

Chemistry 12

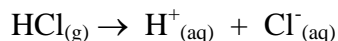
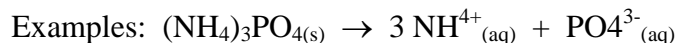
Unit III – Solubility

Notes

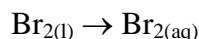
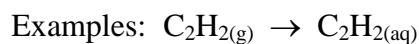
III.1 – A Review Of Solubility

- There are only three classes of compounds that form ionic solutions: ACIDS, BASES and SALTS. **This unit will deal only with SALTS.** Acids and bases will be thoroughly covered in the next unit.

- **Electrolyte:** A substance that dissolves to give an electrically conducting solution containing ions.



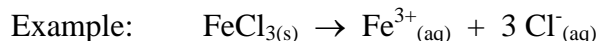
- **Non-Electrolyte:** A substance that dissolves to give a solution that does not conduct electricity and contains only molecules.



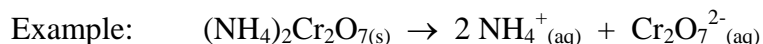
- In summary, we can have either a **molecular solution**, which contains only neutral molecules, or an **ionic solution**, which contains ions. How can we recognize ahead of time whether a molecule will form an ionic or molecular solution?

- Ionic or Molecular Solution: General Rules

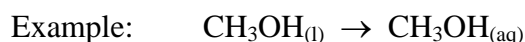
- a) A compound made up of a metal and a non-metal is likely to be ionic (in solution).



- b) A compound made up of species which you know to be polyatomic ions will be ionic in solution.



- c) Covalent compounds (NON-METAL + NON-METAL), especially organic compounds, generally form molecular solutions.



- The “old,” Chemistry 11 definition of solubility was:

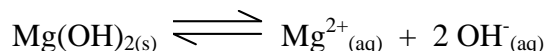
Solubility: the maximum amount of substance that can dissolve in a given amount of solvent at a given temperature.

- A solution, which has dissolved the “maximum amount” of a substance, is said to be **saturated**. Once a solution has been saturated with a substance, the addition of more of the substance will simply cause this extra material to accumulate in undissolved form (usually on the bottom of the container).

- **Saturated Solution:** A solution in which there exists a dissolved substance in equilibrium with the undissolved substance

- In contrast, an **unsaturated solution** contains less than the maximum amount of a substance, which can dissolve. So that there is no undissolved solid present and no equilibrium exists.

- The chemistry 12 definition of solubility is:
Solubility: the equilibrium concentration of the substance in solution at a given temperature.
- The solubility is referred to as the **MOLAR SOLUBILITY** when the concentration is expressed in “moles/litre”
- A **saturated solution** must meet two conditions:
 - a) Some undissolved material must be present.
 - b) Equilibrium must exist between the dissolved and undissolved material.
- We can show that a solution is saturated by writing an *equilibrium equation*:



This equation is interpreted as follows:

When solid Mg(OH)_2 dissolves and enters the solution we have two opposing reactions:

1. Dissolving Reaction: $\text{Mg(OH)}_{2(s)} \rightarrow \text{Mg}^{2+}_{(aq)} + 2 \text{OH}^{-}_{(aq)}$
2. Crystallization Reaction: $\text{Mg}^{2+}_{(aq)} + 2 \text{OH}^{-}_{(aq)} \rightarrow \text{Mg(OH)}_{2(s)}$

Examples: June 2004

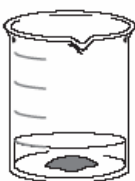
1.

Which of the solutes below can form an ionic solution with the highest conductivity?

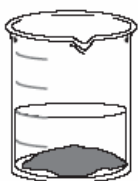
- A. PbS
- B. CH_3Cl
- C. NaNO_3
- D. CH_3COOH

2. June 2001

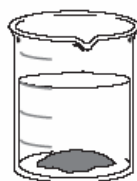
The following three beakers each contain different volumes of a saturated solution of PbI_2 and different masses of solid PbI_2 :



Beaker I



Beaker II



Beaker III

What is the relationship for the $[\text{Pb}^{2+}]$ in the solution in the three beakers?

- A. $\text{I} = \text{II} = \text{III}$
- B. $\text{I} > \text{II} > \text{III}$
- C. $\text{II} > \text{III} > \text{I}$
- D. $\text{III} > \text{II} > \text{I}$

*****Do Hebden Questions #1 - 7, pg 76*****

III.2 - Calculating Solubility and Ion Concentrations

- Once we have experimentally measured the mass of a substance present in **1 L of a solution**, it is straightforward to *calculate the solubility* of the substance.

