6.1 The equilibrium constant

For the reaction

$$aA + bB \rightleftharpoons cC + dD \qquad (6\text{-}1)$$

we write the equilibrium constant, K, in the form

Equilibrium constant: $\qquad K_C = \dfrac{[C]^c[D]^d}{[A]^a[B]^b} \qquad (6\text{-}2)$

where the lowercase superscript letters denote stoichiometry coefficients and each capital letter stands for a chemical species. The symbol [A] stands for the **concentration of A relative to its standard state (defined next). By definition, a reaction is favored whenever K > 1.**

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1. In the thermodynamic derivation of the equilibrium constant, each quantity in Equation 6-2 is expressed as the ratio of the concentration of a species to its concentration in its standard state. For solutes, the standard state is 1 M. For gases, the standard state is 1 bar (10^5 Pa; 1 atm = 1.013 25 bar), and for solids and liquids, the standard states are the pure solid or liquid. It is understood that [A] in Equation 6-2 really means [A]/(1 M) if A is a solute. If D is a gas, [D] really means (pressure of D in bars)/(1 bar). To emphasize that [D] means pressure of D, we usually write P_D in place of [D]. The terms in Equation 6-2 are actually dimensionless; therefore, all equilibrium constants are dimensionless. For the ratios [A]/(1 M) and [D]/(1 bar) to be dimensionless, [A] must be expressed in moles per liter (M), and [D] must be expressed in bars. If C were a pure liquid or solid, the ratio [C]/(concentration of C in its standard state) would be unity (1) because the standard state is the

pure liquid or solid. If C is a solvent, the concentration is so close to that of pure liquid C that the value of [C] is still essentially 1.

1. Concentrations of solutes should be expressed as moles per liter.
2. Concentrations of gases should be expressed in bars.
3. Concentrations of pure solids, pure liquids, and solvents are omitted because they are unity. These conventions are arbitrary, but you must use them if you wish to use tabulated values of equilibrium constants, standard reduction potentials, and free energies.
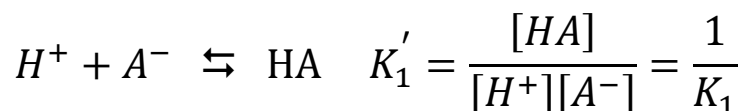
Manipulating Equilibrium Constants
Consider the reaction

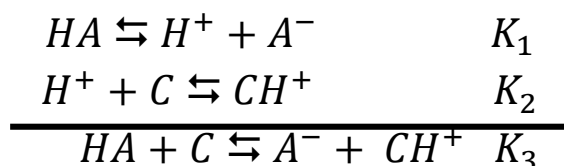$$HA \leftrightarrows H^+ + A^- \qquad K_1 = \frac{[H^+][A^-]}{[HA]}$$
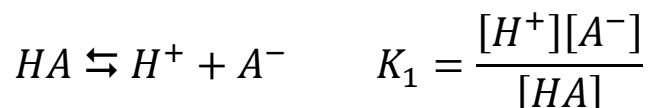
- If the direction of a reaction is **reversed**, the new value of K is simply the reciprocal of the original value of K.

Equilibrium constant for reverse reaction:

$$H^+ + A^- \leftrightarrows HA \qquad K_1' = \frac{[HA]}{[H^+][A^-]} = \frac{1}{K_1}$$

- If two reactions are added, the new K is the product of the two individual values:

$$
\begin{array}{ll}
HA \leftrightarrows H^+ + A^- & K_1 \\
H^+ + C \leftrightarrows CH^+ & K_2 \\
\hline
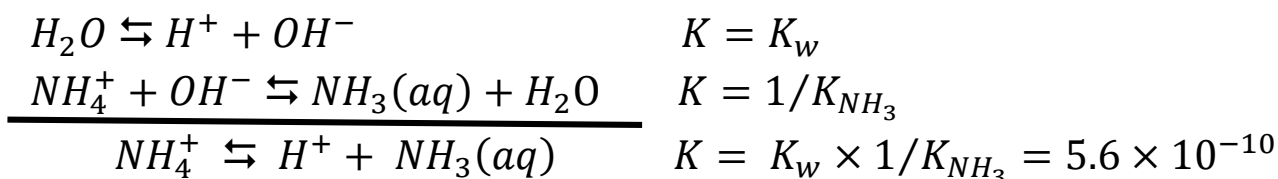HA + C \leftrightarrows A^- + CH^+ & K_3
\end{array}
$$

Equilibrium constant for sum of reactions:

$$K_3 = K_1 K_2 = \frac{[H^+][A^-]}{[HA]} \times \frac{[CH^+]}{[H^+][C]} = \frac{[A^-][CH^+]}{[HA][C]}$$

EXAMPLE Combining Equilibrium Constants

The equilibrium constant for the reaction $H_2O \leftrightarrows H^+ + OH^-$ is called $K_w = [H^+][OH^-]$ and has the value 1.0×10^{-14} at $25°C$. Given that $K_{NH_3} = 1.8 \times 10^{-5}$ for the reaction $NH_3(aq) + H_2O \leftrightarrows NH_4^+ + OH^-$, find K for the reaction $NH_4^+ \leftrightarrows NH_3(aq) + H^+$.

