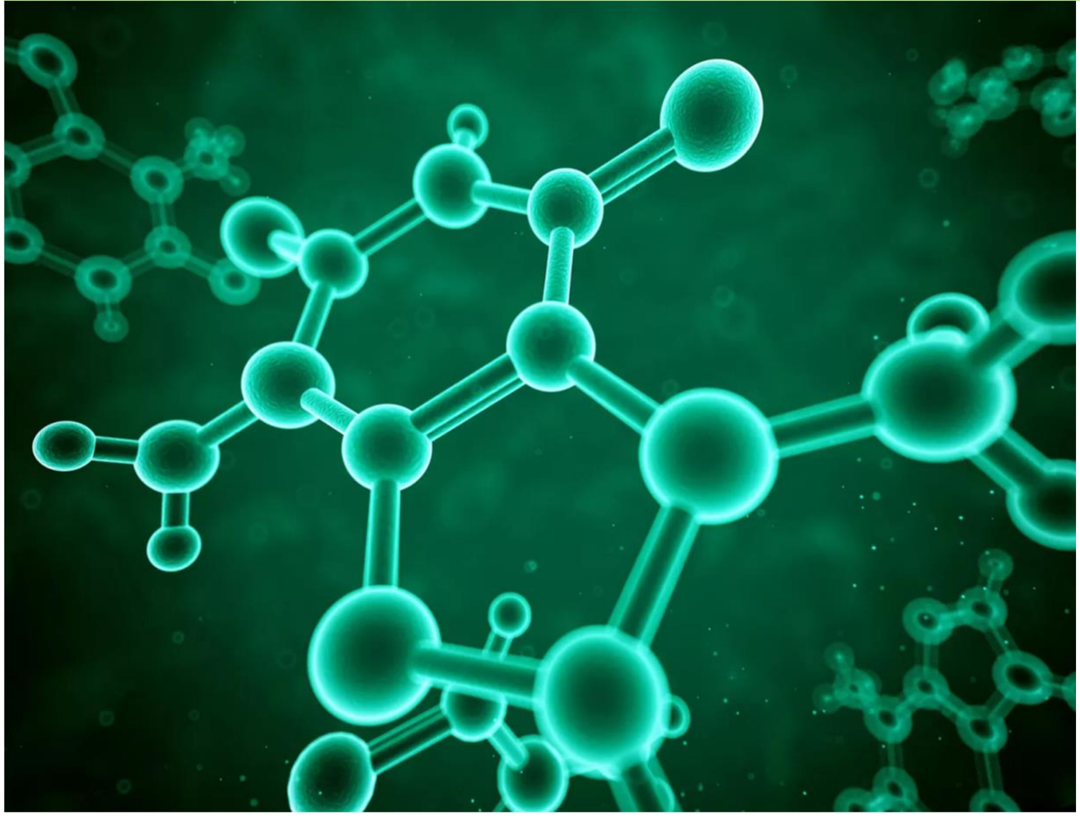
Analytical Chemistry



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Lecture 5

❖ Factors effecting solubility of precipitates :

1. **Temperature :**

As a general role the solubility of must solid in liquids **increased** with an in crease in temperature .

2. **PH (acidity/Basicity) :**

Basic precipitates dissolve in acid, acidic precipitates dissolving in base.

3. **Common ionic effect:**

Adding an excess (increase) of a common ion **reduces** solubility of precipitates. Non common ions can **increase** solubility of precipitates.

4. **Complexation :**

Legands (NH_3) form soluble complexes **increasing** solubility of precipitates.

5. **Particle size :**

Smallar particles have higher solubility than larger ones.

6. **Solvent polarity :**

Ionic precipitates dissolve better in polar solvents(water).for that used **organic solvent (ethanol) to reduce** solubility of precipitates .

❖Post – precipitation

- ✓ When the precipitation is allowed to start in contact with the mother liquor. **A second substance will slowly from a precipitate** with the precipitating agent. Moreover , post precipitation is a slow equilibrium process.
- ✓ This type of contamination can be reduced by:

1. Direct filtration of the main precipitate after precipitation process.
2. Separation of impurities before the precipitation process.

$$\mathbf{Ca^{+2}_{(aq)} + C_2O^{-2}_{4(aq)} \rightarrow CaC_2O_{4(s)}} \quad \textbf{(fast)}$$

$$\mathbf{Mg^{+2}_{(aq)} + C_2O^{-2}_{4(aq)} \rightarrow MgC_2O_{4(s)}} \quad \textbf{(slow)}$$

- ✓ this means that when calcium oxalate is precipitated in the presence of $Mg+^2$, MgC_2O_4 does not precipitates immediately, but it will be precipitated if the solution is allowed to stand too long before filtration of CaC_2o_4.
- ✓ **digestion process increase the precipitation** as it need time .