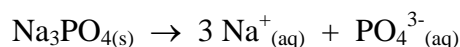
Examples:

- It is experimentally found that 1 L of saturated $\text{Mg}(\text{OH})_{2(\text{aq})}$ contains 1.96g of $\text{Mg}(\text{OH})_2$. What is the solubility of $\text{Mg}(\text{OH})_2$ in moles per litre?
- The solubility of PbI_2 is $1.37 \times 10^{-3}\text{M}$. Express this value in grams per litre.
- Experimentally it is found that 250 mL of saturated CaCl_2 contains 18.6g of CaCl_2 at 20°C . What is the solubility of CaCl_2 in moles per litre?

- A review of calculations involving the concentrations of ions in solution should be beneficial.
- Since a salt will dissociate into ions when it dissolves, we must be able to calculate the concentrations of all ions in the solution.

Examples:

- When 1 mol of Na_3PO_4 is dissolved and diluted to a total volume of 1 L, we have:



moles of particles (in 1 L):	1 mol	3 mol	1 mol
molar concentration (M) :	1 M	3 M	1 M

- What is the concentration of all the ions present in a saturated solution of Ag_2CO_3 having a concentration of $1.2 \times 10^{-4}\text{M}$?

Dilution Calculations

Recall:

$$[\]_{\text{dil}} = [\]_{\text{int}} \times \frac{\text{initial volume}}{\text{Final (total) volume}}$$

3. If 5.0 mL of 0.020 M Cl^- is mixed with 15.0 mL of 0.012 M Br^- , what is the concentration of these ions in the final solution?
4. A 50.0 mL 1.50 M solution of HI is diluted with 50.0 mL of water. Find the final []'s of ions in solution.
5. 36.2 mL of a 1.27 M solution of NaCl is mixed with 73.8 mL of 0.97 M solution of Na_2SO_4 . Find all final ion []'s.

Examples:

1. June 2004

The following data was collected to determine the solubility of a substance:

Mass of solute dissolved	5.00 g
Volume of solvent	250.0 mL
Molar mass of solute	100.0 g/mol
Molar mass of solvent	20.0 g/mol

Which of the following best describes its solubility?

- A. 2.00×10^{-2} g/mL
- B. 5.00×10^{-2} mol
- C. 0.250 mol
- D. 1.00 mol/L

2. August 2002

When 100.0 mL of a saturated solution of BaF_2 is heated and all the water is evaporated, 3.6×10^{-4} mol of solute remains. The solubility of BaF_2 is

- A. 1.9×10^{-10} M
- B. 1.3×10^{-5} M
- C. 3.6×10^{-4} M
- D. 3.6×10^{-3} M

*****Do Hebden Questions #8 - 20, pgs 77 - 81*****

III.3 - Predicting the Solubility of Salts

- Nothing is totally *insoluble* in water. Even glass will dissolve to an extremely small extent in water. However, the amount of glass that dissolves is so small that we say that glass has *negligible solubility* in water.
- Other compounds may dissolve to a somewhat greater extent, such that we cannot neglect the amount that dissolves, but the compound may still be present in the solution in extremely small amounts. Such a substance is said to have *low solubility*.
- **Low Solubility:** A substance is said to have "LOW SOLUBILITY" if a saturated solution of the substance has a concentration of less than 0.1 M.
- Frequently you will see something like the following statement in a problem:

“Equal volumes of 0.2 M compound A and 0.2 M compound B are mixed”. After dilution, both compound A and B are present at 0.1 M solutions. If a precipitate forms when A and B are mixed, the precipitate qualifies as having low solubility.
- When two ions form a compound having “low solubility”, the mixing of the two ions will cause a *precipitate* to form.
- This leads us to the **Solubility Table**, “Solubility of Common Compounds in Water” (See handout).

