

Chemistry 12

Unit III - Solubility

I) Ionic & Covalent Solutions

What is a **solution**?

a homogeneous mixture

homogeneous \Rightarrow one phase

mixture \Rightarrow mix of two or more different types of particles

What are some examples of different types solutions?

solid-solid: metal alloys like brass, steel

liquid-gas: soft drinks

liquid-solid: salt water

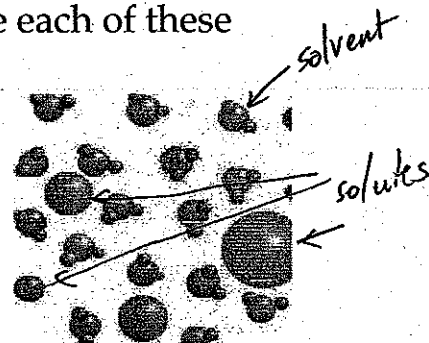
gas-gas: air

liquid-liquid: alcohol + water

Solutions are made up of **solute(s)** and a **solvent**. Define each of these terms:

solute: the component(s) in a solution in lesser amount

solvent: the component in a solution in greatest amount



What is the difference between an **ionic solution** and a **covalent solution**?

ionic solution: an ionic salt in water (table salt in water)

covalent solution: a covalent substance dissolved in water (sugar in water)

What is a salt and what composes a salt?

A salt is an ionic compound composed of metal cations and non-metal anions in a crystal lattice

How does a solid salt such as $\text{NaCl}_{(s)}$ dissolve in water?

http://highered.mcgraw-hill.com/sites/0072512644/student_view0/chapter4/animations_center.html (hydration)

http://preparatorychemistry.com/Bishop_Solubility_frames.htm

<http://mutuslab.cs.uwindsor.ca/schurko/animations/nacl/solutionSalt.htm>

- water molecules collide with the crystal lattice and knock Na^+ cations and Cl^- anions into solution
- water molecules surround the cations and anions

When a salt dissolves in water, it can be described as **dissolving**, but a more accurate term is **dissociation**. Why?

NaCl does not dissolve in water as an NaCl unit. Instead, it dissociates (breaks apart) into Na^+ cations and Cl^- anions.

Sometimes, $\text{NaCl}_{(\text{aq})}$ is used to depict a salt in solution (after dissociation).

How come this is an inaccurate way of writing it?

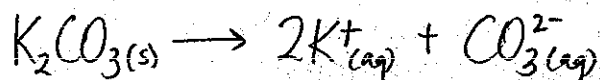
When NaCl is in solution, the sodium and chloride are no longer together. A more accurate description is $\text{Na}^+_{(\text{aq})} + \text{Cl}^-_{(\text{aq})}$.

Dissociation Equation for a salt: $\text{NaCl}_{(\text{s})} \Rightarrow \text{Na}^+_{(\text{aq})} + \text{Cl}^-_{(\text{aq})}$

*In the solubility unit, always write states when writing equations

Compounds that contain polyatomic **ions** are obviously ionic in nature (salts) and would dissociate in water to form ions.

Write the dissociation equation for $\text{K}_2\text{CO}_3_{(\text{s})}$ dissolving in water:



Ions in solution are called electrolytes. Ions, or electrolytes are what allow an ionic solution to conduct electricity.

http://highered.mcgraw-hill.com/sites/0072512644/student_view0/chapter4/animations_center.html#

What is a **molecular** or **covalent** compound composed of?

non-metals i.e. a sugar molecule: $\text{C}_6\text{H}_{12}\text{O}_6$ (C, H, O all non-metals)

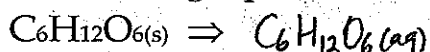
What is different about molecular compounds when they dissolve in water compared to ionic compounds?

Molecular compounds dissolve as whole molecules. They don't dissociate into ions.

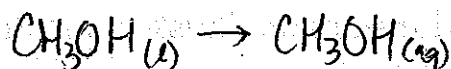
Diagram of sugar ($C_6H_{12}O_6$) dissolving in water:



Example of a dissolving equation for a molecular compound in water:



Write the dissolving equation for CH_3OH (methanol) in water:



Do molecular solutions conduct? Why or why not?

No. They do not create ions in solution

http://highered.mcgraw-hill.com/sites/0072512644/student_view0/chapter4/animations_center.html

What do we call dissolved molecular compounds?

non-electrolytes

II) Solubility

What is a saturated solution?

a solution that has the maximum amount of solute dissolved.

How can you recognize a saturated solution visibly?

you will see undissolved solute at the bottom of the container

*If the excess undissolved solute is filtered off, you can still have a saturated solution with no visible undissolved solute on the bottom

Is a saturated solution static or dynamic?

dynamic \rightarrow it looks static, but particles are continually dissolving as well as re-crystallizing.

What kind of system is a saturated solution?

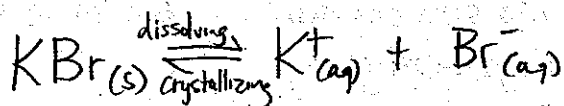
equilibrium

the rate of dissolving EQUALS the rate of crystallization

Therefore, does the amount of undissolved salt at the bottom of a saturated solution change?

No, however much is dissolving, that same amount is simultaneously re-crystallizing

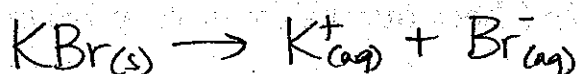
How can a saturated solution equation be written for a saturated solution of KBr?



Explain the difference between the rate of dissolving and rate of precipitation for an **unsaturated** solution:

rate of dissolving > rate of precipitation \therefore eventually all solute dissolves

Write an unsaturated solution equation for KBr:



What's another name for this equation?

dissociation equation

How do the saturated and unsaturated equations differ?

saturated \Rightarrow double arrow

unsaturated \Rightarrow single arrow

Solubility: the solubility of a substance is a quantitative value.

What is it? the molarity at saturation.
(concentration)

Therefore, solubility can only be measured for what types of solutions?

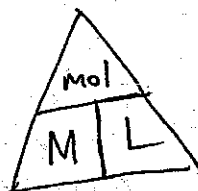
Saturated solutions

What is 'concentration' in chemistry terms?

how much solute is in a certain volume of solution

Concentration is most commonly measured using

$$\text{Molarity (M)} = \frac{\text{moles of solute (mol)}}{\text{litres of solution (L)}}$$



Concentration can also be measured using mass of solute/volume (g/L or g/mL) of solution, as you may see in some examples.

Every salt dissociates to some extent in water, but every salt has a different solubility in water. What does this mean?

- every ionic salt will make a solution in water. However, some become saturated very quickly (at a low molarity) whereas other salts can dissolve quite a lot in water before making a saturated solution (at a high molarity)

Some salts can dissociate to a large extent before becoming saturated, while other salts dissociate very little before becoming saturated.

