University of Baghdad College of Science Department of chemistry

Analytical Chemistry 1

First stage for Chemistry

1st Semester

(صباحي + مسائي)

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The reference :

- Analytical chemistry (An Introduction)(Donglas, A.Skoog and Donald .M.West) 7th (1999).
- Fundamental of Analytical chemistry 8th (2000), skoog and west.
- Analytical chemistry 6th (2004) Gary.D.Christiain.

Contents:

Analytical chemistry (I) Gravimetric method of analysis

- 1. Important weight and concentration units.
- 2. Statistical analysis of data.
- 3. An introduction to gravimetric methods.

* precipitation (ppt) methods.

*volatilization methods

*calculation of results from grav.

*analysis and gravimetric factor.

4. The solubility of precipitates .

* the application of solubility product constant.

*additional variables that effect the solubility of precipitates .

- 5. The particle size and purity of precipitates.
- 6. Application of gravimetric analysis.

<u>Lec.1</u>

Introduction:

What is the analytical chemistry?

Chemistry (Chem.)

- Organic Chem.
- Inorganic Chem.
- Bio Chem.
- Physical Chem.
- Analytical Chem.

The analytical chemistry: is a measurement science of a set of powerful ideas and methods that are useful in all fields of science.

This kind of chem. Specific for separation and determination of the chemical substances.



Qualitative Analysis: reveals chemical identity of elements and compounds. يتم تعيين الهوية الكيميائية للعناصر والمركبات

Quantitative Analysis: determines the relative amounts of each substance in a sample

Analyte or Analyzed: components of a sample that are to be determined



Gravimetric Quant. Anal.:

Precipitation the substance, separation, weight of compound containing species by direct method or loss of weight due to volatilization of species. To get the precipitate we can used organic precipitate or inorganic precipitate or by electro deposition.

• Vol. Quan. Anal.

Measure the volume of standard solution equivalent to unknown by these methods

- 1. Acid-base titration.
- 2. Precipitation titration.
- 3. Oxidation reduction titration.
- 4. Complexometric titration
- Instrumental Quant. Anal.
 - Optical measurement.(Based on intraction of electromagnetic radiation with analyte atoms and molecules, or on the production of radiation by analyte)

2. Electro chemical measurement .(measured electrical properties)

NOTE Quant. Anal. = Quantitative analysis

Chapter One

Important Weight and Concentration Units

Topics

- International System of Units / SI Units
- Mass and Weight
- The Mole
- Units of Concentrations of solutions
- Stoichiometry

<u>Concentration</u> (conc.): The weight (wt.) of solute in known volume of solvent.

Seven SI BASE UNITS

IABLE 4-1	ΤA	В	Ĺ	Е	4	-1	
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Physical Quantity Name of Unit Abbreviation				
Thysical Quantity	Name of Omt	Abbieviation		
Mass	kilogram	kg		
Length	meter	m		
Time	second	S		
Temperature	kelvin	K		
Amount of substance	mole	mol		
Electric current	ampere	А		
Luminous intensity	candela	cd		

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Wt. of solute:

*In laboratory records the mass of substance can be given in

gram(g) ,milligram(mg)[=10 ⁻³ g	$[], microgram(\mu g)[=10^{-6}g],$	Nano
$gram(ng) [=10^{-9}g]$		
*Chemical weight units		
Atomic weight (At.wt.)	Molecular weight (M.wt.)	
Equivelent weight (eq.wt.)	Formula weight (F.wt.)	
Ionic weight (Ion.wt.)		

Table (1) Expression of weight in chemical units

Chemical units	Wt. of unit in	Method of conversation metric
	gram	units to chemical units
Atomic wt. (when the	g.At.wt.	g.At.wt.= $\frac{wt(g)}{At wt(g/g Atwt)}$
analyte is atom)	ex: Na, S,Fe,	
2- Molecular wt. (when	g.M. wt	g. M.wt= $\frac{wt(g)}{M.wtg(g/mole)}$
the sub. is molecular	(ex) O_2 , H_2O ,	$\therefore a M wt = no of moles$
shape).	NH ₃ ect.	$\cdots g.m.wt = no.0j motes$
3- formula wt (when	g.F.wt	g.F.wt= $\frac{wt(g)}{g(g,F)}$
sub. As strong	(ex)NaCl,	g/(g.r.wt)
electrolyte shape).	HClect	
4- Ionic wt (when	g.Ion. Wt	g.ion wt = $\frac{wt(g)}{m wt(g)}$
sub.as ion shape)	(ex) Na ⁺ , Cl ⁻	$m.wt(\frac{1}{g.A.wt})$
	,NH4 ⁺ ect	$wt(e) = 9.11 \text{ x} 10^{-28} \text{ g}$
	$Cl^0 + e = Cl^-$	it is very small.
	$Na^0-e = Na^+$	
5- equivalent wt	g.eq.wt	g.eq.wt = $\frac{wt(g)}{eq.wt(\frac{g}{g.eq.wt})}$
		the cal. depended upon

the reaction of molecules	
---------------------------	--

Examples :-

1- Cal. The g.At.wt of these elements Na, S, Cl, Fe, O in (10g) of each sample .

g.A.wt of Na = $\frac{wt(g)}{A.wt(\frac{g}{g.A.wt})} = \frac{10(g)}{23(\frac{g}{g.A.wt})} = 0.435$ g.A.wt

2- What is the grams of O_2 in 3 moles of it?

Mole =
$$\frac{wt}{m.wt}$$

Wt. of $O_2 = 3$ mole x 32 g/mole = 96 gram.

3- Aqueous solution of Na_2SO_4 have 14.2 gram cal. G- ion wt of Na^+ and SO_4^{-2} and (wt) of each . if M.wt $Na_2SO_4 = 142$ g /mole .

Na₂SO₄
$$\longrightarrow$$
 2Na⁺ + SO₄⁼
0.1 mole 2x0.1g-ion wt Na⁺ 0.1 g-ion wt SO₄⁼
Mole Na₂SO₄ = $\frac{14.2 g}{142 g/mole}$ = 0.1 mole
g.ion wt Na⁺ = 2 x0.1 =0.2
g.ion wt SO₄ = 1x0.1 = 0.1
wt Na⁺ = 0.2 x 23 = 4.6
wt SO₄⁼ = 0.1 x(32+16×4)= 9.6

Concentration

Table (2) : Expression of conc. In chemical units

The system	Symbol	Define method of cal. From chemical unit.
Molarity	М	no.of mole of solute
		vol.of solvent (l)
Molality	m	no.of mole of solute
		wt.of solvent (kg)
Formality	F	no.of g.fwt of solute
		vol.of solvent (l)
Normilty	N	no.of g.eq wtof solute
		vol.of solvent (l)
Mole fraction	M or X	mole.of solute
		mole solute + mole solvent
g/liter	g/l	no.(g)of solute
		vol.of solvent (l)
Weight percent	Wt%	g of solute = x100
	(Wt/Wt) %	$\overline{g \ of \ sample}^{x \ 100}$
		تعبر عن التركيز للكواشف الذائبة بالماء

Vol. percent	Vol %	vol. of solute $r100$
	(Vol/Vol)%	vol. of solvent x100
		للمحاليل المحضرة بالتخفيف لسائل مادة مع سائل اخر
Part per million	ppm	no.of millgrame of solute
		vol. of solvent (l)
		$\frac{mg}{l}$ or $\frac{\mu g}{ml}$
Weight/ volume	Wt./vol.%	
percent		$\frac{wt. of solute(g)}{vol. of solvent(mL)} x100$











1.05 0.90 1.19 1.15 1.42 1.67 1.71
0.90 1.19 1.15 1.42 1.67 1.71
1.19 1.15 1.42 1.67 1.71
1.15 1.42 1.67 1.71
1.42 1.67 1.71
1.67 1.71
1.71
1.84

Back to Concentrations: Parts Per Million, Parts per Billion

- For very dilute solutions, it is convenient to express concentrations in ppm or ppb
- An approximation that is commonly used is that the density of dilute solution approaches the density of water (1.00 g/ml)

$$c_{ppm} = \frac{mass - solute}{mass - solution} \times 10^6 \, ppm$$

$$c_{ppb} = \frac{mass - solute}{mass - solution} \times 10^9 \, ppb$$

Units in numerator and denominator must be consistent!

The calculation used the molarity con.

Molarity: number of moles of solute dissolved in one liter of solvent .

•
$$M = \frac{mole}{l}$$
 or $\frac{m.mole}{ml}$ (units)
• $M = \frac{wt \ of \ solute \ (g)dissolved \ in \ one \ liter}{m.wt}$
 $= \frac{g/l}{g/mole} = \frac{mole}{l}$

Note:

• If the wt. of sub. Like (NaCl) constant the mole is constant because the M.wt constant

• But:- the reaction between vol. and conc. Reversible.
Conc. increase
$$\longrightarrow$$
 vol. decrease
 $M = \frac{mole}{vol}$

•
$$M_1 V_1 = M_2 V_2$$

• $\frac{mole}{V_1} X V_1 = \frac{mole}{V_2} X V_2$: (Mole)₁ = (Mole)₂

Calculation used normality conc.

