

Solubility Equilibria

Applies the principles of equilibrium to ionic solids of low solubility in water

Solubility product (K_{sp})

in a saturated solution, the species in solution is in equilibrium with undissolved material

is characterized by an equilibrium constant K_{sp} called the solubility product

Examples:



$$K_{sp} = [\text{Ag}^+] [\text{Cl}^-] = 1.6 \times 10^{-10}$$

Examples:



$$K_{sp} = [\text{Ag}^+]^2 [\text{CO}_3^{2-}] = 8.1 \times 10^{-12}$$

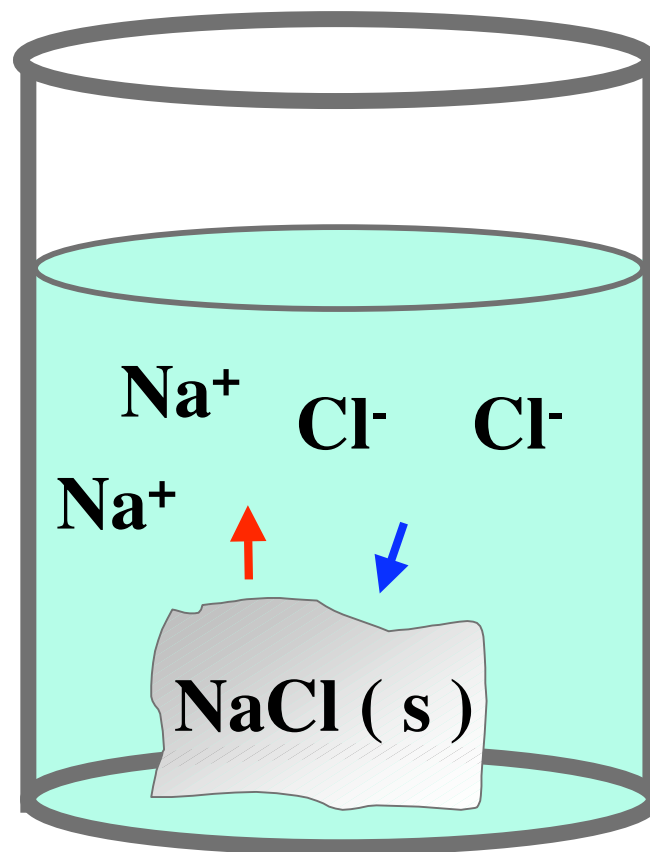
Examples:



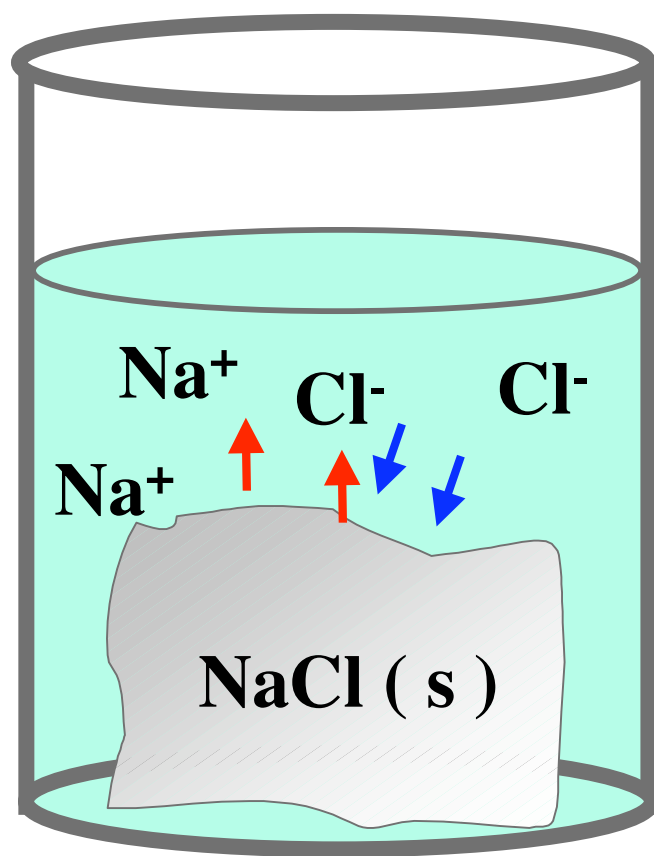
$$K_{sp} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2 = 1.2 \times 10^{-26}$$

**The amount of excess solid present
has no effect on the position of
solubility equilibrium.**

When ions in solution reform solid they do so on the surface of the solid.



