

Gravimetric method of analysis :

Gravimetric methods: The quantitative methods that are based on determining the mass of a pure compound to which the analyte is chemically related.

The principle of Gravimetric Analysis:

The principle behind the gravimetric analysis is that the mass of an ion in a pure compound can be determined. Later, used to find the mass percent of the same ion in a known quantity of an impure compound.

Types of Gravimetric Analysis

- **Precipitation gravimetry:** The analyte is separated from a solution of the sample as a precipitate and is converted to a compound of known composition that can be weighed.
- **Volatilization gravimetry:** The analyte is separated from other constituents of a sample by converting it to a gas of known chemical composition that can be weighed.
- **Electrogravimetry:** The analyte is separated by deposition on an electrode by an electrical current.

Properties of gravimetric analysis:

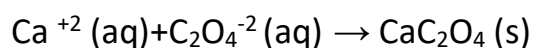
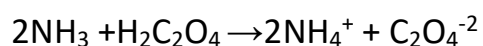
- 1- Tradition method**
- 2- Cheap, easily available apparatus, simple to carry out**
- 3- Slow, especially when accurate results are required**
- 4- Wide range of concentration (ng-kg)**
- 5- No calibration required except for the balance**
- 6- Accurate**

Precipitation gravimetry

The analyte is converted to a sparingly soluble precipitate that is then filtered, washed free of impurities and converted to a product of known composition by suitable heat treatment and weighed.

Ex:

Calcium in water



filtered, dried, ignited



The step required in gravimetric analysis:

- 1- Precipitation
- 2- Digestion
- 3- Filtration
- 4- Washing
- 5- Drying and igniting
- 6- Weighing
- 7- Calculation

Gravimetric factor(GF):

the weight of one substance is converted into the corresponding weight of another substance through substance through multiplication by asset of constant terms .

$$GF = a/b * \text{gfw substance sought} / \text{gfw substance weighed}$$

Species I sought	Species weighed 2	GF
In	In ₂ O ₃	$2/1 * \text{gfw In} / \text{gfw In}_2\text{O}_3$
HgO	Hg ₅ (IO ₆) ₂	$5/1 * \text{gfw HgO} / \text{gfw Hg}_5(\text{IO}_6)_2$
I	Hg ₅ (IO ₆) ₂	$2/1 * \text{gfw I} / \text{gfw Hg}_5(\text{IO}_6)_2$
K ₃ PO ₄	K ₂ PtCl ₆	$2/3 * \text{gfw K}_3\text{PO}_4 / \text{gfw K}_2\text{PtCl}_6$
K ₃ PO ₄	Mg ₂ P ₂ O ₇	$2/1 * \text{gfw K}_3\text{PO}_4 / \text{gfw Mg}_2\text{P}_2\text{O}_7$

Example: Calculate the amount of sulphate as barium sulphate from sodium sulphate. Solution of sodium sulphate (Na₂SO₄) is treated with solution of barium chloride (BaCl₂) to get precipitates of barium sulphate (BaSO₄). The precipitates are then washed, dried and ignited to get free from impurities and then weighed.



Mol. Weight of BaSO₄ = 233.42 gm

Mol. Weight of SO₄⁻ = 96.06 gm

Suppose obtained weight of BaSO₄ precipitates = X · gm

233.42 gm of BaSO₄ = 96.06 gm of SO₄⁻ ions

X · gm of BaSO₄ = ?

$$\text{BaSO}_4 = 96.06 \cdot X / 233.32 = 0.411X \text{ gm of SO}_4^- \text{ ions}$$

Suppose 25 ml solution is consumed, then

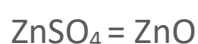
$$25 \text{ ml solution contains} = 0.411X \text{ gm of SO}_4^- \text{ ions}$$

1000ml solution contains?

$$1000 \text{ ml solution contains} = 0.411X \cdot 1000 / 25 = 16.44X \text{ gm of SO}_4^- \text{ ions}$$

Example: Calculate the amount of zinc oxide from zinc sulphate.

A solution of zinc sulphate is boiled to convert it into zinc carbonate by adding solution of sodium carbonate. Sodium carbonate is added to precipitate zinc completely as zinc carbonate. Precipitates of zinc carbonate is boiled for few minutes to convert it into zinc oxide and collected in a tarred Gooch crucible. Precipitates are washed with hot water until it gets free from alkali and then dried, ignited and weighed to a constant weight.



Mol. Weight of $\text{ZnSO}_4 = 168 \text{ gm}$

Mol. Weight of $\text{ZnO} = 81.38 \text{ gm}$

81.38 gm of $\text{ZnO} = 168 \text{ gm of ZnSO}_4$

1 gm of $\text{ZnO} = ?$

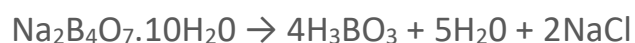
$$= 168 \cdot 1 / 81.38$$

$$= 1.984 \text{ gm}$$

Example: Calculate the amount of Boric acid from Borax.

Borax is an alkaline substance, and reacts with conc. HCl to form Boric acid. Boric acid is freely soluble in boiling water and precipitated out in cold water. To get high grade of Boric acid, Borax is treated with conc. HCl as it is volatile in nature and won't left any residual traces on crystal surface of Boric acid.

Weight and dissolve 5 gm of Borax in 15 ml of distilled water. Add 7 ml of conc. HCl, mix thoroughly with glass rod and mark the original volume with glass rod. Evaporate the solution till the volume reduces to half of the original volume. Allow to cool at room temperature. Keep it aside for few min and add ice water. Filter the residue under suction and dry it in air. Weight the compound preparation.



Mol wt of Borax = 381.37gm

Mol wt of Boric acid = 61.83gm

Practical yield: X gm

381.37 gm of Borax = 4 × 61.83 gm of Boric acid

X gm of Borax = ?

= $X \cdot 4 \cdot 61.83 / 381.37$

= 0.674X gm of Boric acid

Example: The calcium in a 200 mL sample of a natural water was determined by precipitating the cation as CaC_2O_4 . The precipitate was filtered, washed, and ignited in a crucible with empty mass of 26.6002 g. The mass of the crucible and CaO(56.099 g/mol) was 26.7134 g. Calculate the concentration of Ca(40.078 g/mol) in the water in units of grams per 100 mL.

The mass of CaO is

$$26.7134 \text{ g} - 26.6002 \text{ g} = 0.1132 \text{ g}$$

The number of moles Ca in the sample is equal to the number of moles CaO

$$\text{Amount Ca} = 0.1132 \text{ g CaO} \times \frac{1 \text{ mol CaO}}{56.077 \text{ g}} \times \frac{1 \text{ mol Ca}}{1 \text{ mol CaO}} = 2.0168 \times 10^{-3} \text{ mol Ca}$$

$$56.077 \text{ g} \quad \text{mol CaO}$$

$$\text{Mass Ca/100mL} = \frac{2.0186 \times 10^{-3} \text{ mol Ca} \times 40.078 \text{ g Ca/mol Ca}}{100 \text{ mL}} = \mathbf{0.04045 \text{ g/ 100ml}}$$

200 ml sample

EXAMPLE 12-1

The calcium in a 200.0-mL sample of a natural water was determined by precipitating the cation as CaC_2O_4 . 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 (56.077 g/mol) was 26.7134 g. Calculate the concentration of Ca (40.078 g/mol) in water in units of grams per 100 mL of the water.

Solution

The mass of CaO is

$$26.7134\text{g} - 26.6002 = 0.1132\text{g}$$

The number of moles of Ca in the sample is equal to the number of moles of CaO, or

$$\begin{aligned}\text{amount of Ca} &= 0.1132\text{gCaO} \times \frac{1\text{ molCaO}}{56.077\text{gCaO}} \times \frac{1\text{ molCa}}{1\text{ molCaO}} \\ &= 2.0186 \times 10^{-3}\text{ molCa} \\ \text{conc. Ca} &= \frac{2.0186 \times 10^{-3}\text{ molCa} \times 40.078\text{ g Ca/molCa}}{200\text{ mL sample}} \times \frac{100}{100} \\ &= 0.04045\text{ g/100 mL sample}\end{aligned}$$

EXAMPLE 12-2

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 the addition of NH_3 . After filtration and washing, the residue was ignited at a high temperature to give 0.5394 g of pure Fe_2O_3 (159.69 g/mol). Calculate (a) the % Fe (55.847 g/mol) and (b) the % Fe_3O_4 (231.54 g/mol) in the sample.

