18.2 Using Ksp in Calculations

The Common Ion Effect

See Class Web Site

The Common Ion Effect

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

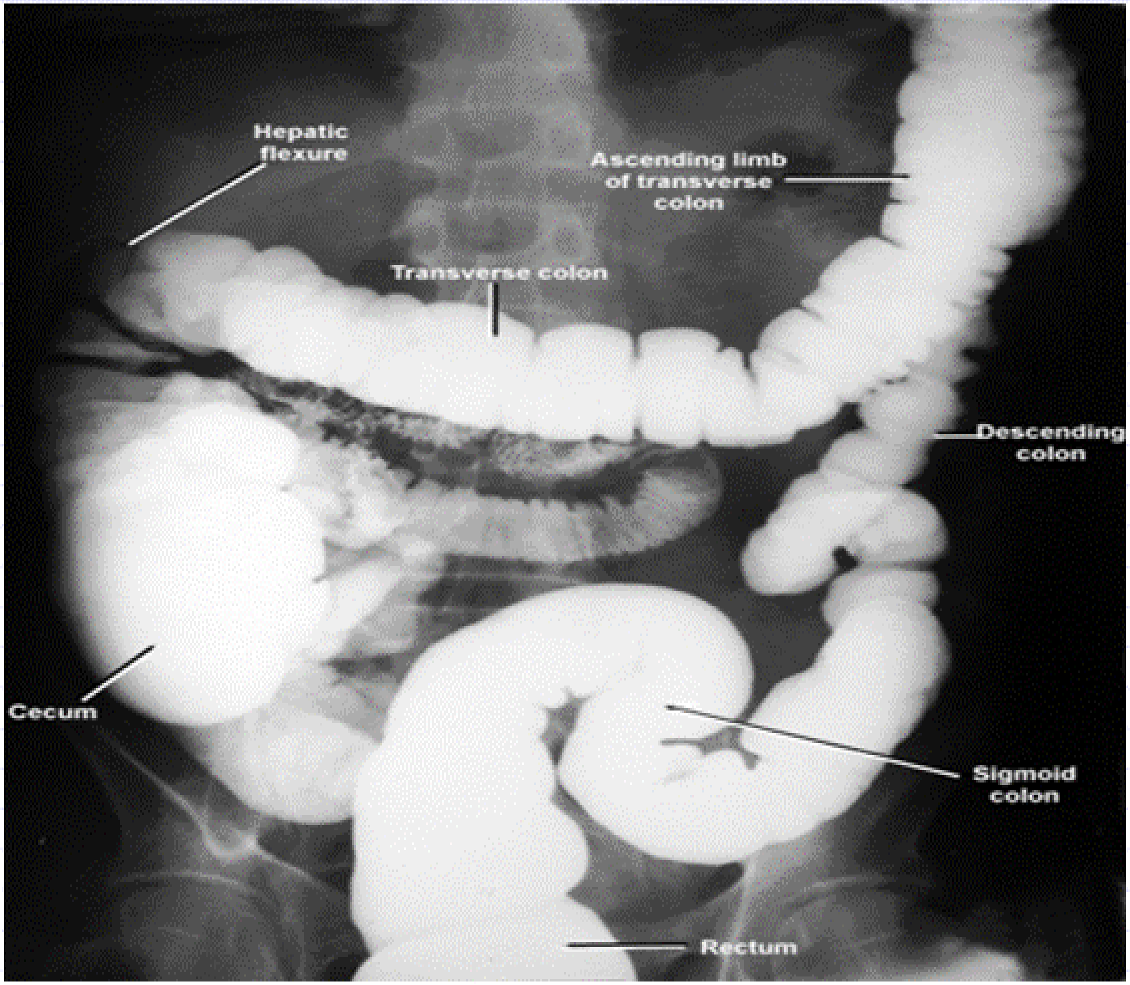
$[Cl^-]$ = 0.00 M

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



$BaSO_{4(s)} \rightleftharpoons Ba^{2+} + SO_4^{2-}$

$K_{sp} = [Ba^{2+}][SO_4^{2-}]$
$= 1.1\times10^{-10}$ @ 25°C

Toxicology : 1-15g ingested

18.2 Using Ksp in Calculations

The Common Ion Effect

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

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

a) In pure water

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

$$Ksp = [Ba^{2+}][SO_4^{2-}]$$
$$1.1 \times 10^{-10} = s(s)$$
$$s^2 = 1.1 \times 10^{-10}$$
$$s = \sqrt{1.1 \times 10^{-10}}$$
$$= 1.05 \times 10^{-5}\ mol.L^{-1}$$

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

s = 0.0025 g.L^{-1}

b) In $Na_2SO_4(aq) = 2Na^+ + SO_4^{2-}$

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

Since $[SO_4^{2-}]_i > 100(1.1 \times 10^{-10})$

$\therefore$ $0.1 + s \approx 0.1$

$$Ksp = [Ba^{2+}][SO_4^{2-}]$$
$$1.1 \times 10^{-10} = s(0.1)$$
$$s = \frac{1.1 \times 10^{-10}}{0.1}$$
$$= 1.1 \times 10^{-9}\ mol.L^{-1}$$

From our previous knowledge on equilibria this is expected.

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

← expected shift

s = 0.00000026 g.L^{-1}

18.4 Simultaneous Equilibria

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

HCN is a weak acid –

$$HCN(aq) + H_2O(l) \Leftrightarrow H_3O^+ + CN^- \qquad Kc = 4.0 \times 10^{-10} @ 25^oC$$

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

