# Precipitation Equilibria

- Solubility Product Constant ($K_{sp}$) - equilibrium constant indicating how soluble the solid is in water
  - ex: dissolution of $MX_2(s)$ in solution

    $$MX_2(s) \rightleftharpoons M^{2+}(aq) + 2X^-(aq)$$

    $$K_{sp} = [M^{2+}][X^-]^2$$

  - ★K is constant for a given temp, independent of ion concentrations, constant for equation as written
- ex. Write the $K_{sp}$ expression for aluminum oxide

  $$Al_2O_3(s) \rightleftharpoons 2Al^{+3}(aq) + 3O^{2-}(aq)$$

  $$K_{sp} = [Al^{3+}]^2[O^{2-}]^3$$

- ex. Write the $K_{sp}$ expression for nickel (II) chloride

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

- ex. Write the $K_{sp}$ expression for potassium permanganate

  $$K_{sp} = [K^+][MnO_4^-]$$

Using Ksp:

- ex. A solution in equilibrium with barium phosphate solid has a barium ion concentration of $5 \times 10^{-4}$ M. Ksp of $Ba_3(PO_4)_2$ is $6 \times 10^{-39}$. Calculate phosphate ion concentration

$$Ba_3(PO_4)_2(s) \rightleftharpoons 3Ba^{2+}(aq) + 2PO_4^{3-}(aq)$$

$$K_{sp} = [Ba^{2+}]^3[PO_4^{3-}]^2$$

$$6 \times 10^{-39} = (5 \times 10^{-4})^3 [PO_4^{3-}]^2$$

$$[PO_4^{3-}] = 7 \times 10^{-15} M$$

- Sulfuric acid is added to a lead nitrate solution. When equilibrium is established $[SO_4^{2-}] = 2.0 \times 10^{-4}$. What is the equilibrium concentration of lead ion?

$$H_2SO_4 + Pb(NO_3)_2 \rightarrow 2HNO_3 + PbSO_4(s)$$

$$K_{sp} = 1.8 \times 10^{-8}$$

$$PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$$

$$K_{sp} = [Pb^{2+}][SO_4^{2-}]$$

$$1.8 \times 10^{-8} = [Pb^{2+}][2.0 \times 10^{-4}]$$

$$[Pb^{2+}] = 9.0 \times 10^{-5}$$

# Ksp and Solubility

- Solubility expressed in mol/L or M.

ex. The measured solubility of $MgF_2$ at 25°C is $2.6 \times 10^{-4}$ mol/L. Calculate Ksp

$$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2F^-(aq)$$

$2.6 \times 10^{-4}$ mol    $2.6 \times 10^{-4}$ mol    $2(2.6 \times 10^{-4} mol) = 5.2 \times 10^{-4}$

$$K_{sp} = [Mg^{2+}][F^-]^2$$
$$= (2.6 \times 10^{-4})(5.2 \times 10^{-4})^2 = 7.0 \times 10^{-11}$$

ex. $BaC_2O_4$ has a solubility of 22mg/L. What is the Ksp for $BaC_2O_4$?

$$BaC_2O_4 \rightleftharpoons Ba^{+2} + C_2O_4^{-2}$$

$$22mg \times \frac{1g}{1000mg} \times \frac{1mol}{225g} = \frac{9.78 \times 10^{-5} mol}{L} BaC_2O_4$$

$$K_{sp} = (9.78 \times 10^{-5})^2 = 9.56 \times 10^{-9}$$

Using Ksp to know whether ppt. forms:

ex. A solution of 0.020M fluoride ions is added to a solution in which the original concentration of barium ions is $1.0 \times 10^{-4}$ M. Will a ppt. form?

Ksp of $BaF_2 = 1.8 \times 10^{-7}$

$BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2F^-(aq)$

$Q = [Ba^{2+}][F^-]^2$

$Q = (1.0 \times 10^{-4})(2.0 \times 10^{-2})$

$Q = 4.0 \times 10^{-8}$

$Q < K_{sp}$ and a ppt. will not form.

see above ex. What concentration of $F^-$ is needed to get a saturated soln?

At saturation $Q = Ksp$.

$Ksp = [Ba^{2+}][F^-]^2$

$1.8 \times 10^{-7} = (1.0 \times 10^{-4})[F^-]^2$

$[F^-] = 4.2 \times 10^{-2}$ M

∴ When $[F^-]$ is greater than $4.2 \times 10^{-2}$ M, there will be a ppt. $(Q > Ksp)$

ex. A soln. originally contains 0.003M $Mg^{2+}$. What concentration of $OH^-$ ions should be added to give an unsaturated, saturated, and supersaturated solution?

