18.2 Using Ksp in Calculations

Predicting Whether a Solid Will Precipitate or Dissolve

When 25.0 mL of a 7.02×10^{-4} M iron(III) bromide solution is combined with 22.0 mL of a 2.10×10^{-4} M sodium sulfide solution does a precipitate form?
Ksp Iron(III) sulfide = 1.4×10^{-88}

a) Yes ✓
b) No

$Fe_2S_3(s) \rightleftharpoons 2\,Fe^{3+} + 3\,S^{2-}$

$Q = [Fe^{3+}]^2[S^{2-}]^3$

Total volume when solutions are mixed $25 + 22 = 47$ mL

$[Fe^{3+}]$:

mol $FeBr_3 = 7.02 \times 10^{-4}(0.025)$
$= 1.755 \times 10^{-5}$

$FeBr_3(aq) = Fe^{3+} + 3Br^-$

mol $Fe^{3+} = 1.755 \times 10^{-5}$
$[Fe^{3+}] = 1.765 \times 10^{-5}/0.047 = 3.73 \times 10^{-4}$

$[S^{2-}]$

mol $Na_2S = 2.10 \times 10^{-4}(0.022)$
$= 4.62 \times 10^{-6}$

$Na_2S(aq) = 2\,Na^+ + S^{2-}$

mol $S^{2-} = 4.62 \times 10^{-6}$
$[S^{2-}] = 4.62 \times 10^{-6}/0.047 = 9.83 \times 10^{-5}$

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

18.2 Using Ksp in Calculations

The Common Ion Effect

The Common Ion Effect

See Class Web Site.