Solution

For both parts of this problem, we need to calculate the number of moles of Fe_2O_3 . Thus,

$$\begin{aligned}\text{amount Fe}_2\text{O}_3 &= 0.5394 \text{ g Fe}_2\text{O}_3 \times \frac{1 \text{ mol Fe}_2\text{O}_3}{159.69 \text{ g Fe}_2\text{O}_3} \\ &= 3.3778 \times 10^{-3} \text{ mol Fe}_2\text{O}_3\end{aligned}$$

(a) The number of moles of Fe is twice the number of moles of Fe_2O_3 , and

$$\begin{aligned}\text{mass Fe} &= 3.3778 \times 10^{-3} \text{ mol Fe}_2\text{O}_3 \times \frac{2 \text{ mol Fe}}{\text{mol Fe}_2\text{O}_3} \times \frac{55.847 \text{ g Fe}}{\text{mol Fe}} \\ &= 0.37728 \text{ g Fe} \\ \% \text{ Fe} &= \frac{0.37728 \text{ g Fe}}{1.1324 \text{ g sample}} \times 100\% = 33.32\%\end{aligned}$$

(b) As shown by the following balanced equation, 3 mol of Fe_2O_3 is chemically equivalent to 2 mol of Fe_3O_4 , that is,

$$\begin{aligned}3\text{Fe}_2\text{O}_3 &\rightarrow 2\text{Fe}_3\text{O}_4 + \frac{1}{2}\text{O}_2 \\ \text{mass Fe}_3\text{O}_4 &= 3.3778 \times 10^{-3} \text{ mol Fe}_2\text{O}_3 \times \frac{2 \text{ mol Fe}_3\text{O}_4}{3 \text{ mol Fe}_2\text{O}_3} \times \frac{231.54 \text{ g Fe}_3\text{O}_4}{\text{mol Fe}_3\text{O}_4} \\ &= 0.52140 \text{ g Fe}_3\text{O}_4 \\ \% \text{ Fe}_3\text{O}_4 &= \frac{0.52140 \text{ g Fe}_3\text{O}_4}{1.1324 \text{ g sample}} \times 100\% = 46.04\%\end{aligned}$$

EXAMPLE 12-3

A 0.2356-g sample containing *only* NaCl (58.44 g/mol) and BaCl₂ (208.23 g/mol) yielded 0.4637 g of dried AgCl (143.32 g/mol). Calculate the percent of each halogen compound in the sample.

Solution

If we let x be the mass of NaCl in grams and y be the mass of BaCl₂ in grams, we can write as a first equation

$$x + y = 0.2356 \text{ g sample}$$

To obtain the mass of AgCl from the NaCl, we write an expression for the number of moles of AgCl formed from the NaCl, that is,

$$\begin{aligned} \text{amount AgCl from NaCl} &= x \cancel{\text{g NaCl}} \times \frac{1 \cancel{\text{mol NaCl}}}{58.44 \cancel{\text{g NaCl}}} \times \frac{1 \text{ mol AgCl}}{\cancel{\text{mol NaCl}}} \\ &= 0.017111x \text{ mol AgCl} \end{aligned}$$

The mass of AgCl from this source is

$$\begin{aligned} \text{mass AgCl from NaCl} &= 0.017111x \cancel{\text{mol AgCl}} \times 143.32 \frac{\text{g AgCl}}{\cancel{\text{mol AgCl}}} \\ &= 2.4524x \text{ g AgCl} \end{aligned}$$

Proceeding in the same way, we can write that the number of moles of AgCl from the BaCl₂ is given by

$$\begin{aligned} \text{amount AgCl from BaCl}_2 &= y \text{ g BaCl}_2 \times \frac{1 \text{ mol BaCl}_2}{208.23 \text{ g BaCl}_2} \times \frac{2 \text{ mol AgCl}}{\text{mol BaCl}_2} \\ &= 9.605 \times 10^{-3} y \text{ mol AgCl} \end{aligned}$$

$$\begin{aligned} \text{mass AgCl from BaCl}_2 &= 9.605 \times 10^{-3} y \text{ mol AgCl} \times 143.32 \frac{\text{g AgCl}}{\text{mol AgCl}} \\ &= 1.3766y \text{ g AgCl} \end{aligned}$$

Because 0.4637 g of AgCl comes from the two compounds, we can write

$$\begin{aligned} 2.4524x \text{ g AgCl} + 1.3766y \text{ g AgCl} &= 0.4637 \text{ g AgCl, or to simplify,} \\ 2.4524x + 1.3766y &= 0.4637 \end{aligned}$$

Our first equation can then be rewritten as

$$y = 0.2356 - x$$

Substituting into the previous equation gives

$$2.4524x + 1.3766(0.2356 - x) = 0.4637$$

which rearranges to $1.0758x = 0.13942$

$$x = \text{mass NaCl} = 0.12960 \text{ g NaCl}$$

$$\% \text{ NaCl} = \frac{0.12960 \text{ g NaCl}}{0.2356 \text{ g sample}} \times 100\% = 55.01\%$$

$$\% \text{ BaCl}_2 = 100.00\% - 55.01\% = 44.99\%$$

Properties of precipitating reagent

- 1- The analyte should selectively react with the Precipitating agent
- 2- Which should preferably have high molecular mass because this will increase the sensitivity of the method
- 3- Lower the conc. Limit of the analyte that can be determined
- 4- The resulting precipitate should have minimum solubility so as de

Properties of good precipitate:

- 1- Easily filtrate and washed free of contamination**
- 2- Low solubility that no significant loss of the analyte accrues during filtration and washing**
- 3- Un reactive with constituents of the atmosphere**
- 4- Of known chemical composition after it is dried or if necessary , ignited.**

Factors that determine the particle size of ppts:

1- Colloidal suspension:

Colloidal ppts are very difficult to filter and are susceptible to peptization a process through which filtered ppt will return to the colloidal state when washed with water whose tiny particles are invisible to the naked eye (10^{-7} - 10^{-4}) cm in diameter.

2- Crystalline suspension:

A crystalline suspension is composed of particles having large diameters about a tenth of a millimeter or greater. The effect of gravity on these large particles is considerably higher than that of colloidal particles. Hence, the particles of the crystalline suspensions tend to settle down spontaneously and are easily filtered. These precipitates are easily purified. The particle size of a precipitate is influenced by precipitate solubility, temperature, reactant concentration and the rate in which the reactants are mixed.

Formation of nuclei versus growth of crystals

Precipitation

This requires addition of a precipitation agent solution to the sample solution upon addition of the first drops of the precipitating agent, supersaturation occurs, then nucleation starts to occur where every few molecules of precipitate aggregate together forming a nucleus. At this point addition of extra precipitating agent will either form new nuclei or will build upon existing nuclei to give a precipitate.

This can be predicted by VonWeimarn ratio where, according to this relation the particles size is inversely proportional to a quantity called the relative supersaturation where:

$$RSS = \frac{Q-S}{S}$$

Q= is the conc. Of reactants before pptn

S= is the solubility of precipitate in the medium from which it is being precipitated

Therefore, in order to get particle growth instead of further nucleation we need to make the relative supersaturation ratio as small as possible.

The optimum conditions for ppt. which make the supersaturation low are:

- a- Pptn using dilute solutions to decrease Q
- b- Slow addition of ppting agent to keep Q as low as possible.
- c- Stirring the solution during addition of ppting agent to avoid conc. Sites and keep Q low
- d- Increase solubility by pptn from hot solution
- e- Adjust the pH in order to increase S but not too much increase as we do not want to lose ppt by dissolution
- f- Usually add a little excess of the ppting agent for quantitative pptn and check for completeness of the pptn

-Generally, precipitation reactions are slow so that, even when a precipitating reagent is added drop by drop to a solution of an analyte, some supersaturation is likely.

- Experimental evidence indicates that the particle size of a precipitate varies inversely with the average relative supersaturation during the time when the reagent is being introduced. Thus, when $(Q - S)/S$ is large, the precipitate tends to be colloidal, and when $(Q - S)/S$ is small, a crystalline solid is more likely.