Re – precipitation :

- in this process the filtered solid is **re dissolved** and **re precipitated**.
- The primary role of re precipitation is to **further purify the precipitate .**

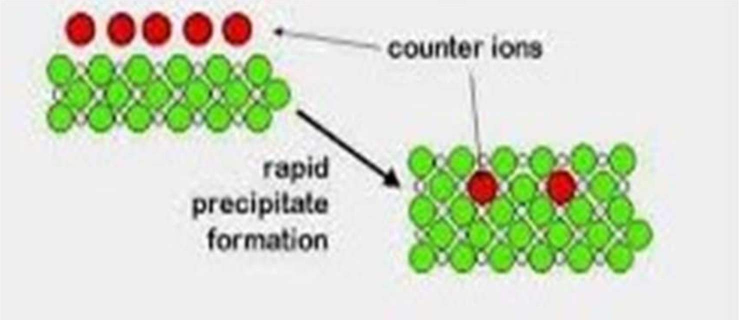
Co – precipitation :

- Precipitate that are **contaminated** from other soluble substances that are soluble in the mother liquor. .
- Co precipitation of impurities is most likely when The impurity is at a **high concentration(concentrated solutions**), for that using dilute solutions and slow precipitation to reduce co precipitation .
- **Homogeneous precipitation** is technique minimizes (decreasing) of the co precipitation.
- Co precipitation occurs when impurities are **trapped** within or adsorbed onto the precipitate, leading to contamination, for that it is a major source of contamination in gravimetric analysis.

❑ There are a number Types of co precipitation :

1. *Occlusion :*

- ✓ when a crystal is a **growing rapidly** during precipitate formation , foreign ions in the solution may became **trapped , or occluded with in the growing crystal.**
- ✓ Occlusion refers to the mechanical trapping of impurities within the crystal structure during rapid precipitation.



- ✓ occlusion can be reduced by (**digestion of precipitate and re precipitation)**

2. *Mixed crystal formation*

- ✓ Mixed-crystal formation occurs when impurities replace ions in the crystal lattice of the precipitate.

3. *Surface adsorption*

- ✓ In surface adsorption, impurities are trapped on the surface of the precipitate due to **electrostatic attraction**.

- ✓ Contamination by surface adsorption can be reduced by **washing the precipitate with a solution containing an electrolyte.**

Post precipitation	**Co precipitation**
The contamination **increase** with the time that the precipitation is left in contact with the mother liquid	decrease
Contamination **increase** the faster is agitated by either mechanical or thermal means .	decrease
Growth of contamination much greater	less
The post precipitation **increases** with tempurature increasing	Less

Precipitation from homogeneous solution :

- It is the a technique in which a precipitating agent is generated in a solution of analyte by a homogeneously (uniformly) slow chemical reaction throughout the solution.
- The precipitating agent appears gradually and homogenously in the solution and reacts immediately with the analyte. As a result the relative supersaturation is kept low during the entire precipitation.
- Solid form (precipitate) by homogeneous precipitation are generally **purer** and more **easily filtered** than precipitates generated by direct addition of a reagent to the analyte solution.
- In generally , homogeneously precipitates both colloidal and crystalline are better suited for analysis than a solid formed by direct addition of a precipitating reagent.
- Precipitation from homogeneous solution is particularly useful in gravimetric analysis because it help minimizing co precipitation and improving filterability.

✓ urea is used as example for the homogeneous generation of hydroxide.

$$(H_2N)_2CO_2 + 3H_2O \xrightarrow{100\ C} CO_2 + 2NH_4^+ + 2OH^-$$

This **hydrolysis process** slowly at temperatures below 100C with 1 to 2 hours needed to complete a typical precipitation and used to determination of Iron or alluminium.

✓ Sulfamic acid can be used to homogeneous generate sulfate ions (SO_4^{-2}) for precipitating $BaSo_4$.(Sulfamic acid hydrolysis to release So_4^- slowly).