Insoluble Salt

- ◉ $PbCl_2$
- ○ AgCl
- ○ CaF_2
- ○ $PbCrO_4$

0.01 g

Common Ion: Cl^-

Soluble Salt

- ◉ NaCl
- ○ KCl
- ○ $NaNO_3$
- ○ $Pb(NO_3)_2$

0.01 M

Solubility: 4.50 g/L

Precipitate: 0.00 g

$[Na^+]$ = 0.00 M

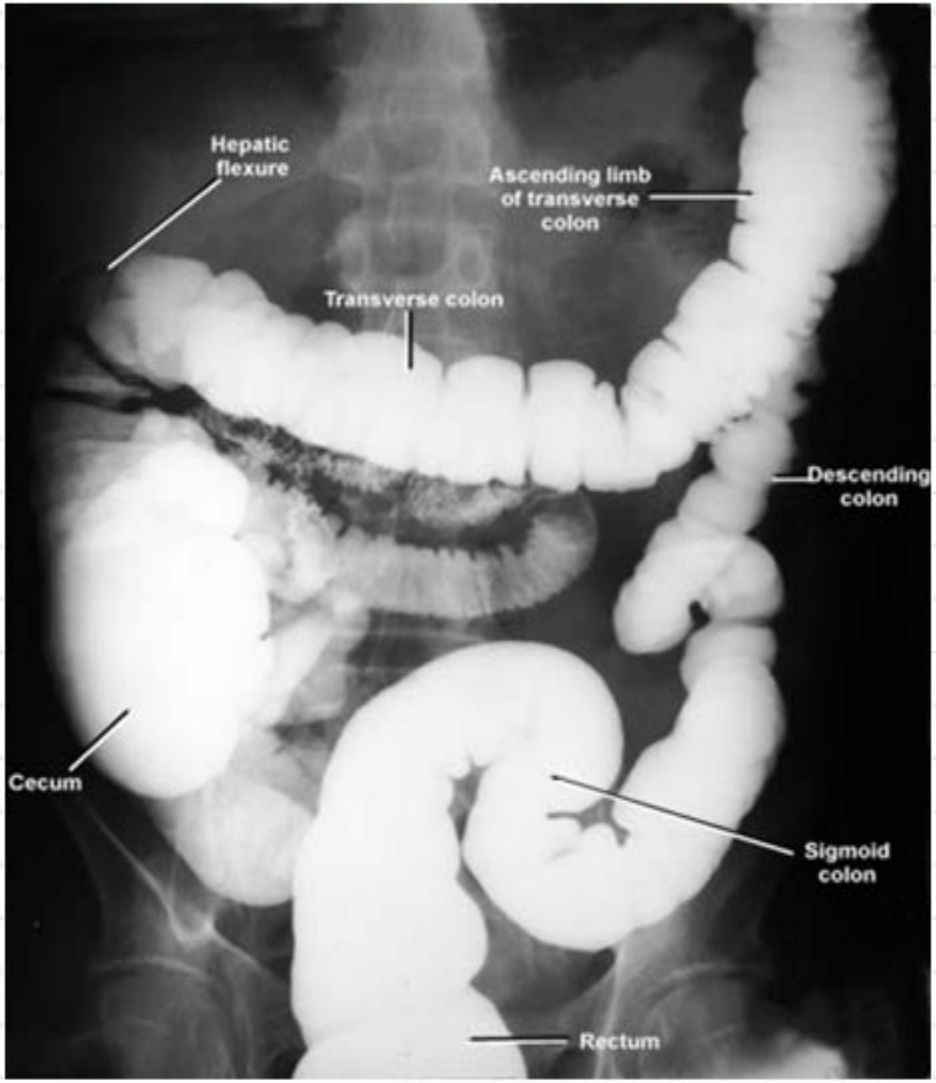
$[Cl^-]$ = 0.00 M

Equation:	$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ Cl^-(aq)$	
Initial Concentration (M)	0.00 M	0.00 M
Change on proceeding to equilibrium	+x	+2x
Equilibrium concentration (M)	x	2x

Solubility = x = 1.62×10^{-2} mol/L

18.2 Using Ksp in Calculations

The Common Ion Effect – Barium Gastrointestinal Images



$BaSO_4(s) \rightleftharpoons Ba^{2+} + SO_4^{2-}$

$K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.1 \times 10^{-10}$ @ 25°C

Toxicology : 1-15 g ingested.

18.2 Using Ksp in Calculations

The Common Ion Effect

a) What is the solubility of $BaSO_4(s)$ in pure water? $K_{sp} = 1.1 \times 10^{-10}$ @ 25°C

b) What is the solubility of $BaSO_4(s)$ in 0.1M Na_2SO_4?

$BaSO_4(s) \rightleftharpoons Ba^{2+} + SO_4^{2-}$

Expected shift ←

	$BaSO_4(s)$	⇌	Ba^{2+}	+	SO_4^{2-}
I	Some		0		0
C	-S		S		S
E			S		S

$K_{sp} = [Ba^{2+}][SO_4^{2-}]$

$1.1 \times 10^{-10} = (S)(S)$

$S^2 = 1.1 \times 10^{-10}$

$S = \sqrt{1.1 \times 10^{-10}} = 1.05 \times 10^{-5}\ mol.L^{-1}$

$BaSO_4$: 233.4 $g.mol^{-1}$

$S = 0.0025\ g.L^{-1}$

$Na_2SO_4(aq) \rightarrow 2\,Na^{+} + SO_4^{2-}$

	$BaSO_4(s)$	⇌	Ba^{2+}	+	SO_4^{2-}
I	Some		0		0.1
C	-S		S		S
E			S		0.1+S

$[SO_4^{2-}]_i > 100\,K_{sp}$: $0.1+S \approx 0.1$

$K_{sp} = [Ba^{2+}][SO_4^{2-}]$

$1.1 \times 10^{-10} = S(0.1)$

$S = 1.1 \times 10^{-9}\ mol.L^{-1}$

$S = 0.00000026\ g.L^{-1}$

18.4 Simultaneous Equilibria

Solubility and pH – Remember me – Le Chatelier's Principle

HCN is a weak acid –

$HCN(aq) + H_2O(l) \Leftrightarrow H_3O^+ + CN^-$ $\quad K_c = 4.0 \times 10^{-10}$ @ 25°C

Addition of OH^- to this equilibrium will cause the $[CN^-]$ to

a) Increase ✓ c) Remain unchanged

b) Decrease d) Impossible to determine

At first look it looks like c) as OH^- is neither a product OR a reactant.

$$HCN(aq) + H_2O(l) \Leftrightarrow H_3O^+ + CN^-$$

$+$

$OH^- = H_2O(l)$

Net result is the removal of a product.