a) Increase ✓

b) Decrease

c) Remain unchanged ? ... No

d) Impossible to determine

Remember this from some time ago!

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

At first glance c looked good as OH^- is neither a reactant or product.

But then came the fact: $H_3O^+ + OH^- = H_2O(l)$

Thus the addition of OH^- was in fact removing a product (H_3O^+) and thus the equilibrium would shift towards more products ... $[CN^-]\uparrow$

What has this got to do with solubility? ... It has a hugh effect :)

18.4 Simultaneous Equilibria

Solubility and pH

$NiCO_3(s) \Leftrightarrow Ni^{2+} + CO_3^{2-}$

$K_{sp} = 1.3\times10^{-7}$ @ 25°C

Very little Ni^{2+} in solution :(

But CO_3^{2-} is not a neutral anion, therefore its a weak base

$NiCO_3(s) \Leftrightarrow Ni^{2+} + CO_3^{2-}$: Now add H_3O^+

$CO_3^{2-} + H_3O^+ = HCO_3^- + H_2O(l)$

We are removing a product!
Expect shift towards products.
More Ni^{2+} will go into solution.

? How much more ??

$HCO_3^- + H_2O(l) \Leftrightarrow H_3O^+ + CO_3^{2-}$ $\quad K_a = 5.5\times10^{-11}$

Reverse it: $H_3O^+ + CO_3^{2-} \Leftrightarrow HCO_3^- + H_2O(l)$ $\quad K = 1.8\times10^{10}$ $\quad K = (1/K_a)$

$NiCO_3(s) \Leftrightarrow Ni^{2+} + CO_3^{2-}$	$K_{sp} = 1.3\times10^{-7}$	
$H_3O^+ + CO_3^{2-} \Leftrightarrow HCO_3^- + H_2O(l)$	$K = 1.8\times10^{10}$	
$NiCO_3(s) + H_3O^+ \Leftrightarrow Ni^{2+} + HCO_3^- + H_2O(l)$	$K' = 2.3\times10^{3}$	$K' = K_{sp} \times K$

19.1 Entropy

A Review of Terminology

… From Chem 111 in which you dealt with heat transfer : ΔH

SYSTEM*: What we are interested in.
For a chemist … the chemical reaction.