Colloidal precipitation

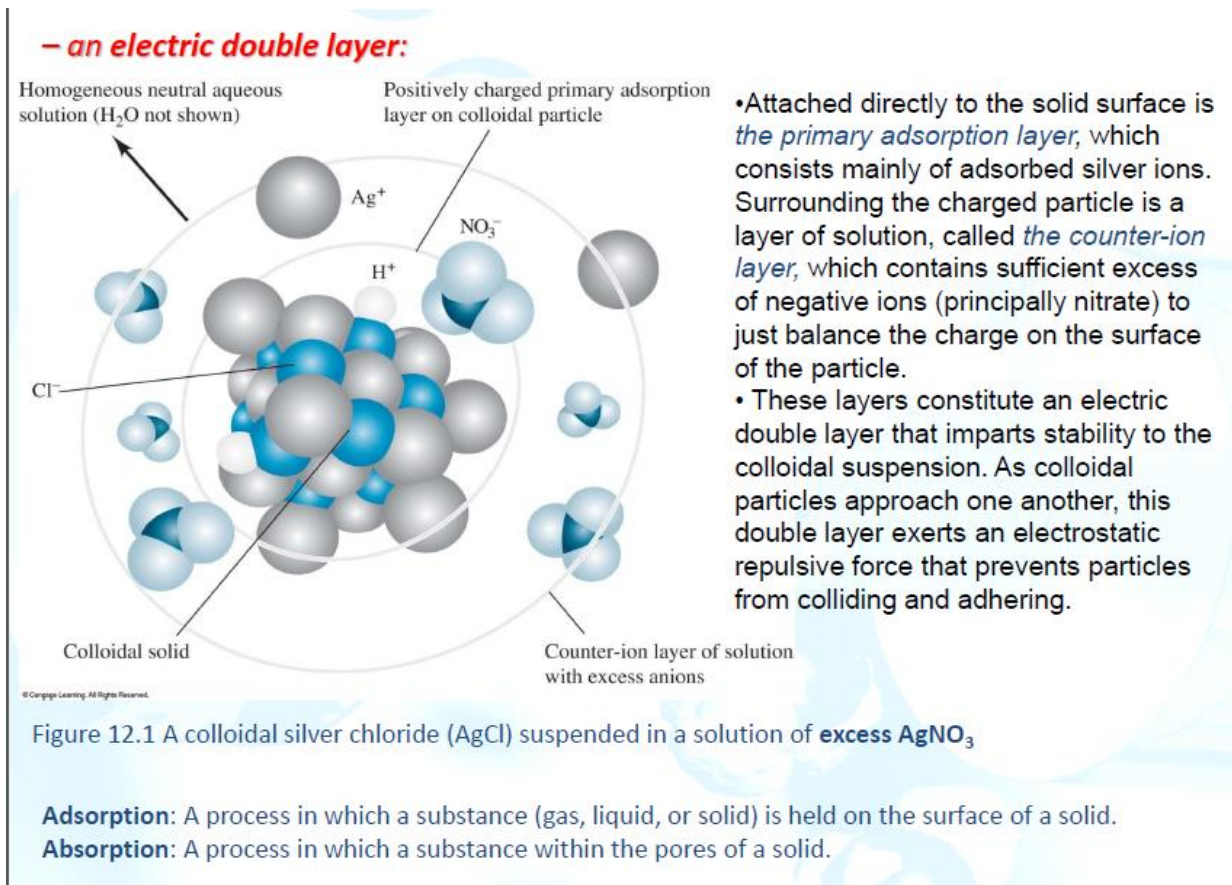
Individual colloidal particles are so small that they are not retained by ordinary filters. Moreover, Brownian motion prevents their settling out of solution under the influence of gravity.

Fortunately, however, we can coagulate, or agglomerate, the individual particles of most colloids to give a filterable, amorphous mass that will settle out of solution.

Coagulation of Colloids

Coagulation can be hastened by heating, by stirring, and by adding an electrolyte to the medium. To understand the effectiveness of these measures, we need to look into why colloidal suspensions are stable and do not coagulate spontaneously.

Colloidal suspensions are stable because all of the particles of the colloid are either positively or negatively charged and thus repel one another. The charge results from cations or anions that are bound to the surface of the particles. We can show that **colloidal particles are charged** by placing them between charged plates where some of the particles migrate toward one electrode while others move toward the electrode of the opposite charge. The process by which ions are retained *on the surface of a solid* is known as **adsorption**.



Coagulation of a colloidal suspension:

When the charge on the colloidal particles is neutralized by the addition of an electrolyte or oppositely charged sol. The pptn takes place thus the process of ppting a colloidal sol. Is known as coagulation or flocculation

Factors governing coagulation:

- 1- A little amount of suitable electrolyte may bring coagulation .*
- 2- Coagulation is brought about by oppositely charged ions of the electrolyte*
- 3- Coagulation also takes place by mixing oppositely charged solution it is called mutual coagulation.*
- 4- Coagulation of a solution is more pronounced at high temp.*
- 5- The coagulation power of different electrolytes is not equal*

Coagulation can be caused by the following methods:

- 1- Electrophoresis*
- 2- Mutual pptn*
- 3- Prolonged dialysis*
- 4- Heating or cooling*

Peptization:

The process by which a coagulated colloid reverts to its original dispersed colloidal suspension state..

(When a coagulated colloid is washed, some of the electrolyte responsible for its coagulation is removed, therefore, the repulsive forces as well as the original colloidal state are reestablished.)

Solution: Use of Volatile electrolyte as washing solution, e.g., HNO_3 , NH_4NO_3 , to avoid peptization.

Practical Treatment of Colloidal Precipitates

Colloids are best precipitated from hot, stirred solutions containing sufficient electrolyte to ensure coagulation. The filterability of a coagulated colloid often improves if it is allowed to stand for an hour or more in contact with the hot solution from which it was formed. During

this process, which is known as **digestion**, weakly bound water appears to be lost from the precipitate. The result is a denser mass that is easier to filter

Digestion

is a process in which a precipitate is heated in the solution from which it was formed (the mother liquor) and allowed to stand in contact with the solution. **Mother liquor** is the solution from which a precipitate was formed.

Crystalline Precipitates

Crystalline precipitates are generally more easily filtered and purified than are coagulated colloids.

- Particle size of crystalline solids can often be improved significantly by minimizing Q (by using dilute solutions, and adding the precipitating reagent slowly, with good mixing) or maximizing S (precipitating from hot solution or by adjusting the pH), or both.

- Digestion improves the purity and filterability of both colloidal and crystalline precipitates.
- The improvement in filterability undoubtedly results from the dissolution and recrystallization that occur continuously and at an enhanced rate at elevated temperatures.
- Recrystallization apparently results in bridging between adjacent particles, a process that yields larger and more easily filtered crystalline aggregates. This view is supported by the observation that little improvement in filtering characteristics occurs if the mixture is stirred during digestion

Coprecipitation:

A process in which normally soluble compounds are carried out of solution by a precipitate. It may result in **impurities** within the desired precipitates. Coprecipitated impurities may cause either negative or

positive errors. There are four types of coprecipitation: surface adsorption, mixed-crystal formation, occlusion, and mechanical entrapment.

Surface Adsorption

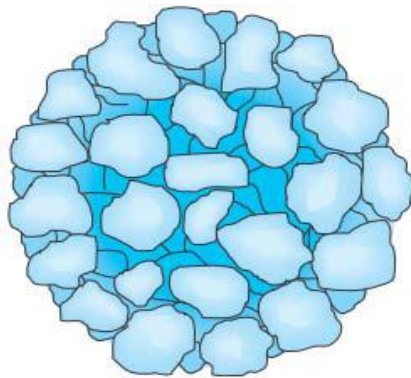
The impurity is chemically or physically adsorbed onto the surface of precipitates

➤ Adsorption is the major source of contamination in coagulated colloids but of no significance in crystalline precipitates.

Minimizing Adsorbed Impurities on Colloids 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.

Reprecipitation:

In this process, the filtered solid is redissolved and reprecipitated. The solution containing the redissolved precipitate has a significantly lower contaminant concentration than the original, and even less adsorption occurs during the second precipitation.



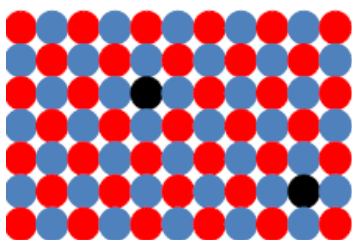
Mixed-Crystal Formation:

A type of coprecipitation in which a contaminant ion replaces an ion in the lattice of a crystal.

Ex

SrSO₄ in BaSO₄

MnS in CdS



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

- Problem solving:
- Change to another more selective precipitating agent
- Reprecipitation

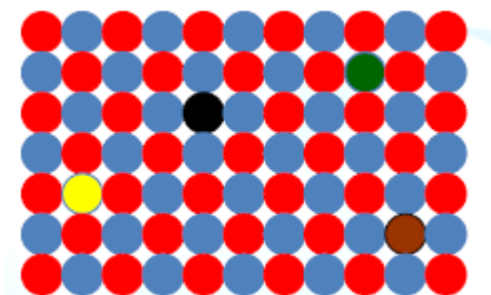
Occlusion:

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.)

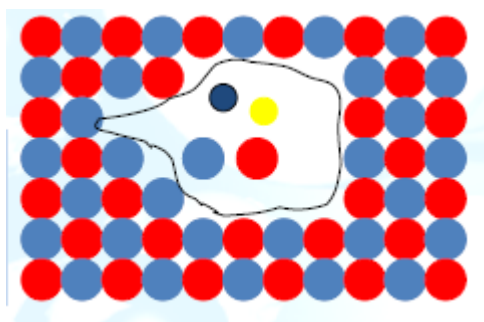


Mechanical Entrapment:

A type of co-precipitation in which coprecipitated 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

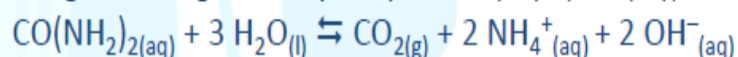


Precipitation from Homogeneous Solution

Homogeneous precipitation

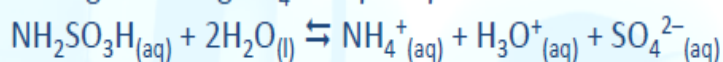
is a process in which a precipitate is formed by slow generation of a precipitating reagent homogeneously throughout a solution. Solids formed by homogeneous precipitation are generally purer and larger in size

Example 1: Urea, for generating OH^- as precipitant (Al(III), Fe(III))



* Generation rate can be controlled by temperature

Example 2: For generating SO_4^{2-} as precipitant



* Generation rate can be controlled by pH

Drying and Ignition of Precipitates

A gravimetric precipitate is heated until its mass becomes constant.