❑ Advantages of the gravimetric methods:

1. These methods do not required the standardization which use the standard solution as in the other method. The gravimetric factor is samply calculated from atomic weights of analyte.
2. more efficient especially one or two sample are needed for the analyis.
3. it can be used for the determination of an analyte at concentration higher than 0.01 getting a good sensitivity.

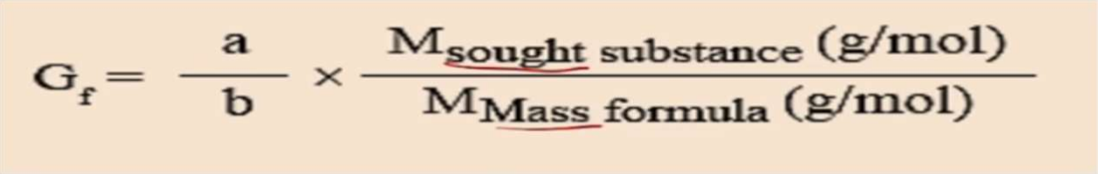
❑ Disadvantages :

1. Less usefulness when a large number of samples needed for analysis .
2. Less sensitivity in the determination of analyte at concenteration below 0.01
3. less faster than other techniques and non specific .

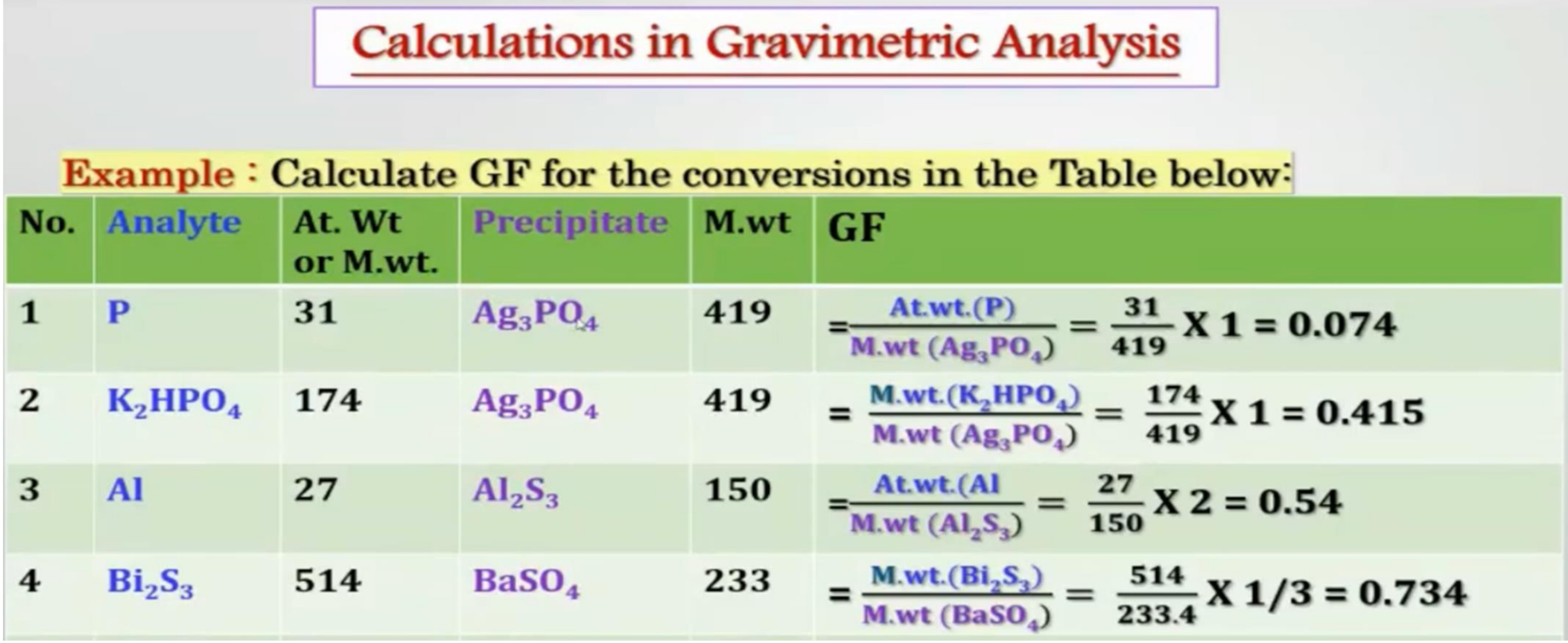
❖ Calculation of results from gravimetric data :

