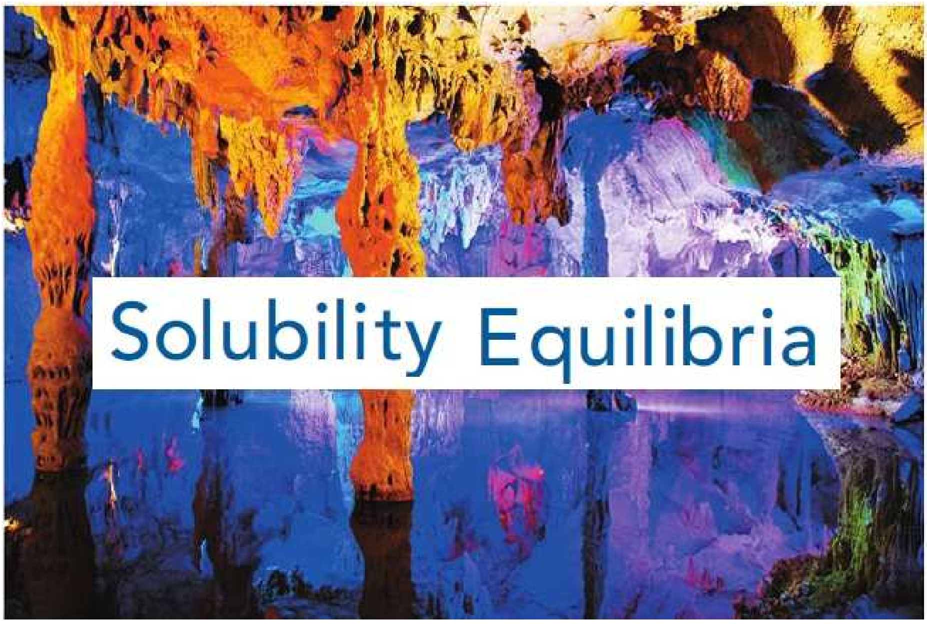


Homogeneous phase chemical reaction

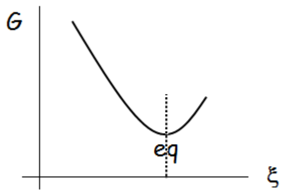
	$A(g)$	$+ \; B(g)$	$\leftrightarrow \; C(g)$
i	p_A	p_B	-
eq	$p_A - x$	$p_B - x$	x

$$K = \frac{x}{(p_A - x)(p_B - x)}$$

Assume $p_A > p_B$

Let $K \uparrow$: $x \rightarrow p_B$, $p_A - x \rightarrow p_A - p_B$

Then, $p_B - x \rightarrow \dfrac{p_B}{(p_A - p_B)\,K}$



Always can reach equilibrium
Never the reaction is 100% complete

Heterogeneous phase chemical reaction

	$A(g)$	+ $B(s)$	$\leftrightarrow C(g)$
i	p_A	n_B	-
eq	$p_A - x$		x

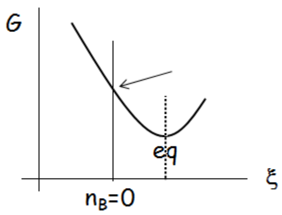
$$K = \frac{x}{(p_A - x)}$$

Assume
$n_B < p_A V/RT$
n_B of gas $\rightarrow p_B$

Let $K \uparrow$ $x \rightarrow p_B$
$p_A - x \rightarrow p_A - p_B$

Then, $p_B - x \rightarrow$ $K = \dfrac{p_B}{(p_A - p_B)}$

Different K for different n_B ??



Need more B to reach equilibrium

Solubility and Solubility Product Constant K_{sp}

dissolution: $$CaF_2(s) \xrightarrow{H_2O} Ca^{2+}(ac) + 2F^-(ac)$$

precipitation: $$Ca^{2+}(ac) + 2F^-(ac) \rightarrow CaF_2(s)$$

$$CaF_2(s) \Leftrightarrow Ca^{2+}(ac) + 2F^-(ac)$$

pure solid, activity =1

Solubility product constant: $$K_{ps} = \left[Ca^{2+}\right]\left[F^-\right]^2$$

Solubility

(or molar solubility), S, is the salt molar concentration in a saturated solution

Relationship Between Solubility and K_{sp}

$$M_m X_x(s) \Leftrightarrow mM(ac) + xX(ac)$$

$$K_{ps} = [M]^m [X]^x$$

$$K_{ps} = (mS)^m (xS)^x = m^m x^x S^{m+x} \qquad \Rightarrow S = \sqrt[m+x]{\frac{K_{ps}}{m^m x^x}}$$

In general, we should not directly compare K_{ps} to estimate solubility ratios!

$$CuS(s) \quad K_{ps} = 8{,}5 \cdot 10^{-45}$$
$$Ag_2S(s) \quad K_{ps} = 1{,}6 \cdot 10^{-49}$$
$$Bi_2S_3(s) \quad K_{ps} = 1{,}1 \cdot 10^{-73}$$

