

1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 01 (Class XI, Semester 01)
Module Name/Title	Equilibrium: Part 5
Module Id	kech_10705
Pre-requisites	Ionization, pH, common ion effect.
Objectives	<p>After going through the contents of this module the learner will be able to:</p> <ul style="list-style-type: none">• Understand and apply the concept of salt hydrolysis;• Calculate pH of an aqueous solution of salt;• Appreciate the formation of buffer solutions;• Calculate solubility product constant;• Explain the dependence of degree of ionization on concentration of the electrolyte and that of the common ion;• Apply solubility product and common ion effect to qualitative salt analysis.
Keywords	Salt hydrolysis, buffers, sparingly soluble, solubility product, common ion effect, qualitative salt analysis.

2. Development Team

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Table of Contents:

1. Introduction
2. Hydrolysis of Salts and the pH of their Solutions
3. Buffer solutions
4. Solubility equilibria of sparingly soluble salts
5. Solubility Product Constant
6. Common Ion Effect on Solubility of Ionic Salts
7. Summary

1. Introduction

In the previous module you studied about the equilibria related to weak acid and weak base in aqueous solutions. Neutralisation of acid and base produces salt and the salt may be acidic, basic or neutral depending upon the strength of acid and base.

Also depending upon the strength of acid and the base involved in the formation of the salt, the salt may be a weak or a strong electrolyte. In this module we will understand and apply the equilibria concerning aqueous solutions of salts which are weak electrolytes.

2. Hydrolysis of Salts and the pH of their Solutions

Salts formed by the reactions between acids and bases in definite proportions, undergo ionization in water. The cations/anions formed 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.

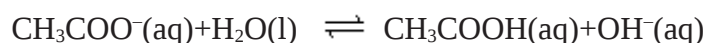
We now consider the hydrolysis of the salts of the following types:

- (i) salts of weak acid and strong base e.g., CH₃COONa.
- (ii) salts of strong acid and weak base e.g., NH₄Cl, and
- (iii) salts of weak acid and weak base, e.g., CH₃COONH₄

In the first case, CH₃COONa being a salt of weak acid, CH₃COOH and strong base, NaOH gets completely ionised in aqueous solution.



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



Acetic acid being a weak acid

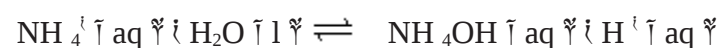
$$(K_a = 1.8$$

$\times 10^{-5})$ 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, NH₄Cl formed from weak base, NH₄OH and strong acid, HCl, in water dissociates completely.



Ammonium ions undergo hydrolysis with water to form NH₄OH and H⁺ ions

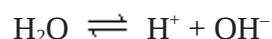
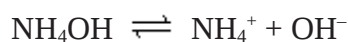
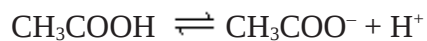


Ammonium hydroxide is a weak base ($K_b = 1.77 \times 10^{-5}$) and therefore remains almost unionised in solution. This results in increased of H⁺ ion concentration in solution making the solution acidic. Thus, the pH of NH₄Cl solution in water is less than 7.

Consider the hydrolysis of CH₃COONH₄ salt formed from weak acid and weak base. The ions formed undergo hydrolysis as follow:



CH_3COOH and NH_4OH , also remain into partially dissociated form:



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:

$$\text{pH} = 7 + \frac{1}{2} (\text{pK}_a - \text{pK}_b) \quad (1)$$

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 1

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

$$\text{pH} = 7 + \frac{1}{2} [\text{pK}_a - \text{pK}_b]$$

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

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

3. 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.

4. Solubility Equilibria of Sparingly Soluble Salts

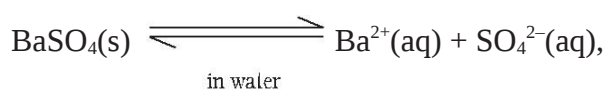
We have already known that the solubility of ionic solids in water varies a great deal. Some of these (like calcium chloride) are so soluble that they are hygroscopic in nature and even absorb water vapour from atmosphere. Others (such as lithium fluoride) have so little solubility that they are commonly 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	$0.01M < \text{Solubility} < 0.1M$
Category III	Sparingly Soluble	Solubility < 0.01M

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

5. Solubility Product Constant

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



The equilibrium constant is given by the equation:

$$K = \frac{[\text{Ba}^{2+}][\text{SO}_4^{2-}]}{[\text{BaSO}_4]}$$

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

$$K = \frac{K[\text{BaSO}_4]}{[\text{SO}_4^{2-}]} = [\text{Ba}^{2+}] \quad (2)$$

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

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

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

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

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 $(\text{Zr}^{4+})_3(\text{PO}_4^{3-})_4$. 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

$$[\text{Zr}^{4+}] = 3S \text{ and } [\text{PO}_4^{3-}] = 4S$$

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

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

A solid salt of the general formula $M_x^{p+} X_y^{q-}$ with molar solubility S in equilibrium with its saturated solution may be represented

by the equation:



