason (R) carefully to mark the correct option out of the options given below:

- **a.** If both assertion and reason are true and the reason is the correct explanation of the assertion.
- **b.** If both assertion and reason are true but reason is not the correct explanation of the assertion.
- c. If assertion is true but reason is false.
- **d.** If the assertion and reason both are false.
- e. If assertion is false but reason is true.
- 71. Assertion: CHCl₃ is more acidic than CHF₃.Reason: The conjugate base of CHCl₃ is more stable than CHF₃.
- 72. Assertion: Addition of silver ions to a mixture of aqueous sodium chloride and sodium bromide solution will first precipitate AgBr rather than AgCl.
 Reason: K_{sp} of AgCl < K_{sp} of AgBr.
- 73. Assertion: Ionic reactions are not instantaneous.Reason: Oppositely charged ions exert strong forces.
- 74. Assertion: pH of hydrochloric acid solution is less than that of acetic acid solution of the same concentration.Reason: In equimolar solutions, the number of titrable protons present in hydrochloric acid is less than that persent in acetic acid.
- **75. Assertion:** A ionic product is used from any types of electrolytes whereas solubility product is applicable only to sparingly soluble salts.

Reason: Ionic product is defined at any stage of the raction whereas solubility product is only appicable to the saturation stage.

- 76. Assertion: A solution of FeCl₃ in water produce brown precipitate on standing.Reason: Hydrolysis of FeCl₃takes place in water
- **77. Assertion:** BaCO₃ is more soluble in NHO₃ than in plain water.

Reason: Carbonate is a weak base and reacts with the H^+ from the strong acid, casuing the barium salt to dissociate.

78. Assertion: The amino acid glycine predominantly exists in the form of ${}^{\oplus}$ NH₃CH₂COO^{\circ}.

Reason: The conjugate acid of glycine is $NH_2CH_2COO^{\circ}$.

- 79. Assertion: The pH of an aqueous solution of CH₃COOH remains unchanged on the addition of CH₃COONa.Reason: The ionization of CH₃COOH is suppressed by the addition of CH₃COONa.
- **80.** Assertion: On addition of NH₄Cl to NH₄OH, pH decreases but remains gemains greater than 7.

Reason: Addition of $\stackrel{\oplus}{NH}_4$ ion decreases ionization of NH₄OH,

thus $[{\stackrel{\scriptscriptstyle \Theta}{O}} H]$ decreases and also pH decreases.

Comprehension Based

Paragraph –I

In qualitative analysis, cations of group II as group II as well as group IV both are precipitated in the form of sulphides. Due to low value of K_{sp} of group II sulphides, group reagent is H_2S in the presence of dil. HCl and due to high value of K_{sp} of group IV sulphides, group reagent is H_2S in the presence of NH₄OH and NH₄Cl. In solution containing 0.1M each of Sn²⁺, Cd²⁺, and Ni²⁺ ions, H_2S gas is passed. K_{sp} of SnS = 8×10^{-29} , K_{sp} of CdS = $15 \ 10^{-28}$, K_{sp} of NiS= 3×10^{-21} , K_1 of $H_2S=1 \times 10^{-7}$, K_2 of $H_2S=1 \times 10^{-14}$

81. If H₂S is passed into the above mixture in the presence of HCl, which ion will be precipitated first?

a. SnS	b. CdS
c. NiS	d. SnS and CdS

82. At what value of pH, NiS will start to precipitate?a. 12.76b. 7

c.	1.24		d
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83. Which of the following sulphides is more soluble in pure water?

4

a. Cds	b. NiS
c. SnS	d. Equal solubility for all

84. If 0.1 M HCl is mixed in the solution containing only 0.1 MCd²⁺ ions and saturated with H₂S, then [Cd²⁺] remaining in the solution after CdS stops to precipitate is:

a. 10^{-8}	b. 8.2×10^{-9}
c. 5.6×10^{-6}	d. 5.6×10^{-10}

Paragraph –II

Acid rain takes place due to combination of acidic oxides with water and it is an environmental concern all over the world. Assuming rain water is uncontaminated with HNO₃ or H_2SO_4 and is in equilibrium with 1.25×10^{-4} atm CO₂. The Henry's law

constant (K_H) is 1.25×10^6 torr. K_{a1} of H₂CO₃ = 4.3×10^{-7} . Given K_fCuCl^{\oplus} = $1.0(K_f$ is formation constant of CuCl^{\oplus})

85.	What is the pH o	f natural rain water?
	a. 5.64	b. 7.00
	c. 5.87	d. 7.40

86. If content is the atmosphere is 0.64 ppm by volume, pH of rain water is (assume 100% ionization of acid rain as monobasic acid).

a. 4.0	b. 5.0
c. 6.0	d. 7.0

Paragraph –III

In acid-base titration reacts rapidly to neutralize each other. Equivalence point is point at which the acid and the base (or oxidising agent and reducing agent) have been added in equivalent quantities. The end point is the point at which the titration stops. Since the purpose of the indicator is to stop the titration close to the point at which the acid and base were added in equivalent quantities, it is important that the equivalent point and the end point be as close as possible. The indicator must change colour at a pH close to that of a solution of the salt of the acid and base. Significantly, the pH changes most rapidly neat the equivalence point. The exact shape of a titration curve depends on K_a and K_b of acid base.