Examples:

1. Is $\text{FeCO}_{3(s)}$ soluble?

2. Will a precipitate form when (equal volumes) 0.2 M solutions of CaS and Na_2SO_4 are mixed?

Special Notes:

- Copper has TWO different ions: Cu^+ and Cu^{2+}
 - Cu^+ has LOW SOLUBILITY when combined with Cl^- , Br^- and I^-
 - Cu^{2+} is soluble when combined with Cl^- , Br^- and I^-
- *You MUST be able to write the chemical formula of a compound formed from two ions.*
- The Solubility Table allows us to make an important generalization:

*****Compounds containing alkali metals, H^+ , NH_4^+ , and NO_3^- will always be soluble in water.*****
- This generalization has two important consequences:
 1. It will be very difficult (or impossible) to remove alkali metals, H^+ , NH_4^+ , and NO_3^- from solution by forming precipitates.

2. If we have to write the formula of a soluble compound containing a specific ion, we should include alkali metals, NH_4^+ , or NO_3^- to ensure the compound will be soluble. (We will omit H^+ from further consideration; acids will be discussed in greater detail in the next unit.)
- a) If you need to get a particular anion into solution, use an alkali metal ion or NH_4^+ to form the compound. **Suggestion: Choose Na^+**
- b) If you need to get a particular cation into solution, use NO_3^- to form the compound. **Suggestion: Choose NO_3^-** . Example: A soluble salt containing Fe^{3+} would be $\text{Fe}(\text{NO}_3)_3$.

Examples:

1. August 2004

Which of the solutes below is both ionic and most soluble?

- A. RbOH
- B. CH_3OH
- C. $\text{Ca}(\text{OH})_2$
- D. $\text{Fe}(\text{OH})_3$

2. January 2001

Which of the following will produce a solution with the highest $[\text{OH}^-]$?

- A. AgOH
- B. $\text{Sr}(\text{OH})_2$
- C. $\text{Fe}(\text{OH})_3$
- D. $\text{Mg}(\text{OH})_2$

3. April 2003

What happens when 10.0 mL of 0.2 M KOH is added to 10.0 mL of 0.2 M CuSO_4 ?

- A. No precipitate forms.
- B. A precipitate of K_2SO_4 forms.
- C. A precipitate of $\text{Cu}(\text{OH})_2$ forms.
- D. Precipitates of K_2SO_4 and $\text{Cu}(\text{OH})_2$ form.

4. January 1999

Consider the following anions:

	ANION
I.	10.0 mL of 0.20 M Cl^-
II.	10.0 mL of 0.20 M OH^-
III.	10.0 mL of 0.20 M SO_3^{2-}

When 10.0 mL of 0.20 M $\text{Pb}(\text{NO}_3)_2$ are added to each of the above, precipitates form in

- A. I and II only.
- B. I and III only.
- C. II and III only.
- D. I, II and III.

*****Do Hebden Questions #21 - 24, pgs 83 - 84*****

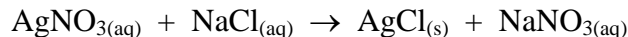
III.4 - Writing Formula, Complete and Net Ionic Equations

- Once we know that a precipitation reaction is possible, we must be able to represent the reaction in three different ways; as a: **Formula Equation, Total Ionic Equation and a Net Ionic Equation.**

Formula Equation

A formula equation is a balanced chemical equation in which all the reactants and products are given by their chemical formulae.

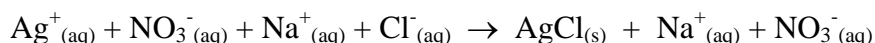
Example:



Total Ionic Equation

A total ionic equation (also called **complete ionic equation**) shows all the **soluble** ionic species broken up into their respective ions.

Example:

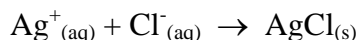


The unreacted ions on the product side are the **spectator ions**. **You should not write a total ionic equation until you have first written a balanced formula equation.**

Net Ionic Equation

A net ionic equation shows only those species which are actively involved in the reaction. The net ionic equation is formed by omitting the spectator ions from the total ionic equation.

Example:



Examples:

1. August 2004

Which of the following best represents the net ionic reaction resulting from the mixing of equal volumes of 0.2 M $\text{Ca}(\text{NO}_3)_2$ and 0.2 M NaOH ?

