EQUILIBRIUM CONSTANT – K_{SP}

This is equilibrium that deals only with the solubility of salts (ionic solids)

- **Insoluble** is defined as anything that dissolves 3g per 100 g of water.
- If something is "suppose to dissolve" it may not, if enough is not added to the solution.
- Insoluble substances MAY dissolve, it is just such a small amount, Ksp tells how much!!
- In other word, soluble and insoluble are not absolute terms.

Example: copper (II) chloride dissolves as follows:

$CuCl_2 \leftarrow\rightarrow Cu^{2+} + 2\ Cl^-$

$Ksp = [Cu^{2+}][Cl^-]^2$ Your solid salt **does not** factor in the equilibrium expression

If a substance has a low Ksp value = less soluble

SOLUBILITY

The solubility rules are not always correct…

Slightly soluble salts establish a dynamic equilibrium.

- Initially when a solid is added to water, **no ions are present**
- As dissolution occurs, the concentration of ions increase until equilibrium is reached.

Solubility Rules
Mnemonic Tricks

Always Soluble NAG SAG	Exceptions PMS and Castro Bear
Nitrates (NO_3^-)	**P** (Pb^{2+}, lead)
Acetates ($C_2H_3O_2^-$)	**M** (mercury, Hg^{2+})
Group 1 (Li^+, Na^+, etc.)	**S** (silver, Ag^+)
Sulfates (SO_4^{2-})	**Ca** $^{2+}$
Ammonium (NH_4^+)	**Sr** $^{2+}$
Group 17 (F^-, Cl^-, etc.)	**Ba** $^{2+}$

sciencenotes.org

- All group 1 salts, all nitrates, all acetates are all soluble
  - the rest below, in theory, should have Ksp values given to determine the solubility.
- All of the halides (group 17) are soluble, except PMS which will precipitate
- Sulfates generally soluble – except PMS and Castro Bear, which form precipitates
- hydroxides - most form precipitates, except Group 1 and Castro Bear dissolve
- Carbonates – Almost all form precipitates, except group 1 and Ammonium will dissolve

RELATIVE SOLUBILITIES – EFFECT K_{SP}

Make sure you can translate names of compounds into a formula

This affects how your proposed salt will dissolve → which in turn affects your **stoichiometry** → which in turn affects your **equilibrium expression**

If the salts being compared produce the same number of ions in solution

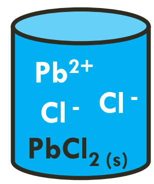
Ksp can be used to directly compare solubility

- NaCl(s), KF(s) → *Ksp* = [cation][anion] = x^2

If the salts being compared produce different numbers of ions

Ksp cannot be directly compared

- Ag_2S(s) → *Ksp* = $[2x]^2[x]$
- Bi_2S_3(s) → *Ksp* = $[2x]^2[3x]^3$



DETERMINING K_{SP}

If the ion concentration is found in a lab setting, that can be used to determine the Ksp of a compound.

Example:

Calculate the Ksp, if the Pb^{+2} concentration in the equation below is 1.62×10^{-2} M

$PbCl_2 \leftarrow\rightarrow Pb^{+2} + 2Cl^-$

Since there are 2 moles of Cl^- then simply multiply the Lead concentration by 2 (think stoich)

Thus $Cl^- = 2(1.62 \times 10^{-2} M) = 3.24 \times 10^{-2} M$

Then use the Ksp expression… $Ksp = [Pb^{+2}][Cl^-]^2$ (raised by 2 because of the mole ratio)

$Ksp = (1.62 \times 10^{-2})(3.24 \times 10^{-2})^2 = 1.70 \times 10^{-5}$ M

The concentration of Br^- in a solution saturated with $PbBr_2(s)$ is 4.28×10^{-2} M. Calculate Ksp for $PbBr_2$

$$PbBr_2(s) \rightarrow Pb^{2+}(aq) + 2\ Br^-(aq)$$

$$Ksp = [Pb^{2+}][Br^-]^2$$

I	0	0
C	+x	+2x
E	x	2x

$$Ksp = (x)(2x)^2$$

$x = 2.14 \times 10^{-2}$ M

$2x = 4.28 \times 10^{-2}$ M

$$Ksp = (2.14 \times 10^{-2})\ (4.28 \times 10^{-2})^2$$

$$Ksp = 3.92 \times 10^{-5}$$

QUALITATIVE ANALYSIS

Example:

You have silver nitrate (soluble), calcium nitrate (soluble), and potassium nitrate are in solution together. You want the silver to drop out first and the calcium to drop out second. You don't want to lose the potassium at all.