87. The following curve represents titration curve of HCl against KOH. The pH at equivalent point is. Examine the titration curve below and answer the question:

a. 3	b. 6
c. 7	d. 8

88.	The curve represents the titration of?					
	a. CsOH by HBr	b. HCl by NaOH				
	c. HCl by KOH	d. NH_3 by HNO_3				
89.	The suitable indicator	for the titration is?				
	a. Methyl orange	b. Bromothymol				
	c. Methyl red	d. All of these				
90.	The pH at equivalence	e point is?				
	a. 2	b. 3				
	c. 7	d. 11				

91. Which of the following curves indicates the titration of a weak diprotic acid by KOH by equivalent strength?



Match the Column

92. Match the statement of Column I with those in Column II:

Column I	Column II						
(A) 0.1 M CH ₃ COH (pK _a	1. Acidic buffer at its						
= 4.74) + 0.1M	maximum capacity						
CH ₃ COONa							
(B) 0.1 MCH ₃ COOH +	2. Buffer solution						
0.1M HCl							
(C) 0.1 MCH ₃ COOH	3. pH < 7at 25°C						
$(pK_a = 4.74) + 0.1M$							
$NH_4OH(pK_a = 4.74)$							
(D) 300 mL of 0.1 M	4. pH = 7at 25°C						
CH ₃ COONa + 100mL							
of 0.1 M HCl							
a. $A \rightarrow 1, B \rightarrow 3, C \rightarrow 4, D \rightarrow 2$							
b. $A \rightarrow 1, B \rightarrow 4, C \rightarrow 4, D \rightarrow 3$							
$\mathbf{a.} A \rightarrow 3, B \rightarrow 1, C \rightarrow 4, D \rightarrow 2$							
d. $A \rightarrow 2, B \rightarrow 3, C \rightarrow 4, D \rightarrow 1$							

93. Match the statement of Column I with those in Column II:

	Column I	Column II
	(A) Solubility of AgCl in 0.1 M HCl	1. $\frac{K_{sp}}{(0.1)^2}$
	(B) Solubility of Ni (OH) ₂ in 0.1 M NaOH	2. $\frac{K_{sp}}{0.1}$
	(C) Solubility of Ni (OH) ₂ in NiCl ₂	3. $\frac{K_{sp}}{(0.1)^3}$
	(D) Solubility of Al (OH) ₃ in 0.1 M NaOH	$4. \left(\frac{K_{sp}}{4 \times 0.1}\right)^{1/2}$
	(E) Solubility of AgCN in a buffer solution of pH=3	$5. \left[K_{sp} \left(1 + \frac{H^{\oplus}}{k_a} \right) \right]^{1/2}$
ę	a. $A \rightarrow 2$, $B \rightarrow 1$, $C \rightarrow 4$, $D \rightarrow 3$, $E \rightarrow 5$	
ł	b. $A \rightarrow 1$, $B \rightarrow 2$, $C \rightarrow 4$, $D \rightarrow 3$, $E \rightarrow 5$	i
(e. $A \rightarrow 2$, $B \rightarrow 3$, $C \rightarrow 4$, $D \rightarrow 1$, $E \rightarrow 5$	
(d. $A \rightarrow 3$, $B \rightarrow 1$, $C \rightarrow 4$, $D \rightarrow 2$, $E \rightarrow 5$	

94. Match the statement of Column I with those in Column II:

Column I	Column II				
(A) HSO_4°	1. Lewis acid				
(B) BF ₃	2. Lewis base				
(C) $\ddot{N}H_{3}$	3. Bronsted acid				
(D) [☉] H	4. Bronsted base				
a. A \rightarrow 3,4, B \rightarrow 1, C \rightarrow 2,4, D \rightarrow	>2,4				
b. A→3,4, B→1, C→2,4, D→2,2					
c. $A \rightarrow 4, 4, B \rightarrow 2, C \rightarrow 1, 4, D \rightarrow 2, 4$					
d. $A \rightarrow 2,4, B \rightarrow 1, C \rightarrow 2,4, D \rightarrow 2,3$					

95. Match the statement of Column I with those in Column II:

Column I	Column II		
(A) Hydrolysis of ethyl	1. Second-order reaction		
acetate in basic solution			
(B) Hydrolysis of ethyl	2. First-order reaction.		
acetate in acidic solution			
(C) The limits of pH values	3. $pK_a \neq 1$		
of a buffer solution.			
(D) The buffer capacity of	4. Equal		
a solution is maximum			
when the concentration			
of salt to the acid is			
a. $A \rightarrow 1$, $B \rightarrow 2$, $C \rightarrow 3$, $D \rightarrow 1,4,2$	2		
b. $A \rightarrow 1$, $B \rightarrow 2$, $C \rightarrow 2$, $D \rightarrow 1,4,3$;		
c. $A \rightarrow 1$, $B \rightarrow 1$, $C \rightarrow 2$, $D \rightarrow 1,3,2$			
d. $A \rightarrow 1$, $B \rightarrow 2$, $C \rightarrow 1$, $D \rightarrow 1,4,4$	ļ		

Integer

- **96.** How many of the conbinations of reactants in (8) above will react until more than 98% of the limiting quantity is used up?
- **97.** The dissociation constant of a substituted benzoic acid at 25° C is 1.1×10^{-1} . Find the pH of a 0.01 M solution of its sodium salt.
- 98. Among the following, find the total number of compounds whose aqueous solution turns red litmus paper blue KCN, K₂SO₄, (NH₄)₂, C₂O₄, NaCl, Zn(NO₃)₂, FeCl₂, K₂CO₃, NH₄NO₂, LiCN.
- **99.** Find the total number of diprotic acids among the following. H₃PO₄, H₂SO₄, H₃ PO₃, H₂CO₃, H₂S₂O₇, H₃BO₃, H₃PO₂, H₂CrO₄, H₂SO₃
- **100.** In 1 L saturated solution of AgCl(K_{sp} of AgCl) =1.6×10⁻¹⁰), 0.1 mol of CuCl (K_{sp} CuCl = 1.0×10⁻⁶) is added. The resultant concentration of Ag⁺ in the solution is 1.6 ×10^{-x}. Calculate the value of x.

