1.3: Varying solubility of ionic compounds

Le Chatelier's principle

When ionic compounds dissolve in water, they dissociate into ions. An equilibrium is established between the ions in water and the undissolved compound. Changes in the concentration of the ions can stress the equilibrium and vary the solubility of the ionic compounds.

Le Chatelier's principle

Le Chatelier's principle states, "When a system at equilibrium is subjected to a change in concentration, temperature, volume, or pressure, the system will change to a new equilibrium, such that the applied change is partially counteracted."

If the ions in the solubility equilibrium are increased or decreased by another reaction going on in parallel, the equilibrium will counteract by decreasing or increasing the compound's solubility. The following explains how to use Le Chatelier's principle to vary the solubility of sparingly soluble ionic compounds with examples.

Common ion effect

Consider dissolution of a sparingly soluble ionic compound $\mathrm{CaF_2}$ in water:

$$\mathrm{CaF_2(s)} \rightleftharpoons \mathrm{Ca^{2+}(aq)} + 2\,\mathrm{F^-(aq)}, \quad K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{F^-}]^2 = 1.5 \times 10^{-10}$$

The solubility (S) can be expressed in the units of mol/L or molarity (M). Similarly, the concentration of any species in square brackets, as $[\mathrm{Ca^{2+}}]$ in the above-mentioned $\mathrm{K_{sp}}$ expression, is also in the units of mol/L or M.

NaF is a water-soluble ionic compound that has $\mathrm{F^-}$ in common with the above equilibrium. The addition of NaF into the mixture will increase the concentration of $\mathrm{F^-}$, causing a decrease in the solubility of $\mathrm{CaF_2}$ because the solubility equilibrium will move in the reverse direction to counteract the rise in the concentration of the common ion. This is called the **common ion effect**.

> The common ion effect refers to the decrease in the solubility of a sparingly soluble ionic compound by adding a soluble ionic compound with an ion in common with the sparingly soluble one.

A quantitative estimate of this common ion effect is given with the help of the following calculations. If solubility of $\mathrm{CaF_2}$ in pure water is S mol/L, then $[\mathrm{Ca^{2+}}]$ = S, and $[\mathrm{F^-}]$ = 2S. Plugging in these values in the $\mathrm{K_{sp}}$ expression and rearranging shows that the solubility of $\mathrm{CaF_2}$ in pure water is 3.3 x 10^{-4} M:

$$K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{F^-}]^2$$

$$1.5 \times 10^{-10} = S(2S)^2$$

$$S = \sqrt[3]{1.5 \times 10^{-10}/4} = 3.310^{-4}\ \mathrm{M}$$

If $\mathrm{F^-}$ concentration is raised to 0.1M by dissolving NaF in the solution, then the molar solubility of $\mathrm{CaF_2}$ changes to a new value $\mathrm{S_i}$, $[\mathrm{Ca^{2+}}] = \mathrm{S_i}$, and $[\mathrm{F^-}] = (0.1 + \mathrm{S_i}) = 0.1$ ($\mathrm{S_i}$ cancels because it is negligible compared to 0.1). Plugging in these values in the $\mathrm{K_{sp}}$ expression and rearranging shows that the new solubility ($\mathrm{S_i}$) of $\mathrm{CaF_2}$ is 1.5 x 10^{-8}M:

$$K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{F^-}]^2$$

$$1.5 \times 10^{-10} = S_i(0.1)^2$$

$$S_i = \frac{1.5 \times 10^{-10}}{(0.1)^2} = 1.5 \times 10^{-8}\ \mathrm{M}$$

It means the common ion effect described above decreases the solubility of $\mathrm{CaF_2}$ by more than twenty thousand times.

> Generally, the solubility of sparingly soluble ionic compounds decreases when a common ion is added to the equilibrium mixture.