✓ Heating removes the solvent and any volatile species carried down with the ppt.

✓ Some precipitates are also ignited to decompose the solid and form a compound of known composition. This new compound is often called the *weighing form*.

- The temperature required to dehydrate a precipitate completely may be as low as 100C or as high as 1000C
- Moisture is completely removed from silver chloride at temperatures higher than 110C, but dehydration of aluminum oxide is not complete until a temperature greater than 1000C is achieved.
- The thermal curve for calcium oxalate is considerably more complex than the others
- Recording thermal decomposition curves is called **thermogravimetric analysis**, and the mass versus temperature curves are termed **thermograms**.

Types of Precipitating agents

1- Inorganic Precipitating Agents: this reagents typically forms lightly soluble saltes or hydrous oxide with the analyte.

TABLE 12-2

Some Inorganic Precipitating Agents	
Precipitating Agent	Element Precipitated*
$\text{NH}_3(aq)$	Be (BeO), Al (Al_2O_3), Sc (Sc_2O_3), Cr (Cr_2O_3)†, Fe (Fe_2O_3), Ga (Ga_2O_3), Zr (ZrO_2), In (In_2O_3), Sn (SnO_2), U (U_3O_8)
H_2S	Cu (CuO)†, Zn (ZnO or ZnSO_4), Ge (GeO_2), As (As_2O_3 or As_2O_5), Mo (MoO_3), Sn (SnO_2)†, Sb (Sb_2O_3), or Sb_2O_5), Bi (Bi_2S_3)
$(\text{NH}_4)_2\text{S}$	Hg (HgS), Co (Co_3O_4)
$(\text{NH}_4)_2\text{HPO}_4$	Mg ($\text{Mg}_2\text{P}_2\text{O}_7$), Al (AlPO_4), Mn ($\text{Mn}_2\text{P}_2\text{O}_7$), Zn ($\text{Zn}_2\text{P}_2\text{O}_7$), Zr ($\text{Zr}_2\text{P}_2\text{O}_7$), Cd ($\text{Cd}_2\text{P}_2\text{O}_7$), Bi (BiPO_4)
H_2SO_4	Li, Mn, Sr , Cd , Pb , Ba (all as sulfates)
H_2PtCl_6	K (K_2PtCl_6 or Pt), Rb (Rb_2PtCl_6), Cs (Cs_2PtCl_6)
$\text{H}_2\text{C}_2\text{O}_4$	Ca (CaO), Sr (SrO), Th (ThO_2)
$(\text{NH}_4)_2\text{MoO}_4$	Cd (CdMoO_4)†, Pb (PbMoO_4)

2- Reducing Agents

convert an analyte to its elemental form for weighing

TABLE 12-3

Some Reducing Agents Used in Gravimetric Methods

Reducing Agent	Analyte
SO ₂	Se, Au
SO ₂ + H ₂ NOH	Te
H ₂ NOH	Se
H ₂ C ₂ O ₄	Au
H ₂	Re, Ir
HCOOH	Pt
NaNO ₂	Au
SnCl ₂	Hg
Electrolytic reduction	Co, Ni, Cu, Zn Ag, In, Sn, Sb, Cd, Re, Bi

3-Organic Precipitating Agents

Some organic reagents react with metal ions then produce insoluble coordination compounds.

✓ Reagents that form coordination compounds of this type are called **chelating agents**, and their products are called **chelates**.

✓ Those metal chelates are relatively nonpolar and have **low solubilities in water**.

✓ Usually, these compounds possess low densities and are often intensely colored. Because they are not wetted by water, coordination compounds are easily freed of moisture at low temperatures.

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 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 ₆ H ₅) ₄ ⁻	K ⁺ , Rb ⁺ , Cs ⁺ , NH ₄ ⁺ , Ag ⁺ , organic ammonium ions
Tetraphenylarsonium chloride	(C ₆ H ₅) ₄ As ⁺ Cl ⁻	Cr ₂ O ₇ ²⁻ , MnO ₄ ⁻ , ReO ₄ ⁻ , MoO ₄ ²⁻ , WO ₄ ²⁻ , ClO ₄ ⁻ , I ₃ ⁻

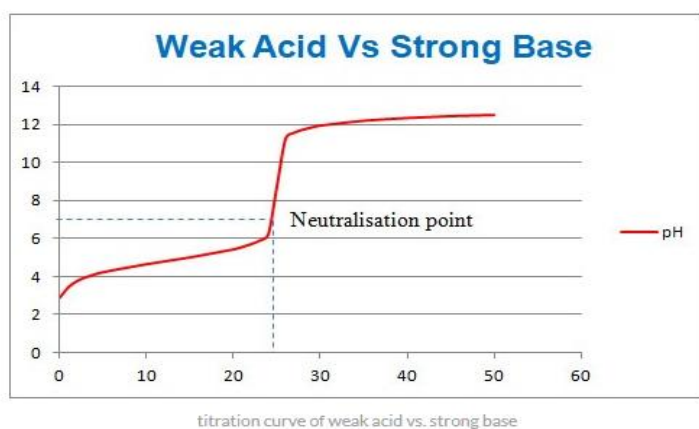
Organic ppting agents have the advantages

- 1- Some of organic ppting agents are very selective and very broad in the number of elements they will ppt.
- 2- Giving pptes with very low solubility in water
- 3- Give a favorable gravimetric factor

Types of titration curves:

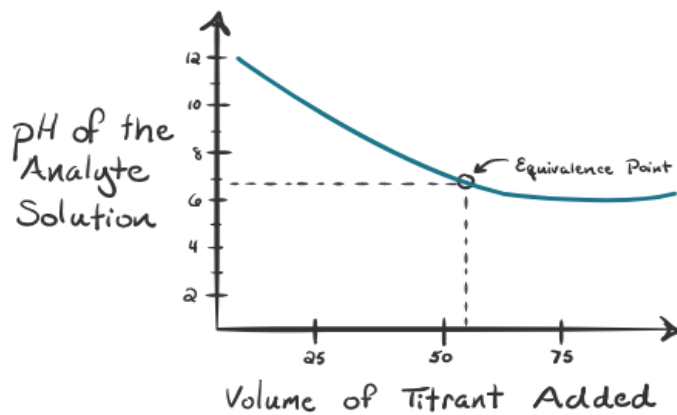
A **titration curve** is a graph of the pH as a function of the amount of titrant (acid or base) added.

- 1- First type called a sigmoidal curve important observations are confined to a small region surrounding the equivalence point the pH – function of analyte as function of reagent volumes.



- 2- A linear segment curve

Measurements are made on both sides of but well away from the equivalence point the vertical axis represents an instrument's reading which is directly proportional to the concentration of the analyte.



The solubility of precipitation

Solubility is a chemical property referring to the ability for a given substance, the solute, to dissolve in a solvent. It is measured in terms of the maximum amount of solute dissolved in a solvent at equilibrium. The resulting solution is called a saturated solution

Ex AgCl slightly dissolve in water giving Cl^- and Ag^+ where



Ex :

What weight of $\text{Ba}(\text{IO}_3)_2$ M.WT (487) can be dissolved in to 500ml of water ?

$$K_{sp} = [\text{Ba}] \cdot [\text{IO}_3]^2$$

$$1.57 \cdot 10^{-9} = S \cdot (2S)^2$$

$$S = 3.72 \cdot 10^{-4} \text{ M}$$

$$\text{Wt } \text{Ba}(\text{IO}_3)_2 = 3.72 \cdot 10^{-4} \cdot 500/1000 \cdot 487$$

$$= 0.178\text{g}$$

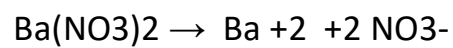
Ex:

Calculate the formal solubility of $\text{Ba}(\text{IO}_3)_2$ in a solution that is 0.02M in $\text{Ba}(\text{NO}_3)_2$?

$$K_{sp} = [\text{Ba}].[\text{IO}_3]^2$$

$$1.57 \cdot 10^{-9} = S \cdot (2S)^2$$

$$S = 3.72 \cdot 10^{-4} \text{ M}$$



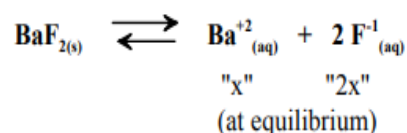
$$0.02 \qquad 0.02 \qquad 2 * 0.02$$

When the $0.02 \geq 1.4 \cdot 10^{-4}$

$$[\text{Ba}] = 0.02 + S \text{ ----- يهمل}$$

EX: Calculating the solubility of a Slightly Soluble Salt in a Solution of a Common Ion

(a) Calculate the **molar** solubility of barium fluoride, BaF_2 , in water at 25°C . The K_{sp} at 25°C is 1.0×10^{-6} .



$$K_{\text{sp}} = [\text{Ba}^{+2}][\text{F}^{-1}]^2$$

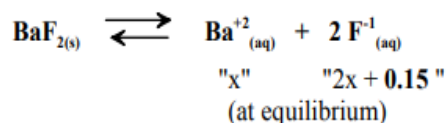
$$1.0 \times 10^{-6} = (x)(2x)^2 = 4x^3 \quad \text{solving for } x, \text{ we get: } \quad x = 6.30 \times 10^{-3} \text{ M}$$

Since "x" represents the molarity of the Ba^{+2} ion, and we get one mole of barium ions for each mole of barium fluoride that dissolves, we obtain a **molar solubility for BaF_2 of $6.30 \times 10^{-3} \text{ M}$** .

