

## Gravimetric Analysis and Precipitation Equilibria

## GRAVIMETRIC METHODS OF ANALYSIS TYPES

1. **Precipitation gravimetry (oldest)**
2. **Electrogravimetry**
3. **Volatilization gravimetry and Thermogravimetry**
4. **Gravimetric titrimetry**
5. **Particulate gravimetry**

- When signal is mass of a precipitate, the method is called **precipitation gravimetry**. For example, determination of  $\text{Cl}^-$  by precipitating it as  $\text{AgCl}$ .
- **Electrogravimetry:** the analyte is deposited on one electrode in an electrochemical cell. For example
  - oxidation of  $\text{Pb}^{2+}$ , and its deposition as  $\text{PbO}_2$  on a Pt anode or
  - reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}$  and its electrodeposition on a Pt cathode, for direct analysis for  $\text{Cu}^{2+}$ .

**Volatilization gravimetry:** when thermal or chemical energy is used to remove a volatile species. For example, determining moisture content using thermal energy to vaporize  $\text{H}_2\text{O}$ . Also carbon and hydrogen in an organic compound may be determined by combustion with  $\text{O}_2$  to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

**Gravimetric titrimetry,** mass of titrant instead of its volume is measured. (Mass measurements are much more accurate and precise)

Finally, in **particulate gravimetry** the analyte is determined following its re-moval from the sample matrix by filtration or extraction. The determination of sus-pended solids is one example of particulate gravimetry.

## Precipitation Gravimetric Analysis

- Gravimetric Analysis – one of the most accurate and precise methods of macro-quantitative analysis.
- Analyte is selectively converted to an insoluble form and precipitated quantitatively from its solution.
- Precipitate is treated to make it easily filterable and then filtered, dried and finally its mass is measured.
- Analyte mass is then calculated on the basis of the chemical composition of ppt and its mass.

## • Why use gravimetric analysis?

- Conducted with simple apparatus.
- Interpretation of results is easy – readings are directly related to analyte amount.
- Provides very accurate and precise results – in fact gravimetric results are used to check the accuracy of other methods.

## How to Perform a Successful Precipitation Gravimetric Analysis?

### What steps are needed?

1. Sample is dried, and triplicate portions weighed
2. The solution is prepared and mixed with ppt agent.
3. Precipitation is completed and ppt is digested for better filtering
4. The ppt is filtered and washed
5. The collected ppt is dried or ignited to a final stable form of known composition.
6. Dried ppt is weighed.
7. The analyte amount is calculated!

## Need to be careful;

- To quantitatively collect all the precipitate
- To know the exact composition of precipitate
  - Precipitation of analyte with known selective/specific agent
  - Volatilization and/or collection of analyte without loss of material during the handling/processing of sample.
  - Free from solvent and other impurities.
- To determine mass accurately and precisely
  - Direct or
  - By difference

## Desirable properties of analytical precipitates:

- Readily and easily filtered and purified
- Low solubility, preventing losses during filtration and washing
- Stable final form (unreactive)
- Known composition after drying or ignition

## Precipitating reagents:

Ideally to be specific and precipitate only one specie, but in real life selective (precipitate a small group of species)

### For example;

- **Ag<sup>+</sup> is a selective reagent**
  - $\text{Ag}^+ + \text{Halides (X}^-) \rightarrow \text{AgX}_{(s)}$
  - $\text{Ag}^+ + \text{CNS}^- \rightarrow \text{AgCNS}_{(s)}$
- **DMG is specific to Ni<sup>2+</sup>**
  - Dimethylglyoxime (DMG)
  - $2 \text{DMG} + \text{Ni}^{2+} \rightarrow \text{Ni(DMG)}_{2(s)} + 2 \text{H}^+$


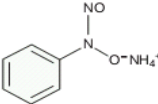
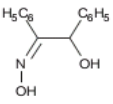
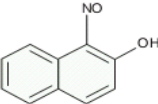
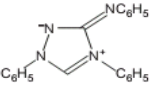
## Selected Gravimetric Method for Inorganic Cations Based on Precipitation

