General Chemistry II
Chapter 16 Lecture Notes

# Acids-Base and Solubility Equilibria

Introduction

This chapter consists of two distinct parts that utilize equilibrium expressions.
Acid-base reactions and acid-base titrations and acid-base buffers are studied using the familiar Ka expressions applied as usual to *homogeneous* systems.

Equilibria involving the precipitation of salts and salt solubility expressions are *heterogeneous* equilibria.

Common Ion Effect

The common ion effect is observed in weak acid and weak base equilibria as well as in solubility problems. The common ion effect is the shift in equilibrium caused by the addition of a species that is part of an equilibrium. Le Chatelier's principle predicts that the equilibrium will shift away from the added species.

Ex: The addition of ammonium or hydroxide ion to an ammonia solution shifts the equilibrium to the left.

$$NH_3(aq) \ + \ H_2O(l) \ \leftrightarrow \ NH_4^{+1}(aq) \ + \ OH^{-1}(aq)$$
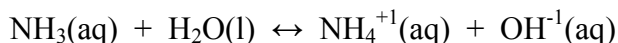
Buffer Solutions

An acid-base buffer is defined as a solution that resists changes in pH. A small amount of HCl or NaOH added to water results in a drastic pH change. It is often desirable to minimize pH changes in a system. In most biological systems, it is absolutely necessary to do so to keep the organism from dying. Human blood pH almost never varies from the range $7.25 - 7.35$ or death can result.

Acid-base buffers typically consist of a weak acid (HA) and its conjugate base (A^{-1}). The weak acid will react with added hydroxide ion, producing just the conjugate (weak) base that is already present, minimizing any pH increase. The conjugate base will react with any added hydrogen ion, producing the weak acid, which is already present, minimizing the pH drop.

The Henderson-Hasselbalch Equation

The pH of a buffer system can be easily determined from the Henderson-Hasselbalch equation.

For any weak acid, HA $\leftrightarrow$ H^{+1} + A^{-1} and K_a -= $[H^{+1}]{\cdot}[A^{-1}]/[HA]$

To find the pH, solve first for $[H^{+1}] \ = \ K_a [HA]/[A^{-1}]$

$\log [H^{-1}] \ = \ \log Ka \ + \ \log[HA]/[A^{-1}]$
$-\log [H^{+1}] \ = \ - \log Ka \ - \ \log[HA]/[A^{-1}]$

$pH = pK_a + \log[A^{-1}]/[HA]$

Note the effect on pH of the pK_a value, and changing the $[A^{-1}]/[HA]$ ratio.

Preparing Buffers with Specific pHs

The H-H equation, $pH = pK_a + \log[A^{-1}]/[HA]$, reduces to $pH = pK_a$ when the acid and conjugate base (salt) concentrations are equal.
To create a buffer system, choose an acid with pK_a as close as possible to the desired pH. The best possible buffer is one with the base/acid ratio close to unity so neither the base nor the acid is near depletion. Since few pK_a values will exactly match a desired pH value, adjust the buffer pH by small changes in the $[A^{-1}]/[HA]$ ratio.

Acid-Base Titrations

Titrations determine the concentration of an acid or a base by comparing it to the concentration of another acid or base.
The titration Equation is $M_A V_A = M_B V_B$ Derived from $n_A = n_B$ at the equivalence point.
(The term **endpoint** refers to a visible change in solution color that may or may not occur exactly at the equivalence point.)

Usually volumes are very well known (to 0.01 mL) so one concentration can be easily determined from the other. One solution is typically dispensed with a pipet and the other by a buret (both to 0.01 mL.)

At the **equivalence point**, the moles of $[H^{+1}]$ equals the moles of $[OH^{-1}]$. Just as in any acid-base reaction the products of the reaction will be a salt and water. The best way to track acid-base titrations is with a pH meter, which gives real-time pH readings to 0.01 pH unit as the titration progresses.

Acid-base titrations are complicated by the fact that the equivalence point does not always occur at pH 7. Consider the nature of the acid-base pair to predict the pH at which the equivalence point will occur.


Strong Base-Strong Acid Titrations

Only a strong acid-strong base titration produces a salt that does not hydrolyze and gives a neutral solution at the equivalence point. Titration of HCl with NaOH gives the salt NaCl at the equivalence point. Neither Na^{+1} nor Cl^{-1} hydrolyzes so the solution is neutral. A pH vs. added NaOH volume graph shows how quickly the pH changes at the equivalence point and how the equivalence point occurs at exactly pH 7.

