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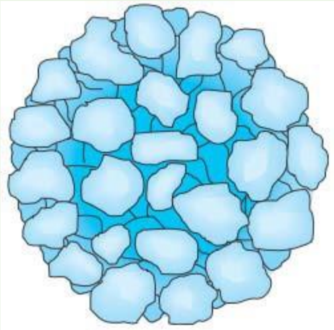
Gravimetric Calculations (II)

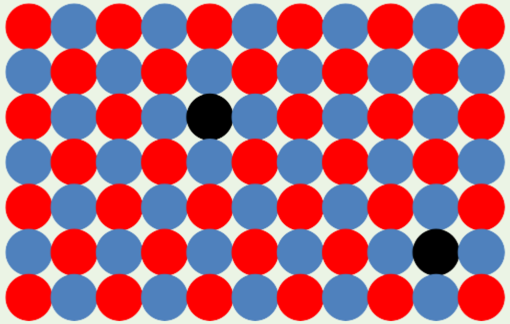
Surface Adsorption

- The impurity is chemically or physically adsorbed onto the surface of precipitates
- Adsorption is the major source of contamination in coagulated colloids but of no significance in crystalline precipitates.
  - *Minimizing Adsorbed Impurities on Colloids, HOW?*
    - *Washing* a coagulated colloid with a solution containing a volatile electrolyte
    - *Digestion*: during this process, water is expelled from the solid to give a denser mass that has a smaller specific surface area for adsorption.
    - *Re-precipitation*: In this process, the filtered solid is re-dissolved and re-precipitated. The solution containing the re-dissolved precipitate has a significantly <u>lower</u> contaminant concentration than the original, and even less adsorption occurs during the second precipitation.



Mixed-Crystal Formation

- A type of co-precipitation in which a contaminant ion replaces an ion in the lattice of a crystal.



Example: $SrSO_4$ in $BaSO_4$

$MgKPO_4$ in $MgNH_4PO_4$

MnS in CdS

- Mixed-crystal formation may occur in both colloidal and crystalline precipitates

- *Problem solving*:
  A. Change to another more selective precipitating agent
  B. Re-precipitation

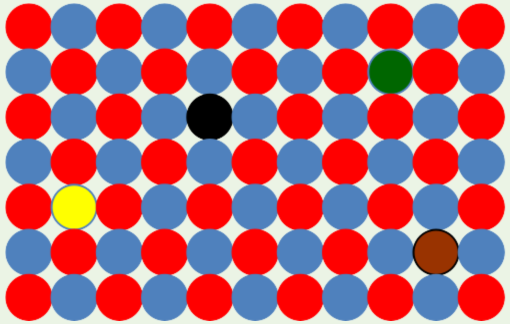
Occlusion

- A type of co-precipitation in which *a compound (foreign ions in the counter-ion layer)* is physically trapped within a precipitate during rapid precipitate formation.

- Problem solving: Digestion

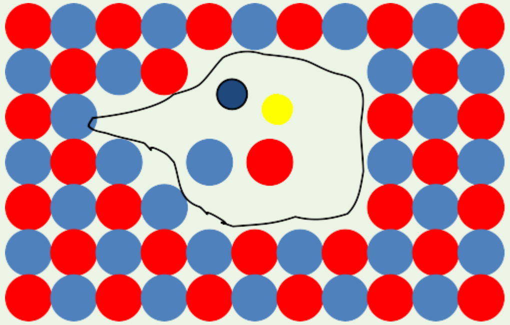
- **Digestion**: The process which has a waiting time to achieve desired outcome.

- (The solubility–precipitation is in a **dynamic equilibrium**, digestion ensures the occluded material is eventually exposed to the supernatant solution.)



Mechanical Entrapment

- A type of co-precipitation in which co-precipitated physically trap a *pocket of solution* within a precipitate during rapid precipitate formation.
- Problem solving: Digestion
- Mixed-crystal formation may occur in both colloidal and crystalline precipitates, but occlusion and mechanical entrapment are confined to crystalline precipitates.



Gravimetric Calculations

- The aim: is to find the weight of analyte from the weight of precipitate.
- We can use the concepts discussed previously in stoichiometric calculations but let us learn something else.
- ***Example***: Assume Cl_2 is to be precipitated as AgCl, then we can write a stoichiometric factor reading as follows: one mole of Cl_2 gives 2 moles of AgCl. We can define a quantity called the gravimetric factor (GF) where:
-
- GF(analyte) = (a/b)*(FW analyte/FW ppt)
- a,b are stoichiometric coefficients
- GF for Cl_2 = (1 mol Cl_2/2 mol AgCl) * (FW Cl_2/FW AgCl)

Gravimetric Stoichiometry

➢ calculations involving mass (**SOLIDS**).