Now, to illustrate the *common ion effect*.

(b) What is the **molar** solubility of barium fluoride in a solution that is 0.15 M NaF at 25°C .

Since the solution is already 0.15 M in F^{-1} ions, we must make an addition to our equilibrium concentrations.



$$K_{\text{sp}} = [\text{Ba}^{+2}][\text{F}^{-1}]^2$$

Because BaF_2 is only slightly soluble, you might expect "2x" to be negligible compared to 0.15. In that case

$$(2x + 0.15) \cong (0.15) \quad \text{and substituting into the } K_{\text{sp}} \text{ expression, we get}$$

$$1.0 \times 10^{-6} = (x)(0.15)^2$$

$$\text{solving for } x, \text{ we get: } \quad x = 4.44 \times 10^{-5} \text{ M}$$

Note that "x" is indeed much smaller than 0.15, so our assumption was correct. Therefore the molar solubility of barium fluoride in 0.15 M NaF is only **$4.44 \times 10^{-5} \text{ M}$** . In pure water, the solubility is $6.3 \times 10^{-3} \text{ M}$, which is over **140 times greater**

EXAMPLE 11-8

Calculate the solubility of AgCl in distilled water.

Solution

$$\begin{aligned}\text{Solubility} = S &= [\text{AgCl}(aq)] + [\text{Ag}^+] \\ [\text{Ag}^+] &= [\text{Cl}^-] \\ [\text{Ag}^+][\text{Cl}^-] &= K_{\text{sp}} = 1.82 \times 10^{-10} \\ [\text{Ag}^+] &= \sqrt{1.82 \times 10^{-10}} = 1.35 \times 10^{-5}\end{aligned}$$

Substituting this value and K_s from Equation 11-25 gives

$$S = 1.35 \times 10^{-5} + 3.6 \times 10^{-7} = 1.38 \times 10^{-5} \text{ M}$$

Note that neglecting $[\text{AgCl}(aq)]$ leads to a 2% error in this example.

EX:

A solution of 0.00016 M lead(II)nitrate, $\text{Pb}(\text{NO}_3)_2$, was poured into 456 mL of 0.00023 M sodium sulfate, Na_2SO_4 . Would a precipitate of lead(II)sulfate, PbSO_4 , be expected to form if 255 mL of the lead nitrate solution were added? (The K_{sp} for lead(II)sulfate is 1.7×10^{-8})

First we must calculate the initial concentrations of Pb^{+2} and SO_4^{-2} in the mixture.

$$(0.00016 \text{ mol/L})(0.255 \text{ L}) = 4.08 \times 10^{-5} \text{ mol Pb}^{+2} \quad (\text{from the 255 mL of Pb}(\text{NO}_3)_2)$$

$$(0.00023 \text{ mol/L})(0.456 \text{ L}) = 1.05 \times 10^{-4} \text{ mol SO}_4^{-2} \quad (\text{from the 456 mL of Na}_2\text{SO}_4)$$

We must now divide each of these results by the cumulative volume of 255 mL + 456 mL = 711 mL

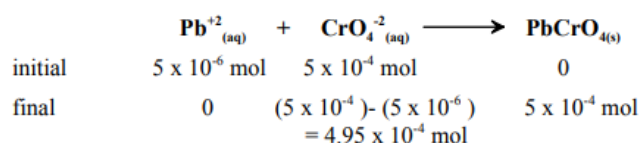
$$[\text{Pb}^{+2}] = \frac{4.08 \times 10^{-5} \text{ mol Pb}^{+2}}{0.711 \text{ L}} = 5.74 \times 10^{-5} \text{ M} \qquad [\text{SO}_4^{-2}] = \frac{1.05 \times 10^{-4} \text{ mol SO}_4^{-2}}{0.711 \text{ L}} = 1.48 \times 10^{-4} \text{ M}$$

Substituting these initial concentrations into the Q_c expression for PbSO_4 , we get;

example:

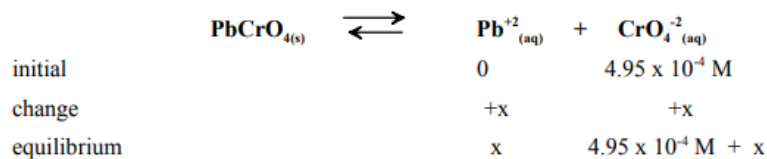
Lead chromate, PbCrO_4 , is a yellow pigment used in paints. Suppose 0.50 L of a $1.0 \times 10^{-5} \text{ M Pb}(\text{C}_2\text{H}_3\text{O}_2)$ and 0.50 L of a $1.0 \times 10^{-3} \text{ M K}_2\text{CrO}_4$ solution are mixed. Calculate the equilibrium concentration of Pb^{+2} ion remaining in the solution after PbCrO_4 precipitates. What is the percentage of Pb^{+2} remaining in solution after the precipitation has occurred. (The K_{sp} for PbCrO_4 is 1.8×10^{-14})

First, let us assume a limiting reagent problem where all the lead chromate that is possible precipitates. Then using the K_{sp} , determine how much could redissolve.



The cumulative volume of the two solutions is now 1.0 L, so we now have $5 \times 10^{-4} \text{ mol}$ solid PbCrO_4 in contact with a solution containing $4.95 \times 10^{-4} \text{ M CrO}_4^{-2}$ ions.

Let us now calculate how much of the solid lead chromate could possibly redissolve in the presence of this excess chromate ion.



Substituting into the K_{sp} expression for lead chromate, we obtain

$$K_{sp} = [\text{Pb}^{+2}][\text{CrO}_4^{-2}]$$

$$K_{sp} = [\text{Pb}^{+2}][\text{CrO}_4^{-2}]$$

$$1.8 \times 10^{-14} = (x)(x + 4.95 \times 10^{-4}) = (x)(4.95 \times 10^{-4}) \dots \text{assuming } x \text{ is negligible compared to } 4.95 \times 10^{-4}$$

$$\text{Solving for "x" we get } x = \frac{1.8 \times 10^{-14}}{4.95 \times 10^{-4}} = 3.64 \times 10^{-11} \text{ M Pb}^{+2} \text{ remaining in solution}$$

The number of moles of Pb^{+2} in the solution prior to precipitation was $5.0 \times 10^{-6} \text{ mol}$, so the percentage of Pb^{+2} remaining in the solution is:

$$\frac{3.64 \times 10^{-11}}{5.0 \times 10^{-6}} \times 100\% = 7.3 \times 10^{-4}\%$$

and would generally be considered a complete precipitation.

Solubility Calculations When the pH Is Constant

Analytical precipitations are usually performed in buffered solutions in which the pH is fixed at some predetermined and known value. The calculation of solubility under this circumstance is illustrated by the following example.

pH and Solubility

- The presence of a common ion **decreases** the solubility.
- Insoluble bases dissolve in acidic solutions
- Insoluble acids dissolve in basic solutions



$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2 = 1.2 \times 10^{-11}$$

$$K_{sp} = (s)(2s)^2 = 4s^3$$

$$4s^3 = 1.2 \times 10^{-11}$$

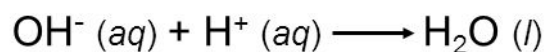
$$s = 1.4 \times 10^{-4} M$$

$$[\text{OH}^-] = 2s = 2.8 \times 10^{-4} M$$

$$\text{pOH} = 3.55 \quad \text{pH} = 10.45$$

At pH less than 10.45

Lower $[\text{OH}^-]$



Increase solubility of Mg(OH)_2

At pH greater than 10.45

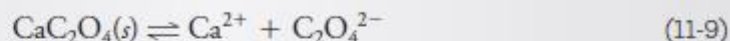
Raise $[\text{OH}^-]$

Decrease solubility of Mg(OH)_2

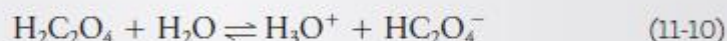
Calculate the molar solubility of calcium oxalate in a solution that has been buffered so that its pH is constant and equal to 4.00.