- A. $\text{Ca}^{2+}_{(aq)} + 2\text{OH}^-_{(aq)} \rightarrow \text{Ca}(\text{OH})_{2(s)}$
- B. $\text{Ca}(\text{NO}_3)_{2(aq)} + 2\text{NaOH}_{(aq)} \rightarrow \text{Ca}(\text{OH})_{2(s)} + 2\text{NaNO}_{3(aq)}$
- C. $\text{Ca}^{2+}_{(aq)} + 2\text{NO}_3^-_{(aq)} + 2\text{Na}^+_{(aq)} + 2\text{OH}^-_{(aq)} \rightarrow \text{Ca}(\text{OH})_{2(s)} + 2\text{NaNO}_{3(aq)}$
- D. $\text{Ca}^{2+}_{(aq)} + 2\text{NO}_3^-_{(aq)} + 2\text{Na}^+_{(aq)} + 2\text{OH}^-_{(aq)} \rightarrow \text{Ca}(\text{OH})_{2(s)} + 2\text{Na}^+_{(aq)} + 2\text{NO}_3^-_{(aq)}$

2. April 2000

The complete ionic equation for the reaction between MgS and $\text{Sr}(\text{OH})_2$ is

- A. $\text{MgS}_{(aq)} + \text{Sr}(\text{OH})_{2(aq)} \rightarrow \text{Mg}(\text{OH})_{2(s)} + \text{SrS}_{(s)}$
- B. $\text{MgS}_{(aq)} + \text{Sr}(\text{OH})_{2(aq)} \rightarrow \text{Mg}(\text{OH})_{2(s)} + \text{SrS}_{(aq)}$
- C. $\text{Mg}^{2+}_{(aq)} + \text{S}^{2-}_{(aq)} + \text{Sr}^{2+}_{(aq)} + 2\text{OH}^-_{(aq)} \rightarrow \text{Mg}^{2+}_{(aq)} + 2\text{OH}^-_{(aq)} + \text{SrS}_{(s)}$
- D. $\text{Mg}^{2+}_{(aq)} + \text{S}^{2-}_{(aq)} + \text{Sr}^{2+}_{(aq)} + 2\text{OH}^-_{(aq)} \rightarrow \text{Mg}(\text{OH})_{2(s)} + \text{Sr}^{2+}_{(aq)} + \text{S}^{2-}_{(aq)}$

*****Do Hebden Questions #25, pg 87*****

III.5 - Separating Mixtures of Ions by Precipitation Methods (Qualitative Analysis)

- One important use of solubility is in the field of *qualitative analysis*.
- Qualitative analysis involves the use of experimental procedures to determine what elements or ions are present in a substance.
- You can try to isolate (precipitate) either cations or anions.
- **Basic idea** = Using the solubility table, try and find an ion that will precipitate one of the anions / cations that you are looking for. Let's try an example...

Example: Assume we have a sample of water from the Chain Lake. We are required to perform a routine check for heavy metal contamination. The metals that we are testing for are: Ag^+ and Sr^{2+} . (For this example, we assume that these are the only two ions in solution.)

- Again, try to find an anion that will precipitate ONE of the two cations (Ag^+ and Sr^{2+}). If a precipitate forms then that cation is present; if no precipitate forms, the cation is absent.
- The table below shows the reactions between the possible cations (left side of the table) and the possible anions that could be added (across the top).
- The five columns correspond to the five groups of ions in the solubility table that can produce a precipitate.
- ' - ' indicates that no precipitate forms and 'ppt' indicates that a precipitate forms

	$\text{Cl}^-, \text{Br}^-, \text{I}^-$	SO_4^{2-}	S^{2-}	OH^-	$\text{PO}_4^{3-}, \text{CO}_3^{2-}, \text{SO}_3^{2-}$
Ag^+	ppt	ppt	ppt	ppt	ppt
Sr^{2+}	—	ppt	—	—	ppt

- As we can see above, no anion will only precipitate Ag^+ . If, for example, CO_3^{2-} is added, it will precipitate **BOTH** Ag^+ and Sr^{2+} .
- However, if Cl^- , S^{2-} , or OH^- were added, then only Ag^+ would precipitate if it were present. (If a precipitate does form, you would have to filter it out (filter paper, centrifuge) before adding more anions).
- Once all the Ag^+ is gone (if present), then you could add PO_4^{3-} and check to see if there is Sr^{2+} . If a precipitate forms after adding PO_4^{3-} , then Sr^{2+} is present.
- Note: is it possible to go to a chemical storeroom and get some Cl^- anions? No, it is not. How could you get those Cl^- ions into solution?

Try this one...

Example: A solution contains one or more of Ag^+ , Ba^{2+} , and Ni^{2+} . What ions could be added, and in what order, to determine which of these cations are present.