- **Write out the balanced equation**
- **Write out the known information under the equation, including mass, molecular weight of the species**
- **Calculation of number of moles of known chemicals**
- **Calculation of the number of moles of unknown using the ration** $\frac{unknown}{known}$
- **Convert moles to mass**

Example

- If you decompose 1.00 g of malachite, or $Cu(OH)_2.CuCO_{3(s)}$, what mass of CuO would be formed using the following reaction:

- $$Cu_{(OH)2}{}_{.}CuCO_3 \rightarrow 2CuO + CO2 + H2O$$

	known	***unknown***
wt =	**1.00 g**	**????**
m.wt=	**221.13**	**79.55**

wt (known) ➞ moles(known) ➞ mole ratio ➞ moles(unknown) ➞ wt (unknown)

Moles of $\mathbf{Cu(OH)_2.CuCO_3} = \dfrac{\mathbf{1.00}}{\mathbf{221.13}}$ **= 0.00452 mole, stoichiometric ratio =** $\dfrac{unknown}{known}$

$$= \frac{\mathbf{2}}{\mathbf{1}}$$

So, moles of CuO = 0.00452/2 = 0.00226 mole

Weight of CuO = 0.00226 * 79.55 = 0.1798 g

Example

- Determine the mass of oxygen required to completely burn 10.0 g of propane.

- $$C_3H_8 + 5O_2 \rightarrow 2CuO + 3CO2 + 4H2O$$

	known	***unknown***
wt =	**10.00 g**	**????**
m.wt=	**44.1**	**32.0**

wt (known) → moles(known) → mole ratio → moles(unknown) → wt (unknown)

Moles of C_3H_8 = $\frac{10.00}{44.11}$ = 0.2267 mole, stoichiometric ratio = $\frac{unknown}{known}$

$$= \frac{5}{1}$$

So, moles of O_2 = 0.2267*5 = 1.1335 mole

Weight of O_2 = 1.1335 * 32.0 = 36.27 g

Gravimetric Calculations

- ***Gravimetric factor***: is an algebraic expression that converts grams of a compound into grams of a single element. It is the ratio of the formula weight (FW) of the substance being sought to that of the substance weighed.
- ***Example 1***. **Fe** is sought, **Fe_2O_3** is weighed:

$$\text{gravimetric factor} = \frac{1\,\cancel{\text{mol}\ Fe_2O_3}}{159.69\,\text{g}\ Fe_2O_3} \times \frac{2\,\cancel{\text{mol}\ Fe}}{\cancel{\text{mol}\ Fe_2O_3}} \times \frac{55.847\,\text{g Fe}}{\cancel{\text{mol Fe}}} = 0.69944\,\frac{\text{g Fe}}{\text{g}\ Fe_2O_3}$$

- ***Example 2***. **Fe_3O_4** is sought, **Fe_2O_3** is weighed:

$$\text{gravimetric factor} = \frac{1\,\cancel{\text{mol}\ Fe_2O_3}}{159.69\,\text{g}\ Fe_2O_3} \times \frac{2\,\cancel{\text{mol}\ Fe_3O_4}}{3\,\cancel{\text{mol}\ Fe_2O_3}} \times \frac{231.54\,\text{g}\ Fe_3O_4}{\cancel{\text{mol}\ Fe_3O_4}} = 0.96662\,\frac{\text{g}\ Fe_3O_4}{\text{g}\ Fe_2O_3}$$

Example

- **Calculate the ratio of weight (mg) of analyte to weight of precipitate for the following: P (at wt =30.97) in Ag_3PO_4 (m.wt = 711.22), Bi_2S_3 m.wt 514.15) in $BaSO_4$ (m.wt = 233.40)**

Solution

$$\mathbf{P \leftrightarrows Ag_3PO_4}$$

mmol P = mmol Ag_3PO_4

mg P/30.97 = mg Ag_3PO_4/711.22

mg P/mg Ag_3PO_4 = 30.97/711.22 = 0.04354

$$\mathbf{Bi_2S_3 \leftrightarrows 3\ BaSO_4}$$

mmol Bi_2S_3 = **1/3** mmol $BaSO_4$

mg Bi_2S_3/***m.wt*** Bi_2S_3 = **1/3** mg $BaSO_4$/***m.wt*** $BaSO_4$

mg Bi_2S_3/514.15 = **1/3** mg $BaSO_4$/233.40

mg Bi_2S_3/ $BaSO_4$ = **1/3** (514.15/ 233.40) = 0.73429

- **Phosphate in a 0.2711 g sample was precipitated giving 1.1682 g of $(NH_4)_2PO_4.12\ MoO_3$ (m.wt = 1876.5). Find percentage P (at wt = 30.97) and percentage P_2O_5 (m.wt = 141.95) in the sample.**

