Chapter 27 Gravimetric and Combustion Analysis

Gravimetric Methods

- **Gravimetric analysis** uses the mass of a product to calculate the quantity of analyte
- Gravimetry was used in Nobel prize-winning work to determine atomic to six digits
  - It was a common procedure for determining industrial materials in the 19th century
  - Too tedious for most applications today, but when used is still one of the most accurate methods

Example Gravimetric Analysis

- A 10.00 mL solution with Cl^- was treated with $AgNO_3$ to precipitate 0.4368 g AgCl (MW=143.321). What was the molarity of Cl^-?

$$Ag^+ + Cl^- \rightarrow AgCl(s)$$

$$\text{mol } Cl^- = \text{mol AgCl} = \frac{0.4368\text{ g AgCl}}{143.321\text{ g/mol AgCl}} = 3.048\times10^{-3}\text{ mol}$$

$$[Cl^-] = \frac{3.048\times10^{-3}\text{ mol}}{0.01000\text{ L}} = 0.3048\text{ M}$$

Some Typical Gravimetric Analyses

Table 27-1 Representative gravimetric analyses

Species analyzed	Precipitated form	Form weighed	Interfering species
Ni^{2+}	Ni(dimethylglyoximate)$_2$	Same	Pd^{2+}, Pt^{2+}, Bi^{3+}, Au^{3+}
Cu^{2+}	CuSCN	CuSCN	NH_4^+, Pb^{2+}, Hg^{2+}, Ag^+
Zn^{2+}	$Zn(NH_4)PO_4\cdot H_2O$	$Zn_2P_2O_7$	Many metals
Ce^{4+}	$Ce(IO_3)_4$	CeO_2	Th^{4+}, Ti^{4+}, Zr^{4+}
Al^{3+}	Al(8-hydroxyquinolate)$_3$	Same	Many metals
Sn^{4+}	Sn(cupferron)$_4$	SnO_2	Cu^{2+}, Pb^{2+}, As(III)
Pb^{2+}	$PbSO_4$	$PbSO_4$	Ca^{2+}, Sr^{2+}, Ba^{2+}, Hg^{2+}, Ag^+, HCl, HNO_3
NH_4^+	$NH_4B(C_6H_5)_4$	$NH_4B(C_6H_5)_4$	K^+, Rb^+, Cs^+
Cl^-	AgCl	AgCl	Br^-, I^-, SCN^-, S^{2-}, $S_2O_3^{2-}$, CN^-
Br^-	AgBr	AgBr	Cl^-, I^-, SCN^-, S^{2-}, $S_2O_3^{2-}$, CN^-
I^-	AgI	AgI	Cl^-, Br^-, SCN^-, S^{2-}, $S_2O_3^{2-}$, CN^-
SCN^-	CuSCN	CuSCN	NH_4^+, Pb^{2+}, Hg^{2+}, Ag^+
CN^-	AgCN	AgCN	Cl^-, Br^-, I^-, SCN^-, S^{2-}, $S_2O_3^{2-}$
F^-	$(C_6H_5)_3SnF$	$(C_6H_5)_3SnF$	Many metals (except alkali metals), SiO_4^{4-}, CO_3^{2-}
ClO_4^-	$KClO_4$	$KClO_4$	
SO_4^{2-}	$BaSO_4$	$BaSO_4$	Na^+, K^+, Li^+, Ca^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Sr^{2+}, Pb^{2+}, NO_3^-
PO_4^{3-}	$Mg(NH_4)PO_4\cdot 6H_2O$	$Mg_2P_2O_7$	Many metals except Na^+, K^+
NO_3^-	Nitron nitrate	Nitron nitrate	ClO_4^-, I^-, SCN^-, CrO_4^{2-}, ClO_3^-, NO_2^-, Br^-, $C_2O_4^{2-}$
CO_3^{2-}	CO_2 (by acidification)	CO_2	(The liberated CO_2 is trapped with Ascarite and weighed.)

Organic Precipitation Reagents

Table 27-2 Common organic precipitating agents

Name	Structure	Ions precipitated
Dimethylglyoxime		Ni^{2+}, Pd^{2+}, Pt^{2+}
Cupferron		Fe^{3+}, VO_2^+, Ti^{4+}, Zr^{4+}, Ce^{4+}, Ga^{3+}, Sn^{4+}
8-Hydroxyquinoline (oxine)		Mg^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, Fe^{3+}, Bi^{3+}, Ga^{3+}, Th^{4+}, Zr^{4+}, UO_2^{2+}, TiO^{2+}
Salicylaldoxime		Cu^{2+}, Pb^{2+}, Bi^{3+}, Zn^{2+}, Ni^{2+}, Pd^{2+}
1-Nitroso-2-naphthol		Co^{2+}, Fe^{3+}, Pd^{2+}, Zr^{4+}
Nitron		NO_3^-, ClO_4^-, BF_4^-, WO_4^{2-}
Sodium tetraphenylborate	$Na^+B(C_6H_5)_4^-$	K^+, Rb^+, Cs^+, NH_4^+, Ag^+, organic ammonium ions
Tetraphenylarsonium chloride	$(C_6H_5)_4As^+Cl^-$	$Cr_2O_7^{2-}$, MnO_4^-, ReO_4^-, MoO_4^{2-}, WO_4^{2-}, ClO_4^-, I_3^-

