

Chem 103

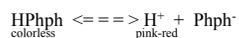
Lecture 5a
Solubility product
(Friday: Test #1)

Last time

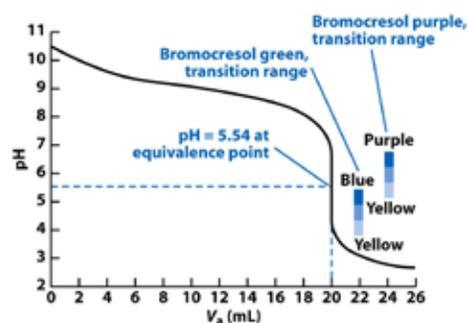
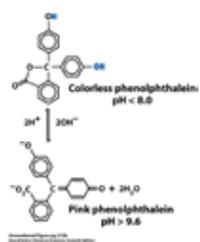
Review buffers, pH calculations
Solution to share-Pair quiz
pH titration curve (pH vs mL)
pH indicators

pH indicators: phenolphthalein (Phph)

pH indicators : example
phenolphthalein is a weak acid



At its pK_a it changes color. If its pK_a is at the center of the equivalence point inflection, then it is ideally suited for the titration...

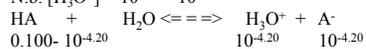


Friday's Pop quiz:

If a 0.100 M solution of a weak acid, HA, has a pH of 4.20, what is its K_a ?

solution:

$$\text{N.b. } [\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4.20}$$



$$K_a = [\text{H}_3\text{O}^+][\text{A}^-]/[\text{HA}] \approx (10^{-4.20})^2/0.100 = 4.0 \times 10^{-8}$$

You draw it for the following:

- weak base (analyte) vs Strong acid (titrant)
- Strong acid (analyte) vs strong base (titrant)
- Strong base (analyte) vs strong acid (titrant)

Solubility and K_{sp}

K_{sp} equilibrium used for *slightly soluble* ionic compounds.

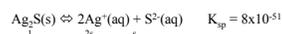
In the sequence: solid \rightleftharpoons aqueous ions

K_{sp} equilibrium constant is a *constant*. The smaller K_{sp} is, the less soluble (for the same stoichiometry of K_{sp})

Solubility (molar) is measure of moles of *formula units* of the compound dissolved per liter.

Example: K_{sp} equilibrium of Ag_2S

K_{sp} for Ag_2S is written:



In a saturated sol'n of Ag_2S in pure water, $[Ag^+] = ?$, etc

$$K_{sp} = [Ag^+]^2[S^{2-}] = 8 \times 10^{-51} = (2s)^2 (s) = 4s^3$$

$$s = \sqrt[3]{(8 \times 10^{-51} / 4)} = 1.3 \times 10^{-17} M \quad (\text{this is the "solubility"})$$

$$[S^{2-}] = 1.3 \times 10^{-17} M \quad \text{and}$$

$$[Ag^+] = 2s = 2(1.3 \times 10^{-17} M) = 2.6 \times 10^{-17} M$$

$$\text{What is } pAg^+? \quad pAg^+ = -\log[Ag^+] = 16.90$$

n.b. $pAg^+ = -\log[Ag^+]$

Q & K_{sp} determine if pptn occurs

Previous example: $[Ag^+] = 2.6 \times 10^{-17}$ and $[S^{2-}] = 1.3 \times 10^{-17} M$

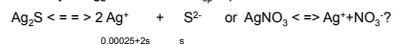
These are determined by K_{sp} and apply to *saturated* solutions

If $Q = [Ag^+]^2[S^{2-}] > K_{sp} \Rightarrow$ supersaturated, precipitn occurs

If $Q < K_{sp}$ precipitation does not occur.

Sample problem: common ion

Suppose we add Ag_2S crystals to a 0.00025M $AgNO_3$ solution, what is the solubility of Ag_2S ? Start with K_{sp} equilibrium!



$$K_{sp} = [Ag^+]^2[S^{2-}] = 8 \times 10^{-51} = (0.00025 + 2s)^2 (s) \approx (0.00025)^2 (s)$$

$$s = 1.3 \times 10^{-43} \quad (\text{compare to } 1.3 \times 10^{-17} M \text{ in pure water})$$

$$\text{Here, } pAg^+ = 42.90 \quad (\text{compare to } 16.90 \text{ in pure water}).$$

Common ion effect decreases solubility

Example: precipitation with 2 substances. $BaSO_4$ and $BaSO_3$.

If you can precipitate 2 different substances in a solution, the first to precipitate will be the less soluble one.

Sample Problem: A solution contains 0.100M Na_2SO_4 and 0.100M K_2SO_3 .

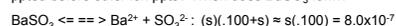
Upon addition of Ba^{2+} ions to the solution, which will precipitate first? What percent of the ions will remain before the other ion starts to precipitate? (K_{sp} 's: $BaSO_4 = 1.1 \times 10^{-10}$ and $BaSO_3 = 8.0 \times 10^{-7}$)

Solution:

Solution to previous problem

Given: K_{sp} 's: $BaSO_4 = 1.1 \times 10^{-10}$ and $BaSO_3 = 8.0 \times 10^{-7}$.

$BaSO_4$ ppts first since $1.1 \times 10^{-10} < 8.0 \times 10^{-7}$. 2nd question: What % SO_4^{2-} is ppted before other ion ppts? When does $BaSO_3$ form?



$s = 8.0 \times 10^{-6}$. Beyond that, $Q > K_{sp}$ and $BaSO_3$ ppts. So what's SO_4^{2-} ?

$$K_{sp} = 1.1 \times 10^{-10} = (8.0 \times 10^{-6}) [SO_4^{2-}]$$

$$\Rightarrow [SO_4^{2-}] = (1.1 \times 10^{-10}) / (8.0 \times 10^{-6}) = 1.4 \times 10^{-5}$$

$$\Rightarrow \% = (1.4 \times 10^{-5} M) / (0.100 M) = 0.014\% \text{ free. } 99.986\% \text{ ppted.}$$