Aqueous Equilibrium 3

CHEM 102
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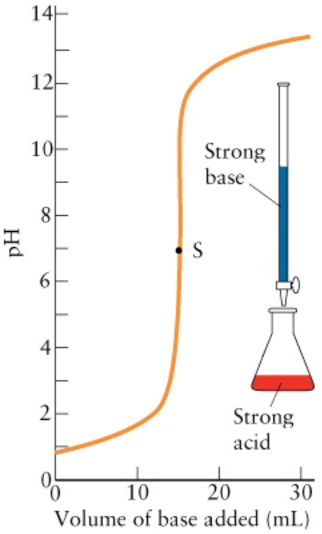
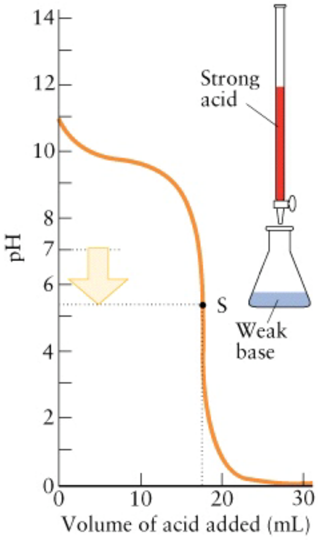
Titrations

- As you have seen in the lab, acid (base) concentrations in samples are determined by controlled addition of known quantities of base (acid) in “neutralization” reactions.
- … and as you have also seen, the first step in a titration involves the preparation of a standard solution to perform the titration.



Strong acid/ Strong Base

Example: Add 0.25 M NaOH to 10 mL 0.375 M HNO_3 solution.



Strong acid/ Weak base

Example: Add 0.20 M HCl to 10 mL 0.35 M $(CH_3)_3N$ solution

$(CH_3)_3N$: pK_b = 4.19

Selection of Indicator

- The purpose of a titration is to find the "stoichiometric point" where

  moles of added standard "titrant"

  = moles of the "analyte"

- Therefore, try to find an indicator for which the pK_a equals the solution's pH at the stoichiometric point (color change for the indicator occurs at the pK_a).

Indicator Choice

- Choose an indicator for the last example.

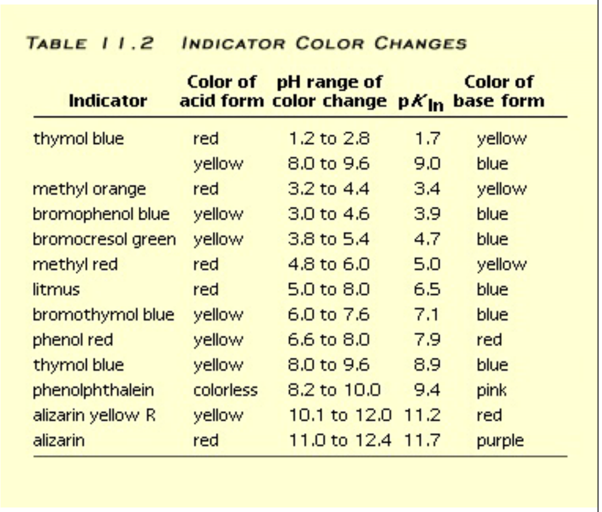
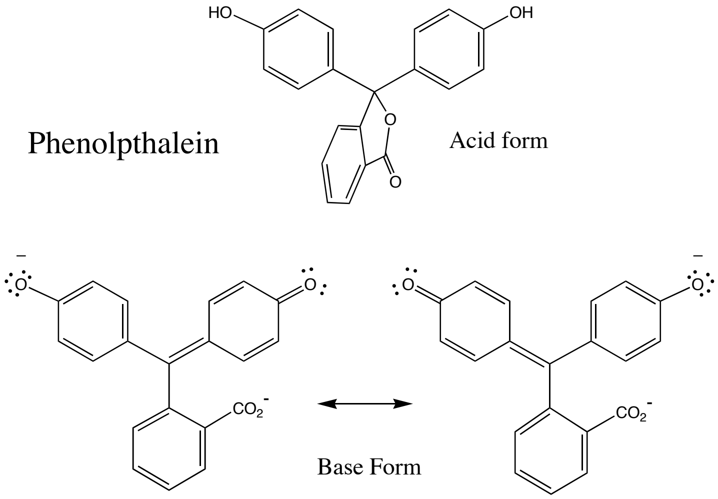