Analyte	Precipitant	Precipitate Formed	Precipitate Weighed
Ba <sup>2+</sup>	(NH <sub>4</sub> ) <sub>2</sub> CrO <sub>4</sub>	BaCrO <sub>4</sub>	BaCrO <sub>4</sub>
Pb <sup>2+</sup>	K <sub>2</sub> CrO <sub>4</sub>	PbCrO <sub>4</sub>	PbCrO <sub>4</sub>
Ag <sup>+</sup>	HCl	AgCl	AgCl
Hg <sub>2</sub> <sup>2+</sup>	HCl	Hg <sub>2</sub> Cl <sub>2</sub>	Hg <sub>2</sub> Cl <sub>2</sub>
Al <sup>3+</sup>	NH <sub>3</sub>	Al(OH) <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>
Be <sup>2+</sup>	NH <sub>3</sub>	Be(OH) <sub>2</sub>	BeO
Fe <sup>3+</sup>	NH <sub>3</sub>	Fe(OH) <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>
Ca <sup>2+</sup>	(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	CaC <sub>2</sub> O <sub>4</sub>	CaCO <sub>3</sub> or CaO
Sb <sup>3+</sup>	H <sub>2</sub> S	Sb <sub>2</sub> S <sub>3</sub>	Sb <sub>2</sub> S <sub>3</sub>
As <sup>3+</sup>	H <sub>2</sub> S	As <sub>2</sub> S <sub>3</sub>	As <sub>2</sub> S <sub>3</sub>
Hg <sup>2+</sup>	H <sub>2</sub> S	HgS	HgS
Ba <sup>2+</sup>	H <sub>2</sub> SO <sub>4</sub>	BaSO <sub>4</sub>	BaSO <sub>4</sub>
Pb <sup>2+</sup>	H <sub>2</sub> SO <sub>4</sub>	PbSO <sub>4</sub>	PbSO <sub>4</sub>
Sr <sup>2+</sup>	H <sub>2</sub> SO <sub>4</sub>	SrSO <sub>4</sub>	SrSO <sub>4</sub>
Be <sup>2+</sup>	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	NH <sub>4</sub> BePO <sub>4</sub>	Be <sub>2</sub> P <sub>2</sub> O <sub>7</sub>
Mg <sup>2+</sup>	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	NH <sub>4</sub> MgPO <sub>4</sub>	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>
Sr <sup>2+</sup>	KH <sub>2</sub> PO <sub>4</sub>	SrHPO <sub>4</sub>	Sr <sub>2</sub> P <sub>2</sub> O <sub>7</sub>
Zn <sup>2+</sup>	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	NH <sub>4</sub> ZnPO <sub>4</sub>	Zn <sub>2</sub> P <sub>2</sub> O <sub>7</sub>

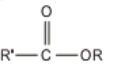

## Selected Gravimetric Methods for Inorganic Anions Based on Precipitation

Analyte	Precipitant	Precipitate Formed	Precipitate Weighed
CN <sup>-</sup>	AgNO <sub>3</sub>	AgCN	AgCN
I <sup>-</sup>	AgNO <sub>3</sub>	AgI	AgI
Br <sup>-</sup>	AgNO <sub>3</sub>	AgBr	AgBr
Cl <sup>-</sup>	AgNO <sub>3</sub>	AgCl	AgCl
ClO <sub>3</sub> <sup>-</sup>	FeSO <sub>4</sub> /AgNO <sub>3</sub>	AgCl	AgCl
SCN <sup>-</sup>	SO <sub>2</sub> /CuSO <sub>4</sub>	CuSCN	CuSCN
SO <sub>4</sub> <sup>2-</sup>	BaCl <sub>2</sub>	BaSO <sub>4</sub>	BaSO <sub>4</sub>