An example of a common ion effect is in the separation of $PbCl_2$ from $AgCl$ and Hg_2Cl_2 precipitates. $PbCl$ is the most soluble in hot water among these three sparingly soluble compounds. So, $PbCl_2$ is selectively dissolved in hot water and separated. The solution is then cooled to room temperate and HCl is added to it as a source of common ion Cl^- to enforce re-precipitation of $PbCl_2$:

$$Pb^{2+}(aq) + 2\,Cl^-(aq) \rightleftharpoons PbCl_2(s)$$

Effect of pH

The pH is related to the concentration of H_3O^+ and OH^- in the solution. Increasing pH increases OH^- and decreases H_3O^+ concentration in the solution, and decreasing pH has the opposite effect. If one of the ions in the solubility equilibrium of a sparingly soluble ionic compound is an acid or a base, its concentration will change with changes in the pH. It is because acids will neutralize with OH^- at high pH, and bases will neutralize with H_3O^+ at low pH. For example, consider the dissolution of $Mg(OH)_2$ in pure water.

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq), \quad K_{sp} = [Mg^{2+}][OH^-]^2 = 2.1 \times 10^{-13}$$

Making the solution acidic, i.e., a decrease in pH adds more H_3O^+ ion that removes OH^- by the following neutralization reaction.

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2\,H_2O(l)$$

According to Le Chatelier's principle, the system moves forward to compensate for the loss of OH^-. In other words, $Mg(OH)_2$ is insoluble in neutral or alkaline water and becomes soluble in acidic water.

> Generally, the solubility of an ionic compound containing basic anion increases by decreasing pH, i.e., in an acidic medium.

In a qualitative analysis of cations, dissociation of H_2S is used as a source of S^{2-} ions:

$$H_2S(g) + 2\,H_2O(l) \rightleftharpoons 2\,H_3O^+(aq) + S^{2-}(aq)$$

The reaction is pH-dependent, i.e., the extent of dissociation of H_2S can be decreased by adding HCl as a source of common ion H_3O^+ or increased by adding a base as a source of OH^- that removes H_3O^+ from the products:

$$OH^-(aq) + H_3O^+(aq) \rightleftharpoons 2\,H_2O(l)$$

> Generally, the solubility of weak acids can be increased by increasing the pH and decreased by decreasing the pH. The opposite is true for the weak bases.

Complex ion equilibria

Transition metal ions, like Ag^+, Cu^{2+}, Ni^{2+}, etc. tend to be strong Lewis acids, i.e., they can accept a lone pair of electrons from Lewis bases. Neutral or anionic species with a lone pair of electrons, like $H_2\ddot{O}:$, $:NH_3$, $:\bar{C}N:$, $:\ddot{\underset{..}{C}}l:^-$, etc. can act as Lewis bases in these reactions. The bond formed by donating a lone pair of electrons of a Lewis base to a Lewis acid is called a **coordinate covalent bond**. The neutral compound or ion that results from the Lewis acid-base reaction is called a **coordination complex** or a **complex ion**. For example, silver ion dissolved in water is often written as $Ag^+_{(aq)}$, but, in reality, it exists as complex ion $Ag(H_2O)_2^+$ in which Ag^+ accepts lone pair of electrons from oxygen atoms in water molecules. Transition metal ion in a coordination complex or complex ion, e.g., Ag^+ in $Ag(H_2O)_2^+$ is called **central metal ion** and the Lewis base like $H_2\ddot{O}:$, in $Ag(H_2O)_2^+$, is called a **ligand**. A ligand's strength is its ability to donate its lone pair of electrons to a central metal ion. If a stronger ligand is added to the solution, it displaces a weaker ligand. For example, if $:NH_3$ is dissolved in the solution containing $Ag(H_2O)_2^+$, the $:NH_3$ displaces $H_2\ddot{O}:$ from the complex ion:

$$Ag(H_2O)_2^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + 2\,H_2O(aq)$$

The lone pair on the ligand is omitted from the equation above and the following equations. Water is usually omitted from the equation for simplicity, that reduces the above reaction to the following:

$$Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) \quad K_f = 1.7 \times 10^7$$

The equilibrium constant for the formation of complex ion is called **formation constant** (K_f), e.g., in the case of the above reaction:

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+] \times [NH_3]^2} = 1.7 \times 10^7$$

