

26

Ionic Equilibria
Solubility Product

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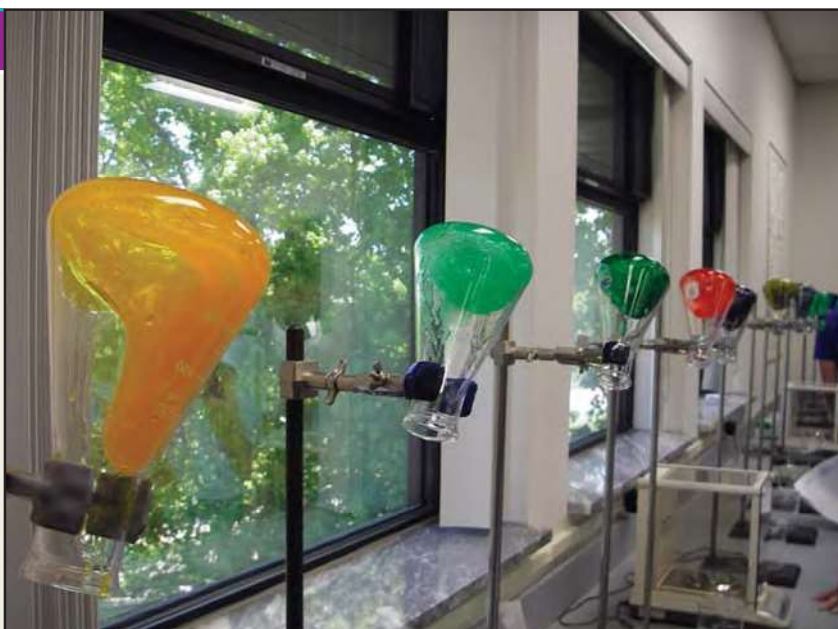
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OSTWALD'S DILUTION LAW

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^- .



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 :

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

$$\text{Rate of combination} = k_2 \times C\alpha \times C\alpha$$

At equilibrium :

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

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

$$\text{or} \quad K_c = \frac{\alpha^2 C}{(1 - \alpha)} \text{ mol litre}^{-1} \quad \dots(1)$$

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

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

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 $1 - \alpha \approx 1$. 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.,**

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

$$\text{or} \quad \alpha = K' \sqrt{V}$$

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,

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

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 $\lambda_\infty = 129.9$

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 $\lambda_v / \lambda_\infty$ 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

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

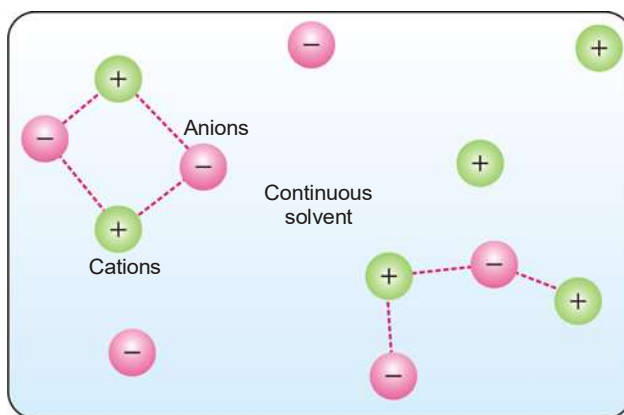
was applicable to univalent strong electrolytes.

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 .

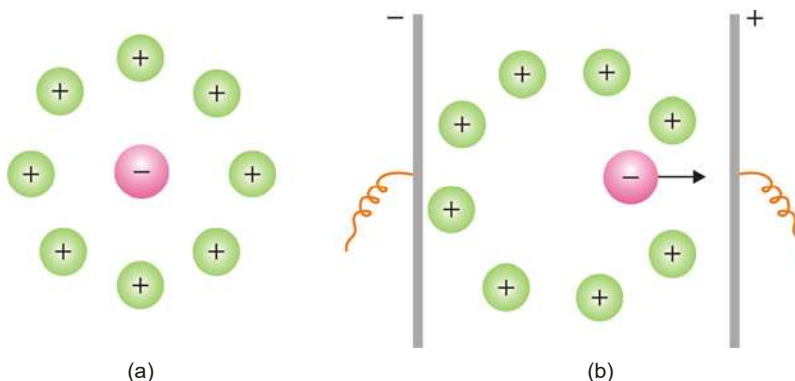
(5) In spite of almost complete ionisation, λ_v is much less than λ_∞ .