TABLE 11.2 INDICATOR COLOR CHANGES

Indicator	Color of acid form	pH range of color change	pK_{In}	Color of base form
thymol blue	red	1.2 to 2.8	1.7	yellow
	yellow	8.0 to 9.6	9.0	blue
methyl orange	red	3.2 to 4.4	3.4	yellow
bromophenol blue	yellow	3.0 to 4.6	3.9	blue
bromocresol green	yellow	3.8 to 5.4	4.7	blue
methyl red	red	4.8 to 6.0	5.0	yellow
litmus	red	5.0 to 8.0	6.5	blue
bromothymol blue	yellow	6.0 to 7.6	7.1	blue
phenol red	yellow	6.6 to 8.0	7.9	red
thymol blue	yellow	8.0 to 9.6	8.9	blue
phenolphthalein	colorless	8.2 to 10.0	9.4	pink
alizarin yellow R	yellow	10.1 to 12.0	11.2	red
alizarin	red	11.0 to 12.4	11.7	purple

How an indicator works



Phenolpthalein

Acid form

Base Form

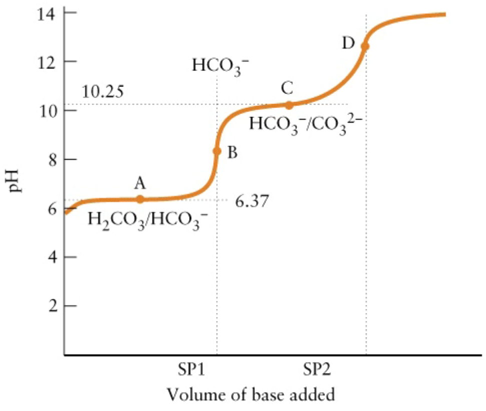
Polyprotic Acid Titrations

Titration curves show a stair step for each proton transferred in the “H_2CO_3”/ HCO_3^-/CO_3^{2-} system.

As in previous examples, the plateaus are buffer regions.

Bromocresol green is used as an indicator in lab. How is that done?

pK_{a1} = 6.37; pK_{a2} = 10.25



Polyprotic Acid Titrations

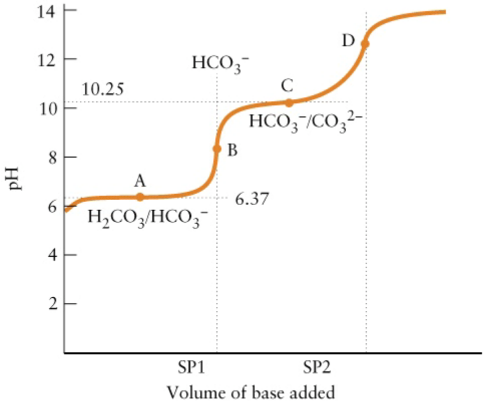
- If we start with 50 mL of a 0.2 M Na_2CO_3 solution, what is the pH at the beginning?
- What is the pH after adding 5 mmol of a strong acid (e.g., gaseous HCl)?

  10 mmol?

  15 mmol?

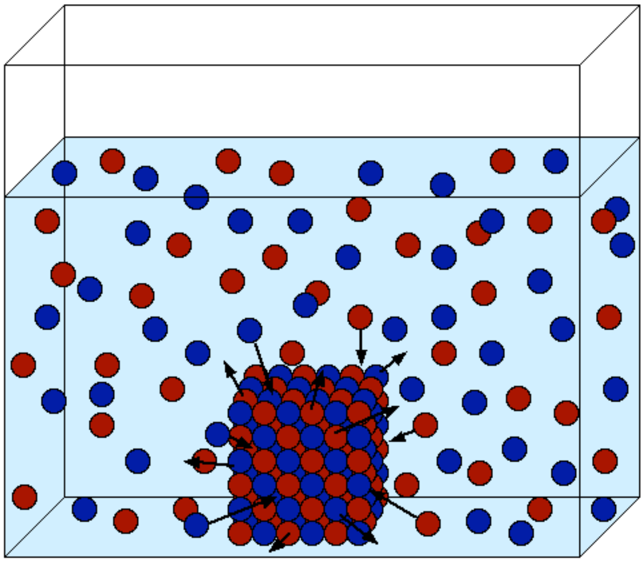
  20 mmol?