ANSWER

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
d	с	b	а	с	а	с	а	d	b
11.	12.	13.	14.	15.	16.	17.	18.	19.	20.
d	d	с	а	b	а	b	с	а	а
21.	22.	23.	24.	25.	26.	27.	28.	29.	30.
b	а	b	b	а	b	а	b	а	с
31.	32.	33.	34.	35.	36.	37.	38.	39.	40.
b	с	с	b	а	с	а	b	с	с
41.	42.	43.	44.	45.	46.	47.	48.	49.	50.
c	с	а	c	а	с	а	а	d	b
51.	52.	53.	54.	55.	56.	57.	58.	59.	60.
a,d	b	b	b	d	а	b	d	с	b
61.	62.	63.	64.	65.	66.	67.	68.	69.	70.
a,d	a,b,c	a,b	c	с	b	а	d	b	b
71.	72.	73.	74.	75.	76.	77.	78.	79.	80.
а	с	e	с	b	а	а	с	d	а
81.	82.	83.	84.	85.	86.	87.	88.	89.	90.
с	c	а	а	с	b	с	а	d	с
91.	92.	93.	94.	95.	96.	97.	98.	99.	100.
а	а	а	а	а	8	8	3	6	7

SOLUTION

Multiple Choice Questions

1. (d) Degree of dissociation $\alpha = ?$

Normality of solution = 0.1 N = $\frac{1}{10}$ N

Volume =10 litre Dissociation constant $K = 1 \times 10^{-5}$

 $K = \frac{\alpha^2}{V}; \ \alpha = \sqrt{KV}$ $= \sqrt{1 \times 10^{-5} \times 10}$ $\alpha = 1 \times 10^{-2}$

(c) Ostwald's dilution formula is α² = K(1-α)/C but for weak electrolyte α is very small.

So that $(1-\alpha)$ is neglected for weak electrolytes. So for

weak electrolyte the dilution formula is $\alpha = \sqrt{\frac{K}{C}}$.

3. **(b)**
$$K_a = C\alpha^2 = 0.2 \times \left(\frac{32}{100}\right)^2$$

= 2.048×10⁻⁴

4. (a)
$$K = \frac{\alpha^2 C}{1 - \alpha}; \alpha = \frac{0.01}{100} \approx 1$$

K =
$$\alpha^2 C = \left[\frac{0.01}{100}\right]^2 \times 1$$

= 1×10^{-8} .

5. (c) According to the Ostwald's dilution formula $\alpha^2 = \frac{K(1-\alpha)}{C}.$

But for weak electrolytes α is very small. So that $(1 - \alpha)$ can be neglected. So that $\alpha = \sqrt{\frac{K_a}{C}}$.

6. (a)
$$\operatorname{BaCl}_2 = \operatorname{Ba}^{2+} + 2\operatorname{Cl}^-$$

Initially 1 0 0
After dissociation $a - \alpha$ α 2α
Total = $1 - \alpha + \alpha + 2\alpha = 1 + 2\alpha$
 $\alpha = \frac{1.98 - 1}{\alpha} = \frac{0.98}{\alpha} = 0.49$
For a mole $\alpha = 0.49$
For 0.01 mole $\alpha = \frac{0.49}{0.01} = 49$

- 7. (c) Polar solvent facilitate ionisation of strong electrolytes due to dipole-ion attraction.
- 8. (a) More is K_a , lesser is $pK_a(pK_a = -\log K_a)$ more is acidic strength.
- **9.** (d) According to Ostwald's dilution law because degree of ionization is directly proportional to the dilution.
- **10.** (b) Because the degree of dissociation is inversely proportional to the concentration of the electrolyte.
- 11. (d) $MgCl_2 \rightleftharpoons Mg^{++} + 2Cl^{-}$ in aqueous solution it is dissociated into ions.
- 12. (d) $CH_3COONa \Longrightarrow CH_3COO^- + Na^+$

 $H_2O \longrightarrow H^+ + OH^-$ CH₃COOH + NaOH

- **13.** (c) $H_2 PO_4^- \longrightarrow H^+ + HPO_4^{2-}$ action.
- 14. (a) Because those acid have higher pK_a value are weak acid.
- **15.** (b) Those substance accept the proton are called Bronsted base and which is donate the proton are called Bronsted acid.

 $HCO_3^- + H^+ \Longrightarrow H_2CO_3$ Bronsted base.

 $HCO_3^- \longrightarrow H^+ + CO_3^{--}$ Bronsted acid.

- 16. (a) Those compound which accept H^+ is called bronstad base NO_3^- accept H^+ and form HNO_3 . So it is a base.
- 17. (b) Those substances which lose proton are called acid. *e.g.* strong acid have a strong tendency to donate a proton.