Precipitation

- Assumptions for gravimetric analysis:
  - Big *K*
  - Easily filtered (particle size not too small)
  - Very pure
  - Known composition
- Conditions can be altered when needed
  - Cooling solution to decrease solubility
  - Avoidance of *colloidal suspensions* (particle size <100nm that pass through filters)

Crystal Growth During Precipitation

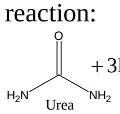
- **Crystallization** occurs in two phases:
  - **Nucleation**, where molecules in solution randomly form small aggregates of molecules
  - **Particle growth** is the addition of more molecules to the aggregate to form a crystal
- In a supersaturated solution, nucleation goes faster than particle growth.
  - This is bad because you wind up with many small particles in solution (a colloid) and few large ones
  - Must do something to promote particle growth

Ways to Promote Particle Growth

- Raise the temperature
  - Increases solubility, decreasing supersaturation
- Add precipitant slowly
  - Avoids localized supersaturation
- Keep volume of solution large
  - Analyte and reagent concentrations are kept low

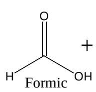
Homogeneous Precipitation

- With **homogeneous precipitation**, the precipitant is generated slowly by a chemical reaction:



Urea

$$+ 3H_2O \xrightarrow{\text{heat}} CO_2 + 2NH_4^+ + 2OH^-$$



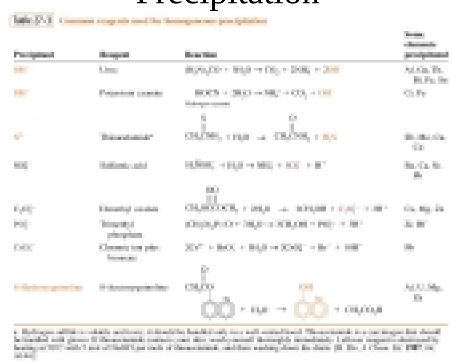
Formic Acid

$$+ OH^- \rightarrow HCO_2^- + H_2O$$

$$3HCO_2^- + Fe^{3+} \rightarrow Fe(HCO_2^-)_3 \cdot H_2O(s)$$

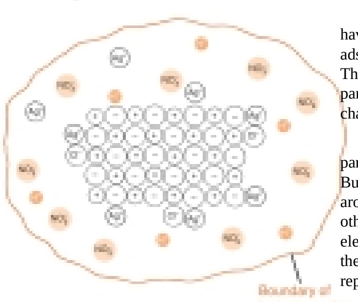
  - Slow OH^- formation enhances particle growth of iron formate

Reagents for Homogeneous Precipitation



Precipitation Using an Electrolyte

- Ionic compounds are usually precipitated in the presence of an electrolyte; for AgCl



The surface of the particle will have a small positive charge due to adsorption of excess silver ions. The *ionic atmosphere* surrounds the particle and has a slight net negative charge.

For particle growth, colloidal particles must collide to coalesce. But the negative atmospheres around the particles repulse each other electrostatically. Adding electrolyte decreases the volume of the ionic atmospheres, allowing repulsion to be overcome.

Steps in a Gravimetric Analysis

- Precipitation (we’ve talked about this!)
- **Digestion**
  - Promotes slow crystallization, increased particle size, and expulsion of impurities from the crystal
- Purification of coprecipitants
  - *Adsorbed* impurities are bound to the surface
  - *Absorbed* impurities are within the crystal
    - Inclusions are random ions of impurity
    - Occlusions are pockets of impurity within the crystal
- Weighing

Purification Procedures

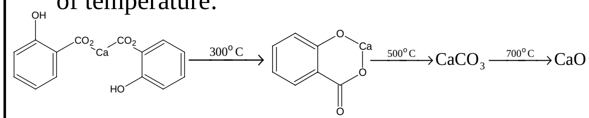
- Many procedures call for *reprecipitation*
  - The impurity concentrations are much lower when redissolved, making coprecipitation much lower
  - A trace impurity can be coprecipitated with a major component of solution using a **gathering** agent
- Some impurities can be masked
  - Typically, formation of a complex ion to keep the impurity in solution can be used

Obtaining a Final Known Composition

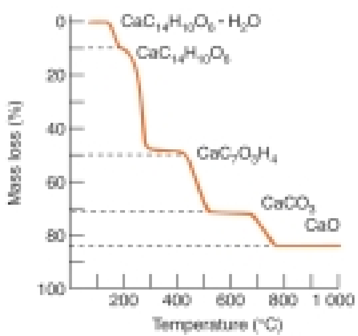
- **Ignition** is often used to drive off water or give an oxide form

$$Fe(HCO_2^-)_3 \cdot H_2O(s) \xrightarrow{850^o C\ 1hr} Fe_2O_3(s) + CO_2(g) + H_2O(g)$$

- **Thermogravimetry** is a form of gravimetric analysis where mass is measured as a function of temperature:

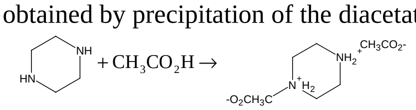


Thermogravimetry



Example 1-Piperazine

- Piperazine content of an impure material can be obtained by precipitation of the diacetate:



- In an experiment, 0.3126 g of sample was dissolved in 25 mL acetone, and 1 mL acetic acid was added. The precipitate was filtered, washed, and dried and found to weight 0.7121 g. What is the wt% piperazine in the sample?