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

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

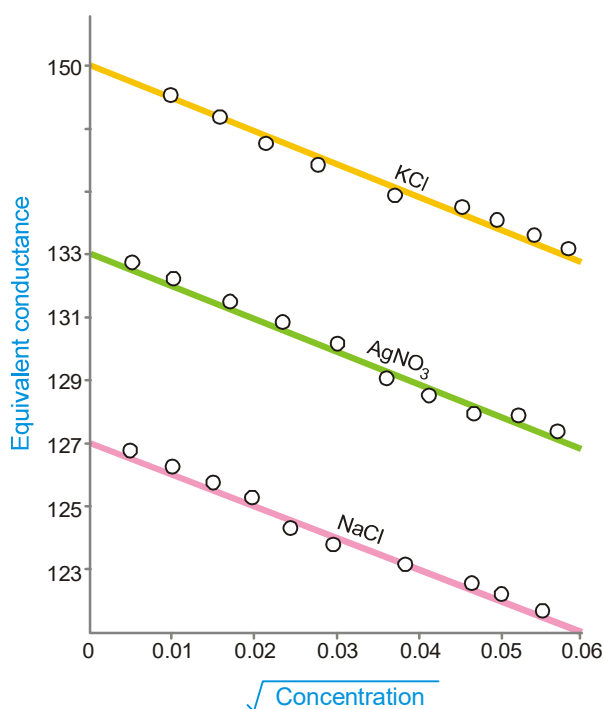
where A and B are constants and c is the concentration in gm-equivalents per litre. These constants depend only on the nature of the solvent and the temperature and are given by the relationships :

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

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 $(60.20 + 0.229\lambda_\infty)$ 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 Onsager equation. The circles represent the observed value of λ_v whereas the dotted line stands for the theoretical values of the slopes expected from the Onsager 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



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.

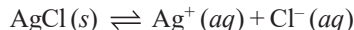


By the addition of the salt (AC), the concentration of A^+ increases. Therefore, according to Le Chatelier's principle, the equilibrium will shift to the left, thereby decreasing the concentration of A^+ ions. Or that, the degree of dissociation of AB will be reduced.

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

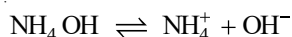
Let us consider a few examples to illustrate the common-ion effect.

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



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 $AgCl$. 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



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 .



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



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 :

$$[\text{HF}] = 1 - x \text{ mol/l}$$

$$[\text{F}^-] = x \text{ mol/l}$$

$$[\text{H}^+] = x \text{ mol/l}$$

Substituting these values in the equilibrium expression, we have

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

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

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

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

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

Thus the degree of dissociation of HF in 1M solution is 2.7×10^{-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 vacuum 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

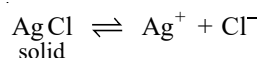
The extent of dissociation of an electrolyte is inversely proportional to the concentration of its solution. The less concentrated the solution, the greater will be the dissociation of the electrolyte. This is obviously due to the fact that in a dilute solution the ratio of solvent molecules to the solute 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 AgCl, we can write the equilibrium equations as follows :



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.

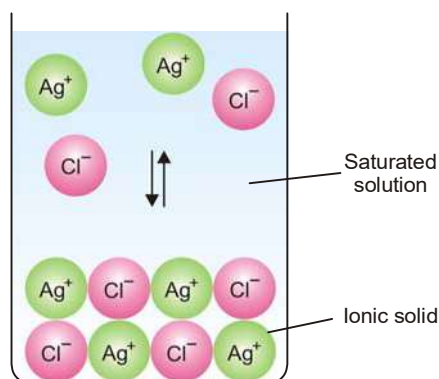


Figure 26.4
Equilibrium between an ionic solid and ions in a saturated solution.