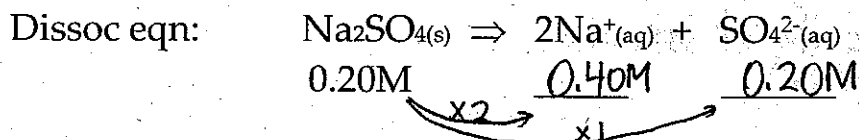
Solubility is also temperature dependent. A general rule for solid-liquid solutions is that solubility increases with increasing temperature.

Assignment 1: Read pages 73-76 (check out the comic on p.76) in Hebden and do Questions #1-5

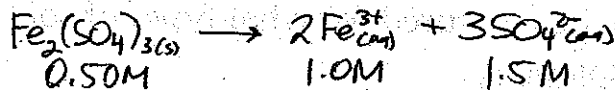
III) Calculating Solubility and Ion Concentrations

Use stoichiometry to calculate the concentration of ions given the concentration of solute.

Calculate $[Na^+]$ and $[SO_4^{2-}]$ in a 0.20M solution of $Na_2SO_4(aq)$



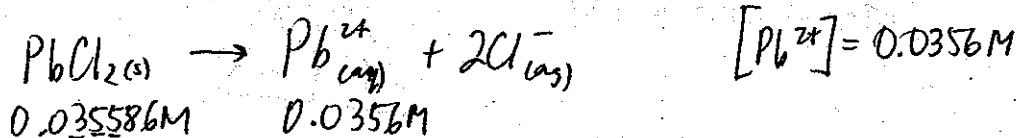
Calculate $[Fe^{3+}]$ and $[SO_4^{2-}]$ in a 0.50M solution of iron III sulphate:



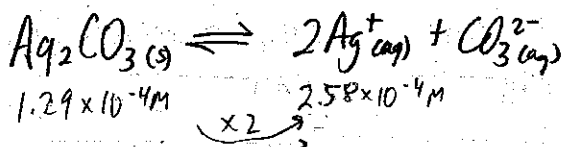
Fe^{3+} SO_4^{2-}
 Fe^{3+} SO_4^{2-}
 SO_4^{2-}

A saturated solution of $PbCl_2$ is found to contain 9.90g of $PbCl_2$ per litre of solution. Find $[Pb^{2+}]$. *change grams to moles, then to M. Then write dissoc eqn and use stoich:

$$\frac{9.90g PbCl_2}{278.2g} \times \frac{1 mol PbCl_2}{1 mol PbCl_2} = 0.035586 mol PbCl_2 \quad [PbCl_2] = \frac{0.035586 mol}{1.00 L} = 0.035586 M$$



Write an equation showing the equilibrium in a saturated solution of silver carbonate. The solubility of Ag_2CO_3 is $1.29 \times 10^{-4} \text{ M}$. Find $[\text{Ag}^+]$ in grams per 100.0mL:



$$\frac{2.58 \times 10^{-4} \text{ mol Ag}^+}{1 \text{ mol Ag}^+} \times \frac{107.9 \text{ g Ag}^+}{1 \text{ mol Ag}^+} = 0.0278 \frac{\text{g Ag}^+}{\text{L}}$$

$$0.0278 \frac{\text{g Ag}^+}{\text{L}} \div 10 = 0.00278 \frac{\text{g}}{100.0 \text{ mL}}$$

A 558mL solution of $\text{Al}_2(\text{SO}_4)_3$ has a concentration of 0.0342M. You then add 325mL of water to it. What is the new concentration?

dilution: $M_i V_i = M_f V_f$

$$M_i = 0.0342 \text{ M}$$

$$V_i = 0.558 \text{ L}$$

$$V_f = 558 + 325 = 883 \text{ mL} = 0.883 \text{ L}$$

$$(0.0342 \text{ M})(0.558 \text{ L}) = M_f (0.883 \text{ L})$$

$$M_f = \underline{0.0216 \text{ M}}$$

$$[\text{Al}_2(\text{SO}_4)_3]_f = \underline{0.0216 \text{ M}}$$

250mL of 0.30M K_2SO_4 and 250mL of 0.80M MgCl_2 are mixed and no precipitate (solid) forms. Calculate the concentration of each ion in the final solution.

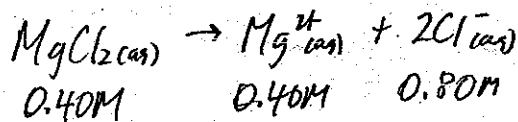
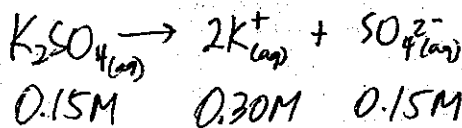
dilution:

$$[\text{K}_2\text{SO}_4]_f = \frac{(0.30 \text{ M})(0.25 \text{ L})}{0.50 \text{ L}}$$

$$= 0.15 \text{ M}$$

$$[\text{MgCl}_2]_f = \frac{(0.80 \text{ M})(0.25 \text{ L})}{0.50 \text{ L}}$$

$$= 0.40 \text{ M}$$



$$[\text{K}^+] = 0.30 \text{ M} \quad [\text{Mg}^{2+}] = 0.40 \text{ M}$$

$$[\text{SO}_4^{2-}] = 0.15 \text{ M} \quad [\text{Cl}^-] = 0.80 \text{ M}$$

Assignment 2: Hebden p.77 # 8, 9 & p.78 #13 & p.81 #18a-d, 20abfg

IV) Using the Solubility Table

The solubility table in the data booklet is used to predict whether a salt is **soluble** in water or **low solubility** in water. **Soluble** salts can dissociate and produce a solution of at least 0.1M before becoming saturated. **Low Solubility** salts dissociate very little as they become saturated before reaching 0.1M.

Identify three soluble salts, and three low solubility salts using the table:

SOLUBLE

NaCl
K₂SO₄
Sr(OH)₂

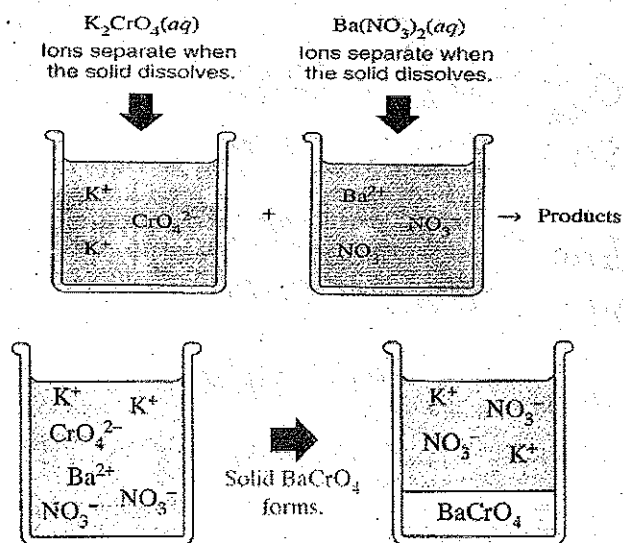
LOW SOLUBILITY

AgCl
CaSO₄
BaCO₃

If two ions that are low solubility with one another are put into the same solution and the resulting concentration exceeds the solubility for that salt (molarity of saturation for that salt), then some of those cations & anions will form together and precipitate (form a solid)

out of solution until the ions have reached their saturation molarity.