Use the titration Equation $M_A V_A = M_B V_B$ to solve either for M_A or M_B, given the accurately measured volumes. At least one volume is determined by a buret to 0.01 mL; the other volume may be measured by a buret, or more commonly, by a 10, 25 or 50 mL pipet that delivers volumes to within 0.01 mL.

Weak Acid-Strong Base Titrations

At the equivalence point, the product is a salt that hydrolyzes to give a **basic** solution.

Titration of HF with NaOH leaves NaF at the equivalence point (when all HF protons have reacted with all NaOH hydroxide ions). The solution at the equivalence point is basic however, because fluoride ion hydrolyzes.

$$F^{-1}(aq) + H_2O(l) \leftrightarrow HF(aq) + OH^{-1}(aq)$$
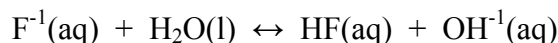
The equivalence point occurs at a basic pH, which can be calculated from the concentration of fluoride ion and its K_b. (A plot of pH vs. added NaOH volume shows a sharp pH change at a value above 7.)

Ex: what is the pH of 0.100 M F^{-1} if the K_b of fluoride is 1.9×10^{-7} ?

The hydrolysis of fluoride is given above with $K_b = [HF]\cdot[OH^{-1}]/[F^{-1}]$.
Assume X is negligibly small compared to $[F^{-1}]$ in the expression $K_b = 1.9 \times 10^{-7} = X^2/(0.100)$.
$X^2 = 1.9 \times 10^{-8}$ $X = 1.4 \times 10^{-4}$ $[OH^{-1}] = 1.4 \times 10^{-4}M$ pOH = 3.85   **pH = 10.15**

(More complex problems start with volumes of added acid and base and ask for pH at various points of the titration, not just the equivalence point.)

Again, the salt formed at the equivalence point hydrolyzes to form a basic solution, the exact pH of which depends on the concentration of the salt and K_b of the conjugate base, which is derived from the acid K_a.

Ex: Calculate the pH at the equivalence point of the titration of 25.00 mL of acetic acid with 17.05 mL of 0.150 M KOH. K_a of acetic acid $= 1.8 \times 10^{-5}$. K_b of the conjugate base acetate ion $= 5.6 \times 10^{-10}$

$M_A V_A = M_B V_B$ gives 1.02×10^{-1} M for the acetic acid or 1.02×10^{-1} mol/L x 0.02500 L $= 2.56 \times 10^{-3}$ mol of acid in the original 25.00 mL sample.
The same number of moles of acetate ion is present at the equivalence point in 42.05 mL of solution, giving an acetate concentration of $= 2.56 \times 10^{-3}$ mol/0.04205 L $= 6.08 \times 10^{-2}$ M.
Substituting into $K_b = [OH^{-1}][HA]/[A^{-1}]$, $5.6 \times 10^{-10} = X^2/(6.08 \times 10^{-2} -X)$, $X = 5.8 \times 10^{-6}$.
X is small enough to ignore relative to $[A^{-1}]$, so no further iterations are necessary.
$[OH^{-1}] = 5.8 \times 10^{-6}$ M, pOH = 5.24 and **pH = 8.76.**

Strong Acid-Weak Base Titrations

By analogy, the equivalence point of a strong acid-weak base titration results in an acidic solution.
The commonest weak base is ammonia, commonly titrated with HCl or HNO_3.
Protons are supplied by the dissociation (not really hydrolysis) of the ammonium ion.

Ex: What is the pH at the equivalence point when 10.00 mL of unknown methylamine solution (CH_3NH_2) is titrated with 23.77 mL of standard 0.100 M HCl?
K_b of methylamine is 4.4×10^{-4}. K_a of methylammonium ion is 2.3×10^{-11}.

$M_AV_A = M_BV_B$ gives 2.38×10^{-1} M for methylamine which gives 2.38×10^{-1} mol/L x 0.01000 L = 2.38 x 10^{-3} mol of methylamine in the original 10.00 mL sample.
At the equivalence point, 2.38×10^{-3} mol of methylammonium ion is also present but in 33.77 mL of solution.
$[CH_3NH_3^{+1}] = 2.38 \times 10^{-3}$ mol/0.03377 L = 7.05×10^{-2} M.