Solution

Step 1. Write Pertinent Equilibria



Oxalate ions react with water to form HC_2O_4^- and $\text{H}_2\text{C}_2\text{O}_4$. Thus, there are three other equilibria present in this solution:



Step 2. Define the Unknown Calcium oxalate is a strong electrolyte so that its molar analytical concentration is equal to the equilibrium calcium ion concentration, that is,

$$\text{solubility} = [\text{Ca}^{2+}] \quad (11-12)$$

Step 3. Write All the Equilibrium-Constant Expressions

$$[\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = K_{\text{sp}} = 1.7 \times 10^{-9} \quad (11-13)$$

$$\frac{[\text{H}_3\text{O}^+][\text{HC}_2\text{O}_4^-]}{[\text{H}_2\text{C}_2\text{O}_4]} = K_1 = 5.60 \times 10^{-2} \quad (11-14)$$

$$\frac{[\text{H}_3\text{O}^+][\text{C}_2\text{O}_4^{2-}]}{[\text{HC}_2\text{O}_4^-]} = K_2 = 5.42 \times 10^{-5} \quad (11-15)$$

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_w = 1.0 \times 10^{-14}$$

Step 4. Mass-Balance Expressions Because CaC_2O_4 is the only source of Ca^{2+} and

Since the problem states that the pH is 4.00, we can also write that

$$[\text{H}_3\text{O}^+] = 1.00 \times 10^{-4} \text{ and } [\text{OH}^-] = K_w/[\text{H}_3\text{O}^+] = 1.00 \times 10^{-10}$$

Step 5. Write Charge-Balance Expression A buffer is required to maintain the pH at 4.00. The buffer most likely consists of some weak acid HA and its conjugate base, A^- . The nature of the three species and their concentrations have not been specified, however, so we do not have enough information to write a charge-balance equation.

Step 6. Count the Number of Independent Equations and Unknowns We have four unknowns ($[\text{Ca}^{2+}]$, $[\text{C}_2\text{O}_4^{2-}]$, $[\text{HC}_2\text{O}_4^-]$, and $[\text{H}_2\text{C}_2\text{O}_4]$) as well as four independent algebraic relationships (Equations 11-13, 11-14, 11-15, and 11-16). Therefore, an exact solution can be obtained, and the problem becomes one of algebra.

Step 7a. Make Approximations It is relatively easy to solve the system of equations exactly in this case, so we will not bother with approximations.

Step 8. Solve the Equations A convenient way to solve the problem is to substitute Equations 11-14 and 11-15 into 11-16 in such a way as to develop a relationship between $[\text{Ca}^{2+}]$, $[\text{C}_2\text{O}_4^{2-}]$, and $[\text{H}_3\text{O}^+]$. Thus, we rearrange Equation 11-15 to give

$$[\text{HC}_2\text{O}_4^-] = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{O}_4^{2-}]}{K_2}$$

Substituting numerical values for $[\text{H}_3\text{O}^+]$ and K_2 gives

$$[\text{HC}_2\text{O}_4^-] = \frac{1.00 \times 10^{-4}[\text{C}_2\text{O}_4^{2-}]}{5.42 \times 10^{-5}} = 1.85[\text{C}_2\text{O}_4^{2-}]$$

Substituting this relationship into Equation 11-14 and rearranging gives

$$[\text{H}_2\text{C}_2\text{O}_4] = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{O}_4^{2-}] \times 1.85}{K_1}$$

Substituting numerical values for $[\text{H}_3\text{O}^+]$ and K_1 yields

$$[\text{H}_2\text{C}_2\text{O}_4] = \frac{1.85 \times 10^{-4}[\text{C}_2\text{O}_4^{2-}]}{5.60 \times 10^{-2}} = 3.30 \times 10^{-3}[\text{C}_2\text{O}_4^{2-}]$$

Substituting these expressions for $[\text{HC}_2\text{O}_4^-]$ and $[\text{H}_2\text{C}_2\text{O}_4]$ into Equation 11-16 gives

$$\begin{aligned} [\text{Ca}^{2+}] &= [\text{C}_2\text{O}_4^{2-}] + 1.85[\text{C}_2\text{O}_4^{2-}] + 3.30 \times 10^{-3}[\text{C}_2\text{O}_4^{2-}] \\ &= 2.85[\text{C}_2\text{O}_4^{2-}] \end{aligned}$$

or $[\text{C}_2\text{O}_4^{2-}] = [\text{Ca}^{2+}]/2.85$

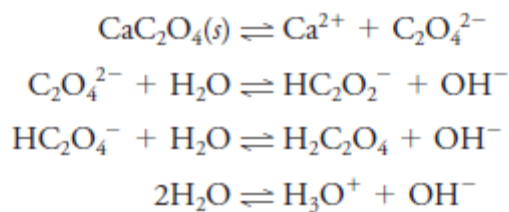
Substituting into Equation 11-13 gives

$$\frac{[\text{Ca}^{2+}][\text{Ca}^{2+}]}{2.85} = 1.7 \times 10^{-9}$$

$$[\text{Ca}^{2+}] = \text{solubility} = \sqrt{2.85 \times 1.7 \times 10^{-9}} = 7.0 \times 10^{-5} \text{ M}$$

Solubility Calculations When the pH Is Variable

Computing the solubility of a precipitate such as calcium oxalate in a solution in which the pH is not fixed and known is considerably more complicated than in the example that we just explored. Thus, to determine the solubility of CaC_2O_4 in pure water, we must take into account the change in OH^- and H_3O^+ that accompanies the solution process. In this example, there are four equilibria to consider



the hydroxide ion concentration now becomes an unknown, and an additional algebraic equation must therefore be developed to calculate the solubility of calcium oxalate.

As in Example 11-7, the solubility is equal to the cation concentration, $[\text{Ca}^{2+}]$.

$$\text{solubility} = [\text{Ca}^{2+}] = [\text{C}_2\text{O}_4^{2-}] + [\text{HC}_2\text{O}_4^-] + [\text{H}_2\text{C}_2\text{O}_4]$$

In this case, however, we must take into account one additional equilibrium—the dissociation of water. The equilibrium-constant expressions for the four equilibria are then

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = 1.7 \times 10^{-9} \quad (11-17)$$

$$K_2 = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{O}_4^{2-}]}{[\text{HC}_2\text{O}_4^-]} = 5.42 \times 10^{-5} \quad (11-18)$$

$$K_1 = \frac{[\text{H}_3\text{O}^+][\text{HC}_2\text{O}_4^-]}{[\text{H}_2\text{C}_2\text{O}_4]} = 5.60 \times 10^{-2} \quad (11-19)$$

$$K_{\text{w}} = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14} \quad (11-20)$$

The charge-balance equation is

$$2[\text{Ca}^{2+}] + [\text{H}_3\text{O}^+] = 2[\text{C}_2\text{O}_4^{2-}] + [\text{HC}_2\text{O}_4^-] + [\text{OH}^-] \quad (11-22)$$

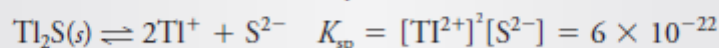
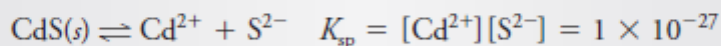
We now have six unknowns ($[\text{Ca}^{2+}]$, $[\text{C}_2\text{O}_4^{2-}]$, $[\text{HC}_2\text{O}_4^-]$, $[\text{H}_2\text{C}_2\text{O}_4]$, $[\text{H}_3\text{O}^+]$, and $[\text{OH}^-]$) and six equations (11-17 through 11-22). Thus, in principle, the problem can be solved exactly.

EX:

Cadmium sulfide is less soluble than thallium(I) sulfide. Find the conditions under which Cd^{2+} and Tl^+ can, in theory, be separated quantitatively with H_2S from a solution that is 0.1 M in each cation.

Solution

The constants for the two solubility equilibria are:



Since CdS precipitates at a lower $[\text{S}^{2-}]$ than does Tl_2S , we first compute the sulfide ion concentration necessary for quantitative removal of Cd^{2+} from solution. As in Example 11-10, we arbitrarily specify that separation is quantitative when all but 1 part in 1000 of the Cd^{2+} has been removed, that is, the concentration of the cation has been lowered to 1.00×10^{-4} M. Substituting this value into the solubility-product expression gives

$$\begin{aligned} K_{\text{sp}} = 10^{-4}[\text{S}^{2-}] &= 1 \times 10^{-27} \\ [\text{S}^{2-}] &= 1 \times 10^{-23} \text{ M} \end{aligned}$$

If we maintain the sulfide concentration at this level or greater, we may assume that quantitative removal of the cadmium will take place. Next, we compute the $[\text{S}^{2-}]$ needed to initiate precipitation of Tl_2S from a 0.1 M solution. Precipitation will begin when the solubility product is just exceeded. Since the solution is 0.1 M in Tl^+ ,

$$\begin{aligned} (0.1)^2[\text{S}^{2-}] &= 6 \times 10^{-22} \\ [\text{S}^{2-}] &= 6 \times 10^{-20} \text{ M} \end{aligned}$$

These two calculations show that quantitative precipitation of Cd^{2+} takes place if $[\text{S}^{2-}]$ is made greater than 1×10^{-23} M. No precipitation of Tl^+ occurs, however, until $[\text{S}^{2-}]$ becomes greater than 6×10^{-20} M.