Precipitate: a solid that forms from a solution due to the mixing of two ions that originated in different solutions, but when mixed together, became 'oversaturated'.



Ba^{2+} and CrO_4^{2-} low solubility together, meaning their molarity at saturation (their solubility) is very low. So some of them will form together as a solid ($BaCrO_4$) and ppt out of solution. A small amount of Ba^{2+} and CrO_4^{2-} ions will remain in solution (the saturated molarity will remain).

<http://www.absorblearning.com/media/item.action?quick=uu>
http://preparatorychemistry.com/Bishop_Solubility_frames.htm

Is it possible that a soluble salt could form a precipitate?

Yes. Any salt will precipitate if its solubility (molarity of saturation) is exceeded.

eg. solubility of NaCl is 6.15M @ 25°C which is about 360g in 1L. What if you put 500g into 1L?

So, saturated solutions of a salt (for example, PbCl_2) can be created in two different ways. What are they?

- ① Add solid PbCl_2 to water until no more PbCl_2 dissolves and just sinks to the bottom
- ② You can mix two solutions - one with Pb^{2+} ions, such as $\text{Pb}(\text{NO}_3)_2$ (aq), and another with Cl^- ions, such as NaCl (aq). If the Pb^{2+} and Cl^- ions are 'oversaturated' when mixed together, a precipitate of PbCl_2 will form, leaving a saturated solution of PbCl_2 (as well as having Na^+ and NO_3^- ions present).

Using your table, which ions are soluble with all other ions?

Alkali ions: Li^+ , Na^+ , K^+ , Cs^+ , Rb^+ , Fr^+ soluble with all anions

H^+ is soluble with all anions

NH_4^+ " " " " "

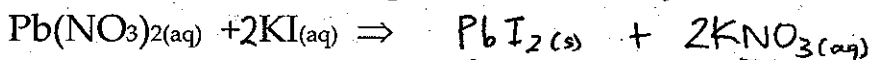
NO_3^- is soluble w/ all cations.

Use your table to predict whether the following salts are soluble, or low solubility (meaning they are likely to form a ppt):

- | | |
|--------------------------|----------------------------|
| 1. Sodium hydroxide S | 2. Ammonium acetate S |
| 3. Calcium sulphate LS | 4. Lead II chloride LS |
| 5. Potassium chloride S | 6. Calcium bromide S |
| 7. Potassium carbonate S | 8. Aluminum sulphate S |
| 9. Lead sulphide LS | 10. Copper II sulphate S |
| 11. Iron II sulphide LS | 12. Barium hydroxide LS |
| 13. Silver bromide LS | 14. Magnesium carbonate LS |
| 15. Copper II chloride S | 16. Copper I chloride LS |

http://highered.mcgraw-hill.com/sites/0072512644/student_view0/chapter4/animations_center.html

i) Will a precipitate form if equal volumes of the following 0.2M solutions are mixed? *do the double replacement and use your table



low solubility on table, so will form a ppt

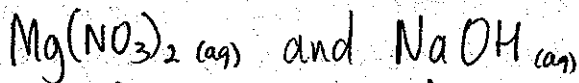
soluble on table - stays aqueous

if equal volumes mixed, molarities diluted to 0.1M, thus anything low solubility will precipitate.

Yes, PbI_2 .

ii) Which 2.0M soluble solutions could be mixed in order to produce a precipitate of $\text{Mg}(\text{OH})_2$?

need to mix two solutions → one with Mg^{2+} and one with OH^-

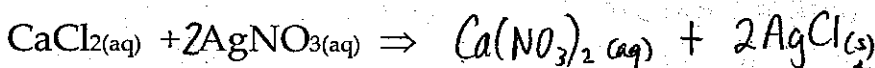


soluble with all cations soluble with all anions.

Assignment 3: Hebden p.83 #21, 22 & p. 84 #24

V) Formula, Complete, and Net Ionic Equations

Formula Equation (double replacement equation):

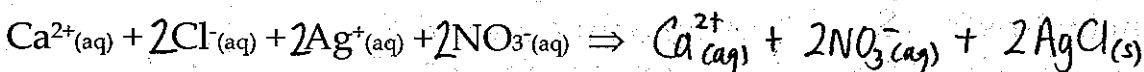


low solubility on table, so it ppts.

Complete Ionic Equation:

In reality, aqueous salts are actually dissociated into ions. Precipitates (solids) are not dissociated, so are written in compound form.

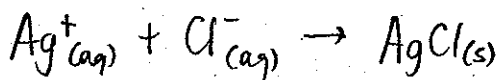
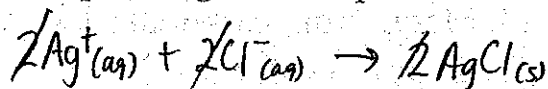
Build and balance the complete ionic equation using the formula equation.



Net Ionic Equation:

Only ions which become a part of the precipitate are written as reactants.

Build the net ionic eqn using the complete ionic eqn as assistance.



Assignment 4: For each of the following, write formula, complete, and net ionic equations:

1. Aqueous magnesium chloride is mixed with aqueous potassium hydroxide.
2. Aqueous lithium carbonate is mixed with aqueous iron (II) sulphate.
3. Aqueous copper I sulphate is mixed with aqueous strontium bromide.
4. Hebden p. 87 #25e,i

VI) Separating Mixtures of Ions by Precipitation

Describe a method to separate Ba^{2+} and Pb^{2+} ions which are in solution together: Cl^- will precipitate Pb^{2+} , but not Ba^{2+}

- ① Add Cl^- as $\text{NaCl}_{(aq)}$ to ppt Pb^{2+} as $\text{PbCl}_{2(s)}$
- ② Filter off the solid PbCl_2 .
- ③ Add SO_4^{2-} as $\text{Na}_2\text{SO}_{4(aq)}$ to ppt Ba^{2+} as $\text{BaSO}_{4(s)}$

