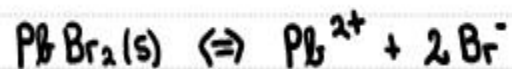


18.1 Solubility Equilibria and K_{sp} The Solubility Product Constant

| Compound | K_{sp} at 25 °C |
|-------------------------------------------------|-----------------------|
| PbBr ₂ | 6.3×10^{-6} |
| AgBr | 3.3×10^{-13} |
| CaCO ₃ | 3.8×10^{-9} |
| CuCO ₃ | 2.5×10^{-10} |
| NiCO ₃ | 6.6×10^{-9} |
| Ag ₂ CO ₃ | 8.1×10^{-12} |
| PbCl ₂ | 1.7×10^{-5} |
| AgCl | 1.8×10^{-10} |
| BaF ₂ | 1.7×10^{-6} |
| CaF ₂ | 3.9×10^{-11} |
| Cu(OH) ₂ | 1.6×10^{-19} |
| Fe(OH) ₃ | 6.3×10^{-38} |
| Ni(OH) ₂ | 2.8×10^{-16} |
| Zn(OH) ₂ | 4.5×10^{-17} |
| Ca ₃ (PO ₄) ₂ | 1.0×10^{-25} |
| CaSO ₄ | 2.4×10^{-5} |
| PbSO ₄ | 1.8×10^{-8} |



Remember that pure liquids and solids do not appear in an equilibrium expression.

$$K = [\text{Pb}^{2+}][\text{Br}^-]^2$$

↑

K_{sp} : Solubility Product Constant.

Note that the salts listed are those during Chem III using Solubility Guide Series we would have considered insoluble.

Looking at the K_{sp} values, these are all reactant-favored equilibria

18.2 Using K_{sp} in Calculations

Estimating Solubility

Which of the following salts is the **least soluble** in water?



- a) AgBr $K_{sp} = 3.3 \times 10^{-13}$ @25°C
 b) Cu(OH)₂ ✓ $K_{sp} = 1.6 \times 10^{-19}$ @25°C
 c) Ca₃(PO₄)₂ $K_{sp} = 1.0 \times 10^{-25}$ @25°C

| | | | | | |
|---|---------|---|-----------------|---|-----------------|
| | AgBr(s) | ⇌ | Ag ⁺ | + | Br ⁻ |
| I | Some | | 0 | | 0 |
| C | -s | | s | | s |
| E | | | s | | s |

$$K_{sp} = [Ag^+][Br^-] : 3.3 \times 10^{-13} = (s)(s)$$

$$s^2 = 3.3 \times 10^{-13}$$

$$s = \sqrt{3.3 \times 10^{-13}} = 5.47 \times 10^{-7}$$

| | | | | | |
|---|-------------------------|---|------------------|---|-------------------|
| | Cu(OH) ₂ (s) | ⇌ | Cu ²⁺ | + | 2 OH ⁻ |
| I | Some | | 0 | | 0 |
| C | -s | | s | | 2s |
| E | | | s | | 2s |

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

$$1.6 \times 10^{-19} = (s)(2s)^2$$

$$4s^3 = 1.6 \times 10^{-19}$$

$$s^3 = 4.0 \times 10^{-20}$$

$$s = \sqrt[3]{4.0 \times 10^{-20}} = 3.42 \times 10^{-7}$$

| | | | | | |
|---|-----------------------------------------------------|---|--------------------|---|---------------------------------|
| | Ca ₃ (PO ₄) ₂ (s) | ⇌ | 3 Ca ²⁺ | + | 2 PO ₄ ³⁻ |
| I | Some | | 0 | | 0 |
| C | -s | | 3s | | 2s |
| E | | | 3s | | 2s |

