

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

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

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

7.13 SOLUBILITY EQUILIBRIA OF SPARINGLY SOLUBLE SALTS

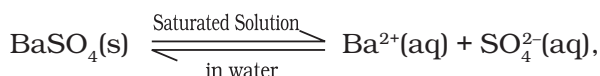
We have already known that the solubility of ionic solids in water varies a great deal. Some of these (like calcium chloride) are so soluble that they are hygroscopic in nature and even absorb water vapour from atmosphere. Others (such as lithium fluoride) have so little solubility that they are commonly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

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

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

7.13.1 Solubility Product Constant

Let us now have a solid like barium sulphate in contact with its saturated aqueous solution. The equilibrium between the 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

$$K_{\text{sp}} = K[\text{BaSO}_4] = [\text{Ba}^{2+}][\text{SO}_4^{2-}] \quad (7.43)$$

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

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

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

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

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

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

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

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:

$$K_{sp} = [M^{p+}]^x [X^{q-}]^y = (xS)^x (yS)^y \quad (7.44)$$

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

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

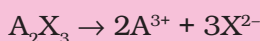
$$S = (K_{sp} / x^x \cdot y^y)^{1/(x+y)} \quad (7.45)$$

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 7.9.

Problem 7.26

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

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

$$\text{therefore, } K_{sp} = (2S)^2(3S)^3 = 108S^5$$

$$= 1.1 \times 10^{-23}$$

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

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

Problem 7.27

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

Solution

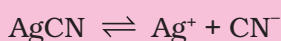
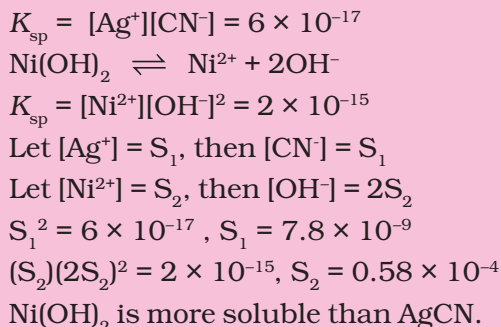


Table 7.9 The Solubility Product Constants, K_{sp} of Some Common Ionic Salts at 298K.

