on ionization of salts either exist as hydrated ions in aqueous solutions or interact with water to reform corresponding acids/bases depending upon the nature of salts. The later process of interaction between water and cations/anions or both of salts is called hydrolysis. The pH of the solution gets affected by this interaction. The cations (e.g., Na^+, K^+, Ca^{2+}, Ba^{2+}, etc.) of strong bases and anions (e.g., Cl^-, Br^-, NO_3^-, ClO_4^- etc.) of strong acids simply get hydrated but do not hydrolyse, and therefore the solutions of salts formed from strong acids and bases are neutral i.e., their pH is 7. However, the other category of salts do undergo hydrolysis.

We now consider the hydrolysis of the salts of the following types :

(i)   salts of weak acid and strong base e.g., CH_3COONa.

(ii) salts of strong acid and weak base e.g., NH_4Cl, and

(iii) salts of weak acid and weak base, e.g., CH_3COONH_4.

In the first case, CH_3COONa being a salt of weak acid, CH_3COOH and strong base, NaOH gets completely ionised in aqueous solution.

$$CH_3COONa(aq) \rightarrow CH_3COO^-(aq) + Na^+(aq)$$

Acetate ion thus formed undergoes hydrolysis in water to give acetic acid and OH^- ions

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

Acetic acid being a weak acid ($K_a = 1.8 \times 10^{-5}$) remains mainly unionised in solution. This results in increase of OH^- ion concentration in solution making it alkaline. The pH of such a solution is more than 7.

Similarly, NH_4Cl formed from weak base, NH_4OH and strong acid, HCl, in water dissociates completely.

$$NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

Ammonium ions undergo hydrolysis with water to form NH_4OH and H^+ ions

$$NH_4^+ (aq) + H_2O (1) \rightleftharpoons NH_4OH(aq) + H^+(aq)$$
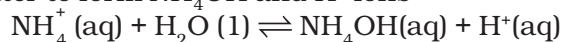
Ammonium hydroxide is a weak base ($K_b = 1.77 \times 10^{-5}$) and therefore remains almost unionised in solution. This results in

increased of H^+ ion concentration in solution making the solution acidic. Thus, the pH of NH_4Cl solution in water is less than 7.

Consider the hydrolysis of CH_3COONH_4 salt formed from weak acid and weak base. The ions formed undergo hydrolysis as follow:

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$
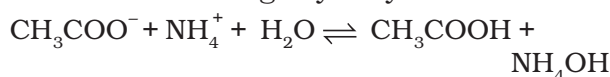
CH_3COOH and NH_4OH, also remain into partially dissociated form:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$
$$H_2O \rightleftharpoons H^+ + OH^-$$
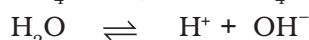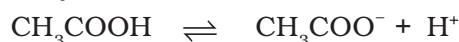
Without going into detailed calculation, it can be said that degree of hydrolysis is independent of concentration of solution, and pH of such solutions is determined by their pK values:

$$pH = 7 + \tfrac{1}{2} (pK_a - pK_b) \qquad (7.38)$$

The pH of solution can be greater than 7, if the difference is positive and it will be less than 7, if the difference is negative.

Problem 7.25

The pK_a of acetic acid and pK_b of ammonium hydroxide are 4.76 and 4.75 respectively. Calculate the pH of ammonium acetate solution.

Solution

$pH = 7 + \tfrac{1}{2} [pK_a - pK_b]$

$\quad = 7 + \tfrac{1}{2} [4.76 - 4.75]$

$\quad = 7 + \tfrac{1}{2} [0.01] = 7 + 0.005 = 7.005$

7.12 BUFFER SOLUTIONS

Many body fluids e.g., blood or urine have definite pH and any deviation in their pH indicates malfunctioning of the body. The control of pH is also very important in many chemical and biochemical processes. Many medical and cosmetic formulations require that these be kept and administered at a particular pH. **The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called Buffer Solutions.** Buffer solutions

of known pH can be prepared from the knowledge of pK_a of the acid or pK_b of base and by controlling the ratio of the salt and acid or salt and base. A mixture of acetic acid and sodium acetate acts as buffer solution around pH 4.75 and a mixture of ammonium chloride and ammonium hydroxide acts as a buffer around pH 9.25. You will learn more about buffer solutions in higher classes.