Doubling the surface area of the solid doubles both the rate of reforming and dissolving. position of equilibrium unchanged



Molar Solubility and Solubility

Molar solubility: the number of moles solute in one liter of a saturated solution (*mol/L*)

Solubility: the number of grams of solute in one liter of a solution (*g/L*)

Depending on the text being used

Solubility v.s. Solubility Product

- **solubility product** is an equilibrium constant and thus has only one value at a certain temperature
- **solubility** is an equilibrium position and has an infinite number of possible values at a given temperature depending on the conditions
ie: the common ion effect

given K_{sp} you should be able to calculate

molar solubility

concentration of anion in a saturated solution

concentration of cation in a saturated solution

**molar solubilities when common-ion effect
comes into play**

Practice Exercise

The solubility of PbCrO_4 is 4.5×10^{-5} g/L.
What is its solubility product ?

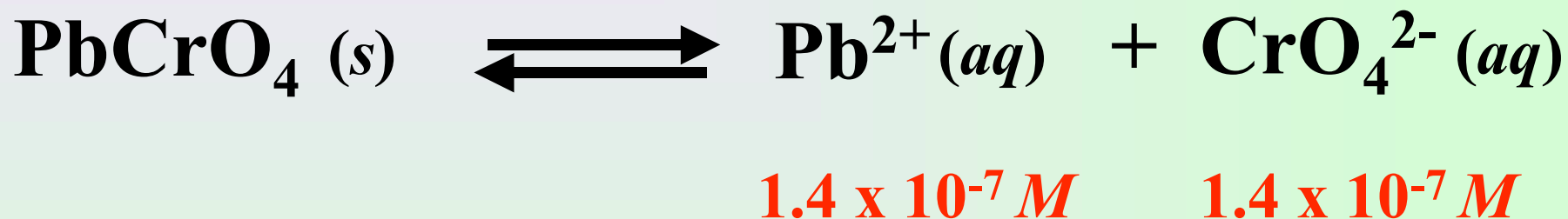
First convert to mol/L



$$4.5 \times 10^{-5} \frac{\text{g}}{\text{L}} \times \frac{1 \text{ mol}}{323.2 \text{ g}} = 1.4 \times 10^{-7} \text{ mol/L}$$

Practice Exercise

The solubility of PbCrO_4 is 4.5×10^{-5} g/L.
What is its solubility product ?



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

$$K_{sp} = (1.4 \times 10^{-7})(1.4 \times 10^{-7})$$

$$K_{sp} = 1.9 \times 10^{-14}$$

Practice Exercise

Calculate the molar solubility of PbCO_3 .

($K_{sp} = 3.3 \times 10^{-14}$)



Init: $0.00 M$ $0.00 M$

final: $+x$ $+x$

$$K_{sp} = [\text{Pb}^{2+}] [\text{CO}_3^{2-}]$$

$$X = 1.8 \times 10^{-7} \text{ mol/L}$$

$$K_{sp} = (x)(x) = (x)^2 = 3.3 \times 10^{-14}$$

Practice Exercise

The K_{sp} value for $\text{Cu}(\text{OH})_2 = 2.2 \times 10^{-20}$ at 25°C . Calculate its solubility in g/L.



Init: 0.00 M 0.00 M

final: $+x$ $+2x$

$$K_{sp} = [\text{Cu}^{2+}] [\text{OH}^-]^2$$

$$K_{sp} = (x)(2x)^2 = (x)(4x^2) = 4x^3 = 2.2 \times 10^{-20}$$

$$4x^3 = 2.2 \times 10^{-20}$$

$$x = \left(\frac{2.2 \times 10^{-20}}{4} \right)^{1/3}$$

$$x = 1.77 \times 10^{-7} \frac{\cancel{\text{mol}}}{\text{L}} \times \frac{97.55 \text{ g}}{1 \cancel{\text{mol}}}$$

