26

Ionic Equilibria Solubility Product

CHAPTER

OSTWALD'S DILUTION LAW

According to the Arrhenius Theory of dissociation, an electrolyte dissociates into ions in water solutions. These ions are in a state of equilibrium with the undissociated molecules. This equilibrium is called the **Ionic equilibrium.** Ostwald noted that **the Law of Mass Action can be applied to the ionic equilibrium as in the case of chemical equilibria.**

Let us consider a binary electrolyte AB which dissociates in solution to form the ions A^+ and B^-.

$$AB \rightleftharpoons A^+ + B^-$$

Let C moles per litre be the concentration of the electrolyte and α (alpha) its degree of dissociation. The concentration terms at equilibrium may be written as :

$$[AB] = C(1-\alpha) \text{ mol litre}^{-1}$$
$$[A^+] = C\alpha \text{ mol litre}^{-1}$$
$$[B^-] = C\alpha \text{ mol litre}^{-1}$$

Applying the Law of Mass Action :

Rate of dissociation $= k_1 \times C(1-\alpha)$

Rate of combination $= k_2 \times C\alpha \times C\alpha$

At equilibrium :

$$k_1 \times C(1-\alpha) = k_2 \times C\alpha \times C\alpha$$

or

$$\frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{k_1}{k_2} = K_c$$

or

$$K_c = \frac{\alpha^2 C}{(1-\alpha)} \text{ mol litre}^{-1} \qquad ...(1)$$

The equilibrium constant K_c is called the **Dissociation constant or Ionization constant.** It has a constant value at a constant temperature.

If one mole of an electrolyte be dissolved in V litre of the solution, then

$$C = \frac{1}{V}$$

V is known as the **Dilution** or the solution. Thus the expression (1) becomes

$$K_c = \frac{\alpha^2}{(1-\alpha)V} \qquad ...(2)$$

This expression which correlates the variation of the degree of dissociation of an electrolyte with dilution, is known as Ostwald's Dilution Law.

For Weak Electrolytes

For weak electrolytes, the value of α is very small as compared to 1, so that in most of the calculation we can take $1 - \alpha \simeq 1$. Thus the Ostwald's Dilution Law expression becomes

$$K_c = \frac{\alpha^2}{V}$$

It implies that **the degree of dissociation of a weak electrolyte is proportional to the square root of the dilution** *i.e.*,

$$\alpha \propto \sqrt{K_c V}$$

or

$$\alpha = K'\sqrt{V}$$

For Strong Electrolytes

For strong electrolytes, the value of α is large and it cannot be neglected in comparison with 1. Thus we have to use the original expression (2). That is,

$$K_c = \frac{\alpha^2}{(1-\alpha)V} \qquad \text{or} \qquad \alpha^2 = K_c V - \alpha K_c V$$

which gives a quadratic equation

$$\alpha^2 + \alpha K_c V - K_c V = 0$$

from this equation the value of α can be evaluated.

Experimental Verification of Ostwald's Law

The Ostwald's Dilution law can be verified if the values of α, the degree of dissociation, at different dilutions are known. The values of α are determined experimentally by using the relation.

$$\alpha = \frac{\lambda_v}{\lambda_\infty}$$

where λ_v and λ_∞ are the equivalent conductances at dilution V and infinite dilution respectively. Their values are found by conductance measurements and Kohlrausch's law. The value of α at various dilutions thus determined are inserted in the expression :

$$K_c = \frac{\alpha^2}{(1 - \alpha)\ V}$$

If the values of K_c come out to be constant, the Ostwald's law stands verified.

Limitation of Ostwald's Law

Ostwald's Dilution law **holds good only for weak electrolytes and fails completely when applied to strong electrolytes.** For strong electrolytes, which are highly ionised in solution, the value of the dissociation constant K, far from remaining constant, rapidly falls with dilution. In Table 26.1, the values of K at different dilutions illustrate the point.

Table 26.1. Dissociation of KCl at 18°C λ_∞ = 129.9			
V	**λ_v**	**$\alpha = \lambda_v / 129.9$**	**$K = \alpha^2 / (1 - \alpha)\ V$**
1	98.27	0.565	2.350
2	102.41	0.7883	1.434
5	107.96	0.831	0.8154
20	115.75	0.891	0.3642
200	119.96	0.9234	0.2221
500	124.41	0.9577	0.1084

Factors that explain the failure of Ostwald's law in case of strong electrolytes

(1)   The law is based on Arrhenius theory which assumes that only a fraction of the electrolyte is dissociated at ordinary dilutions and complete dissociation occurs only at infinite dilution. However, this is true for weak electrolytes. Strong electrolytes are almost completely ionised at all dilutions and λ_v/λ_∞ does not give the accurate value of α.

(2)   The Ostwald's law is derived on the assumption that the Law of Mass Action holds for the ionic equilibria as well. But when the concentration of ions is very high, the presence of charges affects the equilibrium. Thus the Law of Mass Action in its simple form cannot be applied.

(3)   The ions obtained by dissociation may get hydrated and may affect the concentration terms. Better results are obtained by using *activities* instead of concentrations.

THEORY OF STRONG ELECTROLYTES

A number of theories have been put forward by different workers in order to explain the high conductance of strong electrolytes. Southerland (1906) held the view that ions in solution were surrounded by a large number of ions of opposite charge. Due to the weakening of interionic forces, the ionic velocities were accelerated. This resulted in the increase of conductance of the electrolyte solution. However, not much notice was taken of Southerland's view.

Ghosh's Formula

In 1918 J.C. Ghosh revived the above theory. He assumed that though the electrolyte is completely ionised, all the ions are not free to move owing to the influence of electric charges and it is only the *mobile ions* which contribute to the conductance of the solution. The value α represents the "active" proportion of the electrolyte and can be determined by purely electrical data, the Law of Mass Action playing no part whatsoever. His formula

$$\sqrt[3]{V} \log \alpha = K$$

was applicable to univalent strong electrolytes.

Debye-Huckel Theory

In 1923 Debye and Huckel and in 1926 Onsagar put forward the **modern theory of strong electrolytes** in which account is taken of the electrostatic forces between the ions. Without going into its mathematical details, a brief outline of the main ideas of the theory is given below :

(1) **The strong electrolyte is completely ionised at all dilutions.** The present position as it has emerged from the study of Raman spectra, X-ray analysis of crystals, Distribution coefficients and vapour pressures is that there is a very small amount of unionised substance also present and therefore instead of saying 'completely ionised' we should say 'almost completely ionised'.

(2) **Since oppositely charged ions attract each other, it suggests that anions and cations are not uniformly distributed in the solution of an electrolyte but that the cations tend to be found in the vicinity of anions and** *vice-versa* (Fig. 26.1)**.** Though the solution is on the whole neutral, there is in the vicinity of any given ion a predominance of ions of opposite charge which we call as **counter ions.** The ions are all the time on the move in all directions but on the average, more *counter ions* than like *ions* pass by any given ion. This spherical haze of opposite charge is called **ionic atmosphere.**
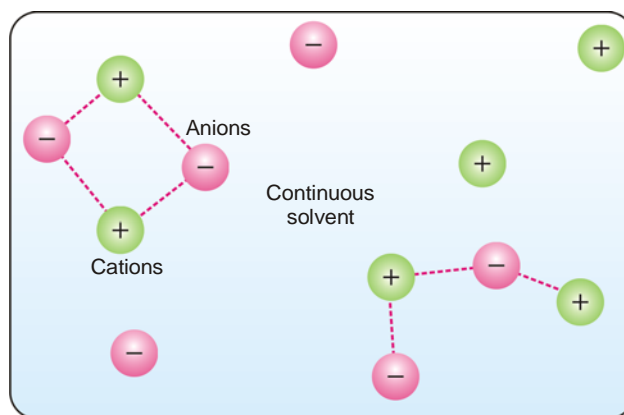
■ **Figure 26.1**
The ions of a particular charge are surrounded by more ions of the opposite charge and solvent molecules. Because of the large number of ions in concentrated solution,the ion activity is reduced due to hindered movement of the ions.

(3) **Decrease in equivalent conductance with increase in concentration is due to fall in mobilities of the ions due to greater inter-ionic effect and** *vice-versa.*

(4) The ratio $\lambda_v / \lambda_\infty$ does not correctly give the degree of dissociation α for strong electrolytes but only the conductance or conductance coefficient f_c.