Solution The third reaction can be obtained by reversing the second reaction and adding it to the first reaction:

$$H_2O \leftrightarrows H^+ + OH^- \qquad\qquad K = K_w$$
$$\underline{NH_4^+ + OH^- \leftrightarrows NH_3(aq) + H_2O \qquad K = 1/K_{NH_3}}$$
$$NH_4^+ \leftrightarrows H^+ + NH_3(aq) \qquad K = K_w \times 1/K_{NH_3} = 5.6 \times 10^{-10}$$

Test Yourself For the reaction $Li^+ + H_2O \leftrightarrows Li(OH)(aq) + H^+$, $K_{Li} = 2.3 \times 10^{-14}$. Combine this reaction with the K_w reaction to find the equilibrium constant for the reaction

$$Li^+ + OH^- \leftrightarrows Li(OH)(aq) \qquad\qquad (Answer: 2.3)$$
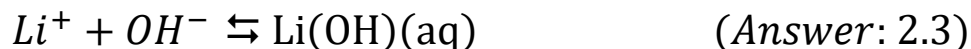
Q1) What is the equilibrium constant for reaction (2) if the equilibrium constant for reaction (1) is K.

Reaction (1): $1/2N_2(g) + 3/2H_2(g) \leftrightarrows NH_3(g)$ (equilibrium constant = K)

Reaction (2): $4NH_3(g) \leftrightarrows 2N_2(g) + 6H_2(g)$

A. $1/K^2$ B. $1/K^8$ C. $1/K$ D. $1/K^4$
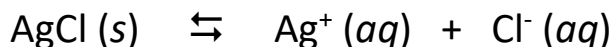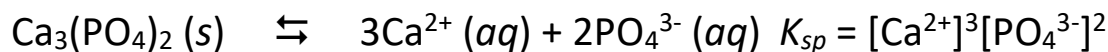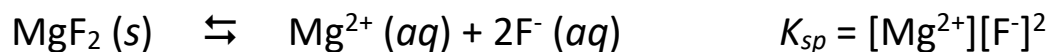
6.3 Solubility Product

In chemical analysis, we encounter solubility in precipitation titrations, electrochemical reference cells, and gravimetric analysis. The effect of acid on the solubility of minerals and the effect of atmospheric CO_2 on the solubility (and death) of coral reefs are important in environmental science.

The solubility product is the equilibrium constant for the reaction in which a solid salt dissolves to give its constituent ions in solution. Solid is omitted from the equilibrium constant because it is in its standard state. Appendix F lists solubility products.

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

$K_{sp} = [Ag^+][Cl^-]$ K_{sp} is the **solubility product constant**

$MgF_2\ (s) \rightleftharpoons Mg^{2+}\ (aq) + 2F^-\ (aq)$ $K_{sp} = [Mg^{2+}][F^-]^2$

$Ag_2CO_3\ (s) \rightleftharpoons 2Ag^+\ (aq) + CO_3^{2-}\ (aq)$ $K_{sp} = [Ag^+]^2[CO_3^{2-}]$

$Ca_3(PO_4)_2\ (s) \rightleftharpoons 3Ca^{2+}\ (aq) + 2PO_4^{3-}\ (aq)$ $K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$

Dissolution of an ionic solid in aqueous solution:

The Reaction Quotient (*Q*)

- *Q* gives the same ratio the equilibrium expression gives, but for a system that is *not* at equilibrium.

$Q < K_{sp}$ Unsaturated solution   No precipitate

$Q = K_{sp}$ Saturated solution

$Q > K_{sp}$ Supersaturated solution   Precipitate will form

Molar solubility (mol/L) is the number of moles of solute dissolved in 1 L of a saturated solution.

Solubility (g/L) is the number of grams of solute dissolved in 1 L of a saturated solution.