$K_a = [H^{+1}][CH_3NH_2]/[CH_3NH_3^{+1}]$. Substituting, $2.3 \times 10^{-11} = X^2/(7.05 \times 10^{-2} -X)$.
X which equals 1.3×10^{-6} can be ignored relative to $[CH_3NH_3^{+1}]$, so no further iterations are necessary.
$[H^{+1}] = 1.3 \times 10^{-6}$ M, **pH = 5.90.**

Acid-Base Indicators

Titrations were commonly done by the low-tech method of using an acid base indicator to signal the endpoint which one hopes will occur close to the equivalence point of the system.
Acid-base indicators are weak acids that change color as a proton is added/removed from the molecule.
$$In(aq) + H^{+1}(aq) \leftrightarrow HIn^{+1}(aq)$$
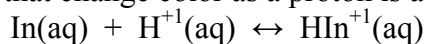
To be useful, an acid-base indicator should have a distinct color change and not over too wide a pH range. (A wide variety of acid-base indicators is available with color change choices across the pH scale. Many are vegetable dyes used to color fabrics.)

Acid-base indicators are chosen for a color change in the same pH range as the titration equivalence point. Phenolphthalein changes from colorless to pink in the pH range 8.3 to 10.0. Once commonly used for most acid-base titrations, it's best used for weak acid-strong base titrations. Bromothymol blue which changes from yellow to blue in the range 6.0 to 7.6 is good for strong acid-strong-base titrations. (Experienced titrators strive for green to get a pH in the middle of that range.) Methyl red which goes from red to yellow in the range 4.2 to 6.3 is used for strong acid-weak base titrations.

Solubility Equilibria

Solubility equilibria make quantitative predictions about the solubilities of many "insoluble" salts. Earlier emphasis was on learning solubility rules for "soluble" and "insoluble" salts. Chemical equilibrium concepts can be extended to quantitative discussion of solubilities and reactions undergone by salts. Even the most insoluble salt releases some ions into solution. These ion concentrations are incorporated into the "solubility product".

Solubility Product

When salts dissolve in water, whether they are very soluble or only slightly soluble, assume the ions in solution are completely dissociated. (When they are not they can cause errors in solubility calculations.)
For instance, for the "insoluble" salt barium sulfate,
$$BaSO_4(s) \leftrightarrow Ba^{+2}(aq) + SO_4^{-2}(aq)$$
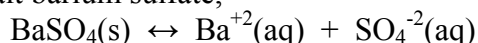
The equilibrium constant expresses the solubility of the salt (in a saturated solution) and since the activity of any solid is unity is given by:

$$K_{sp} = [Ba^{+2}] \cdot [SO_4^{-2}]$$

K_{sp} is called the solubility product and is constant for any aqueous system (usually given at 25ºC). Many K_{sp}
Values listed in table 16.2 show the extreme insolubility of some salts such as PbS.

Molar Solubility And Solubility

Molar solubilities in mol/L can be converted to K_{sp} values by inserting the concentration of each ion into the K_{sp} expression.

Es: The solubility of copper(I) sulfide, Cu_2S is 0.456 g/L. Calculate its molar solubility and the K_{sp}.

0.456 g/L x 1 mol Cu_2S/159.14 g = 2.87 x 10^{-3} mol/L.
K_{sp} = $[Cu^{+2}]^2 \cdot [S^{-2}]$ = (2 x 2.87 x 10^{-3})$^2 \cdot$ (2.87 x 10^{-3}) = 9.43 x 10^{-8}

K_{sp} values are also used to calculate molar and gram solubilities.

Given K_{sp} of BaF_2 = 1.7 x 10^{-6}, what is the molar and gram solubility of BaF_2?
In a saturated BaF_2 solution, $[F^{-1}]$ = 2$[Ba^{+2}]$
K_{sp} = $[Ba^{+2}] \cdot [F^{-1}]^2$. Substituting, 1.7 x 10^{-6} = (2X)$^2 \cdot$ X. 4X^3 = 1.7 x 10^{-6} X = 7.5 x 10^{-3}.
$[Ba^{+2}]$ = $[BaF_2]$= 7.5 x 10^{-3}M
BaF_2 gram solubility = 7.5 x 10^{-3} mol BaF_2/L x 175.3g/mol = 1.3 g/L.

Precipitation Reactions

The precipitation of a salt can be predicted simply by inserting the concentrations of the ions into the ion product formula. If the result is greater than K_{sp}, the salt will precipitate.