(5) In spite of almost complete ionisation, λ_v is much less than λ_∞.

The observed deviations are due to the following reasons :

(1) **Asymmetry or Relaxation Effect.** Imagine a central negative ion. This is surrounded by a number of positively charged ions which form its 'ionic atmosphere.' This atmosphere is symmetrically situated in the absence of any electrical field and the force of attraction exerted by the atmosphere on the central ion is uniform in all directions. When an electric field is applied, the negative ion moves towards the anode and the positive ionic atmosphere towards the cathode. This leaves a large number of positive ions behind it than there are in front of the negative ion with the result that the symmetry

of the atmosphere about the central negative ion is destroyed (Fig. 26.2) and it becomes distorted.

Whereas initially the force of attraction exerted by the atmosphere on the central ion was uniform it becomes greater now behind the ion than in front. As a result of this the negative ion experiences a force which tends to drag it backwards and this slows down its movement in the forward direction. This behavior is known as **Asymmetry Effect.** It may be said that the negative ion which leaves the ionic atmosphere of positive ions behind to die away would build a new ionic atmosphere and the asymmetry would be corrected. If this process of building up and dying away were instantaneous, there would be no cause for asymmetry and the atmosphere would always be symmetrically placed about the ion. But, as it is, the formation of the new ionic atmosphere does not take place at the same rate at which the old one decays and the latter lags behind or takes more time, known as '**relaxation time'.** During this interval, there is a preponderance of positive ions to the left of the central negative ion which is under move and these tend to drag it back. For this reason asymmetry effect is also known as **Relaxation Effect.** Moreover, the central ion moves into a place where there is an excess of ions of its own sign and this has also a retarding effect.
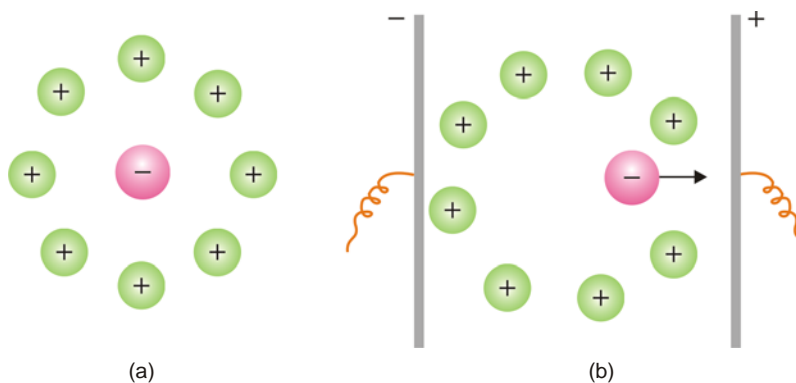
■ **Figure 26.2**
(*a*) **Symmetrical ionic atmosphere at rest; (*b*) Asymmetrical ionic atmosphere under the influence of applied field.**

(2) **Electrophoretic Effect.** Another factor which acts as a drag and tends to retard the motion of an ion in solution is the tendency of the applied field to move the ionic atmosphere (to which solvent molecules are also attached) in a direction opposite to that in which the central ion associated with solvent molecules is moving. Thus the central negative ion moving towards the anode has to make its way through the ionic atmosphere with its associated solvent molecules which is moving in the opposite direction *i.e.*, towards the cathode. This causes a retarding influence on the movement of the ion the effect of which is equal to the increase in the viscous resistance of the solvent. By analogy to the resistance acting on the movement of a colloidal particle under an electrical field (See Chapter 22 on Colloids), this effect is called **Electrophoretic Effect.**

Both the above causes reduce the velocity of the ion and operate in solutions of strong electrolytes with the result that a value of equivalent conductance (λ_v) lower than the value at infinite dilution (λ_∞) is obtained. At infinite dilution since the electrical effects are practically absent, the two values tend to approach each other.

Debye-Huckel-Onsagar Conductance Equation takes these causes into account and for a univalent electrolyte supposed to be completely dissociated is written in the form

$$\lambda_v = \lambda_\infty - (A + B\lambda_\infty)\sqrt{C}$$

where A and B are constants and c is the concentration in gm-equivalents per litre. These constants depend only on the nature of the solvent and the temperature and are given by the relationships :

$$A = \frac{82.4}{(DT)^{1/2}\,\eta} \quad \text{and} \quad B = \frac{8.20 \times 10^5}{(DT)^{3/2}}$$

where D and η are the dielectric constant and coefficient of viscosity of the *medium* respectively at the absolute temperature T. The constant A is a measure of the electrophoretic effect while B is that of the asymmetry effect. For *water* at 25°C with D = 78.5 and $\eta \times 10^3 = 8.95$, the value of A is 60.20 and that of B is 0.229. On substituting these values in the above equation, we have

$$\lambda_v = \lambda_\infty - (60.20 + 0.229\lambda_\infty)\sqrt{C}$$

It follows, therefore, that if the above equation is correct, a straight line of slope equal to (60.20 + 0.229 λ_∞) should be obtained by plotting observed equivalent conductance (λ_v) against the square root of the corresponding concentration *i.e.*, $\sqrt{C}$. The Onsager equation responds to this test favourably and for aqueous solutions of univalent electrolytes, it is closely obeyed at concentrations upto about 2×10^{-3} equivalents per litre (Fig. 26.3). Slight deviations at higher concentrations are attributed to certain approximations assumed in deriving the equation.
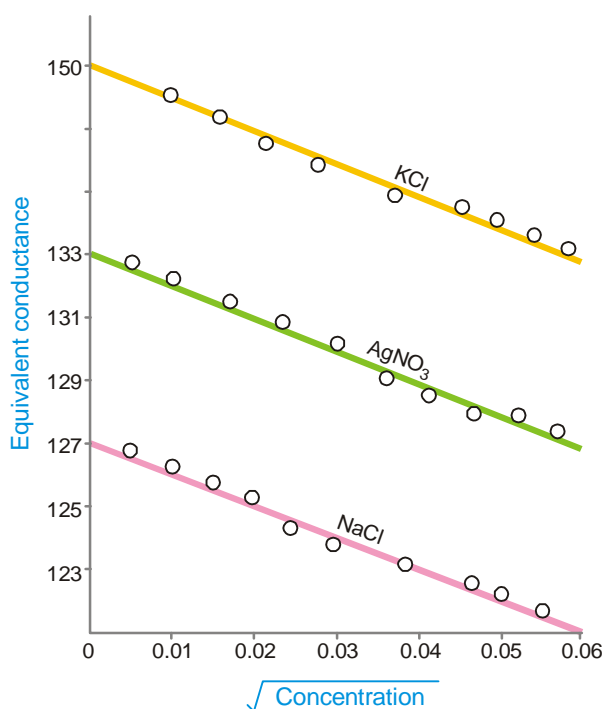
■ Figure 26.3
Testing of Onsagar equation. The circles represent the observed value of I_n whereas the dotted line stands for the theoretical values of the slopes expected from the Onsagar equation.

DEGREE OF DISSOCIATION

When a certain amount of electrolyte $(A^+ B^-)$ is dissolved in water, a small fraction of it dissociates to form ions $(A^+$ and $B^-)$. When the equilibrium has been reached between the undissociated and the free ions, we have

$$AB \rightleftharpoons A^+ + B^-$$

The fraction of the amount of the electrolyte in solution present as free ions is called the Degree of dissociation.

If the degree of dissociation is represented by x, we can write

$$x = \frac{\text{amount dissociated (mol/L)}}{\text{initial concentration (mol/L)}}$$

The value of x can be calculated by applying the Law of Mass Action to the ionic equilibrium stated above :

$$K = \frac{[A^+][B^-]}{[AB]}$$

If the value of the equilibrium constant, K, is given, the value of x can be calculated.

THE COMMON–ION EFFECT

When a soluble salt (say A^+C^-) is added to a solution of another salt (A^+B^-) containing a common ion (A^+), the dissociation of AB is suppressed.

$$AB \rightleftharpoons A^+ + B^-$$

By the addition of the salt (AC), the concentration of A^+ increases. Therefore, according to Le Chatelier's principle, the equilibrium will shift to the left, thereby decreasing the concentration of A^+ ions. Or that, the degree of dissociation of AB will be reduced.

The reduction of the degree of dissociation of a salt by the addition of a common-ion is called the Common-ion effect.