### Selected Gravimetric Methods for Inorganic Cations Based on Precipitation with Organic Precipitants

Analyte	Precipitant	Structure	Precipitate Formed	Precipitate Weighed
Ni <sup>2+</sup>	dimethylglyoxime		Ni(C <sub>4</sub> H <sub>7</sub> O <sub>2</sub> N <sub>2</sub> ) <sub>2</sub>	Ni(C <sub>4</sub> H <sub>7</sub> O <sub>2</sub> N <sub>2</sub> ) <sub>2</sub>
Fe <sup>3+</sup>	cupferron		Fe(C <sub>6</sub> H <sub>5</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>
Cu <sup>2+</sup>	cupron		CuC <sub>14</sub> H <sub>11</sub> O <sub>2</sub> N	CuC <sub>14</sub> H <sub>11</sub> O <sub>2</sub> N
Co <sup>2+</sup>	1-nitroso-2-naphthol		Co(C <sub>10</sub> H <sub>6</sub> O <sub>2</sub> N) <sub>3</sub>	Co or CoSO <sub>4</sub>
K <sup>+</sup>	sodium tetraphenylborate	Na[B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> ]	K[B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> ]	K[B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> ]
NO <sub>2</sub> <sup>-</sup>	nitron		C <sub>20</sub> H <sub>16</sub> N <sub>4</sub> HNO <sub>3</sub>	C <sub>20</sub> H <sub>16</sub> N <sub>4</sub> HNO <sub>3</sub>

### Selected Gravimetric Methods for the Analysis of Organic Functional Groups and Heteroatoms Based on Precipitation

Analyte	Treatment	Precipitant	Precipitate
Organic halides R-X X = Cl, Br, I	Oxidation with HNO <sub>3</sub> in presence of Ag <sup>+</sup>	AgNO <sub>3</sub>	AgX
Organic Halides R-X X = Cl, Br, I	Combustion in O <sub>2</sub> (with Pt catalyst) in presence of Ag <sup>+</sup>	AgNO <sub>3</sub>	AgX
Organic sulfur Organic sulfur	Oxidation with HNO <sub>3</sub> in presence of Ba <sup>2+</sup> Combustion in O <sub>2</sub> (with Pt catalyst) to produce SO <sub>2</sub> and SO <sub>3</sub> , which are collected in dilute H <sub>2</sub> O <sub>2</sub>	BaCl <sub>2</sub>	BaSO <sub>4</sub>
Alkoxy groups R'-OR R = CH <sub>3</sub> or C <sub>2</sub> H <sub>5</sub> or 	Reaction with HI to produce RI	AgNO <sub>3</sub>	AgI
Alkamide group  R = CH <sub>3</sub> , C <sub>2</sub> H <sub>5</sub> N may be 1°, 2°, or 3°	Reaction with HI to produce RI	AgNO <sub>3</sub>	AgI

### Filterability of Precipitates:

- Colloidal suspensions
  - 10<sup>-7</sup> to 10<sup>-4</sup> cm diameter
  - Normally remain suspended
  - Very difficult to filter
- Crystalline suspensions
  - > tenths of mm diameter
  - Normally settle out spontaneously
  - Readily filterable

## Filterability of Precipitates:

- Precipitate formation is affected by RELATIVE SUPERSATURATION (RSS) of solution
  - $RSS = (Q-S)/S$ 
    - S = Equilibrium Solubility of Precipitate
    - Q = Instantaneous Concentration
- Larger Q leads to colloidal precipitates.
- Smaller Q leads to crystalline or flocculated ppts.

## Important Factors for Gravimetric Analysis

- **Nucleation**
  - Individual ions/atoms/molecules coalesce to form “nuclei”
- **Particle Growth**
  - Condensation of ions/atoms/molecules with existing “nuclei” forming larger particles which settle out
- **Colloidal Suspension**
  - Colloidal particles remain suspended due to adsorbed ions giving a net + or - charge

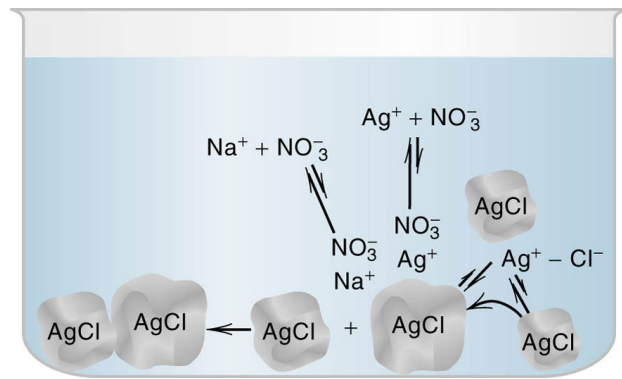
## Important Factors for Gravimetric Analysis