18. (c)
$$H_3PO_4 \xrightarrow{lstep} H^+ + H_2PO_4^-$$

 $H_2PO_4^- \xrightarrow{llstep} H^+ + HPO_4^{--}$
 $HPO_4^{--} \xrightarrow{lllstep} H^+ + PO_4^{---}$

19. (a) M.eq. of 0.2M H₂SO₄

 $= \frac{2 \times 0.2M}{1000} \times 100 = 0.04 \ m/l$ M.eq. of .2M NaOH $= \frac{0.2}{1000} \times 100 = 0.02 \ m/l$ left [H⁺] = .04 - .02 = .02. Total volume = 200 = $\frac{.02}{200}$ = .0001 = 10⁻⁴ M pH = 4.

20. (a) $N_{NaOH} = 1 \times 1 = 1N$

 $N_{H_2SO_4} = 2 \times 10 = 20N$

M.eq. of NaOH $= 1 \times 100 = 100$

M.eq. of $H_2SO4 = 20 \times 10 = 200$

Thus M.eq. of acid are left and therefore pH < 7, so the resulting mixture will be acidic.

- **21.** (b) Hydrolysis of Fe^{3+} $Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+$
- **22.** (a) Because of F⁻ is a highly electronegative. So it is easily lose the electron and reaction occur rapidly.
- 23. (b) CH₃COOH + HF → CH₃COOH⁺₂ + F⁻.
 HF gives H⁺ to the CH₃COOH.
 So it is a conjugate base of HF.
- **24.** (b) The basic character of hydride decreases down the group.
- 25. (a) H₃BO₃ + H₂O = [B(OH)₄]⁻ + H⁺
 H₃BO₃ is a weak monobasic acid if does not act as a H⁺
 donor but behaves as a Lewis acid.
- 26. (b) Cu(II) complexes are blue. The four water molecules are attached with secondary valencies of the metal atom *e.g.*, [Cu(H₂O)₄]SO₄. H₂O.

27. (a) The species which can accept as well as donate H⁺ can act both as an acid and a base.

$$\begin{array}{c} HSO_{4}^{-} + H^{+} & \longrightarrow & H_{2}SO_{4} \\ HSO_{4}^{-} & \longrightarrow & SO_{4}^{2-} + H^{+} \\ \end{array}$$

28. (b) Ag⁺ is an electron deficient compound and hence is a Lewis acid.

29. (a)
$$Mg(OH)_2 \implies Mg^{++} + 2OH^-_{(2X)^2} K_{sp} = 4X^3$$

30. (c)
$$BaSO_4 \implies Ba^{++} + SO_4^{--}$$

 $(S) = 0.01 \times S$
 $K_{sp} = S^2 = S \times S = 0.01 \times S$
 $S_{(SO_4^{--})} = \frac{K_{sp}}{S_{(Ba^{++})}} = \frac{1 \times 10^{-9}}{0.01} = 10^{-7} \text{ mole/litre}$

- **31.** (b) $\operatorname{CaF}_2 \rightleftharpoons \operatorname{Ca}_{(S)}^{++} + 2F^-_{(2S)^2}; K_{sp} = 4S^3$
- **32.** (c) Because it is a strong base.
- 33. (c) It is a strong acid and they lose proton in a solution.
- 34. (b) pH of the solution A = 3 $[H^+]_A = 10^{-3} M.$ pH of the solution B = 2 $[H^+]_B = 10^{-2} M$ $[H^+] = 10^{-3} + 10^{-2} = 10^{-3} + 10 \times 10^{-3}$ $= 11 \times 10^{-3}.$ pH = $-\log(11 \times 10^{-3}) = 3 - \log 11$ = 3 - 1.04 = 1.95
- **35.** (a) $CN^- + H_2O \longrightarrow HCN + OH^-$

Because OH⁻ concentration is increased.

36. (c) 0.001 M of NaOH means $[OH^{-}] = .001$

 $= 10^{-3} M \Rightarrow pOH = 3$ pH + pOH = 14 \Rightarrow pH = 14 - 3 = 11

- **37.** (a) $KCN + H_2O \longrightarrow KOH + HCN$, KOH is a strong base and HCN is a weak acid.
- **38.** (b) $[H^+] = [OH^-]$ $K_w = [H^+][OH^-] = 10^{-14}$
- \therefore [H⁺] = 10⁻⁷, pH = -log[H⁺] = 7.
- 39. (c) It is a strong base.
 1 M NaOH has maximum [OH⁻] and minimum [H⁺] and maximum pH.

40. (c)
$$HA \implies H^+ + A^-$$

 $[H^+] = 0.1 \text{ M}; [H^+]^2 = K_a \times C$
 $[H^+] = \sqrt{K_a \times C}$
 $= \sqrt{1 \times 10^{-5} \times 0.1} = \sqrt{10^{-6}}$
 $[H^+] = 10^{-3} \text{ M}; \text{ pH} = 3$
41. (c) $H_2O \implies [H^+] [OH^-]$
 $HCl \implies [H^+] = [H^+]_{H_2O} + [H^+]_{HCl}$
 $= 10^{-7} + 10^{-8}$
 $= 10^{-7} + 10^{-8}$
 $= 10^{-7} [1 + 10^{-1}]$
 $[H^+] = 10^{-7} \times \frac{11}{10}$
 $pH = -\log[H^+] = -\log\left(10^{-7} + \frac{11}{10}\right);$
 $pH = 6.958$
42. (c) (i) 20 *ml* of 0.5 *N HCl*
 $0.5N \implies 1000 \text{ ml } 0.5 \text{ mole HCl}$ is present in