Assignment 5: Ion Separation Exercises

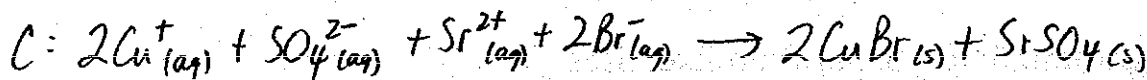
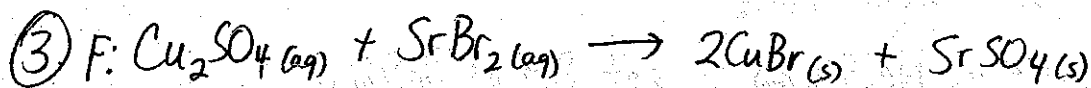
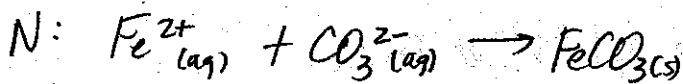
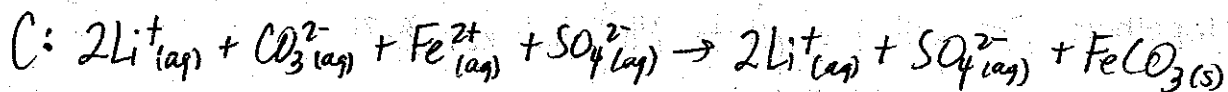
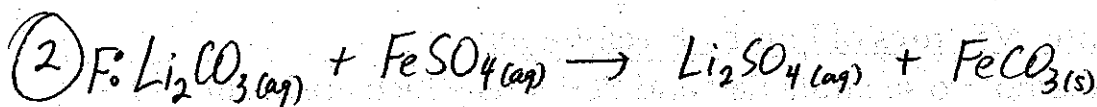
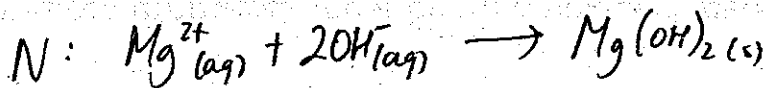
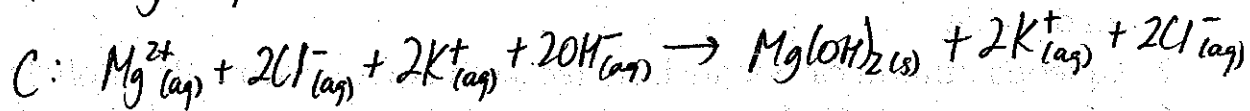
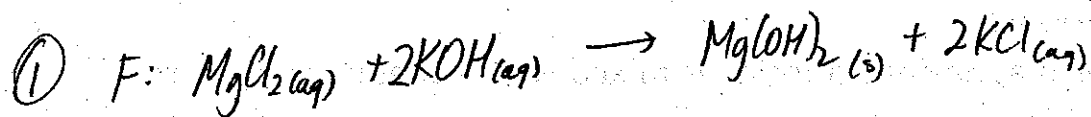
1. Describe a method to separate Cl^- and OH^- that are in solution together. Whatever cation you choose in each step, add it as component of a salt with nitrate (since nitrate is soluble with any cation).
2. A solution is known to possibly contain one or more of the following ions: Mg^{2+} , Ca^{2+} , Pb^{2+}
What steps can you carry out to find the composition of the solution?
3. You have a solution known to contain any or all of Cu^+ , Ca^{2+} , Fe^{3+} , and Sr^{2+} . You have the following 'test' solutions available: 1M Na_2CO_3 , 1M Na_2SO_4 , 1M NaOH , 1M NaCl , 1M Na_2S . In what order would you add each of the above test solutions to test for the presence of each cation?
4. Hebden p. 90 #28, 31, 32

VII) Quantitative Solubility

A saturated solution is in equilibrium because the rate of

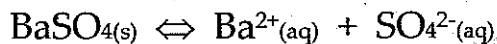
dissolving equals the rate of precipitation.

Assignment 4



N: same as complete ionic eqn.

dissolving
→
← precipitation



Because equilibrium exists, there can be an equilibrium constant. The equilibrium constant for a saturated solution is called a K_{sp} .

Write the K_{sp} equation for the saturated solution above:

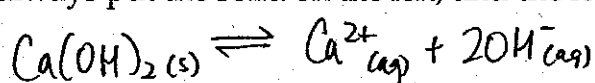
$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

The 'sp' stands for solubility product because...

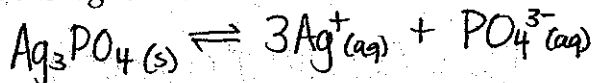
product is the result of a multiplication. A K_{sp} is always simply a multiplication (never a denominator) because the substance on the left side (reactant side) of the reaction equation is always a solid.

Write the balanced saturated solution equations, and then K_{sp} equations for saturated solutions of $\text{Ca}(\text{OH})_2$ and Ag_3PO_4 .

*When writing saturated solution equations that will be used to make a K_{sp} equation, always put the solid on the left, and the ions on the right.



$$K_{sp} = [\text{Ca}^{2+}][\text{OH}^{-}]^2$$



$$K_{sp} = [\text{Ag}^{+}]^3[\text{PO}_4^{3-}]$$

Would **soluble** salts have large or small K_{sp} values? Why?

Large. Soluble salts have high ion concentrations in solution. This would result in large K_{sp} values.

What about **low solubility** salts?

Small. Low solub. salts have very small ion concs. in solution.

Notice that the K_{sp} table in the data booklet (p.5) only lists K_{sp} constants for **low solubility** salts (salts that easily form precipitates).

Notice they are all small values (much less than 1), as they should be.

VIII) Type A Problems: Calculating K_{sp}

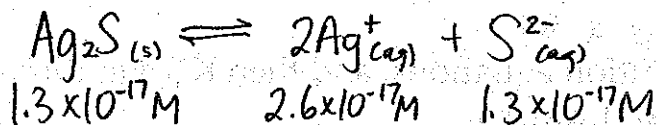
K_{sp} constants can be calculated for **soluble** or **low solubility** salts, as long as there is information available about the respective **saturated** solution.

Examples:

1. If the solubility of Ag_2S in water is $1.3 \times 10^{-17}M$, calculate the K_{sp} .

*What is solubility again? *molarity at saturation.*

*Write an equilibrium equation for Ag_2S and use stoichiometry to find the concentrations of the ions in the saturated solution



$$K_{sp} = [Ag^+]^2 [S^{2-}]$$

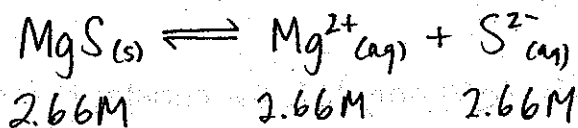
$$K_{sp} = (2.6 \times 10^{-17})^2 (1.3 \times 10^{-17})$$
$$= \underline{8.8 \times 10^{-51}}$$

↑ Ag_2S is a low solubility substance as K_{sp} very small.

2. Calculate the K_{sp} of MgS if a maximum of 300.0g can be dissolved in 2.00L of water.

$$\frac{300.0g}{56.4g MgS} \times \frac{1 \text{ mol } MgS}{1} = \underline{5.319 \text{ mol } MgS}$$

$$[MgS] = \frac{5.319 \text{ mol}}{2.00L} = 2.66M$$



$$K_{sp} = [Mg^{2+}] [S^{2-}]$$
$$= (2.66)(2.66)$$

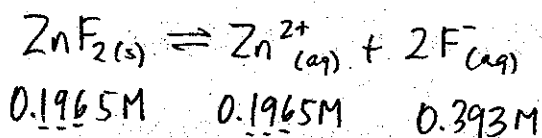
$$= \underline{7.07} \leftarrow \text{large } K_{sp} \text{ so } MgS \text{ soluble.}$$

3. A 25.00mL sample of a ZnF_2 saturated solution (with no excess solid on the bottom) was evaporated to dryness. The mass of the residue was 0.508g. Calculate the solubility product constant of ZnF_2 .