- **Coagulation, agglomeration (desired)**
  - Suspended colloidal particles coalesce to form larger filterable particles (inert electrolyte allows closer approach)
- **Peptization (undesired)**
  - Re-dissolution of coagulated colloids by washing and removing inert electrolyte

## Important Factors for Gravimetric Analysis

- **Co-precipitation (undesired)**
  - Normally soluble compounds carried down with insoluble precipitate (surface adsorption, occlusion, mixed crystals, entrapment)
- **Digestion (good)**
  - Precipitation heated for hour(s) in contact with solution from which it was formed. Helps coagulate and get rid of water from ppt.

During digestion at elevated temperature:  
 Small particles tend to dissolve and reprecipitate on larger ones.  
 Individual particles agglomerate.  
 Adsorbed impurities tend to go into solution.



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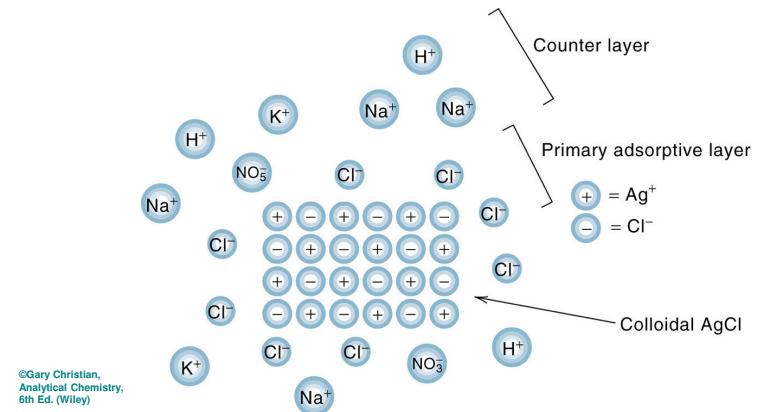
Fig. 10.1. Ostwald ripening.

Cl<sup>-</sup> adsorbs on the particles when in excess (primary layer).

A counter layer of cations forms.  
 neutral double layer causes the colloidal particles to coagulate.

The

Washing with water will dilute the counter layer and the primary layer charge causes the particles to revert to the colloidal state (peptization).  
 So we wash with an electrolyte that can be volatilized on heating (HNO<sub>3</sub>).



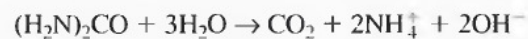
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Fig. 10.2. Representation of silver chloride colloidal particle and adsorptive layers when Cl<sup>-</sup> is in excess.

Homogeneous precipitation is a process in which a precipitate is formed by slow generation of a precipitating reagent homogeneously throughout a solution.

Precipitates formed by homogeneous precipitation are generally purer and more easily filtered than precipitates generated by direct addition of a reagent to the analyte

Urea is often used for the homogeneous generation of hydroxide ion. The reaction can be expressed by the equation



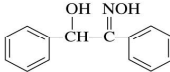
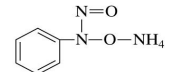
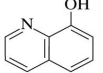
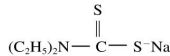
## Homogeneous Precipitation

- What?
  - Precipitating agent generated slowly by chemical reaction in analyte solution
- Why?
  - Precipitant appears gradually throughout
  - Keeps relative supersaturation low
  - Larger, less-contaminated particles
- How?
  - (OH<sup>-</sup>) by urea decomposition
  - $(NH_2)_2CO \rightarrow 2 OH^- + CO_2 + 2 NH_4^+$
  - (S<sup>=</sup>) by thioacetamide decomposition
  - $CH_3CSNH_2 \rightarrow H_2S + CH_3CONH_2$
  - (DMG) from biacetyl + hydroxylamine
  - $CH_3C(=O)-C(=O)CH_3 + 2 H_2NOH \rightarrow DMG + 2 H_2O$