7.12.1 Designing Buffer Solution

Knowledge of pK_a, pK_b and equilibrium constant help us to prepare the buffer solution of known pH. Let us see how we can do this.

Preparation of Acidic Buffer
To prepare a buffer of acidic pH we use weak acid and its salt formed with strong base. We develop the equation relating the pH, the equilibrium constant, K_a of weak acid and ratio of concentration of weak acid and its conjugate base. For the general case where the weak acid HA ionises in water,

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$
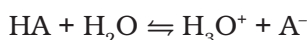
For which we can write the expression

$$K_a = \frac{[H_3O^+] [A^-]}{[HA]}$$

Rearranging the expression we have,

$$[H_3O^+] = K_a \frac{[HA]}{[A^-]}$$

Taking logarithm on both the sides and rearranging the terms we get —

$$pK_a = pH - \log \frac{[A^-]}{[HA]}$$

Or

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \qquad (7.39)$$

$$pH = pK_a + \log \frac{[\text{Conjugate base, } A^-]}{[\text{Acid, HA}]}$$

$$(7.40)$$

The expression (7.40) is known as **Henderson–Hasselbalch equation.** The quantity $\frac{[A^-]}{[HA]}$ is the ratio of concentration of

conjugate base (anion) of the acid and the acid present in the mixture. Since acid is a weak acid, it ionises to a very little extent and concentration of [HA] is negligibly different from concentration of acid taken to form buffer. Also, most of the conjugate base, [A−], comes from the ionisation of salt of the acid. Therefore, the concentration of conjugate base will be negligibly different from the concentration of salt. Thus, equation (7.40) takes the form:

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

In the equation (7.39), if the concentration of [A−] is equal to the concentration of [HA], then pH = pK_a because value of log 1 is zero. Thus if we take molar concentration of acid and salt (conjugate base) same, the pH of the buffer solution will be equal to the pK_a of the acid. So for preparing the buffer solution of the required pH we select that acid whose pK_a is close to the required pH. For acetic acid pK_a value is 4.76, therefore pH of the buffer solution formed by acetic acid and sodium acetate taken in equal molar concentration will be around 4.76.

A similar analysis of a buffer made with a weak base and its conjugate acid leads to the result,

$$pOH = pK_b + \log \frac{[\text{Conjugate acid, BH}^+]}{[\text{Base, B}]}$$

$$(7.41)$$

pH of the buffer solution can be calculated by using the equation pH + pOH = 14.

We know that pH + pOH = pK_w and $pK_a + pK_b = pK_w$. On putting these values in equation (7.41) it takes the form as follows:

$$pK_w - pH = pK_w - pK_a + \log \frac{[\text{Conjugate acid, BH}^+]}{[\text{Base, B}]}$$

or

$$pH = pK_a + \log \frac{[\text{Conjugate acid, BH}^+]}{[\text{Base, B}]} \qquad (7.42)$$

If molar concentration of base and its conjugate acid (cation) is same then pH of the buffer solution will be same as pK_a for the base. pK_a value for ammonia is 9.25; therefore a buffer of pH close to 9.25 can be obtained by taking ammonia solution and ammonium

chloride solution of same molar concentration. For a buffer solution formed by ammonium chloride and ammonium hydroxide, equation (7.42) becomes:

$$pH = 9.25 + \log \frac{[\text{Conjugate acid}, BH^+]}{[\text{Base}, B]}$$

pH of the buffer solution is not affected by dilution because ratio under the logarithmic term remains unchanged.

