Solubility Equilibrium

The Basics (should be mostly review)

Solubility is defined as the maximum amount of a substance which can be dissolved in a given solute at a given temperature. The solubility of a substance is the equilibrium concentration of a given solution at a given temperature.

Saturated solutions are those that can no longer accept any more solute in solution, and are in equilibrium: rate of dissolving = rate of crystallization. Supersaturated solutions have been heated up, and cooled down with a concentration greater than the accepted solubility.

We CAN have molecular solutions (ex. sugar in water) but we will be only working with ionic solutions for this unit.

Many ways to measure concentration of solutions (g/mL, %wt, %vol etc...) but we use molarity (mol/L or M) for concentrations unless otherwise specified. Use square brackets to denote [ ] concentration in M.

Ionic Solutions

Ions form in aqueous solutions from ionic compounds; AKA salts; AKA electrolytes (in solution) – they conduct electricity.

When they dissolve (dissolution) they form aqueous ions in separate cationic and anionic forms.

Dissolving

$$Ag_2CO_{3(s)} \rightleftharpoons 2\ Ag^+_{(aq)} + CO_3{}^{2-}_{(aq)}$$

Crystallization

$$2\ Ag^+_{(aq)} + CO_3{}^{2-}_{(aq)} \rightleftharpoons Ag_2CO_{3(s)}$$

Formulae

Formula Equation (same as grade 10) – disregards that ions dissociate

$$Ca(NO_3)_{2(aq)} + K_2CO_{3(aq)} \rightleftharpoons 2\ KNO_{3(aq)} + CaCO_{3(s)}$$

This is a simple double replacement reaction like you do in grade 10 and 11

Complete Ionic Equation – includes ALL ions

$$Ca^{2+}{}_{(aq)} + 2NO_3{}^{-}{}_{(aq)} + 2K^{+}{}_{(aq)} + CO_3{}^{2-}{}_{(aq)} \rightleftharpoons 2K^{+}{}_{(aq)} + 2NO_3{}^{-}{}_{(aq)} + CaCO_{3(s)}$$

We take in to account that in solution all ionic species (that are dissolved) are actually in aqueous ionic form; separated and not part of a crystal. Notice that there are 2 nitrate and 2 potassium ions on BOTH sides of the equation… these do not take place in the reaction and are known as "spectator ions"

Net Ionic Equation – omits spectator ions (only ions involved in reaction)

$$Ca^{2+}{}_{(aq)} + CO_3{}^{2-}{}_{(aq)} \rightleftharpoons CaCO_{3(s)}$$

Since the nitrate and potassium ions are not involved in the reaction, we remove them from the equation.

Predicting Solubility

Using the solubility chart (found on your data tables, and in the back of the text) we can determine if a combination of anion and cation will be soluble. Alkali ions, ammonium, and hydrogen are universally soluble cations, and nitrate is a universally soluble anion.

Ex.	Calcium and chloride	soluble
	Uranium and sulphite	non-soluble
	Strontium and hydroxide	soluble
	Momeyerium and nitrate	soluble

Homework questions on pages 73-87 in Hebden, Questions 1-25

Qualitative Analysis (III.5 in Hebden)

Imagine you have a sample of unknown concentration, but you know that it contains the toxic metals; Pb^{2+} and Ba^{2+}. Is there a way to isolate the two cations so you can analyze the concentrations?

Then look at all the anions that can be combined using the solubility table. The trick is finding an anion that will precipitate ONLY one of these cations.

	NO_3^-	Cl^-, Br^-, I^-	SO_4^{2-}	S^{2-}	OH^-	CO_3^{2-}, PO_4^{2-}, SO_3^{2-}
Pb^{2+}	--	ppt	ppt	ppt	ppt	ppt
Ba^{2+}	--	--	ppt	--	ppt	ppt

So we could add Cl^-, Br^-, I^- or S^{2-} with a non-precipitating cation (alkali ion, H^+ or NH_4^+) **Ex.** HCl or Na_2S could be added (you can't just add Br^- ions)

Try these examples below to see if you really understand what's going on:

Ex. A sample containing: Sr^{2+} and Ag^+...

A sample containing: Ca^{2+} and U^{3+}...

A sample containing: CO_3^{2-} and SO_4^{2-} ...

A sample containing: OH^- and SO_3^{2-} ...

Homework questions on pages 88-91 in Hebden, Questions 26-39

The Solubility Product Constant (K_{sp})

Low solubility compounds form an $Eq^{\underline{m}}$ between the solid & its aqueous ions.

$$\text{Solid} \rightleftharpoons n(\text{cations}) + m(\text{anions})$$

$$K_{eq} = [\text{cations}]^n + [\text{anions}]^m$$

If both [ion] are large then the K_{sp} is large and implies a high solubility

A. Examples finding solubility

Ex. Find the solubility of copper (I) iodide; $K_{sp} = 1.3 \times 10^{-12}$

$CuI_{(s)} \rightleftharpoons Cu^{+}_{(aq)} + I^{-}_{(aq)}$ $\qquad K_{sp} \neq \frac{[Cu^+][I^-]}{[CuI]}$ (<u>don't include solids</u>)

$K_{sp} = [Cu^+][I^-] = 1.3 \times 10^{-12}$

Because there is 1 Cu^+ ion for every 1 I^- ion their [ ]'s will be equal, we can call this [ ] = **x**

