V. POLYPROTIC ACID IONIZATION

A. Polyprotic acids are acids with two or more acidic hydrogens.

monoprotic: $HC_2H_3O_2$, HCN, HNO_2, HNO_3

diprotic: H_2SO_4, H_2SO_3, H_2S } polyprotic

triprotic: H_3PO_4, H_3BO_3 } polyprotic

B. Polyprotic acids ionize in steps - one H^+ is removed at a time - with a different K_a for each step.

Examples:

1. H_3PO_4:

Step 1: $H_3PO_4(aq) + H_2O(l) \leftrightharpoons H_3O^+(aq) + H_2PO_4^-(aq)$ $K_{a1} = 7.1 \times 10^{-3}$

Step 2: $H_2PO_4^-(aq) + H_2O(l) \leftrightharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$ $K_{a2} = 6.3 \times 10^{-8}$

Step 3: $HPO_4^{2-}(aq) + H_2O(l) \leftrightharpoons H_3O^+(aq) + PO_4^{3-}(aq)$ $K_{a3} = 4.4 \times 10^{-13}$

NOTICE: $K_{a1} > K_{a2} > K_{a3}$

2. H_2S

3. H_2SO_4

C. Polyprotic Acid Ionization Calculations

Calculate $[H_3O^+]$, $[H_3PO_4]$, $[H_2PO_4^-]$, $[HPO_4^{2-}]$ and $[PO_4^{3-}]$ for a solution of 0.200 M H_3PO_4.

Step 1: $H_2O + H_3PO_4 \leftrightharpoons H_3O^+ + H_2PO_4^-$

	H_3PO_4	H_3O^+	$H_2PO_4^-$
I	.2	0	0
Δ	-x	+x	+x
[Eq]	0.2-x	x	x

$K_{a1} = 7.1 \times 10^{-3}$

$[H_3O^+] = x$

$[H_3PO_4] = 0.2 - x$

$[H_2PO_4^-] = x$

Step 2: $H_2O + H_2PO_4^- \leftrightharpoons H_3O^+ + HPO_4^{2-}$

	$H_2PO_4^-$	H_3O^+	HPO_4^{2-}
I	x	x	0
Δ	-y	+y	+y
[Eq]	x-~~y~~	x+~~y~~	y

$K_{a2} = 6.3 \times 10^{-8}$

$[HPO_4^{2-}] = y = K_{a2}$

Step 3: $H_2O + HPO_4^{2-} \leftrightharpoons H_3O^+ + PO_4^{3-}$

	HPO_4^{2-}	H_3O^+	PO_4^{3-}
I	y	x	0
Δ	-z	+z	+z
[Eq]	y-~~z~~	x+~~z~~	z

$K_{a3} = 4.4 \times 10^{-13}$

$[PO_4^{3-}] = z = (K_{a2} \cdot K_{a3}) \div [H_3O^+]$

VI. HYDROLYSIS

A. Hydrolysis is the reaction of one or both **ions** of a **salt** with water to produce a weak base (and H_3O^+) or a weak acid (and OH^-) or both.

B. Which Salts Hydrolyze?

1. Salt of a Strong Acid & Strong Base (note: of course all of these are *soluble* salts)

   example: NaCl: Does NaCl hydrolyze, and will an aqueous solution of NaCl be acidic, basic, or neutral?

1. Salt of a Weak Acid and a Strong Base

   example: NaCN: Does NaCN hydrolyze, and will an aqueous solution of NaCN be acidic, basic, or neutral?

3. Salt of a Strong Acid and a Weak Base

   example: NH_4Br: Does NH_4Br hydrolyze, and will an aqueous solution of NH_4Br be acidic, basic, or neutral?

4. Salt of a Weak Acid and a Weak Base

example: NH_4F: Does NH_4F hydrolyze, and will an aqueous solution of NH_4F be acidic, basic, or neutral?

5. Salt of a weak polyprotic acid and a strong base

example: Na_2S: Does Na_2S hydrolyze, and will an aqueous solution of Na_2S be acidic, basic, or neutral?

6. Salt that contains anion from first ionization step of polyprotic weak acid

example: $NaHCO_3$: Does $NaHCO_3$ hydrolyze, and will an aqueous solution of $NaHCO_3$ be acidic, basic, or neutral?