Shift towards products. $[CN^-]\uparrow$

18.4 Simultaneous Equilibria

Solubility and pH

→ Expected equilibrium shift.

$NiCO_3(s) \Leftrightarrow CO_3^{2-} + Ni^{2+}$; $K_{sp} = 1.3 \times 10^{-7}$ @ 25°C in pure water

+

Add acid: $H_3O^+ = HCO_3^- + H_2O(l)$: Strong acid + Weak Base ... 100%

$HCO_3^- + H_2O \Leftrightarrow H_3O^+ + CO_3^{2-}$ $K_a = 5.5 \times 10^{-11}$

Reverse: $H_3O^+ + CO_3^{2-} \Leftrightarrow HCO_3^- + H_2O$ $K = 1.8 \times 10^{10}$ $(1/K_a)$

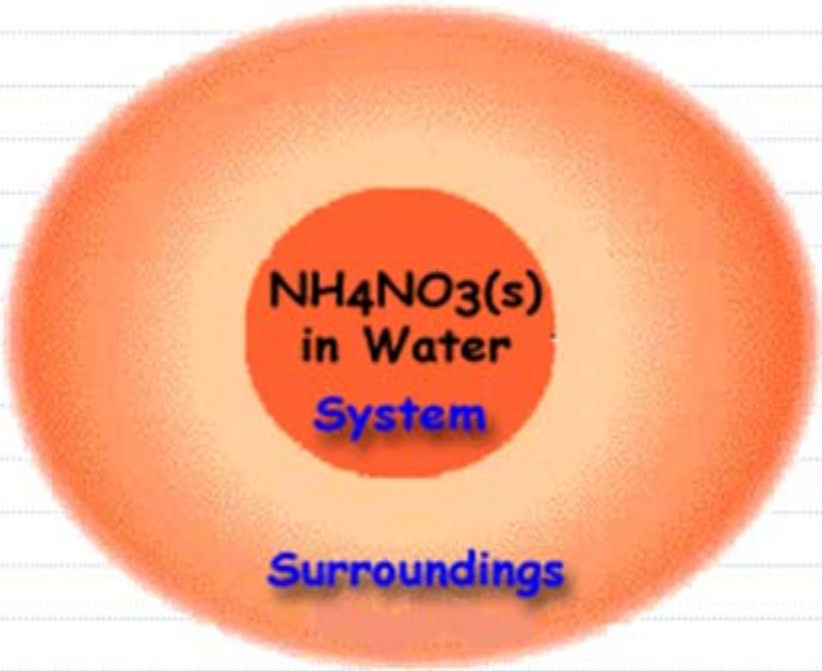
$NiCO_3(s) \Leftrightarrow Ni^{2+} + CO_3^{2-}$ $K_{sp} = 1.3 \times 10^{-7}$

$H_3O^+ + CO_3^{2-} \Leftrightarrow HCO_3^- + H_2O(l)$ $K = 1.8 \times 10^{10}$

$NiCO_3(s) + H_3O^+ \Leftrightarrow Ni^{2+} + HCO_3^- + H_2O(l)$ $K = 2.3 \times 10^{3}$

19.1 Entropy

A Review of Terminology



System: What we are interested in ... the chemical reaction.

Surroundings: Everything else.

Universe = System + Surroundings

Chem III: Heat Transfer (Enthalpy) in the system.

$$\Delta H^\circ_{RXN} = \sum \Delta H^\circ_f \text{(products)} - \sum \Delta H^\circ_f \text{(reactants)}$$

$\Delta H^\circ_{RXN} < 0$: Exothermic

$\Delta H^\circ_{RXN} > 0$: Endothermic

19.1 Entropy

Spontaneous Process V Nonspontaneous Process

Butane burner

Electrolysis of $H_2O(l)$

Spontaneous:

Any process that is able to occur without being continously driven by an external source of energy

- May require an initial input of energy to overcome E_a to get it started.

↑

Requires a continuously external energy source.

Nonspontaneous