The 0.508g that remained after evaporation was the amount of ZnF_2 that was originally dissolved to make a saturated solution.

$$\frac{0.508g ZnF_2}{103.4g ZnF_2} \times 1 \text{ mol } ZnF_2 = 4.913 \times 10^{-3} \text{ mol}$$

$$[ZnF_2] = \frac{4.913 \times 10^{-3} \text{ mol}}{0.02500L} = 0.1965M$$



$$K_{sp} = [Zn^{2+}][F^{-}]^2$$

$$= (0.1965)(0.393)^2$$

$$= 3.04 \times 10^{-2}$$

Assignment 6: Type A Exercises

- At 25°C, only 0.00245g of $BaSO_4$ can be dissolved in 1.0L of H_2O . Calculate the K_{sp} for $BaSO_4$. 1.1×10^{-10}
- At 25°C, the solubility of Ag_3PO_4 is $1.8 \times 10^{-5}M$. Calculate the K_{sp} for Ag_3PO_4 . 2.8×10^{-18}
- An experiment showed that a maximum of 1.49g of $AgBrO_3$ can dissolve in 1.00L of water at 25°C. What is the K_{sp} for $AgBrO_3$ at this temperature? 3.99×10^{-5}
- A saturated solution of CaF_2 contains $4.15 \times 10^{-4}mol$ of CaF_2 in 2.0L of solution. What is the K_{sp} for CaF_2 ? 3.6×10^{-11}
- A solution in equilibrium with solid Ag_2S on the bottom of the beaker was found to contain $1.6 \times 10^{-16}M S^{2-}$ and $2.5 \times 10^{-18}M Ag^{+}$. Calculate the solubility product constant of Ag_2S . 1.0×10^{-51}

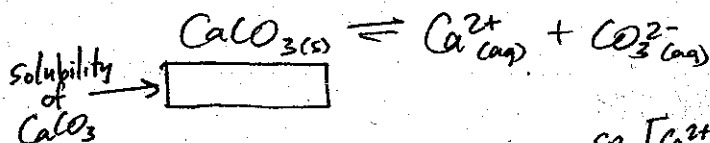
IX) Type B Problems: Calculating Solubility

In Type B problems, you must calculate the solubility of a salt using the K_{sp} constant from p.5 of the data booklet.

Remember that **solubility** means the **molarity of the salt at equilibrium** (when it is **saturated**).

Examples:

1. Calculate the solubility of CaCO_3 in water at 25°C .



$$K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$$

$$K_{sp} \text{ from table} = 5.0 \times 10^{-9}$$

$$\text{Let } x = [\text{Ca}^{2+}] = [\text{CO}_3^{2-}]$$

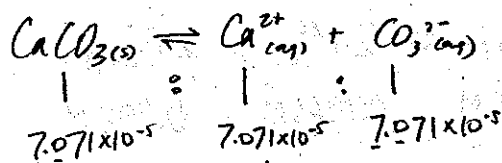
$$5.0 \times 10^{-9} = (x)(x)$$

$$x^2 = 5.0 \times 10^{-9}$$

$$x = \sqrt{5.0 \times 10^{-9}}$$

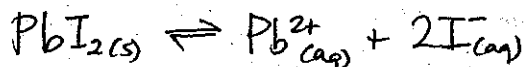
$$x = \underline{7.071 \times 10^{-5}}$$

$$\text{so } [\text{Ca}^{2+}] = [\text{CO}_3^{2-}] = \underline{7.071 \times 10^{-5}}$$



$$\therefore \text{solubility of } \text{CaCO}_3 = \underline{\underline{7.1 \times 10^{-5} \text{ M}}}$$

2. Calculate the solubility of PbI_2 in g/L.



$$K_{sp} = [\text{Pb}^{2+}][\text{I}^{-}]^2$$

$$K_{sp} \text{ from table} = 8.5 \times 10^{-9}$$

$$\text{Let } x = [\text{Pb}^{2+}]$$

$$\text{then } 2x = [\text{I}^{-}]$$

$$8.5 \times 10^{-9} = (x)(2x)^2$$

$$8.5 \times 10^{-9} = 4x^3$$

$$x = \sqrt[3]{\frac{8.5 \times 10^{-9}}{4}}$$

$$x = \underline{\underline{1.286 \times 10^{-3}}}$$

$$\therefore \text{solubility of } \text{PbI}_2 = \underline{\underline{1.286 \times 10^{-3} \text{ M}}}$$

change moles to grams:

$$\frac{1.286 \times 10^{-3} \text{ mol} \quad | \quad 461.0 \text{ g PbI}_2}{1 \text{ mol PbI}_2}$$

$$= \underline{\underline{0.59 \text{ g/L}}}$$

3. How many grams of PbBr_2 can be dissolved in 250.0 mL of water at 25°C ? $\text{PbBr}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{Br}^-(aq)$

find solubility of PbBr_2 first:

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

$$K_{sp} \text{ from table} = 6.6 \times 10^{-6}$$

$$\text{Let } x = [\text{Pb}^{2+}]$$

$$\text{then } 2x = [\text{Br}^-]$$

$$6.6 \times 10^{-6} = 4x^3$$

$$x = \sqrt[3]{\frac{6.6 \times 10^{-6}}{4}}$$

$$x = 0.011817$$

$$[\text{Pb}^{2+}] = 0.011817 \text{ M}$$

Solubility = 0.011817 M
of PbBr_2

now must change $\frac{\text{mol}}{\text{L}}$ to $\frac{\text{g}}{250\text{mL}}$

(i) change moles to grams

$$\frac{0.011817 \text{ moles PbBr}_2}{1 \text{ mol PbBr}_2} \times 367.0 \text{ g PbBr}_2 = 4.3368 \frac{\text{g}}{\text{L}}$$

(ii) change L to 250 mL \Rightarrow divide by 4

$$4.3368 \div 4 = \underline{\underline{1.1 \text{ g PbBr}_2}}$$

Assignment 7: Type B Exercises

- The K_{sp} at a certain temperature for $\text{Ni}(\text{OH})_2$ is 1.6×10^{-16} . Calculate the solubility of $\text{Ni}(\text{OH})_2$. $3.4 \times 10^{-6} \text{ M}$
- Find the solubility of CaSO_4 in g/L. 1.1 g/L
- Which saturated solutions at 25°C will have a greater $[\text{Ag}^+]$, AgCl or Ag_2CO_3 ? $\text{Ag}_2\text{CO}_3 \text{ w/ } [\text{Ag}^+] = 2.6 \times 10^{-4} \text{ M}$ vs. $\text{AgCl} \text{ w/ } [\text{Ag}^+] = 1.3 \times 10^{-5} \text{ M}$
- Calculate the mass of MgCO_3 which could be dissolved in 3.0 L of water at 25°C . 0.66 g
- What mass of PbSO_4 will dissolve in 5.0 L of water at 25°C ? $2.0 \times 10^{-4} \text{ g}$

X) Type C Problems: Trial K_{sp}

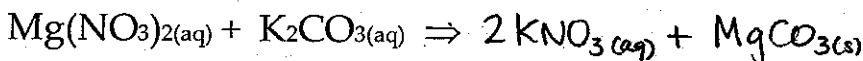
When two soluble solutions are mixed, a cation from one solution is introduced to an anion from the other solution, and *visa versa*. One or both of the new ion combinations (cation and anion) could have low solubility. If this is the case, and there are too many of the low solubility ions present (more than what is necessary for a saturated solution), a precipitate will result. If there are not enough of the low solubility ions present to reach the saturation concentration, a precipitate will not form and the ions will stay dissolved in solution.

