

Lecture 9: Getting Quantitative About Solubility

Our first 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 concentration of material that dissolves. We will be using concepts from Lectures 5 and 6 in which the RICE expression was introduced. We will also see be introduced to strategies for simplifying the equilibrium problem--making approximations that reduce cubics and quartics to quadratics and first order expressions that permit simpler calculations.

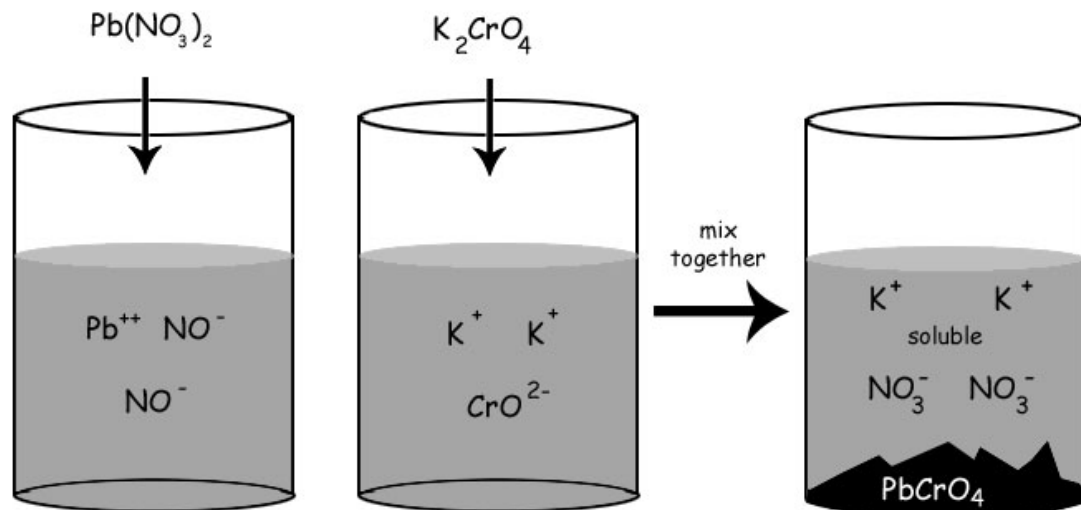
Also, although we will spend just a single lecture on solubility calculations, it will be instructive to relate what you learn here to the month-long introduction to acid/base equilibria that will follow--it will really help reinforce your general understanding of dissociation equilibria if you can see the parallels between solubility equilibria and acid-base equilibria.

Throwing salts in water—the qualitative background developed in high school chemistry and in CH301.

You may not know it, bu have been introduced to two qualitative strategies for explaining 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

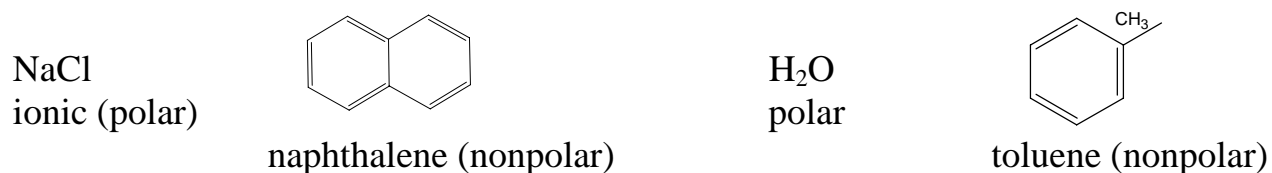
Solubility rules predict the chemistry we see in the laboratory, like the classic reaction to yield lead chromate, a yellow precipitate.



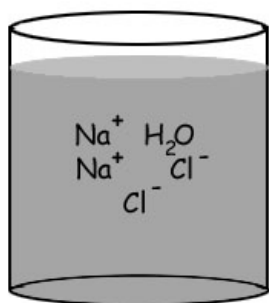
2. Concepts from physical equilibria in Lecture 3: the physical reasons for why things dissolve

- 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

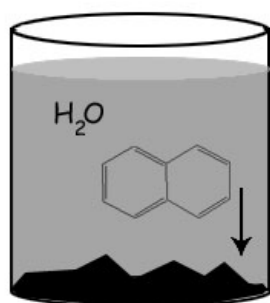
For example, let’s look at “Like dissolves like” again and predict– what happens when you mix combinations of the four chemicals



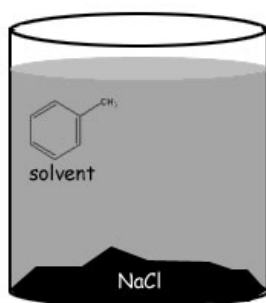
case 1:
soluble



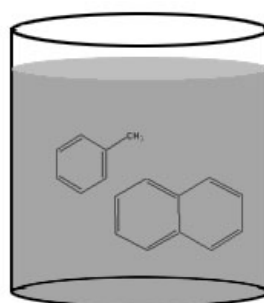
case 2:
insoluble



case 3:
insoluble



case 4:
soluble



Well on to method 3--we get quantitative about the solubility reaction by using concepts from chemical equilibria using K values.

For example, we will set up chemical reactions involving solubility and use the K values to tell us that:

- 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 Lecture 5 and 6 chemical equilibria 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 result based on "strong electrolytes" and "weak electrolytes."

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 salts (strong electrolytes):

$NaCl \rightleftharpoons Na^+ + Cl^-$	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 K_{sp} 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.
 $8g \text{ NaCl} / 58.9 \text{ g/mol} \rightarrow 0.137 \text{ moles} / 50\text{mL of solution} \rightarrow 2.7\text{M} !!$
- And since we will learn that $K_{sp} = [Na^+][Cl^-]$ then $K_{sp} = (2.7)(2.7) = 7.3$ 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

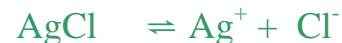
Salts of form AB



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

← just like weak acid

example:



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 A₂B or AB₂



C _{AB2}	0	0
-x	+x	+2x
C _{AB2-x}	x	x

← just like weak acid

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 A₂B or AB₂

Example. What is the molar solubility of Mg⁺⁺ in MgF₂ if of $K_{SP} = 4 \times 10^{-12}$?

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

example:



C _{MgF2}	0	0
-x	+x	+2x
C _{MgF2-x}	x	2x

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

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

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

Now you do AB₃ 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



2 ions so take a square root

Examples: AgCl

$$K_{SP} = 1 \times 10^{-12}$$

$$[Ag^+] \sim (10^{-12})^{1/2}$$

$$[Ag^+] \sim 10^{-6}$$

AB₂ or A₂B



3 ions so take a cubed root

CaF₂

$$K_{SP} = 4 \times 10^{-12} \sim 10^{-12}$$

$$[Ca^{2+}] \sim (10^{-12})^{1/3}$$

$$[Ca^{2+}] \sim 10^{-4}$$

AB₃ or A₃B



4 ions so take a 4th root

Fe(OH)₃

$$K_{SP} = 10^{-40}$$

$$[Fe^{3+}] \sim (10^{-40})^{1/4}$$

$$[Fe^{3+}] \sim 10^{-10}$$

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.