Normality: number (g.eq.wt) of solute dissolved in one liter.

1- N =
$$\frac{g.eq wt}{l}$$
 or N = $\frac{mg.eq wt}{ml}$ (unit)
2- N = $\frac{no.gram of solute dissolved in one liter}{eq.wt}$
N = $\frac{g/l}{g/(g.eq wt)}$ = $\frac{g.eq wt}{l}$

3-
$$N_1 V_1 = N_2 V_2$$

 $\frac{(g.eq wt)_1}{v_1} xv_1 = \frac{(g.eq wt)_2}{v_2} x v_2$

 $(g.eq wt)_1 = (g.eq wt)_2$

Note:

- (M) have one value because its depended upon M.wt &M. wt of sub. Constant and not change with reaction .
- (N) have many value because its depended upon (eq. wt.) and (eq. wt.) change with reaction of substance .

<u>Lec.2</u>

Calculation of equivalent weight



* mono basic acid> HCl, HNO₃,....ect

* di basic acid.....> H₂SO₄, H₂S....ect

* tri basic acid>
$$H_3PO_4$$
,....ect
* eq.wt. $HCl = \frac{M.wt}{no \ of \ H+ \ ion \ reacted} = M.wt/1$
*eq.wt H_2SO_4 half state
 H_2SO_4 +NaOH = NaHSO_4 + H_2O
eq.wt $H_2SO_4 = M.wt/1$
neutral state
if H_2SO_4 + 2NaOH = Na_2SO_4+ 2H_2O
eq.wt $H_2SO_4 = M.wt/2$
* Cal. the eq.wt of H_3PO_4 (have 3 value)
eq.wt of substance react as acid
av SO_4 CO_4 B:O_4 = oct

ex SO₃, CO₂, P₂O₅,.....ect
eq.wt of SO₃ =
$$\frac{M.wt \ of \ so3}{no.of \ H+ion \ react \ with \ it}$$

SO₃ + H₂O = $\frac{M.wt \ of \ so3}{2}$

or

2.

$$SO_{3} + 2 NaOH = Na_{2}SO_{4} + H_{2}O$$

eq wt SO_{3} =
$$\frac{M.wt \ of \ so3}{no.of \ OH-ion \ react \ with \ it}$$
$$= \frac{M.wt \ of \ so3}{2}$$

3. eq.wt of base

NaOH, Ca(OH)₂, Al(OH)₃,ect eq.wt base = $\frac{M.wt}{no.of (OH)group}$

- eq.wt of $Al(OH)_3 = M.wt/3$
- 4. eq.wt of sub. React as base

Na₂O, CaO,.....ect

eq.wt of CaO=
$$\frac{M.wt \ of \ CaO}{no.of \ H+react \ with \ it}$$

 $CaO + 2HCl = CaCl_2 + H_2O$ eq.wt CaO = M.wt/2

5. eq.wt of salts

AgCl, BaCl₂, Ca₃(PO₄)₂.....ect

eq-wt of salt = $\frac{M.wt \ of \ salt}{total \ no.of \ (+)ion}$ or total no.of (-)ion

eq.wt of $Ca_3(PO_4)_2 = M.wt/6$

6. eq.wt of reduction agent. Or eq.wt of oxidation agent .

eq.wt of reduction agent = $\frac{M.wt}{no.of \ (e)lose \ in \ (one)molecules}$ eq.wt of oxidation agent = $\frac{M.wt}{no.of \ (e)accepted \ for \ (one)molecules}$

ex:



Oxidation : it is lose in (e) with increase with charge.

Reduction : it is accepted of (e) with decrease in charge

eq.wt of Zn = At.wt/2

eq.wt of HCl= M.wt /1

Ex:

 $5Fe^{2+} +MnO_4^- +10H^+ \longrightarrow Mn^{++} + 5Fe^{3+} + 5H_2O$

eq.wt of Fe = At.wt/1

eq.wt Mn = M.wt/5

Examples:-

1- Cal. The molality of solution have (15%) of NaOH in water if At.wt Na= 23, H=1, O=16

solution :

wt. NaOH = 15g , wt. H₂O = 85g

$$m = \frac{mole \ of \ NaOH}{wt \ of \ H2O(Kg)}$$

m= $\frac{15g/(\frac{40g}{mole})}{(85/1000)(Kg)}$ =mole/kg

2- 100g of solution content 0.03 mg Na $^+$, Cal. The percentage of Na $^+$ %

Solution:

•

g=1000mg , 0.03/1000 mg =0.00003g

$$\% \text{Na}^{+} = \frac{\text{wt solule}}{\text{wt sample}} \times 100$$
$$= \frac{3x10^{5} - 5g}{100g} \times 100 = 3x10^{5} \%$$

3- 50 ml of HCl have 0.1N mix with 25 ml HCl have 0.2N, cal. The new normilty

Solution:

HC1	+	HC1	 →	HC1
50x0.1		25x0.2		75x??
$N_1V_1 + N_2V_2$	= N	V_3V_3		
N ₃ =				

4- 30 ml of 0.1 N HCl added to 15ml 0.2 N of NaOH , what is the product solution (acid-base, neutral) cal .(N) of product solution and (N) of product salt.

Solution :

HCl	+	NaOH	\longrightarrow	$NaOH + H_2O$
Before reaction 30x	0.15	15	x0.2	
4.5 mg	g.q wt	3mg.e	q wt	
After reaction	1.5		zero	3mg.eq wt
The solution ne mg .eq wt of H	cutral w $Cl \equiv m$	hen g.eq wt of	NaOH	
4.5-3=1.5 exce	ss of act	id		
The solution pr	oduct is	s (acid)		
(N) product sol	ution =	mg.eq wt total vol		
	$=\frac{1}{2}$	$\frac{1.5}{45} = 0.033$		
Csalt=3/45 = 0	0.066			
Note:				
To charge (M) or	(N) con	ncn to (ppm	n) used this re	lation

• $ppm = M.wt \ge M \ge 1000$

g/mole x mole/l x1000

= g/l x1000 = (mg/l)

• ppm = eq.wt x N x1000

• ppm =
$$\frac{wt \ of \ solute}{wt \ of \ sample} \ge 10^6$$

Eq. wt for acid == $\frac{Mwt \ of \ acid}{no \ .of \ H+}$
Eq.wt. for base = $\frac{Mwt \ of \ base}{no \ of \ OH-}$
Eq. wt. for salt = $\frac{Mwt \ of \ salt}{no \ .of \ metal \ atom * no \ .of \ oxidation \ number}$
Eq. wt. for oxidant regent = $=\frac{Mwt \ of \ for \ oxidant}{no \ of \ accept \ e_{-}}$
Eq. wt. for reductant regent = $\frac{Mwt \ of \ for \ reductant}{no \ .of \ loss \ e_{-}}$
Eq. wt. for precipitation reaction $=\frac{Mwt \ of \ salt}{no \ of \ ion \ valence}$
Eq. wt. for complexation reaction $=\frac{Mwt for possative ion}{no .of valance of possative ion}$
Molality (m) = $\frac{\text{no.of mole (solute)}}{\text{one kg of solution}}$
$m = \frac{wt}{M.wt} \times \frac{1}{wt.kg \text{ solution}}$
Formality (F) = $\frac{\text{sp.g} \times \% \times 1000}{\text{F.wt}}$ for liquid (d or sp. g)
$F = \frac{wt}{F.wt} \times \frac{1000}{v(ml)} $ for solid
Molarity (M) = $\frac{\text{wt.}}{\text{M.wt}} \times \frac{1000}{\text{v(ml)}}$ for solid
$M = \frac{\text{sp.g} \times \% \times 1000}{\text{M.wt}} \qquad \text{for liquid (d or sp.g)}$
Normality (N) = $\frac{\text{wt.}}{\text{eq.wt}} \times \frac{1000}{\text{v(ml)}}$ for solid
$N = \frac{\text{sp.g} \times \% \times 1000}{\text{eq.wt}} \qquad \text{for liquid (sp.g or d)}$

Wt . (g) = M . * M. wt . * V (L)
Wt . (mg) = M . * M. wt . * V (ml)
$Wt_{(g)} = N * Eq . wt * V (L)$
$Wt_{(mg)} = N * Eq. wt. * V (ml)$
ppm = M . * M . wt * 1000
ppm = N * Eq. wt * 1000
no . of mole $. = M * V$
$N_1V_1 = N_2V_2$, $M_1V_1 = M_2V_2$, $F_1V_1 = F_2V_2$

<u>Lec.3</u>

Chapter Two

Statistical analysis of data

CHAPTER OUTLINE:

The student will be able to:-

1. The types of errors

2. The definition of accuracy, mean value, precision, deviation, standard deviation, absolute error, and relative error.

3. The types of rejection of measurement result.

Statistical: Statistical techniques must be never applied unless adequate data have been collected. Nevertheless the results obtained in the investigation of a new method should be set out in such a way that another chemist or statistician can use them.