$pK_{a1} = 6.37; pK_{a2} = 10.25$



Solubility Equilibrium

The process is in equilibrium when rate of ions (or molecules) leaving the solid = rate returning to the solid. That is, when dissolution rate = precipitation rate



Solubility Product, K_{sp}

$$A_xB_y(s) \rightleftharpoons x\,A^{y+}(aq) + y\,B^{x-}(aq)$$

$$eg., \quad BaCl_2(s) \rightleftharpoons Ba^{2+}(aq) + 2\,Cl^{-}(aq)$$

- What is the form of the equilibrium constant?

$$K_{eq} = \frac{\text{activities of products}}{\text{activities of reactants}} \quad \text{(at equilibrium)}$$

- Use of concentrations is meaningful only for sparingly soluble or nearly insoluble salts.

K_{sp} from solubility

- In a saturated aqueous solution of MgF_2, the concentration of Mg^{2+} ions is 1.14×10^{-3} M. (Note: the solution must be saturated or no equilibrium is operative.)

Compute K_{sp} for MgF_2.

Solubility from K_{sp}

- K_{sp} for PbI_2 is 9.7 × 10^{-9}.
- K_{sp} for $PbSO_4$ is 1.8 × 10^{-8}.

Which compound has the greater molar solubility?

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More of the Common Ion Effect

- Solubility product equilibria can operate even the original source of the ions involved is not the salt that is precipitated.

Example: How much $AgNO_3$ must be added to a 10 M NaCl solution before a precipitate forms (What is the precipitate? What information do we need?)

K_{sp} for AgCl is 1.6×10^{-10}.

Common Ions - Predicting Precipitation

- K_{sp} for $PbCl_2$ is 1.7×10^{-5}.

What are the concentrations of of all species in solution when 2.78 g of $PbCl_2$ is added to 1.0 L of water? (Neglect the volume change.)

What are the concentrations of of all species in solution when 2.92 g of NaCl is added to the solution above? (Neglect the volume change.)

Selective Precipitation

- Differences in solubility can sometimes be used to separate mixtures of ions.
- Such differences are the basis of qualitative analysis schemes.
- Example: an acidic soln. contains 1.0 ´10^{-3} M of $Bi(NO_3)_3$, $Cr(NO_3)_3$, and $Co(NO_3)_3$. In what order do the hydroxides of each metal precipitate as solid NaOH is added? At what $[OH^-]$ and pH do each begin to precipitate?

K_{sp}'s:		
	$Bi(OH)_3$	3.2×10^{-40}
	$Cr(OH)_3$	6.7×10^{-31}
	$Co(OH)_3$	4.0×10^{-45}

Selective Precipitation

- Example, cont.: What % of Co^{3+} is still in solution when $Bi(OH)_3$ just begins to precipitate? What % of Bi^{3+} is still in solution when $Cr(OH)_3$ just begins to precipitate?

K_{sp}'s:

$Bi(OH)_3$	3.2×10^{-40}
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Complex Ion Formation

- Metal ions form complexes with various "ligands" (Lewis bases):
- Examples: Ag^+ forms a cyanide and ammine complexes

$$Ag^+ + 2\ CN^- \rightleftharpoons Ag(CN)_2^- \quad K_f = 5.6 \times 10^8$$

$$Ag^+ + 2\ NH_3 \rightleftharpoons Ag(NH_3)_2^+ \quad K_f = 1.6 \times 10^7$$

- Fe^{2+} and Fe^{3+} form very stable cyanide complexes:

$$Fe^{2+} + 6\ CN^- \rightleftharpoons Fe(CN)_6^{4-} \quad K_f = 7.7 \times 10^{36}$$

$$Fe^{3+} + 6\ CN^- \rightleftharpoons Fe(CN)_6^{3-} \quad K_f = 7.8 \times 10^{43}$$