Gravimetric factor(Gf):

The ratio of molar mass of the sought substance (analyte) to molar mass of gravimetric formula (precipitate) is called as Gravimetric factor



$$G_f = \frac{a}{b} \times \frac{M_{\text{sought substance}}\,(\text{g/mol})}{M_{\text{Mass formula}}\,(\text{g/mol})}$$

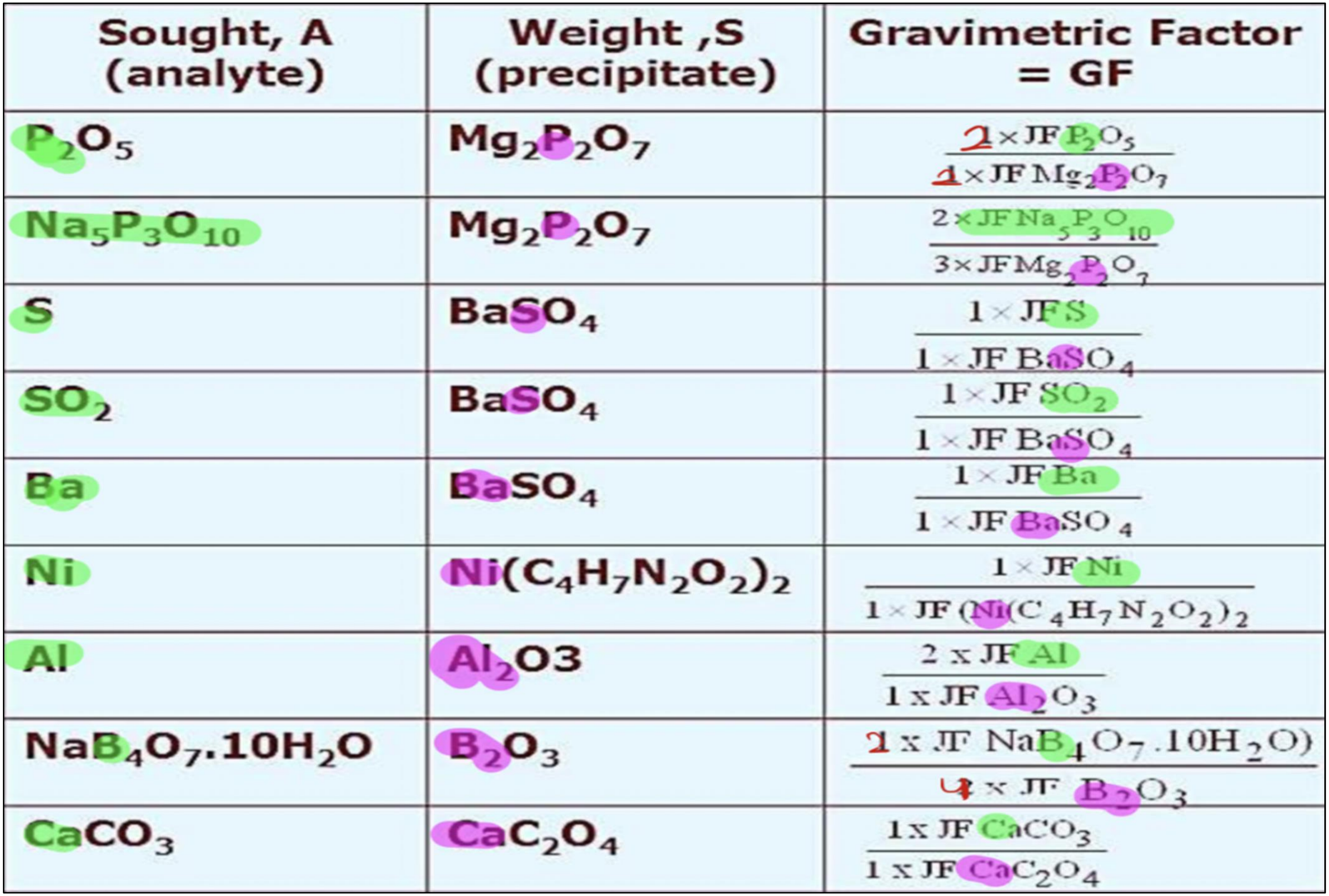


Calculations in Gravimetric Analysis

Example : Calculate GF for the conversions in the Table below:

No.	Analyte	At. Wt or M.wt.	Precipitate	M.wt	GF
1	P	31	Ag_3PO_4	419	$= \frac{\text{At.wt.(P)}}{\text{M.wt }(Ag_3PO_4)} = \frac{31}{419} \text{ X } 1 = 0.074$
2	K_2HPO_4	174	Ag_3PO_4	419	$= \frac{\text{M.wt.}(K_2HPO_4)}{\text{M.wt }(Ag_3PO_4)} = \frac{174}{419} \text{ X } 1 = 0.415$
3	Al	27	Al_2S_3	150	$= \frac{\text{At.wt.(Al}}{\text{M.wt }(Al_2S_3)} = \frac{27}{150} \text{ X } 2 = 0.54$
4	Bi_2S_3	514	$BaSO_4$	233	$= \frac{\text{M.wt.}(Bi_2S_3)}{\text{M.wt }(BaSO_4)} = \frac{514}{233.4} \text{ X } 1/3 = 0.734$

❖ Calculation of result from gravimetric data



Sought, A (analyte)	Weight ,S (precipitate)	Gravimetric Factor = GF
P_2O_5	$Mg_2P_2O_7$	$\frac{2 \times \text{JF}\ P_2O_5}{1 \times \text{JF}\ Mg_2P_2O_7}$
$Na_5P_3O_{10}$	$Mg_2P_2O_7$	$\frac{2 \times \text{JF}\ Na_5P_3O_{10}}{3 \times \text{JF}\ Mg_2P_2O_7}$
S	$BaSO_4$	$\frac{1 \times \text{JF}\ S}{1 \times \text{JF}\ BaSO_4}$
SO_2	$BaSO_4$	$\frac{1 \times \text{JF}\ SO_2}{1 \times \text{JF}\ BaSO_4}$
Ba	$BaSO_4$	$\frac{1 \times \text{JF}\ Ba}{1 \times \text{JF}\ BaSO_4}$
Ni	$Ni(C_4H_7N_2O_2)_2$	$\frac{1 \times \text{JF}\ Ni}{1 \times \text{JF}\ (Ni(C_4H_7N_2O_2)_2}$
Al	Al_2O3	$\frac{2\ x\ \text{JF}\ Al}{1\ x\ \text{JF}\ Al_2O_3}$
$NaB_4O_7.10H_2O$	B_2O_3	$\frac{2\ x\ \text{JF}\ NaB_4O_7.10H_2O)}{4\ x\ \text{JF}\ B_2O_3}$
$CaCO_3$	CaC_2O_4	$\frac{1 x\ \text{JF}\ CaCO_3}{1\ x\ \text{JF}\ CaC_2O_4}$

- **The following equation is used to calculate the percentage of the sought substance(analyte) found in sample.**

$$\text{Percentage of sought substance } \% = \frac{G_f \times m_{\text{mass formula}}\,(g)}{m_{\text{sample}}\,(g)} \times 100\%$$

Example : Calculate the % Phosphorus in a 0.3516 g detergent sample. Final yield is 0.2161 g Mg2P2O4.

