The Role of the Ion Product (Q_{sp}) In Solubility Calculations

Consider a saturated solution of AgCl in water.

$$\mathrm{AgCl}(s) \xrightleftharpoons{\mathrm{H_2O}} \mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq)$$

Because AgCl is a 1:1 salt, the concentrations of the Ag^+ and Cl^- ions in this solution are equal.

Saturated solution of AgCl in water:

$$[\mathrm{Ag}^+] = [\mathrm{Cl}^-]$$

Imagine what happens when a few crystals of solid $AgNO_3$ are added to this saturated solution of AgCl in water. According to the solubility rules, silver nitrate is a soluble salt. It therefore dissolves and dissociates into Ag^+ and NO_3^- ions. As a result, there are two sources of the Ag^+ ion in this solution.

$$\mathrm{AgNO_3}(s) \rightarrow \mathrm{Ag}^+(aq) + \mathrm{NO_3}^-(aq)$$

$$\mathrm{AgCl}(s) \xrightleftharpoons{\mathrm{H_2O}} \mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq)$$

Adding $AgNO_3$ to a saturated AgCl solution therefore increases the Ag^+ ion concentrations. When this happens, the solution is no longer at equilibrium because the product of the concentrations of the Ag^+ and Cl^- ions is too large. In more formal terms, we can argue that the **ion product (Q_{sp})** for the solution is larger than the solubility product (K_{sp}) for AgCl.

$$Q_{sp} = (\mathrm{Ag}^+)(\mathrm{Cl}^-) > K_{sp}$$

The ion product is literally the product of the concentrations of the ions at any moment in time. When it is equal to the solubility product for the salt, the system is at equilibrium.

The reaction eventually comes back to equilibrium after the excess ions precipitate from solution as solid AgCl. When equilibrium is reestablished, however, the concentrations of the Ag^+ and Cl^- ions won't be the same. Because there are two sources of the Ag^+ ion in this solution, there will be more Ag^+ ion at equilibrium than Cl^- ions:

Saturated solution of AgCl to which $AgNO_3$ has been added:

$$[\mathrm{Ag}^+] > [\mathrm{Cl}^-]$$

Now imagine what happens when a few crystals of NaCl are added to a saturated solution of AgCl in water. There are two sources of the chloride ion in this solution.

$$\mathrm{NaCl}(s) \xrightarrow{\mathrm{H_2O}} \mathrm{Na}^+(aq) + \mathrm{Cl}^-(aq)$$

$$\mathrm{AgCl}(s) \xrightleftharpoons{\mathrm{H_2O}} \mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq)$$

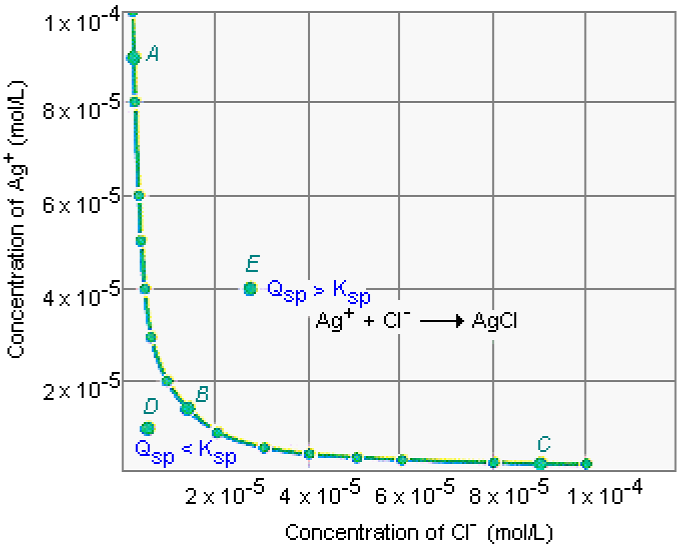
Once again, the ion product is larger than the solubility product $Q_{sp} = (\mathrm{Ag}^+)(\mathrm{Cl}^-) > K_{sp}$

This time, when the reaction comes back to equilibrium, there will be more Cl- ion in the solution than Ag^+ ion.

Saturated solution of AgCl to which NaCl has been added:

$$[\mathrm{Ag}^+] < [\mathrm{Cl}^-]$$

The figure below shows a small portion of the possible combinations of the Ag^+ and Cl^- ion concentrations in an aqueous solution. Any point along the curved line in this graph corresponds to a system at equilibrium, because the product of the Ag^+ and Cl^- ion concentrations for these solutions is equal to K_{sp} for AgCl.



Point *A* represents a solution at equilibrium that could be produced by dissolving two sources of the Ag^+ ion — such as $\mathrm{AgNO_3}$ and AgCl — in water. Point *B* represents a saturated solution of AgCl in pure water, in which the $[\mathrm{Ag}^+]$ and $[\mathrm{Cl}^-]$ terms are equal. Point *C* describes a solution at equilibrium that was prepared by dissolving two sources of the Cl^- ion in water, such as NaCl and AgCl.

Any point that is not along the solid line in the above figure represents a solution that is not at equilibrium. Any point *below* the solid line (such as Point *D*) represents a solution for which the ion product is smaller than the solubility product.

$$\text{Point } D\text{:} \quad Q_{sp} < K_{sp}$$

If more AgCl were added to the solution at Point *D*, it would dissolve.

$$\text{If } Q_{sp} < K_{sp}\text{:} \quad \mathrm{AgCl}(s) \longrightarrow \mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq)$$

Points *above* the solid line (such as Point *E*) represent solutions for which the ion product is larger than the solubility product.

$$\text{Point } E\text{:} \qquad Q_{sp} > K_{sp}$$

The solution described by Point *E* will eventually come to equilibrium after enough solid AgCl has precipitated.

$$\text{If } Q_{sp} > K_{sp}\text{:} \qquad \mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq) \longrightarrow \mathrm{AgCl}(s)$$