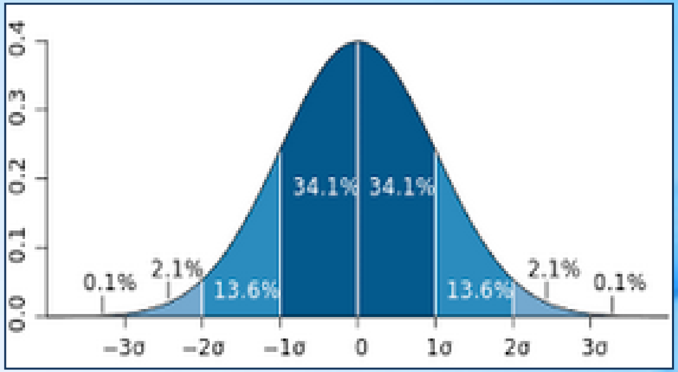
2nd YEAR - 1st Sem
2024 - 2025

Gravimetric Analysis
Solubility
Analytical Statistics



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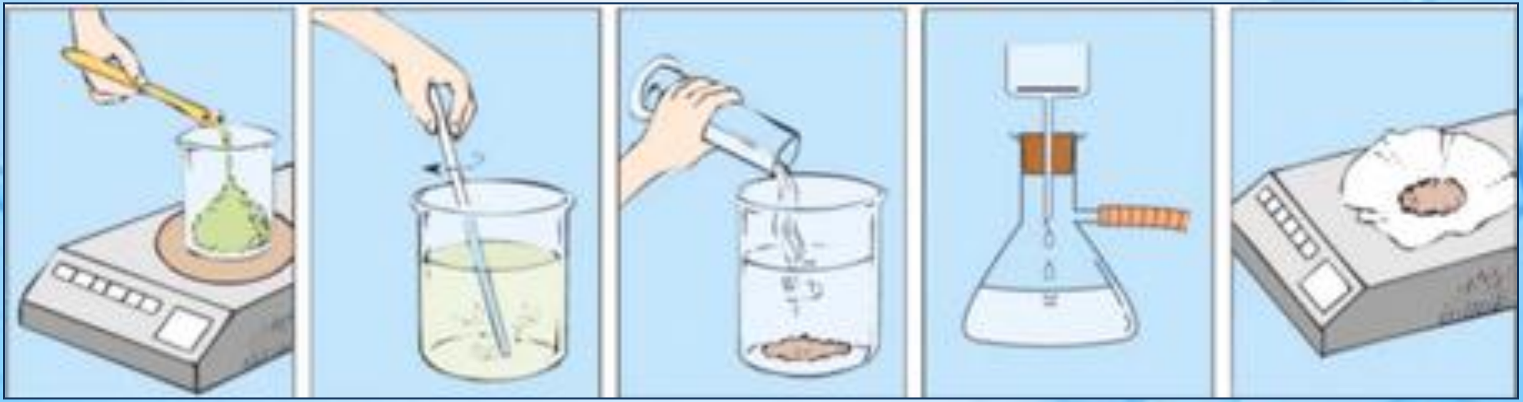


It's not about being the BEST, it's about being BETTER than you were yesterday. (Anonymous)

Gravimetric analysis

Gravimetric analysis is an analytical technique used for the quantitative determination of an analyte based on the mass of solid.

Gravimetric Analysis is based on the principle the mass of the ion present in the pure compound can be determined by estimating the mass percentage of the same ion in the known quantity of an impure compound.

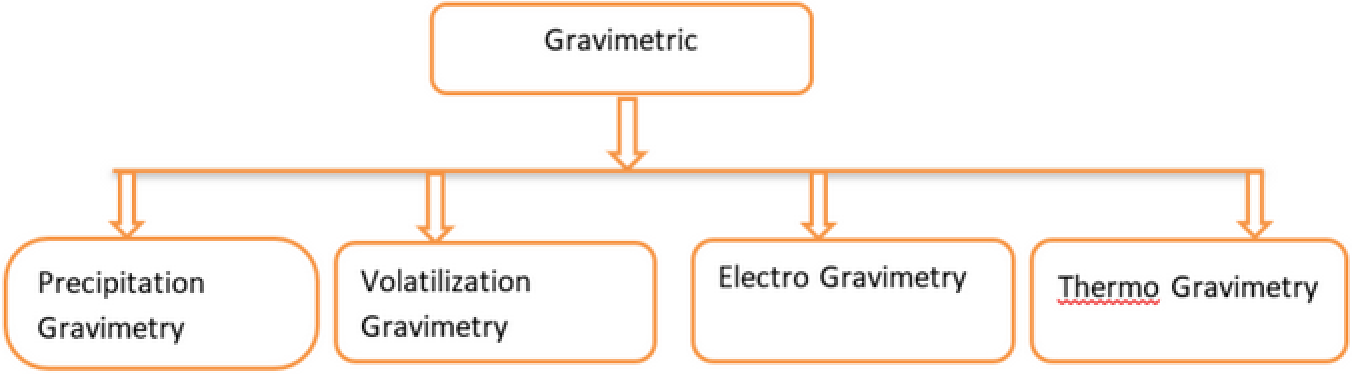
The element to be identified is precipitated from a solution using this method of analysis by the addition of a suitable precipitating agent.

The precipitate should either have a known composition or, through heating, should be changed into another compound with a known composition.

For example, to determine the sulphate ions (SO_4^{2-}) contained in ammonium sulphate $(NH_4)_2SO_4$ solution, the solution is treated with barium chloride ($BaCl_2$) first. When all sulphate ions have precipitated as barium sulphate ($BaSO_4$), the precipitate of barium sulphate is filtered, washed, dried, ignited, and finally weighed. By knowing the weight of the precipitate, $BaSO_4$, the amount of sulphate ion present in the given volume of ammonium sulphate can be determined using a suitable stiochiometric relationship.

Classification of Gravimetric Analysis

Gravimetric analysis is broadly classified into following types:



Gravimetric

Precipitation Gravimetry

Volatilization Gravimetry

Electro Gravimetry

Thermo Gravimetry

Precipitation gravimetry

Precipitation gravimetric analysis separates ions from a solution by using the precipitation process (the reaction that creates an insoluble solid product from the reaction of two soluble solid products). The chemical responsible for precipitate formation in the precipitation reaction is referred to as the precipitating agent.

For instance, the white precipitate of silver chloride is produced when aqueous silver nitrate and sodium chloride solutions react. Sodium chloride is utilized as a precipitating agent in this process.

$$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$$

(a) Weighing the sample to be analysed

(b) Dissolving this sample in water

(c) Adding a suitable chemical to form a precipitate

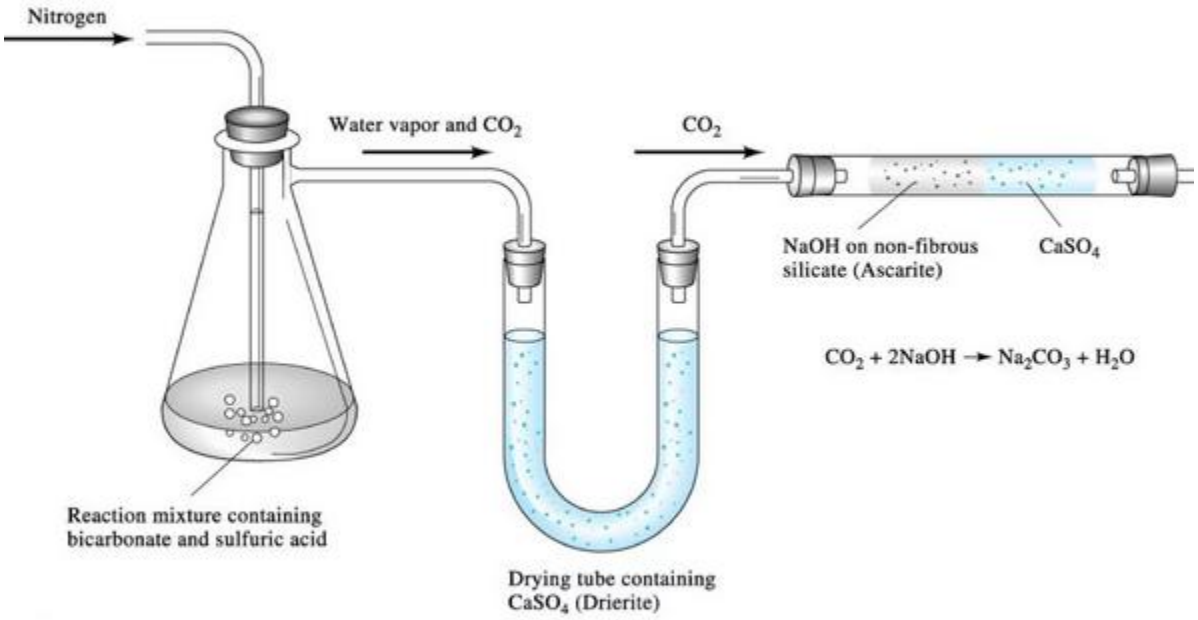
(d) Filtering to collect the precipitate

(e) Repeated drying and weighing until a constant mass of precipitate is obtained

Volatilization gravimetry

The analytical technique of gravimetric volatilization separates the masses using thermal or chemical energy to determine their masses. In this method solid reactant molecules are converted into gaseous molecules using thermal or chemical energy. Different volatile gases (that can be easily evaporative), like carbon dioxide, chlorine, etc., can be separated with the help of volatilization gravimetry.
For example, the aqueous solution of sulphuric acid helps to separate carbon dioxide gas (a volatile gas) molecules from sodium bicarbonate.

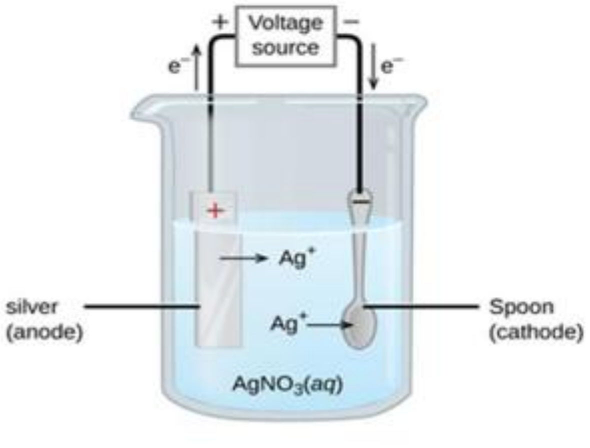
$$2NaHCO_3\,(aq) + H_2SO_4\,(aq) \rightarrow 2CO_2\,(g) + 2H_2O\,(l) + Na_2SO_4\,(aq)$$

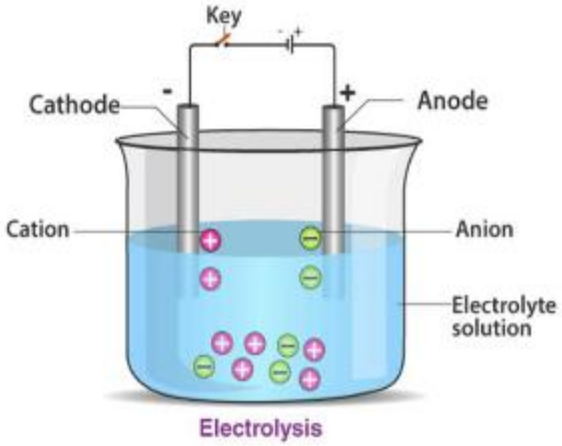


Electrogravimetry

Electrogravimetry is a method used to separate and quantify ions of a substance, usually a metal. It is similar to conventional gravimetric analysis. However, in electrogravimetry the product is deposited quantitatively on an electrode by an electrolytic reaction and the amount of the product is determined by weighing the electrode before and after electrolysis. The material is deposited on an electrode by the application of a potential instead of chemical precipitation from a solution. Hence the name electrogravimetry (weighing of the product after electrolysis).

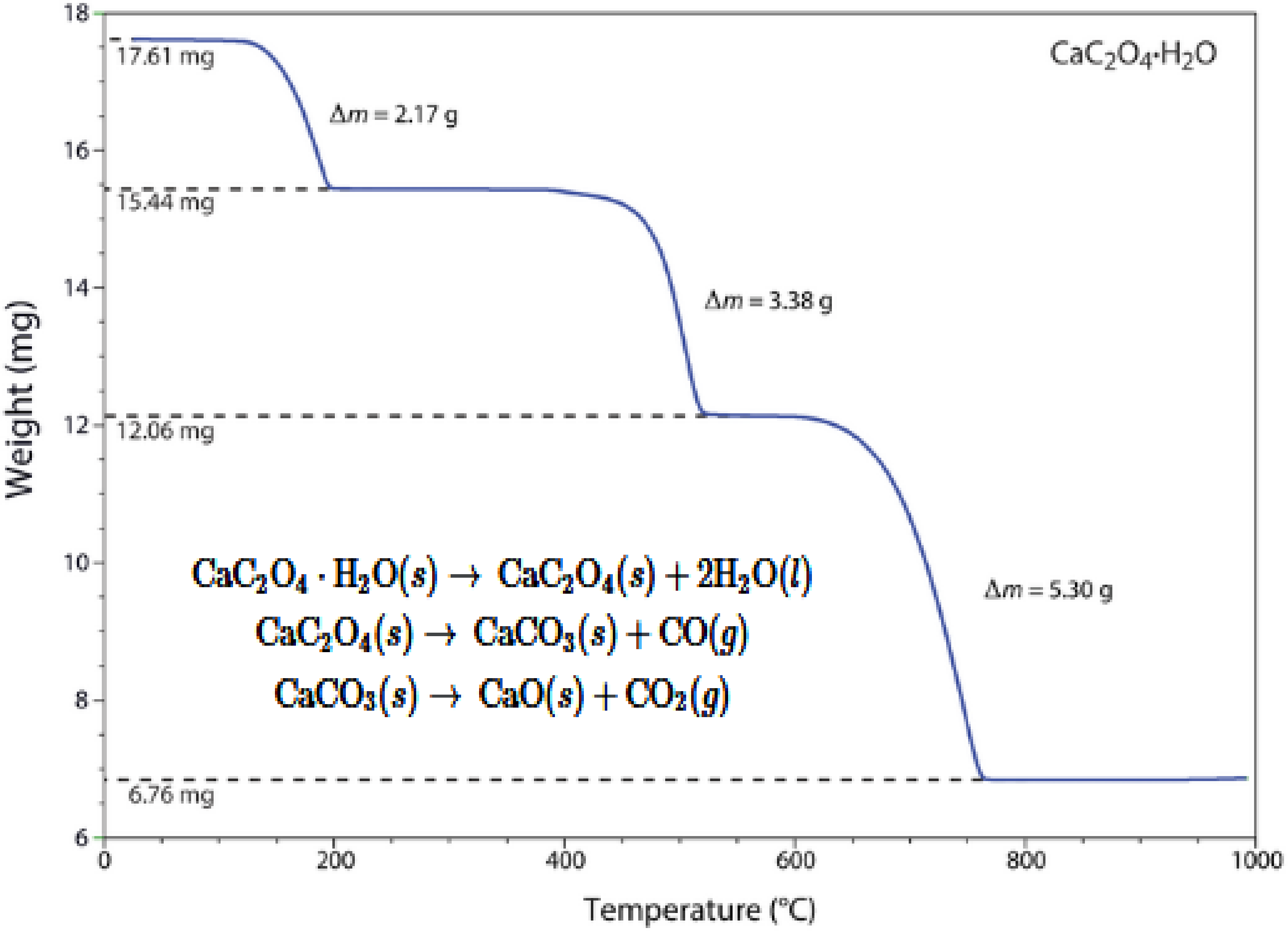
When a current is passed through a solution containing two or more electroactive species, the electrochemical process with the most positive reduction potential will occur first at the cathode. For example, if the solution contains copper, hydrogen, and cadmium ions, copper will deposit first. As copper deposits, the electrode potential becomes more negative until it reaches a point where hydrogen ions are reduced and hydrogen gas is formed at the cathode