Ex: If a 0.100 M $Pb(NO_3)_2$ solution is made 0.030 M in NaCl, will $PbCl_2$ precipitate?
K_{sp} = $[Pb^{+2}] \cdot [Cl^{-1}]^2$ = 2.4 x 10^{-4}.

Substituting the concentrations given into $[Pb^{+2}] \cdot [Cl^{-1}]^2$ gives (0.100) (0.030)^2 = 9.0 x 10^{-5}.
$PbCl_2$ will not precipitate.

Separation of Ions by Fractional Precipitation

Two similar ions can be separated if their salts with another ion have sufficiently different solubilities.
For instance barium carbonate and strontium carbonate have almost the same K_{sp} values, 8.1 x 10^{-9} and
1.6 x 10^{-9}, respectively, so the two metal ions cannot be separated by precipitating their carbonates. On
the other hand, barium sulfate and strontium sulfate have K_{sp} values of 1.1 x 10^{-10} and 3.8 x 10^{-7}.

Ex: A solution is 0.100 M $BaCl_2$ and 0.100 M $SrCl_2$. Na_2SO_4 solution added slowly will precipitate $BaSO_4$ and not $SrSO_4$ if the concentration of sulfate does not exceed the solubility product of $SrSO_4$.

$$K_{sp} = [M^{+2}] [SO_4^{-2}]$$

To precipitate $BaSO_4$, $SO_4^{-2}(aq) = K_{sp}/[Ba^{+2}] = (1.1 \times 10^{-10})/0.100 = 1.1 \times 10^{-9}$ M
To precipitate $SrSO_4$, $SO_4^{-2}(aq) = K_{sp}/[Sr^{+2}] = (3.8 \times 10^{-7})/0.100 = 3.8 \times 10^{-6}$ M

The Common Ion Effect and Solubility

The simplified equation $AB(s) \leftrightarrow A^+(aq) + B^-(aq)$ describes the equilibrium between a solid salt and its ions in solution. For this reaction,

$$K_{sp} = [A^+]\cdot[B^-]$$

Adding either $A^+(aq)$ or $B^-(aq)$ from a separate source (such as a soluble salt with an inert counterion) decreases the concentration of the other ion and decrease the solubility of the salt AB (without, of course affecting the value of K_{sp} which is a constant).

Ex: Barium ion is extremely toxic, yet $BaSO_4$ is given routinely as an x-ray contrast medium to visualize the digestive tract. $BaSO_4$ is safe to give alone but it is sometimes given with soluble $MgSO_4$ to hurry its expulsion and to reduce $[Ba^{+2}]$ in the digestive tract.
What is the solubility of $BaSO_4$ in water and what is its solubility in 0.200 M $MgSO_4$?
$BaSO_4$ $K_{sp} = 1.0 \times 10^{-10} = [Ba^{+2}] \cdot [SO_4^{-2}]$
$s = [BaSO_4] = [Ba^{+2}] = [SO_4^{-2}]$ when ions from other sources are not present.
$s^2 = [Ba^{+2}] \cdot [SO_4^{-2}]$
$s = 1.0 \times 10^{-5}$ M $= [BaSO_4]$ when ions from other sources are not present. (~1.4 mg Ba^{+2}/L)

When $[SO_4^{-2}] = 0.200$ M from added $MgSO_4$, $K_{sp} = 1.1 \times 10^{-10} = [Ba^{+2}] \cdot (0.200)$
$[Ba^{+2}] = [BaSO_4] = 5.5 \times 10^{-10}$ M. (~8 x 10^{-5} mg Ba^{+2}/L)

pH And Solubility

If the concentration or form of an ion in a solubility equilibrium is affected by the solution pH, then pH will affect the solubility of that salt, acid or base.
Ions whose concentration changes with pH include carbonate, fluoride, hydroxide, nitrite, sulfide and cyanide, but not chloride, bromide, iodide, sulfate* or nitrate.

Ex: At what pH will calcium hydroxide begin to dissolve?
$Ca(OH)_2$ has $K_{sp} = 8.0 \times 10^{-6}$
In saturated $Ca(OH)_2$ solution, $[Ca^{+2}] = 1.26 \times 10^{-2} \cong 1.3 \times 10^{-2}$ M and $[OH^{-1}] = 2.5 \times 10^{-2}$ M.
pOH $= 1.60$ and pH $= 12.40$.
$Ca(OH)_2$ dissolves to a greater extent below pH 12.40 because hydroxide ion is depleted by $[H^{+1}]$.