Solution

$$P \leftrightarrows (NH_4)_2PO_4.12\ MoO_3$$

Stoichiometric ration: 1 : 1

So, mole *P* = mole $(NH_4)_2PO_4.12\ MoO_3$

wt P/at wt P = wt $(NH_4)_2PO_4.12\ MoO_3$**/ *m.wt*** $(NH_4)_2PO_4.12\ MoO_3$

wt P = at wt P x (wt $(NH_4)_2PO_4.12\ MoO_3$**/ *m.wt*** $(NH_4)_2PO_4.12\ MoO_3$**)**

wt P = 30.97 (1.1682 / 1876.5) = 0.0192 mg

% P = (0.0192/0.2711) x 100 = 7.1%

The same procedure is applied for finding the percentage of P_2O_5

$$P_2O_5 \leftrightarrows 2\ (NH_4)_2PO_4.12\ MoO_3$$

Stoichiometric ratio: 2 : 1

so, mole P_2O_5 = 1/2 mole $(NH_4)_2PO_4.12\ MoO_3$

wt P_2O_5/*m.wt* P_2O_5 = 1/2 (wt $(NH_4)_2PO_4.12\ MoO_3$/ *m.wt* $(NH_4)_2PO_4.12\ MoO_3$)

wt P_2O_5 = 1/2 x *m.wt* P_2O_5 x (wt $(NH_4)_2PO_4.12\ MoO_3$/ *m.wt* $(NH_4)_2PO_4.12\ MoO_3$)

wt P_2O_5 = 1/2 x 141.95 (1.1682/1876.5) = 0.0442 g

% P_2O_5 = (0.0442/0.2711) x 100 = 16.30%

- Advantages of Gravimetric Analysis
- If the methods are followed carefully, **it provides exceedingly precise analysis**. It is used **to determine the atomic masses of many elements to six-figure accuracy**. It **provides a little room for instrumental error** and **does not require a series of standards for calculation of an unknown**.

- Disadvantages of Gravimetric Analysis
- It usually **provides only for the analysis of a single element, or a limited group of elements, at a time. Comparing modern dynamic flash combustion coupled with gas chromatography with traditional combustion analysis**.

PRECIPITATING REAGENTS (PRECIPITANTS)

Precipitants are chosen for their ability to be selective and to form highly insoluble precipitates (easily filtered) and of reproducible stoichiometry.

- **Types of precipitant: inorganic and organic reagents.**

INORGANIC PRECIPITANTS

- **Form slightly soluble salts or hydrous oxides with the analyte.**

- **Most inorganic reagents are not very selective.**

- **Two common inorganic precipitating agents are,**
- **silver nitrate, which is used to precipitate halide ions such as chloride,**

- **barium chloride, which is used to precipitate sulfate ion.**

Common Inorganic Precipitants

Precipitant	Analyte	Precipitate Formed	Precipitate Weighed
NH_4OH	Al	$Al(OH)_3$	Al_2O_3
	Fe	$Fe(OH)_3$	Fe_2O_3
HCl	Ag	AgCl	AgCl
$AgNO_3$	Cl	AgCl	AgCl
$NaSO_4$	Ba	$BaSO_4$	$BaSO_4$
$BaCl_2$	SO_4^{2-}	$BaSO_4$	$BaSO_4$

ORGANIC PRECIPITANTS

- Very useful precipitating agents for metals.

- Advantages by using organic reagents as a precipitant ;

  It forms chelate compounds with cations which are very insoluble in water. So, that metal ions may be quantitatively precipitated.

  - The organic precipitant often has a large molecular weight. Thus a small amount of metal may yield a large weight of precipitate.

  - Some of the organic reagents are fairly selective, yielding precipitates with only a limited number of cation. By controlling such factors as pH and the concentration of masking reagents, the selectivity of an organic reagent can be enhanced.

  - The precipitates obtained with organic reagents are often coarse and bulky, and hence easily handle or filtered.

Examples:
8- hydrixyquinoline (oxine)

It can precipitates many elements but can be used for group separation by controlling pH.

Aluminium ion can be precipitated at pH 4. A higher pH is required to precipitate magnesium.

Other organic precipitants:

DMG – Ni^{2+} and Co^{2+}
Cupferron – Fe^{2+}, Ce^{4+}
Nitron – NO^{3-}, ClO_4^-
tetraphenyiarsonium chloride – $Cr_2O_7^{2-}$, MnO_4^-