Thermogravimetry

Thermo gravimetric analysis is a type of thermal analysis in which the mass of a sample is determined as a result of temperature change. It gives information on both physical and chemical phenomena, such as phase transitions, absorption, thermal degradation, and so on.



$$CaC_2O_4 \cdot H_2O(s) \rightarrow CaC_2O_4(s) + 2H_2O(l)$$

$$CaC_2O_4(s) \rightarrow CaCO_3(s) + CO(g)$$

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

Gravimetric analysis steps (precipitation)

1. **Preparation of the sample solution**
2. **Precipitation process**
3. **Digestion**
4. **Filtration and washing**
5. **Drying and Igniting**
6. **Weighing**
7. **Calculation**

➧ Preparation of the solution

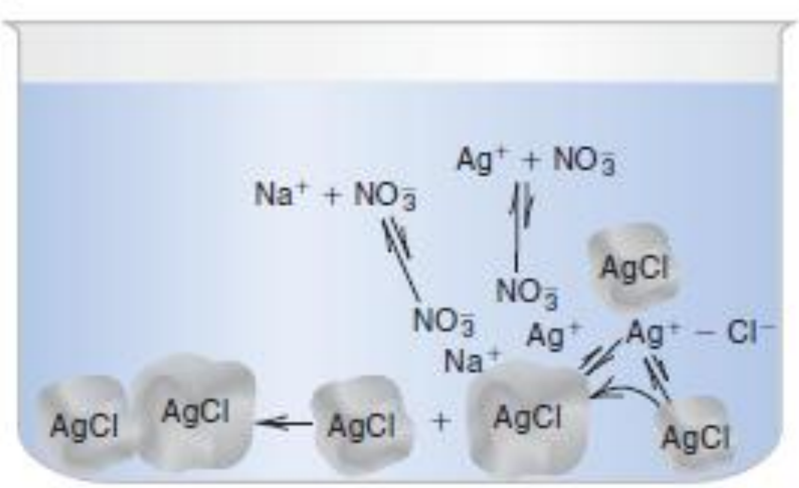
This may involve several steps including adjustment of the pH of the solution in order for the precipitate to occur quantitatively and get a precipitate of desired properties, removing interferences, adjusting the volume of the sample to suit the amount of precipitating agent to be added.

➧ Precipitation

This requires addition of a precipitating 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 nucleous. At this point, addition of extra precipitating agent will either form new nuclei or will build up on existing nuclei to give a precipitate.

➧ Digestion of the precipitate

The precipitate is left hot (below boiling) for 30 min to 1 hour in order for the particles to be digested. Digestion involves dissolution of small particles and reprecipitation on larger ones resulting in particle growth and better precipitate characteristics. This process is called Ostwald ripening.
Ostwald ripening is the phenomenon in which molecules on the surface of a small particle dissolve and then crystallize on the surface of a larger particle



An important advantage of digestion is observed for colloidal precipitates where large amounts of adsorbed ions cover the huge area of the precipitate. Digestion forces the small colloidal particles to agglomerate which decreases their surface area and thus adsorption. The precipitate often contains ions that were trapped when the precipitate was
formed. This is mostly a problem for crystalline precipitates. If the trapped ions are not volatile, then their presence will corrupt the weighing step. Concentration of interfering species may be reduced by digestion. Unfortunately , postprecipitation as we will see later will increase during digestion.

➡ Filtration and washing

Problems with surface adsorption may be reduced by careful washing of the precipitate. With some precipitates, peptization occurs during washing. Each particle of the precipitate has two layers, in primary layer certain ions are adsorbed and in the outer layer other ions of opposite charge are adsorbed . This situation makes the precipitate settle down. If the outer layer ions are removed then all the particles will have the same charge so the particles will be dissonant .This is called peptization. This results in the loss of part of the precipitate because the colloidal form may pass through on filtration. , in case of colloidal precipitates we should not use water as a washing solution since peptization would occur. In such situations dilute volatile electrolyte such as nitric acid, ammonium nitrate, or dilute acetic acid may be used.

Drying and ignition

If the collected precipitate is in a form suitable for weighing, it must be heated to remove water and to remove the adsorbed electrolyte from the wash liquid. This drying can usually be done by heating at 110 to 120$^{\circ C}$ for 1 to 2 h. Ignition at a much higher temperature (>250$^{\circ C}$) is usually required if a precipitate must be converted to a more suitable form for weighing. For example, magnesium ammonium phosphate, $MgNH_4PO_4$, is decomposed to the pyrophosphate, $Mg_2P_2O_7$, by heating at 900$^{\circ C}$.
Hydrous ferric oxide, $Fe_2O_3.xH_2O$, is ignited to the anhydrous ferric oxide.
Many metals that are precipitated by organic reagents (e.g., 8-hydroxyquinoline) or by sulfide can be ignited to their oxides.

Weighing

The precipitate cannot be weighed with the necessary accuracy in place on the filter Paper; nor can the precipitate be completely removed from the filter paper in order to weigh it. The precipitate can be carefully heated in a crucible until the filter paper has burned away; this leaves only the precipitate. (As the name suggests, "ashless" paper is used so that the precipitate is not contaminated with ash.) . If you use Goosh crucible then after the precipitate is allowed to cool (preferably in a desicator to keep it from absorbing moisture), it is weighed (in the crucible). The mass of the crucible is subtracted from the combined mass, giving the mass of the precipitated analyte. Since the composition of the precipitate is known, it is simple to calculate the mass of analyte in the original sample.

➧ Precipitant or precipitating agent

Precipitant or precipitating agent refers to the chemical that is used to cause precipitation. Ideally, a gravimetric precipitating agent should react specifically or at least selectively with the analyte. Specific reagents, which are rare, react only with a single chemical species.
It is important to understand that the term specificity is used to tell something about the method's ability responding to one single analyte only, while selectivity is used when the method is able to respond to several different analytes in the sample.
Specifically react only with a single chemical species, i.e., Dimethylglyoxime – Ni^{+2}
Selectively react with a limited number of species, i.e., $AgNO^{3-}$ Cl^-, Br^-, I^- and SCN^-

Selective reagents, which are more common, react with a limited number of species.
In addition to specificity and selectivity, the ideal precipitating reagent would react with the analyte to give a product that is:

1. easily filtered and washed free of contaminants
2. of sufficiently low solubility that no significant loss of the analyte occurs during filtration and washing
3. unreactive with constituents of the atmosphere
4. of known chemical composition after it is dried or, if necessary, ignited

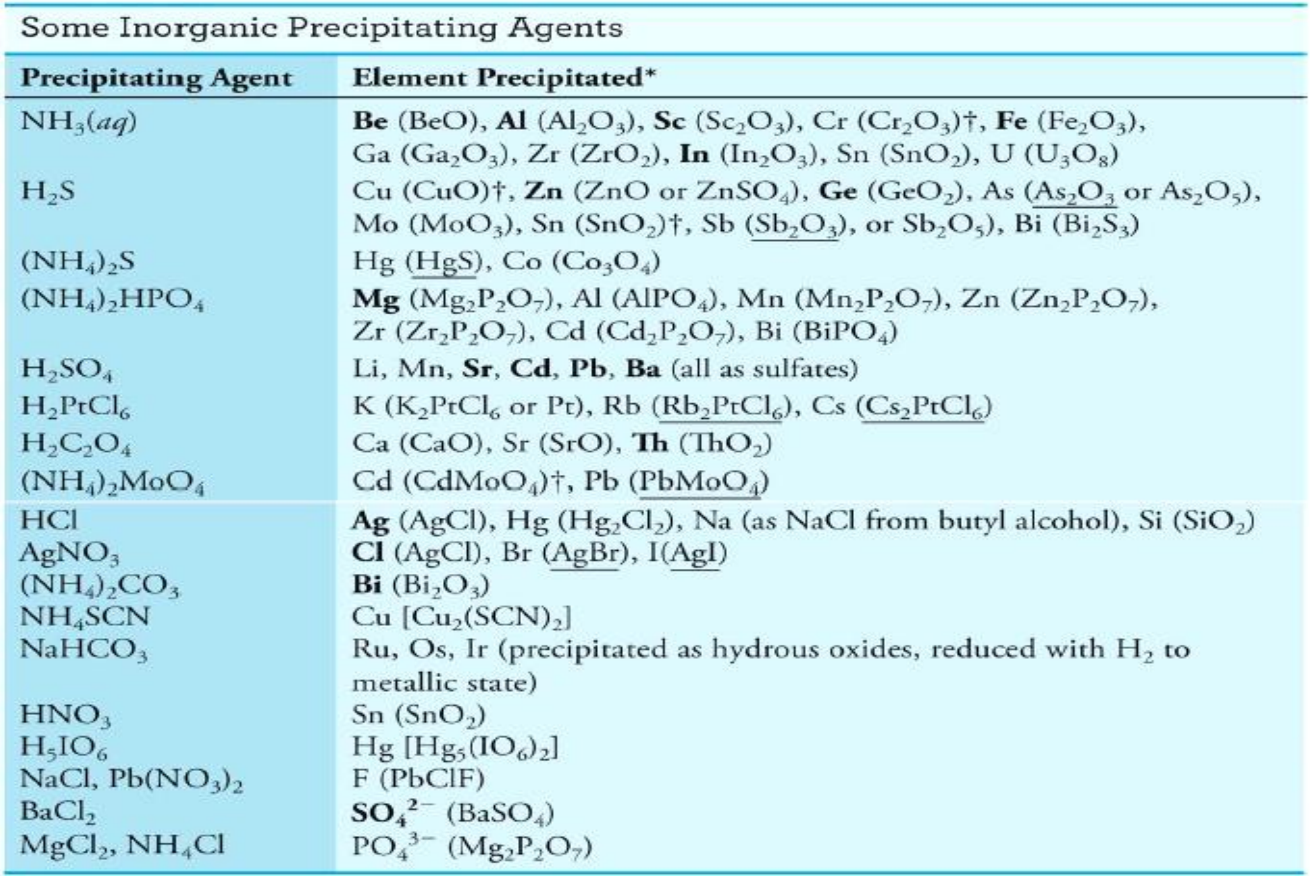
➧ Inorganic precipitating agents

Common inorganic precipitants can be used to determine several cations and anions. In some cases, the formation of the same precipitate can be used to determine the cation and the anion. For example, the reaction of barium and chromate ions to give barium chromate is used to determine both barium and chromate. However, precipitates such as hydroxides, oxalates, and metal ammonium phosphates are first converted to a weighable form. Precipitation methods can also be applied to determine organic functional groups such as organic halides, carbonyl, alkoxy groups, aromatic nitro, azo, and phosphate.

Organic precipitating agent

Organic precipitating agents have the advantages of giving precipitates with very low solubility in water and a favorable gravimetric factor. Most of them are **chelating agents** that form slightly soluble, uncharged chelates with the metal ions.

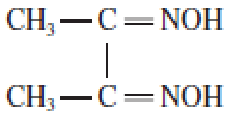
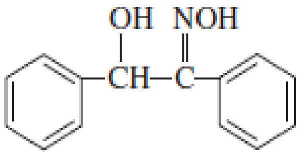
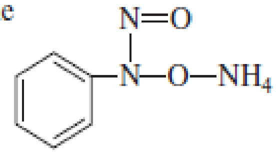
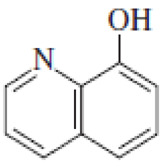
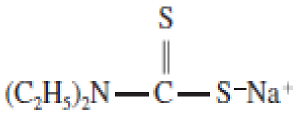
A chelating agent is a type of complexing agent that has two or more groups capable of complexing with a metal ion. The complex formed is called a chelate. Since chelating agents are weak acids, the number of elements precipitated, and thus the selectivity, can usually be regulated by adjustment of the pH. Some of these precipitates are not stoichiometric, and more accurate results are obtained by igniting them to form the metal oxides.



