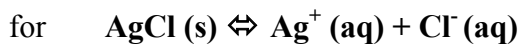


Solubility Equilibrium

Solubility Product

If an “insoluble” or slightly soluble material placed in water then there is Equilibrium between solid and ions in solution



$$K = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]} \quad \text{but there is no conc for pure solid } [\text{AgCl}]$$

so just write

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

K_{sp} is solubility product

K_{sp} is function of temperature table of values at 25°C

Concentration is in mol/L

$$K_{sp} (\text{AgCl}) = 1.7 \times 10^{-10}$$

$$K_{sp} (\text{PbCl}_2) = 1.6 \times 10^{-5}$$

More soluble then more ions in solution and K_{sp} is larger value

Example - Bismuthium Sulfide



$$\text{Write } K_{sp} = [\text{Bi}^{3+}]^2 [\text{S}^{2-}]^3$$

Must account for all ions present but not solid

K_{sp} Problems

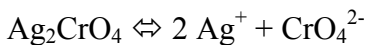
1. Know concentrations find K_{sp}
2. Know K_{sp} find concentrations

Example (1) :

For Silver Chromate

Maximum 7.8×10^{-5} mol Ag_2CrO_4 dissolves in 1 L of water

Find $K_{sp} = ?$



$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

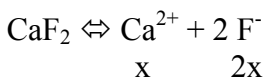
$$K_{sp} = (7.8 \times 10^{-5})^2 (7.8 \times 10^{-5})$$

$$K_{sp} = 1.9 \times 10^{-12}$$

Example (2):

For CaF_2 given that $K_{sp} = 3.9 \times 10^{-11}$

find concentrations in saturated solution $[\text{Ca}^{2+}] = ?$ $[\text{F}^-] = ?$



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

$$3.9 \times 10^{-11} = [x] [2x]^2$$

$$3.9 \times 10^{-11} = 4x^3$$

$$x = 2.1 \times 10^{-4}$$

So...

$$[\text{Ca}^{2+}] = 2.1 \times 10^{-4} \text{ mol/L}$$

$$[\text{F}^-] = 4.2 \times 10^{-4} \text{ mol/L}$$

Corrections to Model (can ignore)

Complications in this model occur and less correct if:

1. at higher concentrations
2. if other ions present

A more complex analysis uses activities in place of concentrations but we can ignore this correction.

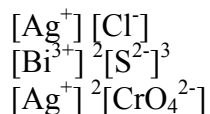
Example when K_{sp} does not predict correctly due to salt effect – solubility of a salt is increased by presence of other ions in solution

AgCl 20% more soluble in 0.20 M KNO_3 , other ions surround ions in solution so more stable and tend to stay in solution

Normally don't have such complications for dilute solutions

Precipitation

The formula for the concentrations used to calculate the K_{sp} is the ion product



Ion product (IP) – actual concentrations present

Relation between K_{sp} and ion product

Ion product $< K_{sp}$ Unsaturated solution

Ion product $= K_{sp}$ Saturated solution

Ion product $> K_{sp}$ Supersaturated solution

Supersaturated dissolve at one temperature where K_{sp} greater, then allow temp to come to desired value if ions stay in solution then $IP > K_{sp}$

Normally,

Unless special information given

$IP > K_{sp}$ Precipitate will form

$IP \leq K_{sp}$ No precipitate

IP Example- Will precipitate form from

10 mL of 0.010M $AgNO_3$ and 10 mL 0.0001 M NaCl mixed

if $K_{sp} = 1.7 \times 10^{-10}$ $AgCl$?

(Conc.) (Vol.) = (mol)

moles of $Ag^+ = (0.01 \text{ mol/L}) (0.010 \text{ L}) = 1.0 \times 10^{-4} \text{ mol}$

$Cl^- = (1.0 \times 10^{-4} \text{ mol/L}) (0.010 \text{ L}) = 1.0 \times 10^{-6} \text{ mol}$

Conc. after dilution $(1.0 \times 10^{-4} \text{ mol}) / (0.020 \text{ L}) = 5.0 \times 10^{-3} \text{ M}$

$(1.0 \times 10^{-6} \text{ mol}) / (0.020 \text{ L}) = 5.0 \times 10^{-5} \text{ M}$

$[Ag^+][Cl^-] = 2.5 \times 10^{-7} > K_{sp}$

$AgCl$ will precipitate!

IP Example - Will precipitate form from?

0.001M $\text{Mg}(\text{NO}_3)_2$

pH = 9.0

$K_{sp} = 8.98 \times 10^{-12}$ $\text{Mg}(\text{OH})_2$

So first find pOH = 5.0

then $[\text{OH}^-] = 1.0 \times 10^{-5}$

$$\begin{aligned} \text{IP} &= [\text{Mg}^{2+}] [\text{OH}^-]^2 \\ &= [1.0 \times 10^{-3}] [1.0 \times 10^{-5}]^2 \\ &= 1.0 \times 10^{-13} < K_{sp} \end{aligned}$$

No precipitate!