What is the solubility of silver chloride in g/L?

$$AgCl\ (s) \rightleftharpoons Ag^+\ (aq) + Cl^-\ (aq) \qquad K_{sp} = 1.6 \times 10^{-10}$$

Initial (M)	0.00	0.00	$K_{sp} = [Ag^+][Cl^-]$
Change (M)	+s	+s	$K_{sp} = s^2$
Equilibrium (M)	s	s	$s = \sqrt{K_{sp}}$
$[Ag^+] = 1.3 \times 10^{-5}\ M$		$[Cl^-] = 1.3 \times 10^{-5}\ M$	$s = 1.3 \times 10^{-5}$

$$Solubility\ of\ AgCl = \frac{1.3 \times 10^{-5}\ mol\ AgCl}{1\ L\ soln} \times \frac{143.5\ g\ AgCl}{1\ mol\ AgCl} = 1.9 \times 10^{-3}\ g/L$$

TABLE 16.3 Relationship Between K_{sp} and Molar Solubility (s)

Compound	K_{sp} Expression	Cation	Anion	Relation Between K_{sp} and s
AgCl	$[Ag^+][Cl^-]$	s	s	$K_{sp} = s^2; s = (K_{sp})^{\frac{1}{2}}$
BaSO$_4$	$[Ba^{2+}][SO_4^{2-}]$	s	s	$K_{sp} = s^2; s = (K_{sp})^{\frac{1}{2}}$
Ag$_2$CO$_3$	$[Ag^+]^2[CO_3^{2-}]$	2s	s	$K_{sp} = 4s^3; s = a\frac{K_{sp}}{4}b^{\frac{1}{3}}$
PbF$_2$	$[Pb^{2+}][F^-]^2$	s	2s	$K_{sp} = 4s^3; s = a\frac{K_{sp}}{4}b^{\frac{1}{3}}$
Al(OH)$_3$	$[Al^{3+}][OH^-]^3$	s	3s	$K_{sp} = 27s^4; s = a\frac{K_{sp}}{27}b^{\frac{1}{4}}$
Ca$_3$(PO$_4$)$_2$	$[Ca^{2+}]^3[PO_4^{3-}]^2$	3s	2s	$K_{sp} = 108s^5; s = a\frac{K_{sp}}{108}b^{\frac{1}{5}}$

If 2.00 mL of 0.200 M NaOH are added to 1.00 L of 0.100 M CaCl$_2$, will a precipitate form?

The ions present in solution are Na$^+$, OH$^-$, Ca^{2+}, Cl$^-$.

Only possible precipitate is Ca(OH)$_2$ (solubility rules).

Is $Q > K_{sp}$ for Ca(OH)$_2$?

$[Ca^{2+}]_0 = 0.100\ M$ $\qquad\qquad$ $[OH^-]_0 = 4.0 \times 10^{-4}\ M$

$Q = [Ca^{2+}]_0[OH^-]_0$ $\qquad\qquad$ $0.10 \times (4.0 \times 10^{-4})^2 = 1.6 \times 10^{-8}$

$K_{sp} = [Ca^{2+}][OH^-]^2 = 8.0 \times 10^{-6}$

$Q < K_{sp}$ $\qquad$ No precipitate will form

The Common Ion Effect and Solubility

The presence of a common ion **decreases** the solubility of the salt.

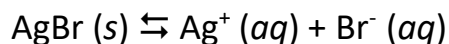**What is the molar solubility of AgBr in (a) pure water and (b) 0.0010 _M_ NaBr?**

(a) AgBr (_s_) ⇆ Ag⁺ (_aq_) + Br⁻ (_aq_)

K_{sp} **= 7.7 x 10⁻¹³**

$s^2 = K_{sp}$

s = 8.8 x 10⁻⁷ _M in pure water_

(b) NaBr (_s_) → Na⁺ (_aq_) + Br⁻ (_aq_)

[Br⁻] = 0.0010 _M_

AgBr (_s_) ⇆ Ag⁺ (_aq_) + Br⁻ (_aq_)

[Ag⁺] = _s_

[Br⁻] = 0.0010 + _s_ ≈ 0.0010

K_{sp} = 0.0010 x _s_

s = 7.7 x 10⁻¹⁰ _M in 0.0010 M NaBr_

Calculate the molar solubility of Hg_2Cl_2 in distlled water

$$Hg_2Cl_2(s) \quad\quad ⇆ \quad\quad Hg_2^{2+} \quad + \quad 2Cl^-$$

initial: 0   0

final: x   2x

molar solubility = $[Hg_2^{2+}] = \frac{1}{2}[Cl^-]$

The solubility product

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2 = 1.2 \times 10^{-18} = 4x^3$$
$$x = 6.7 \times 10^{-7} \, M = [Hg_2^{2+}] \quad and \, [Cl^-] = 1.3 \times 10^{-6} \, M$$

What is the molar solubility of Hg_2Cl_2 in 0.030 M NaCl?