42. (c) (1) 20 ml of 0.5 N HCl $0.5N \Rightarrow 1000 \text{ ml } 0.5 \text{ mole HCl}$ is present in 20 ml 20×0.5 1 0...10⁻²

$$=\frac{1000}{1000} = 1.0 \times 10$$

(ii) 35 ml of 0.1 N NaOH

 $0.1N \Rightarrow 1000ml \text{ of } 0.1 \text{ mole NaOH is } 35 ml$

$$=\frac{35\times0.1}{1000}=0.35\times10^{-2}$$

Total = 20 + 35 = 55 ml.

$$\Rightarrow (1.0-0.35)10^{-2} = 0.65 \times 10^{-2} \text{mole HCl}$$
$$\text{HCl} = \text{H}^{+}+\text{Cl}^{-}$$

 $\Rightarrow [HCl] = [H^+] + [Cl^-]$ 55 ml contains 0.65 × 10⁻² mole of H⁺ ions 0.65 × 10⁻² × 10³ 6.5

$$1000 \text{ ml} - \frac{0.63 \times 10^{-1} \times 10^{-1}}{55} = \frac{0.5}{55}$$
$$pH = -\log[H^{+}] = -\log(6.5/55)$$
$$= \log 55 - \log 6.5 = 0.92$$

Due to acidic nature of solutions the colour of phenolphthalein becomes pink.

43. (a) An acid buffer solution consists of solution of weak acid with strong base of its salt.

44. (c) pH + pOH = 14;

pH = 14 - pOH;pH = 14 - 6 = 8. 45. (a) $X^- + H_2O \longrightarrow OH^- + HX$ $K_b = \frac{[OH^-][HX]}{[X^-]}$ $HX \longrightarrow H^+ + X^ K_a = \frac{[H^+][X^-]}{[HX]}$ $\therefore \quad K_a \times K_b = [H^+][OH^-] = K_w = 10^{-14}$ Hence $K_a = 10^{-4}$ Now as $[X^-] = [HX]$, $pH = pK_a = 4$. 46. (c) $pH = pK_a + \log \frac{[Salt]}{[Acid]}$.

For small concentration of buffering agent and for maximum buffer capacity

$$\frac{[Salt]}{[Acid]} \approx 1 \; .$$

M HCl = $\frac{0.10}{1000} \times 40 = 0.004$ M

M.eq. of 0.45 M NaOH

$$= \frac{0.45 \times 10}{1000} = 0.0045M$$

Now left [OH⁻] = 0.0045 - 0.004
= 5 \times 10⁻⁴ M

Total volume = 50 ml.

$$[OH^{-}] = \frac{5 \times 10^{-4}}{50} \times 1000$$
$$[OH^{-}] = 1 \times 10^{-2}$$
$$pOH = 2 ; pH = 14 - pOH = 12.$$

- **48.** (a) pH will decrease because [OH⁻] increased due to this pOH is decreased.
- **49.** (d) In $\frac{N}{10}$ NaOH have $[OH^-] = 10^{-1}$ M means pOH = 1 and then pH + pOH = 14 pH = 14 - pOH = 13.
- 50. (b) pH > 7 = BasicIt means contain more hydroxide ions than carbonate ions.
- 51. (a,d) M.eq. of 0.01 M HCl = $\frac{.01 \times 100}{1000} = 1 \times 10^{-3}$ pH = 3

M.eq. of .02 M H₂SO₄ =
$$\frac{.04 \times 50}{1000} = 2 \times 10^{-3}$$

M.eq. of .02 M NaOH = $\frac{0.02 \times 50}{1000} = 1 \times 10^{-3}$
Left [H⁺] = $2 \times 10^{-3} - 1 \times 10^{-3}$
= 1×10^{-3} ; pH = 3

52. (b) Solubility of $Al_2(SO_4)_3$

$$Al_{2}(SO_{4})_{3} = 2Al^{+++} + 3SO_{4}^{-}$$
$$K_{sp} = [Al^{3+}]^{2} [SO_{4}^{2-}]^{3}$$

53. (b) $MX_2 \xrightarrow{} M_S^{2+} + 2X_{2S}^{-}$ $K_{sp} = (2S)^2(S) = 4S^3$ $\Rightarrow S = 2\sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{4 \times 10^{-12}}{4}}$ $= 1.0 \times 10^{-4} M.$

54. (b)
$$MX_2 \xrightarrow{M^+} M_{(S)}^+ + 2X_{(2S)^2}^- K_{sp} = 4S^3$$

 $S = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{1 \times 10^{-11}}{4}}$
 $= 1.35 \times 10^{-4}$

55. (d) The concentration of S^{2-} ions in group II is lowered by maintaining acidic medium in the presence of NH_4Cl . The ionization of H_2S is supressed due to common ion effect. So the ionic product is less than solubility product.

56. (a)
$$K_{sp} = 4s^{3}$$

 $S = \sqrt[3]{\frac{K_{sp}}{4}}$
 $= \sqrt[3]{\frac{1.0 \times 10^{-6}}{4}}$
 $= 6.3 \times 10^{-3}.$

57. (b) The solubility of BaSO₄ in g/litre is given 2.33×10^{-3}

$$\therefore$$
 in mole/litre. n = $\frac{W}{m. wt}$

$$=1\times10^{-5}=\frac{2.33\times10^{-3}}{233}$$

Because BaSO₄ is a compound

$$K_{sp} = S^2 = [1 \times 10^{-5}]^2 = 1 \times 10^{-10}$$

(d) Common ion effect is noticed only for weak electrolyte dissociation. H₂SO₄ is strong electrolyte.