Some Inorganic Precipitating Agents

Precipitating Agent	Element Precipitated*
$NH_3(aq)$	**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)
$(NH_4)_2S$	Hg (HgS), Co (Co_3O_4)
$(NH_4)_2HPO_4$	**Mg** ($Mg_2P_2O_7$), Al ($AlPO_4$), Mn ($Mn_2P_2O_7$), Zn ($Zn_2P_2O_7$), Zr ($Zr_2P_2O_7$), Cd ($Cd_2P_2O_7$), 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)
$H_2C_2O_4$	Ca (CaO), Sr (SrO), **Th** (ThO_2)
$(NH_4)_2MoO_4$	Cd ($CdMoO_4$)†, Pb ($PbMoO_4$)
HCl	**Ag** ($AgCl$), Hg (Hg_2Cl_2), Na (as NaCl from butyl alcohol), Si (SiO_2)
$AgNO_3$	**Cl** ($AgCl$), Br ($AgBr$), I(AgI)
$(NH_4)_2CO_3$	**Bi** (Bi_2O_3)
NH_4SCN	Cu [$Cu_2(SCN)_2$]
$NaHCO_3$	Ru, Os, Ir (precipitated as hydrous oxides, reduced with H_2 to metallic state)
HNO_3	Sn (SnO_2)
H_5IO_6	Hg [$Hg_5(IO_6)_2$]
$NaCl$, $Pb(NO_3)_2$	F ($PbClF$)
$BaCl_2$	**SO_4^{2-}** ($BaSO_4$)
$MgCl_2$, NH_4Cl	PO_4^{3-} ($Mg_2P_2O_7$)

Some Organic Precipitating Agents

Reagent	Structure	Metals Precipitated
Dimethylglyoxime	 $\begin{array}{l}CH_3-C=NOH\\ \qquad\ \ \vert\\ CH_3-C=NOH\end{array}$	Ni(II) in NH_3 or buffered HOAc; Pd(II) in HCl ($M^{2+} + 2HR \rightarrow \underline{MR_2} + 2H^+$)
α -Benzoinozime (cupron)		Cu(II) in NH_3 and tartrate; Mo(VI) and W(VI) in H^+ ($M^{2+} + H_2R \rightarrow \underline{MR} + 2H^+$; $M^{2+} = Cu^{2+}$, MoO_2^{+}, WO_2^{2+}) Metal oxide weighed
Ammonium nitrosophenylhydroxylamine (cupferron)		Fe(III), V(V), Ti(IV), Zr(IV), Sn(IV), U(IV) ($M^{n+} + nNH_4R \rightarrow \underline{MR_n} + nNH_4^+$) Metal oxide weighed
8-Hydroxyquinoline (oxine)		Many metals. Useful for Al(III) and Mg(II) ($M^{n+} + nHR \rightarrow \underline{MR_n} + nH^+$)
Sodium diethyldithiocarbamate	 $(C_2H_5)_2N-\overset{\overset{S}{\|}}{C}-S^-Na^+$	Many metals from acid solution ($M^{n+} + nNaR \rightarrow \underline{MRn} + nNa^+$)
Sodium tetraphenylboron	$NaB(C_6H_5)_4$	K^+, Rb^+, Cs^+, Tl^+, Ag^+, Hg(I), Cu(I), NH_4^+, RNH_3^+, $R_2NH_2^+$, R_3NH^+, R_4N^+. Acidic solution ($M^+ + NaR \rightarrow \underline{MR} + Na^+$)
Tetraphenylarsonium chloride	$(C_6H_5)_4AsCl$	$Cr_2O_7^{2-}$, MnO_4^-, ReO_4^-, MoO_4^{2-}, WO_4^{2-}, ClO_4^-, I_3^-. Acidic solution ($A^{n-} + nRCl \rightarrow R_nA + nCl^-$)

Errors in Gravimetric analysis

There are different causes of errors in gravimetric analysis these are as follows:

- Inaccurate weighing.
- Incomplete and imperfect precipitation.
- Ignition of precipitate at either too low or too high temperature.
- Exposure of ignited precipitate to the atmosphere.
- Use of sub standard reagent and apparatus.
- Haste and impatience.

Precaution to avoid the errors in gravimetric analysis

Gravimetric analysis has several possible causes of error, however, a careful analyst with adequate technical skill would avoid frequent mistakes.

For a successful gravimetric analysis, the following precaution should be used.

- ✓ Since gravimetric analysis is a lengthy and tedious process, each step must be conducted with considerable patience.
- ✓ Dilute solutions should be used for the precipitation since they prevent co-precipitation.
- ✓ The precipitant should be slowly introduced with constant stirring. This helps in large crystal growth, and the level of super-saturation is also decreased.
- ✓ Precipitation should be performed under hot conditions since precipitation is most effective in hot solutions.
- ✓ A slight excess of the precipitant should be added throughout the precipitation process, but significant excess must be avoided since they will contaminate the precipitate.

Advantages of gravimetric analysis

1. Although there are numerous sources of inaccuracy in gravimetric analysis, when conducted correctly, this method remains the most accurate method for chemical analysis.
2. his procedure employs low-cost equipments.
3. It allows for very little instrumental error and does not necessitate a set of standards to calculate the constituent to be determined.
4. It is an analytical method that helps to determine the quantity of analyte based on the density of the solid.
5. This approach has been developed and standardized for practically all cations and anions.
6. This technique can also be used with neutral species like iodine, carbon dioxide, water, and sulfur dioxide.
7. This method has been successfully used to estimate a wider range of organic compounds, including lactose in milk products, salicylates in medications, nicotine in pesticides, and cholesterol in cereals, among others.
8. Possible sources of error i.e. presence of impurities can be checked easily.

Disadvantages of gravimetric analysis

1. It is a macroscopic approach since a large amount of sample is needed.
2. The study of a single element or small group of elements may generally only be done via gravimetric analysis at one time.
3. The steps in this method are frequently complex, and a single mistake in the process can frequently cause trouble for the study.
4. This method is time-consuming and difficult because it requires so many steps.

Requirements of gravimetric analysis

1. The component that needs to be estimated must be fully precipitated.
2. The precipitate should be pure before it weighs.
3. The precipitate must be suitable for handling, such as filtering, washing, weighing, etc.
4. The most fundamental requirement for the gravimetric analysis is the selection of an insoluble precipitate of the constituent to be determined which has sufficient stability and is suitable for manipulation.

Gravimetric factor (GF)

Gravimetric factor (GF), which represents the weight of analyte per unit weight of precipitate. It is obtained from the ratio of the formula weight of the analyte to that of the precipitate, multiplied by the moles of analyte per mole of precipitate obtained from each mole of analyte, that is,

$$\boxed{\begin{aligned} \text{GF} &= \frac{\text{fw analyte (g/mol)}}{\text{fw precipitate (g/mol)}} \times \frac{a}{b}(\text{mol analyte/mol precipitate}) \\ &= \text{g analyte/g precipitate} \end{aligned}}$$

Example 1

Calculate the grams of analyte per gram of precipitate for the following conversions:

Analyte	*Precipitate*
P	Ag_3PO_4
K_2HPO_4	Ag_3PO_4
Bi_2S_3	$BaSO_4$

Solution

$$\text{g P/g } Ag_3PO_4 = \frac{\text{at wt P (g/mol)}}{\text{fw } Ag_3PO_4 \text{ (g/mol)}} = \frac{1}{1}\ (\text{mol P/mol } Ag_3PO_4)$$

$$\text{GF} = \frac{30.97 \text{ (g P/mol)}}{418.58 \text{ (g } Ag_3PO_4\text{/mol)}} \times \frac{1}{1} = 0.07399 \text{ g P/g } Ag_3PO_4$$

$$\text{g } K_2HPO_4/\text{g } Ag_3PO_4 = \frac{\text{fw } K_2HPO_4 \text{ (g/mol)}}{\text{fw } Ag_3PO_4 \text{ (g/mol)}} \times \frac{1}{1} \text{ (mol } K_2HPO_4/\text{mol } Ag_3PO_4)$$

$$GF = \frac{174.18 \text{ (g } K_2HPO_4/\text{mol)}}{418.58 \text{ (g } Ag_3PO_4/\text{mol)}} \times \frac{1}{1} = 0.41612 \text{ g } K_2HPO_4/\text{g } Ag_3PO_4$$

$$\text{g } Bi_2S_3/\text{g } BaSO_4 = \frac{\text{fw } Bi_2S_3 \text{ (g/mol)}}{\text{fw } BaSO_4 \text{ (g/mol)}} \times \frac{1}{3} \text{ (mol } Bi_2S_3/\text{mol } BaSO_4)$$

$$GF = \frac{514.15 \text{ (g } Bi_2S_3/\text{mol)}}{233.40 \text{ (g } BaSO_4/\text{mol)}} \times \frac{1}{3} = 0.73429 \text{ g } Bi_2S_3/\text{g } BaSO_4$$

$$\boxed{\begin{aligned} \text{Weight of substance sought (g)} &= \text{weight of precipitate (g)} \\ &\quad \times \frac{\text{fw substance sought (g/mol)}}{\text{fw precipitate (g/mol)}} \\ &\quad \times \frac{a}{b} \text{ (mol substance sought/mol precipitate)} \\ &= \text{weight of precipitate (g)} \\ &\quad \times \text{GF (g sought/g precipitate)} \end{aligned}}$$

$$\boxed{\% \text{ A} = \frac{g_A}{g_{\text{sample}}} \times 100\%}$$

$$\boxed{\% \text{ sought} = \frac{\text{weight of precipitate (g)} \times \text{GF (g sought/g precipitate)}}{\text{weight of sample (g)}} \times 100\%}$$

Example 2

Orthophosphate (PO_4^{3-}) is determined by weighing as ammonium phosphomolybdate, $(NH_4)PO_4 \cdot 12MoO_3$. Calculate the percent P in the sample and the percent P_2O_5 if 1.1682 g precipitate (ppt) were obtained from a 0.2711-g sample. Perform the % P calculation using the gravimetric factor and just using dimensional analysis.

$$\% \text{ P} = \frac{1.1682 \text{ g ppt} \times \dfrac{\text{P}}{(NH_4)_3PO_4 \cdot 12MoO_3} \text{(g P/g ppt)}}{0.2711 \text{ g sample}} \times 100\%$$

$$= \frac{1.1682 \text{ g} \times (30.97/1876.5)}{0.2711 \text{ g}} \times 100\% = 7.111\%$$

$$\% \text{ P}_2\text{O}_5 = \frac{1.1682 \text{ g ppt} \times \dfrac{P_2O_5}{2(NH_4)_3PO_4 \cdot 12MoO_3} \text{(g } P_2O_5\text{/g ppt)}}{0.2711 \text{ g sample}} \times 100\%$$

$$= \frac{1.1682 \text{ g} \times [141.95/(2 \times 1876.5)]}{0.2711 \text{ g}} \times 100\%$$

$$= 16.30\%$$

Let's do the same calculation using dimensional analysis for the % P setup.

$$\% \text{ P} = \frac{1.982 \text{ g } \cancel{(NH_4)_2PO_4 \cdot 12MoO_3} \times (30.97/1867.5)\text{g P/g } \cancel{(NH_4)_2PO_4 \cdot 12MoO_3}}{0.2771 \text{ g sample}}$$

$$\times 100\%$$

$$= (7.111 \text{ g P/g sample}) \times 100\% = 7.111\% \text{ P}$$

Note that the $(NH_4)_2PO_4 \cdot 12MoO_3$ species cancel one another (dimensional analysis), leaving only g P in the numerator.

Example 3

An ore is analyzed for the manganese content by converting the manganese to Mn_3O_4 and weighing it. If a 1.52-g sample yields Mn_3O_4 weighing 0.126 g, what would be the percent Mn_2O_3 in the sample? The percent Mn?

Solution

$$\% \text{ Mn}_2\text{O}_3 = \frac{0.126 \text{ g Mn}_3\text{O}_4 \times \dfrac{3\text{Mn}_2\text{O}_3}{2\text{Mn}_3\text{O}_4}(\text{g Mn}_2\text{O}_3/\text{g Mn}_3\text{O}_4)}{1.52 \text{ g sample}} \times 100\%$$

$$= \frac{0.126 \text{ g} \times [3(157.9)/2(228.8)]}{1.52 \text{ g}} \times 100\% = 8.58\%$$

$$\% \text{ Mn} = \frac{0.126 \text{ g Mn}_3\text{O}_4 \times \dfrac{3\text{Mn}}{\text{Mn}_3\text{O}_4}(\text{g Mn}/\text{g Mn}_3\text{O}_4)}{1.52 \text{ g sample}} \times 100\%$$

$$= \frac{0.126 \text{ g} \times [3(54.94)/228.8]}{1.52 \text{ g}} \times 100\% = 5.97\%$$

Example 4

What weight of pyrite ore (impure FeS_2) must be taken for analysis so that the $BaSO_4$ precipitate weight obtained will be equal to one-half that of the percent S in the sample?

Solution

If we have A% of S, then we will obtain $\frac{1}{2}$ A g of $BaSO_4$. Therefore,

$$A\%\ S = \frac{\frac{1}{2}A(\text{g } BaSO_4) \times \frac{S}{BaSO_4}(\text{g S/g } BaSO_4)}{\text{g sample}} \times 100\%$$

or

$$1\%\ S = \frac{\frac{1}{2} \times \frac{32.064}{233.40}}{\text{g sample}} \times 100\%$$

$$\text{g sample} = 6.869 \text{ g}$$

Example 5

A mixture containing only $FeCl_3$ and $AlCl_3$ weighs 5.95 g. The chlorides are converted to the hydrous oxides and ignited to Fe_2O_3 and Al_2O_3. The oxide mixture weighs 2.62 g. Calculate the percent Fe and Al in the original mixture.

Solution

There are two unknowns, so two simultaneous equations must be set up and solved. Let $x =$ g Fe and $y =$ g Al. Then, for the first equation,

$$\text{g FeCl}_3 + \text{g AlCl}_3 = 5.95 \text{ g} \tag{1}$$

$$x\left(\frac{\text{FeCl}_3}{\text{Fe}}\right) + y\left(\frac{\text{AlCl}_3}{\text{Al}}\right) = 5.95 \text{ g} \tag{2}$$

$$x\left(\frac{162.21}{55.85}\right) + y\left(\frac{133.34}{26.98}\right) = 5.95 \text{ g} \tag{3}$$

$$2.90x + 4.94y = 5.95 \text{ g} \tag{4}$$

$$\text{g Fe}_2\text{O}_3 + \text{g Al}_2\text{O}_3 = 2.62 \text{ g} \tag{5}$$

$$x\left(\frac{\text{Fe}_2\text{O}_3}{2\text{Fe}}\right) + y\left(\frac{\text{Al}_2\text{O}_3}{2\text{Al}}\right) = 2.62 \text{ g} \tag{6}$$

$$x\left(\frac{159.69}{2 \times 55.85}\right) + y\left(\frac{101.96}{2 \times 26.98}\right) = 2.62 \text{ g} \tag{7}$$

$$1.43x + 1.89y = 2.62 \text{ g} \tag{8}$$

Solving (4) and (8) simultaneously for x and y:

$$x = 1.07 \text{ g}$$

$$y = 0.58 \text{ g}$$

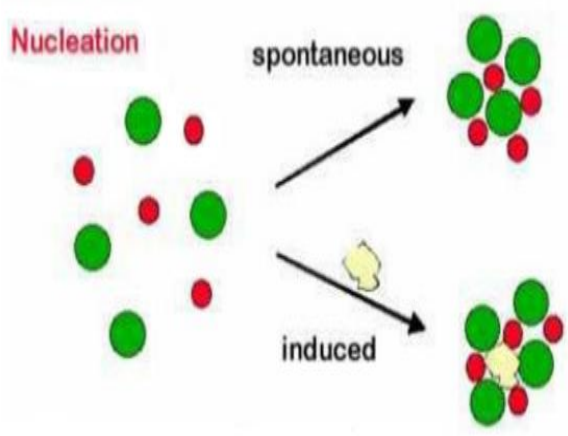
$$\%\ \text{Fe} = \frac{1.07 \text{ g}}{5.95 \text{ g}} \times 100\% = 18.0\%$$

$$\%\ \text{Al} = \frac{0.58 \text{ g}}{5.95 \text{ g}} \times 100\% = 9.8\%$$

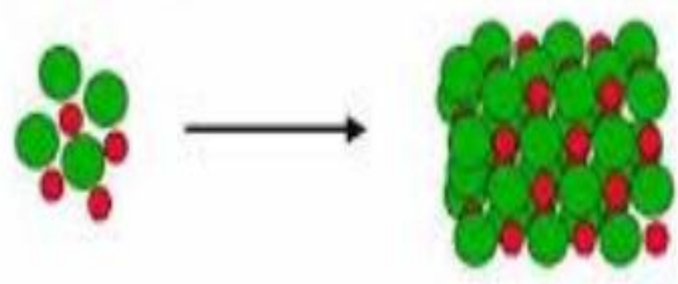
Mechanism of Precipitation (how particles are formed?)