$$Hg_2Cl_2(s) \quad \leftrightarrows \quad Hg_2^{2+} \quad + \quad 2Cl^-$$

initial: 0   0.030

final: x   2x + 0.030

molar solubility = $[Hg_2^{2+}]$

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2 = 1.2 \times 10^{-18} = x(0.030)^2$$

x = 1.3 x 10^{-15} M
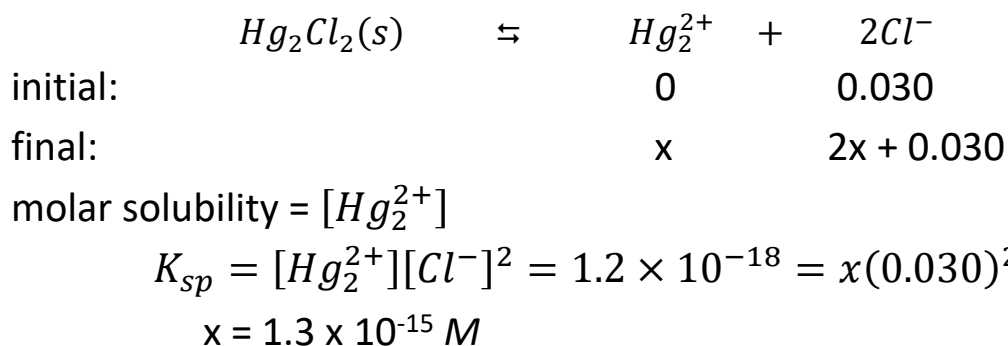
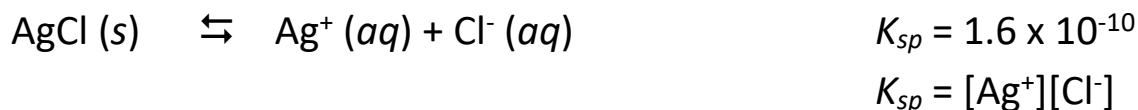- **solubility is REDUCED by adding COMMON ION.**

Separation by Precipitation

What concentration of Ag$^+$ is required to precipitate ONLY AgBr in a solution that contains both Br$^-$ and Cl$^-$ at a concentration of 0.02 M?

K_{sp} of AgCl = 1.6 x 10^{-10} and K_{sp} of AgBr = 7.7 x 10^{-13}

AgCl (s) $\leftrightarrows$ Ag$^+$ (aq) + Cl$^-$ (aq) K_{sp} = 1.6 x 10^{-10}

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

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.6 \times 10^{-10}}{0.02} = 8.0 \times 10^{-9} \ M$$

AgCl will precipitate when $[Ag^+] > 8.0 \times 10^{-9} \ M$

AgBr (s) $\leftrightarrows$ Ag$^+$ (aq) + Br$^-$ (aq)

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

$$[Ag^+] = \frac{K_{sp}}{[Br^-]} = \frac{7.7 \times 10^{-13}}{0.02} = 3.9 \times 10^{-11} \ M$$

AgBr will precipitate when $[Ag^+] > 3.9 \times 10^{-11} \ M$

$$3.9 \ x \ 10^{-11} \ M < [Ag^+] < 8.0 \ x \ 10^{-9} \ M$$

Consider 0.010 M, Pb^{2+}, Hg_2^{2+} ions

each forms insoluble iodide.

PbI_2(s) $\leftrightarrows$ Pb^{2+} + 2I⁻   **K_{sp} = 7.9 × 10⁻⁹**

Hg_2I_2(s) $\leftrightarrows$ Hg_2^{2+} + 2I⁻   **K_{sp} = 4.6 × 10⁻²⁹**

Is it *possible to separate* Pb^{2+} and Hg_2^{2+} ions?

(instead of complete separation, 99.99 % of Hg_2^{2+})

$$0.01\% \; Hg_2^{2+} \; ion \; exists$$

We are asking whether we can lower [Hg_2^{2+}] to 0.010% of 0.010 M = 1.0×10^{-6} M without precipitating Pb^{2+}.

$$K_{sp} = [Hg_2^{2+}][I^-]^2 = (1.0 \times 10^{-6})(x)^2 = 4.6 \times 10^{-29}$$

$$X = [I^-] = 6.8 \times 10^{-12} \; M$$

Will this concentration of I^- cause 0.010 M Pb^{2+} to precipitate? That is, is the solubility product of PbI_2 exceeded?

$$Q = [Pb^{2+}][I^-]^2 = (0.010)(6.8 \times 10^{-12})^2$$

$$= 4.6 \times 10^{-25} < K_{sp} \text{ (for PbI}_2\text{)}$$

The reaction quotient, is less than K_{sp} for PbI_2 = **7.9 × 10⁻⁹**. Therefore, Pb^{2+} will not precipitate and separation of Pb^{2+} and Hg_2^{2+} is feasible. We predict that adding I^- to a solution of Pb^{2+} and Hg_2^{2+} will precipitate virtually all the mercury(I) before any lead(II) precipitates.

(when $[I^-]$ larger than 6.8 x 10⁻¹² M, Hg_2^{2+} further precipitates).