Let us consider a few examples to illustrate the common-ion effect.

Example 1. In a saturated solution of silver chloride, we have the equilibrium

$$AgCl\,(s) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq)$$
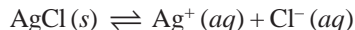
When sodium chloride is added to the solution, the concentration of Cl^- ions will increase. The equilibrium shown above will be shifted to the left to form more of solid Ag Cl. Thus the solubility of AgCl, a typical sparingly soluble salt, will decrease.

Example 2. When solid NH_4Cl is added to NH_4OH solution, the equilibrium

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$
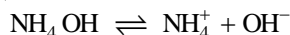
shifts to the left. Thereby the equilibrium concentration of OH^- decreases. This procedure of reducing the concentration of OH^- ions is used in qualitative analysis.

Example 3. The common-ion effect can also be applied to the ionic equilibrium of a weak acid as HF.

$$HF \rightleftharpoons H^+ + F^-$$

NaF is added to the equilibrium mixture. The concentration of F^- (common ion) is increased. Thus the equilibrium shifts to the left. In other words, the degree of dissociation of HF decreases. It was found by experiment that the degree of dissociation of HF in 1M solution is 2.7, while the value reduces to 7.2×10^{-4} after the addition of 1M NaF.

> **SOLVED PROBLEM.** Find the degree of dissociation of HF in 1M aqueous solution. The value of K for the ionic equilibrium $HF \rightleftharpoons H^+ + F^-$ is 7.2×10^{-4}.
>
> **SOLUTION**
>
> HF dissociates in water to form H^+ and F^- ions. On reaching the equilibrium we have
>
> $$HF \rightleftharpoons H^+ + F^-$$
>
> Thus one mole of HF taken initially dissociates to yield 1 mole of H^+ and 1 mole of F^-.
>
> If x be the degree of dissociation, the concentration terms at equilibrium are :

$$[HF] = 1-x \text{ mol/l}$$
$$[F^-] = x \text{ mol/l}$$
$$[H^+] = x \text{ mol/l}$$

Substituting these values in the equilibrium expression, we have

$$K = 7.2 \times 10^{-4} = \frac{[H^+][F^-]}{[HF]} = \frac{(x)(x)}{1.00-x}$$

If x is very small compared to 1, we can write :

$$7.2 \times 10^{-4} = \frac{x^2}{1.00}$$

$\therefore \qquad x^2 = (7.2 \times 10^{-4})(1.00) = 7.2 \times 10^{-4}$

or $\qquad x = \sqrt{7.2 \times 10^{-4}} = 2.7 \times 10^{-2}$

Thus the degree of dissociation of HF in 1M solution is $\mathbf{2.7 \times 10^{-2}}$

FACTORS WHICH INFLUENCE THE DEGREE OF DISSOCIATION

The *degree of dissociation* of an electrolyte in solution depends upon the following factors :

(1) Nature of Solute

The nature of solute is the chief factor which determines its degree of dissociation in solution. Strong acids and strong bases, and the salts obtained by their interaction are almost completely dissociated in solution. On the other hand, weak acids and weak bases and their salts are feebly dissociated.

(2) Nature of the solvent

The nature of the solvent affects dissociation to a marked degree. It weakens the electrostatic forces of attraction between the two ions and separates them. This effect of the solvent is measured by its '*dielectric constant*'. The **dielectric constant** of a solvent may be defined as its capacity to weaken the force of attraction between the electrical charges immersed in that solvent.

The dielectric constant of any solvent is evaluated considering that of vaccum as unity. It is 4.1 in case of ether, 25 in case of ethyl alcohol and 80 in case of water. The higher the value of the dielectric constant the greater is the dissociation of the electrolyte dissolved in it because the electrostatic forces vary inversely as the dielectric constant of the medium. Water, which has a high value of dielectric constant is, therefore, a strong dissociating solvent. The electrostatic forces of attraction between the ions are considerably weakened when electrolytes are dissolved in it and as a result, the ions begin to move freely and there is an increase in the conductance of the solution.

(3) Concentration

The extent of dissociation of an electrolyte is inversely proportional to the concentration of its solution. The less concentrated the solution, the greater will be the dissociation of the electrolyte. This is obviously due to the fact that in a dilute solution the ratio of solvent molecules to the solute molecules is large and the greater number of solvent molecules will separate more molecules of the solute into ions.

(4) Temperature

The dissociation of an electrolyte in solution also depends on temperature. The higher the temperature greater is the dissociation. At high temperature the increased molecular velocities overcome the forces of attraction between the ions and consequently the dissociation is great.

SOLUBILITY EQUILIBRIA AND THE SOLUBILITY PRODUCT

When an ionic solid substance dissolves in water, it dissociates to give separate cations and anions. As the concentration of the ions in solution increases, they collide and reform the solid phase. Ultimately, a dynamic equilibrium is established between the solid phase and the cations and anions in solution. For example, for a sparingly soluble salt, say Ag Cl, we can write the equilibrium equations as follows :

$$\underset{\text{solid}}{Ag\,Cl} \rightleftharpoons Ag^+ + Cl^-$$
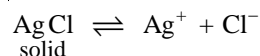
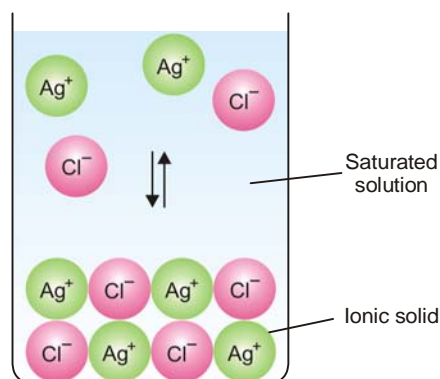At equilibrium the solute continues to dissolve at a rate that exactly matches the reverse process, the return of solute from the solution. Now the solution is said to be saturated.

■ Figure 26.4
Equilibrium between an ionic solid and ions in a saturated solution.

A Saturated solution is a solution in which the dissolved and undissolved solute are in equilibrium.

A saturated solution represents the limit of a solute's ability to dissolve in a given solvent. This is a measure of the "solubility" of the solute.

The Solubility (S) of a substance in a solvent is the concentration in the saturated solution. Solubility of a solute may be represented in grams per 100 ml of solution. It can also be expressed in moles per litre.

Molar Solubility is defined as the number of moles of the substance per one litre (l) of the solution.

The value of solubility of a substance depends on the solvent and the temperature.

Applying the Law of Mass Action to the above equilibrium for Ag Cl, we have

$$K = \frac{[Ag^+]\,[Cl^-]}{[Ag\,Cl]}$$

The amount of Ag Cl in contact with saturated solution does not change with time and the factor [Ag Cl] remains the same. Thus the equilibrium expression becomes

$$K_{sp} = [Ag^+]\,[Cl^-]$$

where $[Ag^+]$ and $[Cl^-]$ are expressed in mol/L. The equilibrium constant in the new context is called the **Solubility Product Constant** (or simply the **Solubility Product**) and is denoted by K_{sp}. The value of K_{sp} for a particular solubility equilibrium is constant at a given temperature. The product $[Ag^+]\,[Cl^-]$ in the K_{sp} expression above is also called the **Ionic Product** or **Ion Product.**

TABLE 26.2. SOLUBILITY PRODUCT VALUES FOR SOME SPARINGLY SOLUBLE SALTS		
Substance	Formula	K_{sp} at 25°C
Aluminium hydroxide	$Al(OH)_3$	$[Al^{3+}][OH^-]^3 = 1.6 \times 10^{-33}$
Barium fluoride	BaF_2	$[Ba^{2+}][F^-]^2 = 1.7 \times 10^{-6}$
Barium carbonate	$BaCO_3$	$[Ba^{2+}][CO_3^{2-}] = 8.1 \times 10^{-9}$
Calcium fluoride	CaF_2	$[Ca^{2+}][F^-]^2 = 4.0 \times 10^{-11}$
Copper (I) bromide	CuBr	$[Cu^{+1}][Br^-] = 4.2 \times 10^{-8}$
Copper (I) sulphide	Cu_2S	$[Cu^+]^2[S^{2-}] = 8.5 \times 10^{-45}$
Iron (III) hydroxide	$Fe(OH)_3$	$[Fe^{3+}][OH^-]^3 = 2.0 \times 10^{-39}$
Lead (II) bromide	$PbBr_2$	$[Pb^{2+}][Br^-]^2 = 7.9 \times 10^{-5}$
Lead (II) iodide	PbI_2	$[Pb^{2+}][I^-]^2 = 1.4 \times 10^{-8}$
Silver Chloride	AgCl	$[Ag^+][Cl^-] = 1.8 \times 10^{-10}$