- Set up a table of solubilities and fill in the columns with ‘-’ or ‘ppt’

	Cl^- , Br^- , I^-	SO_4^{2-}	S^{2-}	OH^-	PO_4^{3-} , CO_3^{2-} , SO_3^{2-}
Ag^+					
Ba^{2+}					
Ni^{2+}					

- Once the table is filled in, decide what order to add the different anions to check for each cation.

Example: A solution contains Cl^- and SO_4^{2-} . Describe a procedure to separate these anions

- Set up a table of solubilities and fill in the columns with ‘-’ or ‘ppt’

	Ag^+	Pb^{2+}	Cu^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
SO_4^{2-}						
Cl^-						

Examples:

1. August 2005

Which of the following solutions could be used to separate the anions SO_4^{2-} and CO_3^{2-} from each other by precipitation?

- A. $\text{NaNO}_3(\text{aq})$
- B. $\text{AgNO}_3(\text{aq})$
- C. $\text{Fe}(\text{NO}_3)_3(\text{aq})$
- D. $\text{Ba}(\text{NO}_3)_2(\text{aq})$

2. January 2003

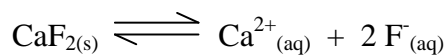
Using the solubility table, determine which of the following ions could not be used to separate S^{2-} from SO_4^{2-} by precipitation?

- A. Be^{2+}
- B. Ca^{2+}
- C. Ba^{2+}
- D. Sr^{2+}

*****Do Hebden Questions #26 - 39, pgs 90 - 91*****

III.6 - The Solubility Product

- The salt $\text{CaF}_{2(s)}$ is only slightly soluble in water, such that very little $\text{CaF}_{2(s)}$ is required to form a saturated aqueous solution:



- The equilibrium expression that corresponds to the dissociation equation above is called the **Solubility Product Expression**:

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^{-}]^2 \quad \text{where } K_{sp} = \text{the } \underline{\text{Solubility Product Constant}}$$

(K_{sp} is simply the special name given to K_{eq} when we are dealing with the dissociation reaction for a slightly soluble salt.)

- **Note:** You have to predict if a compound has low solubility, use the solubility table. If you need to calculate/compare relative solubilities, you **MUST** use the K_{sp} table.
- **Important:** Since the value of K_{sp} depends on the concentration of ions in solution, a larger K_{sp} indicates a more soluble salt, while a smaller value indicates a less soluble salt.
 - **Solubility** – amount of substance required to make a saturated solution
 - **Molar Solubility** – is the molar concentration (mols/liter) of a saturated solution.
 - **Solubility Product** – is the K_{sp} value obtained when the concentrations of the ions in a saturated solution are multiplied together.

Solubility and Solubility Product are DIFFERENT CONCEPTS...don't get them confused!!!
- Solving Solubility Product Problems:

There are really only two types solubility problems when dealing with the solubility product expression:

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

1. We can be given the values directly for $[\text{Ca}^{2+}]$ and $[\text{F}^{-}]$ (or we may have to find the values indirectly from the amount of the salt which dissolves to produce the ions) and be required to find the value of K_{sp} .
2. We can be given the value of K_{sp} and be required to find the individual concentrations of the ions.

It is very strongly, strongly, strongly, STONGLY suggested that for EVERY K_{sp} problem you...

- Write out the equilibrium equation showing the dissolving of the salt
- Write out the solubility product constant

Examples:

1. A solution in equilibrium with a precipitate of BaF_2 contains $4.59 \times 10^{-2} \text{ M Ba}^{+2}$ and $2.00 \times 10^{-3} \text{ M F}^{-}$. What is the K_{sp} for BaF_2 ?

2. A saturated solution of CaF_2 contains 2.15×10^{-4} mol of CaF_2 in 1.00 L of solution. What is K_{sp} for CaF_2 ?
3. $K_{sp} = 3.98 \times 10^{-11}$ for $\text{CaF}_{2(s)}$. What is the $[\text{Ca}^{2+}]$ in a saturated solution of CaF_2 ?
4. What mass of CaF_2 will dissolve in 250 mL of water?

Examples:

1. April 2004

For a saturated solution, the K_{sp} expression does not contain any solid solute term. What is the reason for this?

- A. The solid solute is a product.
- B. The solid solute is a reactant.
- C. The solid solute continues to change in amount.
- D. The solid solute does not change in concentration.

2. April 2003

Which of the following expressions represents $[\text{Fe}^{3+}]$ in a saturated $\text{Fe}(\text{OH})_3$ solution?