A Trial K_{sp} (same concept as a trial K_{eq}) can be calculated for these mixtures to deduce whether a precipitate will form or not when the two solutions are mixed.

If the trial K_{sp} is larger than the actual K_{sp} , the concentrations of low solubility ions mixed together is greater than saturation, so a precipitate will result. If the trial K_{sp} is smaller than the actual K_{sp} , the concentrations of low solubility ions mixed together has not yet reached saturation, therefore a precipitate will not form.

Examples:

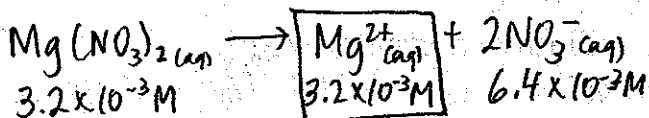
1. Will a precipitate form if 40.0mL of $8.0 \times 10^{-3}M$ $Mg(NO_3)_2$ is mixed with 60.0mL of $1.0 \times 10^{-2}M$ K_2CO_3 ?



Since two solutions are being mixed, dilution occurring:

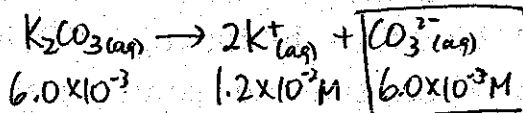
$$[Mg(NO_3)_2]_f = \frac{(8.0 \times 10^{-3}M)(0.0400L)}{0.1000L}$$

$$= 3.2 \times 10^{-3}M$$

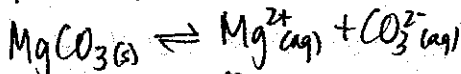


$$[K_2CO_3]_f = \frac{(1.0 \times 10^{-2}M)(0.0600L)}{0.1000L}$$

$$= 6.0 \times 10^{-3}M$$



possible ppt is $MgCO_3$:



$$K_{sp} = [Mg^{2+}][CO_3^{2-}]$$

$$K_{sp} \text{ from table} = 6.8 \times 10^{-6}$$

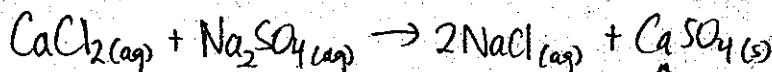
$$\text{Trial } K_{sp} = (3.2 \times 10^{-3})(6.0 \times 10^{-3})$$

$$= 1.9 \times 10^{-5}$$

$$\text{Trial } K_{sp} > K_{sp}$$

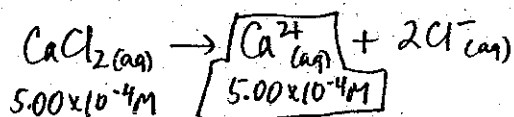
\therefore a ppt of $MgCO_3$ will form.

2. Will a precipitate form if 50.0 mL of 0.00100 M CaCl_2 is added to 50.0 mL of 0.0100 M Na_2SO_4 ?



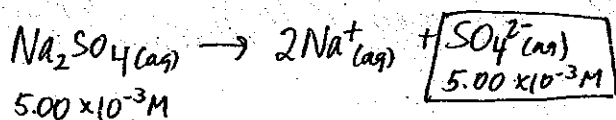
$$[\text{CaCl}_2]_f = \frac{(0.00100\text{M})(0.0500\text{L})}{0.1000\text{L}}$$

$$= 5.00 \times 10^{-4}\text{M}$$

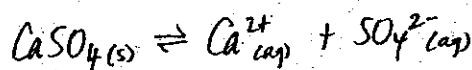


$$[\text{Na}_2\text{SO}_4]_f = \frac{(0.0100\text{M})(0.0500\text{L})}{0.1000\text{L}}$$

$$= 5.00 \times 10^{-3}\text{M}$$



possible ppt is CaSO_4 :



$$K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]$$

$$K_{sp} \text{ from table} = 7.1 \times 10^{-5}$$

$$\text{Trial } K_{sp} \text{ or } 'Q' = (5.00 \times 10^{-4})(5.00 \times 10^{-3})$$

$$Q = 2.5 \times 10^{-6}$$

Since $Q < K_{sp}$

a ppt of CaSO_4 will not form.

Assignment 8: Type C Exercises

1. Will a precipitate form when 1.0 L of $3.0 \times 10^{-10}\text{M}$ $\text{Zn}(\text{NO}_3)_2$ is added to 1.0 L of $2.0 \times 10^{-11}\text{M}$ Na_2S ? $Q = 1.5 \times 10^{-21}$ a ppt will form

2. Will a precipitate form when 2.0 L of $6.7 \times 10^{-3}\text{M}$ SrS is added to 1.0 L of $4.3 \times 10^{-4}\text{M}$ K_2SO_4 ? $Q = 6.4 \times 10^{-7}$ a ppt will form

3. Will a precipitate form when 1.0 L of $5.0 \times 10^{-4}\text{M}$ MgCl_2 is added to 1.0 L of $2.0 \times 10^{-2}\text{M}$ Na_2CO_3 ? $Q = 2.5 \times 10^{-6}$ a ppt will not form

4. $2.5 \times 10^{-7}\text{M}$ of $\text{Fe}(\text{NO}_3)_2$ is mixed with $1.0 \times 10^{-5}\text{M}$ NaOH . Will a precipitate be observed? $Q = 3.1 \times 10^{-18}$ a ppt will not be observed. equal volumes of these two solutions are mixed

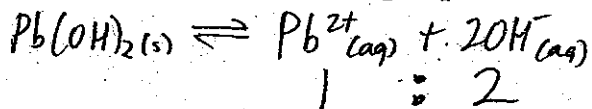
XI) Type D Problems: Determining the Concentration of a Specific Ion in a Saturated Solution

Recall that there are two ways to make a saturated solution. What are they (use $\text{Pb}(\text{OH})_2$ as an example)?

1. add solid $\text{Pb}(\text{OH})_2$ to water until no more will dissolve.

2. Mix two soluble solutions together: one that contains $\text{Pb}^{2+}_{(aq)}$ such as $\text{Pb}(\text{NO}_3)_2_{(aq)}$ and one that contains $\text{OH}^-_{(aq)}$ such as $\text{NaOH}_{(aq)}$. When mixed, if $[\text{Pb}^{2+}]$ and $[\text{OH}^-]$ exceed the saturation molarity (their solubility), some will precipitate out as $\text{Pb}(\text{OH})_2_{(s)}$ and you'll be left with a saturated $\text{Pb}(\text{OH})_2_{(aq)}$ solution (with NO_3^- and Na^+ ions also present).

