Lecture 14: Getting Quantitative About Solubility

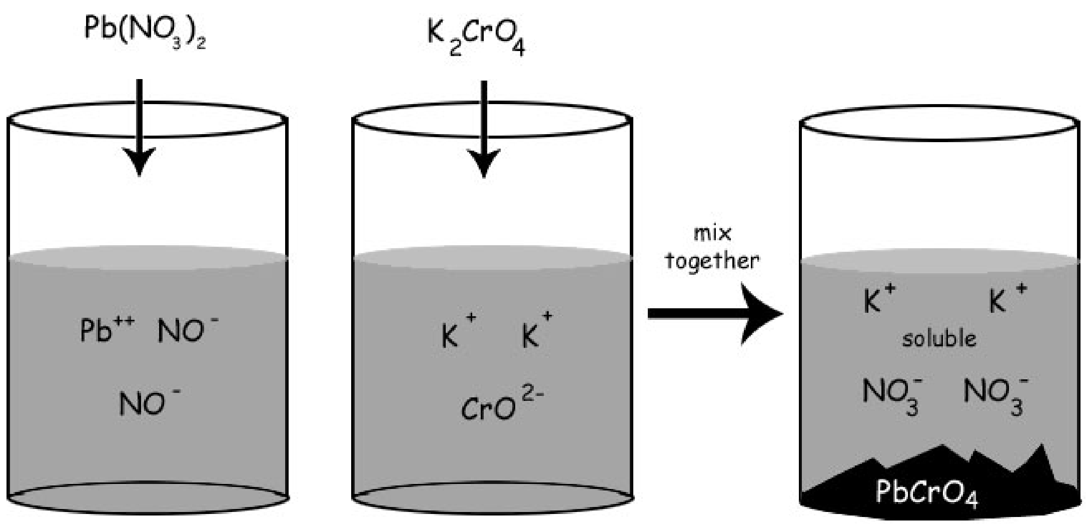
Our last lecture on "simple" equilibria concerns what happens when you throw a salt that can dissociate into water and try to assign some numbers to the amount of material that dissolves. We will find that a process similar to what we did using the RICE expression applied to dissociating acids and bases will apply here as well, and that the notion of strong and weak acids have parallels to soluble and slightly soluble salts. We will also see that the strategies for simplifying the equilibrium problem by making approximations will allow us to create very simple calculation strategies. So as much as anything, look for parallels to acid/base equilibria to help reinforce your understanding of dissociation equilibria.

Throwing salts in water—our qualitative background.

What we have learned three different ideas over the course of the year that can explain solubility:

1. The solubility rules. These include facts such as:
    - CO_3^{2-}, S^{2-}, OH^-, PO_4^{-3} don't dissolve
    - K^+, Na^+, NO_3^-, NH_4^+ do dissolve

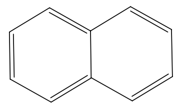
Example of how we use solubility rules to explain the chemistry we see, a metathesis reaction:



2. Chapter 8 Physical Equilibria Rules: the physical reasons for why things dissolve
    - multiply charged salts have a high heat of hydration and therefore are less soluble in water
    - "like dissolves like" because of intermolecular force arguments so polar dissolves polar, non-polar dissolves non-polar

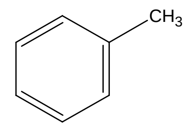
Let's look an example of "Like dissolves like" – what happens when you mix combinations of the four chemicals

NaCl
ionic (polar)



naphthalene (nonpolar)

H_2O
polar



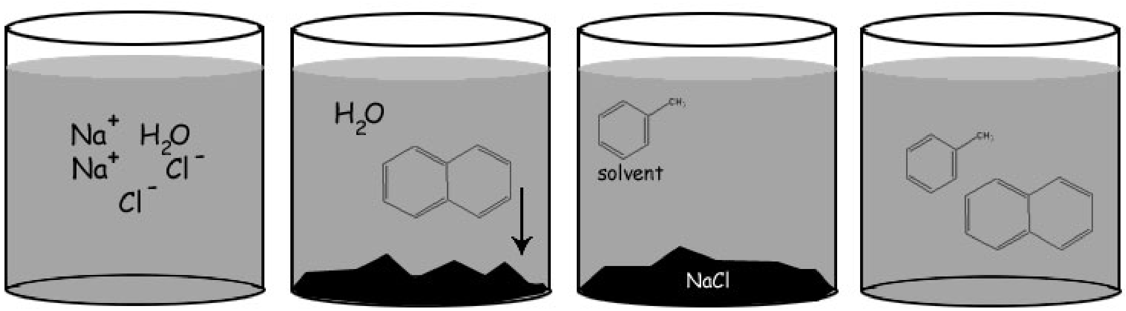
toluene (nonpolar)

case 1: soluble

case 2: insoluble

case 3: insoluble

case 4: soluble



3. Chapter 9—chemical equilibria, creating a numerical basis for solubility using K values (equilibrium theory)
   For example, set up a chemical reaction involving solubility and use the K values to tell us:
    - stuff dissolves because the reaction shifts right, K is large
    - stuff doesn't dissolve because the reaction shifts left, K is small

The rest of the lecture will focus on these Chapter 9 chemical equilbria concepts, looking at the dissolving of salts in water and write equilibrium expressions like those below

Creating Chemical Equilibrium Expressions and the K values that results: note two categories just like for acids and bases.

Examples of sparingly soluble salts: K_{sp} (note the small number for K means rxn stays left and nothing happens)

$PbS \rightleftharpoons Pb^{2+} + SO_4^{2-}$	10^{-28}	
$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$	10^{-10}	
$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$	10^{-12}	
$Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$	10^{-40}	

Example of soluble

$NaCl \rightleftharpoons Na^+ + Cl^-$	infinity	assume reaction goes to completion
$NaOH \rightleftharpoons Na^+ + OH^-$	infinity	hey, the strong base case is just like NaCl, everything dissolves

Time out for an experiment to find out whether Ksp for NaCl is actually infinity (of course it isn't, but how good is our assumption?)