Error: may be defined as a deviation from the absolute value or from the true average of a large number of results.

Two types of errors are recognized determinate (constant) and indeterminate (random or accidental).

Types of errors:

- 1. Gross careless errors.
- 2. Random errors (indeterminate errors or accidental errors)
- **3.** Systematic errors (determinate errors or constant errors)

<u>Gross careless errors</u>: are those due to mistakes that are not likely to be repeated in similar determinations. Examples, are the spilling of apportion of sample recording the wrong value for one of weights used, reading the wrong number for the volume of liquid in a burette.....etc. when a series of careful measurement contains one result that differs widely from the others of errors has occurred.

<u>Random (indeterminate) errors:</u> are due to (a) inherent limitations of the equipment (b) to limitations of observations, and (c) to lack of care in making the measurement. They can minimized by using high grade equipment and by careful work with this equipment, but these can never be completely eliminated.

<u>Systematic (determinate) errors:</u> can never be detected from the results of a single series of measurements, but only by comparing results of separate measurements using different instruments or method.

Chemical analysis are often subject to systematic errors. The use of impure materials for standardization of solutions, incorrect weights, in properly calibrated volumetric apparatus, even inadequate methods of analysis— all these and many other factors may lead to systematic errors.

Many of the possible systematic errors of analysis may be avoided by certain

routine precautions, such as calibration of measuring apparatus,

determination of a blank, performing an analysis by two or more independent

methods, and testing a method by a control analysis on a sample of known composition.

Types of systematic errors: (a) <u>personal errors</u>,(b) <u>operative errors</u>,(c) instrumental errors and (d) methodic.

The Mean X : The mean, arithmetic mean, and average are refer to the numerical value of the various measurements and dividing the total by number N of the measurements. In mathematical notation, the arithmetic mean for a small group of values expressed as:

$$\bar{\mathbf{X}} = \frac{\sum xi}{N}$$
or $\bar{\mathbf{X}} = \frac{\sum x1 + x2 + x3 + \dots \cdot xx}{N}$

For example: we have these numerical value-31.60, 31.60, 31.70, 31.76, 31.71, 31.53, 31.62, 31.47, 31.64. the total divided by the number of individual results.

 $\bar{\mathbf{X}} = 31.60 + 31.60 + 31.70 \dots + 31.64/9 = 31.67$

Median:-

is the central member of series there are equal number of observation smaller and greater than the median.

Measures of Central Tendency

Median

- middle result when replicate date are arranged in increasing or decreasing order
 - For <u>odd number</u> of results, locate the middle
 - For <u>even number</u> of results, average value of middle pair

Mode

- value that has the highest frequency

Ex/ cal. The mean and median for these observation:-

10.06, 10.20, 10.08, 10.10

$$Mean = \frac{10.06 + 10.20 + 10.08 + 10.10}{4} = 10.11$$

الحل 1- رتب الاعداد تصاعديا او تنازليا

(اذا كانت القياسات زوجية) 10.06,10.08,10.10, 10.20

The median is gives by the average of middle pair of results

Median $=\frac{10.08+10.10}{2} = 10.09$

اما اذا كانت القياسات فردية فتؤخذ القيمة الوسطية

Ex: 10.06, 10.08, <u>10.09</u>, 10.10, 10.20

<u>Precision:</u> is a measure of the agreement among the values in a group of data. That have been made in identical fashion.

<u>Accuracy</u>: is the agreement between the data (mean value) and the true value. Indeterminate or chance errors influence the precision of the results, and the measurement of the precision is accomplished best by statistical mean. Determinate or constant errors affect the accuracy of data.

Indeterminate errors obey the laws of probability, both positive or negative errors being equally probable, and larger errors being less probable than smaller ones. <u>Presentation of data</u>: There is no standard method of presenting data. The criteria must be that the data sufficient, the statistics legitimate and the definitions clear enough to be understood by another analyst.

Terms such as (mean error, relative error, and error) are ambiguous. For a series of results it is desirable to give the following data:

Precision data (1) Arithmetic mean. (2) Range, i.e. the difference between the highest and lowest results. (3) Average deviation, i.e. the average difference, without regard to sign, of each result in the series from the mean. (4) Standard deviation, i.e. the square root of the sum of the squares of the differences of each result from the mean after division by one less than the total number of results.

Accuracy data (5) Average difference, i.e. the average difference with regard to sign of each result in the series from the ' true' result. (6)

Average recovery, i.e. the mean of series of results as a percentage of the true'result. Accuracy data are not statistical measures and need only be calculated if it is suspected that the method under examination has a systematic bias. The actual systematic bias of any method can often only be found after collaborative, or inter laboratory studies, for the results of a single worker may have a bias owing to, e.g. an inaccurate standard solution. An example may help to clarify the methods involved. Strength of sulfuric acid method: Titration with N sodium hydroxide. The following series were carried out at different times by one chemist, but conditions for each series were the same. All results are expressed as percent by weight.

Series	1	2	3	4
	98.44	98.49	98.54	98.53
	98.51	98.49	98.51	98.49
	98.49	98.51	98.51	98.49
Mean of Series x	98.48	98.497	98.52	98.503
Precision data				
Range w	0.07	0.02	0.03	0.04
Mean Range $w = 0.04$				
Average Deviation	0.026	0.009	0.013	0.018
Standard Deviation s	0.036	0.012	0.017	0.023
Accuracy Data. The 'true' value f laboratories was 98.	ound by 05	a large nu	umber of c	collaborating
Average Difference				
with regard to sign +	0.43 +0	0.447 +	-0.47 -	+0.45

Measures of Spread

1. Range

- difference between the largest and smallest values in the data set
- 2. Deviation
- 3. Average deviation
- 4. Standard deviation
 - describes the spread of individual measurements about the mean
- 5. Variance – square of standard deviation
- 6. Relative Standard Deviation (RSD)
 - can be expressed in terms of ppt or %
 - coefficient of Variation (CV)

<u>Absolute errors (E)</u>: The absolute error can be defined as E = O - A, where the error E is the difference between the observed value (O) and the accepted value or true value (A).

suppose that the accepted value for the percentage chloride in sample is 24.34 percent.

E = 24.29 - 24.34 = -0.5 percent.

Here, we ordinarily retain the sign of the error to indicate whether the result is high or low.

Mean Error: The difference between the sample arithmetic mean and the true value gives a measure of the accuracy of an operation; is known as *mean error*. Example, if the arithmetic mean is 0.90 and the true value is 1. The mean error in this case is

1.00-0.90 = 0.10 g

Relative Error: Is obtained by dividing the mean error by the true value. It can be expressed as a percentage by multiplying by 100, or in parts per thousand by multiplying

by 1000. It is easier to compare several sets of results by using relative error rather than

the absolute mean error. The relative error in the case just cited is $0.10/1.00 \times 100 = 10\%$

Deviation (D): Is the numerical difference without regard to sign between an experimental value and the mean or average for a set of data that includes that value.

To illustrate, suppose that the following results were obtained for chloride analysis.

Sample	Percent Cl	Deviation from mean
1	24.39	0.10
2	24.20	0.09
3	24.28	0.01

The mean value is 24.29 percent and the first result has a deviation from the mean of 0.10 percent. the set exhibits an average deviation from the mean of 0.07.

Mean (average) Deviation: The *mean deviation d* for a sample, that is, the deviation of an individual observation from the arithmetic mean of the sample, is obtained by taking the difference between each individual value X_i and the arithmetic mean X, (adding the differences without regard to the algebraic signs), and dividing by the sum of the number of values to obtain the average . the mean deviation of a sample is expressed as:

$$d = \frac{\sum (X_{I} - \overline{X})}{N}$$

Standard Deviation(s): The standard deviation σ (sigma) is the square root of the mean of the squares of the deviations. This parameter is used to measure the dispersion or variability of a large number of measurements, for example, the weights of contents of several million capsules. This set of items or measurements approximates the *population*

or the *universe*, and σ is therefore called the *standard deviation of the universe*. The standard deviation of the population is known as the *sample standard deviation* and is designed by the letter *s*. In which $\Sigma | X_i - X |$ is the sum of the absolute deviations from the mean. The formula is written as: (the *s* for very large number of measurements).

Population mean deviation = δ

مقياس التشتت measure of dispersion *

1- variane $\equiv S^2$ التباین

S² =
$$\frac{\sum(Xi-X)^2}{(N-1)}$$
 used For small number of measurements
Or $\sigma^2 = \frac{\sum(Xi-X)^2}{N}$ used For large number of measurements

The number N-1 is known as the *number of degrees of freedom*. It replaces N to reduce the bias of the standard deviation s, which on the average is lower than the universe standard deviation .

The difference between the arithmetic mean and the *true* or *absolute* value express the *error* that can often be used as a measure of *accuracy* of the method.