Complex Ion Formation

- The complexation of metal ions can compete with other equilibria.
- Example: complexation by cyanide can compete with bromide for Ag^+ ions:

$$Ag^+ + 2\,CN^- \rightleftharpoons [Ag(CN)_2]^- \quad K_f = 5.6 \times 10^8$$

What is the solubility of AgBr in a 0.10 M KCN solution? For AgBr, $K_{sp} = 7.7 \times 10^{-13}$

Complex Ion Formation

- Solution. What we know:

$$Ag^+ + 2\,CN^- \rightleftharpoons [Ag(CN)_2]^- \quad K_f = 5.6 \times 10^8$$

$$AgBr \rightleftharpoons Ag^+ + Br^- \qquad K_{sp} = 7.7 \times 10^{-13}$$

The Ag^+ concentration will be very low, because Ag^+ is being “tied-up” in both the precipitate and the complex. It is easier to consider the reaction

$$AgBr + 2\,CN^- \rightleftharpoons [Ag(CN)_2]^- + Br^- \qquad K_{eq}$$

$$K_{eq} = K_{sp}K_f = 4.31 \times 10^{-4}$$

Complex Ion Formation

- Solution, cont.

$$AgBr + 2\,CN^- \rightleftharpoons [Ag(CN)_2]^- + Br^-$$

$$(0.1-2x) \qquad x \qquad x$$

$$K_{eq} = 4.31 \times 10^{-4} = x^2/(0.1-2x)^2$$

$$2.077 \times 10^{-2} = x/(0.1-2x)$$

$$\text{Solubility} = x = 1.99 \times 10^{-3}\ \text{mol/L}$$

Competing Equilibria can give Tricky Problems

- One of the two problems, (a) & (b), is easy and the other is not so easy. ($K_{sp}(MgF_2) = 6.4 \times 10^{-9}$)

Calculate the solubility of:

(a) MgF_2 in a 2.5×10^{-3} M solution of $Mg(NO_3)_2$.

(b) MgF_2 in a 1.0×10^{-1} M solution of KF.

- Which one is tricky?

The tricky problem

At first, it doesn't seem so bad:

$$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2F^-(aq)$$

$$x + (2.5 \times 10^{-3}) \quad 2x$$

Set-up and solve:

$6.4 \times 10^{-9} = (x + 2.5 \times 10^{-3})(2x)^2$

$x = 1.09 \times 10^{-3}$ - solved graphically

Bad News: This is wrong! Why?

(Hint: K_a(HF) = 3.47×10^{-4} — it gets messy!)

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Solubility Rules

1. The nitrates, chlorates and acetates of all metals are soluble in water. Silver acetate is sparingly soluble.
2. All sodium, potassium and ammonium salts are soluble in water.
3. The chlorides, bromides and iodides of all metals except lead, silver and mercury(I) are soluble in water. HgI_2 is insoluble in water. $PbCl_2$, $PbBr_2$, and PbI_2 are soluble in hot water. The water-insoluble chlorides, bromides and iodides are also insoluble in dilute acids.

Solubility Rules, cont.

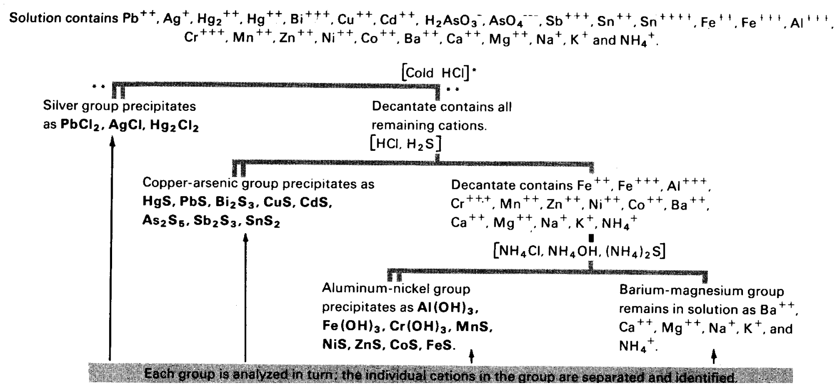
4. The sulfates of all metals except lead, mercury(I), barium and calcium are soluble in water. Silver sulfate is slightly soluble. The water-insoluble sulfates are also insoluble in dilute acids.
5. The carbonates, phosphates, borates, sulfites, chromates and arsenates of all metals except sodium, potassium and ammonium are insoluble in water but soluble in dilute acids. $MgCrO_4$ is soluble in water; $MgSO_3$ is slightly soluble in water.