**Organic precipitating agents are chelating agents.**

**They form insoluble metal chelates.**

**Some Organic Precipitating Agents**

Reagent	Structure	Metals Precipitated
Dimethylglyoxime	$\text{CH}_3-\text{C}=\text{NOH}$ $\text{CH}_3-\text{C}=\text{NOH}$	Ni(II) in $\text{NH}_3$ or buffered HOAc; Pd(II) in HCl ( $\text{M}^{2+} + 2\text{HR} \rightarrow \text{MR}_2 + 2\text{H}^+$ )
$\alpha$ -Benzoinozone (cupron)		Cu(II) in $\text{NH}_3$ and tartrate; Mo(VI) and W(VI) in $\text{H}^+$ ( $\text{M}^{2+} + \text{H}_2\text{R} \rightarrow \text{MR} + 2\text{H}^+$ ; $\text{M}^{2+} = \text{Cu}^{2+}$ , $\text{MoO}_2^{2+}$ , $\text{WO}_2^{2+}$ ) Metal oxide weighed
Ammonium nitrosophenylhydroxylamine (cupferron)		Fe(III), V(V), Ti(IV), Zr(IV), Sn(IV), U(IV) ( $\text{M}^{n+} + n\text{NH}_2\text{R} \rightarrow \text{MR}_n + n\text{NH}_4^+$ ) Metal oxide weighed
8-Hydroxyquinoline (oxine)		Many metals. Useful for Al(III) and Mg(II) ( $\text{M}^{n+} + n\text{HR} \rightarrow \text{MR}_n + n\text{H}^+$ )
Sodium diethyldithiocarbamate		Many metals from acid solution ( $\text{M}^{n+} + n\text{NaR} \rightarrow \text{MR}_n + n\text{Na}^+$ )
Sodium tetraphenylboron	$\text{NaB}(\text{C}_6\text{H}_5)_4$	$\text{K}^+$ , $\text{Rb}^+$ , $\text{Cs}^+$ , $\text{Tl}^+$ , $\text{Ag}^+$ , $\text{Hg}(\text{I})$ , $\text{Cu}(\text{I})$ , $\text{NH}_4^+$ , $\text{RNH}_3^+$ , $\text{R}_2\text{NH}_2^+$ , $\text{R}_3\text{NH}^+$ , $\text{R}_4\text{N}^+$ . Acidic solution ( $\text{M}^+ + \text{NaR} \rightarrow \text{MR} + \text{Na}^+$ )
Tetraphenylarsonium chloride	$(\text{C}_6\text{H}_5)_4\text{AsCl}$	$\text{Cr}_2\text{O}_7^{2-}$ , $\text{MnO}_4^-$ , $\text{ReO}_4^-$ , $\text{MoO}_4^{2-}$ , $\text{WO}_4^{2-}$ , $\text{ClO}_4^-$ , $\text{I}_3^-$ . Acidic solution ( $\text{A}^{n-} + n\text{RCl} \rightarrow \text{R}_n\text{A} + n\text{Cl}^-$ )

**Methods for Homogeneous Generation of Precipitating Agents**

Precipitating Agent	Reagent	Generation Reaction	Elements Precipitated
$\text{OH}^-$	Urea	$(\text{NH}_2)_2\text{CO} + 3\text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{NH}_4^+ + 2\text{OH}^-$	Al, Ga, Th, Bi, Fe, Sn
$\text{PO}_4^{3-}$	Trimethyl phosphate	$(\text{CH}_3\text{O})_3\text{PO} + 3\text{H}_2\text{O} \rightarrow 3\text{CH}_3\text{OH} + \text{H}_3\text{PO}_4$	Zr, Hf
$\text{C}_2\text{O}_4^{2-}$	Ethyl oxalate	$(\text{C}_2\text{H}_5)_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{C}_2\text{O}_4$	Mg, Zn, Ca
$\text{SO}_4^{2-}$	Dimethyl sulfate	$(\text{CH}_3\text{O})_2\text{SO}_2 + 4\text{H}_2\text{O} \rightarrow 2\text{CH}_3\text{OH} + \text{SO}_4^{2-} + 2\text{H}_3\text{O}^+$	Ba, Ca, Sr, Pb
$\text{CO}_3^{2-}$	Trichloroacetic acid	$\text{Cl}_3\text{CCOOH} + 2\text{OH}^- \rightarrow \text{CHCl}_3 + \text{CO}_3^{2-} + \text{H}_2\text{O}$	La, Ba, Ra
$\text{H}_2\text{S}$	Thioacetamide*	$\text{CH}_3\text{CSNH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CONH}_2 + \text{H}_2\text{S}$	Sb, Mo, Cu, Cd
DMG†	Biacetyl + hydroxylamine	$\text{CH}_3\text{COCOCH}_3 + 2\text{H}_2\text{NOH} \rightarrow \text{DMG} + 2\text{H}_2\text{O}$	Ni
HOQ‡	8-Acetoxyquinoline§	$\text{CH}_3\text{COOQ} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{HOQ}$	Al, U, Mg, Zn