- A. $\frac{K_{sp}}{3[\text{OH}^-]}$
- B. $\frac{K_{sp}}{[\text{OH}^-]^3}$
- C. $\sqrt[3]{\frac{K_{sp}}{[\text{OH}^-]}}$
- D. $K_{sp} \times [\text{OH}^-]^3$

*****Do Hebden Questions #40 - 55, pgs 91 - 95*****

III.7 - Predicting Whether a Precipitate Will Form

- Whenever we have two solutions containing ions, we can ask the question, “If we mix these two solutions, will a precipitate form?” Such a situation requires us to make a decision, similar to the situation that existed when we calculated a trial value, Q for K_{eq} .
- **The Ion Product / Trial Ion Product (TIP) / Trial $K_{sp} = Q$**
- Q is the product of the ion concentrations which actually exist in solution = “What we have”
- K_{sp} is the product of the ion concentrations required to establish a solubility equilibrium = “What we need to form a saturated solution”
- When solutions are mixed, there are three possible outcomes...

1. $Q < K_{sp}$

“What we have” is less than “what we need to form a saturated solution”. There are not enough ions in solution to form a precipitate.

Conclusion: A precipitate **WILL NOT** form

2. $Q = K_{sp}$

“What we have” is just equal to “what we need to form a saturated solution”. Minimum possible amount of precipitate forms at this point. (i.e. This is when precipitation just starts...)

Conclusion: A barely saturated solution is formed

3. $Q > K_{sp}$

“What we have” is more than “what we need to form a saturated solution”. Therefore, a precipitate forms and will continue to form until the excess ions have been removed from solution and $Q = K_{sp}$

Conclusion: A precipitate **will** form

Examples:

1. Will a precipitate form when 5.0 mL of 6.0×10^{-5} M Ag^+ is mixed with 10.0 mL of 4.0×10^{-6} M Cl^- ? (Remember, when two solutions are mixed they DILUTE each other. Dilution calculations first!!!)
2. $K_{sp} = 8.5 \times 10^{-9}$ for PbI_2 . If 25.0 mL of 4.50×10^{-3} M $\text{Pb}(\text{NO}_3)_2$ is mixed with 35.0 mL of 2.80×10^{-3} M MgI_2 , will a precipitate form?
3. What $[\text{Cl}^-]$ is required to just start precipitation of $\text{AgCl}_{(s)}$ from a 3.6×10^{-3} M solution of Ag^+ ?

Examples:

1. August 2002

What happens when equal volumes of 0.2 M AgNO_3 and 0.2 M NaCl are combined?

- A. A precipitate forms because the trial ion product $> K_{sp}$
- B. A precipitate forms because the trial ion product $< K_{sp}$
- C. No precipitate forms because the trial ion product $> K_{sp}$
- D. No precipitate forms because the trial ion product $< K_{sp}$

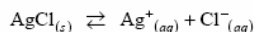
2. January 2004

Two salt solutions were mixed and a Trial K_{sp} was calculated to be 2.0×10^{-9} . The K_{sp} value is 1.0×10^{-10} . From this information, which of the following is a true statement?

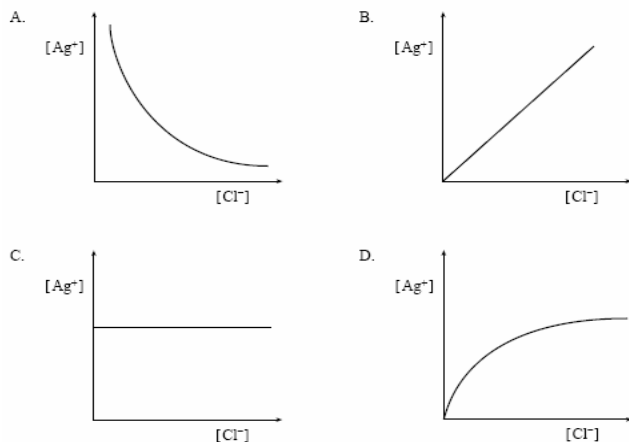
	K_{sp} comparison	Outcome
A.	Trial $K_{sp} < K_{sp}$	precipitate forms
B.	Trial $K_{sp} > K_{sp}$	precipitate forms
C.	Trial $K_{sp} < K_{sp}$	no precipitate forms
D.	Trial $K_{sp} > K_{sp}$	no precipitate forms

3. January 1998

Consider the following equation:



Which of the following graphs represents the relationship between $[\text{Ag}^+]$ and $[\text{Cl}^-]$ in this system at a constant temperature?