Measures of Spread $s = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N - 1}} = \sqrt{\frac{\sum_{i=1}^{N} d_i^2}{N - 1}}$ $RSD = s_r = \frac{s}{\bar{x}}$ $RSD \text{ in ppt} = \frac{s}{\bar{x}} \times 1000 \text{ ppt}$ $CV = RSD \text{ in percent} = \frac{s}{\bar{x}} \times 100\%$

Ex1:	Consider	the	foll	lowing	sets	of data
The second secon	Comprace		101	io wing	0.000	or auto

31.60	31.76	31.62
31.60	31.71	31.47
31.71	31.53	31.64

Calculate mean, deviation- average deviation, and standard deviation.

الانحراف القياسي (SD) الانحراف القياسي

The positive square root of the variance

$$S = \sqrt{\sum \frac{(Xi-x)^2}{N-1}} \qquad \qquad \sigma = \sqrt{\sum \frac{(Xi-x)^2}{N}}$$

3. Range the range between the highest and lowest value of a set of results.

4. Relative standard deviation الانحراف القياسي النسبي
$$RSD = \frac{s}{x}$$

Or coefficient of variance معامل التباین : It is the relative standard deviation as percentage

الانحراف القياسي النسبي بالمئة
$$Cv = \frac{s}{x} \times 100 \equiv RSD\%$$

Lec.4

* Accuracy and precision

1. The rang of analytical value is near to true value التوافق (الاتقان)

2. The precision (الدقه) The rang of analytical value (one near from other) without observe to true value.



CHARACTERIZING EXPERIMENTAL ERRORS

Accuracy

- Measure of how close a measure of central tendency is to the true or expected value (μ)
- Expressed in terms of:
 - 1. Absolute Error

$$E = x_i - x_t$$

2. Relative Error

$$E_r = \frac{x_i - x_t}{x_t} \times 100\%$$

CHARACTERIZING EXPERIMENTAL ERRORS

Precision

- Measure of spread of data about a central value
- Errors affecting the distribution of measurements around a central value are called indeterminate and are characterized by a random variation in both magnitude and direction

CHARACTERIZING EXPERIMENTAL ERRORS



H.W : three student make experiment in lab rotary to determine the percentage of sample have true value equal (12-10) determine acc. And pre. For each one ??

А	В	С
12.12	12.10	12.21
12.09	12.30	12.19
12.10	11.90	12.20

3. there are several methods for reporting the precision of data.

* deviation from mean The deviation between an experimental value and average of set of data

$$\mathbf{D} \equiv \mathbf{d} \equiv \mathbf{x}\mathbf{i} - \mathbf{x}$$

 $Xi \equiv$ any measured $x \equiv$ average of all measured.

* Average deviation (d)

$$d = \frac{\sum d}{N}$$

ex/ A sample containing chloride ion, the percentage of $Cl^{\text{-}}$ ion was determined , calculate \bar{X} , d, and \bar{d}

Sample	%Cl	X	d	d
1	24.39			
2	24.28			
3	24.20			

4. Method of expressing accuracy

* Absolute error (E) الخطا المطلق Different between true value and measured value .

E=Xi-Xt

Xi = measured value Xt = true value (accepted value)

مقياس الخطأ المطلق (النسبى) relative error *

$$\mathbf{Er} = \frac{xi - xt}{xt} \equiv \frac{E}{xt}$$

% $\mathbf{Er} = \frac{xi - xt}{xt} \mathbf{x100}$

* % Recovery (الاستردادية) = % Rec
$$\equiv \frac{xt-E}{xt} \ge 100$$
 (theoretical)

$$\% \text{Rec} = \frac{Exp.value}{True \ value} \ \text{x100} \quad (\text{practical})$$

Example: suppose :- you have (3) sample

True value	Experimental value	%Rec.
3ppm	2.99	%Rec= $\frac{Exp.value}{True value}$ x100
		$=\frac{2.99}{3}$ x100
4ppm	3.96	
5ppm	4.98	

The % Rec. for method =

The average of all $\% \text{Rec} = (\% \text{Rec})_1 + (\% \text{Rec})_2 + (\% \text{Rec})_3 / 3$

 $x^- \equiv$ Average of Absorbance results.(measured)

مناطق الثقة Confidence intervals

The confidence level (CL) is the probability that the true mean lies within a certain interval and is often expressed as a percentage.

The probability that a result is outside the confidence interval is often called the significance level.

 \Box If we make a single measurement x from a distribution of known σ , we can say that the true mean should lie in the interval x± z δ with a probability dependent on z.

$$CI for \mu = x \pm z\sigma$$

 \Box However, we rarely estimate the true mean from a single measurement. Instead, we use the experimental mean(\bar{x}) of N measurements as a better estimate of μ .

**(C.L) when $s \equiv \sigma$ (it is called confidence limit) حدود الثقة

$$\mathbf{C} \cdot \mathbf{L} = \bar{\mathbf{x}} \pm \frac{Z\sigma}{\sqrt{N}}$$

Z= statistical factor based upon normal error.

This table value of Z for various confidence levels)

لمستوبات ثقة مختلفة

%C.L	Ζ
50	0.67
80	1.29
90	1.64
95	1.86
99	2.28
99.9	3.29

Finding the confidence interval when δ is unknown

 \Box In case of limitations in time or in the amount of sample available, a single set of replicate measurements must provide not only a mean but also an estimate of precision.

 \Box s calculated from a small set of data may be quite uncertain.

 \Box Thus, confidence intervals are necessarily broader when we must use a small sample value of s as our estimate of δ .

 \Box To account for the variability of s, we use the important statistical parameter t, which is defined in exactly the same way as *z*, except that *s* is substituted for δ .

For the mean of N measurements

$$\mathbf{C}.\mathbf{L} \equiv \mathbf{U}^{-} = \mathbf{X} \pm \frac{t \, s}{\sqrt{N}}$$

Like z, *t* depends on the desired confidence level as well as on the number of degrees of freedom in the calculation of s.

t approaches z as the number of degrees of freedom becomes large.

* The confidence interval for the mean of N replicate measurements can be calculated from t as

C.L =
$$\vec{X} \pm \frac{t s}{\sqrt{N}}$$
 Example:

The standard deviation (σ) for chloride analysis is (0.2 percent) estimate the (90) percent confidence limit for sample have 52-10 percent chloride base upon

- a) Single analysis
- b) Triplicate analysis
- c) Average of (5) analysis.

Solution:

a) %C.L =
$$52.10 \mp \frac{(1.64)(0.2)}{\sqrt{1}}$$

= 52.10 ∓ 0.33 percent.
b) %90 C.L =52.10 $\mp \frac{(1.64)(0.2)}{\sqrt{3}}$ = 52.10 \mp 0.19 percent. c) %90 C.L = 52.10 $\mp \frac{(1.64)(0.2)}{\sqrt{5}}$

Note: C.L	(increase)) when r	neasured	increased

	Experimental	Accepted
a)	12.67	12.81
b)	60.08	59.94
c)	27.33	27.25

A clinical chemist obtained the following data for the alcohol content of a sample of blood: $% C_{a}H_{s}OH$: 0.084, 0.089, and 0.079. Calculate the 95% confidence interval for the mean assuming that (a) the three results obtained are the only indication of the precision of the method and that (b), from previous experience on hundreds of samples, we know that the standard deviation of the method $s = 0.005\% C_{a}H_{s}OH$ and is a good estimate of σ .

Solution

(a) $\sum x_i = 0.084 + 0.089 + 0.079 = 0.252$ $\sum x_i^2 = 0.007056 + 0.007921 + 0.006241 = 0.021218$ $s = \sqrt{\frac{0.021218 - (0.252)^2/3}{3 - 1}} = 0.0050\% \text{ C}_2\text{H}_5\text{OH}$

In this instance, $\bar{x} = 0.252/4 = 0.084$. Table 7-3 indicates that t = 4.30 for two degrees of freedom and the 95% confidence level. Thus, using Equation 7-5,

95% CI =
$$\bar{x} \pm \frac{ts}{\sqrt{N}} = 0.084 \pm \frac{4.30 \times 0.0050}{\sqrt{3}}$$

= 0.084 ± 0.012% C₂H₅OH

(b) Because s = 0.0050% is a good estimate of σ , we can use z and Equation 7-2

95% CI =
$$\bar{x} \pm \frac{z\sigma}{\sqrt{N}}$$
 = 0.094 ± $\frac{1.96 \times 0.0050}{\sqrt{3}}$
= 0.084 ± 0.006% C₂H₅OH

Note that a sure knowledge of σ decreases the confidence interval by a significant amount even though s and σ are identical.

Home work:

- 1. Calculate the absolute error and percent error for the following value :
- 2. Consider the following set of data

Α	В	С
21.63	78.91	3.16
21.40	79.05	3.19
21.56	79.17	3.18
21.53	78.97	3.23

Cal.: mean, median, range, average deviation from mean, standard deviation.