$$K_{sp} = [Ca^{2+}]^3 [PO_4^{3-}]^2$$

$$1.0 \times 10^{-25} = (3s)^3 (2s)^2$$

$$108s^5 = 1.0 \times 10^{-25}$$

$$s^5 = 9.3 \times 10^{-28}$$

$$s = \sqrt[5]{9.3 \times 10^{-28}} = 3.9 \times 10^{-6}$$



18.2 Using K_{sp} in Calculations

Estimating Solubility

| General Formula | Example | K_{sp} Expression | K_{sp} as a Function of Molar Solubility (x) | Solubility (x) as a Function of K_{sp} |
|-------------------------------|-------------------------------------------------|---------------------------------|----------------------------------------------------|----------------------------------------------|
| MY | AgCl | $K_{sp} = [M^+][Y^-]$ | $K_{sp} = (x)(x) = x^2$ | $x = \sqrt{K_{sp}}$ |
| MY ₂ | HgI ₂ | $K_{sp} = [M^{2+}][Y^-]^2$ | $K_{sp} = (x)(2x)^2 = 4x^3$ | $x = \sqrt[3]{\frac{K_{sp}}{4}}$ |
| MY ₃ | BiI ₃ | $K_{sp} = [M^{3+}][Y^-]^3$ | $K_{sp} = (x)(3x)^3 = 27x^4$ | $x = \sqrt[4]{\frac{K_{sp}}{27}}$ |
| M ₂ Y ₃ | Fe ₂ (SO ₄) ₃ | $K_{sp} = [M^{3+}]^2[Y^{2-}]^3$ | $K_{sp} = (2x)^2(3x)^3 = 108x^5$ | $x = \sqrt[5]{\frac{K_{sp}}{108}}$ |

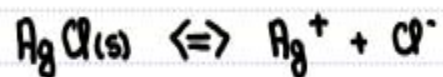
Instead of MEMORIZING these simply use the ICE method.

Note that in the ICE table for solubility we use 's' instead of 'x' simply because by solving for s, we have determined the solubility in mol.L⁻¹ ... M