| Name of the Salt | Formula | K_{sp} |
|---------------------|-------------|-----------------------|
| Silver Bromide | AgBr | 5.0×10^{-13} |
| Silver Carbonate | Ag_2CO_3 | 8.1×10^{-12} |
| Silver Chromate | Ag_2CrO_4 | 1.1×10^{-12} |
| Silver Chloride | AgCl | 1.8×10^{-10} |
| Silver Iodide | AgI | 8.3×10^{-17} |
| Silver Sulphate | Ag_2SO_4 | 1.4×10^{-5} |
| Aluminium Hydroxide | $Al(OH)_3$ | 1.3×10^{-33} |
| Barium Chromate | $BaCrO_4$ | 1.2×10^{-10} |
| Barium Fluoride | BaF_2 | 1.0×10^{-6} |
| Barium Sulphate | $BaSO_4$ | 1.1×10^{-10} |
| Calcium Carbonate | $CaCO_3$ | 2.8×10^{-9} |
| Calcium Fluoride | CaF_2 | 5.3×10^{-9} |
| Calcium Hydroxide | $Ca(OH)_2$ | 5.5×10^{-6} |
| Calcium Oxalate | CaC_2O_4 | 4.0×10^{-9} |
| Calcium Sulphate | $CaSO_4$ | 9.1×10^{-6} |
| Cadmium Hydroxide | $Cd(OH)_2$ | 2.5×10^{-14} |
| Cadmium Sulphide | CdS | 8.0×10^{-27} |
| Chromic Hydroxide | $Cr(OH)_3$ | 6.3×10^{-31} |
| Cuprous Bromide | CuBr | 5.3×10^{-9} |
| Cupric Carbonate | $CuCO_3$ | 1.4×10^{-10} |
| Cuprous Chloride | CuCl | 1.7×10^{-6} |
| Cupric Hydroxide | $Cu(OH)_2$ | 2.2×10^{-20} |
| Cuprous Iodide | CuI | 1.1×10^{-12} |
| Cupric Sulphide | CuS | 6.3×10^{-36} |
| Ferrous Carbonate | $FeCO_3$ | 3.2×10^{-11} |
| Ferrous Hydroxide | $Fe(OH)_2$ | 8.0×10^{-16} |
| Ferric Hydroxide | $Fe(OH)_3$ | 1.0×10^{-38} |
| Ferrous Sulphide | FeS | 6.3×10^{-18} |
| Mercurous Bromide | Hg_2Br_2 | 5.6×10^{-23} |
| Mercurous Chloride | Hg_2Cl_2 | 1.3×10^{-18} |
| Mercurous Iodide | Hg_2I_2 | 4.5×10^{-29} |
| Mercurous Sulphate | Hg_2SO_4 | 7.4×10^{-7} |
| Mercuric Sulphide | HgS | 4.0×10^{-53} |
| Magnesium Carbonate | $MgCO_3$ | 3.5×10^{-8} |
| Magnesium Fluoride | MgF_2 | 6.5×10^{-9} |
| Magnesium Hydroxide | $Mg(OH)_2$ | 1.8×10^{-11} |
| Magnesium Oxalate | MgC_2O_4 | 7.0×10^{-7} |
| Manganese Carbonate | $MnCO_3$ | 1.8×10^{-11} |
| Manganese Sulphide | MnS | 2.5×10^{-13} |
| Nickel Hydroxide | $Ni(OH)_2$ | 2.0×10^{-15} |
| Nickel Sulphide | NiS | 4.7×10^{-5} |
| Lead Bromide | $PbBr_2$ | 4.0×10^{-5} |
| Lead Carbonate | $PbCO_3$ | 7.4×10^{-14} |
| Lead Chloride | $PbCl_2$ | 1.6×10^{-5} |
| Lead Fluoride | PbF_2 | 7.7×10^{-8} |
| Lead Hydroxide | $Pb(OH)_2$ | 1.2×10^{-15} |
| Lead Iodide | PbI_2 | 7.1×10^{-9} |
| Lead Sulphate | $PbSO_4$ | 1.6×10^{-8} |
| Lead Sulphide | PbS | 8.0×10^{-28} |
| Stannous Hydroxide | $Sn(OH)_2$ | 1.4×10^{-28} |
| Stannous Sulphide | SnS | 1.0×10^{-25} |
| Strontium Carbonate | $SrCO_3$ | 1.1×10^{-10} |
| Strontium Fluoride | SrF_2 | 2.5×10^{-9} |
| Strontium Sulphate | $SrSO_4$ | 3.2×10^{-7} |
| Thallos Bromide | TlBr | 3.4×10^{-6} |
| Thallos Chloride | TlCl | 1.7×10^{-4} |
| Thallos Iodide | TlI | 6.5×10^{-8} |
| Zinc Carbonate | $ZnCO_3$ | 1.4×10^{-11} |
| Zinc Hydroxide | $Zn(OH)_2$ | 1.0×10^{-15} |
| Zinc Sulphide | ZnS | 1.6×10^{-24} |



7.13.2 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 silver ion as silver chloride, ferric ion as its hydroxide (or hydrated ferric oxide) and barium ion as its sulphate for quantitative estimations.

Problem 7.28

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 .

$$K_{sp} = 2.0 \times 10^{-15} = [\text{Ni}^{2+}][\text{OH}^-]^2$$

$$= (S)(0.10 + 2S)^2$$

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

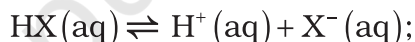
Hence,

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

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

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.,

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



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

$$[\text{X}^-] / [\text{HX}] = K_a / [\text{H}^+]$$

Taking inverse of both side and adding 1 we get

$$\frac{[\text{HX}]}{[\text{X}^-]} + 1 = \frac{[\text{H}^+]}{K_a} + 1$$

$$\frac{[\text{HX}] + [\text{H}^+]}{[\text{X}^-]} = \frac{[\text{H}^+] + K_a}{K_a}$$

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

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

$$S = \{K_{sp} ([\text{H}^+] + K_a) / K_a\}^{1/2} \quad (7.46)$$

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