C. Practice writing equations for hydrolysis of following salts:

1. KNO_2

2. N_2H_5Cl

D. Hydrolysis Calculations

1. Calculate the pH of a 0.020 M solution of NH_4Br. (K_b for NH_3 is 1.8×10^{-5})

2. Calculate the percent hydrolysis and the pH of a 0.100 M solution of NaCN. (K_a for HCN is 4.0×10^{-10})

VII. ACID-BASE TITRATION

A. Acid-Base Titration: Procedure for determining the amount of acid (or base) in solution by measuring the volume of base (or acid) solution of known concentration required to completely react with it - that is - to reach the equivalence point.

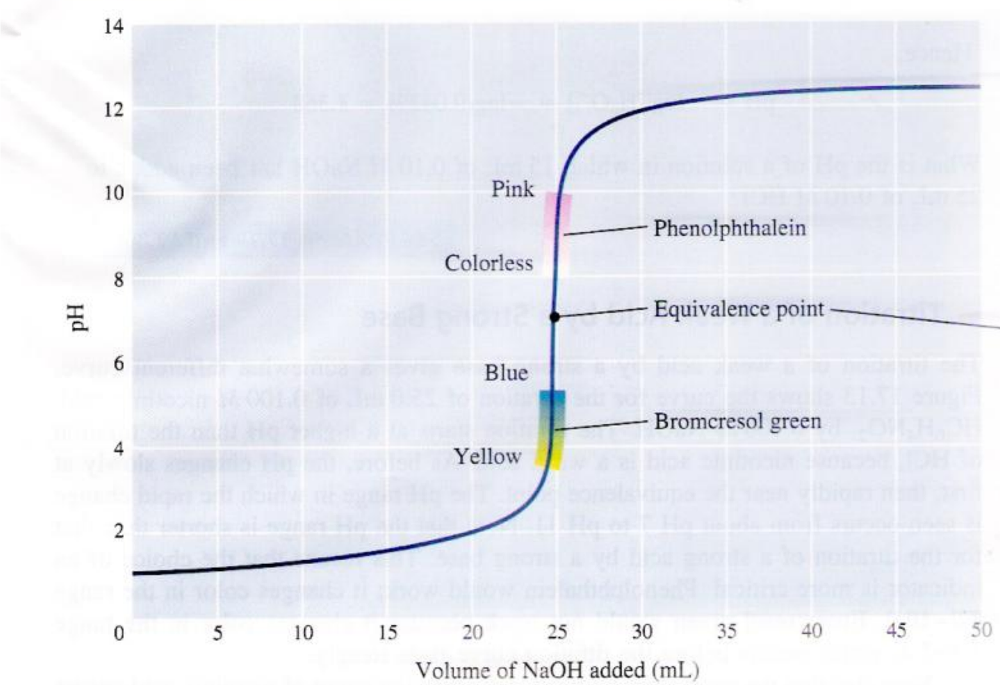
Equivalence point:

B. Acid-Base Titration Curve

1. Definition: A plot of the pH of a solution (of acid or base) being titrated versus the volume of titrant (base or acid solution) added.

2. Curve for Titration of a Strong Acid with a Strong Base

Titration of 25.0 mL of 0.100 M HCl with 0.100 M NaOH.



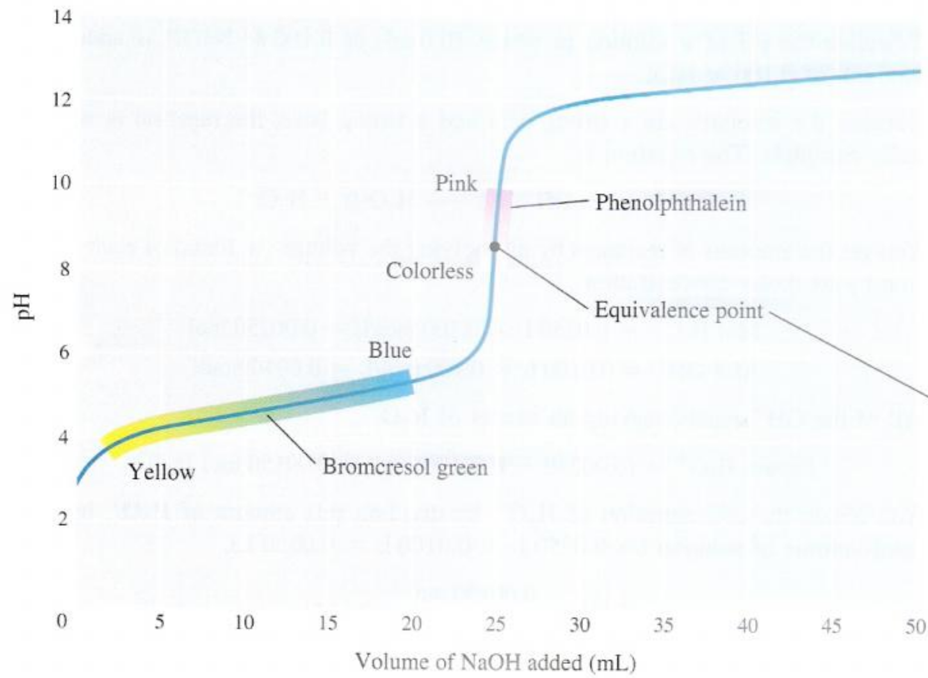
Volume NaOH added (mL)	pH
0	1.00
5	1.18
10	1.37
15	1.60
20	1.95
21	2.06
22	2.20
23	2.38
24	2.69
25	7.00
26	11.29
27	11.59
28	11.75
29	11.87
30	11.96
35	12.22
40	12.36
45	12.46
50	12.52