(where $x \times p^+ = y \times q^-$)

And its solubility product constant is given by:

$$K_s = [M^{p+}]^x [X^{q-}]^y$$

$$= (xS)^x (yS)^y \quad (3)$$

$$= x^x \cdot y^y \cdot S^{(x+y)}$$

$$S^{(x+y)} = K_{sp} / x^x \cdot y^y$$

$$S = (K_{sp} / x^x \cdot y^y)^{1/(x+y)} \quad (4)$$

The term K_{sp} in equation is given by Q_{sp} (section 7.6.2) when the concentration of one or more species is not the concentration under equilibrium. Obviously under equilibrium conditions $K_{sp} = Q_{sp}$ but otherwise it gives the direction of the processes of precipitation or dissolution. The solubility product constants of a number of common salts at 298K are given in Table 1.

Problem 2

Calculate the solubility of A_2X_3 in pure water, assuming that neither kind of ion reacts with water. The solubility product of A_2X_3 , $K_{sp} = 1.1 \times 10^{-23}$.

Solution



$$K_{sp} = [A^{3+}]^2 [X^{2-}]^3 = 1.1 \times 10^{-23}$$

If S = solubility of A_2X_3 , then

$$[A^{3+}] = 2S; [X^{2-}] = 3S$$

$$\begin{aligned} \text{Therefore, } K_{sp} &= (2S)^2(3S)^3 = 108 S^5 \\ &= 1.1 \times 10^{-23} \end{aligned}$$

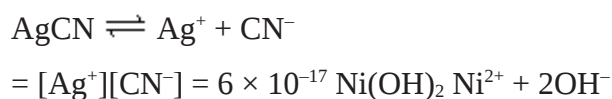
$$\text{Thus, } S^5 = 1 \times 10^{-25}$$

$$S = 1.0 \times 10^{-5} \text{ mol/L.}$$

Problem 3

The values of K_{sp} of two sparingly soluble salts $\text{Ni}(\text{OH})_2$ and AgCN are 2.0×10^{-15} and 6×10^{-17} respectively. Which salt is more soluble? Explain.

Solution



$$K_{sp} = [\text{Ni}^{2+}][\text{OH}^-]^2 = 2 \times 10^{-15}$$

$$\text{Let } [\text{Ag}^+] = S_1, \text{ then } [\text{CN}^-] = S_1$$

$$\text{Let } [\text{Ni}^{2+}] = S_2, \text{ then } [\text{OH}^-] = 2S_2$$

$$S_1^2 = 6 \times 10^{-17}, S_1 = 7.8 \times 10^{-9} \quad (S_2)(2S_2)^2 = 2 \times 10^{-15}, S_2 = 0.58 \times 10^{-4}$$

$\text{Ni}(\text{OH})_2$ is more soluble than AgCN

6. Common Ion Effect on Solubility of Ionic Salts

It is expected from Le Chatelier's principle that if we increase the concentration of any one of the ions, it should combine with the ion of its opposite charge and some of the salt will be precipitated till once again $K_{sp} = Q_{sp}$. Similarly, if the concentration of one of the ions is decreased, more salt will dissolve to increase the concentration of both the ions till once again $K_{sp} = Q_{sp}$. This is applicable even to soluble salts like sodium chloride except that due to

higher concentrations of the ions, we use their activities instead of their molarities in the expression for Q_{sp} . Thus if we take a saturated solution of sodium chloride and pass HCl gas through it, then sodium chloride is precipitated due to increased concentration (activity) of chloride ion available from the dissociation of HCl. Sodium chloride thus obtained is of very high purity and we can get rid of impurities like sodium and magnesium sulphates. The common ion effect is also used for almost complete precipitation of a particular ion as its sparingly soluble salt, with very low value of solubility product for gravimetric estimation.

Thus we can precipitate :

- (i) silver ion as silver chloride,
- (ii) ferric ion as its hydroxide (or hydrated ferric oxide)
- (iii) barium ion as its sulphate for quantitative estimations.
- (iv) pass HCl gas through a saturated solution of sodium chloride to get high purity NaCl

Problem 4

Calculate the molar solubility of $\text{Ni}(\text{OH})_2$ in 0.10 M NaOH. The ionic product of $\text{Ni}(\text{OH})_2$ is 2.0×10^{-15} .