## 7.13 SOLUBILITY EQUILIBRIA OF SPARINGLY SOLUBLE SALTS

We have already known that the solubility of ionic solids in water varies a great deal. Some of these (like calcium chloride) are so soluble that they are hygroscopic in nature and even absorb water vapour from atmosphere. Others (such as lithium fluoride) have so little solubility that they are commonly termed as insoluble. The solubility depends on a number of factors important amongst which are the lattice enthalpy of the salt and the solvation enthalpy of the ions in a solution. For a salt to dissolve in a solvent the strong forces of attraction between its ions (lattice enthalpy) must be overcome by the ion-solvent interactions. The solvation enthalpy of ions is referred to in terms of solvation which is always negative i.e. energy is released in the process of solvation. The amount of solvation enthalpy depends on the nature of the solvent. In case of a non-polar (covalent) solvent, solvation enthalpy is small and hence, not sufficient to overcome lattice enthalpy of the salt. Consequently, the salt does not dissolve in non-polar solvent. As a general rule , for a salt to be able to dissolve in a particular solvent its solvation enthalpy must be greater than its lattice enthalpy so that the latter may be overcome by former. Each salt has its characteristic solubility which depends on temperature. We classify salts on the basis of their solubility in the following three categories.

Category I	Soluble	Solubility > 0.1M
Category II	Slightly Soluble	0.01M<Solubility< 0.1M
Category III	Sparingly Soluble	Solubility < 0.01M

We shall now consider the equilibrium between the sparingly soluble ionic salt and its saturated aqueous solution.

7.13.1 Solubility Product Constant

Let us now have a solid like barium sulphate in contact with its saturated aqueous solution. The equilibrium between the undisolved solid and the ions in a saturated solution can be represented by the equation:

$$BaSO_4(s) \underset{\text{in water}}{\overset{\text{Saturated Solution}}{\rightleftharpoons}} Ba^{2+}(aq) + SO_4^{2-}(aq),$$
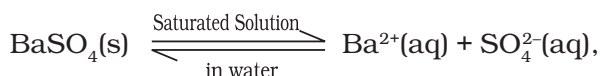
The equilibrium constant is given by the equation:

$$K = \{[Ba^{2+}][SO_4^{2-}]\} / [BaSO_4]$$

For a pure solid substance the concentration remains constant and we can write

$$K_{sp} = K[BaSO_4] = [Ba^{2+}][SO_4^{2-}] \qquad (7.43)$$

We call K_{sp} the *solubility product constant* or simply *solubility product*. The experimental value of K_{sp} in above equation at 298K is 1.1×10^{-10}. This means that for solid barium sulphate in equilibrium with its saturated solution, the product of the concentrations of barium and sulphate ions is equal to its solubility product constant. The concentrations of the two ions will be equal to the molar solubility of the barium sulphate. If molar solubility is S, then

$$1.1 \times 10^{-10} = (S)(S) = S^2$$

or $\qquad\qquad S = 1.05 \times 10^{-5}.$

Thus, molar solubility of barium sulphate will be equal to 1.05×10^{-5} mol L^{-1}.

A salt may give on dissociation two or more than two anions and cations carrying different charges. For example, consider a salt like *zirconium phosphate* of molecular formula $(Zr^{4+})_3(PO_4^{3-})_4$. It dissociates into 3 zirconium cations of charge +4 and 4 phosphate anions of charge –3. If the molar solubility of zirconium phosphate is S, then it can be seen from the stoichiometry of the compound that

$$[Zr^{4+}] = 3S \text{ and } [PO_4^{3-}] = 4S$$

$$\text{and } K_{sp} = (3S)^3 (4S)^4 = 6912 (S)^7$$

$$\text{or } S = \{K_{sp} / (3^3 \times 4^4)\}^{1/7} = (K_{sp} / 6912)^{1/7}$$