Figure 17.12

Curve for the titration of a strong acid by a strong base
Here 25.0 mL of 0.100 *M* HCl is titrated by 0.100 *M* NaOH. The portions of the curve where indicators bromcresol green and phenolphthalein change color are shown. Note that both indicators change color where the pH changes rapidly (the nearly vertical part of the curve).

2. Curve for Titration of a Weak Acid with a Strong Base

Titration of 25.0 mL of 0.100 M nicotinic acid. ($K_a = 1.4 \times 10^{-5}$) with 0.100 M NaOH.



Volume NaOH added (mL)	pH
0	2.92
1	3.47
2	3.79
3	3.98
4	4.13
5	4.25
10	4.67
15	5.03
20	5.45
21	5.57
22	5.72
23	5.91
24	6.23
25	8.78
26	11.29
27	11.59
28	11.75
29	11.87
30	11.96
35	12.22
40	12.36
45	12.46
50	12.52

Figure 17.13

Curve for the titration of a weak acid by a strong base
Here 25.0 mL of 0.100 *M* nicotinic acid, a weak acid, is titrated by 0.100 *M* NaOH. Note that bromcresol green changes color during the early part of the titration, well before the equivalence point. Phenolphthalein changes color where the pH changes rapidly (near the equivalence point). Thus, phenolphthalein could be used as an indicator for the titration, whereas bromcresol green could not.

VIII. SOLUBILITY EQUILIBRIA

A. SOLUBILITY PRODUCT

1. In a **saturated solution** of a salt, equilibrium exists between the undissolved salt and its dissolved ions.

   For example, a saturated aqueous solution of AgBr:

   $$AgBr_{(s)} \leftrightharpoons Ag^{+}_{(aq)} + Br^{-}_{(aq)}$$

   Equilibrium constant expression:

   $$K = \frac{[Ag^{+}][Br^{-}]}{[AgBr]}$$

   $$\underbrace{K \cdot [AgBr]}_{K_{sp}} = [Ag]\,[Br]$$

   Since [AgBr] is constant, (the concentraton in mole/liter of a solid is given by its density, which is constant, and is not dependent on the quantity of the solid) [AgBr] may be included with K.

   $$K_{sp} = [Ag^{+}]\,[Br^{-}]$$

   K_{sp} **solubility product constant**

2. K_{sp} expression differs from other K expressions

   a. There is no denominator term.

   b. Concentrations are often squared or cubed, etc.

   examples:

   $$Fe(OH)_{2(s)} \leftrightharpoons Fe^{2+}_{(aq)} + 2\,OH^{-}_{(aq)} \qquad K_{sp} = [Fe^{2+}]\,[OH^{-}]^2$$

   $$Bi_2S_{3(s)} \leftrightharpoons 2\,Bi^{3+}_{(aq)} + 3\,S^{2-}_{(aq)} \qquad K_{sp} = [Bi^{3+}]^2\,[S^{2-}]^3$$

3. K_{sp} value depends on temperature since solubility depends on temperature

B. DISSOLVING REACTIONS

1. Simple K_{sp} Calculations

a. Calculate K_{sp} given solubility and molar mass.