$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$ $Ksp = 6 \times 10^{-12}$

$Ksp = [Mg^{2+}][OH^-]^2$

$6 \times 10^{-12} = [.003][OH^-]^2$

$[OH^-] = 4.4 \times 10^{-5}$ saturated

$> 4.4 \times 10^{-5}$ supersaturated

$< 4.4 \times 10^{-5}$ unsaturated

# Using Ksp: Mixing Solutions

ex. Will a ppt. form when 200.0 mL of 0.100M $Al(NO_3)_3$ is mixed with 300.0 mL $Ba(OH)_2$?

Determine the ppt. using solubility rules:

$$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq)$$

$$K_{sp} = 2\times10^{-31}$$

Is there enough $Al^{3+}$ and $OH^-$ ions in solution for $Q > K_{sp}$?

For $Al^{3+}$: $0.200L \times \frac{.100 mol\ Al(NO_3)_3}{1L} \times \frac{1 mol\ Al^{3+}}{1 mol\ Al(NO_3)_3} =$

$$.0200 mol\ Al^{3+} \times \frac{1}{.200L + .300L} = .0400M\ Al^{3+}$$

For $OH^-$: $0.300L \times \frac{.200 mol\ Ba(OH)_2}{1L} \times \frac{2 mol\ OH^-}{1 mol\ Ba(OH)_2} =$

$$.120 mol\ OH^- \times \frac{1}{.200L + .300L} = 0.240M\ OH^-$$

$$Q = [Al^{3+}][OH^-]^3$$

$$Q = [.0400][.240]^3 = 5.53\times10^{-4}$$

$Q > K$, ∴ a ppt. will form

ex. Will a ppt. form if 250.0mL of 0.400M ammonium phosphate are mixed with 450.0mL of 0.125M calcium chloride?

$$2(NH_4)_3PO_4(aq) + 3CaCl_2(aq) \rightleftharpoons \underset{\text{ppt}}{\boxed{Ca_3(PO_4)_2(s)}} + 6NH_4Cl(aq)$$

For $PO_4^{3-}$

$$0.25L \times \frac{.4\text{ mol }(NH_4)_3PO_4}{1L} \times \frac{1\text{ mol }PO_4^{3-}}{1\text{ mol }(NH_4)_3PO_4} = \frac{.1\text{ mol }PO_4^{3-}}{.7L} = .143M = [PO_4^{3-}]$$

For $Ca^{2+}$

$$0.45L \times \frac{0.125\text{ mol }CaCl_2}{1L\ CaCl_2} \times \frac{2\text{ mol }Ca^{2+}}{1\text{ mol }CaCl_2} = \frac{0.05625\text{ mol }Ca^{2+}}{.7L} = 0.08M = [Ca^{2+}]$$

$$Ca_3(PO_4)_2 \rightarrow 3Ca^{2+} + 2PO_4^{3-}$$

$$Q = [Ca^{2+}]^3[PO_4^{3-}]^2 = 1.047 \times 10^{-5}$$

$Q > K$ ∴ precipitate forms

Predicting which precipitate forms:

ex.

A soln. contains 0.02M of $Mg^{2+}$ and 0.02M of $Sr^{2+}$. Sufficient carbonate is added so that the carbonate ion concentration is $2 \times 10^{-7}$M. Does a ppt. form and if so what is?

For: $MgCO_3$ $K_{sp} = 6.8 \times 10^{-6}$

$Q = [Mg^{2+}][CO_3^{2-}]$

$= (.02)(2 \times 10^{-7}) = 4 \times 10^{-9}$

$Q < K$, ∴ no ppt. forms

For: $SrCO_3$ $K_{sp} = 5.6 \times 10^{-10}$

$Q = [Sr^{2+}][CO_3^{2-}]$

$= (0.02)(2 \times 10^{-7}) = 4 \times 10^{-9}$

$Q > K$, ∴ $SrCO_3$ precipitates

ex. A soln. contains 0.0040M $Ba^{2+}$ and 0.0060M $Pb^{2+}$. What concentration ~~add past~~ of $F^-$ will precipitate just one of the ions?

$BaF_2 \rightleftharpoons Ba^{2+} + 2F^-$

$K_{sp} = 1.8 \times 10^{-7}$

$1.8 \times 10^{-7} = [.004][F^-]^2$

$[F^-] = 6.7 \times 10^{-3}$

.0067M

$PbF_2 \rightleftharpoons Pb^{2+} + 2F^-$

$K_{sp} = 1.5 \times 10^{-7}$

$1.5 \times 10^{-7} = [.006][F^-]^2$

$[F^-] = .005$

only $BaF_2$ will ppt.

∴ $Pb^{2+}$ precipitates selectively when $[F^-]$ is below $6.7 \times 10^{-3}$M