- 59. (c) $\operatorname{NaCl}_{(s)} \longrightarrow \operatorname{Na}^{+}_{(aq)} + \operatorname{Cl}^{-}_{(aq)}$ $\operatorname{HCl} \longrightarrow \operatorname{H}^{+} + \operatorname{Cl}^{-}$ The increase in [Cl⁻] brings in an increase in [Na⁺] [Cl⁻] which will lead for backward reaction because $K_{sp} \operatorname{NaCl} = [\operatorname{Na}^{+}] [\operatorname{Cl}^{-}].$
- **60.** (b) Solubility is directly proportional to the K_{sp} .

NCERT Exemplar Problems

More than One Answer

61. (a, d) M.eq. of 0.01 M HCl =
$$\frac{.01 \times 100}{1000} = 1 \times 10^{-3}$$
 pH = 3
M.eq. of .02 M H₂SO₄ = $\frac{.04 \times 50}{1000} = 2 \times 10^{-3}$
M.eq. of .02 M NaOH = $\frac{0.02 \times 50}{1000} = 1 \times 10^{-3}$
Left [H⁺] = $2 \times 10^{-3} - 1 \times 10^{-3} = 1 \times 10^{-3}$; pH = 3

62. (**a**, **b**, **c**) Because buffer solution are mixture of weak acid or weak base and their salt.

63. (a, b)
$$pK_a = -\log(3 \times 10^{-5}) = -0.48 + 5 = 4.52$$

 $H_{ind} \longrightarrow Ind^{\circ} + H^{\oplus}$
(a) 75% 25%
(b) 25% 75%
(a) $pH = 4.52 + \log\left(\frac{25}{75}\right)$
 $= 4.52 + \log\frac{1}{3} = 4.52 - 0.48 = 4.04$
(b) $pH = 4.52 + \log\left(\frac{25}{75}\right)$
 $= 4.52 + 0.48 = 5.0$

- 64. (c) Colour of electrolyte depends on the nature of both ions. *e.g.* $CuSO_4$ is blue because Cu^{2+} ions are blue.
- 65. (c) CH₃COOH is weak acid shows dissociation equilibrium as CH₃COOH \implies CH₃COO⁻ + H⁺
- **66.** (b) For pure water $[H^+] = [OH^-]$,
- :. $K_w = 10^{-12}$ is
- 67. (a) Solubility of $Al(OH)_3$ is lesser than $Zn(OH)_2$
- **68.** (d) CH₃COONa is a salt of weak acid, (CH₃COOH) and strong base (NaOH).

69. (b) The equilibrium will shift in the backward direction.

70. (b)
$$Mg(OH)_2 \implies Mg^{2+} + 2OH^-$$

 $K_{sp} = [Mg^{2+}][OH^-]^2$
 $1 \times 10^{-12} = 0.01[OH^-]^2$
 $[OH^-]^2 = 1 \times 10^{-10}$
 $\Rightarrow [OH^-] = 10^{-5}$
 $[H^+] = 10^{-14} / 10^{-5} = 10^9$
 $pH = -log[H^+] = -log[10^{-9}] = 9$

Assertion and Reason

- **71.** (a) The conjugate base of CHCl₃ is more stable than conjugate base of CHF₃(CF₃)CCl₃ stabilized by -I effect of chlorine atoms as well as by the electrons. But conjugate base of CH₃(CH₃) is stabilized only by -I effect of flourine atoms. Here both assertion and reason are true and reason is correct explanation of assertion.
- **72.** (c) Ionic product of AgBr is greater than that of AgCl in comparison with their solubility product AgBr will precipitate. First rather than that of AgCl.
- **73.** (e) It is fact that ionic reactions are instantaneous due to the fact that oppositely charged ions exert strong forces and combine immediately.
- 74. (c) HCl is a strong electrolyte since it will produce more H^+ , comparison than that of CH_3COOH . Hence assertion is true but reason false.
- **75.** (b) For sparingly soluble salts, reason is not a correct explanation. Hence both assertion and reason are true but reason is not a correct explanation of assertion.
- **76.** (a) Aq. solution of FeCl₃ on standing produce brown ppt. Due to hydrolysis it produce ppt. of $Fe(OH)_3$ which is of brown colour. Hence both are correct and reason is a correct explanation.
- 77. (a) Barium carbonate is more soluble in HNO₃ than in water become carbonate is a weak base and reacts with the H^+ ion of HNO₃ causing the barium salt to dissociate. BaCO₃ + HNO₃ \longrightarrow Ba(NO₃)₂ + CO₂ + H₂O
- 78. (c) Assertion is correct. It exists as Zwitter ion. Reason is wrong. The conjugate acid is $\stackrel{\oplus}{N}H_2CH_2COOH$
- **79.** (d) Assertion is wrong. It forms acidic buffer and this pH changes. Reason is correct. Due to common ion (CH_3COO°) , ionization of is CH₃COOH suppressed.

80. (a) But Assertion and Reason are true. A basic buffer is formed whose pH is always >7.