Substituting these two values for $[\text{S}^{2-}]$ into Equation 11-42 permits us to calculate the $[\text{H}_3\text{O}^+]$ range required for the separation.

and

$$[\text{H}_3\text{O}^+]^2 = \frac{1.2 \times 10^{-22}}{6 \times 10^{-20}} = 2.0 \times 10^{-3}$$

$$[\text{H}_3\text{O}^+] = 0.045 \text{ M}$$

By maintaining $[\text{H}_3\text{O}^+]$ between approximately 0.045 and 3.5 M, we should be able to separate Cd^{2+} quantitatively from Tl^+ . Because of the high ionic strength of such acidic solutions, it may be necessary to correct for activity effects.

Titration curve for mixture

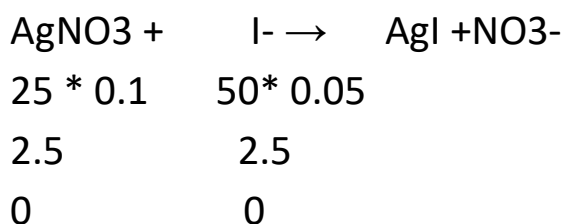
Titration 50ml of (0,05M I⁻ + 0,08M Cl⁻) with 0,1M AgNO₃ K_{sp}
AgCl = $1.82 \cdot 10^{-10}$, K_{sp} AgI = $8.3 \cdot 10^{-17}$

I⁻ Ppt first

A) At zero addition

$$\begin{aligned} \text{PI} &= -\log [\text{I}^-] \\ &= -\log (0.05) \end{aligned}$$

B) After addition of 25ml



$$K_{sp} = [\text{Ag}][\text{Cl}]$$

$$[\text{Ag}] = K_{sp} / [\text{I}^-]$$

$$K_{sp} \text{ AgCl} = K_{sp} / [\text{I}^-] / [\text{Cl}^-]$$

$$[\text{I}^-] = 4.56 \cdot 10^{-7} [\text{Cl}^-]$$

$$[\text{Cl}^-] = 50 \cdot 0.08 / 75 = 0.0533$$

$$[\text{I}^-] = 2.36 \cdot 10^{-8}$$

$$\begin{aligned} [\text{Ag}] &= 1.82 \cdot 10^{-10} / 0.0533 \\ &= 3.41 \cdot 10^{-9} \end{aligned}$$

$$\text{P}_{\text{Ag}} = 0.47$$

C) At 30ml addition

$$\begin{aligned} [\text{Cl}^-] &= 50 \cdot 0.08 + 50 \cdot 0.05 / 80 = \\ &= 0.043 \text{M} \end{aligned}$$

$$\begin{aligned} [\text{Ag}] &= 1.82 \cdot 10^{-10} / 0.0438 \\ &= 4.16 \cdot 10^{-9} \end{aligned}$$

$$P_{Ag} = 8.38$$

Indicators for ppting titration

Three types of end points encountered in titration with silver nitrate:

1- Potentiometric end points:

Are obtained by measuring the potential between a silver electrode and reference electrode whose potential is constant and independent of the added reagent

2- Amperometric end point

The current generated between a pair of silver microelectrodes in the solution of the analyte is measured and plotted as a function of reagent volume

3- Achemical end point

Usually consists of a color change appearance or disappearance of turbidity in the solution [being titrated]

The requirements for an indicator in precipitation titration

- 1- The color change should occur over a limited range of p- function of the reagent or the analyte
- 2- The color change should take place within the steep portion of T.C for the analyte

Examples of indicators for pption titration:

Mohar method

Mohr method of determination of chlorides by titration with silver nitrate is one of the oldest titration methods still in use - it was researched and published by Karl Friedrich Mohr in 1856.

The idea behind is very simple - chlorides are titrated with the silver nitrate solution in the presence of chromate anions. End point is signalled by the appearance of the red silver chromate.

Intense yellow color of chromate may make detection of first signs of formation of red silver chromate precipitation difficult. As some excess of silver must be added before precipitate starts to form, if concentration of titrant is below 0.1M, we may expect significant positive error. To correct for this error we can determine a blank, titrating a solution of the indicator potassium chromate with standard silver nitrate solution. To make result more realistic we can add small amount of chloride free calcium carbonate to the solution to imitate the white silver precipitate.

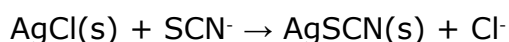
Solution during titration should be close to neutral. In low pH silver chromate solubility grows due to the protonation of chromate anions, in high pH silver starts to react with hydroxide anions, precipitating in form of AgOH and Ag₂O. Both processes interfere with the determination accuracy.

Exactly the same approach can be used for determination of bromides. Other halides and pseudohalides, like I⁻ and SCN⁻, behave very similarly in the solution, but their precipitate tends to adsorb chromate anions making end point detection difficult.

2-Volhard method

In the Volhard method chlorides are first precipitated with excess silver nitrate, then excess silver is titrated with potassium (or sodium) thiocyanate. To detect end point we use Fe^{3+} cations, which easily react with the thiocyanate, creating distinct wine red complex.

There is a problem though. Silver thiocyanate solubility is slightly lower than solubility of silver chloride, and during titration thiocyanate can replace chlorides in the existing precipitate:



To avoid problems we can filtrate precipitated AgCl before titration. However, there exist much simpler and easier procedure that gives the same result. Before titration we add some small volume of a heavy organic liquid that is not miscible with water (like nitrobenzene, chloroform or carbon tetrachloride). These liquids are better at wetting precipitate than water. Once the precipitate is covered with non polar liquid, it is separated from the water and unable to dissolve.

Precipitate solubility is not a problem during determination of I^- and Br^- , as both AgBr and AgI have much lower solubilities than AgSCN.

3- Fajans method

Fajan's method makes use of a reaction between the indicator and the precipitate formed during the titration. A dye such as dichlorofluorescein is the indicator, and exists as an anion in solution. In a solution of chloride, since chloride ions are in excess, they form the primary layer on the precipitate, with the cations of sodium held as the secondary layer. On completion of the reaction, at the end point, the silver ion is in excess. As a result, the primary layer is now the silver ion which is positively charged and attracts the anion of the indicator to form the secondary layer. The color of the free indicator is different from that of the adsorbed

indicator. This provides a visible end point to signal that the reaction is complete.

Compleximetric reaction and titration

omplexometric titration is a form of volumetric analysis in which the formation of a colored complex is used to indicate the end point of a titration. Complexometric titrations are particularly useful for the determination of a mixture of different metal ions in solution. An indicator capable of producing an unambiguous color change is usually used to detect the end-point of the titration.

Effect of pH on the composition of EDTA

The strength and stability of EDTA complexes is pH dependent.

The total concentration of EDTA will be the sum of all equilibrium species

$$C_T = [H_4Y] + [H_3Y^-] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]$$

where C_T is the total molar concentration of *uncomplexed* EDTA.

The fraction of any species can be found if desired where:

$$\alpha_0 = [H_4Y]/C_T$$

$$\alpha_1 = [H_3Y^-]/C_T$$

$$\alpha_2 = [H_2Y^{2-}]/C_T$$

$$\alpha_3 = [HY^{3-}]/C_T$$

The values may be estimated from a graph or calculated.

The value of $\alpha_{Y^{4-}}$ depends only on the concentration of H_3O^+ and the acid dissociation constants for EDTA.