4. June 1999

The maximum $[\text{SO}_4^{2-}]$ that can exist in 1.0×10^{-3} M $\text{Ca}(\text{NO}_3)_2$ without a precipitate forming is

- A. 7.1×10^{-5} M
- B. 1.0×10^{-3} M
- C. 8.4×10^{-3} M
- D. 7.1×10^{-2} M

*****Do Hebden Questions #56 - 69, pgs 98 - 99*****

III.9 - Removing Pollution and Hardness from Water by Precipitation Methods

- A. *Removing metal ion pollutants by precipitation.*

- Although biological systems within living organisms can generally tolerate lighter ions such as sodium and magnesium, heavy metal ions such as Cu^{2+} , Hg^{2+} and Pb^{2+} interfere with many biochemical reactions and are therefore toxic to the organism ingesting them.
- The toxicity of heavy metal ions is proportional to their concentrations: the greater the concentration, the greater the toxicity. Therefore, we can take advantage of precipitation processes to lower the concentrations of unwanted metal ions.

Example: $K_{\text{sp}} = 2.2 \times 10^{-14}$ for $\text{Cd}(\text{OH})_2$. Wastewater in the “tailings” pond of a mining operation had cadmium ion concentration of about 0.005 M. Before discharging the wastewater into an adjacent river, the mine had to lower the $[\text{Cd}^{2+}]$ to at most 1.0×10^{-5} M. What $[\text{OH}^-]$ would be required to bring the $[\text{Cd}^{2+}]$ to acceptable values?

- B. *Removing “hardness” from water.*

- “Hardness” in water results from the presence of Mg^{2+} and Ca^{2+} cations that have dissolved from rocks at the source of the water.

There are *three* undesirable effects of hardness in water:

- a) Hard water has a bitter taste which many people find objectionable. The presence of Ca^{2+} and Mg^{2+} directly causes the bitterness.
- b) Hard water prevents proper cleaning action in soaps. This effect is due to the fact that the effective “cleaning ingredient” in most soap is a large organic molecule called the stearate ion: $\text{C}_{17}\text{H}_{35}\text{COO}^-$. Since calcium stearate and magnesium stearate have a low solubility,

$$\begin{aligned}K_{\text{sp}} &= 1 \times 10^{-12} \text{ for } \text{Ca}(\text{C}_{17}\text{H}_{35}\text{COO})_2 \\K_{\text{sp}} &= 5 \times 10^{-13} \text{ for } \text{Mg}(\text{C}_{17}\text{H}_{35}\text{COO})_2\end{aligned}$$

the presence of Ca^{2+} or Mg^{2+} in soapy water causes a gray-white, curd-like precipitate of calcium stearate and magnesium stearate to form. This removes both unwanted ions, but it also uses up the soap.

- c) The precipitate of calcium stearate and magnesium stearate is most of what we call soap scum (or ring around the tub). These deposits can also accumulate inside steam pipes and kettles as rock-hard material that can clog the steam lines and interfere with the heating coils in kettles.
- How can we get rid of Ca^{2+} and Mg^{2+} in “hard” water to “soften” the water?

The most common method of **softening** water is to add “washing soda” which is simply sodium carbonate, Na_2CO_3 . The Solubility Table indicates that calcium carbonate and magnesium carbonate have low solubility in water, so the addition of the carbonate ion precipitates the unwanted calcium and magnesium ions.

- If water contains Ca^{2+} and or Mg^{2+} and DOES NOT contain HCO_3^- , the water is said to be **permanently hard**. This refers to the fact that the only way to soften the water is to perform a precipitation reaction.
- If the water does contain HCO_3^- , the HCO_3^- can be decomposed by heat. Therefore, water containing $\text{Ca}^{2+} / \text{Mg}^{2+}$ and HCO_3^- is said to be **temporarily hard**.

Example: $K_{\text{sp}} = 2.6 \times 10^{-5}$ for MgCO_3 . If hard water contains 0.0050 M Mg^{2+} , what mass of “washing soda”(Na₂CO₃) is required to just start precipitation of MgCO_3 from 10.0 L of hard water?

Examples:

1. August 2002

The magnesium and calcium ions in hard water can be removed by the addition of

- A. NaI
- B. NaNO₃
- C. Na₂CO₃
- D. Na₂SO₄

2. August 2005

Which pair of ions would be suitable for removing the cations responsible for hard water?