Comprehension Based

81. (c)
$$[S^{2-}]_{min}$$
 for $SnS = \frac{K_{sp}(SnS)}{[Sn^{2+}]}$;
 $[S^{2-}]_{min}$ for $CdS = \frac{K_{sp}(CdS)}{[Cd^{2+}]}$;
 $[S^{2-}]_{min}$ for $NiS = \frac{K_{sp}(NiS)}{[Ni^{2+}]}$;
and $K_{sp}(NiS) < K_{sp}(SnS) < K_{sp}(CdS)$

: NiS will precipitate first.

82. (c)
$$H_2S \longrightarrow 2H^{\oplus} + S^2$$

$$\Rightarrow K_1 K_2 = \frac{[H^{\oplus}]^2 [S^{2^-}]}{[H_2 S]} = 10^{-21}$$

$$[S^{2^-}] = \frac{K_{sp} (NiS)}{[Ni^{2^+}]}$$

$$= \frac{3 \times 10^{-21}}{0.1} = 3 \times 10^{-20}$$

$$\frac{[H^{\oplus}]^2 (3 \times 10^{-20})}{0.1} = 10^{-21}, [H^{\oplus}] = \left(\frac{10^{-21} \times 0.1}{3 \times 10^{-20}}\right)^{-20}$$

$$= \sqrt{0.33} \times 10^{10^{-1}} = 5.74 \times 10^{-2}$$

$$\Rightarrow$$
 pH = 1.24

83. (a) Solubility of either CdS, NiS, SnS = $\sqrt{K_{sp}} \Rightarrow$ look for highest K_{sp}. CdS is more soluble.

84. (a)
$$K_1 K_2 = \frac{[H^+]^2 [S^{2-}]}{[H_2 S]}$$

 $\Rightarrow K_1 K_2 = \frac{[H^{\oplus}]^2 [S^{2-}]}{[H_2 S]}$
 $\Rightarrow [S^{2-}]_{min} = 10^{-20} M$
 $\Rightarrow [Cd^{2+}]_{allowed} = \frac{K_{sp}(CdS)}{[S^{2-}]_{salt}} = 10^{-8} M$

85. (c) By Henry's Law:

$$Pco_2 = x_{CO_2}K_H$$

$$x_{CO_2} = \frac{pCO_2}{K_H} = \frac{(1.25 \times 10^{-4} \text{ atm}) \times 760 \text{ torr}}{1.25 \times 10^6 \text{ torr}}$$

= 0.76 × 10¹⁰⁻⁷ = $\frac{n_{CO_2}}{1.25 \times 10^{-4} \text{ torr}}$

n Total

$$x_{H_2}O = (1 - 0.76 \times 10^{10-7}) \approx 1 = \frac{n_{H_2O}}{n \text{ Total}}$$

$$\therefore \frac{x_{CO_2} / n \text{ total}}{n_{H_2O} / n \text{ total}} = \frac{n_{CO_2}}{n_{H_2O}}$$

$$= \frac{0.76 \times 10^{10-7}}{1} \approx 0.76 \times 10^{10-7}$$
Molality of CO₂ solution
$$= \frac{x_{CO_2} \times 1000}{x_{H_2O} \times M_W H_2O} = \frac{n_{CO_2} \times 1000}{n_{H_2O} \times M_{WH_2O}}$$

$$= \frac{0.76 \times 10^{10-7} \times 1000}{18}$$

$$= 4.22 \times 10^{10-6} \text{ m} \approx 4.22 \times 10^{10-6} \text{ M.}$$

$$H_2CO_3 \longleftrightarrow H^{\oplus} + HCO_3^{\odot}$$

$$K = \frac{[H^{\oplus}][HCO_3^{\odot}]}{[H_2CO_3]} = \frac{[H^{\oplus}]^2}{[H_2CO_3]}$$

$$= \sqrt{4.3 \times 10^{-7} \times 4.22 \times 10^{-6}}$$

$$= \sqrt{1.814} \times 10^{-6}$$

$$= 1.345 \times 10^{-6} \text{ M}$$

$$pH = 5.87$$

86. (b) 0.64 ppm = 0.64 g is 10^6 mL.

$$= \frac{0.64 \times 10^{3} \text{ mL}}{64 \times 10^{6} \text{ mL}}$$
$$= 10^{-5} \text{ M} \text{ (Mw SO}_{2} = 64)$$

$$[\mathrm{H}^{\oplus}] = [\mathrm{SO}_2] = 10^{-5} \mathrm{M}$$

- \Rightarrow pH = 5.0
- 87. (c) pH of titration of strong acid with strong base is 7.
- **88.** (a) Since the curve starts at higher pH (12.5), so it should be strong base and pH changes most rapidly near the equivalence point, so it should be strong acid. Hence the titration is strong base with strong acid (*i.e.*, CsOH by HBr).
- **89.** (d) The suitable indicator for the titration are Methyl orange, Bromothymol and Methyl red .
- **90.** (c) The pH at equivalence point is 7. pH value of solutions do not give immediate idea of their relative strength.
- **91.** (a) In Fig (a), there are two equivalence point and pH changes most rapidly at that point, so it is a titration of a weak diprotic acid by a strong base. At the end pH is very high and suggest a strong base.

Figs.(b),(c) and (d) do not have high, pH at the end. So strong base is not possible. Moreover pH does not change rapidly at equivalence point.