SURROUNDINGS: Everything else.

UNIVERSE = SYSTEM + SURROUNDINGS

Chem 111: Heat transfer (Enthalpy) in the system.

$$\Delta H^\circ_{RXN} = \Sigma \Delta H^\circ_f \text{(PRODUCTS)} - \Sigma \Delta H^\circ_f \text{(REACTANTS)}$$

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

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

* Disclaimer, if you are a Chemical Engineer then our thermodynamic worlds are reversed.
Chemist … interest is the System.
Engineer … interest is the Surroundings …
which is why they make more $:)

19.1 Entropy

Spontaneous Process V Nonspontaneous Process

Butane Burner

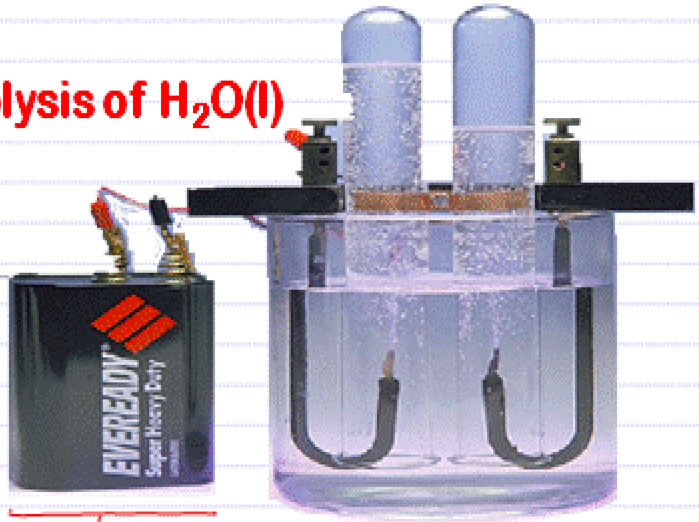
Spontaneous:

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

May require an initial input of energy to overcome the Activation Energy to get it started. Once started it continues until a reactant is consumed.

The butane burner depicted does not start to burn by simply turning on the butane, it needs a spark.

Electrolysis of $H_2O(l)$



Without the continous use of this battery this reaction will not occur.

Nonspontaneous

19.1 Entropy

Enthalpy a Measure of Spontaneity?

Nonspontaneous

$$2\,H_2O(l) = 2\,H_2(g) + O_2(g)$$

$\Delta H^\circ_{RXN} = 2\,\Delta H^\circ_f\,H_2(g) + \Delta H^\circ_f\,O_2(g) - 2\,\Delta H^\circ_f\,H_2O(l)$

$2(0) \quad + \quad 0 \quad - 2(-285.8)$

$= 571.6\ kJ$

Endothermic ☺

Note the red line!
Chem 111 Reminder that the Enthalpy of Formation (ΔH°_f) of any element in its standard state is **zero**.

Both Hydrogen and Oxygen are in their standard state, ie both are diatomics and both are gases.

Spontaneous

$$2\,C_4H_{10}(g) + 13\,O_2(g) = 8\,CO_2(g) + 10\,H_2O(g)$$

$\Delta H^\circ_{RXN} = 8\,\Delta H^\circ_f\,CO_2(g) + 10\,\Delta H^\circ_f\,H_2O(g) - 2\,\Delta H^\circ_f\,C_4H_{10}(g) - 13\,\Delta H^\circ_f\,O_2(g)$

$= 8(-393.5) + 10(-241.8) - 2(-125.6) - 13(0)$

$= -5{,}314.8\ kJ$

Exothermic ☺

$$H_2O(l) = H_2O(g)$$

$\Delta H^\circ_{RXN} = \Delta H^\circ_f\,H_2O(g) - \Delta H^\circ_f\,H_2O(l)$

$= -241.8 - (-285.8)$

$= 44\ kJ$

Endothermic ☹ ... There goes that idea.
As they say, 'back to the drawing board'