- A. H⁺ and Cl⁻
- B. NO₃⁻ and I⁻
- C. S²⁻ and SO₄²⁻
- D. CO₃²⁻ and PO₄³⁻

3. August 1998

Two ions found in hard water are Ca^{2+} and Mg^{2+} . Which of the following will precipitate only one of these ions?

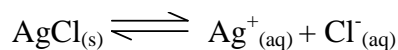
- A. I⁻
- B. S²⁻
- C. SO₄²⁻
- D. CO₃²⁻

*****Do Hebden Questions #76 - 80, pg 104 *****

III.10 - The Common Ion Effect and Other Ways to Alter the Solubility of a Salt

- Both increasing and decreasing the solubility of a salt work on a similar principle.

According to Le Chatelier's principle, changing the concentration of the dissolved ions in the equilibrium



will shift the equilibrium either to the solid side (*decreasing the solubility of the solid*) or to the ions side (*increasing the solubility of the solid*).

In other words, "increasing and decreasing the solubility" refers to the solid salt, but the changes in solubility are accomplished by altering the concentration of the dissolved ions.

- Common Ion Effect:** The lowering of the solubility of one salt by adding a second salt with a common ion.
- A. *Decreasing the Solubility of a Salt*

- If we increase one of the ions in solution, the equilibrium will shift and use up some of the added ions and cause more solid to form.
- Consider the following equilibrium...



Can increase the Ag⁺ concentration by adding a soluble salt containing Ag⁺, such as AgNO₃

Or...

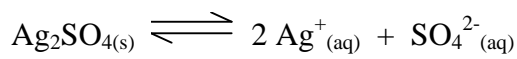
Can increase the BrO₃⁻ concentration by adding a soluble salt containing BrO₃⁻, such as NaBrO₃.

- B. *Increasing the Solubility of a Salt*

- If we decrease the concentration of one of the ions in solution, then the equilibrium will shift so as to dissolve more of the solid and bring the concentration of the ions back up again.
- Consider the following...

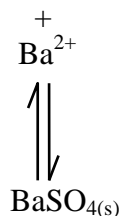
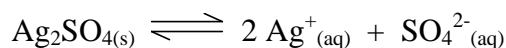
There are two ways that we can increase the amount of Ag₂SO_{4(s)} which can go into solution.

- a) By adding an ion such as Cl⁻ which precipitates Ag⁺:



As the Ag⁺ in solution is removed by precipitation in the form of AgCl_(s) the equilibrium involving Ag₂SO_{4(s)} must shift to the ions side to replace the lost Ag⁺, and thereby dissolve more of the Ag₂SO_{4(s)}.

- b) By adding an ion such as Ba²⁺ which precipitates SO₄²⁻:

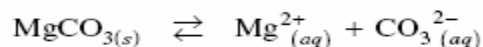


As the SO₄²⁻ in solution is removed by precipitation in the form of BaSO_{4(s)}, the equilibrium involving Ag₂SO_{4(s)} must shift to the ions side to replace the lost SO₄²⁻, and thereby dissolve more of the Ag₂SO_{4(s)}.

Examples:

1. June 2003

Consider the following equilibrium:

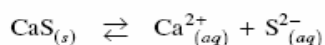


Adding which of the following would cause the solid to dissolve?

- A. HCl
- B. K_2CO_3
- C. MgCO_3
- D. $\text{Mg}(\text{NO}_3)_2$

2. June 2003

Consider the following equilibrium:

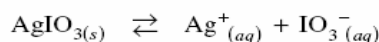


When $\text{Ca}(\text{NO}_3)_2(aq)$ is added to this solution, the equilibrium shifts to the

- A. left and $[\text{S}^{2-}]$ increases.
- B. left and $[\text{S}^{2-}]$ decreases.
- C. right and $[\text{S}^{2-}]$ increases.
- D. right and $[\text{S}^{2-}]$ decreases.

3. April 2002

Consider the following equilibrium:



A few crystals of NaIO_3 are added to the above equilibrium. When equilibrium is re-established, how do the new ion concentrations compare with the original equilibrium concentrations?

	$[\text{Ag}^{+}]$	$[\text{IO}_3^{-}]$
A.	decreased	decreased
B.	decreased	increased
C.	increased	decreased
D.	increased	increased

*****Do Hebden Questions #81 - 86, pg 108 *****