The K_{sp} expression may be stated as : **the product of the concentration of ions (mol/l) in the saturated solution at a given temperature is constant.** This is sometimes called the **Solubility product principle.**

NUMERICAL PROBLEMS

While discussing numerical problems on solubility product principle, three cases may arise:

Case 1. Calculation of K_{sp} from Solubility

The solubility of a sparingly soluble salt as AgCl may be defined as **the moles of solid AgCl which dissolve per one litre (1.0 l) of solution to reach the equilibrium with the excess solid.**

Here, the equilibrium reaction is

$$AgCl\,(s) \rightleftharpoons Ag^+ + Cl^-$$
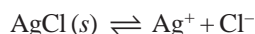
One mole of AgCl gives one mole of Ag^+ ion and one mole of Cl^- ion. If S mol/l be the solubility of AgCl, the equilibrium concentrations of Ag^+ and Cl^- are :

$$[Ag^+] = S \text{ mol/l}$$
$$[Cl^-] = S \text{ mol/l}$$

Substituting the values in the K_{sp} expression,

$$K_{sp} = [Ag^+][Cl^-]$$
$$= [S \text{ mol/l}][S \text{ mol/l}]$$
$$= S^2 \text{ mol}^2/l^2$$

Knowing the value of S, K_{sp} can be calculated.

The units for K_{sp} values are usually omitted.

SOLVED PROBLEM. The solubility of CuBr is found to be 2.0×10^{-4} mol/l at 25°C. Calculate K_{sp} value for CuBr.

SOLUTION

The solubility of CuBr is $= 2.0 \times 10^{-4}$ mol/l. This means that the equilibrium concentration of CuBr $= 2.0 \times 10^{-4}$ mol/l.

From the reaction

$$\underset{\text{solid}}{CuBr} \rightleftharpoons Cu^+ + Br^-$$

it is evident that 1 mole of CuBr yields one mole of Cu^+ and one mole of Br^-. Thus 2.0×10^{-4} mole of CuBr would yield 2.0×10^{-4} mole of Cu^+ and 2.0×10^{-4} mole of Br^-.

$\therefore$ Equilibrium concentration of $\quad Cu^+ \; = \; 2.0 \times 10^{-4} \, mol \, l^{-1}$
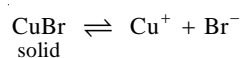
Equilibrium concentration of $\qquad Br^- \; = \; 2.0 \times 10^{-4} \, mol \, l^{-1}$

Substituting these in the expression

$$
\begin{aligned}
K_{sp} \; &= \; [Cu^+][Br^-] \\
&= \; [2.0 \times 10^{-4} \, mol \, l^{-1}][2.0 \times 10^{-4} \, mol \, l^{-1}] \\
&= \; \mathbf{4.0 \times 10^{-8} \, mol^2 \, l^{-2}}
\end{aligned}
$$

Case 2. Calculation of Solubility from K_{sp}

We have seen how the experimentally determined value of solubility of an ionic solid can be used to calculate its K_{sp} value. The reverse is also possible. We can calculate the solubility of an ionic compound if the K_{sp} value is given. Here, we assume that the solubility is S. Then the equilibrium concentrations of the ions into which the compound dissociates are found. The value of K_{sp} is found by substituting these in the K_{sp} expression.

SOLVED PROBLEM 1. Calculate the solubility of $NiCO_3$ in moles per litre and grams per litre. The value of K_{sp} for $NiCO_3 = 1.4 \times 10^{-7}$.

SOLUTION
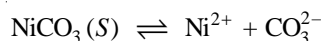
$$NiCO_3 \, (S) \; \rightleftharpoons \; Ni^{2+} + CO_3^{2-}$$

$$K_{sp} = [Ni^{2+}][CO_3^{2-}]$$

$$1.4 \times 10^{-7} = [Ni^{2+}][CO_3^{2-}]$$

In the above equilibrium reaction, one mole of $NiCO_3$ dissociates to produce one mole of Ni^{2+} and one mole of CO_3^{2-}. If S mol/l be the solubility of $NiCO_3$, the equilibrium concentration of Ni^{2+} is S mol/l and that of CO_3^{2-} also it is S mol/l.

Substituting these values in the K_{sp} expression, we have

$$1.4 \times 10^{-7} = [S \, mol/l][S \, mol/l]$$

or $\qquad\qquad\qquad S^2 = 1.4 \times 10^{-7}$

$$S = \sqrt{1.4 \times 10^{-7}} = 3.7 \times 10^{-4} \, mol/l$$

This means that the solubility of $NiCO_3$ is 3.7×10^{-4} mol/l. Therefore, the solubility in g/l is

$= 3.7 \times 10^{-4} \times 118.7 = \mathbf{0.044 \, g/l}$ where 118.7 is the molecular mass of $NiCO_3$.

SOLVED PROBLEM 2. Calculate the K_{sp} for Bismuth sulphide (Bi_2S_3), which has a solubility of 1.0×10^{-15} mol/L at 25°C.

SOLUTION

Here, the equilibrium reaction is

$$Bi_2S_3 \; \rightleftharpoons \; 2Bi^{3+} + 3S^{2-}$$

One mole of Bi_2S_3 gives two moles of Bi^{3+} ion and three moles of S^{2-} ion. Thus 1.0×10^{-15} mole Bi_2S_3 will give $2(1.0 \times 10^{-15}$ mole) of Bi^{3+} and $3(1.0 \times 10^{-15}$ mole) of S^{2-}. We can write the equilibrium concentrations of Bi^{3+} and S^{2-} as :

$$[Bi^{3+}] = 2.0 \times 10^{-15} \, mol/l$$

$$[S^2] = 3.0 \times 10^{-15} \, mol/l$$

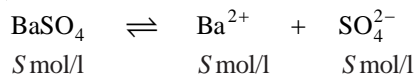Substituting these values in the K_{sp} expression

$$K_{sp} = [Bi^{3+}]^2 [S^{2-}]^3$$
$$= (2.0 \times 10^{-15})^2 (3.0 \times 10^{-15})^3$$
$$= 1.08 \times 10^{-73}$$

Thus the value of K_{sp} is **1.08×10^{-73}.**

SOLVED PROBLEM 3. The solubility of $BaSO_4$ is 2.33×10^{-4} g/ml at 20°C. Calculate the solubility product of $BaSO_4$ assuming that the salt is completely ionised.

SOLUTION

$$BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$$
$$S \text{ mol/l} \qquad S \text{ mol/l} \qquad S \text{ mol/l}$$

Where S represents the solubility of $BaSO_4$ at 20°C.

Amount of $BaSO_4$ in one ml $= 2.3 \times 10^{-4}$ g

Amount of $BaSO_4$ in one l $= 2.3 \times 10^{-4} \times 10^3$ g

No. of moles of $BaSO_4$ per litre $= \dfrac{2.3 \times 10^{-4} \times 10^3}{233} = 1.0 \times 10^{-3}$

$\therefore \qquad K_{sp} = [Ba^{2+}] [SO_4^{2-}]$
$$= (1.0 \times 10^{-3}) (1.0 \times 10^{-3})$$
$$= 1.0 \times 10^{-6}$$

Thus the solubility product of $BaSO_4$ at 25°C is **1.0×10^{-6}**.

Case 3. Whether precipitation will occur on mixing solutions

When two reacting solutions are mixed, calculate the concentration of each ion in the solution in which precipitation is produced. The ionic product, Q, is then calculated. We know that K_{sp} is the ionic product when the ions are in contact with the solid substance. Therefore, the precipitation will occur for any higher ion concentrations. In other words, the precipitation will take place if $Q > K_{sp}$.

If $Q < K_{sp}$, no precipitation will occur.