$$x = 1.72 \times 10^{-5} \text{ g/L}$$

Relative Solubilities

Salt	K_{sp}
AgCl	8.3×10^{-17}
CuI	5.1×10^{-12}
CaSO ₄	6.1×10^{-5}

all K_{sp} expressions are of the form

$$K_{sp} = [X][Y]$$

Therefore, solubility decreases in the order



Relative Solubilities

Salt	K_{sp}
CuS	8.3×10^{-45}
Ag ₂ S	1.6×10^{-49}
Bi ₂ S ₃	1.1×10^{-73}

K_{sp} expressions are of the form
[Cu²⁺] [S²⁻], [Ag⁺]² [S²⁻], [Bi³⁺]² [S²⁻]³

Therefore, need to do a calculation

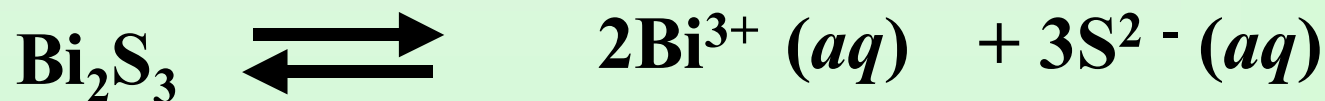
Relative Solubilities



$$8.3 \times 10^{-45} = [\text{Cu}^{2+}] [\text{S}^{2-}] = x^2$$



$$1.6 \times 10^{-49} = [\text{Ag}^+]^2 [\text{S}^{2-}] = 4x^3$$



$$1.1 \times 10^{-73} = [\text{Bi}^{3+}]^2 [\text{S}^{2-}]^3 = 108x^5$$

Relative Solubilities

Salt	K_{sp}	Molar solubility
CuS	8.3×10^{-45}	9.2×10^{-23}
Ag ₂ S	1.6×10^{-49}	3.4×10^{-17}
Bi ₂ S ₃	1.1×10^{-73}	1.0×10^{-15}

Predicting Precipitation Reactions

Ion Product

$$Q = \frac{[\text{products}]^x}{[\text{reactants}]^y}$$

- analogous to reaction quotient
- tells us whether a precipitate will form under a given set of reaction conditions

$Q_c > K_{sp}$: precipitate will form

$Q_c = K_{sp}$: saturated solution

$Q_c < K_{sp}$: no precipitate will form;
substance dissolves

Practice Exercise

If 2.00 ml of 0.200 *M* NaOH are added to 1.0 L of 0.100 *M* CaCl₂, will a precipitate form?

Practice Exercise

If 2.00 ml of 0.200 *M* NaOH are added to 1.0 L of 0.100 *M* CaCl₂, will a precipitate form?

$$K_{sp} = 8.0 \times 10^{-6}$$





$$\text{Ca}^{2+} = 1.0 \text{ L} \times \frac{0.10 \text{ mol}}{\text{L}} = .1 \text{ mol}$$

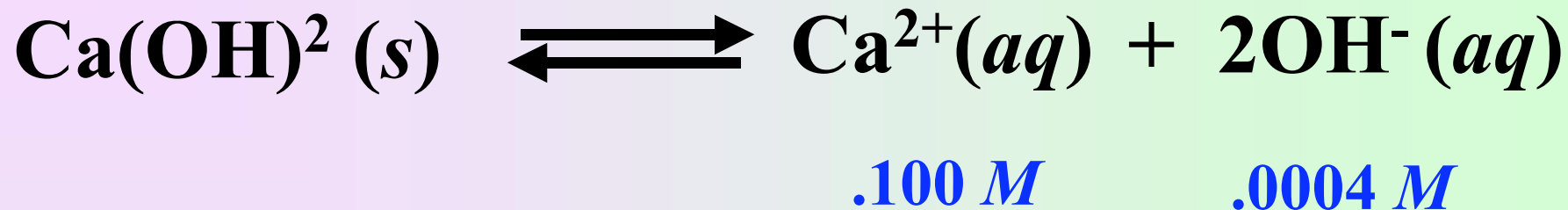
$$\text{OH}^- = 2.0 \times 10^{-3} \text{ L} \times \frac{0.20 \text{ mol}}{\text{L}} = 4.0 \times 10^{-4} \text{ mol}$$