- Supersaturated solution formed ... *The ionic product of concentrations ≥ the solubility product.*
- Nucleation ...*a few atoms, ions or molecules join together to give a stable solid called nuclei.*
- Particle growth ...*the process where more ions are added to the nucleus to form colloids with sizes in the range of 1-100nm in diameter.*

When a solution of a precipitating agent is added to a test solution to form a precipitate, such as in the addition of $AgNO_3$ to a chloride solution to precipitate AgCl, the actual precipitation occurs in a series of steps. The precipitation process involves heterogeneous equilibria and, as such, is not instantaneous.
First, **supersaturation occurs**, that is, the solution phase contains more of the dissolved salt than it can carry at equilibrium. This is a metastable condition, and the driving force will be for the system to approach equilibrium (saturation). This is started by **nucleation**.



For nucleation to occur, a minimum number of particles must come together to produce microscopic nuclei of the solid phase. The higher the degree of supersaturation, the greater the rate of nucleation. The formation of a greater number of nuclei per unit time will ultimately produce more total crystals of smaller size. The total crystal surface area will be larger, and there will be more danger that impurities will be adsorbed. Although nucleation should theoretically occur spontaneously, it is usually induced, for example, on dust particles, scratches on the vessel surface, or added seed crystals of the precipitate (not in quantitative analysis).



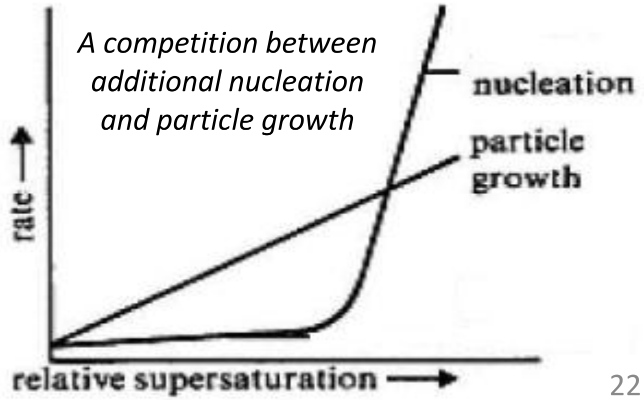
Following nucleation, the initial nucleus will grow by depositing other precipitate particles to form a crystal of a certain geometric shape. Again, the greater the supersaturation, the more rapid the crystal growth rate. An increased growth rate increases the chances of imperfections in the crystal and trapping of impurities.

How particle size is controlled ?

1. Precipitate from **dilute solution**. This keeps Q low.
2. Add dilute precipitating reagents slowly, with effective **stirring**. This also keeps Q low. Stirring prevents local excesses of the reagent.
3. Precipitate from **hot solution**. This increases S. The solubility should not be too great or the precipitation will not be quantitative (with less than 1 part per thousand remaining). The bulk of the precipitation may be performed in the hot solution, and then the solution may be coold to make the precipitation quantitative.
4. Precipitate at as **low a pH** as is possible to maintain quantitative precipitation. Many precipitates are more soluble in acid medium, and this slows the rate of precipitation. They are more soluble because the anion of the precipitate (which comes from a weak acid) combines with protons in the solution.

VonWeimarn discovered that the particle size of precipitates is inversely proportional to the relative supersaturation of the solution during the precipitation process:
Where:
Q *is the concentration of the mixed reagents before precipitation occurs, S is the* solubility of the precipitate at equilibrium,
Q – S *is the degree of supersaturation.*
The ratio, ***(Q – S)/S****, relative supersaturation, is also called the VonWeimarn ratio.*

When a solution is supersaturated, it is in a state of metastable equilibrium, and this favors rapid nucleation to form a large number of small particles. That is, Obviously, then, we want to keep *Q low and S high* during precipitation


A competition between additional nucleation and particle growth

- Solubility of the precipitate *... Increase solubility by precipitating from hot solution or adjusting the pH*

- Relative Supersaturated (RSS) *...as small as possible*

RSS = (Q-S)/S (Von Weimarn ... Particles size inversely RSS)

Q: conc. of the solute
S: equilibrium solubility
(Q-S) is a measure of the degree of supersaturation

- Solutions *...as diluted as possible*

- Addition of precipitating agent *...as slow as possible*

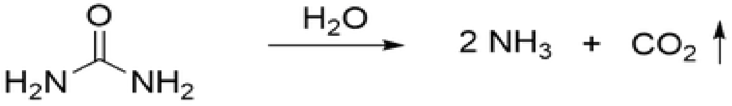
Large particle size (**crystalline solid**) ⇨ S ↑ + RSS ↓ + Q ↓ (dil. & slow)

Small particle size (**colloid**) ⇨ S ↓ + RSS ↑+ Q ↑ (conc. & fast)

Precipitation from homogeneous solution

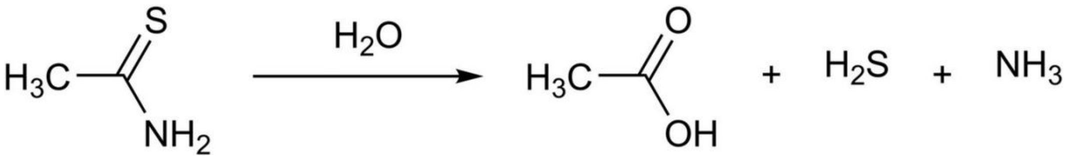
Homogeneous precipitation is a process in which a precipitate is formed by slow generation of an precipitating reagent homogeneously throughout a solution. Solids formed by homogeneous precipitation are generally purer and larger in size.

Hydrolysis of urea



Urea

Hydrolysis of thioacetamide



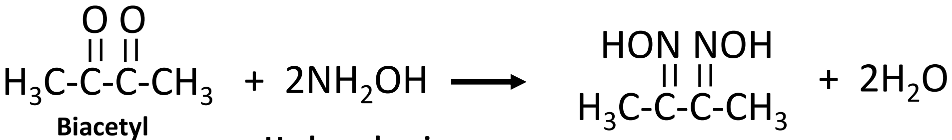
Thioacetamide

Acetic acid

Hydrogen sulfide

Ammonia

Formation of DMG



$$H_3C\text{-}\overset{\overset{O}{\|}}{C}\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_3 + 2NH_2OH \longrightarrow H_3C\text{-}\overset{\overset{HON}{\|}}{C}\text{-}\overset{\overset{NOH}{\|}}{C}\text{-}CH_3 + 2H_2O$$

Biacetyl (2,3-diketobutane)

Hydroxylamine

Dimethylglyoxime

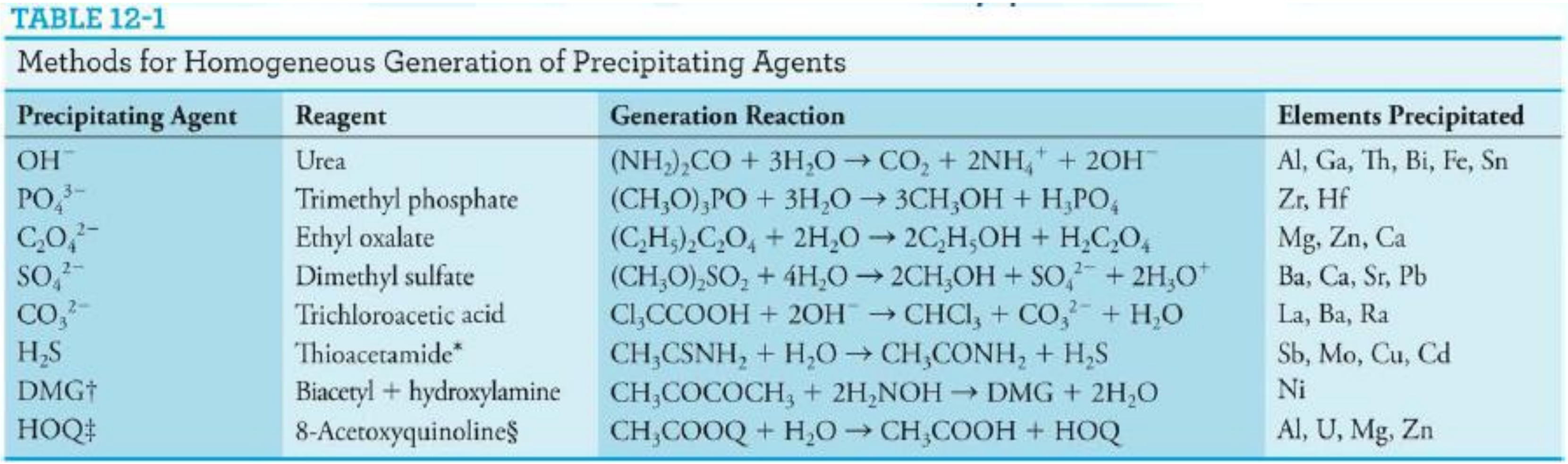


TABLE 12-1

Methods for Homogeneous Generation of Precipitating Agents

Precipitating Agent	Reagent	Generation Reaction	Elements Precipitated
OH^-	Urea	$(NH_2)_2CO + 3H_2O \rightarrow CO_2 + 2NH_4^+ + 2OH^-$	Al, Ga, Th, Bi, Fe, Sn
PO_4^{3-}	Trimethyl phosphate	$(CH_3O)_3PO + 3H_2O \rightarrow 3CH_3OH + H_3PO_4$	Zr, Hf
$C_2O_4^{2-}$	Ethyl oxalate	$(C_2H_5)_2C_2O_4 + 2H_2O \rightarrow 2C_2H_5OH + H_2C_2O_4$	Mg, Zn, Ca
SO_4^{2-}	Dimethyl sulfate	$(CH_3O)_2SO_2 + 4H_2O \rightarrow 2CH_3OH + SO_4^{2-} + 2H_3O^+$	Ba, Ca, Sr, Pb
CO_3^{2-}	Trichloroacetic acid	$Cl_3CCOOH + 2OH^- \rightarrow CHCl_3 + CO_3^{2-} + H_2O$	La, Ba, Ra
H_2S	Thioacetamide*	$CH_3CSNH_2 + H_2O \rightarrow CH_3CONH_2 + H_2S$	Sb, Mo, Cu, Cd
DMG†	Biacetyl + hydroxylamine	$CH_3COCOCH_3 + 2H_2NOH \rightarrow DMG + 2H_2O$	Ni
HOQ‡	8-Acetoxyquinoline§	$CH_3COOQ + H_2O \rightarrow CH_3COOH + HOQ$	Al, U, Mg, Zn

➧ Types of precipitates

There are two types of precipitates, according to the size of the formed particles

1.colloidal (1- 100 μm diameter) or amorphous.
2.crystalline (> 100 μm diameter) precipitates

Colloidal particles are very small (1 to 100 nm) and have a very large surface to-mass ratio, which promotes surface adsorption. They are formed by virtue of the precipitation mechanism. As a precipitate forms, the ions are arranged in a fixed pattern.

Primary adsorption layer:

- It will have a positive or negative charge, depending on the excess reagent.
- If the excess reagent is the cation of the solute, then the overall charge will be positive. For example, excess silver nitrate added to sodium chloride. The primary adsorption layer will be predominately silver ions.

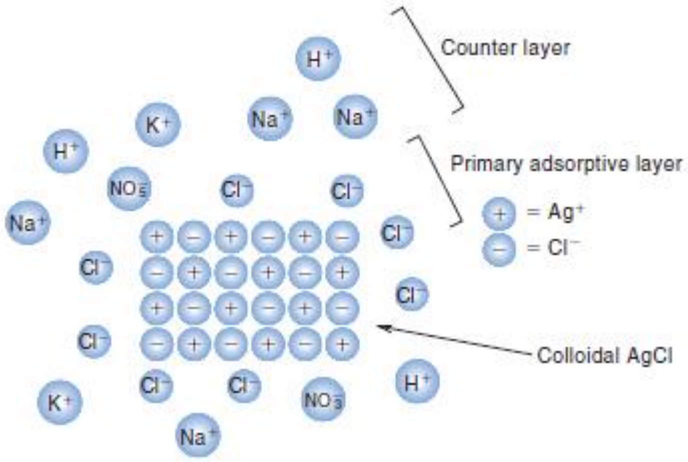
Counter-ion layer:

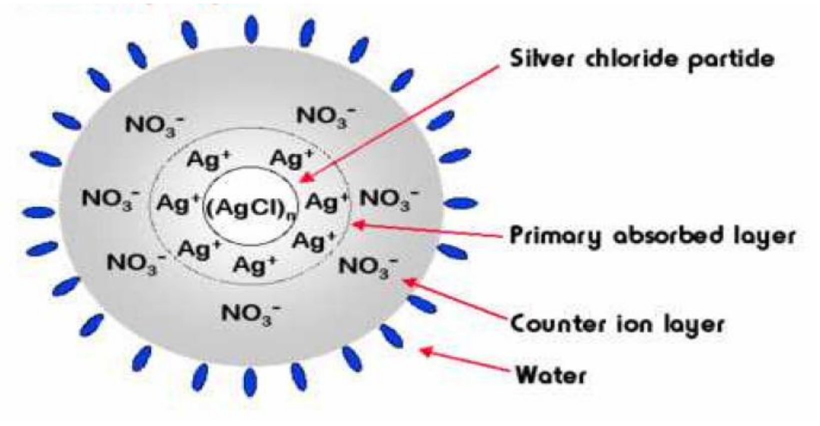
- Because of the overall charge of the adsorption layer, a second layer called the counter-ion layer forms.
- This is also composed of the excess reagent along with other ions in solution.
- It will impart the opposite overall charge to the entire colloidal particle.
- So if the adsorption layer is positive, the counter-ion layer will be negative.

Electrical double layer:

Together, the two layers comprise what is called an electrical double layer surrounding a solid core.