Match the Column

- 92. (a) $A \rightarrow 1, B \rightarrow 3, C \rightarrow 4, D \rightarrow 2$
- (A) Acidic buffer (mixture of W_A + salt of W_A/S_B)

$$pH = pK_a + \log\left(\frac{Salt}{Acid}\right)$$
$$= 4.74 + \log\left(\frac{0.1}{0.1}\right) = 4.74$$

Thus, it is acidic buffer at maximum buffer capacity. Because buffer limits are $pH \pm 1$.

When $pH = pK_a$, it is a buffer at maximum buffer capacity.

- (B) It is mixture of W_A and S_A . SO pH of 0.1 M HCl will predominate and pH<7.
- (C) It will form salt of W_A/W_B . Since $pK_a = pK_b$,

Thus
$$pH = 7.\left(pH = \frac{1}{2}(pK_w + pK_a + pK_b)\right)$$

(D) mmol of CH₃COONa = $300 \times 0.1 = 30$ m mol of HCl = HCl = $100 \times 0.1 = 10$. CH₃COONa + HCl \longrightarrow CH₃COOH + NaCl Initial 30 mmol 10 mmol 0 0 Final (30–10)=20 (10–10)=0 10 ---It is a mixture of W_A and salt of W_A / S_B. It forms acidic

buffer.

$$pH = pK_{a} + \log\left(\frac{Salt}{Acid}\right)$$
(Total volume = 300+100=400 mL)
$$= 4.74 + \log\left[\frac{20/400}{10/400}\right]$$

$$= 4.74 + 0.3 = 5.03$$

- 93. (a) $A \rightarrow 2$, $B \rightarrow 1$, $C \rightarrow 4$, $D \rightarrow 3$, $E \rightarrow 5$
- 94. (a) $A \rightarrow 3,4, B \rightarrow 1, C \rightarrow 2,4, D \rightarrow 2,4$ $HSO_4^{\circ} + H_2O \longrightarrow H_2O^{\oplus} + SO_4^{2-}(Bronsted acid)$ $HSO_4^{\circ} + H^{\oplus} \longrightarrow H_2SO_4(Bronsted base)$

 BF_3 (e⁻ deficient and hence Lewis acid).

H₃N; (It can donate lone pair of electrons and acts as Lewis base)

$$NH_3 + H_2O \longrightarrow NH_4 + O^-H$$
 (Accepts H^+ and acts as
Bronsted base)

O⁻H (It is bronsted bas e by accepting H^+) It can donate lone pair of electrons and acts as Lewis base also.

95. (a) $A \rightarrow 1$, $B \rightarrow 2$, $C \rightarrow 3$, $D \rightarrow 1,4,2$ All factual statements

Integer

96. (8) c. $CH_{3}COO^{-} + H_{3}O^{+} \longrightarrow CH_{3}COOH + H_{2}O(>98\%)$ d. $CH_{3}COOH + O^{-}H \longrightarrow CH_{3}COO^{-} + H_{2}O(>98\%)$ e. $CH_{3}COO^{-} + H_{3}O^{+} \longrightarrow CH_{3}COOH + H_{2}O(>98\%)$ f. $HCl + H_{2}O \longrightarrow H_{3}O^{+} + Cl^{-}(>98\%)$ i. $N^{+}H_{4} + O^{-}H \longrightarrow NH_{3} + H_{2}O(>98\%)$ j. $N^{+}H_{4} + O^{-}H \longrightarrow NH_{3} + H_{2}O(>98\%)$ l. $NH_{3} + H_{3}O^{+} \longrightarrow N^{+}H_{4} + H_{2}O(>98\%)$ m. $NH_{3} + H_{3}O^{+} \longrightarrow N^{+}H_{4} + H_{2}O(>98\%)$ 97. (8) For a salt of weak acid and strong base,

$$pH = 7 + \frac{1}{2}pK_{a} + \frac{1}{2}\log C$$
$$= 7 + \frac{1}{2}(-\log \times 10^{-4}) + \frac{1}{2}\log 0.01 = 8$$

98. (3) Salts of strong bases and weak acids turn red litmus to blue.

KCN, H₃PO₃, LiCN

99. (6) Diprotic acids are those which furnish two protons per molecule.

 $H_{2}SO_{4}, H_{3}PO_{3}, H_{2}CO_{3}, H_{2}S_{2}O_{7}, H_{3}CrO_{4}, H_{2}SO_{3}$ $H_{3}BO_{3} + H_{2}O \longrightarrow B(OH)_{4}^{-} + H^{+}(Monobasic)$

$$H - O - S - O - H (Diabasic)$$
$$H - O - S - O - H (Diabasic)$$
$$H - O - S - O - H (Diabasic)$$

Only those hydrogens are replaceable from oxy-acids of phosphorous and sulphur which are attached to oxygen. H_3PO_4 (Tribasic)

H₃PO₃ (Dibasic)

H₃PO₂ (Monobasic)

100. (7) AgCl → Ag⁺ + Cl⁻_(S'+x)(K_{sp} = 1.6×10⁻¹⁰)
CuCl → Cu⁺ + Cl⁻_(X+S')(K_{sp} = 1×10⁻⁶)
∴ S'(S' + x) = 1.6×10⁻¹⁰
x(x + S') = 10⁻⁶

$$\frac{S'}{x} = 1.6 \times 10^{-4}$$

∴ S' = (1.6×10⁻⁴)x.
⇒ x(x + 1.6×10⁴ x) = 10⁻⁶
⇒ x = 10⁻³
∴ S' = 1.6×10⁻⁷
= 1.6×10^{-x} (The value of x = 7)

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