$\mathbf{x} \cdot \mathbf{x} = 1.3 \times 10^{-12}$ $\qquad \sqrt{X^2} = \sqrt{1.3x10^{-12}}$

$\mathbf{x} = 1.1 \times 10^{-6}$ M

Ex. Find the solubility of lead (II) chloride; $K_{sp} = 1.2 \times 10^{-5}$

$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$

Ex. Find the solubility of $Al(OH)_3$; $K_{sp} = 3.7 \times 10^{-15}$

B. The Reverse: Calculating K_{sp} from solubility (Easier)

Ex. Saturated solution of $PbSO_4$ has a $[Pb^{2+}] = 1.05 \times 10^{-4}$ M,
Find K_{sp}

Since $[Pb^{2+}] = [SO_4^{2-}]$
therefore K_{sp} expression = $[Pb^{2+}][SO_4^{2-}]$

Ex. Saturated solution of $PbCl_2$ has $[Pb^{2+}] = 3.56 \times 10^{-2}$ M,
Find K_{sp}

C. Finding the Concentration of Another Ion

Ex. Saturated solution of $PbSO_4$ has a $[Pb^{2+}] = 1.0 \times 10^{-3}$ M,
if $K_{sp} = 1.8 \times 10^{-8}$ what's the max $[SO_4^{2-}]$?

Ex. A solution of $PbCl_2$ has $[Pb^{2+}]$ = 2.0 x 10^{-3} M, the K_{sp} = 1.2 x 10^{-5}. What's the max $[Cl^-]$?

D. Trial Ion Product (TIP or *Q*)

We use the TIP to determine IF a ppt (precipitate) will form when two ionic solutions are mixed.

Use the same K_{sp} equation and just "plug-in" the values to get the TIP

If Q is smaller than K_{sp} then there are less products than required to establish an equilibrium and no ppt forms.

IF:

$Q < K_{sp} \rightarrow$ no ppt
$Q = K_{sp} \rightarrow$ saturated solution (but no ppt)
$Q > K_{sp} \rightarrow$ ppt forms & $eq^{\underline{m}}$ forms

Ex. Will a ppt form if 100.0mL of 0.10M Fe^{3+} is added to a solution of 1.0L of 0.0020M OH^-?

$Fe(OH)_{3(s)} \rightleftharpoons Fe^{3+}{}_{(aq)} + 3OH^-{}_{(aq)}$ & $K_{sp} = [Fe^{3+}][OH^-]^3$

$[Fe^{3+}] \rightarrow \boldsymbol{M_i \times V_i = M_f \times V_f} \rightarrow \frac{0.1000\ \text{L x } 0.10\ \text{M}}{1.1\ \text{L}} = 0.0091\ \text{M}$

$[OH^-] = \frac{1.0\ \text{L x } 0.0020\ \text{M}}{1.1\ \text{L}} = 0.0018\ \text{M}$

$Q = (0.0091)(0.0018)^3 = 5.5 \times 10^{-11}$

K_{sp} (from the booklet) = 2.6 x 10^{-39}

<u>Because **$Q > K_{sp}$** therefore a **ppt forms** (YES)</u>

Ex. Will a ppt form if 25.0mL of 1.0×10^{-4} M $ZnCl_2$ is added to 45.0mL of 1.0×10^{-3} M Na_2S?

$ZnS_{(s)} \rightleftharpoons Zn^{2+}{}_{(aq)} + S^{2-}{}_{(aq)}$ & $K_{sp} = [Zn^{2+}][S^{2-}]$

Ex. If a 0.10M Ag^+ solution is added dropwise to a solution containing: 0.10M Cl^-, 0.10M $SO_4{}^{2-}$, 0.10M OH^- different ions

K_{sp}	Ag_2SO_4	$= 1.2 \times 10^{-5}$
	AgOH	$= 1.5 \times 10^{-8}$
	AgCl	$= 1.8 \times 10^{-10}$

E. Common Ion Effect

Recall that ***Solubility*** is the amount of a given solid that dissolves in a liter of solution. Therefore:

⇑ Solubility = more solid dissolves (⇑ rate shift towards products →)
⇓ Solubility = more solid crystalizes (⇓ rate shift towards reactants ←)

$$AB_{(s)} \rightleftharpoons A^{+}_{(aq)} + B^{-}_{(aq)}$$

So, if we can increase rate of dissolving we ⇑ solubility.
if we can increase rate of crystallization we ⇓ solubility.

According to Le Chatelier if we stress one side of the eq$^{\underline{m}}$ it shifts to relieve the stress. So if we add an ion (A^+ or B^-) the eq$^{\underline{m}}$ shifts to make a solid (AB): ⇓ solubility.

If we remove an ion the eq$^{\underline{m}}$ shifts to make more ions: ⇑ solubility.

Ex. Will the solubility of $AgCl_{(aq)}$ ***increase or decrease*** if we add:

$$AgCl_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$$

a. $AgNO_{3(aq)}$

b. $NaCl_{(aq)}$

c. $AgCl_{(s)}$

d. $NaOH_{(aq)}$

e. $KBr_{(aq)}$

f. $KNO_{3(aq)}$

g. $Pb(NO_3)_{2(aq)}$

h. Adding H_2O