$$\frac{.1 \text{ mol}}{1.002 \text{ L}}$$

$$\frac{4.0 \times 10^{-4} \text{ mol}}{1.002 \text{ L}}$$

$$[\text{Ca}^{2+}] .100 \text{ M}$$

$$[\text{OH}^-] .0004 \text{ M}$$



$$Q = [\text{Ca}^{2+}] [\text{OH}^-]^2$$

$$Q = (.100) (.0004)^2$$

$$Q = 1.6 \times 10^{-8}$$

$$K_{\text{sp}} = 8.0 \times 10^{-6}$$

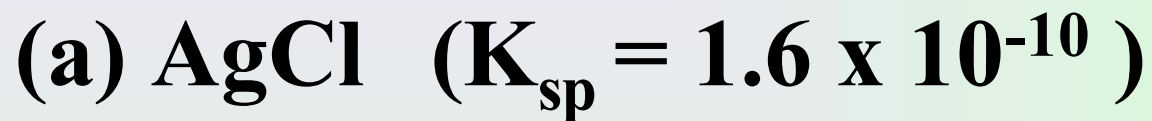
$$Q < K_{\text{sp}} ; \text{precipitate will not form}$$

Separation of Ions by Fractional Precipitation

When a solution contains several ions can one be removed by precipitation, leaving all the others in solution?

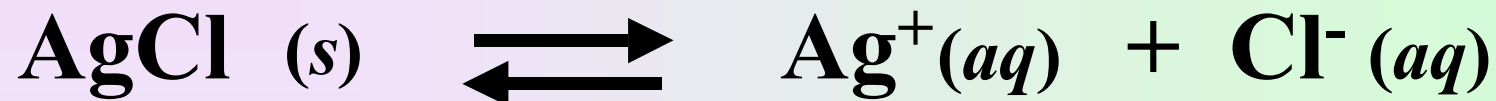
Practice Exercise

Calculate the concentration of Ag^+ necessary to cause precipitation of



from a solution in which Cl^- and PO_4^{3-} are each present at a concentration of 0.10 M .

Practice Exercise



$$[\text{Cl}^-] = 0.1 \text{ M}; \quad K_{sp} = 1.6 \times 10^{-10}$$



$$[\text{PO}_4^{3-}] = 0.1 \text{ M}; \quad K_{sp} = 1.8 \times 10^{-18}$$

Practice Exercise

calculate the concentration of Ag^+ at which AgCl begins to precipitate



$$[\text{Cl}^-] = 0.1 \text{ M}; \quad K_{sp} = 1.6 \times 10^{-10}$$

$$1.6 \times 10^{-10} = [\text{Cl}^-] [\text{Ag}^+]$$

$$1.6 \times 10^{-10} = (0.1) [\text{Ag}^+]$$

$$[\text{Ag}^+] = 1.6 \times 10^{-9}$$

Practice Exercise

calculate the concentration of Ag^+ at which Ag_3PO_4 begins to precipitate



$$[\text{PO}_4^{3-}] = 0.1 \text{ M}; \quad K_{sp} = 1.8 \times 10^{-18}$$

$$1.8 \times 10^{-18} = [\text{Ag}^+]^3 [\text{PO}_4^{3-}]$$

$$1.8 \times 10^{-18} = (0.10) [\text{Ag}^+]^3$$

$$[\text{Ag}^+]^3 = 1.8 \times 10^{-17}$$

$$[\text{Ag}^+] = 2.6 \times 10^{-6}$$

Practice Exercise

[Ag⁺] to begin precipitation of:

$$\text{Cl}^- = 1.6 \times 10^{-9}$$

$$\text{PO}_4^{3-} = 2.6 \times 10^{-6} \text{ M}$$

AgCl precipitates before Ag₃PO₄

Practice Exercise

What is $[\text{Cl}^-]$ when Ag_3PO_4 begin precipitate ?

PO_4^{3-} begins to precipitate when $[\text{Ag}^+]$ reaches $2.6 \times 10^{-6} \text{ M}$.

$$K_{sp} = 1.6 \times 10^{-10} = [\text{Ag}^+] [\text{Cl}^-]$$

$$1.6 \times 10^{-10} = (2.6 \times 10^{-6}) [\text{Cl}^-]$$

$$[\text{Cl}^-] = 6.2 \times 10^{-5}$$