**Calculations of analyte content requires knowledge of :**

- Chemistry
- Stoichiometry
- Composition of precipitate

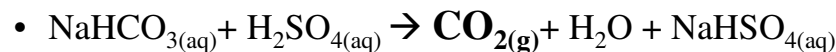
**Gravimetry and Solution Equilibria**

- Thermal Conversion to Measurable Form
- Removal of volatile reagents & solvent by extended heating at 110 to 115 °C

**Chemical conversion to known stable form**



**Volatilization & trapping of component**



## Volatilization & trapping of component

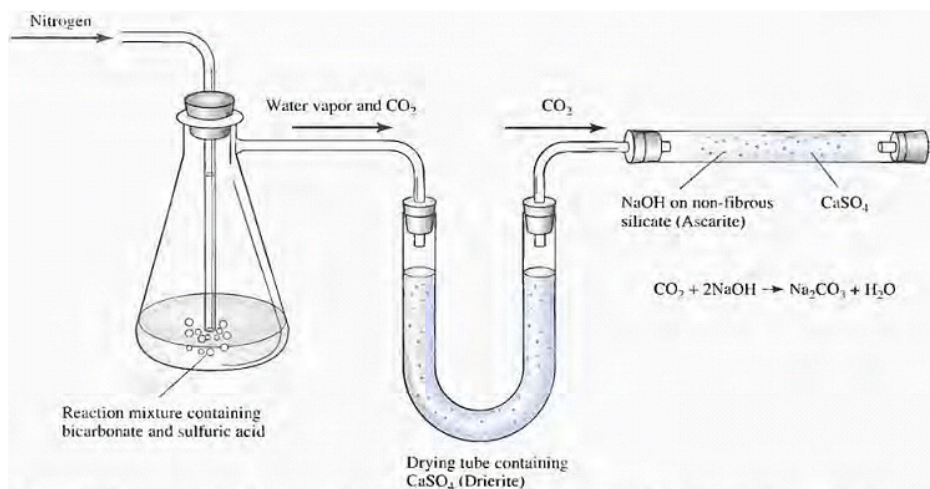
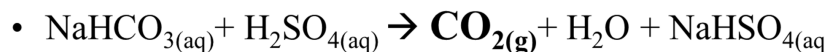


Figure 12-8 Apparatus for determining the sodium hydrogen carbonate content of antacid tablets by a gravimetric volatilization procedure.

## Gravimetric Errors

- Unknown Stoichiometry:
- Consider  $\text{Cl}^-$  determination with  $\text{AgNO}_3$
- $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}$
- $\text{Ag}^+ + 2 \text{Cl}^- \rightarrow \text{AgCl}_2$

## Gravimetric Errors

### Co-precipitation: (w/AgCl)

<u>Co-precipitant</u>	<u>Error</u>	<u>Rationale</u>
NaF	Positive	All NaF is excess
NaCl	Negative	Fwt Na < Ag
AgI	Positive	All AgI is excess
$\text{PbCl}_2$ (fwt 278.1)	Negative	Gravimetric Factors decreases

## Precipitation Equilibria:

### The Solubility Product

- Solubility of Slightly Soluble Salts:
- $\text{AgCl}_{(s)} \rightleftharpoons (\text{AgCl})_{(aq)} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$
- Solubility Product  $K_{\text{SP}} = \text{ion product}$
- $K_{\text{SP}} = [\text{Ag}^+][\text{Cl}^-]$
- $\text{Ag}_2\text{CrO}_{4(s)} \rightleftharpoons 2 \text{Ag}^+ + \text{CrO}_4^{2-}$
- $K_{\text{SP}} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}]$



The molar solubility depends on the stoichiometry of the salt.