Here are the steps of the experiment:

- Create a saturated equilibrium solution of NaCl in water by letting it settle until there is salt on bottom of the beaker and the solution is clear (but filled with Na+ and Cl-)
- Weigh a beaker
- Decant 50 ml of the saturated solution of NaCl
- Heat the saturated solution to dryness
- Weigh the crusty beaker
- After subtracting the weight of the beaker there is 8g of dried salt that had been dissolved in the water
- Now do the math to find the concentration of NaCl.

  8g NaCl / 58.9 g/mol → 0.137 moles / 50mL of solution → 2.7M !!
- And since we will learn that Ksp = [Na+][Cl-] then Ksp = (2.7)(2.7) = 7.3 not exactly a million, but definitely a reaction that "happens"

And for the first time, after a year of hand waving about dissolving salts in water, we can be quantitative. Instead of saying, we see that instead of saying and instead of "gee, that is really salty" we can say: "hey, K_{sp} for NaCl is 7!!"

Using RICE to create a general solution for solubility calculations

- First the good news: these are the equilibrium calculations to do, and more good news, we derive from them RICE using exactly the procedure we developed for acids/bases

- Now the bad news: these are so easy and the acid base calculations will be so much more involved, that it is easy to not bother with these until the exam. So pay attention and work some problems.

To start: In these problems we almost always want to calculate the "molar solubility" of an ion which is a fancy way to say we want to know how many moles of an ion are in a liter of solution. This is just like calculating $[H^+]$ or $[OH^-]$ but it varies from salt to salt, and because the stoichiometry is not always one to one as it is with H^+ and OH^-, things can get messier.

Recall that all salts have similar forms and therefore similar equilibrium expressions based on stoichiometric relationships of the cations and anions. For example:

Type	AB	AB_2 or A_2B	AB_3 or A_3B
Example:	NaCl, $BaCO_3$	CaF_2, Na_2O	$Al(OH)_3$ or Na_3N

Let's look at each using RICE concepts

Salts of form AB

$AB \rightleftharpoons A^+ + B^-$

C_{AB}	0	0
-x	+x	+x
C_{AB} -x	x	x

←just like weak acid

example: $AgCl \rightleftharpoons Ag^+ + Cl^-$

C_{AgCl}	0	0
-x	+x	+x
C_{AgCl} -x	x	x

BUT!! C-x = 1 because it is a solid so

$K_{SP} = [A^+][B^-]$

$K_{SP} = = [A^+][B^-] = x^2$

So molar solubility is just $x = K_{SP}^{1/2}$ for salts of form AB

$K_{SP} = [Ag^+][Cl^-]$

$K_{SP} = [Ag^+][Cl^-] = x^2$

$[Ag^+] = x = K_{SP}^{1/2}$

Example. What is the molar solubility of $K_{SP} = 10^{-12}$? $[Ag^+] = x = K_{SP}^{1/2} = (10^{-12})^{1/2} = 10^{-6}$ M

Salts of form A_2B or AB_2

$AB_2 \rightleftharpoons A^{++} + 2B^-$

C_{AB2}	0	0
-x	+x	+2x
C_{AB2} -x	x	x

←just like weak acid

example: $MgF_2 \rightleftharpoons Mg^{++} + 2F^-$

C_{MgF2}	0	0
-x	+x	+2x
C_{MgF2}-x	x	2x

BUT!! C-x = 1 because it is a solid so

$K_{SP} = [A^{++}][B^-]^2$

$K_{SP} = = [A^{++}][B^-]^2 = x(2x)^2 = 4x^3$

So molar solubility is just $x = (K_{SP}/4)^{1/3}$ for salts of form A_2B or AB_2

$K_{SP} = [Mg^{++}][F^-]^2$

$K_{SP} = [Mg^{++}][F^-]^2 = x(2x)^2 = 4x^3$

$[Mg^{++}] = x = (K_{SP}/4)^{1/3}$

Example. What is the molar solubility of Mg^{++} in MgF_2 if of $K_{SP} = 4 \times 10^{-12}$?

$[Mg^{++}] = x = (K_{SP}/4)^{1/3} = (4 \times 10^{-12}/4)^{1/3} = 10^{-4}$ M

Now you do AB_3 type (no doubt this kind of problem will be on the exam)

How to estimate when doing solubility product problems.

And finally, a nice rule of thumb. The molar solubility of a pure salt in water is approximately the root of the number of ions. All the rest of the calculation is a coefficient that is often insignificant if the exponents of K are large numbers (positive or negative). Thus, for

AB	AB_2 or A_2B	AB_3 or A_3B
↓	↓	↓
2 ions so take a square root	3 ions so take a cubed root	4 ions so take a 4^{th} root
Examples: AgCl	CaF_2	$Fe(OH)_3$
$K_{SP} = 1x10^{-12}$	$K_{SP}=4x10^{-12} \sim 10^{-12}$	$K_{SP}=10^{-40}$
$[Ag^+] \sim (10^{-12})^{1/2}$	$[Ca^{2+}] \sim (10^{-12})^{1/3}$	$[Fe^{3+}] \sim (10^{-40})^{1/4}$
$[Ag^+] \sim 10^{-6}$	$[Ca^{2+}] \sim 10^{-4}$	$[Fe^{3+}] \sim 10^{-10}$

Of course to be exact, you need to correct for a coefficient (1, 4, 27, ….) but often the approximation is the best way to get to an answer quickly. You will see an example of this on the worksheet.