Now, assume a divalent metal reacts with EDTA, Y^{4-} , the following equilibrium will be observed in alkaline medium:

$$M^{2+} + Y^{4-} \rightleftharpoons MY^{2-}$$

$$K_f = \frac{[MY^{2-}]}{[M^{2+}][Y^{4-}]}$$

Y^{4-} concentration is dependent on pH and, therefore, should be calculated as follows:

$$\alpha_4 = \frac{K_1 K_2 K_3 K_4}{[H_3O^+]^4 + K_1 [H_3O^+]^3 + K_1 K_2 [H_3O^+]^2 + K_1 K_2 K_3 [H_3O^+] + K_1 K_2 K_3 K_4}$$

$$[Y^{4-}] = \alpha_4 C_T$$

Ex

Find the conc. Of all species in solution at equilibrium resulting from mixing 50ml of 0.2M Ca with 50ml of 0.1MEDTA adjusted to PH= 10. α_4 is 0.35 $K_f=5 \cdot 10^{10}$.



$$0.05 - x \quad \alpha_4 x \quad 0,05 + x$$

$$\text{Mmole } Ca^{+2} = 0.2 * 50 = 10 \text{ mmol}$$

$$\text{Mmole EDTA} = 0.1 * 50 = 5 \text{ mmol}$$

$$\text{Excess} = 10 - 5 = 5 \text{ mmole}$$

$$[\text{Ca}^{+2}] = 5/100 = 0.05\text{M}$$

$$[\text{CaY}^{-2}] = 5/100 = 0.05\text{M}$$

$$K_f = [\text{CaY}^{-2}] / [\text{Ca}^{+2}] \alpha_4 C_T$$

$$[\text{Ca}^{+2}] = C_T$$

$$5 \cdot 10^{10} = 0.05 / 0.05 \cdot 0.35 \cdot x$$

$$x = 5.6 \cdot 10^{-11} \text{ M}$$

$$[\text{Y}^{-2}] = \alpha_4 C_T$$

$$= 0.35 \cdot 5.6 \cdot 10^{-11}$$

$$= 1.9 \cdot 10^{-11} \text{ M}$$

EX: calculate the molar conc. Of Ni^{+2} in a 0.015M solution of NiY^{-2} that has been buffered to pH a) 3
b) 8



$$x \quad \alpha_4 C_T \quad 0.015 - x$$

$$[\text{Ni}^{+2}] = [\text{Y}^{-4}] + [\text{HY}^{-3}] + [\text{H}_2\text{Y}^{-2}] + [\text{H}_3\text{Y}^{-1}] + [\text{H}_4\text{Y}] = C_T$$

a)

$$K_f = [\text{NiY}^{-2}] / [\text{Ni}^{+2}] \alpha_4 C_T$$

$$4.2 \cdot 10^{18} = 0.015 / [\text{Ni}^{+2}]^2 \cdot 2.5 \cdot 10^{-11}$$

$$= 1.2 \cdot 10^{-5} \text{ M}$$

b)

$$K_f = [\text{NiY}^{-2}] / [\text{Ni}^{+2}]^2 \alpha_4$$

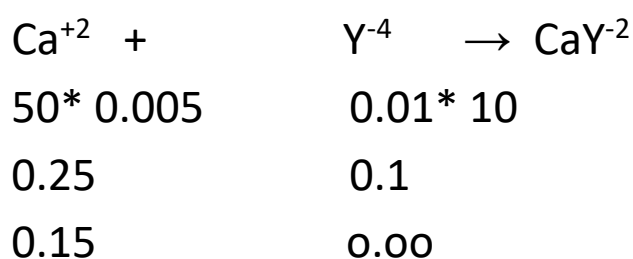
$$4.2 \cdot 10^{18} = 0.015 / [\text{Ni}^{+2}]^2 \cdot 5.4 \cdot 10^{-3}$$

$$= 8.1 \cdot 10^{-10} \text{ M}$$

Ex: drive a curve relating p Ca to the volume of EDTA added in the titration of 50ml of 0.005M Ca⁺² with 0.01M EDTA in a solution buffered to a pH= 10, α₄= 0.35

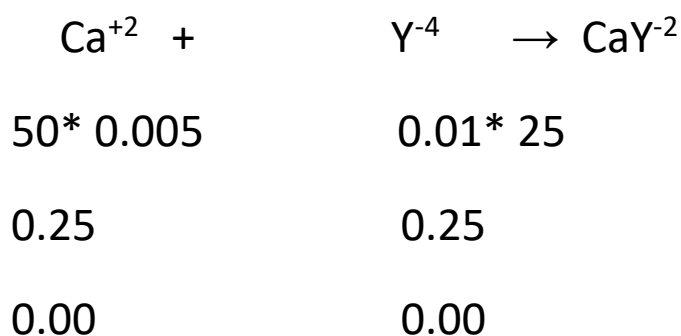
At (10, 25, 30)ml

A) 10 ml added EDTA



$$[\text{Ca}^{+2}] = 0.15 / 60 = 2.5 \cdot 10^{-3} \text{ M}$$

B) 25 ml added EDTA eq.point



$$[\text{CaY}^{-2}] = 0.25 / 75 = 3.33 \cdot 10^{-3} \text{ M}$$

$$[\text{Ca}^{+2}] = \text{CT}$$

$$K_f = [\text{CaY}^{-2}] / [\text{Ca}^{+2}]^2 \alpha_4$$

$$5 \cdot 10^{10} = 0.0033 / [\text{Ca}^{+2}]^2 \cdot 0.35$$

$$= 4.36 \cdot 10^{-7}$$

$$\text{pCa} = 6.36$$

c) At 35ml EDTA added



$$50 \cdot 0.005 \qquad 0.01 \cdot 35$$

$$0.25 \qquad 0.35$$

$$0.00 \qquad 0.1$$

$$[\text{CaY}^{-2}] = 0.25 / 85$$

$$= 2.94 \cdot 10^{-3} \text{M}$$

$$\text{CT} = 0.1 / 85$$

$$= 1.18 \cdot 10^{-3} \text{M}$$

$$K_f = [\text{CaY}^{-2}] / [\text{Ca}^{+2}] \alpha_4 \text{CT}$$

$$5 \cdot 10^{10} = 2.94 \cdot 10^{-3} / [\text{Ca}^{+2}] \cdot 0.35 \cdot 1.18 \cdot 10^{-3}$$

$$[\text{Ca}^{+2}] = 1.42 \cdot 10^{-10}$$

$$\text{pCa} = 9.85$$

sharpness of the end point

the end point is affected two major factors

- 1- Stability constant of the metal ion –EDTA complex .
- 2- The concentration of the metal ion and EDTA

As the value of both factors is increased sharper end points.

Very low stability constants diffuse end points of less sharpness and large errors.

Solutions are typically buffered at basic condition ,higher pH give sharp end point and formation metal-EDTA complex.

APPLICATION OF EDTA Techniques.

EDTA titrations can be performed in many ways, let's look at a few Since several of these techniques are pretty specialized and you won't see them again I will just talk about the first and last, Direct titrations and Masking

Direct Titrations

In direct titrations you simply add an indicator to a solution of the metal ion and titrate with EDTA. Before you start the titration you need to check that the pH of the solution gives a good K_f' and that the pH is consistent with your indicator color change as well. auxiliary complexing agents like ammonia, tartrate, or citrate may be added to block formation of insoluble OH complexes

Back Titrations

In a back titration an excess of EDTA is added to the metal ion solution, and the excess EDTA is titrated with a known concentration of a second metal ion. The second metal ion must form a weaker complex with EDTA than the analyte ion so the second metal does not displace the analyte ion from its complex with EDTA. Back titration are used when the metal ion blocks the indicator when the metal-EDTA complex forms too slowly, or when the metal precipitates in the absence of EDTA.

Displacement Titrations

For metal ions that do not have a good indicator a second titration method is the displacement titration. Here the analyte is treated with an excess of a second metal bound to EDTA. The analyte ion displaces the second metal from the EDTA complex, and then the second metal is titrated with EDTA. A typical displacement titration involves Hg_{2+} as the analyte and MgEDTA at the displacement titrant.

Indirect Titrations

With a little clever thought EDTA can be used as a titrant for anions like SO_4^{2-} . BaSO_4 is insoluble to one way to determine SO_4^{2-} is to precipitate with Ba, filter and wash the ppt, then boil in excess EDTA to complex all the Ba. Back titrate to determine how much Ba you had, and that, in turn, tells you how much SO_4^{2-} you had.

Types of solvent :

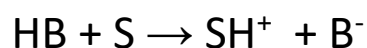
1- Aprotic solvent

Which may be considered Chemically neutral and virtually unreactive under the condition employed they are frequently used to dilute reaction mixture. carbon tetrachloride and toluene

Come in this group they possess low dielectric constant don't cause ionization in solutes and do not undergo reaction with acids and bases.

2- Protophilic solvent :

Are the substance that possess a high affinity for proton the overall reaction



The equilibrium in this reversible reaction will be generally influenced by the nature of the acid and the solvent

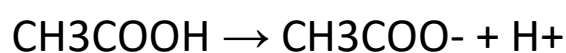
3- Protogenic solvent

Are acidic in nature and readily donate protons anhydrous acids such as hydrogen fluoride and sulphuric acid fall in this category because of their strength and ability to

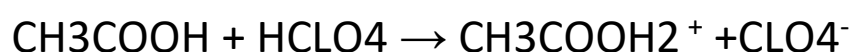
donate proton they enhanced the strength of weak bases.

4- Amphiprotic solvent

Consist of liquids such as water , alcohols and weak organic acid which are slightly ionized and combine both protogenic and protolitic properties in being able to donate protons and accept proton ethanoic acid displace acidic properties



In the presence of perchloric acid stronger acid



$\text{CH}_3\text{COOH}_2^+$ ion can very readily give up its proton to react with a base , basic properties of base is enhanced titration between weak base and perchloric acid can often be accurately carried out using ethanoic acid as solvent.

5- Leveling solvents:

Strongly protophilic solvents are important to force equilibrium equation to the right this effect is so powerful is strongly protophilic

solvent all acids act as of similar strength . the covers accrue with strongly protogenic solvent which cause all bases to act as they were of similar strength solvent which act in this way known a leveling solvent.