Solubility Rules

6. The sulfides of all metals except barium, calcium, magnesium, sodium, potassium and ammonium are insoluble in water. BaS, CaS and MgS are sparingly soluble.

7. The hydroxides of sodium, potassium, and ammonium are very soluble in water. The hydroxides of calcium and barium are moderately soluble. The oxides and hydroxides of all other metals are insoluble.

Qualitative Analysis



Solution contains Pb^{++}, Ag^{+}, Hg_2^{++}, Hg^{++}, Bi^{+++}, Cu^{++}, Cd^{++}, $H_2AsO_3^{-}$, AsO_4^{---}, Sb^{+++}, Sn^{++}, Sn^{++++}, Fe^{++}, Fe^{+++}, Al^{+++}, Cr^{+++}, Mn^{++}, Zn^{++}, Ni^{++}, Co^{++}, Ba^{++}, Ca^{++}, Mg^{++}, Na^{+}, K^{+} and NH_4^{+}.

[Cold HCl]*

**

Silver group precipitates as **$PbCl_2$, $AgCl$, Hg_2Cl_2**

**

Decantate contains all remaining cations.

[HCl, H_2S]

Copper-arsenic group precipitates as **HgS, PbS, Bi_2S_3, CuS, CdS, As_2S_5, Sb_2S_3, SnS_2**

Decantate contains Fe^{++}, Fe^{+++}, Al^{+++}, Cr^{+++}, Mn^{++}, Zn^{++}, Ni^{++}, Co^{++}, Ba^{++}, Ca^{++}, Mg^{++}, Na^{+}, K^{+}, NH_4^{+}

[NH_4Cl, NH_4OH, $(NH_4)_2S$]

Aluminum-nickel group precipitates as **$Al(OH)_3$, $Fe(OH)_3$, $Cr(OH)_3$, MnS, NiS, ZnS, CoS, FeS.**

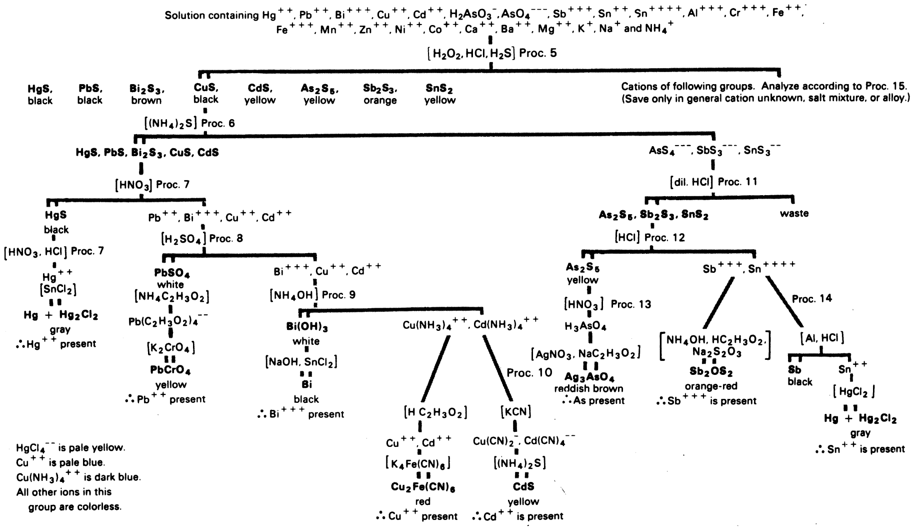
Barium-magnesium group remains in solution as Ba^{++}, Ca^{++}, Mg^{++}, Na^{+}, K^{+}, and NH_4^{+}.

Each group is analyzed in turn; the individual cations in the group are separated and identified.

*A bracketed formula [cold HCl] means that the substance (HCl in this case) is added as a reagent.

**The notation means separation by centrifuging and decanting. The double vertical parallel lines at the left refer to the precipitate and the one vertical line at the right refers to the decantate.

Qualitative Analysis



$HgCl_4^{--}$ is pale yellow.
Cu^{++} is pale blue.
$Cu(NH_3)_4^{++}$ is dark blue.
All other ions in this group are colorless.