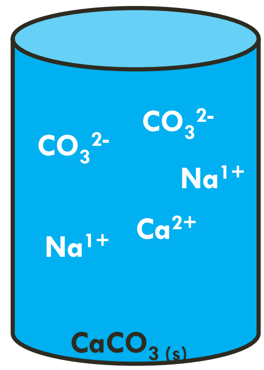
Suggest an approach to accomplish your goal?

Answer (one way) –

1. Add any sort of chloride (KCl would work) - the silver will precipitate out as AgCl. You can decant your solution.
2. Now you are left with potassium ions, calcium ions, nitrate ions, and chloride ions. Calcium will form a lot of insoluble salts. Take your pick of reagents, NaOH is easy. Calcium hydroxide is very insoluble.
3. Now you only have potassium ions in solution. You have accomplished your goal.

There are many ways, this is just one approach

COMMON ION EFFECT



If you add a solid to water (or any solvent) -- Like calcium carbonate ($CaCO_3$). It is not very soluble on its own, but a little will dissolve.

You'll have (in your beaker), mostly water, solid calcium carbonate, and a little ionic calcium (2+) and ionic carbonate (2-).

To see the equation: $CaCO_3 \leftarrow\rightarrow Ca^{2+} + CO3^{2-}$

Next let's dissolve some Na_2CO_3 in solution (which is soluble).

Now we have plenty $CO_3{}^{2-}$ in solution. How much $CaCO_3$ dissolves now? (more or less?)

Answer?

Even less. Remember, this is equilibrium. We don't care how extra carbonate got there. It just got there. Calcium carbonate has a small Ksp. One of the two product is already in solution. That makes it harder for calcium carbonate to dissolve.

Don't let the specialized name confuse you. It's an equilibrium effect, plain and simple.

Calculate the solubility of $Ce(IO_3)_3$ in a 0.20 M KIO_3 solution.
$Ce(IO_3)_3$ Ksp is 3.5×10^{-10}

$$Ce(IO_3)_3(s) \rightarrow Ce^{3+}(aq) + 3\ IO_3^-(aq)$$

$$Ksp = [Ce^{3+}][IO_3^-]^3$$

I	0	0.20 M
C	+x	+3x
E	x	0.20M + 3x

$$3.5 \times 10^{-10} = (x)(0.20\ M + 3x)^3$$

Assume: 3x is negligible since Ksp is so small compared to 0.20 M

$$3.5 \times 10^{-10} \approx (x)(0.20\ M)^3$$

$$x = 4.38 \times 10^{-8}\ M$$

REACTION QUOTIENT (Q) AND KSP

Determined the same way as before but new "meanings"

- **If Q > Ksp** – precipitate forms (supersaturated solution)
- If **Q < Ksp** – no precipitate forms (unsaturated solution)
- If **Q = Ksp** – it's at equilibrium (no precipitate) (saturated solution)

This is used to determine if a precipitate will be formed in a solution

Steps:

1. Calculate the Cation and Anion concentrations after the solutions have mixed.
   - Use $M_1V_1 = M_2V_2$ for each ion.
2. Place into the Q expression and solve
3. Use the above conditions compared to K to see if a precip is formed.

Will a precipitate form when :
50.0 mL of 0.20 M $Ca(NO_3)_2$ is added to 50.0 mL of 0.30 M Na_3PO_4
(Ksp for $Ca_3(PO_4)_2$ = 1.3 x 10^{-32})

$Ca_3(PO_4)_2 = 3Ca^{2+} + 2\,PO_4^{3-}$

$$M_1V_1 = M_2V_2$$

$Ca^{2+} \rightarrow (0.20\ M)(50.0\ mL) = x(100.0\ mL)$

$Ca^{2+} \rightarrow x = 0.10\ M$

$$M_1V_1 = M_2V_2$$

$PO_4^{3-} \rightarrow (0.30\ M)(50.0\ mL) = x(100.0\ mL)$

$PO_4^{3-} \rightarrow x = 0.15\ M$

$Q = \left[Ca^{2+}\right]^3 \left[PO_4^{3-}\right]^2$

$Q = \left[0.10\ M\right]^3 \left[0.15\ M\right]^2$

$Q = 2.3 \times 10^{-5}$

$Q > Ksp$

ppt will form