SOLVED PROBLEM 1. A 200 ml of 1.3×10^{-3} M $AgNO_3$ is mixed with 100 ml of 4.5×10^{-5} M Na_2S solution. Will precipitation occur ? ($K_{sp} = 1.6 \times 10^{-49}$)

SOLUTION

The reaction that would cause precipitation is
$$2Ag^+ + S^{2-} = Ag_2S \,(s)$$
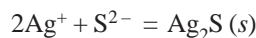
The ion product is
$$Q = [Ag^+]^2 [S^{2-}]$$

Let us now calculate the molar concentrations of Ag^+ and S^{2-} ions :

$$[Ag^+] = 1.3 \times 10^{-3} \text{ M} \times \frac{200 \text{ ml}}{(200 + 100) \text{ ml}} = 8.7 \times 10^{-4} \text{ M}$$

$$[S^{2-}] = 4.5 \times 10^{-5} \text{ M} \times \frac{100 \text{ ml}}{300 \text{ml}} = 1.5 \times 10^{-5} \text{ M}$$

$\therefore \qquad Q = (8.7 \times 10^{-4}) (1.5 \times 10^{-5}) = 13.05 \times 10^{-9}$

$\qquad K_{sp}$ for the reaction is $= 1.6 \times 10^{-49}$ (given)

$\therefore \qquad Q > K_{sp}$ and **precipitation will occur**.

SOLVED PROBLEM 2. 50 ml of 6.0×10^{-3} M $CaCl_2$ is mixed with 30 ml of 0.04 M NaF_2. Will precipitation of CaF_2 occur ? (K_{sp} for $CaCl_2 = 4.0 \times 10^{-11}$)

SOLUTION

The reaction that can cause precipitation is
$$Ca^{2+} + 2F^- = CaF_2(s)$$
The concentration of each ion in solution is :
$$[Ca^{2+}] = 6.0 \times 10^{-3} \text{ M} \times \frac{50.0 \text{ ml}}{(50.0 + 30.0) \text{ ml}} = 3.75 \times 10^{-3} \text{ M}$$
$$[F^-] = 0.040 \text{ M} \times \frac{30.0 \text{ ml}}{80.0 \text{ ml}} = 0.015 \text{ M}$$
$$\therefore \qquad Q = [Ca^{2+}][F^-]^2 = (3.75 \times 10^{-3})(0.015)^2 = 8.4 \times 10^{-7}$$
Since $Q > K_{sp}$, **precipitation will occur**.

Case 4. Calculation of solubility in presence of a common ion

Let us consider how to find the solubility of a solid when water contains an ion in common with the dissolving salt. Assuming that S m/L is the solubility, the concentrations of ions are expressed in terms of S. It may be noted that the concentration of the common ion is added to the equilibrium concentration to get the final concentration. The values of the final concentrations are then substituted into the K_{sp} expression and the value of S calculated.

SOLVED PROBLEM. Calculate the solubility of silver chromate, Ag_2CrO_4, in a 0.100 M solution of $AgNO_3$. (K_{sp} for $Ag_2CrO_4 = 9.0 \times 10^{-12}$)

SOLUTION

Ag_2CrO_4 dissolves according to the equilibrium reaction
$$Ag_2 CrO_4(s) \rightleftharpoons 2Ag^+ + CrO_4^{2-}$$
If S mol/l be the solubility, we can say that :
$$S \text{ mol/l } Ag_2CrO_4 \longrightarrow 2S \text{ mol/l } Ag^+ + S \text{ mol/l } CrO_4^{2-}$$
$\therefore$ The equilibrium concentrations in terms of S are
$$[Ag^+] = 0.100 \quad (\text{already present} + 2S)$$
$$[CrO_4^{2-}] = S$$
Substituting these in the K_{sp} expression, we have
$$9.0 \times 10^{-12} = [Ag^+][CrO_4^{2-}] = (0.100 + 2S)^2$$
$$= (0.100)^2 (S)$$
(Since S is very small compared to 0.100 M, the factor $2S^2$ is ignored)
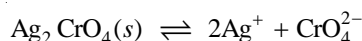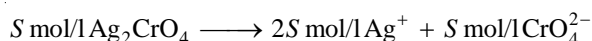
Hence
$$S = \frac{9.0 \times 10^{-12}}{(0.100)^2} = 9.0 \times 10^{-10} \text{ mol/l}$$
Therefore, the solubility of Ag_2CrO_4 in 0.1 M $AgNO_3$ is $S = \textbf{9.0} \times \textbf{10}^{-10} \textbf{ mol/l}$.

APPLICATION OF SOLUBILITY PRODUCT PRINCIPLE IN QUALITATIVE ANALYSIS

Precipitation reactions are used to identify cations present in an unknown mixture of salts.

The Ion product and K_{sp}. The solubility product (K_{sp}) of an insoluble substance is the product of the concentrations of its ions at equilibrium. However, **the ion product is the product of actual concentrations of ions** which may or may not be in equilibrium with the solid. For example,
$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$$
If S be the solubility of AgCl, we have
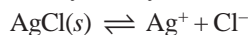
$$K_{sp} = [S \text{ mol/l Ag}^+][S \text{ mol/l Cl}^-]$$

Suppose 0.25 mol/L excess of HCl is added to the solution. Then Q, the ion product, will be

$$Q = [S \text{ mol/l Ag}^+][(S + 0.25) \text{ mol/l Cl}^-]$$

The increase in concentration of Cl^- will shift the equilibrium to the left to form a precipitate of AgCl.

Thus, if

$$\begin{array}{ll} Q > K_{sp} & \text{the precipitation will occur} \\ Q = K_{sp} & \text{the solution is saturated} \\ Q < K_{sp} & \text{no precipitation will occur,} \\ & \text{more solid salt will dissolve} \end{array}$$

SELECTIVE PRECIPITATION

The scheme of Qualitative Analysis is based on the **Principle of Selective Precipitation.** Let us consider a mixture containing Ag^+, Cu^{2+} and Fe^{3+}.

Step 1 : Add dil HCl to the solution of the mixture. Ag^+ will precipitate as AgCl. It is removed by filtration.

Step 2 : Pass H_2S through the filtrate. Cu^{2+} is precipitated as CuS and removed by filtration.

Step 3 : Add NH_4OH or NaOH solution to filtrate. Fe^{3+} is precipitated as $Fe(OH)_3$.

In this way ions are precipitated from solution one by one. **The precipitation of cations from solution one at a time is called Selective precipitation.**

Separation of the Basic ions into Groups

Qualitative analysis of a mixture containing all the common cations involves first their separation into six major Groups based on solutions. Each group is then treated further to separate and identify the individual cations. The scheme of separation of cations into different Groups is listed in Fig.26.5.

Group I — Insoluble Chlorides

When excess dil HCl is added to a solution containing a mixture of common cations, only Ag^+, Pb^{2+} and Hg^{2+} will be precipitated as insoluble chlorides. The K_{sp} of these chlorides is very low and is easily exceeded. The K_{sp} value of other chlorides is high and they remain dissolved. For example, the K_{sp} of CuCl is 1.9×10^{-7} and, therefore, it will not be precipitated.

Group II — Sulphides insoluble in acid solution

After removing the insoluble chlorides in Group I, the solution is still acidic. When H_2S is passed through this solution, only the insoluble sulphides of Hg^{2+}, Cd^{2+}, Bi^{3+}, Cu^{2+}, and Sn^{4+} will precipitate. It is so as the concentration of S^{2-} ion is relatively low because of the higher concentration of H^+ (Common Ion effect).

$$H_2S \text{ (g)} \rightleftharpoons 2H^+ + S^{2-} \quad \text{(equilibrium shifted to left)}$$

Other cations Mn^{2+}, Zn^{2+}, Ni^{2+}, CO^{2+} with higher value of K_{sp} of the respective sulphides will remain dissolved because the ionic product is less than K_{sp}.

Group III — Insoluble Hydroxide in $NH_4OH + NH_4Cl$

To the filtrate from Group II is added NH_4Cl and then NH_4OH. NH_4OH is a weak base and the concentration of OH^- is low. NH_4Cl provides more NH_4^+ ions which shifts the equilibrium to the left (Common Ion effect).

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$
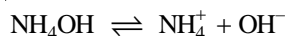
Thus some OH^- ions are converted to undissociated NH_4OH. So that the concentration of OH^- ions becomes extremely low. But the ion product, Q, is greater than K_{sp} values for the hydroxides of Al^{3+}, Fe^{3+} and Cr^{3+} which precipitate out. On the other hand, the ion product is lower than the K_{sp} values for $Zn(OH)_2$ $Mn(OH)_2$, and $Mg(OH)_2$ which remain dissolved.