A large value of K_f in the above reaction shows that the reaction is highly favored in the forward direction. If ammonia is present in water, it increases the solubility of $AgCl$ by removing the Ag^+ ion from the products, just like acid (H_3O^+) increases the solubility of $Mg(OH)_2$ by removing OH^- from the products:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \quad K_f = 1.8 \times 10^{-10}$$

$$Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) \quad K_f = 1.7 \times 10^7$$

$$\text{Adding above reactions: } AgCl(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq) \quad K = 3.0 \times 10^{-3}$$

The equilibrium constant for the dissolution of $AgCl(s)$ changes from 1.8 x 10^{-10} in pure water to 3.0 x 10^{-3} in the water containing dissolved ammonia, i.e., a 17 million times increase. It makes insoluble $AgCl(s)$ quite soluble. This reaction is used to separate silver ions from mercury ions in a mixture of $AgCl$ and Hg_2Cl_2 mixture precipitates.

Generally, adding a strong ligand to the solution increases the solubility of metal compounds containing metals capable of coordinate complex formation.

Manipulating chemical equations

The chemical equations can be manipulated like algebraic equations, i.e., multiplied or divided by a constant, added, and subtracted, as demonstrated in the example of the silver ammonia complex formation reactions above. Note that the species on the right side of the equation cancels the same species on the left side of any other equation like algebraic equations, e.g., Ag^+ is canceled in the final equation.

When two equilibrium reactions are added, their equilibrium constants are multiplied to get the equilibrium constant of the overall reaction, i.e., $K = K_{sp} \times K_f$ in the above reactions.

Redox reactions

There are three major types of chemical reactions: precipitation reactions, acid-base reactions, and redox reactions.

Precipitation reactions

Precipitation reactions of ionic compounds are double replacement reactions where the cation of one compound combines with the anion of another and vice versa, such that one of the new combinations is an insoluble salt.

For example, when silver nitrate ($AgNO_3$) solution is mixed with sodium chloride ($NaCl$) solution, an insoluble compound silver chloride ($AgCl$) precipitates out of the solution:

$$AgNO_3(aq) + HCl(aq) \longrightarrow AgCl(s)\downarrow + NaNO_3(aq)$$

Acid-base reactions

Acid-base reactions are the reactions involving the transfer of a proton.

For example, H_2S dissociates in water by donating its proton to water molecules:

$$H_2S(g) + 2\,H_2O(l) \rightleftharpoons 2\,H_3O^+(aq) + S^{2-}(aq)$$

Redox reactions

Redox reactions are reactions involving the transfer of electrons.

For example, when sodium metal (Na) reacts with chlorine gas (Cl_2), sodium loses electrons and becomes Na^+ cation and chlorine gains electrons and becomes Cl^- anion that combine to form $NaCl$ salt:

$$2\,Na(s) + 2\,Cl_2(g) \longrightarrow NaCl(s)$$

An example of a redox reaction in qualitative analysis of cations is the dissolution of NiS precipitate by adding an oxidizing acid HNO_3. The S^{2-} is a weak base that can be removed from the product by adding a strong acid like HCl:

$$S^{2-}(aq) + 2\,H_3O^+(aq) \rightleftharpoons H_2S(aq) + 2\,H_2O(l)$$

Therefore, addition of HCl is sufficient to dissolve FS precipitate by removal of S^{2-} from the products:

$$FeS(s) + 2\,H_3O^+(aq) \rightleftharpoons Fe^{2+}(aq) + H_2S(aq) + 2\,H_2O(l)$$

However, the addition of HCl does not remove S^{2-} sufficient enough to dissolve a relatively less soluble NiS precipitate. Nitric acid (HNO_3) that is a source of an oxidizing agent NO_3^- is needed to remove S^{2-} to a higher extent for dissolving NiS:

$$3\,S^{2-}(aq) + 2\,NO_3^-(aq) + 8\,H_3O^+(aq) \longrightarrow 3\,S(s, yellow)\downarrow + 2\,NO(g)\uparrow + 12\,H_2O(l)$$

In this reaction, sulfur is oxidized from an oxidation state of -2 in S^{2-} to an oxidation state of zero in S, and nitrogen is reduced from an oxidation state of +5 in NO_3^- to an oxidation state of +2 in NO.

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