Ex: For which of the following compounds will pH affect the solubility?
FeS, $FeSO_4$, $PbCl_2$, AgI, $Cd(OH)_2$, CaF_2

Ex: At what ammonia concentration will 0.0100 M Fe^{+2}(aq) precipitate as $Fe(OH)_2$(s)?
Iron (II) hydroxide begins to precipitate when $[Fe^{+2}]$ and $[OH^{-1}]$ exceed the solubility product 1.6 x 10^{-14}.
Calculate the $[OH^{-1}]$ necessary to exceed the solubility product for 0.0100 M Fe^{+2}(aq) and calculate the
ammonia concentration needed to produce that $[OH^{-1}]$.

$K_{sp} = [Fe^{+2}] \cdot [OH^{-1}]^2$ 1.6 x 10^{-14} = (0.0100) s^2 s^2 = 1.6 x 10^{-12} s = 1.3 x 10^{-6}
$[OH^{-1}]$ = 1.3 x 10^{-6} M   (pH = 8.10, not very basic)
What ammonia concentration is needed to produce this $[OH^{-1}]$?
K_b of ammonia is 1.8 x 10^{-5}.
$K_b = [NH_4^{+1}] \cdot [OH^{-1}]/[NH_3]$ Assume $[NH_4^{+1}] = [OH^{-1}]$
Substitution gives 1.8 x 10^{-5} = $[OH^{-1}]^2/[NH_3]$
$[NH_3]$ = = $[OH^{-1}]^2 /K_b$ = (1.3 x 10^{-5})^2/ (1.8 x 10^{-5}) $[NH_3]$ = 9.4 x 10^{-6} M, very low!
(Al(III) and Fe(III) hydroxides precipitate even in acidic solutions because of low K_{sp} values near 10^{-33}.)

Complex Ions and Solubility

Many metal ions, particularly transition metal ions, act as Lewis acids and form complexes with Lewis
bases (electron pair donors) called ligands. The formation of these complexes effectively lowers the
concentration of the metal ion in solution, increasing the solubility of that metal's salts.

Transition metal ions have partially occupied d orbitals that serve as electron pair acceptors to ligands
such as water, ammonia, cyanide, halide ions, etc.
Commonly encountered complexes are $Ag(NH_3)_2^{+1}$, $CoCl_4^{-2}$, $Cu(NH_3)^{+2}$, $Al(OH)_4^{-1}$, etc.
Complex formation is used to dissolve insoluble precipitates such as AgCl, $Cu(OH)_2$, $Al(OH)_3$, etc.
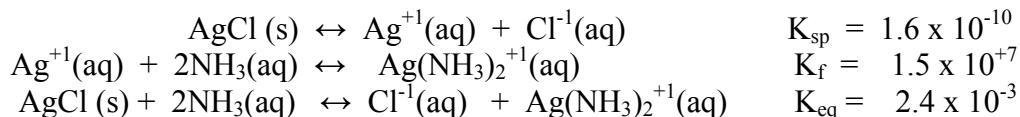
The equation for the formation of a metal ion-ligand complex often has a large equilibrium constant
symbolized by K_f. If K_f is large, the metal ion concentration at equilibrium will be very low.
For instance, for Ag^{+1}(aq) + $2NH_3$(aq) $\leftrightarrow$ $Ag(NH_3)_2^{+1}$(aq)
$K_{eq} = K_f = [Ag(NH_3)_2^{+1}]/ [Ag^{+1}] \cdot [NH_3]^2 = 1.5$ x 10^{+7}

The large K_f of $Ag(NH_3)_2^{+1}$ explains why ammonia is used to dissolve silver chloride and silver bromide
precipitates in analytical procedures. AgI does not dissolve in excess ammonia because its solubility
product is 5 x 10^6 times smaller than that of AgCl.