Example 1 (Cont.)

- Find the moles of product:

$$\text{mol Pip diAc}^- = \frac{0.7121\text{g}}{206.240\ \text{g/mol}} = 3.453\times10^{-3}\text{mol} = \text{mol Pip}$$

- Mass of reactant:

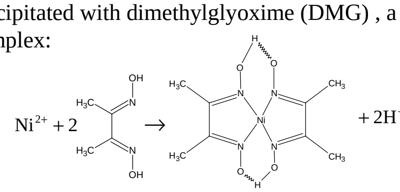
$$\text{g Pip} = (3.453\times10^{-3}\text{mol})(86.136\ \text{g/mol}) = 0.2974\ \text{g}$$

- Weight percent:

$$\text{Wt \% Pip} = \frac{0.2974\ \text{g}}{0.3126\text{g}}\times100 = 95.14\ \%$$

Example 2-Calculating Reagent to Use

- Nickel in steel can be measured by dissolving the alloy in 12 M HCl and neutralized. Nickel can be precipitated with dimethylglyoxime (DMG) , a red complex:



- If the nickel content is ~ 3 wt%, and you wish to analyze 1 g of steel, what volume of 1.0 wt% DMG should be used to give 50% excess DMG? The density of DMG solution is 0.79 g/mL

Example 2 (Cont)

- What first?
  - Find the mol of Ni in the steel sample

$$\text{mol Ni} = \frac{(1.0\text{ g})(0.03)}{58.69\text{ g/mol}} = 5.11\times10^{-4}\text{ mol}$$

- How much DMG is required?

$$\text{g DMG} = 2(5.11\times10^{-4}\text{ mol})(116.12\text{ g/mol}) = 0.119\text{ g DMG}$$

$$50\%\text{ excess DMG} = 1.5(0.119\text{ g DMG}) = 0.178\text{ g}$$

- How much volume?

$$\text{mL soln.} = \frac{0.178\text{ g DMG}}{0.010\text{ g DMG/g soln.}}/(0.79\text{ g soln./mL}) = 23\text{ mL}$$

Example 2 (Cont)

- If 1.163 g steel gave 0.1795 g precipitate, what % of Ni is in the steel?
  - There is 1 mol of precipitate for 1 mol of Ni:

$$\text{mol Ni(DMG)}_2 = \frac{0.1795\text{ g Ni(DMG)}_2}{288.91\text{ g/mol Ni(DMG)}_2} = 6.213\times10^{-4}\text{ mol}$$

  - Ni in the alloy:

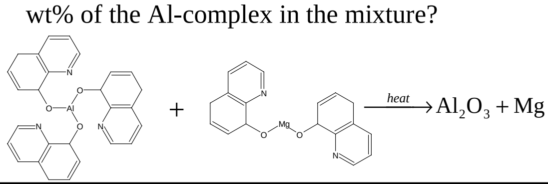
$$(6.213\times10^{-4})(58.69\text{ g/mol}) = 0.03646\text{ g Ni}$$

  - Wt percent of Ni in the steel:

$$\frac{0.03646\text{ g Ni}}{1.1634\text{ g steel}}\times100 = 3.314\,\%$$

Example 3--A Mixture

- 8-hydroxyquinoline (Q) can complex and precipitate many metals. A mixture of the aluminum and magnesium complexes weighed 1.0843 g (MW=459.43; 312.61). When ignited, the mixture decomposed and left a residue of Al_2O_3 and MgO weighing 0.1344 g. What is the wt% of the Al-complex in the mixture?



Example 3 (Cont)

- If the mass of AlQ_3 is x and mass of MgQ_2 is y:

$$x + y = 1.0843\text{ g}$$

- If we then find the mass of product oxides:

$$\text{mol Al} = \frac{x}{459.43} \qquad \text{mol Mg} = \frac{y}{312.61}$$

$$\text{mol Al}_2\text{O}_3 = \frac{1}{2}\cdot\frac{x}{459.43} \qquad \text{mol MgO} = \frac{y}{312.61}$$

$$\frac{1}{2}\left(\frac{x}{459.43}\right)(101.96) + \frac{y}{312.61}(40.304) = 0.1344\text{ g}$$

- Substituting the 1st equation into the 2nd:

$$\frac{1}{2}\left(\frac{x}{459.43}\right)(101.96) + \frac{1.0843 - x}{312.61}(40.304) = 0.1344\text{ g}$$

$$x = 0.3003\text{ g} \qquad \%\text{AlQ}_3 = \frac{0.3003\text{ g}}{1.0843\text{ g}}\times100 = 27.70\%$$