$PbCl_2$ has a solubility of 4.43 g/L. What is its K_{sp}? ($PbCl_2$ = 278.1 g/mole)

b. Calculate solubility given K_{sp} and molar mass
The K_{sp} for Ag_2CrO_4 is 1.9×10^{-12}. Calculate its solubility in g/L.
(Ag_2CrO_4 = 331.73 g/mole)

2. Common Ion Effect on Solubility.

a. The presence of a common ion will decrease the solubility of a salt.

b. Example: calculate the molar solubility of PbI_2 in
(a) in water
(b) in a 0.010 M NaI solution. (K_{sp} of PbI_2 is 7.47×10^{-9})

D. PRECIPITATION REACTIONS

1. DETERMINING WHETHER A PRECIPITATE WILL FORM

a. Ion Product

The ion product (IP) is calculated just as the K_{sp} is. For example:

$$Bi_2S_{3(s)} \leftrightarrows 2\ Bi^{3+}{}_{(aq)} + 3\ S^{2-}{}_{(aq)}$$

$$\mathbf{K_{sp}} = [Bi^{3+}]^2\ [S^{2-}]^3 \qquad \text{and} \qquad \mathbf{IP} = (\underline{M}\ Bi^{3+})^2\ (\underline{M}\ S^{2-})^3$$

However, the K_{sp} is calculated using **equilibrium** concentrations only, whereas the ion product is calculated using non-equilibrium (initial) concentrations.

b. Comparison of IP and K_{sp} values to determine whether or not a precipitate will form:

(1) $IP = K_{sp}$

(2) $IP > K_{sp}$

(3) $IP < K_{sp}$

a. Problem: $NaIO_3$ and $Cu(C_2H_3O_2)_2$solutions are mixed. Initially, the mixture is 0.020 M in $NaIO_3$ and 0.010 M in $Cu(C_2H_3O_2)_2$. Will a precipitate of $Cu(IO_3)_2$ form?
K_{sp} of $Cu(IO_3)_2$ is 1.4×10^{-7}

2. SEPARATION OF IONS BY SELECTIVE PRECIPITATION

a. It is possible to separate two ions from each other when they are present together in solution, by adding an ion that will precipitate one ion but not the other.

   ***Example*:** a solution containing Na^+ and Ag^+

b. In the event that the added ion precipitates both ions, it is still possible to achieve some separation.

   ***Example*:** a solution containing Ba^{2+} and Ca^{2+} - selective precipitation with sulfate ion

   Solid Na_2SO_4 is added slowly to a solution that is 0.0050 M in Ba^{2+} and 0.20 M in Ca^{2+} ion.

   (1) Which sulfate will precipitate first?
   (2) Calculate the concentration of the ion of the less soluble sulfate at the point where the solution is saturated with respect to both salts. (That is, when the second salt is just ready to precipitate.)

   K_{sp} of $BaSO_4 = 1.5 \times 10^{-9}$ K_{sp} of $CaSO_4 = 2.4 \times 10^{-5}$

3. SEPARATION OF METAL IONS BY SULFIDE PRECIPITATION

Consider the effect of adding a strong acid to a solution on Zn^{2+} and Pb^{2+} ions. Now you saturate the solution with H_2S gas. The H_3O^+ from the strong acid represses the ionization of H_2S, giving a lower concentration of S^{2-} ion. By adjusting the H_3O^+ concentration, you can control the S^{2-} concentration and therefore the ion products for ZnS and PbS. You can adjust the hydrogen ion concentration so that only PbS precipitates when the solution is saturated with H_2S.

To determine the H_3O^+ concentration necessary to prevent some ions from precipitating while others form the sulfides, you need to look at the overall equation for the Ionization of H_2S. You can determine this by adding the equations for the two steps of acid ionization:

$$H_2S(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + HS^-(aq)$$
$$HS^-(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + S^{2-}(aq)$$

$$H_2S(aq) + 2\,H_2O(l) \leftrightarrows 2\,H_3O^+(aq) + S^{2-}(aq)$$

The equilibrium constant for the overall equation is determined by multiplying the equilibrium constants for the two reactions that were added together.

$$K_{a_1} \bullet K_{a_2} = \frac{[H_3O^+]^2[S^{2-}]}{[H_2S]}$$

$$K_{a_1} = 8.9 \times 10^{-8}$$

$$K_{a_2} = 1.2 \times 10^{-13}$$

Therefore, $K_{a_1} \bullet K_{a_2} = 1.1 \times 10^{-20}$

A saturated solution of hydrogen sulfide is 0.10 M H_2S, and this is not significantly altered by changes in the hydronium ion concentration. Substitute this into the equilibrium expression:

$$K_{a_1} \bullet K_{a_2} = \frac{[H_3O^+]^2[S^{2-}]}{[H_2S]}$$

$$1.1 \times 10^{-20} = \frac{[H_3O^+]^2[S^{2-}]}{0.10} \qquad (K_{a_1} \bullet K_{a_2} = 1.1 \times 10^{-20})$$

$$1.1 \times 10^{-21} = [H_3O^+]^2[S^{2-}]$$

Note that as the $[H_3O^+]$ increases, $[S^{2-}]$ decreases. Therefore, by adjusting the hydronium ion concentration, you can obtain any desired sulfide ion concentration.

a. ***Example 1***: A solution that is 0.30 M in H_3O^+, 0.050 M in Pb^{2+}, and 0.050 M in Fe^{2+} is saturated with H_2S. Should PbS and/or FeS precipitate. K_{sp} of PbS = 7×10^{-29}

K_{sp} of FeS = 4×10^{-19}.

b. ***Example 2***: What must be the hydronium ion concentration of a solution that is 0.050 M in Ni^{2+} to prevent the precipitation of NiS when the solution is saturated with H_2S.