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 AgCl, we have

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

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

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

where $[\text{Ag}^+]$ and $[\text{Cl}^-]$ 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 $[\text{Ag}^+][\text{Cl}^-]$ 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	$\text{Al}(\text{OH})_3$	$[\text{Al}^{3+}][\text{OH}^-]^3 = 1.6 \times 10^{-33}$
Barium fluoride	BaF_2	$[\text{Ba}^{2+}][\text{F}^-]^2 = 1.7 \times 10^{-6}$
Barium carbonate	BaCO_3	$[\text{Ba}^{2+}][\text{CO}_3^{2-}] = 8.1 \times 10^{-9}$
Calcium fluoride	CaF_2	$[\text{Ca}^{2+}][\text{F}^-]^2 = 4.0 \times 10^{-11}$
Copper (I) bromide	CuBr	$[\text{Cu}^+][\text{Br}^-] = 4.2 \times 10^{-8}$
Copper (I) sulphide	Cu_2S	$[\text{Cu}^+]^2[\text{S}^{2-}] = 8.5 \times 10^{-45}$
Iron (III) hydroxide	$\text{Fe}(\text{OH})_3$	$[\text{Fe}^{3+}][\text{OH}^-]^3 = 2.0 \times 10^{-39}$
Lead (II) bromide	PbBr_2	$[\text{Pb}^{2+}][\text{Br}^-]^2 = 7.9 \times 10^{-5}$
Lead (II) iodide	PbI_2	$[\text{Pb}^{2+}][\text{I}^-]^2 = 1.4 \times 10^{-8}$
Silver Chloride	AgCl	$[\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$

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.**

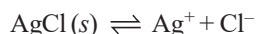
NUMERICAL PROBLEMS

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



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 :

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

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

Substituting the values in the K_{sp} expression,

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

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

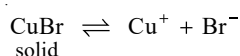
The units for K_{sp} values are usually omitted.

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



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 $\text{Cu}^+ = 2.0 \times 10^{-4} \text{ mol l}^{-1}$

Equilibrium concentration of $\text{Br}^- = 2.0 \times 10^{-4} \text{ mol l}^{-1}$

Substituting these in the expression

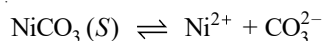
$$\begin{aligned} K_{\text{sp}} &= [\text{Cu}^+][\text{Br}^-] \\ &= [2.0 \times 10^{-4} \text{ mol l}^{-1}][2.0 \times 10^{-4} \text{ mol l}^{-1}] \\ &= 4.0 \times 10^{-8} \text{ mol}^2 \text{ l}^{-2} \end{aligned}$$

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 $\text{NiCO}_3 = 1.4 \times 10^{-7}$.

SOLUTION



$$K_{\text{sp}} = [\text{Ni}^{2+}][\text{CO}_3^{2-}]$$

$$1.4 \times 10^{-7} = [\text{Ni}^{2+}][\text{CO}_3^{2-}]$$

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 $S \text{ mol/l}$ be the solubility of NiCO_3 , the equilibrium concentration of Ni^{2+} is $S \text{ mol/l}$ and that of CO_3^{2-} also it is $S \text{ mol/l}$.

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

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

or

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

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

This means that the solubility of NiCO_3 is $3.7 \times 10^{-4} \text{ mol/l}$. Therefore, the solubility in g/l is $= 3.7 \times 10^{-4} \times 118.7 = 0.044 \text{ g/l}$ 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 $1.0 \times 10^{-15} \text{ mol/L}$ at 25°C .

SOLUTION

Here, the equilibrium reaction is



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 $2(1.0 \times 10^{-15} \text{ mole})$ of Bi^{3+} and $3(1.0 \times 10^{-15} \text{ mole})$ of S^{2-} . We can write the equilibrium concentrations of Bi^{3+} and S^{2-} as :

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

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

Substituting these values in the K_{sp} expression