A 1:1 salt is less soluble than a nonsymmetric salt with the same  $K_{sp}$ .

Table 10.3

Solubility Product Constants of Selected Slightly Soluble Salts

Salt	$K_{sp}$	Solubility, $s$ (mol/L)
PbSO <sub>4</sub>	$1.6 \times 10^{-8}$	$1.3 \times 10^{-4}$
AgCl	$1.0 \times 10^{-6}$	$1.0 \times 10^{-5}$
AgBr	$4 \times 10^{-13}$	$6 \times 10^{-7}$
AgI	$1 \times 10^{-16}$	$1 \times 10^{-8}$
Al(OH) <sub>3</sub>	$2 \times 10^{-32}$	$5 \times 10^{-9}$
Fe(OH) <sub>3</sub>	$4 \times 10^{-38}$	$2 \times 10^{-10}$
Ag <sub>2</sub> S	$2 \times 10^{-49}$	$4 \times 10^{-17}$
HgS	$4 \times 10^{-53}$	$6 \times 10^{-27}$

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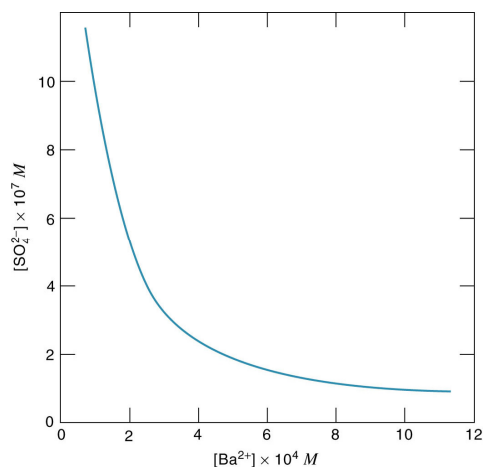
## Precipitation Equilibria: The Common Ion Effect

- Common Ion Effect
- Will decrease the solubility of a slightly soluble salt.

The common ion effect is used to decrease the solubility.

Sulfate concentration is the amount in equilibrium and is equal to the BaSO<sub>4</sub> solubility.

In absence of excess barium ion, solubility is  $10^{-5}$  M.



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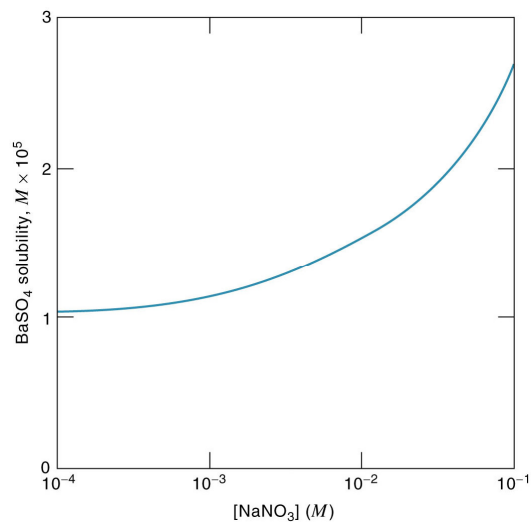
Fig. 10.3. Predicted effect of excess barium ion on solubility of BaSO<sub>4</sub>.

## Diverse Ion Effect on Solubility:

- Presence of diverse ions will increase the solubility of precipitates due to shielding of dissociated ion species.
- $K_{SP}^{\circ}$  and Activity Coefficients
- $\text{AgCl}_{(s)} \rightleftharpoons (\text{AgCl})_{(aq)} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$
- Thermodynamic solubility product  $K_{SP}^{\circ}$
- $K_{SP}^{\circ} = a_{\text{Ag}^+} \cdot a_{\text{Cl}^-} = [\text{Ag}^+]f_{\text{Ag}^+} \cdot [\text{Cl}^-]f_{\text{Cl}^-}$
- $K_{SP}^{\circ} = K_{SP} f_{\text{Ag}^+} \cdot f_{\text{Cl}^-}$
- $K_{SP} = K_{SP}^{\circ} / (f_{\text{Ag}^+} \cdot f_{\text{Cl}^-})$

$$K_{sp} = K_{sp}^0 / f_{Ag^+} f_{SO_4^{2-}}$$

Solubility increases with increasing ionic strength as activity coefficients decrease.