Solution

Let the solubility of $\text{Ni}(\text{OH})_2$ be equal to S. Dissolution of S mol/L of $\text{Ni}(\text{OH})_2$ provides

S mol/L of Ni^{2+} and 2S mol/L of OH^- , but the total concentration of $\text{OH}^- = (0.10 + 2S)$ mol/L because the solution already contains 0.10 mol/L of OH^- from NaOH.

$$\begin{aligned}K_{sp} &= 2.0 \times 10^{-15} = [\text{Ni}^{2+}] [\text{OH}^-]^2 \\ &= (S) (0.10 + 2S)^2\end{aligned}$$

As K_{sp} is small, $2S \ll 0.10$, thus, $(0.10 + 2S) \approx 0.10$

Hence,

$$2.0 \times 10^{-15} = S (0.10)^2$$

$$S = 2.0 \times 10^{-13} \text{ M} = [\text{Ni}^{2+}]$$

The solubility of salts of weak acids like phosphates increases at lower pH. This is because at lower pH the concentration of the anion decreases due to its protonation. This in turn increases the solubility of the salt so that $K_{sp} = Q_{sp}$. We have to satisfy two equilibria simultaneously i.e.

$$K_{sp} = [\text{M}^+] [\text{X}^-]$$



$$[\text{X}^-] / K_a = \frac{[\text{H}^+ (\text{aq})] [\text{X}^- (\text{aq})]}{[\text{HX} (\text{aq})]} \quad [\text{HX}] = K_a / [\text{H}^+]$$

Taking inverse of both side and adding 1 we get

Now, again taking inverse, we get

$[\text{X}^-] / \{[\text{X}^-] + [\text{HX}]\} = f = K_a / (K_a + [\text{H}^+])$ and it can be seen that 'f' decreases as pH decreases. If S is the solubility of the salt at a given pH then

$$K_{sp} = [S] [f S] = S^2 \{K_a / (K_a + [\text{H}^+])\} \quad \text{and}$$

$$S = \{K_{sp} ([\text{H}^+] + K_a) / K_a\}^{1/2} \quad (13)$$

Thus solubility S increases with increase in $[\text{H}^+]$ or decrease in pH.

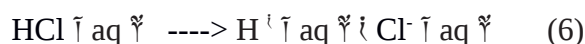
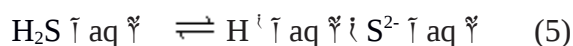
Application of Common ion effect and K_{sp} in Qualitative Salt Analysis

(i) Group I: Lead gets precipitated as chlorides on addition of dil.HCl when $Q_{sp} > K_{sp}$.

(ii) Group II: Bismuth, copper, cadmium and antimony get precipitated as sulphides when H_2S gas is passed through acidified solution of salt.

Explanation: H₂S is a weak acid. In presence of common ion H⁺ its ionization is suppressed; so the concentration of S²⁻ is sufficient only for Q_{sp} to exceed the K_{sp} of sulphides of ions of group II: Bi³⁺, Cu²⁺, Cd²⁺, Sb³⁺.

K_{sp} of sulphide salts of subsequent groups is too high to get precipitated at low S²⁻ concentration.



Owing to the presence of common ion H⁺, reaction (5) shifts in the backward direction according to Le Chatelier's principle thus decreasing the concentration of sulphide ions.

(iii) Group III: Al³⁺, Fe²⁺, Fe³⁺, Mn²⁺, and Cr³⁺ get precipitated as hydroxides when NH₄OH is added to aqueous salt solution containing NH₄Cl.

Explanation: NH₄OH is a weak base and in presence of common ion NH₄⁺, its ionization is suppressed; so the concentration of OH⁻ is sufficient only for Q_{sp} to exceed the K_{sp} of ions of group III. K_{sp} of hydroxide salts of subsequent groups is too high to get precipitated at low OH⁻ concentration.



Owing to the presence of common ion NH₄⁺, reaction (7) shifts in the backward direction according to Le Chatelier's principle thus decreasing the concentration of hydroxide ions.

(iv) Group IV: Co²⁺, Ni²⁺, Mn²⁺ and Zn²⁺ get precipitated as sulphides when H₂S gas is passed through ammoniacal solution of salt.

Explanation: In group IV, H₂S gas is passed through an aqueous solution of salt containing NH₄OH in excess. The OH⁻ ions from equilibrium (7) and H⁺ ions from equilibrium (5) combine and shift the equilibrium in the forward direction.



Owing to the forward shift of reaction (5) according to Le Chatelier's principle, the concentration of sulphide ions in the solution increases. This increased concentration of sulphide ions is sufficient for Q_{sp} to exceed the K_{sp} of sulphides of group IV cations Co²⁺, Ni²⁺, Mn²⁺ and Zn²⁺.

(v) **Group V:** precipitated as carbonates when $Q_{sp} > K_{sp}$

7. Summary

The salts of strong acid and weak base, weak acid and strong base, and weak acid and weak base undergo hydrolysis in aqueous solution. The definition of **buffer solutions**, and their importance are discussed briefly. The solubility equilibrium of sparingly soluble salts is discussed and the equilibrium constant is introduced as **solubility product constant** (K_{sp}). Its relationship with solubility of the salt is established. The conditions of precipitation of the salt from their solutions or their dissolution in water are worked out. The role of common ion and the solubility of sparingly soluble salts is also discussed.