In AgCl, for example, there will be alternating Ag^+ and Cl^- ions on the surface (see figures below). While there are localized + and − charges on the surface, the net surface charge is zero. However, the surface does tend to adsorb the ion of the precipitate particle that is in excess in the solution, for example, Ag^+ if precipitating Cl^- with an excess of Ag^+; this imparts a charge. (With crystalline precipitates, the degree of such adsorption will generally be small in comparison with particles that tend to form colloids.) The adsorption creates a **primary layer** that is strongly adsorbed and is an integral part of the crystal. It will attract ions of the opposite charge in a **counter layer or secondary layer** so the particle will have an overall neutral charge. There will be solvent molecules interspersed between the layers. Normally, the counter layer completely neutralizes the primary layer and is close to it, so the particles will collect together to form larger particles; that is, they will **coagulate**. However, if the secondary layer is loosely bound, the primary surface charge will tend to repel like particles, maintaining a colloidal state.





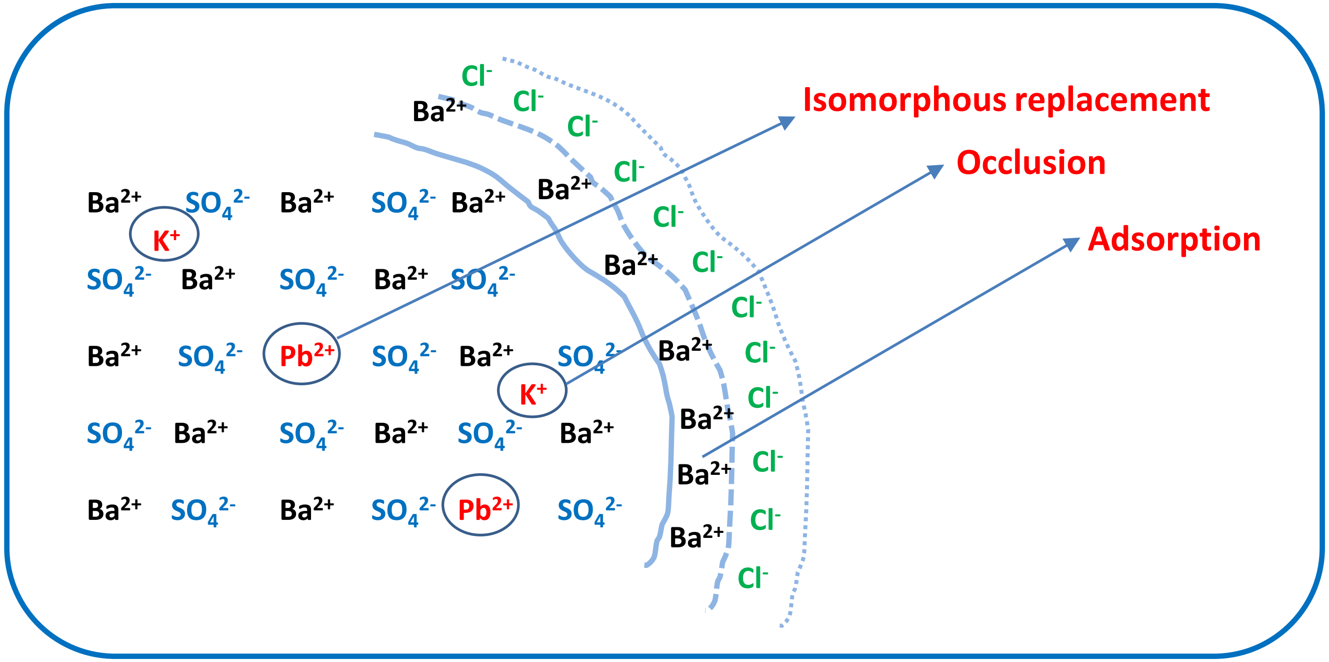
Crystalline precipitates are generally more easily filtered and purified than are coagulated colloids. In addition, the size of individual crystalline particles, and thus their filterability, can be controlled to some extent.

Impurities in Precipitates

Precipitates tend to carry down from the solution other constituents that are normally soluble, causing the precipitate to become contaminated. This process is called **coprecipitation.** The process may be equilibrium based or kinetically controlled.
There are a number of ways in which a foreign material may be coprecipitated.

1. Co-precipitation

- Inclusion ... *trap a pocket of solution*
- Occlusion ...*impurities trapped inside the growing crystal*
- Surface adsorption ...*on the surface*
- Isomorphous replacement (mixed crystal) ...*occupy crystal lattice*



An example of Co-precipitation of $PbSO_4$ in $BaSO_4$

Occlusion

In the process of occlusion, material that is not part of the crystal structure is trapped within a crystal. For example, water may be trapped in pockets when $AgNO_3$ crystals are formed, and this can be removed to a degree by dissolution and recrystallization. If such mechanical trapping occurs during a precipitation process, the water will contain dissolved impurities.

Inclusion

Inclusion occurs when ions, generally of similar size and charge, are trapped within the crystal lattice (isomorphous inclusion, as with K_+ in NH_4MgPO_4 precipitation). These are not equilibrium processes.

Occluded or included impurities are difficult to remove. Digestion may help some but is not completely effective. The impurities cannot be removed by washing. Purification by dissolving and re-precipitating is helpful.

Surface adsorption

The surface of the precipitate will have a primary adsorbed layer of the lattice ions in excess. This results in surface adsorption, the most common form of contamination. For example, after barium sulfate is completely precipitated, the lattice ion in excess will be barium, and this will form the primary layer. The counter ion will be a foreign anion, for example, nitrate two for each barium. The net effect then is an adsorbed layer of barium nitrate, an equilibrium-based process. These adsorbed layers can often be removed by washing, or they can be replaced by ions that are readily volatilized. Gelatinous precipitates are especially troublesome, though. Digestion reduces the surface area and, therefore, the adsorbed amount.

Isomorphous replacement

Two compounds are said to be isomorphous if they have the same type of formula and crystallize in similar geometric forms. When their lattice dimensions are about the same, one ion can replace another in a crystal, resulting in a mixed crystal. This process is called isomorphous replacement or isomorphous substitution. For example, in the precipitation of Mg^{2+} as magnesium ammonium phosphate, K^+ has nearly the same ionic size as NH_4^+ and can replace it to form magnesium potassium phosphate. Isomorphous replacement, when it occurs, causes major interference, and little can be done about it. Precipitates in which it occurs are seldom used analytically.

2. Post-precipitation

Sometimes, when the precipitate is allowed to stand in contact with the mother liquor, a second substance will slowly form a precipitate with the precipitating reagent. This is called **postprecipitation.** For example, when calcium oxalate is precipitated in the presence of magnesium ions, magnesium oxalate does not immediately precipitate because it tends to form supersaturated solutions. But it will precipitate if the solution is allowed to stand too long before being filtered. Similarly, copper sulfide will precipitate in acid solution in the presence of zinc ions without zinc sulfide being precipitated, but eventually zinc sulfide will precipitate.

Solubility and solubility product

- **Solubility**

... is the **maximum amount** of solute that can be dissolved in a solvent at a given temperature at a given volume at equilibrium.

- **Equilibrium**

... when the concentrations of products and reactants have become **equal** after the reaction has taken place

- **Concentration**

... is the **amount** of solute that can be dissolved in a solvent at a given volume

- **Solubility product constant(Ksp)**

... is the product of the **equilibrium** concentrations of the ions in a **saturated** solution of a salt. Each concentration is raised to the power of their stoichiometric coefficients in the balanced equation.

$$PbCl_{2\,(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2\,Cl^{-}_{(aq)}$$

$$Ksp = [Pb^{2+}]\,[Cl^{-}]^{2}$$

Ksp is considered unitless because it is derived from the ratio of activities or concentrations that cancel out, reflecting the equilibrium state of the system without specific units.

⇨ **Shortcut method of Ksp expression (without ion common)**

$AB_{(s)} \rightarrow Ksp = x^1 * x^1 = x^2$ **(ratio 1:1)**

$AB_{2\,(s)} \rightarrow Ksp = x^1 * (2x)^2 = 4x^3$ **(ratio 1:2)**

$AB_{3\,(s)} \rightarrow Ksp = x^1 * (3x)^3 = 27x^4$ **(ratio 1:3)**

$A_3B_{2\,(s)} \rightarrow Ksp = (3x)^3 * (2x)^2 = 108x^5$ **(ratio 3:2)**

Calculating molar solubility from Ksp

Example 6

Calculate the molar solubility of CaF_2(s) in its saturated solution, given that ksp $_{CaF2}$ = $3.2*10^{-11}$

$$\mathrm{CaF_2} \leftrightarrow \mathrm{Ca^{2+}} + \mathrm{2F^-}$$

$$K_{sp} = [Ca^{2+}]\,[F^-]^2$$

$$3.2 * 10^{-11} = [x][2x]^2 = 4x^3$$

$$x = \sqrt[3]{\frac{3.2 * 10^{-11}}{4}} = 0.0002\,\frac{mol}{L}$$

Calculating Ksp from molar solubility

Example 7

The solubility of Ag_2S in water is 8x10 $^{-15}$g/L, calculate the solubility product (Ksp), given that the M.wt of Ag_2S is 248 gm/mole

$$\frac{\mathrm{g}}{\mathrm{L}} = \mathrm{M}\,\frac{\cancel{\mathrm{mol}}}{\mathrm{L}} * \mathrm{M.wt}\,\frac{\mathrm{g}}{\cancel{\mathrm{mol}}}$$

$$\mathrm{M} = \frac{\mathrm{g/L}}{\mathrm{M.wt}} = \frac{8 * 10^{-15}\ \mathrm{g/L}}{248\ \mathrm{g/mol}} = 3.226 * 10^{-17}\ \mathrm{mol/L}$$

$$\mathrm{Ag_2S} \leftrightarrow \mathrm{2Ag^+} + \mathrm{S^{2-}}$$

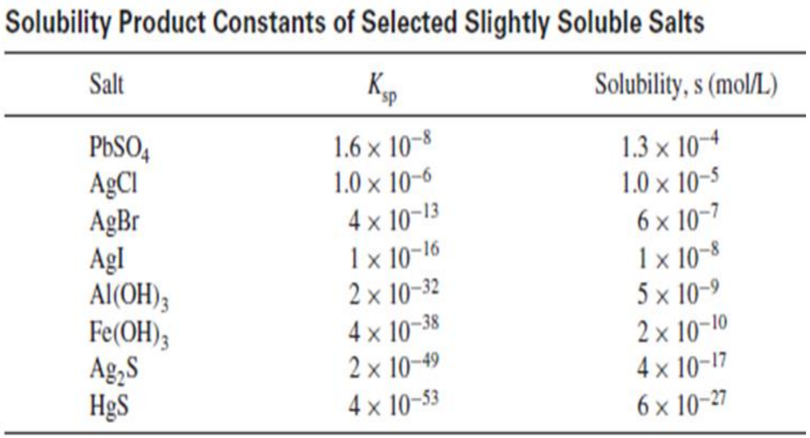
$$K_{sp} = [Ag^+]^2[S^{2-}]$$

$$K_{sp} = [2x]^2\,[x] = 4x^3$$

$$K_{sp} = 4(3.226 * 10^{-17})^3 = 1.34 * 10^{-49}$$

Solubility depends on the stoichiometry

The molar solubility is not necessarily directly proportional to the Ksp value since it depends on the stoichiometry of the salt.
The K_{sp} of AgI is 5 × 10^{15} larger than that of $Al(OH)_3$, but its molar solubility is only twice that of $Al(OH)_3$. That is, a 1:1 salt has a lower solubility than a non-symmetric salt for a given Ksp.



Solubility Product Constants of Selected Slightly Soluble Salts

Salt	K_{sp}	Solubility, s (mol/L)
$PbSO_4$	1.6×10^{-8}	1.3×10^{-4}
AgCl	1.0×10^{-6}	1.0×10^{-5}
AgBr	4×10^{-13}	6×10^{-7}
AgI	1×10^{-16}	1×10^{-8}
$Al(OH)_3$	2×10^{-32}	5×10^{-9}
$Fe(OH)_3$	4×10^{-38}	2×10^{-10}
Ag_2S	2×10^{-49}	4×10^{-17}
HgS	4×10^{-53}	6×10^{-27}

Example 8
Calculate the molar solubility of $PbSO_4$ and compare it with that of PbI_2.

$$\begin{aligned} PbSO_4 &\rightleftharpoons Pb^{2+} + SO_4{}^{2-} \\ [Pb^{2+}][SO_4{}^{2-}] &= 1.6 \times 10^{-8} \\ (s)(s) &= 1.6 \times 10^{-8} \\ s &= 1.3 \times 10^{-4}\ M \end{aligned}$$

Although the Ksp of PbI_2 (7.1 × 10^{-9}) is smaller than that of $PbSO_4$ (1.6 × 10^{-8}), the solubility of PbI^2 is greater, due to the non-symmetrical nature of the precipitate.

For electrolytes of the same valence type, the order of solubility will be the same as the order of the corresponding solubility products. But when we compare salts of different valence type, the order may be different. Compound AB will have a smaller molar solubility than compound AC_2 when both have identical Ksp values.
A smaller Ksp with a non-symmetrical precipitate does not necessarily mean a smaller solubility compared to a symmetrical one.

Predicting precipitation [*Ionic product (Q) Vs solubility product (Ksp)*]

The *ionic product (Q)* of a salt is the product of the concentrations of the ions in solution raised to the same powers as in the solubility product expression. It is analogous to the reaction quotient (*Q*) for gaseous equilibria. Whereas K_{sp} describes equilibrium concentrations, the ion product describes concentrations that are not necessarily equilibrium concentrations. An ion product can in principle have *any* positive value, depending on the concentrations of the ions involved. Only in the special case when its value is identical with K_s does it become the solubility product. A solution in which this is the case is said to be *saturated* .

Thus when $[Ag^+]^2\ [CrO_2{}^{-4}]=2.76\times10^{-12}$

at the temperature and pressure at which this value *Ksp* of applies, we say that the "solution is saturated in silver chromate".

The Relationship between Q and K_{sp}. If Q is less than K_{sp}, the solution is unsaturated and more solid will dissolve until the system reaches equilibrium ($Q = K_{sp}$). If Q is greater than K_{sp}, the solution is supersaturated and solid will precipitate until $Q = K_{sp}$. If $Q = K_{sp}$, the rate of dissolution is equal to the rate of precipitation; the solution is saturated, and no net change in the amount of dissolved solid will occur.