- **3.** Experimental results obtained from analysis KIO3 is (0.8mg) calculate the percentage relative error if the amount of KIO3 in sample are :
 - a) 10 mg
 - b) 0.04 g
 - c) 160 mg
 - d) 0.8 g
- 4. Calculate the standard deviation for each sets of data :
 - a) 4.06, 4.08, 4.14, 4.12
 - b) 17.91, 18.04, 17.95
- 5. These data are obtained when a sample known contain (21.68) percent (Fe) was analyzed by new method

Sample	% Fe
1	21.46
2	21.80
3	21.77
4	21.40
5	21.74

Cal. Mean, median, range, standard deviation, variance, relative standard deviation percent, absolute error, relative error, recovery percent.

6. The percentage of sulphate in sample were (0.75, 0.69, 0.72) % and the standard deviation (s) of the method was equal to 0.5%. Calculate the confidence limit at %95 confidence level of analysis (t value equals 3.1).

Lec.5 <u>CHAPTER (3)</u>

Introduction to Gravimetric analysis methods

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

<u>Gravimetric analysis</u>(G.A) is a quantitative determination of the amount of analyte through a precipitation process, precipitate isolation, and determination of isolated product weight.

There are two general analysis in G.A

Direct analysis
 Measured the weight of product of reaction that have known structure
 AgNO₃ + NaCl → AgCl + NaNO₃
 Measured (wt) AgCl after drying and washing .
 Indirect analysis
 Measured the loss in weight by: * volatilization of species
 Ex/ determination of water in CaCO₃. X H₂O
 CaCO₃.xH₂O → CaCO₃ + H₂O↑
 Different in weight before and after heating equivalent (wt) H₂O

Different in weight before and after heating equivalent (wt) H₂O Heating Ex/ CaCO₃ \longrightarrow CaO + CO₂↑ (*Different in weight equivalent CO*₂) 900C⁰ Ex/ when adsorption H_2O or CO_2 by these substances H_2SO_4 , P_2O_5 , $CaCl_2$.

or Isolation of species $Ex/sample content (Ag^++ Pb^{++})$ in mixture we can isolation one from other by ppt as AgCl+ PbCl₂, the hot water can dissolved PbCl₂ and by centrifuge in order to separated PbCl₂ as dissolved solution from AgCl as precipitate.

Types of Gravimetric Methods

<u>Precipitation gravimetry</u>: 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.

<u>Electrogravimetry</u>: The analyte is separated by deposition on an electrode by an electrical current

<u>Particulate gravimetry</u> The analyte is determined by separating it from the sample's matrix using a filtration or an extraction. The determination of total suspended solids is one example of particulate gravimetry.

Gravimetric methods	Definition	Application
Precipitation gravimetry	A gravimetric method in which the signal is the mass of a precipitate	Suspended solid: determination of Cl ⁻ by AgNO ₃ precipitating to AgCl (filtration)
Electrogravimetry	A gravimetric method in which the signal is the mass of an electrodeposit on the cathode or anode in an electrochemical cell	Aqueous ion: determination of Pb ²⁺ by oxidizes to PbO ₂ and deposited on Pt anode (chemical converting)

TYPES OF GRAVIMETRIC METHODS

Volatilization gravimetry	A gravimetric method in which the loss of a volatile species gives rise to the signal (remove the volatile species)	Moisture: determination of water in food content by heat or thermal or chemical energy (heating
Particulate gravimetry	A gravimetric method in which the mass of a particulate analyte is determined following its separation from its matrix	Suspended solid: determination of solid that can be separated from the sample (filtration or extraction)

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. for determining the $[Ca^{2+}]$ in water:

$$2NH_{3(aq)} + H_{2}C_{2}O_{4(aq)} \rightarrow 2NH_{4(aq)}^{+} + C_{2}O_{4(aq)}^{2-}$$

$$Ca^{2+} + C_{2}O_{4(aq)}^{2-} \rightarrow CaC_{2}O_{4(s)}$$
filtered, dried, ignited
$$CaC_{2}O_{4(s)} \xrightarrow{\Delta} CaO_{(s)} + CO_{(g)} + CO_{2(g)}$$

After cooling, the precipitate is weighed and the mass is determined.

STEPS IN GRAVIMETRIC ANALYSIS

Gravimetric Analysis

- 1. Dissolve a sample after weighing.
- 2. A precipitating agent with excess amount is added to this solution.
- 3. The resulting precipitate is filtered, dried (or ignited) and weighed.

4. Determine the amount of the original ion from the mass of the precipitate (known composition).

5. Stoichiometry is important (write down the chemical equation!).





TYPES OF PRECIPITATING REAGENTS

Selective (react with a few analytes) Example: AgNO3 $Ag^+ + Halides (X^-) \longrightarrow AgX(s)$ $Ag^+ + CNS^- \longrightarrow AgCNS(s)$

Specific (react with 1 analyte only) Example: Dimethylglyoxime (DMG) that precipitates only Ni²⁺ from alkaline solutions 2 DMG + Ni²⁺ ____ Ni(DMG)₂(s) + 2 H⁺
*Specific reagents: react only with a single chemical species.
Selective reagents: react with a limited number of species.

Properties of Precipitates and Precipitating Reagents

A gravimetric **precipitating agent** should react **specifically** or at least **selectively** with the **analyte** and give **precipitates** that is:

1. Enough **particle size** for retaining on filter paper (Filterability)

It must be possible to isolate the precipitate quantitatively from the liquid phase by filtration method, its depended upon particle size, when particles (small) filtration process is difficult

2. High purity (The precipitate should be free from impurities and free of contaminants)

3.Low solubility that no significant loss of the analyte occurs during filtration and washing

The ppt must have low solubility

* when ksp small (S) small

* when ksp large (S) large

For example AgCl have ksp = 10^{-10} AgCl more stable than PbCl₂

PbCl₂ have ksp = 10^{-4}

4. Unreactive with air (stable) The precipitate may be constant at room temperature and not adsorption H_2O or CO_2 from air.

5.Known stoichimetric composition after it is dried or, if necessary, ignited. The

precipitate must be known chemical composition to weight and calculate the percent composition of the sample.

Lec.6

GRAVIMETRIC ANALYSIS

The result of G.A are generally computed from two experimental measurement :-

- 1- wt of sample
- 2- wt product of known composition derive from that sample.

* GF: used to determine percent of element or compound which its form the ppt .

Calculations of analyte content requires knowledge of :

Chemistry Stoichiometry Composition of precipitate

For example: determination of silver or chloride by the formation of AgCl (s).

 $Ag^+ + Cl^- \longrightarrow AgCl(s)$ •Precipitation occurs when the value of [Ag⁺][Cl⁻] exceeds the solubility product Ksp of AgCl (1.8×10^{-10}) .

The precipitate obtained is usually different from the weight of the analyte we want to report.

•The gravimetric factor (GF): weight of analyte per unit weight of precipitate.

$$GF = \frac{FW \text{ analyte } (g/mol)}{FW \text{ precipitate } (g/mol)} \times \frac{a}{b} (mol \text{ analyte } /mol \text{ precipitate})$$

Gravimetric Factor (GF): a = moles of analyte b = moles of precipitate

$$GF = \frac{a}{b} * \frac{fwt \ analyte}{fwt \ precipitate}$$
(g/mol) (g/mol)

GF = g analyte / g precipitate % analyte = (weight analyte (g) / weight sample (g)) x 100%

% (w/w) analyte (g) = ((wt precipitate (g) x GF) / wt sample) x 100%

M.wt known

Table 2 explain the way to calculate GF

unk.sub.	Known sub.	GF
BiCl ₂	Bi ₂ O	M.wt.BiCl2
		M.wt Bi203 x1
KNO ₃	K_2PtCl_6	$\underline{M.wt.KNO3 x2}$
		M.wt K2PtCl6 x1
K ₃ PO ₄	K ₂ PtCl ₆	<i>M.wt.K3P04 x2</i>
		M.wt K2PtCl6x3
Fe ⁺³	CaCO ₃	$eq.wtFe - \frac{At.wtFe}{3}$
		$\frac{1}{eq.wt \ CaCO3} = \frac{M.wt \ CaCO3}{2}$
P ₂ O ₃	Mg ₂ P ₂ O ₇	<i>M.wt</i> . <i>P205 x</i> 1
		<i>M.wt Mg2P207 x1</i>
Р	Mg ₂ P ₂ O ₇	At.wt.P x2
		<i>M.wt P207 x</i> 1
Ι	$Hg_5(IO_6)_2$	At. wt. I x2
		$\overline{M.wt} \operatorname{Hg5}(106)2 x1$
HgO	Hg5(IO6)2	M.wt.HgOx5
		<i>M.wt</i> Hg5(I06)2 <i>x</i> 1
Bi ₂ S ₃	3 BaSO ₄	<i>M.wt</i> .Bi2S3 <i>x</i> 1
		<i>M.wt</i> BaSO4 <i>x</i> 3

EXAMPLE 1:



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

Analyte:	Precipitate:
NaCl	AgCl

$$g \frac{\text{NaCl}}{\text{AgCl}} = \frac{\text{FW NaCl}(g/\text{mol})}{\text{FW AgCl}(g/\text{mol})} \times \frac{1}{1} (\text{mol NaCl/mol AgCl})$$
$$\text{GF} = \frac{1}{1} \times \frac{58.44 \text{ g/mol}}{143.32 \text{ g/mol}} = 0.4078 \text{ g NaCl/mol AgCl}$$

EXAMPLE 2: Calculate the grams of analyte per gram of precipitate for the following conversions:

Analyte:	Precipitate:
2K ₂ HPO ₄	$Mg_2P_2O_7$

$$g \frac{K_{2}HPO_{4}}{Mg_{2}P_{2}O_{7}} = \frac{FW K_{2}HPO_{4} (g/mol)}{FW Mg_{2}P_{2}O_{7} (g/mol)} \times \frac{2}{1} (mol_{2}HPO_{4}/mol_{2}Mg_{2}P_{2}O_{7})$$

$$GF = \frac{2}{1} \times \frac{174.2 g/mol}{222.6 g/mol} = 1.565 g_{2}HPO_{4}/mol_{2}Mg_{2}P_{2}O_{7}$$

Ex/ Calculate the weight AgCl when added excess of AgNO₃ to 0.75g of BaCl₂ if M.wt AgCl=143.3 and M.wt BaCl₂ =208.3

Solution :

 $AgNO_3 + BaCl_2 \rightarrow AgCl \downarrow + BaNO_3$

$$GF = \frac{eq.wt \ AgCl}{eq.wt \ BaCl2} = \frac{\frac{143.4}{1}}{\frac{208.3}{2}} = 1.38$$

Wt. AgCl =wt. BaCl₂ x GF

= 0.75 x1.38 =104 gram.

Ex/ Calculate the $\,$ GF of change Fe to Fe_2O_5 . Fe_3O_4 and $Fe_7S_5,$ if At.wt:- $Fe{=}55.8$, $\,O{=}16,\,S{=}32.$

Solution :

Fe: known and

Fe₂O₅, Fe₃O₄ and Fe₇S₅ (unknown)

GF Fe₂O₅ =
$$\frac{M.wt Fe_{2}O5 X1}{At.wt Fe X2}$$
 = 1.43

GF Fe₇S₅ = $\frac{M.wt \text{ Fe7S5 } X1}{At.wt \text{ Fe } x7}$ =1.5

$$GF Fe_3O_4 = \frac{M.wt Fe_3O4 X1}{At.wt Fe X3} = 1.38$$

Ex/ pure sample of NaCl have (2.5g) give (6.3g) of AgCl when added AgNO₃, of At.wt of Cl=35.5, Ag=107.8, Calculate the At.wt of Na.

Solution :

the relation between (wt.) & M.wt. :

$$\frac{wt \, NaCl}{M.wt \, NaCl} = \frac{wt \, AgCl}{M.wt \, AgCl}$$

$$M.wt \, NaCl = \frac{wt \, NaCl \, x \, M.wt \, AgCl}{wt \, AgCl}$$

$$At.wt \, Na +35.5 = \frac{(2.5)x(107.8+35.5)}{6.3} = 23$$

Ex/ 0.4 g sample of mixture containing only ($K_2SO_4+Na_2SO_4$) was dissolved. The sulphate ion was precipitated as (BaSO₄) when BaCl₂ is added, the weight of BaSO₄ was found (0.576) gram, calculate the percent of Na₂SO₄ and k₂SO₄ in sample, the M.wt BaSO₄ = 233.4,

M.wt $K_2SO_4 = 174.2$, and M.wt $Na_2SO_4 = 142.0$

Solution :

You have (2) unknown

wt. K_2SO_4 +wt NaSO₄ =0.4g

wt. $K_2SO_4 = 0.4$ -wt. $NaSO_4$(1)

wt. BaSO₄ (from NaSO₄) +wt. BaSO₄ (From K_2SO_4) =0.575.....(2)

OR $X_1 + X_2 = 0.575 \dots (2)$

1- To determine value of X1 :-

BaSO ₄	Na_2SO_4
233.4	142
X1	wt. Na ₂ SO ₄
$X_1 = \frac{wt.NaSO4 \ x \ 233.4}{142}$	
2- To determine	value of X ₂
<u>BaSO4</u>	$\underline{K_2SO_4}$
233.4	174
<u>X2</u>	wt. K ₂ SO ₄
$X2 = \frac{wt.K2SO4X233.4}{174}$	

2 تعويض قيم x1, x2 ي معادلة رقم x1, x2 $\therefore \frac{wt \, Na2SO4 \, X233.4}{142} + \frac{wt \, K2SO4 \, X233.4}{174} = 0.575....(2)$ 0.575= 1.644wt. Na2SO4 + 1.341wt. K2SO4

1.644wt. Na2SO4= 0.575 -1.341wt. K2SO4

1.644 بقسمة طرفي المعادلة على1.644 wt.Na₂SO₄= 0.3497- 0.8156wt.K₂SO₄(3) 1 تعويض معادلة رقم 3 في معادلة رقم ث wt. K₂SO₄ =0.268 % K₂SO₄ = $\frac{0.268}{0.4}$ X100 =67% % Na₂SO₄=100-67=33%

HOME WORK:

- 1- Sample as FeCO₃ dissolved and after oxidation and precipitation to FeO₃ (wt.=1g) ,calculate wt. of (Fe) as [FeCO₃ or Fe or FeO) in sample .
- 2- Calculate the percent of (P) in sample have (0.68g), then it was precipitated as MgNH₄PO₄ and it oxidized by heating to MgP₂O₇ with weight of 0.435g.
- 3- Calculate the percent of Fe and Fe₃O₄ in sample (0.04g), this sample dissolved and oxidized toFe₂O₃ (wt.=0.09g).
- 4- 0.87g sample of mixture of sodium bromide and potassium Bromide, when added AgNO₃ it yield silver Bromide (wt.=1.5g), what are the percent of two salts in sample?

ملاحظة: نحتاج الى الأوزان الذرية نجدها في اي مصدر لمادة الكيمياء التحليلية.

5- Suppose you wish to determine the amount of iron in a sample. Which of the following compounds—FeO, Fe₂O₃, or Fe₃O₄—provides the greatest sensitivity?

To determine which form has the greatest sensitivity, we use a conservation of mass for iron to find the relationship between the precipitate's mass and the mass of iron.

$$g \text{ FeO} = g \text{ Fe} \times \frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} \times \frac{71.85 \text{ g FeO}}{\text{mol Fe}} = 1.286 \times \text{g Fe}$$
$$g \text{ Fe}_2\text{O}_3 = g \text{ Fe} \times \frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} \times \frac{159.70 \text{ g Fe}_2\text{O}_3}{2 \text{ mol Fe}} = 1.430 \times \text{g Fe}$$
$$g \text{ Fe}_3\text{O}_4 = g \text{ Fe} \times \frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} \times \frac{231.55 \text{ g Fe}_3\text{O}_4}{3 \text{ mol Fe}} = 1.382 \times \text{g Fe}$$

Of the three choices, the greatest sensitivity is obtained with Fe2O3 because it provides the largest value for *GF*.

Lec.7

Chapter (4)

<u>The solubility of precipitates</u>

All precipitation gravimetric analysis share two important attributes. **First**, *the precipitate must be of low solubility, of high purity*, and of *known composition if its mass is to accurately reflect the analyte's mass*. **Second**, *the precipitate must be easy to separate from the reaction mixture*.

precipitate's solubility must be minimal. The accuracy of a total analysis technique typically is better than $\pm 0.1\%$, which means that the precipitate must account for at least 99.9% of the analyte. Extending this requirement to 99.99% ensures that the precipitate's solubility does not limit the accuracy of a gravimetric analysis.

We can minimize solubility losses by carefully controlling the conditions under which the precipitate forms. This, in turn, requires that we account for every equilibrium reaction affecting the precipitate's solubility. For example, we can determine Ag+ gravimetrically by adding NaCl as a precipitant, forming a precipitate of AgCl.

$$\operatorname{Ag}^+(aq) + \operatorname{Cl}^-(aq) \rightleftharpoons \operatorname{AgCl}(s)$$

If this is the only reaction we consider, then we predict that the precipitate's solubility, S_{AgCl} , is given by the following equation.

$$S_{AgCl} = [Ag^+] = \frac{K_{sp}}{[Cl^-]}$$

It suggests that we can minimize solubility losses by adding a large excess of Cl⁻. In fact, adding a large excess of Cl⁻ increases the precipitate's solubility.

Ksp = solubility product constant

The constant (ksp) : is an equilibrium condition for saturated solution of slightly soluble strong electrolytes.

[Cl⁻][Ag⁺]< Ksp unsaturated solution هذا لايحدث ترسيب [Cl⁻][Ag⁺]= Ksp saturated solution لايحدث ترسيب [Cl⁻][Ag⁺]> Ksp super saturated solution يحدث ترسيب يقل تركيز كلا الايونين الى ان نصل الى الحالة: [Cl⁻][Ag⁺]= Ksp][Cl⁻]

* The solubility (s) : disappearance of atoms or molecules or ions of solute between atoms or molecules of solvent

* solution : homogenous mixture of two substance solute and solvent.