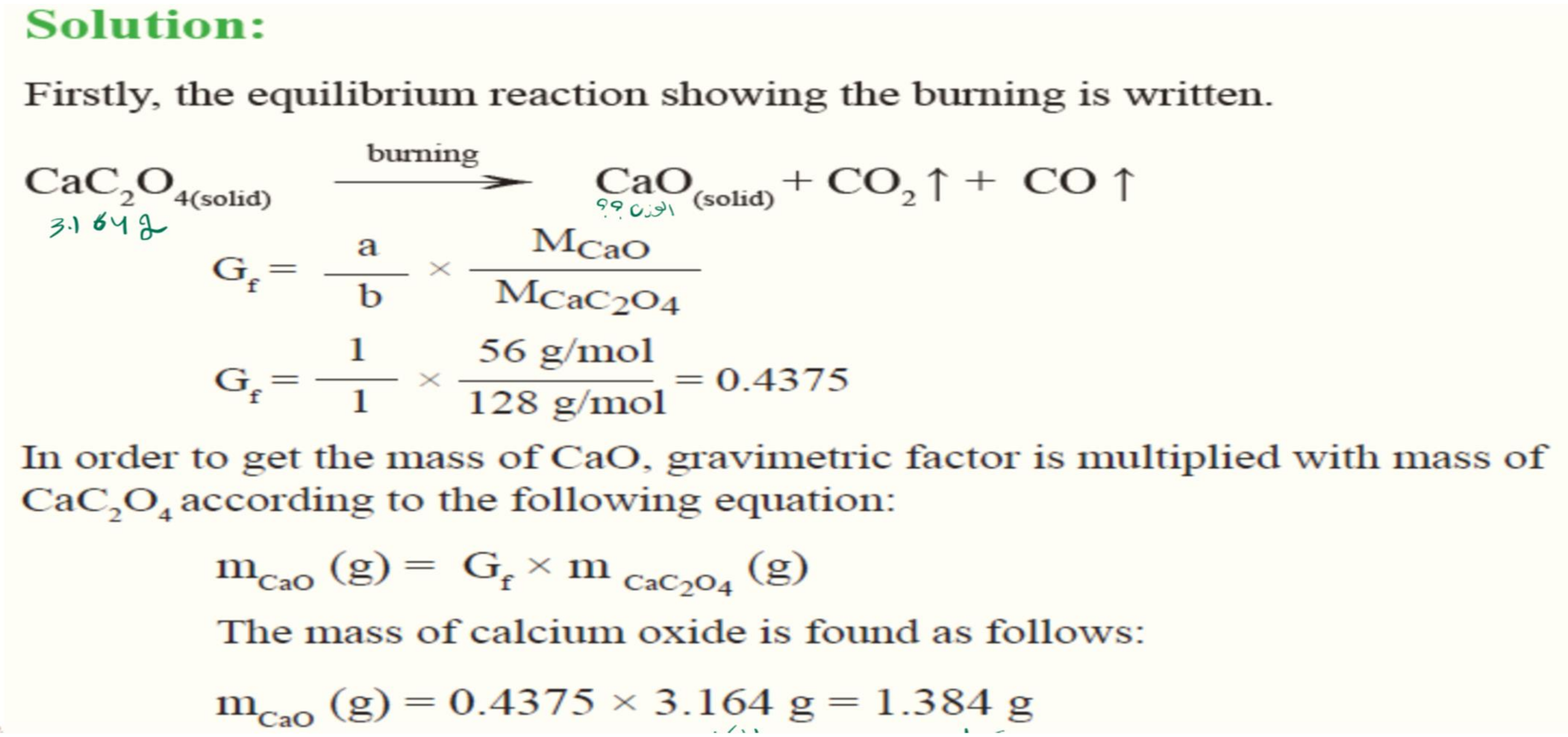
(formula weight of P : 30.97 g , formula weight of Mg2P2O4 : 222.57 g)

$$\text{Gf} = \frac{a}{b} \text{ x } \frac{\text{FW analyte}\,(P)}{\text{FW sample}\,(Mg_2P_2O_4)}$$

$$\text{Gf} = \frac{\boxed{2}}{1} \text{ x } \frac{30.97g}{222.57g} = 0.27833$$

$$\%P = \frac{(0.2161g\ Mg_2P_2O_7)(0.27833)}{0.3516g} \text{x} 100 = 17.10\%$$

- ☐ **Example :** What is the mass of calcium oxide (CaO) formed by complete burning of 3.164 g of calcium oxalate (CaC2O4) ?



Solution:

Firstly, the equilibrium reaction showing the burning is written.

$$CaC_2O_{4(solid)} \xrightarrow{\text{burning}} CaO_{(solid)} + CO_2\uparrow + CO\uparrow$$

3.164 g

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$$G_f = \frac{a}{b} \times \frac{M_{CaO}}{M_{CaC_2O_4}}$$

$$G_f = \frac{1}{1} \times \frac{56\ g/mol}{128\ g/mol} = 0.4375$$

In order to get the mass of CaO, gravimetric factor is multiplied with mass of CaC_2O_4 according to the following equation:

$$m_{CaO}\,(g) = G_f \times m_{CaC_2O_4}\,(g)$$

The mass of calcium oxide is found as follows:

$$m_{CaO}\,(g) = 0.4375 \times 3.164\ g = 1.384\ g$$