The process of calculating the value of the ion product and comparing it with the magnitude of the solubility product is a straightforward way to determine whether a solution is unsaturated, saturated, or supersaturated. More important, the ion product tells chemists whether a precipitate will form when solutions of two soluble salts are mixed.

$$BaSO_{4\,(s)} \underset{\text{Precipitation}}{\overset{\text{Dissolution}}{\rightleftharpoons}} Ba^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$$

$$Ksp = [Ba^{2+}]_{eq}\,[SO_4{}^{2-}]_{eq}$$

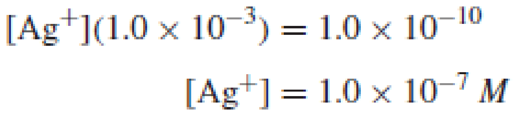
$$Q = [Ba^{2+}]_0\,[SO_4{}^{2-}]_0$$

Ksp at equilibrium, Q at anytime

Q < Ksp	$\longrightarrow$	*Dissolution*	... the solution is *unsaturated* **(C < S)**
Q = Ksp	$\rightleftharpoons$	*Equilibrium*	... the solution is *saturated* **(C = S)**
Q > Ksp	$\longleftarrow$	*Precipitation*	... the solution is *supersaturated* **(C > S)**

Example 9

What must be the concentration of added Ag^+ to just start precipitation of AgCl in a 1.0×10^{-3} M solution of NaCl?



$$[Ag^+](1.0 \times 10^{-3}) = 1.0 \times 10^{-10}$$

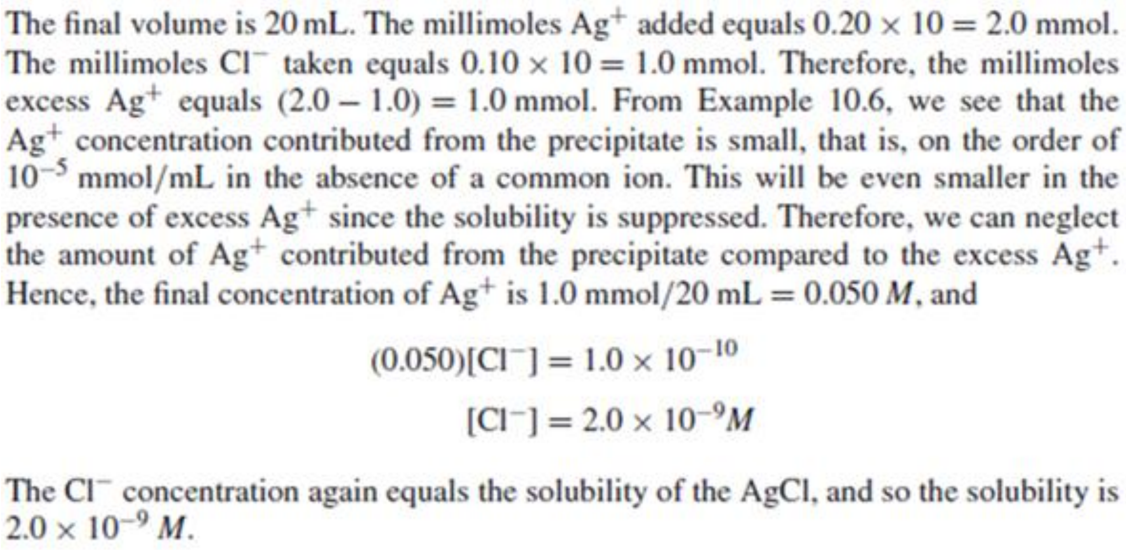
$$[Ag^+] = 1.0 \times 10^{-7}\ M$$

The concentration of Ag^+ must, therefore, just exceed 10^{-7} M to begin precipitation.

In reality supersaturation is needed before precipitation begins. In practice it is unlikely that precipitation will begin when Ag^+ just exceeds 10^{-7} M

Example 10

Ten milliliters of 0.20M $AgNO_3$ is added to 10 mL of 0.10M NaCl. Calculate the concentration of Cl^- remaining in solution at equilibrium, and the solubility of the AgCl.



The final volume is 20 mL. The millimoles Ag^+ added equals $0.20 \times 10 = 2.0$ mmol. The millimoles Cl^- taken equals $0.10 \times 10 = 1.0$ mmol. Therefore, the millimoles excess Ag^+ equals $(2.0 - 1.0) = 1.0$ mmol. From Example 10.6, we see that the Ag^+ concentration contributed from the precipitate is small, that is, on the order of 10^{-5} mmol/mL in the absence of a common ion. This will be even smaller in the presence of excess Ag^+ since the solubility is suppressed. Therefore, we can neglect the amount of Ag^+ contributed from the precipitate compared to the excess Ag^+. Hence, the final concentration of Ag^+ is 1.0 mmol/20 mL = 0.050 *M*, and

$$(0.050)[Cl^-] = 1.0 \times 10^{-10}$$

$$[Cl^-] = 2.0 \times 10^{-9} M$$

The Cl^- concentration again equals the solubility of the AgCl, and so the solubility is 2.0×10^{-9} *M*.

Because the Ksp product always holds, precipitation will not take place unless the product of $[Ag^+]$ and $[Cl^-]$ exceeds the ksp. If the product is just equal to Ksp, all the Ag^+ and Cl^- remains in solution.

- ➢ The solubility product must be exceeded for precipitation to occur.

Factors effecting solubility

1. Effect of temperature on solubility

Temperature has a significant impact on the solubility of substances in solvents, and its effects can vary depending on the nature of the solute and solvent involved. Here are the key effects of temperature on solubility:

1. **Increased Solubility of Solids**: For most solid solutes, solubility tends to increase with an increase in temperature. This is because higher temperatures provide more kinetic energy to the molecules, allowing them to overcome intermolecular forces and dissolve more readily. For example, sugar dissolves more easily in hot water than in cold water.

2. **Decreased Solubility of Gases**: In contrast to solids, the solubility of gases in liquids generally decreases with an increase in temperature. As temperature rises, gas molecules gain kinetic energy and are more likely to escape from the liquid phase into the gas phase. This is why carbonated beverages lose their fizz more quickly when warmed.

3. **Endothermic vs. Exothermic Dissolution**: The effect of temperature on solubility can also depend on whether the dissolution process is endothermic (absorbs heat) or exothermic (releases heat):
- **Endothermic Dissolution**: If the dissolution process absorbs heat, increasing the temperature will increase solubility. An example is ammonium nitrate, which dissolves endothermically.
- **Exothermic Dissolution**: If the dissolution process releases heat, increasing the temperature may decrease solubility. An example is calcium sulfate, which dissolves exothermically.

4. **Equilibrium Considerations**: According to Le Chatelier's principle, if a system at equilibrium is subjected to a change in temperature, the equilibrium will shift to counteract that change. For endothermic dissolutions, increasing temperature shifts the equilibrium to favor more solute dissolving, while for exothermic dissolutions, it shifts to favor the formation of solid.

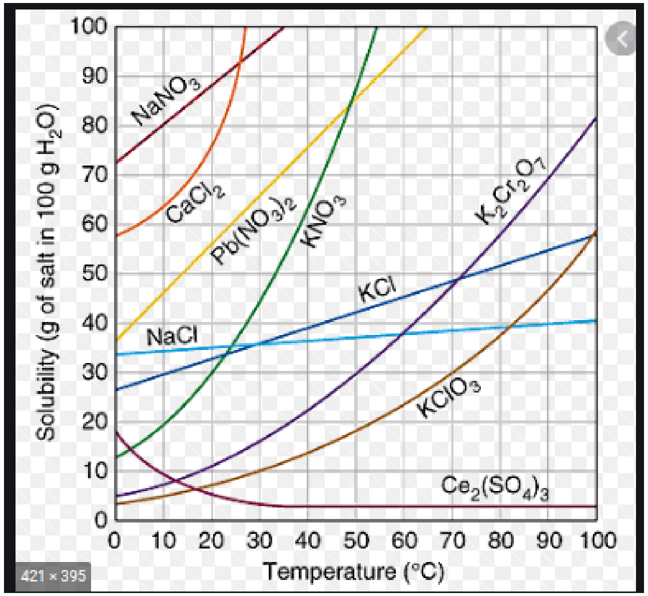
Example 11

Based on the diagram, answer the following questions:

⇨ Which substance is least soluble at 0°C? $KClO_3$

⇨Which substance is the most soluble at 0°C? $NaNO_3$

⇨What is the solubility of $K_2Cr_2O_7$ at 30°C? 15gm

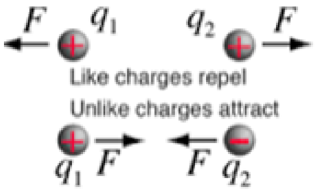


2. Effect of solute's nature on solubility

When ionic charge increases, the attraction between ions increases, and this leads to decrease the solubility.

Small ions are less soluble than large ions, as the bond between small ions is stronger that the bond between large ions with the same charge (see coulomb's law below).

The higher the charges on the ions, the stronger their electrostatic attraction for each other, and the harder it is for the solvent (i.e., water) to pull them apart. For example, if the calcium carbonate in marble were to dissolve too easily, think of how many buildings and statues would dissolve in the rain.

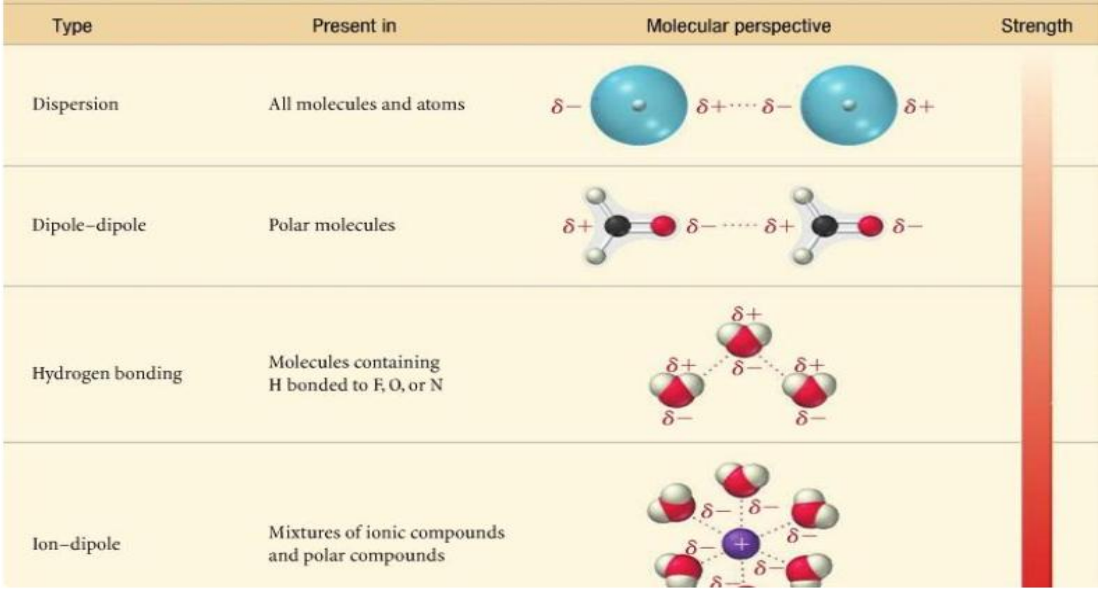


$$F = \frac{kq_1q_2}{r^2} = \frac{q_1q_2}{4\pi\varepsilon_0 r^2}$$

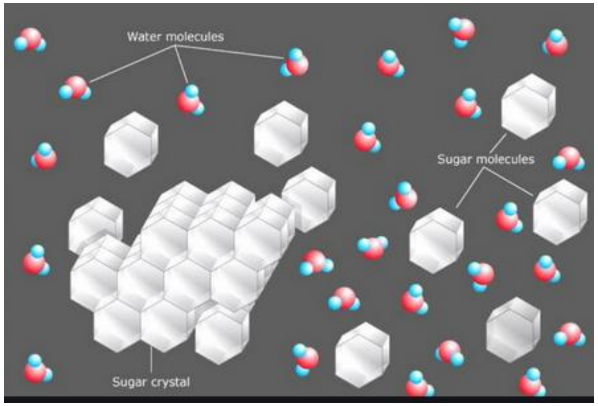
3. Effect of solvent’s nature on solubility

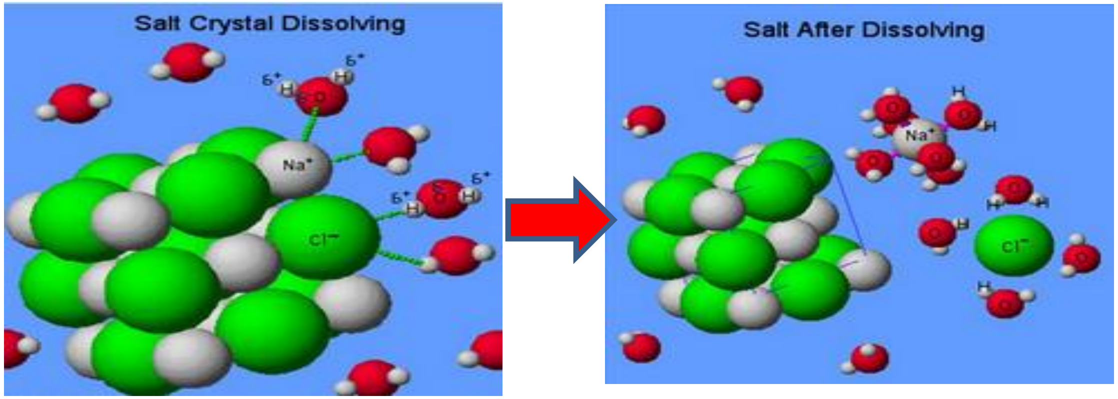
“Like dissolves like”

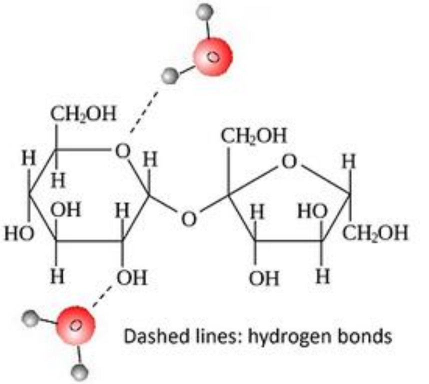
⇨Substances that exhibit similar types of intermolecular force dissolve in each other.
⇨Polar molecules and ionic compounds (like salt) will be more soluble in polar solvents (like water).
⇨Nonpolar molecules (like oil) will be more soluble in nonpolar solvents (like hexane).
If you introduce a solute into a solvent where it is not compatible, it may not dissolve effectively.