K_{sp} of NiS =3×10^{-21}

4. USING COMMON ION EFFECT TO PREVENT PRECIPITATION

The common ion effect may be used to prevent the formation of a precipitate. Consider the precipitation of magnesium hydroxide from a solution that contains Mg^{2+} ions:

$$Mg(OH)_{2(s)} \leftrightharpoons Mg^{2+}(aq) + 2\ OH^{-}(aq)$$

If the hydroxide ion is provided by ammonia:

$$NH_{3(aq)} + H_2O(l) \leftrightharpoons NH_4^{+}(aq) + OH^{-}(aq)$$

Precipitation can be prevented by keeping the concentration of OH^- low, for example by adding NH_4^+.

Example: What concentration of NH_4^+, derived from NH_4Cl, is necessary to prevent the formation of an $Mg(OH)_2$ precipitate in a solution that is 0.50 M in Mg^{2+} and 0.50 M in NH_3?

K_{sp} of $Mg(OH)_2 = 8.9 \times 10^{-12}$ K_b of $NH_3 = 1.8 \times 10^{-5}$

IX. HETEROGENEOUS EQUILIBRIA

Heterogeneous equilibria are equilibrium reactions whose reactants and products are not all in the same phase.

For example:

$$Ca(HCO_3)_{2(aq)} \leftrightharpoons CaCO_{3(s)} + H_2O_{(l)} + CO_{2\,(g)}$$

$$K = \frac{[CaCO_3][H_2O][CO_2]}{[Ca(HCO_3)_2]}$$

$$\underbrace{\frac{K}{[CaCO_3][H_2O]}} = \frac{[CO_2]}{[Ca(HCO_3)_2]}$$

The concentrations of pure solids and pure liquids are never included in the equilibrium constant expression.

$$K_c = \frac{[CO_2]}{[Ca(HCO_3)_2]}$$

K_c is a constant that depends only on temperature.

X. GASEOUS EQUILIBRIA

A. EQUILIBRIUM CONSTANTS: K_c and K_p

$$N_{2(g)} + 3\ H_{2(g)} \rightleftharpoons 2\ NH_{3(g)}$$

1. $K_c = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$ [ ] = concentration of gas in mole/liter

2. K_p: since partial pressures of gases are proportional to molar concentration, the K expression can be written showing partial pressures:

   $K_p = \dfrac{p^2_{NH_3}}{p_{N_2}\ p^3_{H_2}}$ p = partial pressure of gas

3. K_p is not **numerically** equal to K_c, but may be calculated from K_c as follows:

   $K_p = K_c\,(RT)^{\Delta n}$ where Δn = total moles products – total moles reactants (from coefficients in equation)

   and

   $K_c = K_p\,(RT)^{-\Delta n}$

B. Review of Le Chatelier's Principle

1. Effect of concentration change

2. Effect of temperature change

3. Effect of pressure and volume changes at constant temperature.
   (applies only to gases since solids and liquids are not compressible.)

4. Effect of catalyst

C. GASEOUS EQUILIBRIUM CALCULATIONS

1. Consider the following equation:

$$H_2O(g) + CO(g) \leftrightarrows CO_{2}(g) + H_{2}(g)$$

At 200°C the system is at equilibrium and there are 0.200 moles H_2O, 0.400 moles CO, 0.500 moles CO_2 and 0.800 moles H_2 in a 2.00 liter vessel. In another experiment at 200°C, 0.600 moles H_2O and 0.600 moles CO are placed in a 2.00 liter container and allowed to come to equilibrium. Calculate the equilibrium concentrations of all species.

2. 3.00 moles N_2 and 4.00 moles H_2 are placed in a 1.00 liter reaction vessel and allowed to come to equilibrium. At equilibrium, the H_2 concentration is 3.40 M. Calculate K_c

$$N_{2(g)} + 3\,H_{2(g)} \leftrightharpoons 2\,NH_{3\,(g)}$$