Ex: Calculate the minimum ammonia concentration in 100 mL of solution needed to dissolve 1.00 mmol
of an AgCl precipitate (K_{sp} = 1.6 x 10^{-10}). 1.00 mmol/100.0 mL = 1.00 x 10^{-2} M Ag^{+1}

$$AgCl \text{ (s)} \leftrightarrow Ag^{+1}\text{(aq)} + Cl^{-1}\text{(aq)} \qquad K_{sp} = 1.6 \text{ x } 10^{-10}$$
$$Ag^{+1}\text{(aq)} + 2NH_3\text{(aq)} \leftrightarrow Ag(NH_3)_2^{+1}\text{(aq)} \qquad K_f = 1.5 \text{ x } 10^{+7}$$
$$AgCl \text{ (s)} + 2NH_3\text{(aq)} \leftrightarrow Cl^{-1}\text{(aq)} + Ag(NH_3)_2^{+1}\text{(aq)} \qquad K_{eq} = 2.4 \text{ x } 10^{-3}$$

When the precipitate is fully dissolved, $[Cl^{-1}]$ = $[Ag(NH_3)_2^{+1}]$ = 1.00 x 10^{-2} M

$K_{eq} = 2.4 \times 10^{+3} = [Cl^{-1}] \cdot [Ag(NH_3)_2^{+1}]/[NH_3]^2$

$[NH_3]^2 = (1.00 \times 10^{-2})^2/(2.4 \times 10^{-3}) = 4.2 \times 10^{-2}$

$[NH_3] = 2.0 \times 10^{-1}$ M, easily attained by using 6M NH_3

Ex: AgBr will not dissolve in 6M NH_3 but will in 15 M NH_3. Calculate the minimum ammonia concentration in 100 mL solution needed to dissolve 1.00 mmol of AgBr precipitate if $K_{sp} = 7.7 \times 10^{-13}$. (When the precipitate is dissolved, $[Ag^{+1}] = 1.00 \times 10^{-2}$ M $= [Ag(NH_3)_2^{+1}]$ as in the AgCl example.)

$$AgBr(s) + 2NH_3(aq) \leftrightarrow Br^{-1}(aq) + Ag(NH_3)_2^{+1}(aq) \qquad K_{eq} = 1.2 \times 10^{-5}$$
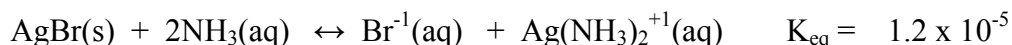
When the precipitate is fully dissolved, $[Br^{-1}] = [Ag(NH_3)_2^{+1}] = 1.00 \times 10^{-2}$ M

$K_{eq} = 1.2 \times 10^{-5} = [Br^{-1}] \cdot [Ag(NH_3)_2^{+1}]/[NH_3]^2$
$[NH_3]^2 = (1.00 \times 10^{-2})^2/(1.2 \times 10^{-5}) = 8.3$
$[NH_3] = 2.9$ M, attainable by using 15 M $[NH_3]$

Ex: Calculate the reason for the insolubility of AgI in 15M $[NH_3]$:

K_{sp} of AgI $= 8.3 \times 10^{-17}$

$$AgI(s) + 2NH_3(aq) \leftrightarrow I^{-1}(aq) + Ag(NH_3)_2^{+1}(aq) \qquad K_{eq} = 1.2 \times 10^{-9}$$

$[NH_3]^2 = (1.00 \times 10^{-2})^2/(1.2 \times 10^{-9}) = 8.3 \times 10^4$
$[NH_3] = 290$ M, which is unattainable

Applying the Solubility Product to Qualitative Analysis

Qualitative analysis of certain metal ions:
Titration and gravimetric analysis are commonly used to analyze metal ions quantitatively.
Flame photometry used for qualitative and quantitative work.
An older method uses selective precipitation of metal ions with anions.
One scheme groups cations in five groups (not related to periodic table groups).

Group 1: Ag^{+1}, Hg_2^{+2}, Pb^{+2}; Precipitated by chloride ion
Group 2: Bi^{+3}, Cd^{+2}, Sn^{+2}; Precipitated by acid H_2S
Group 3: Al^{+3}, Co^{+2}, Cr^{+3}, Fe^{+2}, Mn^{+2}, Ni^{+2}, Zn^{+2}; Precipitated by basic H_2S (or OH^{-1})
Group 4: Ba^{+2}, Ca^{+2}, Sr^{+2}; Precipitated by carbonate
Group 5: K^{+1}, Na^{+1}, NH_4^{+1}; No common precipitants

After precipitation, other tests must be done to distinguish within a group.
In group 5, K^{+1} and Na^{+1}, NH_4^{+1} are distinguished by flame emission colors.
NH_4^{+1} is proven by odor and basicity of volatile ammonia.