Type	Present in	Molecular perspective	Strength
Dispersion	All molecules and atoms	δ− δ+····δ− δ+	
Dipole–dipole	Polar molecules	δ+ δ−·····δ+ δ−	
Hydrogen bonding	Molecules containing H bonded to F, O, or N	δ+ δ− δ+ δ− δ+ δ−	
Ion–dipole	Mixtures of ionic compounds and polar compounds	δ− δ− δ− δ− δ− δ− +	







Sucrose dissolved in water

4. Effect of common ion on solubility

The common ion effect refers to the decrease in solubility of an ionic compound when a common ion is added to the solution. This happens due to Le Chatelier's principle, which states that a system at equilibrium will shift to counteract changes. For example, consider the solubility of silver chloride (AgCl) in water. Without any common ions, AgCl has a certain solubility. If you add sodium chloride (NaCl), which provides a common ion (Cl^-), the equilibrium of AgCl dissociation shifts left, resulting in less AgCl dissolving in the solution. So, if the solubility of AgCl is 0.001 mol/L in pure water, adding NaCl could reduce its solubility to 0.0005 mol/L, effectively demonstrating the common ion effect.

Example 12

The Ksp for $BaSO_4$ is $1*10^{-10}$, calculate the solubility of barium sulphate $BaSO_4$ in a D.W and 0.002M $BaCl_2$.

In D.W

$$BaSO_4 \leftrightarrow Ba^{2+} + SO_4^{2-}$$

$$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]$$

$$1 * 10^{-10} = [x][x] = x^2$$

$$x = [Ba^{2+}] = [SO_4^{2-}] = \sqrt[3]{1 * 10^{-10}} = 1 * 10^{-5}\,\frac{mol}{L}$$

Use the concentration of the common ion as the initial concentration

In 0.002M $BaCl_2$

$$BaSO_4 \leftrightarrow Ba^{2+} + SO_4^{2-}$$

I		0.002	0
C		+x	+x
E		0.002+x	x

you can only ignore X when it is being added or subtracted

$$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]$$

$$1 * 10^{-10} = [0.002 + \cancel{x}][x]$$

$$1 * 10^{-10} = 0.002x$$

$$x = \frac{1 * 10^{-10}}{0.002} = 5 * 10^{-8}\,mol/L$$

Note that the solubility of $BaSO_4$ has been decreased by 200 times due to the affect of common ion Ba^{2+}

5. Effect of pH on solubility

pH can influence solubility by means of:

Acid-Base Reactions: For solutes that are weak acids or weak bases, pH can significantly impact solubility.

Weak Acids: The solubility of weak acids typically increases in a more basic (high pH) environment. This is because the weak acid (HA) dissociates into its conjugate base (A^-) and hydrogen ions (H^+). In a basic solution, the concentration of H^+ is lower, so the equilibrium shifts to produce more of the conjugate base, which enhances the solubility of the weak acid.

Weak Bases: Conversely, the solubility of weak bases generally increases in a more acidic (low pH) environment. Weak bases (B) accept protons to form their conjugate acids (BH^+). In an acidic solution, there are more H^+ ions available, which shifts the equilibrium to form more of the conjugate acid and increases the solubility of the weak base.

Salt Solubility: For salts formed from a strong acid and a strong base (like NaCl), pH usually doesn't have a significant effect on solubility because both the acid and base completely dissociate in water. However, for salts formed from a weak acid and a strong base (or vice versa), pH can impact solubility:

Salts of Weak Acids: Salts formed from weak acids and strong bases (like sodium acetate) can become more soluble in acidic solutions because the added H^+ ions shift the equilibrium to dissolve more of the salt to counteract the increase in H^+.

Salts of Weak Bases: Salts formed from weak bases and strong acids (like ammonium chloride) can become more soluble in basic solutions because the added OH^- ions react with the H^+ ions, reducing the concentration of H^+ and shifting the equilibrium to dissolve more of the salt.

Overall :

Increased pH (more basic): Generally increases the solubility of weak acids and decreases the solubility of weak bases.

Decreased pH (more acidic): Generally increases the solubility of weak bases and decreases the solubility of weak acids.

pH effect on solubility (illustration)

- Occurs when one of the ions in the salt is an acid or base $Mg(OH)_2 \leftrightarrow Mg^{2+} + 2OH^-$
- Occurs when the salt is a conjugated base of a weak acid (BaC_2O_4, $CaCO_3$, ...)
- If the anion (A-) of the salt/precipitate is that of a weak acid, the salt/precipitate will dissolve more when in a strong acid (H+ ions will form HA with A^-)
- However, if the anion of the precipitate is that of a strong acid, adding a strong acid will have no effect on the precipitate dissolving more.

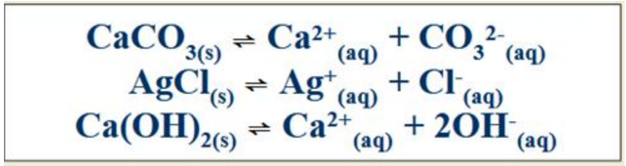
The stronger the acid, the weaker the conjugate base

A conjugate base of a strong acid (**weak base**) (e.g. Cl^-) ⇒ **no effect**

A conjugate base of a weak acid (**strong base**) (e.g. S^{2-}) ⇒ **S ↑**

e.g. How would the addition of HCl affect the solubility of $PbCl_2$? *No effect*

e.g. Predict the effect on solubility of adding a strong acid? *Increase ($CaCO_3$ & $Ca(OH)_2$), no effect on AgCl*



$$CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$$
$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$
$$Ca(OH)_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$$

Example 13

The Ksp value of $Mg(OH)_2$ is $8.9\text{x}10^{-12}$, what is the pH of a saturated solution of $Mg(OH)_2$?

$$Mg(OH)_2 \leftrightarrow Mg^{2+} + 2OH^-$$

	Mg^{2+}	$2OH^-$
I	0	0
C	+x	+2x
E	x	2x

$$K_{sp} = [Mg^{2+}]\,[OH^-]$$

$$8.9 * 10^{-12} = [x][2x]^2 = 4x^3$$

$$x = 1.305 * 10^{-4}\,\frac{mol}{L}$$

$$[OH] = 2x = 2 * 1.305 * 10^{-4} = 2.61 * 10^{-4}$$

$$pH = 14 - pOH = 14 - 3.583 = 10.4$$

Example 14

What pH is required to just precipitate iron (III) hydroxide from a 0.10M FeCl3 solution?

$$Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$$

$$[Fe^{3+}][OH^-]^3 = 4 \times 10^{-38}$$

$$(0.1)[OH^-]^3 = 4 \times 10^{-38}$$

$$[OH^-] = \sqrt[3]{\frac{4 \times 10^{-38}}{0.1}} = 7 \times 10^{-13}\ \text{M}$$

$$\text{pOH} = -\log 7 \times 10^{-13} = 12.2$$

$$\text{pH} = 14.0 - 12.2 = 1.8$$

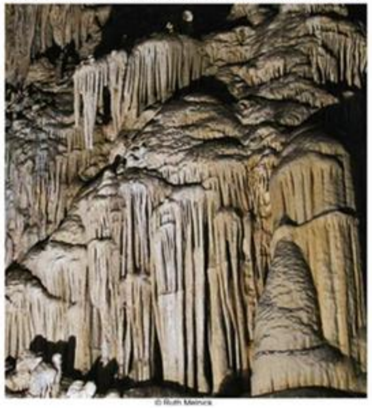
$Fe(OH)_3$ actually precipitates in acid solution due to the small $K_{sp.}$

Note: that precipitation generally will not begin exactly at the calculated pH, as supersaturation is needed.

Applications of pH effect on solubility

Limestone cave in Nerja, Málaga, Spain.

Limestone is mostly $CaCO_3$ ($K_{sp} = 3.3 \times 10^{-9}$).



© Ruth Melnick

Ground water rich in CO_2 trickles over $CaCO_3$, causing it to dissolve. This gradually carves out a cave.

Water containing HCO_3^- and Ca^{2+} ions drips from the cave ceiling. The air has a lower P_{CO2} than the soil, causing CO_2 to come out of solution. A shift in equilibrium results in the precipitation of $CaCO_3$ to form stalagmites and stalactites.

If limestone ($CaCO_3$) deposit is near surface…sinkhole

Jamal and Associates, Orlando, Fl

Figure 62. Spectacular, sudden collapse of the land surface commonly accompanies the formation of a sinkhole, such as this one that formed at Winter Park, just north of Orlando, Fla., in 1981.

6. Effect of complex-ion formation on solubility

A complex ion forms from a metal ion and a ligand because of a Lewis acid–base interaction. The positively charged metal ion acts as a Lewis acid, and the ligand, with one or more lone pairs of electrons, acts as a Lewis base.

When a solute forms a complex ion with a ligand, the solubility of the original solute can increase. This is often because the complex ion is more stable in solution than the individual ions.

Consider a metal salt like silver chloride (AgCl), which is only sparingly soluble in water. When chloride ions (Cl^-) are present, they can form complex ions with silver ions (Ag^+) in the presence of a complexing agent (such as ammonia, NH_3).

The complex ion formed $[Ag(NH_3)_2]^+$ can increase the solubility of AgCl in the solution because the formation of the complex ion effectively reduces the concentration of free Ag^+ ions, shifting the dissolution equilibrium of AgCl to dissolve more of the solid.

Practically NH_3 dissolves only AgCl which has relatively large K_{sp} value because the value of K_f for $Ag(NH_3)^{2+}$ is small.

The larger the K_{sp} value of the salt and the value of K_f of the metal complex the more the effect of the complexing agent on dissolving the salt and vice versa.

Example 15

Calculate the molar solubility of AgCl (Ksp = 1.8×10^{-10}) in pure water and in 3M NH_3?

$$AgCl_s \leftrightarrow Ag^+ + Cl^-$$

		Ag^+	Cl^-
I		0	0
C		+x	+x
E		x	x

$$K_{sp} = [Ag^+]\,[Cl^-]$$

$$1.8 * 10^{-10} = [x][x] = x^2$$

$$x = \sqrt[2]{1.8 * 10^{-10}} = 1.3 * 10^{-5}\,\frac{mol}{L}$$

$$\cancel{Ag}^+ + 2NH_3 \leftrightarrow Ag(NH_3)_2^+ \qquad K_f = 1.6x10^7$$

$$AgCl_s \leftrightarrow \cancel{Ag}^+ + Cl^- \qquad K_{sp} = 1.8x10^{-10}$$

$$AgCl_s + 2NH_{3\,(aq)} \leftrightarrow Ag(NH_3)^+_{2\,(aq)} + Cl^-_{(aq)} \qquad K = K_{sp} * K_f = 2.9x10^{-3}$$

	NH_3	$Ag(NH_3)_2^+$	Cl^-
I	3.0	0	0
C	-2x	+x	+x
E	3.0-2x	x	x

$$k = \frac{[Ag(NH_3)_2^+]^1[Cl^-]^1}{[NH_3]^2}$$

$$2.9x10^{-3} = \frac{[x]^1[x]^1}{[3.0 - 2x]^2}$$

$$x = 0.14\ M$$

Note that the solubility of AgCl has been increased due to the affect of complex-ion formation

The NH_3 ligand remove Ag^+ and shifts the equilibrium to the right, increasing the solubility of AgCl

7. Effect of ionic strength on solubility

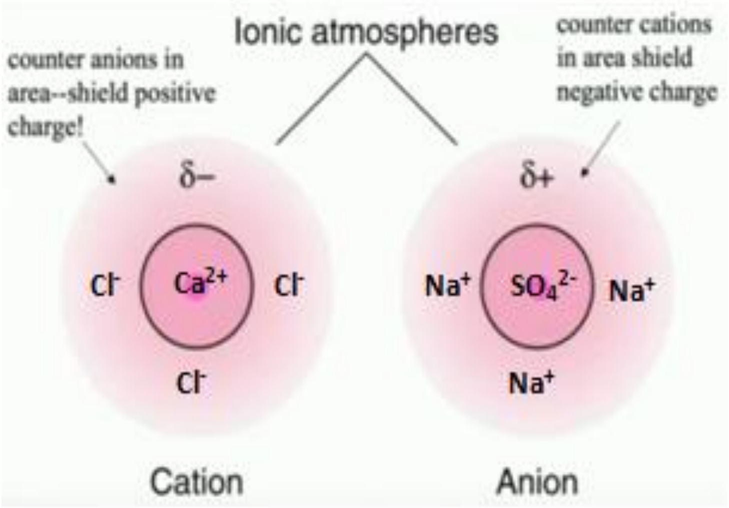
Ionic strength refers to the concentration of ions in a solution and significantly affects the solubility of ionic compounds. As ionic strength increases, solubility often increases due to reduced electrostatic interactions between ions. This phenomenon occurs because higher ionic strength leads to more shielding of charged ions, effectively reducing the force of attraction between oppositely charged ions in a solid.
For example, consider calcium sulfate ($CaSO_4$). In a solution with low ionic strength, the solubility might be around 0.2 g/L. However, if a salt like sodium chloride (NaCl) is added to the solution, increasing the ionic strength, the solubility of calcium sulfate could rise to 0.5 g/L or more.

Ionic strength (μ)
- Addition of salt to solution increases ionic strength
- Added salt is inert ➔ does not interact or react with other ions

In general, *increasing* ionic strength *increases* salt solubility

The *greater* the ionic strength of a solution, the *higher* the charge in the ionic atmospheres

Ionic strength: measure of the total concentration of ions in solution
Sum extends over *all* ions in solution



More ions added, more ions can be present in ionic atmospheres

$$\mu = \frac{1}{2}\left(c_1 z_1^2 + c_2 z_2^2 + \ldots\right) = \frac{1}{2}\sum_i c_i z_i^2$$

Where: C_i is the concentration of the ith species and z_i is its charge

Example 16
A solution contains 0.100 M sodium nitrate ($NaNO_3$) and 0.200 M $MgCl_2$. Find the ionic strength of the solution? *(Answer: 0.7 M)*

Factors affecting solubility (summary)

- **Temperature (S↑)**

... Solubility increases with temperature

- **Nature of Solute**

... When ionic charge increases, the attraction between ions increases, solubility decreases

... Small ions is less soluble than large ions, as the bond between small ions is stronger that the bond between large ions with the same charge.

- **Nature of Solvent**

... Like dissolves like

- **Common ion (S↓)**

... the presence of common ions reduce solubility

- **pH the solution (S↑ OR S↓)**

... Occurs when one of the ions in the salt is an acid or base $Mg(OH)_2 \leftrightarrow Mg^{2+} + 2OH^-$

... Occurs when the salt is a conjugated base of a weak acid (BaC_2O_4, $CaCO_3$, ...)