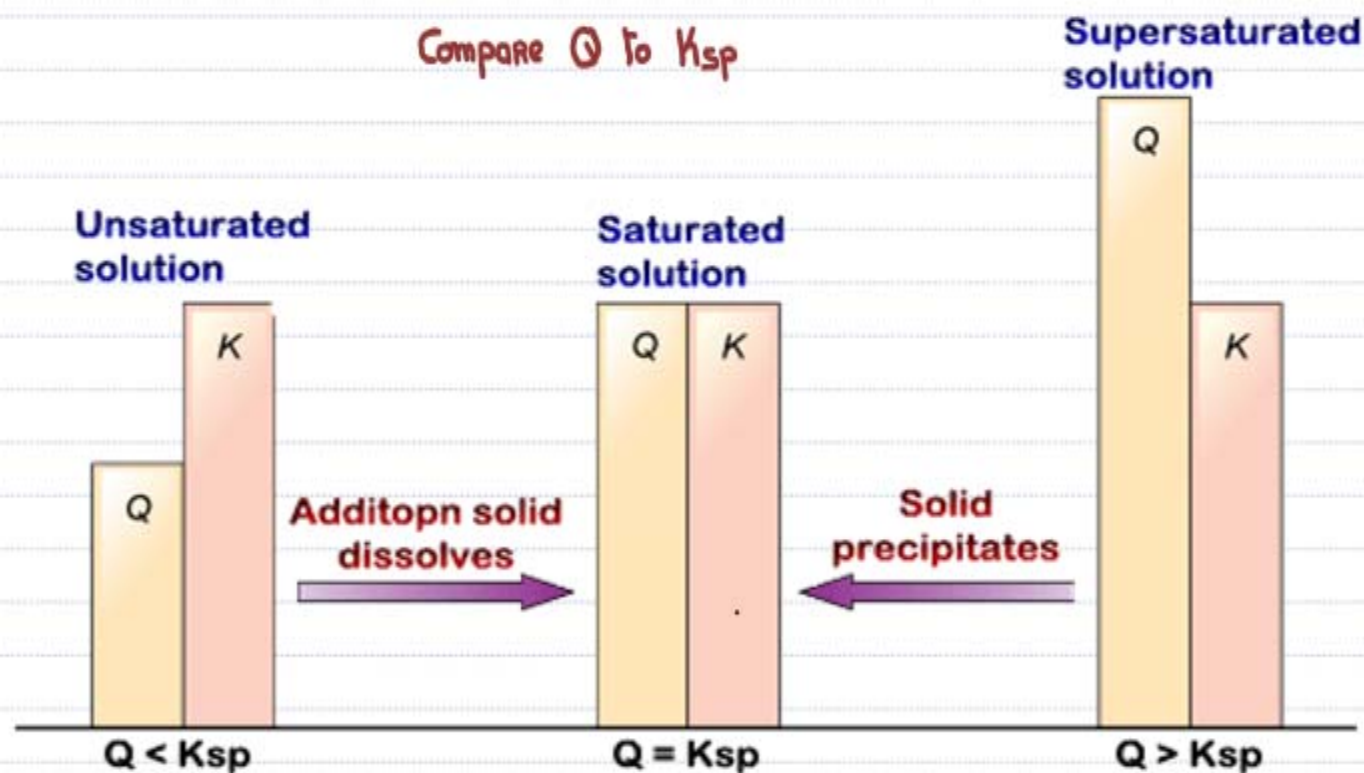
18.2 Using K_{sp} in Calculations

Predicting Whether a Solid Will Precipitate or Dissolve



$$Q = [\text{Ag}^+][\text{Cl}^-]$$

Compare Q to K_{sp}



18.2 Using K_{sp} in Calculations

Predicting Whether a Solid Will Precipitate or Dissolve

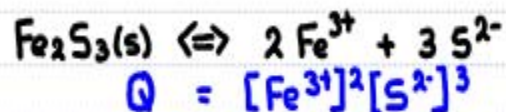
When 25.0 mL of a $7.02 \times 10^{-4} \text{ M}$ iron(III) bromide solution is combined with 22.0 mL of a $2.10 \times 10^{-4} \text{ M}$ sodium sulfide solution does a precipitate form?

K_{sp} Iron(III) sulfide = 1.4×10^{-88}



a) Yes ✓

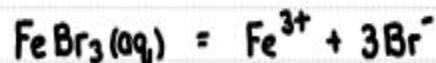
b) No



Total volume when solutions are mixed $25 + 22 = 47 \text{ mL}$

$[\text{Fe}^{3+}]$:

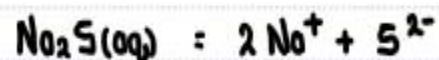
$$\begin{aligned} \# \text{ mol FeBr}_3 &= 7.02 \times 10^{-4} (0.025) \\ &= 1.755 \times 10^{-5} \end{aligned}$$



$$\begin{aligned} \# \text{ mol Fe}^{3+} &= 1.755 \times 10^{-5} \\ [\text{Fe}^{3+}] &= 1.755 \times 10^{-5} / 0.047 = 3.73 \times 10^{-4} \end{aligned}$$

$[\text{S}^{2-}]$

$$\begin{aligned} \# \text{ mol Na}_2\text{S} &= 2.10 \times 10^{-4} (0.022) \\ &= 4.62 \times 10^{-6} \end{aligned}$$



$$\begin{aligned} \# \text{ mol S}^{2-} &= 4.62 \times 10^{-6} \\ [\text{S}^{2-}] &= 4.62 \times 10^{-6} / 0.047 = 9.83 \times 10^{-5} \end{aligned}$$

$$\begin{aligned} Q &= (3.73 \times 10^{-4})^2 (9.83 \times 10^{-5})^3 \\ &= 1.32 \times 10^{-19} > K_{sp} \end{aligned}$$



18.2 Using K_{sp} in Calculations

The Common Ion Effect

The Common Ion Effect

See Class Web Site.