	$Zn(OH)_2$	$Mn(OH)_2$	$Mg(OH)_2$
K_{sp}	4.5×10^{-17}	4.6×10^{-14}	1.5×10^{-11}

Group IV — Insoluble Sulphides in basic solution

The filtrate from Group III contains OH^- ions and is basic. H_2S is passed through it. In the presence of OH^- ions, the H^+ ions produced from H_2S form unionised water.

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

$$H^+ + OH^- \longrightarrow H_2O \text{ (nonionised)}$$
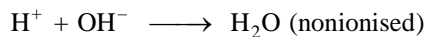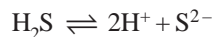
Thus the above equilibrium shifts to the right and the concentration of S^{2-} ions increases. This increases the actual ion product for the reaction

$$\underset{\text{metal sulphide}}{MS(s)} \rightleftharpoons M^{2+} + S^{2-}$$
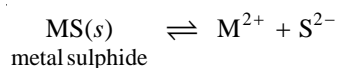
which becomes greater than the K_{sp} value for the insoluble sulphides of Mn^{2+}, Zn^{2+}, Ni^{2+}, and CO^{2+}. Thus MnS, ZnS, NiS and CoS are therefore, precipitated.

K_{sp} at 25°C

Add dil HCl	→ Precipitate	AgCl	1.6×10^{-10}
		Hg_2Cl_2	1.1×10^{-18}
		$PbCl_2$	1.6×10^{-5}

Pass H_2S in acid solution	→ Precipitate	Bi_2S_3	1.6×10^{-72}
		CdS	1.0×10^{-28}
		CuS	8.5×10^{-45}
		HgS	1.6×10^{-54}
		Sb_2S_3	1.6×10^{-93}

Add NH_4Cl and NH_4OH	→ Precipitate	$Al(OH)_3$	2×10^{-32}
		$Fe(OH)_3$	6.8×10^{-38}
		$Cr(OH)_3$	6.7×10^{-31}

Pass H_2S in basic solution	→ Precipitate	MnS	2.3×10^{-13}
		ZnS	2.5×10^{-22}
		NiS	3×10^{-21}
		CoS	5×10^{-22}

Add $(NH_4)_2CO_3$	→ Precipitate	$BaCO_3$	1.6×10^{-9}
		$SrCO_3$	7×10^{-10}
		$CaCO_3$	8.7×10^{-9}
		$MgCO_3$	1×10^{-15}

■ Figure 26.5
Precipitation into the qualitative analysis groups.

Group V — Insoluble Carbonates

To the filtrate from Group IV is added excess of sodium carbonate solution. The excess CO_3^{2-} ions in solution will drive the equilibrium to the left for $BaCO_3$, $SrCO_3$, $MgCO_3$ and $CaCO_3$. Thus,

$$BaCO_3 \rightleftharpoons Ba^{2+} + \underset{\text{(excess)}}{CO_3^{2-}}$$
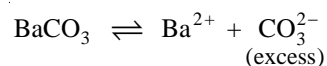
This leads to the precipitation of the carbonates of Ba^{2+}, Sr^{2+}, Mg^{2+}, and Ca^{2+} to completion.

Group VI. The cations Na^+ and K^+, if present in the mixture, are identified by individually testing by the flame test.

EXAMINATION QUESTIONS

1. Define or explain the following terms :
   - (a) Ostwald's dilution law
   - (b) Degree of dissociation
   - (c) Common ion effect
   - (d) Solubility equilibria
   - (e) Solubility product

2. (a) Define the terms 'Solubility' and 'Solubility product'. Explain the use of solubility product in qualitative analysis.
   (b) The solubility of $BaSO_4$ is 2.33×10^{-4} g per cc at 20°C. Calculate the solubility product of $BaSO_4$ assuming that the dissolved salt is completely ionised.

   Answer. (b) 1.0×10^{-6}

3. (a) Give the relation between solubility and solubility product.
   (b) The solubility product of silver chromate in water is 2.0×10^{-12} at 25°C. Calculate the solubility at that temperature.

   Answer. (b) 7.935×10^{-5} mol/litre

4. (a) State the principle of solubility product. How is the solubility of a salt is affected by the presence of a common ion?
   (b) The solubility product of lead bromide is 8.0×10^{-5}. If the salt is 80% dissociated in the saturated solution, find the solubility of the salt.

   Answer. 12.44 g/litre

5. Define :
   (a) (i) Solubility; and (ii) Solubility product.
   (b) The solubility of silver chloride at 25°C is 1.05×10^{-5} moles per litre. Calculate the solubility product.

   Answer. 1.1025×10^{-10}

6. (a) How will you determine the solubility and solubility product of sparingly soluble salts through conductometric measurements?
   (b) The specific conductivity of a saturated solution of silver chloride is 1.33×10^{-6} mhos at 25°C. Given that the ionic conductivities for Ag^+ and Cl^- ions are 56.9 and 68.4 mhos respectively. Calculate the solubility and solubility product of the silver chloride.

   Answer. (b) 1.523×10^{-3} g l^{-1}; 1.1264×10^{-10}

7. (a) Zinc sulphide is precipitated by hydrogen sulphide from ammoniacal solution. Explain.
   (b) The solubility of $BaSO_4$ at 18°C is 0.00233 g per litre. Calculate the solubility product of $BaSO_4$. (Molecular weight of $BaSO_4$ is 233).

   Answer. 1×10^{-10}

8. (*a*) What is the Henderson equation?

   (*b*) Calculate the pH value of a solution obtained by mixing 500 ml of 0.1N CH_3COOH and 500 ml of 0.1N CH_3COONa. K_a for acetic acid is 1.8×10^5.

   Answer. 4.774

9. (*a*) State Ostwald's dilution law. How is it experimentally verified?

   (*b*) Calculate pH value of a solution whose hydrogen ion concentration is 0.006 gm ion/litre.

   Answer. (*b*) 2.5

10. (*a*) What is meant by pH of a solution? A solution has a pH = 6. Is it acidic or alkaline?

    (*b*) Calculate the pH of (*i*) 10^{-8} N aqueous HCl solution; and (*ii*) 10^{-7} aqueous NaOH solution.

    Answer. (*a*) Acidic; (*b*) (*i*) 8; (*ii*) 7

11. State and explain Ostwald's Dilution law. Can this law be applied to the dissociation of HCl in aqueous solution?

12. What is the ionic strength of an electrolyte? Explain how mean activity coefficient of an electrolyte can be determined from the Debye-Huckel theory of activity coefficients? (*Delhi BSc, 2000*)

13. How does the stability constant of a complex ion in solution predict about the stability of complex towards its dissociation. (*Himachal Pradesh BSc, 2000*)

14. Explain briefly how does Debye-Huckel theory explain the increase in equivalent conductance with dilution in case of strong electrolyte. (*Punjabi BSc, 2000*)

15. Define mean activity and mean activity coefficient of an electrolyte $A_x B_y$. (*Jammu BSc, 2000*)

16. With the help of conductivity how can you determine :

    (*i*) Solubility product of AgCl

    (*ii*) Degree of dissociation of a weak electrolyte

    (*iii*) Ionic product of water (*Panjab BSc, 2000*)

17. Briefly discuss the Debye-Huckel theory of activity coefficients of strong electrolytes.

    (*Guru Nanak Dev BSc, 2001*)

18. Define solubility and solubility product. Give its two applications. (*Jiwaji BSc, 2001*)

19. What is Ostwald's dilution law? How it is verified? What are its limitations? (*HS Gaur BSc, 2002*)

20. Define and explain ionic product of water. (*Punjabi BSc, 2002*)

21. Explain any two applications of common ion effect. (*Venkateshwar BSc, 2003*)

22. Explain how conductance measurements can be used to determine the solubility of sparingly soluble salts. (*Mizoram BSc, 2002*)

23. The dissociation constant of a weak mono basic acid is 4×10^{-10}. Calculate the hydrogen ion concentration of 0.1 N solution of this acid.

    Answer. 5.198 (*Jiwaji BSc, 2002*)

24. How do you determine the degree of ionisation of an electrolyte by conductance method?

    (*Sambalpur BSc, 2003*)

25. (*a*) What is solubility product of an electrolyte? Explain giving three examples, the use of solubility product in qualitative analysis.

    (*b*) At 20°C the solubility of silver chloride in water is 1.435×10^{-3} g per litre. Find the solubility product of AgCl.