*solubility : amount of solute can dissolved in known size of solvent.

Note:

The substance may divided to polar substance and nonpolar substance

 \ast polar sub. As :NaCl , HCl, NaOH (salt, acid, base) dissolved in H2O (H2O polar solvent).

 \ast non polar sub. as: Benzen (organic compound) not dissolved in H_2O and it dissolved in organic solvent .

The mechanism of solubility

AgCl as precipitate slightly soluble in H2O because , it have small value of solubility product constant ($ksp=10^{-10}$)

But the precipitate $PbCl_2$ have (ksp=10⁻⁴) it dissolved in hot water.

Ex/

AgCl (s) $\stackrel{\mathrm{K}_1}{\leftrightarrow}$ AgCl (aq).....(1)

 $K_1 = \frac{AgCl(aq)}{AgCl(s)}$ for first equation

 $K_2 = \frac{[Ag^+][Cl^-]}{AgCl(aq)}$ for second equation

$$\mathbf{K}_1 \ge \mathbf{K}_2 = \frac{AgCl(aq)}{AgCl(s)} \ge \frac{[Ag^+][Cl^-]}{AgCl(aq)}$$

If :

 $[AgCl_{(s)}] = 1$ (at constant temp.)

 $K_1 X k_2 = ksp = [Ag^+][Cl^-] \dots (3)$

Ex/ Calculate the weight of Barium iodate $Ba(IO_3)_2$ if it dissolved in 500ml of distilled water (D.W) at $25C^0$ if M.wt of ppt. = 487 g/mole and ksp= 1.57×10^{-9} .

Solution :

Ba(IO₃)₂ ↔ Ba⁺⁺ + 2IO₃⁻ S 25 Ksp= [B⁺⁺][IO₃⁻]² 1.57 X10⁻⁹ = (S)(2S)² S=7.3 x10⁻⁴ mole/l M= $\frac{mole}{l} = \frac{\frac{wt}{m.wt}}{\frac{v}{l}} = \frac{wt}{m.wt} x \frac{1000}{v}$ $\therefore wt = \frac{m.m.wt xv}{1000} = \frac{7.3 x10^{-4} x 487 x500}{1000}$ wt.= 487 g

The rules for solubility of inorganic compounds in water

The application of solubility product constant ksp.

Ksp is used in nonhomogeneous system.

The most application :

* formation ppt or not

Ex/ when AgNO₃ added to NaCl the ppt (AgCl) form or not???

 $AgNO_3 \rightarrow Ag^+ + NO_3^ NaCl \rightarrow Na^+ + Cl^-$

 $Ag^+ + Cl^- \rightarrow AgCl\downarrow$

Ksp (AgCl) =10⁻¹⁰

I.P = Ionic product

If:

- I.P < ksp unsaturated solution. (no ppt)
- I.P= ksp saturated solution (no ppt)
- I.P> ksp super saturated solution. (ppt form).

Ex/ When equal volume of 0.001 M AgNO₃ mixed with 0.02 MKBrO₃, explain the AgBrO₃ as ppt. appear or not, if ksp = $6x10^{-5}$?

Solution :

* KBr	$O_3 \rightarrow K$	$+ BrO_3^-$
0.02	2	0.02
* AgN	$O_3 \rightarrow A$	$g^{+} + NO_{3}^{-}$
0.00	0.	001
Ag^+	+ BrC	$O_3^- \leftrightarrow AgBrO_3$
0.001	0.02	,
2	2	-
-	-	
Note :		

The relation between (M&v) reversible when the vol. increase (became double) the concn decrease .(M= $\frac{mole}{v}$)

$$\therefore I.P = [Ag^+] [BrO_3^-]$$

$$\frac{0.001}{2}$$
 × $\frac{0.02}{2}$ = 5 x10⁻⁶

 \therefore I.P =5 x10⁻⁶ < ksp [=6x10⁻⁵]

Unsaturated solution (no ppt. is appeared).

Home work:

5 ml of 10^{-5} M H₂SO₄ added to 5ml of 10^{-5} M BaCl₂, explain the BaSO₄ (ppt) formation or not? ksp (BaSO₄)= 10^{-10} .

Ex/ 50 ml of 0.001 M H₂SO₄ added to 10 ml of 0.02 M BaCl₂, explain the formation of BaSO₄ as ppt. or not ?? ksp (BaSO₄)= 10^{-10} .

Solution:

The new conc. of H₂SO₄ and BaCl after the mixture is added are :-Total vol. became =60ml $50x0.001 = (50+10) M_{H2SO4}$

$$M_{H2SO4} = \frac{1}{60} = \dots [SO_4^{-1}]$$

$$10 \ge 0.02 = (50+10) M_{BaCl2}$$

$$M_{BaCl2} = \frac{10 \ge 0.02}{60} = \dots [Ba^{++}]$$

$$I.P = [Ba^{++}] [SO_4^{-1}]$$

$$(\frac{10 \ge 0.02}{60}) (\frac{50 \ge 0.001}{60})$$

$$I.P = \dots, Ksp = \dots$$

Lec.8

The solubility and solubility product constant are affected with several factors, as following;

1- Common Ion effect.

From Le chatelier principle the (s) of an electrolyte should be lower by prescens in solution , an excess of one of ions common to the compound.

In G.A using an excess of precipitating agent to minimize solubility . "تقل الذوبانية بوجود الايون المشترك في المحلول"

Ex/



Ex/ what is the solubility of Ba(IO₃)₂ in 0.02 M solution of KIO₃ if ksp for Ba(IO₃)₂ = 1.7×10^{-9} .

Solution :

$$Ba(IO_3)_2 \leftrightarrow Ba^{++} + 2 IO_3^{-}$$
(S) (2S)

Ksp =[S][2S]² In (D.W) S= 7.3×10^{-4} In (D.W)

*when 0.02 M KIO₃ added to solution.

Ba(IO₃)₂ ↔ Ba⁺⁺ + 2IO₃⁻ (S) (2S) KIO₃ → K⁺ + IO₃⁻ 0.02 0.02 Ksp = [S][2S +0.02]² ↓ Small value = negligible

 $Ksp = [S][0.02]^2$

 $1.5 \text{ x}10^{-9} = [S][0.02]^2$, $S=3.9 \text{ x}10^{-6} \text{ S} = 3.9 \text{ x} 10^{-6}$

Note

[S] decrease in present common ion If:
* the conc. Of common ion less than %10
* the solubility increase when the conc. of common ion more than %10

Home work:

Calculate the solubility of CaF₂? If ksp [CaF₂]=4x10⁻⁴

- In water
- In 0.01 M CaCl₂
- In 0.01 M NaF

2. effect of PH on (S) and (ksp)

The solubility effect by conc. of (H_3O^+) and $[OH^-]$ in solution Ex/ if we have Mg(OH)₂ ppt. Mg(OH)₂ \leftrightarrow Mg⁺⁺ + 2OH⁻ *1ST when $[OH^-]$ increase Mg(OH)₂ \leftrightarrow Mg⁺⁺ + 2OH⁻ Back reaction \leftarrow \uparrow increase [S] decrease when $[OH^-]$ increase *2nd when $[H_3O^+]$ increase.

Ex/

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

When $[H_3O^+]$ increase [S] increase because $[H_3O^+]$ react with (F^-) to form (HF)

 F^- decrease the reaction go forward and the solubility of CaF_2 increase (this type is more complicated than the first type.)

ثابت حاصل الاذابة المؤثر.(Effective solubility product (Keff

Value of Keff change with (pH)

pH depended upon \propto

∝: conc. Fraction كسر التركيز

 $\propto_0 + \propto + \propto 2 \dots \propto \infty = 1$

The weak acid for example (HA)

 $HA \leftrightarrow H^+ + A^-$ (partial dissociation).....(1)

The solution have two species

[HA] : conc. of acid

 $[A^-]$: ion acid

Ca: conc. of acid (total conc.) \blacksquare Ca= [HA]+ [A⁻]

لتأين التأين Ka=
$$\frac{[H^+][A^-]}{[HA]}$$
(2)

Rearrangement :

$$[HA] = \frac{[A^{-}][H^{+}]}{Ka} \dots (3)$$

$$: ext{ isometry } ext{ if } ca = [HA] + [A^{-}]$$

$$: Ca = \frac{[A^{-}][H^{+}]}{Ka} + [A^{-}]$$

$$Ca = \frac{[A^{-}][H^{+}] + [A^{-}]Ka}{Ka}$$

$$Ca = \frac{[A^{-}][H^{+} + Ka]}{Ka} \dots (4)$$

When rearrangement this eq. $\propto 1 = \frac{[A^-]}{Ca} = \frac{Ka}{[H^+ + Ka]}$

 $[A^{\text{-}}] = Ca \times \propto 1$

Note: $\propto \equiv conc. fraction$

To calculate (∝) depended upon constant (ka value) &(pH value)

The salts come from reaction of acid + base \rightarrow give salt +H₂O

1- The salt (MA)
ionization
MA
$$\longrightarrow$$
 M⁺ + A⁻ NOTE: A⁻ derived from mono acid HA

At known value of (pH)

Ksp=
$$[M^+]$$
 [Ca× \propto 1]
Or $\frac{ksp}{\alpha 1} = [M^+]$ [Ca] \equiv keff.