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Predicted effect of increased ionic strength on solubility of BaSO<sub>4</sub>. Solubility at zero ionic strength is 1.0 × 10<sup>-5</sup> M.

This is an example of a direct analysis since the iron in the analyte, Fe<sub>3</sub>O<sub>4</sub>, is part of the isolated precipitate, Fe<sub>2</sub>O<sub>3</sub>. Applying a conservation of mass to Fe, we write

$$3 \times \text{moles Fe}_3\text{O}_4 = 2 \times \text{moles Fe}_2\text{O}_3$$

Using formula weights, FW, to convert from moles to grams in the preceding equation leaves us with

$$\frac{3 \times \text{g Fe}_3\text{O}_4}{\text{FW Fe}_3\text{O}_4} = \frac{2 \times \text{g Fe}_2\text{O}_3}{\text{FW Fe}_2\text{O}_3}$$

which can be solved for grams of Fe<sub>3</sub>O<sub>4</sub> and %w/w Fe<sub>3</sub>O<sub>4</sub> in the sample.

$$\frac{2 \times \text{g Fe}_2\text{O}_3 \times \text{FW Fe}_3\text{O}_4}{3 \times \text{FW Fe}_2\text{O}_3} = \frac{2 \times 0.8525 \text{ g} \times 231.54 \text{ g/mol}}{3 \times 159.69 \text{ g/mol}} = 0.82405 \text{ g Fe}_3\text{O}_4$$

$$\frac{\text{g Fe}_3\text{O}_4}{\text{g sample}} \times 100 = \frac{0.82405 \text{ g}}{1.5419 \text{ g}} \times 100 = 53.44\% \text{ w/w Fe}$$

## Calculating Results from Gravimetric Data

\*An ore containing magnetite, Fe<sub>3</sub>O<sub>4</sub>, was analyzed by dissolving a 1.5419-g sample in concentrated HCl, giving a mixture of Fe<sup>2+</sup> and Fe<sup>3+</sup>. After adding HNO<sub>3</sub> to oxidize any Fe<sup>2+</sup> to Fe<sup>3+</sup>, the resulting solution was diluted with water and the Fe<sup>3+</sup> precipitated as Fe(OH)<sub>3</sub> by adding NH<sub>3</sub>. After filtering and rinsing, the residue was ignited, giving 0.8525 g of pure Fe<sub>2</sub>O<sub>3</sub>. Calculate the %w/w Fe<sub>3</sub>O<sub>4</sub> in the sample.

## Calculating Results from Gravimetric Data

- The calcium in a 200.0 mL sample of a natural water was determined by precipitating the cation as CaC<sub>2</sub>O<sub>4</sub>. The precipitate was filtered, washed, and ignited in a crucible with an empty mass of 26.6002 g. The mass of the crucible plus CaO (fwt 56.077 g/mol) was 26.7134 g. Calculate the concentration of Ca (fwt 40.078 g/mol) in the water in units of grams per 100 mL.

### Calculating Results from Gravimetric Data

- An iron ore was analyzed by dissolving a 1.1324 g sample in concentrated HCl. The resulting solution was diluted with water, and the iron(III) was precipitated as the hydrous oxide  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  by addition of  $\text{NH}_3$ . After filtration and washing, the residue was ignited at high temperature to give 0.5394 g pure  $\text{Fe}_2\text{O}_3$  (fwt 159.69 g/mol). Calculate (a) the % Fe (fwt 55.847 g/mol) and (b) %  $\text{Fe}_3\text{O}_4$  (fwt 231.54 g/mol) in the sample.

### Calculating Results from Gravimetric Data

- A 0.2356 g sample containing only NaCl (fwt 58.44 g/mol) and  $\text{BaCl}_2$  (fwt 208.23 g/mol) yielded 0.4637 g of dried AgCl (fwt 143.32 g/mol). Calculate the percent of each halogen compound in the sample.