    Answer. 1×10^{-10} (*Agra BSc, 2004*)

26. What is the pH of the buffer composed of 0.1M solution of HCN in 0.1M KCN? The dissociation constant of HCN is 0.01 M.

    Answer. 2 (*Jammu BSc, 2004*)

27. Calculate the solubility product of silver chromate Ag_2CrO_4 at 25 °C if the concentration of Ag^+ ion 1.5×10^{-4} mol lit^{-1} is in a saturated solution of silver chromate at 25 °C.

    Answer. $K_{sp} = 1.6875 \times 10^{-12}$ (*Sri Venkateswara BSc, 2005*)

28. The solubility of lead sulphate in water 0.038 g lit^{-1} at 25 °C. Calculate its solubility product at 25 °C. (molar mass of $PbSO_4$ = 303).

    Answer. 1.5725×10^{-8} (*HS Gaur BSc, 2005*)

29. When one litre of saturated solution of lead chloride, $PbCl_2$ is evaporated to dryness, the residue is found to weight 4.5 g. Calculate the value of K_{sp} for $PbCl_2$.

    Answer. 1.7×10^{-5} (*Jammu BSc, 2006*)

30. The solubility product of AgCl in water is 1.5×10^{-10}. Calculate its solubility in 0.01 M NaCl solution.

    Answer. 1.5×10^{-8} mol lit^{-1} (*Delhi BSc, 2006*)

31. Calculate the solubility product of AgCl if its solubility at 20 °C is 1.435×10^{-5} g/litre.

    Answer. 1×10^{-10} (*Arunachal BSc, 2006*)

MULTIPLE CHOICE QUESTIONS

1. The Ostwald's dilution law when applied to a binary electrolyte gives the expression (α is degree of dissociation)

   (a) $K_c = \dfrac{\alpha^2}{(1-\alpha)V}$ (b) $K_c = \dfrac{\alpha}{(1-\alpha)V}$

   (c) $K_c = \dfrac{\alpha^2}{(1-\alpha)V^2}$ (d) $K_c = \dfrac{\alpha^2}{(1-\alpha)^2 V}$

   Answer. (*a*)

2. Which of the following expression holds good for a weak electrolyte (α is the degree of dissociation)

   (a) $K_c = \dfrac{\alpha}{V}$ (b) $K_c = \dfrac{\alpha^2}{V}$

   (c) $K_c = \dfrac{\alpha}{V^2}$ (d) $K_c = \dfrac{\alpha^2}{V^2}$

   Answer. (*b*)

3. If λ_∞ and λ_v are the equivalent conductances at infinite dilution and at V dilution, the degree of dissociation, α, is given by

   (a) $\lambda = \dfrac{\lambda_\infty}{\lambda_v}$ (b) $\lambda = \dfrac{\lambda_\infty}{\lambda_v^2}$

   (c) $\lambda = \dfrac{\lambda_v}{\lambda_\infty}$ (d) none of these

   Answer. (*c*)

4. Which of the following statement is true?

   (a) Ostwald's dilution law holds good only for strong electrolytes and fails completely when applied to weak electrolytes

   (b) Ostwald's dilution law holds good only for weak electrolytes and fails completely when applied to strong electrolytes

   (c) Ostwald's dilution law holds good for both weak and strong electrolytes

   (d) Ostwald's dilution law does not hold good for both weak and strong electrolytes

   Answer. (*b*)

5. The failure of Ostwald's dilution law in case of strong electrolytes is due to

   (a) strong electrolytes are almost completely dissociated at all dilutions and λ_v/λ_α does not give accurate value of α

(b) the law of mass action in its simple form cannot be applied when the concentration of ions is very high

(c) the ions get hydrolysed and affect the concentration terms

(d) all of the above

Answer. (*d*)

6. Which of the following postulates of Debye-Huckel theory is/are true?

(*a*) the strong electrolyte is completely ionised at all dilutions

(*b*) the oppositely charged ions are completely distributed in the solution but the cations tend to be found in the vicinity of anions and vice-versa

(*c*) decrease in equivalent conductance with increase in concentration is due to fall in mobilities of ions due to inter-ionic effect

(*d*) all of the above

Answer. (*d*)

7. The effect that tends to retard the mobilities of ions in solution is

(*a*) asymmetry effect   (*b*) relaxation effect

(*c*) electrophoretic effect   (*d*) all of these

Answer. (*d*)

8. The value of equilibrium constant K for the equilibrium $AB \rightleftharpoons A^+ + B^-$ is

(*a*) $K = \dfrac{[AB]}{[A^+][B^-]}$ (*b*) $K = \dfrac{[A^+][B^-]}{[AB]}$

(*c*) $K = \dfrac{[AB]^2}{[A^+][B^-]}$ (*d*) $K = \dfrac{[AB]}{[A^+]^2 \, [B^-]^2}$

Answer. (*b*)

9. When a salt is added to a solution of another salt having a common ion, the degree of dissociation, α,

(*a*) increases   (*b*) remains the same

(*c*) decreases   (*d*) none of these

Answer. (*c*)

10. When NH_4Cl is added to a solution of NH_4OH, the equilibrium $NH_4OH \rightleftharpoons NH_4^+ + OH^-$ shifts towards

(*a*) left   (*b*) right

(*c*) remains unchanged   (*d*) none of these

Answer. (*a*)

11. Which of the following electrolytes when added to the equilibrium $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ disturbs the equilibrium towards left thereby decreasing the solubility of AgCl.

(*a*) KBr   (*b*) NaCl

(*c*) $NaNO_3$ (*d*) HNO_3

Answer. (*b*)

12. The degree of dissociation of an electrolyte depends upon

(*a*) nature of solute   (*b*) nature of solvent

(*c*) concentration of solute   (*d*) all of these

Answer. (*d*)

13. A saturated solution is that in which

(*a*) the concentration of dissolved and undissolved solute is the same

(*b*) there exists an equilibrium between dissolved and undissolved solute

(*c*) the concentration of undissolved solute is almost negligible

(*d*) none of the above

Answer. (*b*)

14. The solubility (*s*) of a substance in a solvent is the concentration in _____ solution.

   (*a*) unsaturated   (*b*) supersaturated

   (*c*) saturated   (*d*) none of these

   Answer. (*c*)

15. Molar solubility is the number of _____ of the substance per litre of the solution.

   (*a*) grams   (*b*) kilograms

   (*c*) g-equivalents   (*d*) moles

   Answer. (*d*)

16. The solubility product of AgCl is given by the expression

   (*a*) $K_{sp} = [Ag^+][Cl^-]$ (*b*) $K_{sp} = [Ag^+]^2[Cl^-]^2$

   (*c*) $K_{sp} = [Ag^+][Cl^-]^2$ (*d*) none of these

   Answer. (*a*)

17. The product of concentration of ions (mol lit^{-1}) in the saturated solution at a given temperature is called

   (*a*) ionic product   (*b*) solubility product

   (*c*) solubility   (*d*) solubility constant

   Answer. (*c*)

18. If '*s*' is the solubility of AgCl in water the solubility product K_{sp} is given by

   (*a*) $K_{sp} = s$ (*b*) $K_{sp} = s^2$

   (*c*) $K_{sp} = s^3$ (*d*) $K_{sp} = \sqrt{s}$

   Answer. (*b*)

19. For CuBr, the solubility is 2.0×10^{-4} mol lit^{-1} at 298 K. The solubility product would be

   (*a*) 1.0×10^{-4} mol^2 lit^{-2} (*b*) 1.414×10^{-2} mol^2 lit^{-2}

   (*c*) 4.0×10^{-8} mol^2 lit^{-2} (*d*) none of these

   Answer. (*c*)

20. If '*s*' is the solubility of CaF$_2$, the solubility product would be given by the expression

   (*a*) $K_{sp} = s^2$ (*b*) $K_{sp} = s^3$

   (*c*) $K_{sp} = 4s^3$ (*d*) $K_{sp} = 4s^2$

   Answer. (*c*)

21. The precipitation of a salt takes place if its ionic product is

   (*a*) equal to its solubility product   (*b*) less than its solubility product

   (*c*) greater than its solubility product   (*d*) none of the above

   Answer. (*c*)

22. When excess of dil HCl is added to a solution containing a mixture of common cations, only Ag$^+$, Pb^{2+} and Hg$^+$ will be precipitated. This is because of the reason that K_{sp} of these chlorides is

