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:

$$AgCl\,(s) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq)$$

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

Examples:

$$Ag_2CO_3\,(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}\,(aq)$$

$$K_{sp} = [Ag^+]^2\,[CO_3^{2-}] = 8.1 \times 10^{-12}$$

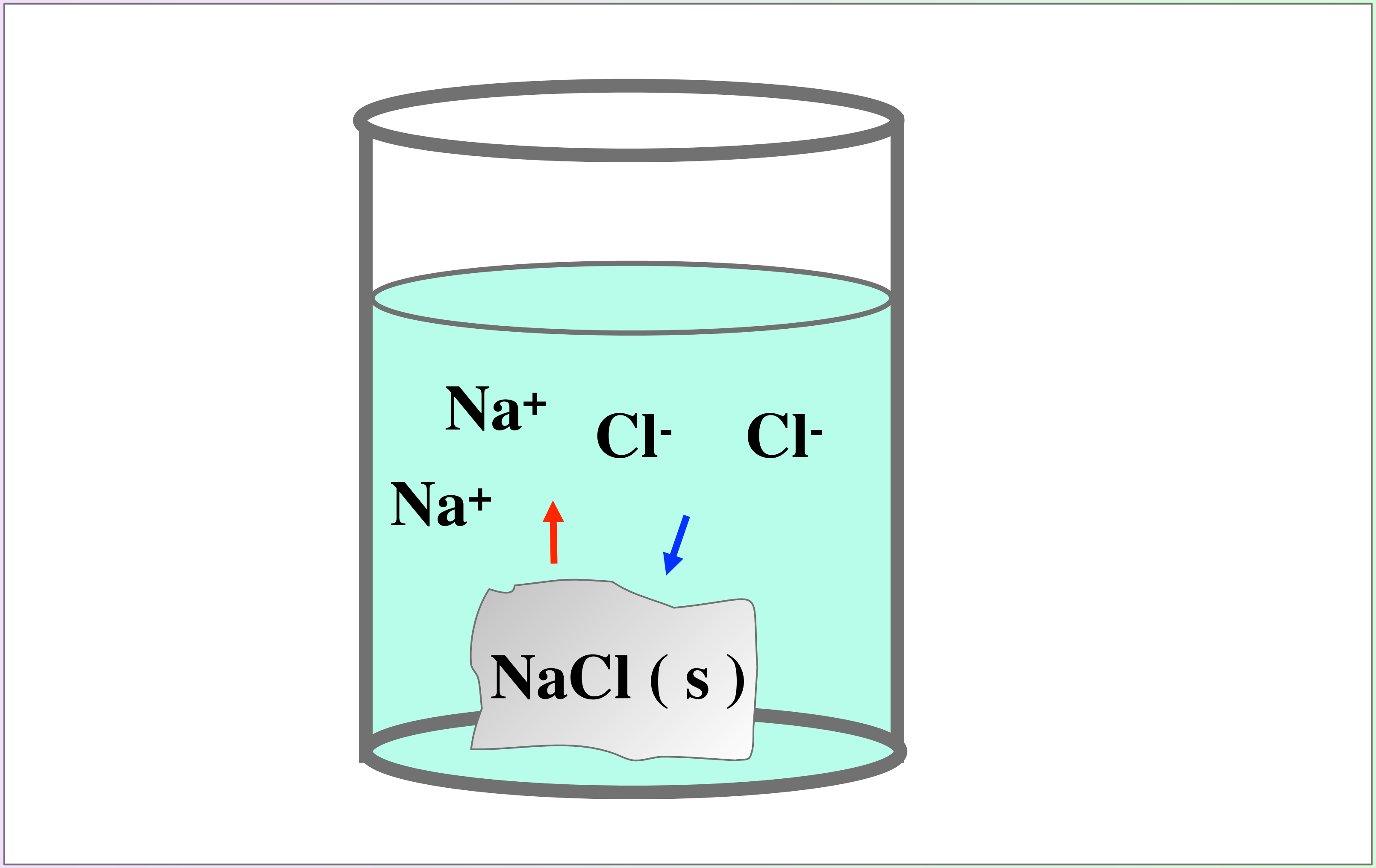
Examples:

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

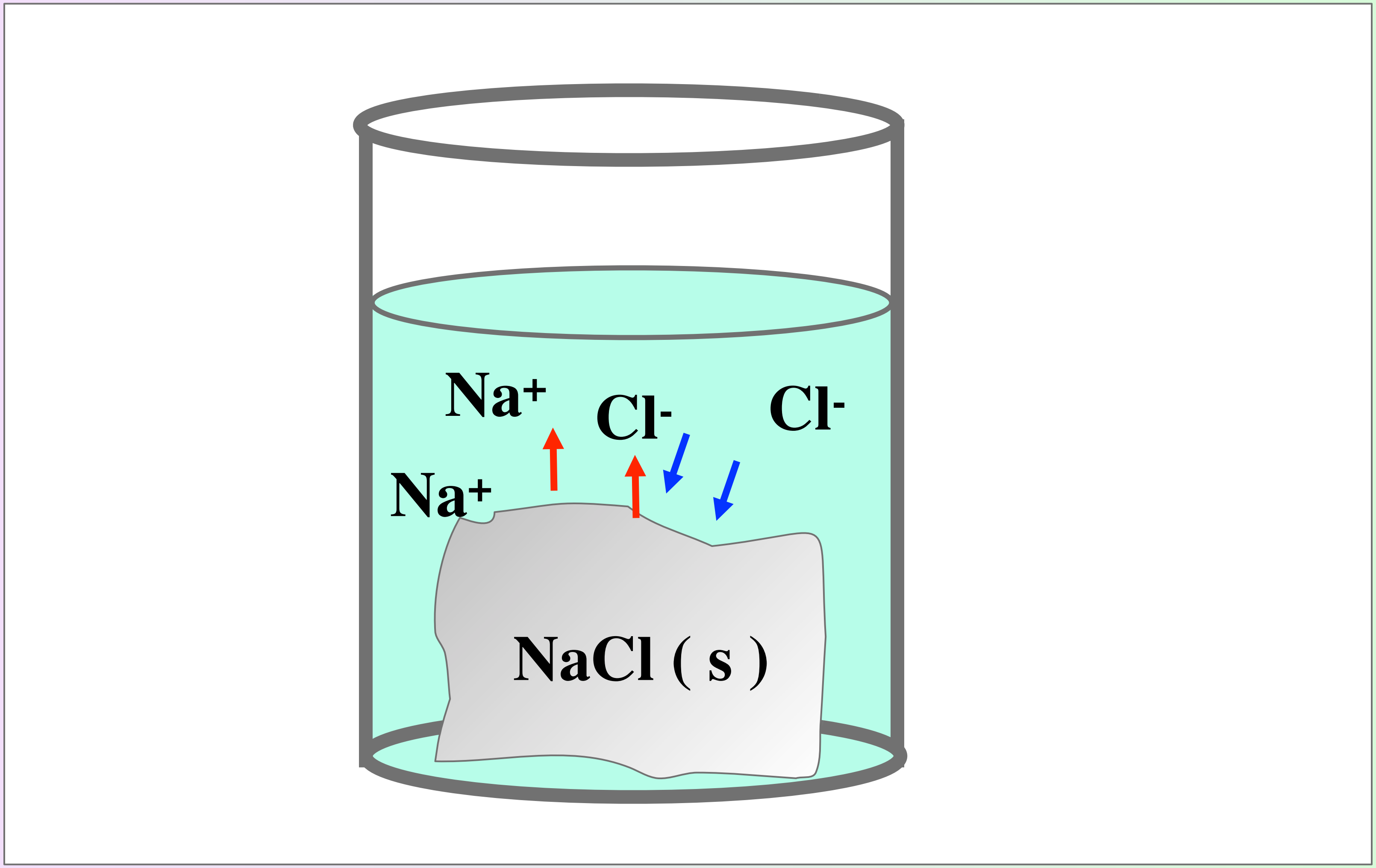
$$K_{sp} = [Ca^{2+}]^3 [PO_4^{3-}]^2 = 1.2 \times 10^{-26}$$

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

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

Solubility v.s. Solubility Product

- **solubility product** is an equilibrium constant and thus has only one value at a certain temperature

$$K_{sp}$$

- **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 1.4×10^{-7} mol/L. What is its solubility product ?

$$PbCrO_4\,(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$$

1.4×10^{-7} mol/L

Practice Exercise

The solubility of $PbCrO_4$ is 1.4×10^{-7} mol/L. What is its solubility product ?

