Separation by Precipitation

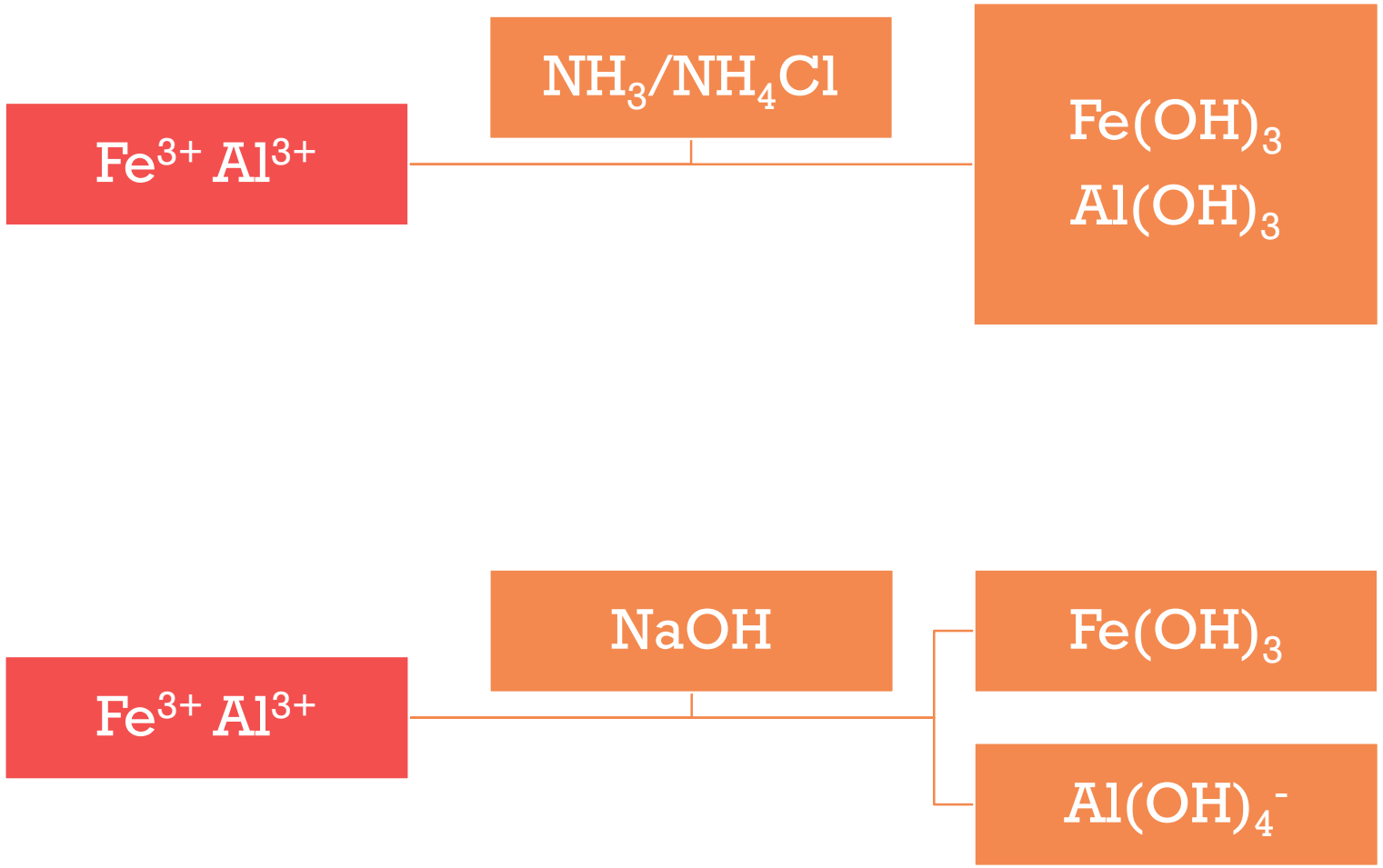
Ideally, a gravimetric precipitating agent should react specifically or at least selectively with the analyte.

Reagent	Solution	Analyte	Specific or Selective
$AgNO_3$	Acidic	I^- Br^- Cl^- SCN^-	Selective
Dimethylglyoxime	Alkaline	Ni^{2+}	Specific

- Separations by precipitation require **large solubility differences between the analyte and potential interferents**.
- The theoretical feasibility of this type of separation can be determined by **solubility calculations**.
- Unfortunately, several other factors (**coprecipitation phenomena**) may preclude the use of precipitation to achieve a separation.
- Finally, when precipitates form as colloidal suspensions, **coagulation** may be difficult and slow, particularly when the isolation of a small quantity of a solid phase is attempted.
- Many precipitating agents have been used for quantitative inorganic separations.

Separations Based on Control of Acidity

- Many separations based on pH control are in theory possible. In practice, these separations can be grouped in three categories:
  - those made in relatively concentrated solutions of strong acids,
  - those made in buffered solutions at intermediate pH values
  - those made in concentrated solutions of sodium or potassium hydroxide


Fe^{3+} Al^{3+}
NH_3/NH_4Cl
$Fe(OH)_3$
$Al(OH)_3$
Fe^{3+} Al^{3+}
NaOH
$Fe(OH)_3$
$Al(OH)_4^-$

Sulfide Separations

- Sulfide ion forms precipitates with heavy metal cations that have solubility products that vary from 10^{-10} to 10^{-90} or smaller.
- In addition, the concentration of S^{2-} can be varied over a range of about 0.1 M to 10^{-22} M by controlling the pH of a saturated solution of hydrogen sulfide.
- To illustrate the use of hydrogen sulfide to separate cations based on pH control, consider the precipitation of the divalent cation M^{2+} from a solution that is kept **saturated with hydrogen sulfide by bubbling the gas continuously** through the solution.

Separations by Other Inorganic Precipitants

- No other inorganic ions are as generally useful for separations as hydroxide and sulfide ions.
- **Phosphate**, **carbonate**, and **oxalate** ions are often used as precipitants for cations, but they are not selective.
- **Chloride** and **sulfate** are useful because of their highly selective behavior.

Separations by Organic Precipitants

- There are two types of organic reagents:
  - one forms slightly soluble nonionic products called coordination compounds,
  - the other forms products in which the bonding between the inorganic species and the reagent is largely ionic.

8-Hydroxyquinoline (Oxine)

- Two dozen cations form sparingly soluble chelates with 8-hydroxyquinoline.
- The solubilities of metal 8-hydroxyquinolates vary widely from cation to cation and are pH dependent because 8-hydroxyquinoline is always deprotonated during a chelation reaction.

Dimethylglyoxime

- Dimethylglyoxime is an organic precipitating agent of unparalleled specificity.
- Only nickel(II) is precipitated from a weakly alkaline solution.

Sodium Tetraphenylborate

- Sodium tetraphenylborate is an important example of an organic precipitating reagent that forms salt-like precipitates.
- In cold mineral acid solutions, it is a near-specific precipitating agent for potassium and ammonium ions.