⇨ Ex. ionic compound with basic anion

solubility will increase as the pH of the solution decreases (H+ reacts with the basic anion)

$$CaCO_3\ (s) \rightleftarrows Ca^{2+}\ (aq) + CO_3^{2-}\ (aq) \quad \xrightarrow[\text{Shift to the right}]{\text{Anion decreases}}$$

$$CO_3^{2-}\ (aq) + H^+\ (aq) \rightarrow HCO_3^-\ (aq)$$

- **Formation of complex ion (S↑)**

The solubility of an ionic compound may increase dramatically if a solution containing a Lewis base is added

As the complex ion forms, [cation] in solution decreases

$$AgCl\ (s) \rightleftarrows Ag^+\ (aq) + Cl^-\ (aq)$$

$$Ag^+\ (aq) + 2\ NH_3\ (aq) \rightleftarrows [Ag(NH_3)_2]^+\ (aq)$$

- **Electrolyte strength (S↑)** ... The presence of other electrolytes increase solubility
- **Particle size** ... Smaller particles are more dissolved

When a solute dissolves, the action takes place only at the surface of each particle. When the total surface area of the solute particles is increased, the solute dissolves more rapidly.

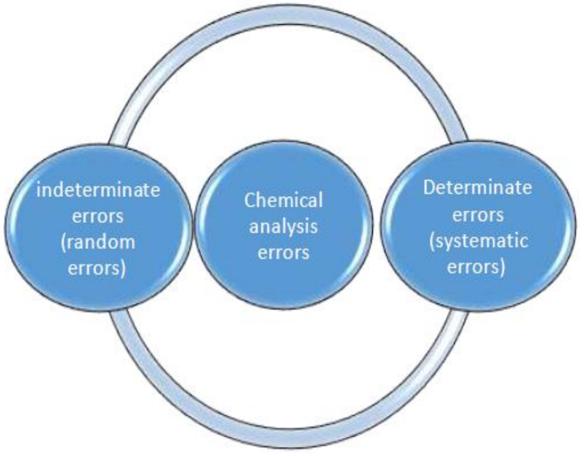
Analytical Statistics

Errors in chemical analysis

It is impossible to perform a chemical analysis that is totally free of errors or uncertainties, but only to minimize errors to acceptable values. Errors can be caused by faulty equipment or bad laboratory practice; proper equipment maintenance, appropriate training, calibrations, standardizations, and analyses of known samples can sometimes be used to lessen all. Errors must be controlled and assessed so that valid analytical measurements can be made and reported.

Type of errors in a chemical analysis

Basically, chemical analysis are affected by two types of errors which include determinate errors (also known as systematic errors), and indeterminate errors (also known as random errors).



Determinate errors

Determinate errors (also known as systematic errors) have a definite value from identified sources. There are three types of systematic errors that include instrumental error, method error, and personal error.

1. Instrumental errors are caused by non-ideal instrument behavior, by faulty calibrations, or by use under inappropriate conditions. Pipettes, burettes, and volumetric flasks may hold or deliver volumes slightly different from those indicated by their graduations. Calibration eliminates most systematic errors of this type. Errors of these types usually are detectable and correctable.

2. Method errors are initiated by the non-ideal chemical or physical behavior of the reagents and reactions on which an analysis is based; often introduce systematic method errors. Such sources of non-ideality include the slowness of some reactions, the incompleteness of others, the instability of some species, the lack of specificity of most reagents, and the possible occurrence of side reactions that interfere with the measurement process. Errors inherent in a method are often difficult to detect and hence, these errors are usually the most difficult to identify and correct.

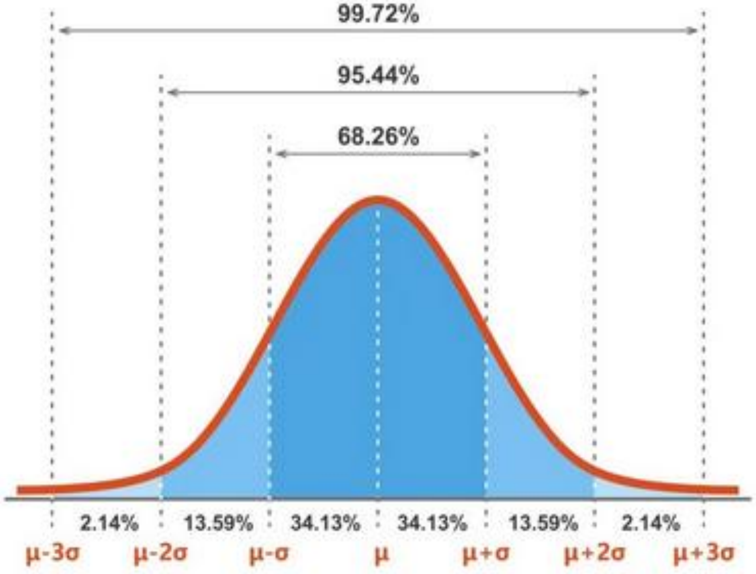
3.Personal Errors result from the experimenter's carelessness, inattention, or personal limitations. Many measurements require personal judgments. Examples include estimating the position of a pointer, the color of a solution at the end point in a titration, or the level of a liquid with respect to a graduation in a pipette or burette. Digital and computer displays on pH meters, laboratory balances, and other electronic instruments eliminate number bias because no judgment is involved in taking a reading.
Determinate errors that lead to a higher value or result than a true or accepted one are said to show a positive bias; those leading to a lower value or result are said to show a negative bias.

- **Indeterminate errors**

Indeterminate errors (known as random errors) are caused by the many uncontrollable variables that accompany every measurement. It is impossible to eliminate them, but they can be minimised by careful experimental design and control. Environmental factors such as temperature, pressure and humidity, and electrical properties such as current, voltage and resistance are all susceptible to small continuous and random variations described as noise. These contribute to the overall indeterminate error in any physical or physicochemical measurement, but no specific source can be identified.

The distribution of errors was first studied by Carl F. Gauss. When a large number of replicate readings, at least 50 numbers are taken of a continuous variable, the results attained will usually be distributed about the mean in a roughly symmetrical manner. The mathematical model that best satisfies such a distribution of random error is called the normal Gaussian distribution.
Gaussian distribution curve is a bell-shaped that is symmetrical about the mean as shown in the figure.
This curve satisfies the equation:

$$\boxed{1/(\sigma\sqrt{2\pi})\ e^{-(x-\mu)^2/2\sigma^2}}$$

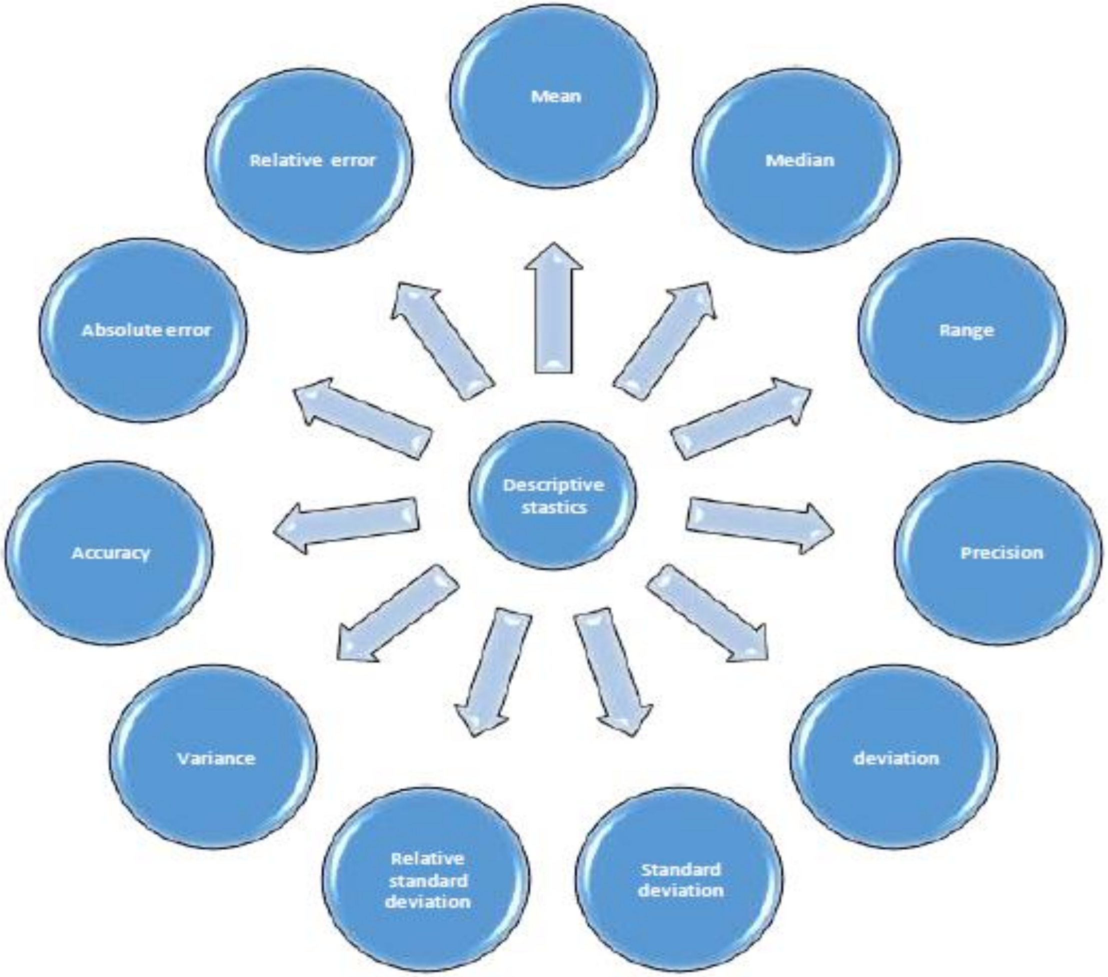


Normal or Gaussian distribution curve

Where, σ = standard deviation μ = mean of total population.

➧ Descriptive statistics

There are certain terms in statistics which must be defined; as they form the basis defining the measure of dispersion of data that causes errors in analytical results:



The mean or average is obtained by dividing the sum of replicate measurements by the number of measurements in the set.

$$\bar{x} = \frac{\sum_{i=1}^{N} x_i}{N}$$

The symbol Σxi means to add all of the values xi for the replicates; xi represents the individual values of x making up the set of N replicate measurements.

Example 17

If a titration is repeated four times and titre values are 10.1, 9.9, 10.0 and 10.2 mL, calculate the mean?

Mean = 10.1+ 9.9+ 10 + 10.2/4 = 40.2/4 = 10.05 mL

The median is the middle value in a set of data that has been arranged in numerical order. For an odd number of values, the middle value is the median, for an even no value, the average of the two middle values is the median.

For the odd values 18, 19, 20, 21, and 22, the median is equal to (20).

For the even values 18, 19, 20, 21, 22, and 23, the median is equal to 20+21/2 =20.5**.**

The range is the difference between the greatest and least values of data.

Precision is the agreement between multiple measurements made in the same way. It implies nothing about their relation to the true value. Describes the reproducibility of measurements. The precision of a set of replicate data may be expressed as standard deviation, relative standard deviation, and variance.

Deviation is how much each measurement differs from the mean. This is an important number and is called the deviation.

Standard deviation (S) is the square root of the sum of the individual deviations squared, divided by the number of readings based on the normal error (Gaussian) curve. It is an important term in the analysis of random numbers.

$$s = \sqrt{\frac{\sum_{i=1}^{i=N} (x_i - \bar{x})^2}{N-1}}$$

Relative standard deviation (RSD) (also known as coefficient of variation (CV)) is the standard deviation expressed as a percentage of the measured value.

Relative standard deviation (RSD) % = (S/ mean) × 100

The variance is the square of standard deviation, which is designated as S^2. The variance is fundamentally more important in statistics than is S itself. Variance, S^2 = (Standard deviation)^2

$$S^2 = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n - 1}$$

Example 18

An iron core gives the following results during the Fe estimation as the value 7.08, 7.21, 7.12, 7.09, 7.16, 7.14, 7.07, 7.14, 7.18, 7.11. Calculate the mean, the standard deviation, relative standard deviation, and variance for the values.

The mean, $\bar{x}$= (7.08 + 7.21 + 7.12 + 7.09 + 7.16 + 7.14 + 7.07 + 7.14 + 7.18 + 7.11)/10
= 71.3/10
=7.13
Standard deviation = S = $\sqrt{}(7.08-7.13)^2 + (7.21-7.13)^2 + \ldots\ldots\ldots\ldots(7.18-7.13)2 + (7.11-7.13)^2 /9$
S = $\sqrt{}181.98 \times 10^{-4} /9$
S = 4.49×10^{-2}
S = 0.0449
Relative standard deviation (RSD) = (S/mean) × 100
RSD = 0.0449/7.13 × 100
RSD = 0.62 %
Variance (S2) = $181.98 \times 10^{-4}/9$
S2= 2×10^{-2}
S2=0.002

Accuracy is the closeness of a measurement or the mean of multiple measurements, to its true or accepted value. The term accuracy is commonly stated in terms of absolute error and relative error.

Absolute errors refers to the difference between a measured value and the true or known value:

Where E is the absolute error, X_i is the measured or experimental value and X_t is the true value. If the measurement result is low, the sign is negative; if the measurement result is high, the sign is positive.

$$E = Xi - Xt$$

The relative error of a measurement is the absolute error divided by the true value. Relative error may be expressed in percent, parts per thousand, or parts per million, depending on the magnitude of the result:

$$Er = \frac{E}{Xt} \times 100$$

$$Er = \frac{Xi - Xt}{Xt} \times 100$$

Where E_r is expressed as percentage relative error, E is the absolute error, X_i is the measured or experimental value and X_t is the true value.

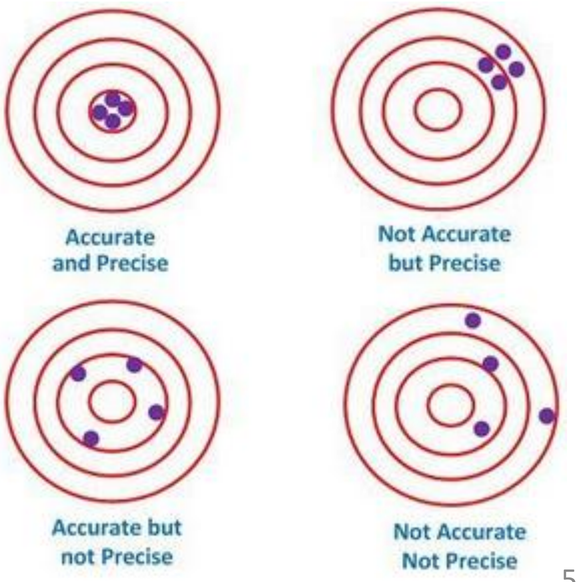
Example 19

The measured weight of a pineapple is approximate as 682.325 g, but the original weight is 684.075 g. Determine the absolute and relative error in the weighing?

Absolute error = 682.325 – 684.075 = -1.75 g

Relative error = -1.75/684.075 × 100 = -0.25

The relationship between precision and accuracy are demonstrated in the figures:



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