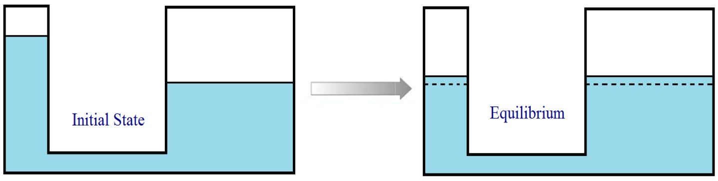
Salt	K_{ps}	Solubility (mol/L)
CuS	$8{,}5 \cdot 10^{-45}$	$9{,}2 \cdot 10^{-23}$
Ag_2S	$1{,}6 \cdot 10^{-49}$	$3{,}4 \cdot 10^{-17}$
Bi_2S_3	$1{,}1 \cdot 10^{-73}$	$1{,}0 \cdot 10^{-15}$

solubility: $Bi_2S_3(s) > Ag_2S(s) > CuS(s)$

K_{Ps}: $Bi_2S_3(s) < Ag_2S(s) < CuS(s)$

Common-Ion Effect in Solubility Equilibria

Mecanical image of the LeCatelier principle



Numerical example:

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

$$K_{ps} = [Ag^+][Cl^-] = 1,7{\cdot}10^{-10}$$

In pure water

$$[Ag^+] = \sqrt{1,7{\cdot}10^{-10}} = 1,3{\cdot}10^{-5}\,M$$

In NaCl 0,1 M solution

$$K_{ps} = [Ag^+][Cl^-] = 1,7{\cdot}10^{-10}$$

$$[Ag^+] = s$$

$$[Cl^-] = \cancel{s} + 0.1$$

$$[Ag^+] = \frac{K_{ps}}{[Cl^-]} = \frac{1,7{\cdot}10^{-10}}{0,1} = 1,7{\cdot}10^{-9}$$

10000 times smaller!

Equilibria Involving Complex Ions

$$AgCl(s) \rightleftharpoons \cancel{Ag^+(aq)} + Cl^-(aq) \qquad K_{sp} = 1.8 \times 10^{-10}$$

$$\cancel{Ag^+(aq)} + 2\,NH_3(aq) \rightleftharpoons [Ag(NH_3)_2{}^+](aq) \qquad K_f = 1.6 \times 10^7$$

$$AgCl(s) + 2\,NH_3(aq) \rightleftharpoons [Ag(NH_3)_2{}^+](aq) + Cl^-(aq)$$

$$K = K_{sp} \times K_f = 1.8 \times 10^{-10} \times 1.6 \times 10^7 = 2.9 \times 10^{-3}$$

$$K = \frac{[[Ag(NH_3)_2]^+][Cl^-]}{[NH_3]^2} = \frac{s \cdot s}{(0.100 - 2s)^2} = \left(\frac{s}{0.100 - 2s}\right)^2 = 2.9 \times 10^{-3}$$

$$s = 4.9 \times 10^{-3}$$

… while in pure water: $s^2 = K_{Ps} \rightarrow$ s= 1.3 10^{-5} M

By means of balances

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = 1.8 \times 10^{-10}$$

$$Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons [Ag(NH_3)_2{}^+](aq) \qquad K_f = 1.6 \times 10^7$$

$$s = [Ag^+] + [Ag(NH_3)_2{}^+]$$

$$[NH_3]_0 = [NH_3] + 2\,[Ag(NH_3)_2{}^+]$$

$$K_f = \frac{[[Ag(NH_3)_2]^+][Cl^-]}{K_{sp}\ [NH_3]^2} = \frac{s \cdot s}{(0.100 - 2s)^2} = \left(\frac{s}{0.100 - 2s}\right)^2 = 2.9 \times 10^{-3}$$

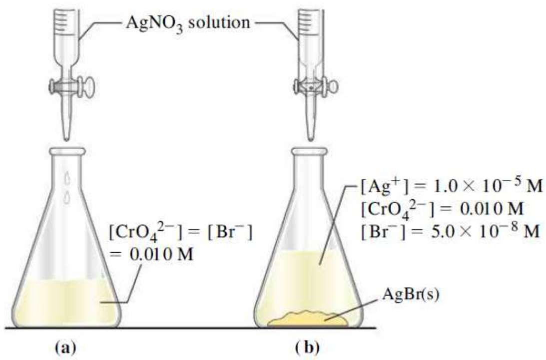
$$s = 4.9 \times 10^{-3}$$

… while in pure water: $s^2 = K_{Ps} \rightarrow$ s= 1.3 10^{-5} M

Fractional Precipitation

(a) $AgNO_3(aq)$ is slowly added to a solution that is 0.010 M in Br^- and 0.010 M in $CrO_4{}^{2-}$.

(b) Essentially all the Br^- has precipitated as pale yellow AgBr(s), $[Br^-]$ in solution = 5.0×10^{-8} M.
Red-brown $Ag_2CrO_4(s)$ is just about to precipitate.



Convention: we say that the precipitation of an ion is complete when its concentration is reduced one thousand times.