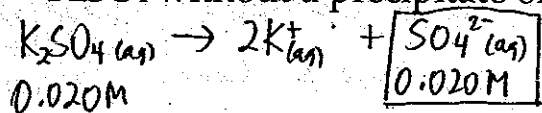
It is important to recognize that ion stoichiometry for a saturated solution is only a reality when the saturated solution is made from dissolving the salt in water (dissolving $\text{Pb}(\text{OH})_2$ solid in water until you have a saturated solution – method #1 above). What would be the proportion of $[\text{OH}^-]$ compared to $[\text{Pb}^{2+}]$ in this case?



If a saturated solution of a salt (such as $\text{Pb}(\text{OH})_2$) is made by combining two different solutions, such as $\text{Pb}(\text{NO}_3)_2_{(aq)}$ and $\text{NaOH}_{(aq)}$, the $[\text{Pb}^{2+}]$ relative to the $[\text{OH}^-]$ could be anything, depending on the proportions of the solutions mixed. So, you can't rely on 2 OH^- to 1 Pb^{2+} stoichiometry because the ions came from different sources. However, the K_{sp} equation can still be relied upon in these situations to do calculations for saturated solutions, as you'll see in Type D problems.

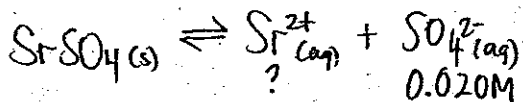
Examples:

1. What is the maximum $[\text{Sr}^{2+}]$ that can be dissolved in a 0.020M solution of K_2SO_4 without a precipitate of SrSO_4 forming?



$$K_{sp} \text{ from table} = 3.4 \times 10^{-7}$$

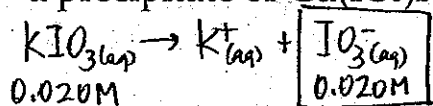
$$3.4 \times 10^{-7} = [\text{Sr}^{2+}](0.020\text{M})$$



$$[\text{Sr}^{2+}] = \underline{\underline{1.7 \times 10^{-5}\text{M}}}$$

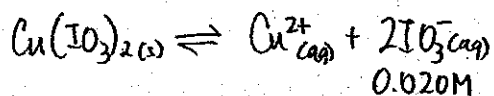
$$K_{sp} = [\text{Sr}^{2+}][\text{SO}_4^{2-}]$$

2. If Cu^{2+} is slowly added to a solution of 0.020M KIO_3 , at what $[\text{Cu}^{2+}]$ does a precipitate of $\text{Cu}(\text{IO}_3)_2$ just start to form?



$$K_{sp} \text{ from table} = 6.9 \times 10^{-8}$$

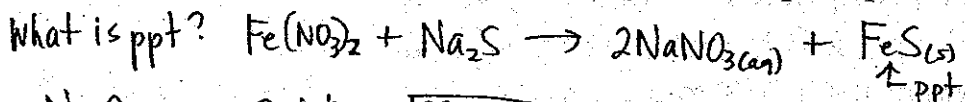
$$6.9 \times 10^{-8} = [\text{Cu}^{2+}](0.020\text{M})^2$$



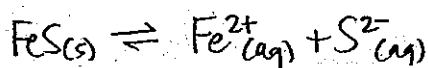
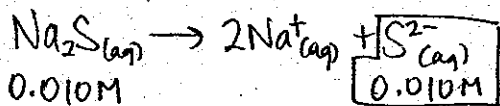
$$[\text{Cu}^{2+}] = \underline{1.7 \times 10^{-4} \text{ M}}$$

$$K_{sp} = [\text{Cu}^{2+}][\text{IO}_3^-]^2$$

3. $\text{Fe}(\text{NO}_3)_2$ is slowly added to a 2.0L solution of $0.010\text{M Na}_2\text{S}$. What mass of $\text{Fe}(\text{NO}_3)_2$ would be required to just start precipitation?



\uparrow
 $\text{Fe}(\text{NO}_3)_2$ added as a solid and then dissociates into solution.



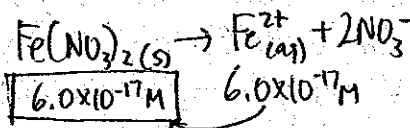
$$K_{sp} = [\text{Fe}^{2+}][\text{S}^{2-}]$$

$$K_{sp} \text{ from table} = 6.0 \times 10^{-19}$$

$$6.0 \times 10^{-19} = [\text{Fe}^{2+}](0.010\text{M})$$

$$[\text{Fe}^{2+}] = 6.0 \times 10^{-17}\text{M}$$

When $\text{Fe}(\text{NO}_3)_2$ is sprinkled into solution, $[\text{Fe}^{2+}]$ becomes $6.0 \times 10^{-17}\text{M}$



mass $\text{Fe}(\text{NO}_3)_2$:

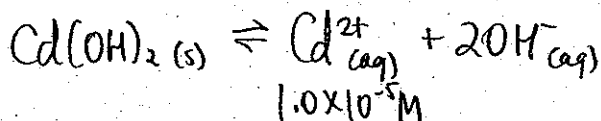
$1.2 \times 10^{-16} \text{ mol}$	179.8 g
	$1 \text{ mol Fe}(\text{NO}_3)_2$

$$= \underline{2.2 \times 10^{-14} \text{ g}}$$

$$\text{moles Fe}(\text{NO}_3)_2 = (6.0 \times 10^{-17}\text{M})(2.0\text{L}) = 1.2 \times 10^{-16} \text{ moles}$$

4. Removing pollution by precipitation:

Waste water from a mining operation was found to have a $[\text{Cd}^{2+}]$ exceeding environmental standards. Before discharging the water into an adjacent river, the $[\text{Cd}^{2+}]$ in the tank had to be lowered to $1.0 \times 10^{-5}\text{M}$. What $[\text{OH}^-]$ would be required to bring the $[\text{Cd}^{2+}]$ to an acceptable level? $K_{sp} = 2.2 \times 10^{-14}$ for $\text{Cd}(\text{OH})_2$



$$K_{sp} = [\text{Cd}^{2+}][\text{OH}^-]^2$$

$$[\text{OH}^-] = \underline{4.7 \times 10^{-5}\text{M}}$$

$$2.2 \times 10^{-14} = (1.0 \times 10^{-5})[\text{OH}^-]^2$$

$$[\text{OH}^-] = \sqrt{\frac{2.2 \times 10^{-14}}{1.0 \times 10^{-5}}}$$

Assignment 9: Type D Exercises

1. What $[S^{2-}]$ must be present to just start precipitation from a 0.20M solution of $CuCl_2$? $3.0 \times 10^{-36} M$
2. What $[Cu^{2+}]$ would be required to just start precipitation of $Cu(IO_3)_2$ from a 0.20M solution of KIO_3 ? $1.7 \times 10^{-6} M$
3. $AgNO_3$ is added to a 0.10M solution of $NaCl$. What $[Ag^+]$ must be present in order to observe a precipitate? $1.8 \times 10^{-9} M$
4. What is the maximum $[SO_4^{2-}]$ that can be present in 0.010M $CaBr_2$ solution without a precipitate forming? $7.1 \times 10^{-3} M$
5. What $[Ba^{2+}]$ must be present to just start a precipitation in a $5.0 \times 10^{-4} M$ solution of K_2CrO_4 ? $2.4 \times 10^{-7} M$

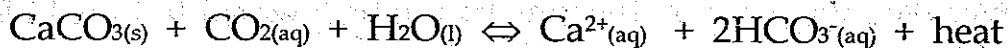
XII) Hard Water

Hard water is caused by a high concentration of Ca^{2+} and/or Mg^{2+} ions in water. It is a problem in areas of the world rich in limestone ($CaCO_3$). Water from rivers, lakes, and streams pass over limestone rock, and Ca^{2+} ends up in water by the two processes below.