   (*a*) very low   (*b*) very high

   (*c*) equal to zero   (*d*) equal to infinity

   Answer. (*a*)

23. ZnS is not precipitated when H$_2$S is passed through the filtrate of group I during salt analysis. This is so because

   (*a*) the K_{sp} for ZnS is very high   (*b*) the K_{sp} for ZnS is very low

   (*c*) Zns evaporates   (*d*) none of these

   Answer. (*a*)

24. The 'solubility' of an electrolyte of type AB$_2$ is *s* (ignoring the units), the expressions for solubility product will be

   (*a*) $K_{sp} = s^2$ (*b*) $K_{sp} = 4s^2$

   (*c*) $K_{sp} = 4s^3$ (*d*) $K_{sp} = 4s^4$

   Answer. (*c*)

25. The expression for the solubility product of $Al(OH)_3$ would be (s is its solubility)
    (a) $K_{sp} = s \times 3s^2$
    (b) $K_{sp} = s \times 9s^2$
    (c) $K_{sp} = s \times 9\ s^3$
    (d) $K_{sp} = s \times 4s^2$
    Answer. (c)

26. A solution is unsaturated if its
    (a) ionic product $< K_{sp}$
    (b) ionic product $= K_{sp}$
    (c) ionic product $> K_{sp}$
    (d) none of these
    Answer. (a)

27. For a supersaturated solution, the ionic product is
    (a) greater than the solubility product
    (b) equal to its solubility product
    (c) lesser than its solubility product
    (d) none of these
    Answer. (a)

28. For an electrolyte of 1:2 type, the solubility is given by the expression
    (a) $s = \sqrt{K_{sp}}$
    (b) $s = \sqrt[3]{K_{sp}}$
    (c) $s = \sqrt{\dfrac{K_{sp}}{4}}$
    (d) $s = \sqrt[3]{\dfrac{K_{sp}}{4}}$
    Answer. (d)

29. For $Fe(OH)_3$, the solubility 's' is related to its solubility product K_{sp} by the relation
    (a) $s = \sqrt[3]{\dfrac{K_{sp}}{4}}$
    (b) $s = \sqrt[3]{\dfrac{K_{sp}}{27}}$
    (c) $s = \sqrt[4]{\dfrac{K_{sp}}{27}}$
    (d) $s = \sqrt[4]{\dfrac{K_{sp}}{4}}$
    Answer. (c)

30. The solubility product of $BaSO_4$ in water is 1.5×10^{-9}. Its solubility would be
    (a) 3.87×10^{-5} mol lit^{-1}
    (b) 1.224×10^{-5} mol lit^{-1}
    (c) 3.87×10^{-4} mol lit^{-1}
    (d) 12.24×10^{-5} mol lit^{-1}
    Answer. (a)

31. The solubility of $Mg(OH)_2$ in pure water is 1.65×10^{-4} mol lit^{-1}. Its solubility product would be
    (a) 1.796×10^{-11}
    (b) 17.96×10^{-11}
    (c) 4.49×10^{-12}
    (d) 4.49×10^{-11}
    Answer. (a)

32. When NH_4Cl is added to NH_4OH solution, the dissociation of NH_4OH is suppressed. It is due to
    (a) NH_4Cl is more soluble than NH_4OH
    (b) NH_4Cl is having one ion common to NH_4OH
    (c) the K_{sp} of NH_4Cl is greater than that of NH_4OH
    (d) NH_4Cl is easily oxidised
    Answer. (b)

33. The solubility product of a salt of the type AB_3 is 4×10^{-12}. Its solubility in mol lit^{-1} would be
    (a) 1×10^{-3}
    (b) 1×10^{-4}
    (c) 1×10^{-6}
    (d) 1.587×10^{-4}
    Answer. (b)

34. The solubility of a salt is 's' and the solubility product is $4s^3$. The ratio of cations to anions in the salt is
    (a) 1:1
    (b) 1:2
    (c) 1:3
    (d) 2:3
    Answer. (b)

35. The solubility product of a salt is equal to the square of its solubility. The ratio of cations to anions in the salt is
    (a) 1:2   (b) 1:3
    (c) 2:3   (d) 1:1
    Answer. (d)

36. The addition of HCl will not suppress the ionisation of
    (a) CH_3COOH (b) H_2SO_4
    (c) H_2S (d) C_6H_5COOH
    Answer. (b)

37. Pure NaCl gets precipitated when HCl gas is passed through the saturated solution of NaCl. It is because
    (a) the ionic product of NaCl becomes more than its solubility product
    (b) the ionic product of NaCl becomes lesser than its solubility product
    (c) the ionic product of NaCl becomes equal to its solubility product
    (d) the ionic product of NaCl becomes zero
    Answer. (a)

38. Ostwald's dilution law is applicable to
    (a) all electrolytes   (b) strong electrolytes
    (c) weak electrolyte   (d) non-electrolytes
    Answer. (c)

39. Which pair, out of the following, will show common ion effect?
    (a) $HCl + NHO_3$ (b) $HCl + H_2S$
    (c) $HCl + H_2SO_4$ (d) $HCl + NaCl$
    Answer. (b)

40. Which of the following pairs of electrolytes will not show common ion effect?
    (a) $NH_4Cl + NH_4OH$ (b) $HCl + H_2S$
    (c) $HCl + CH_3COOH$ (d) $NaCl + NH_4Cl$
    Answer. (d)

41. The solubility of an electrolyte of the type AB_3 is 0.25×10^{-4} mol lit^{-1}. Its solubility product will be
    (a) 1.56×10^{-14} (b) 6.25×10^{-14}
    (c) 6.25×10^{-10} (d) 1.56×10^{-12}
    Answer. (b)

42. The solubility of a salt of the type A_3B_2 type in water is s moles lit^{-1}. Its solubility product will be
    (a) $25\ s^2$ (b) $125\ s^3$
    (c) $81\ s^4$ (d) $108\ s^5$
    Answer. (d)

43. The solubility product of a salt AB_2 is 4.0×10^{-9}. Its solubility will be
    (a) 2×10^{-3} mol lit^{-1} (b) 1×10^{-3} mol lit^{-1}
    (c) 1.58×10^{-3} mol lit^{-1} (d) 1.33×10^{-3} mol lit^{-1}
    Answer. (b)

44. For the equilibrium $PbCl_2 \rightleftharpoons Pb^{2+} + 2Cl^-$ the solubility product is
    (a) $K_{sp} = [Pb^{2+}]^2\,[Cl^-]^2$ (b) $K_{sp} = [Pb^{2+}]\,[Cl^-]^2$
    (c) $K_{sp} = [Pb^{2+}]^2\,[Cl^-]$ (d) $K_{sp} = [Pb^{2+}]\,[Cl^-]$
    Answer. (b)

45. If the solubility of $Mg(OH)_3$ is $\sqrt{2}$, its solubility product will be
    (a) 8   (b) $4\sqrt{2}$

(c) $8\sqrt{2}$ (d) $9\sqrt{2}$

Answer. (c)

46. The solubility of Calcium fluoride is 1×10^{-4} mol lit^{-1}. Its solubility product will be

    (a) 2×10^{-8} (b) 4×10^{-8}

    (c) 8×10^{-12} (d) 4×10^{-12}

    Answer. (d)

47. Which pair out of the following will have similar expression for solubility product?

    (a) $AgCl, PbCl_2$ (b) $PbCl_2, Hg_2Cl_2$

    (c) $Mg(OH)_2, CaF_2$ (d) $MgCl_2, AlCl_3$

    Answer. (c)

48. When HCl gas is passed through a saturated solution of NaCl, the solubility of NaCl

    (a) will increase   (b) will remain the same

    (c) will decrease   (d) will become zero

    Answer. (c)

49. The solubility product of a salt A_2B with mol mass 100 is 4.0×10^{-9}. How many grams of it will dissolve in water to make one litre of saturated solution?

    (a) 0.1 g   (b) 0.01 g

    (c) 0.001 g   (d) 0.0001 g

    Answer. (a)

50. The solubility product of salt of bivalent metal with chloride ions is 4×10^{-6}. Its solubility in mol lit^{-1} will be

    (a) 10^{-1} (b) 10^{-2}

    (c) 10^{-3} (d) 10^{-4}

    Answer. (b)

Top