Insoluble Salt

- PbCl₂
- AgCl
- CaF₂
- PbCrO₄

0.01 g

Common Ion: Cl⁻



Soluble Salt

- NaCl
- KCl
- NaNO₃
- Pb(NO₃)₂

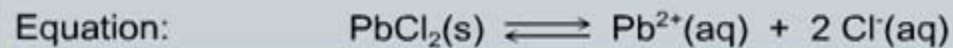
0.01 M

Solubility: 4.50 g/L

Precipitate: 0.00 g

[Na⁺] = 0.00 M

[Cl⁻] = 0.00 M



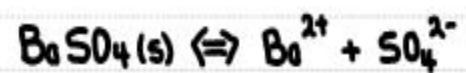
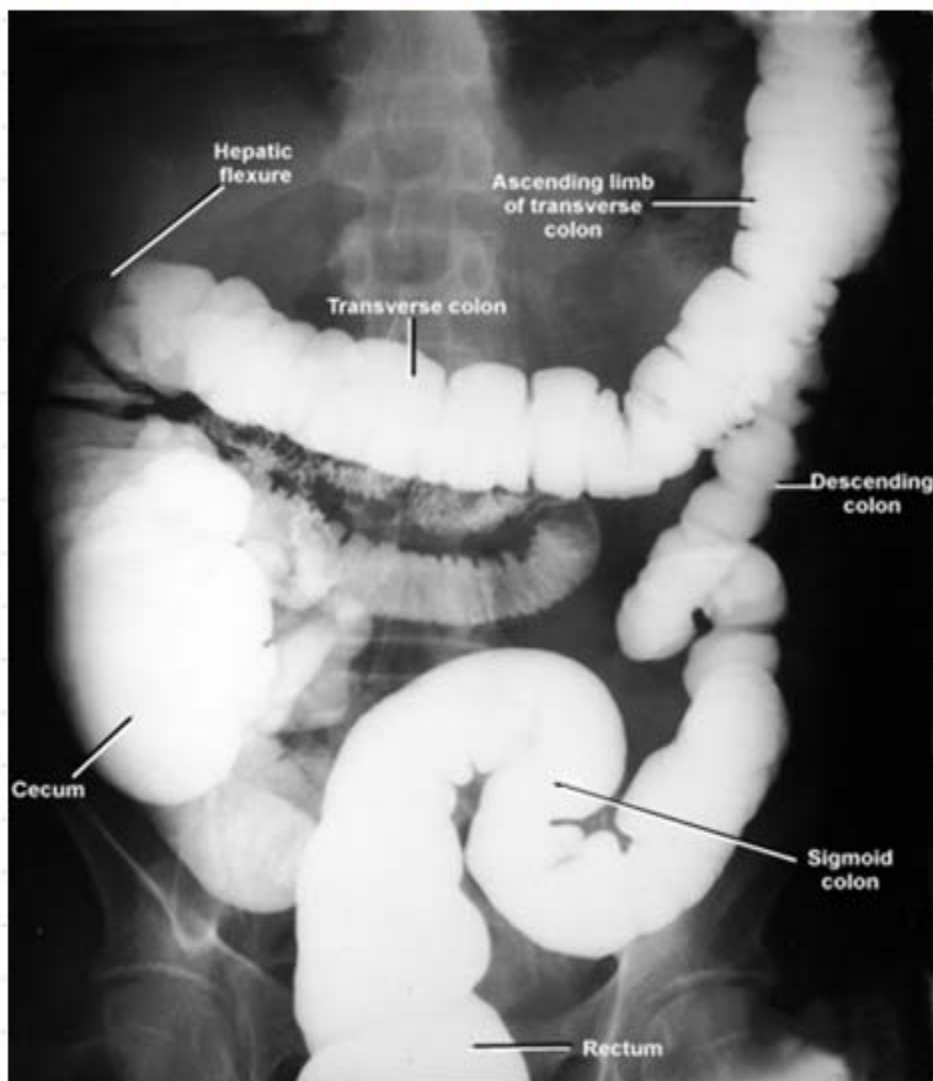
| | | |
|-------------------------------------|--------|--------|
| Initial Concentration (M) | 0.00 M | 0.00 M |
| Change on proceeding to equilibrium | +x | +2x |
| Equilibrium concentration (M) | x | 2x |

Solubility = $x = 1.62 \times 10^{-2} \text{ mol/L}$



18.2 Using K_{sp} in Calculations

The Common Ion Effect – Barium Gastrointestinal Images



$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.1 \times 10^{-10} @ 25^\circ\text{C}$$

Toxicology : 1-15 g ingested.