1. Permanent Hard Water is formed by Acidic Water (water containing H^+) due to Acid Rain. It is deemed 'permanent' because the reaction is not reversible:



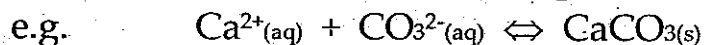
2. Temporary Hard Water is due to CO_2 dissolved in regular rainwater. It is deemed 'temporary' because it's a reversible reaction



How do you soften hard water (lower the $[Ca^{2+}]$ and/or $[Mg^{2+}]$) ?

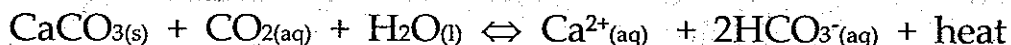
Permanently hard water:

Use washing soda (Na_2CO_3), or any substance that contains an anion that is low solubility with and will precipitate Ca^{2+} and/or Mg^{2+}



Temporary hard water:

Use heat (increase temperature) to reverse the direction of the formation of $\text{Ca}^{2+}_{(aq)}$, as the equilibrium will shift left (endo).



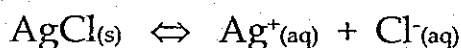
What's inconvenient about hard water: <http://www.absorblearning.com/media/item.action?quick=v1>

another way to soften hard water: <http://www.absorblearning.com/media/item.action?quick=v2>

Assignment 10: Read Hebden p. 103-104 and do p. 104 #76-80

XIII) Altering the Solubility of a Salt

Saturated solution equations (solid on the left, ions on the right) are simply equilibrium equations. In the equilibrium unit, we studied how concentration changes cause a **shift**.



What if $[\text{Ag}^{+}]$ was increased? What would happen to the equilibrium?

shift left

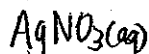
How would the $\text{AgCl}_{(s)}$ change?

amount of $\text{AgCl}_{(s)}$ would increase

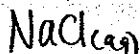
Because the amount of $\text{AgCl}_{(s)}$ would increase, we can say that the solubility of AgCl (it's ability to dissolve) has decreased.

By adding more Ag^{+} to increase $[\text{Ag}^{+}]$ or more Cl^{-} to increase $[\text{Cl}^{-}]$, the equilibrium is driven left, resulting in more $\text{AgCl}_{(s)}$.

This is called the common ion effect, because an ion that is already part of the equilibrium (common to the equilibrium) is being added. However, laboratories don't have solutions that contain solely $\text{Ag}^{+}_{(aq)}$ available to add to the equilibrium to increase $[\text{Ag}^{+}]$, so what can be used as a source of $\text{Ag}^{+}_{(aq)}$ which can be added to the equilibrium?



What can be used as a source of $\text{Cl}^{-}_{(aq)}$?



Summary: To decrease the solubility, add a common ion (common ion effect) to shift the equilibrium left.

What if we want to shift the equilibrium to the right? How can we achieve

this? $\text{AgCl}_{(s)} \rightleftharpoons \text{Ag}^+_{(aq)} + \text{Cl}^-_{(aq)}$

find a way to decrease $[\text{Ag}^+]$ or $[\text{Cl}^-]$

A shift to the right causes more $\text{AgCl}_{(s)}$ to dissolve, thereby increasing its solubility.

What can be done to the equilibrium to decrease $[\text{Ag}^+]$ or $[\text{Cl}^-]$ to cause a shift to the right? $\text{AgCl}_{(s)} \rightleftharpoons \text{Ag}^+_{(aq)} + \text{Cl}^-_{(aq)}$

Add an ion that is low solubility with Ag^+ or Cl^- , causing one of those two ions to form a solid and ppt out of solution, thereby decreasing the ion conc and causing a shift right.

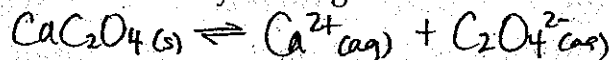
For example, adding $\text{Pb}(\text{NO}_3)_2_{(aq)}$. The Pb^{2+} would ppt with the Cl^- to form $\text{PbCl}_2_{(s)}$.

$[\text{Cl}^-]$ would decrease, causing a shift right, causing more $\text{AgCl}_{(s)}$ to dissolve, thereby increasing its solubility.

Summary: By adding an ion that will precipitate out one of the product ions, the equilibrium is driven right resulting in more $\text{AgCl}_{(s)}$ dissolving, and hence an increase in solubility.

Examples:

1. In which of the following 0.10M solutions would CaC_2O_4 be least soluble in and most soluble in? *Start by writing a saturated solution equation for CaC_2O_4



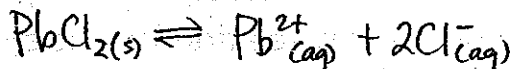
NaOH,
↑
low solub w/ Ca^{2+}
thus $\text{Ca}(\text{OH})_2$ ppt
∴ $[\text{Ca}^{2+}] \downarrow$ ∴ shift
right ∴ inc solubility
∴ most soluble

KCl,
neither
 K^+ or Cl^-
will affect
the equil

$\text{Ca}(\text{NO}_3)_2$
↑
 $\text{Ca}^{2+} \Rightarrow$ common ion ∴ $[\text{Ca}^{2+}] \uparrow$
∴ shift left ∴ least soluble

2. In which of the following 0.10M solutions would PbCl_2 be most soluble?

Least soluble?



HCl,
↑
Common ion
less soluble
0.10M Cl^- added

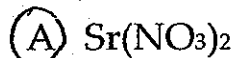
MgCl_2 ,
↑
Common ion
less soluble
 $2\text{Cl}^- = 0.20\text{MCl}^-$ added
least
soluble

AgNO_3 ,
↑
ppts with Cl^-
to form AgCl
∴ $[\text{Cl}^-] \downarrow$
∴ more
soluble
most soluble

NH_4NO_3
no
effect

Assignment 11:

1. In which of the following 0.10M solutions would $\text{Sr}(\text{OH})_2$ be least soluble in?



2. In which of the following 0.10M solutions would NaCl be most soluble in?



3. Hebden p. 108 #81, 82, 84-86