$$PbCrO_4\,(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$$

$1.4 \times 10^{-7}\,M$ $\quad$ $1.4 \times 10^{-7}\,M$

$$K_{sp} = [Pb^{2+}]\,[CrO_4^{2-}]$$

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

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

Practice Exercise

Calculate the molar solubility of $PbCO_3$.
($K_{sp} = 3.3 \times 10^{-14}$)

$$PbCO_3\ (s) \rightleftharpoons Pb^{2+}(aq) + CO_3^{2-}(aq)$$

		Pb^{2+}	CO_3^{2-}
Init:		0.00 *M*	0.00 *M*
final:		+x	+x

$$K_{sp} = [Pb^{2+}]\ [CO_3^{2-}]$$

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

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

Practice Exercise

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

$$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$$

Init:		0.00 *M*	0.00 *M*
final:		+x	+2x

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

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

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

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

$$\boxed{x = 1.77 \times 10^{-7}\ \text{mol/L}}$$

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

$CaSO_4$ > CuI > AgCl

Relative Solubilities

Salt	K_{sp}
CuS	8.3×10^{-45}
Ag_2S	1.6×10^{-49}
Bi_2S_3	1.1×10^{-73}

K_{sp} expressions are of the form

$[Cu^{2+}]\,[S^{2-}]$, $[Ag^{+}]^2\,[S^{2-}]$, $[Bi^{3+}]^2\,[S^{2-}]^3$

Therefore, need to do a calculation

Relative Solubilities

$$CuS \rightleftharpoons Cu^{2+}\,(aq) + S^{2-}\,(aq)$$

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

$$Ag_2S \rightleftharpoons 2Ag^{+}\,(aq) + S^{2-}\,(aq)$$

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

$$Bi_2S_3 \rightleftharpoons 2Bi^{3+}\,(aq) + 3S^{2-}\,(aq)$$

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

Relative Solubilities

Salt	K_{sp}	Molar solubility
CuS	8.3×10^{-45}	9.2×10^{-23}
Ag_2S	1.6×10^{-49}	3.4×10^{-17}
Bi_2S_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* $CaCl_2$, 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* $CaCl_2$, will a precipitate form?

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

$$Ca(OH)_2\,(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^{-}(aq)$$

$$Ca(OH)^2\,(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$$

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

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

$$\frac{.1\ mol}{1.002\ L} \qquad \frac{4.0 \times 10^{-4}\ mol}{1.002\ L}$$

$\boxed{[Ca^{2+}]\ .100\ M}$ $\boxed{[OH\ ]\ .0004\ M}$

$$Ca(OH)^2\ (s) \rightleftharpoons Ca^{2+}(aq) + 2OH^{-}(aq)$$

.100 *M* .0004 *M*

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

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

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

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

$$Ca(OH)^2\ (s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$$

.100 M .0004 M

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

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

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

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

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

The Common Ion Effect and Solubility

A common ion suppresses the solubility of an ionic substance

Practice Exercise

Calculate the solubility of AgBr (K_{sp} = 7.7 x 10^{-13}) in:

(a) pure water

$\boxed{\text{(b) 0.0010 M NaBr}}$

$$AgBr\ (s) \rightleftharpoons Ag^{+}(aq) + Br^{-}(aq)$$

Practice Exercise

Calculate the solubility of AgBr ($K_{sp} = 7.7 \times 10^{-13}$) in:

(a) pure water

$\boxed{\text{(b) 0.0010 M NaBr}}$

$$AgBr\ (s) \rightleftharpoons Ag^{+}(aq) + Br^{-}(aq)$$

Le Chatelier's principle: the solubility is less in a solution of NaBr than in pure water

Practice Exercise

Calculate the solubility of AgBr ($K_{sp} = 7.7 \times 10^{-13}$) in:

(a) pure water

$$AgBr\ (s) \rightleftharpoons Ag^{+}(aq) + Br^{-}(aq)$$

$$K_{sp} = [Ag^{+}][Br^{-}] = 7.7 \times 10^{-13}$$

$$x^2 = 7.7 \times 10^{-13}$$

$$x = 8.8 \times 10^{-7}\ M$$

Practice Exercise

Calculate the solubility of AgBr (K_{sp} = 7.7 x 10^{-13}) in:

(b) 0.0010 *M* NaBr

$$AgBr\ (s) \rightleftharpoons Ag^{+}(aq) + Br^{-}(aq)$$

$$K_{sp} = [Ag^{+}]\,[Br^{-}] = 7.7 \times 10^{-13}$$

$$[Ag^{+}]\,(0.0010) = 7.7 \times 10^{-13}$$

$$[Ag^{+}] = 7.7 \times 10^{-10}\ M$$