2- If the salt
$$MA_2$$

ionization
 $MA_2 \longrightarrow M^{++} + 2A^{-}$

First state: [A⁻] derive from mono acid [HA] in this salt used two part of acid or two molecules (2HA)

$$\therefore keff = \frac{ksp}{(\alpha 1)^2}$$

Second state: If the salt derived from (H₂A) acid

$$H_{2}A \leftrightarrow HA^{-} + H^{+} \qquad k_{1} = \frac{[HA -][H +]}{[H2A]}$$

$$HA \leftrightarrow A^{-2} + H^{+} \qquad k_{2} = \frac{[A - 2][H +]}{[HA -]}$$

$$Ca = H_{2}A + HA^{-} + A^{=} \qquad \therefore \alpha 2 = \frac{K1K2}{[H^{+}]^{2} + [H^{+} \times K1] + K1K2}$$

$$\propto A^{=} = \propto 2 \qquad \therefore keff = \frac{ksp}{\propto 2}$$

Note $\cdot \propto A^{=} - \propto 2 -$	$[A^{=}]$	جزء
$\mathbf{NOIE}: \mathbf{A} = \mathbf{A} \mathbf{Z} =$	${[H2A]+[HA^-]+[A^=]}$	

EX/ Calculate the molar solubility of CaF₂ in acidic solution of HCl have PH=3 if ksp CaF₂= $4x10^{-11}$, ka(HF) = $6 x10^{-4}$.

Solution:

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

Salt derive from two molecules of [HF] weak acid

 $[H^{+}] = 10^{-PH} = 10^{-3}$ $\therefore \alpha 1 = \frac{Ka}{H^{+} + Ka} = \frac{4x10^{-4}}{10^{-3} + 610^{-4}} = 0.38$ $(\propto 1)^{2} = 0.14$ $Keff = \frac{Ksp}{(\propto 1)^{2}} = \frac{4x10^{-11}}{0.14} = 2.9x \ 10^{-10}$ $CaF_{2} \rightarrow Ca^{++} + 2F^{-}$ $S \qquad 2S$ $Keff = [Ca^{++}][F^{-}]^{2}$ OR $Keff = [S][2S]^{2}$ $2.9x \ 10^{-10} = 4S^{3}$

Home work

 $S = 4.2 \text{ x} 10^{-4} \text{ M}.$

Calculate the molar solubility of CaC_2O_4 in solution of HCl have PH=3 if ksp $(CaC_2O_4) = 2 \times 10^{-9}$ and $k1 = 6.5 \times 10^{-2}$, $k2 = 6.1 \times 10^{-5}$.

3. Effect of Complex ion formation on solubility

The solubility of precipitated may be effect by presence in solution an ion that will react with anion or cation of (ppt) to form soluble complex.

 $Al(OH)_3 \leftrightarrow Al^{3+} + 3OH^{-}$

In presence (F⁻) in solution

 Al^{3+} + $6F^{-}$ \leftrightarrow $[AlF_6]^{=}$

Soluble complex

 Al^{3+} decrease - the ppt $Al(OH)_3$ dissolved and the reaction go forward reaction the (S) of ppt increase

and (S) increase.

Ex/Calculate the best pH to start ppt of $Fe(OH)_3$ in solution content 0.1M of positive ion if ksp of $Fe(OH)_3=10^{-34}$

SOLUTION :

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

Ksp= $[Fe]^{3+}[OH^{-}]^{3} \longrightarrow 10^{-34} = (10^{-1})(OH^{-})^{3}$

$$(OH^{-})^{3} = \frac{10^{-34}}{10^{-1}} = 10^{-33}$$

 $[OH^{-}]=10^{-11}$, POH=11 \implies PH=14-POH=14-11=3

HOME WORK:

Calculate the best pH to start (ppt) $Mg(OH)_2$ in solution content 0.1 M of positive ion if $ksp(Mg(OH)_2)=10^{-11}$

4-Effect of temperature on solubility

PbCl₂ dissolved partially in room temp., but it dissolved very easy when temp. *increase (S) increase when temp increase and value of ksp increase*.

Ex. / ksp of Mg(OH)₂= 3.4×10^{-11} at room temp:

- a) Calculate the number of grams of dissolved (Mg⁺⁺) ion in 100 ml of 0.1 M NH₄OH if $k_b(NH_3)=1.75 \times 10^{-5}$
- b) Calculate the number of gram of dissolved (Mg⁺⁺) ion in 100ml of 0.1 M NH₄OH content (2M) of [NH₄⁺] ion (At.wt. Mg⁺⁺=24.3 g/mole).

Solution:

a) NH⁴OH \leftrightarrow NH4⁺ +OH⁻ Kb= $\frac{[NH4^+][OH^-]}{[NH4OH]}$

$$1.7x10^{-5} = \frac{[OH^{-}]^{2}}{0.1}, [OH^{-}] = 1.3x10^{-3} \text{ M.}$$

$$Mg(OH)_{2} \leftrightarrow Mg^{++} + 2OH^{-} \text{ Ksp} = [Mg^{++}][OH^{-}]^{2}$$

$$S 2S$$

$$Ksp = [Mg^{++}][2 \times 1.3 x10^{-3}]^{2}$$

$$[Mg^{++}] = 2x10^{-5} \text{ M}$$

$$M = \frac{mole}{l} \longrightarrow M = \frac{wt.}{At.wt} \times \frac{1000}{Vol.(ml)}$$

$$Wt = M \times \text{ At.wt} \times \frac{100}{1000}$$

$$Wt = 2 x10^{-5} x24.3 x (1/10) = 4.9 x10^{-5} \text{ g/ } 100 \text{ ml}$$

$$b) \text{ kb} \frac{[NH4^{+}][OH^{-}]}{[NH4OH]} \text{ *common ion effect}$$

$$1.75 = \frac{2 \times [OH^{-}]}{0.1}, \quad [OH^{-}] = 8.8x10^{-7}$$

$$Ksp = [Mg^{++}][OH^{-}]^{2}$$

$$3.4 x10^{-11} = [Mg^{++}][2 \times 8.8 x 10^{-7}]^{2}$$

 $[Mg^{++}] = \dots, wt. = \dots$

Home work:

- 1- The value of PbSO₄ dissolved in water equal 0.038g/L, calculate the ksp of PbSO₄ if M.wt of PbSO₄ =303 g/mole.
- 2- The conc. of $[Ag^+] = 2.2 \times 10^{-4}$ in saturated solution of Ag_2CrO_4 calculate the ksp of Ag_2CrO_4 .
- 3- Ksp Fe(OH)₃=10⁻³⁶ A-Calculate the weight (Fe³⁺) not ppt in 100ml of 0.1 M NH₄OH if kb(NH₃) =1.7 x10⁻⁵ B- Calculate the weight (Fe³⁺) not ppt in 100 ml of 2 M NH⁴⁺ and 0.1 M NH₄OH , if At.wt Fe=55.8.

Ionic strength

- the electrolyte effect is highly dependent on the charges of the participants in an equilibrium. When only neutral species are involved, the position of equilibrium is essentially independent of electrolyte concentration. With ionic participants, the magnitude of the electrolyte effect increases with charge.
- Note, for example, that, in a 0.02 M solution of potassium nitrate,

the solubility of barium sulfate with its pair of doubly charged ions is larger than it is in pure water by a factor of 2. This same change in electrolyte concentration increases the solubility of barium iodate by a factor of only 1.25 and that of silver chloride by 1.2. The enhanced effect due to doubly charged ions is also reflected in the greater slope of curve B in Figure

- The solubility (s) increase in solution of electrolyte than in pure water .
- the effect of added electrolyte on equilibria is independent of the chemical nature of the electrolyte but depends on a property of the solution called the ionic strength. This quantity is defined as :

Ionic strength $\equiv \mu$ $\mu = 1/2(M_1Z_1^2 + M_2Z_2^2 + M_3Z_3^2 + \dots ect)$ M_1, M_2, M_3, \dots molar conc. of ions. Z_1, Z_2, Z_3, \dots charge of that ions..

Calculate the ionic strength of (a) a 0.1 M solution of KNO_3 and (b) a 0.1 M solution of Na_2SO_4 .

Solution

(a) For the KNO₃ solution, $[K^{+1}]$ and $[NO_3^-]$ are 0.1 M

and

 μ =0.5× (0.1 M × 1² + 0.1 M × 1²) = 0.1 M

(b) For the Na₂SO₄ solution, $[Na^+] = 0.2$ M and $[SO_4^{-2}] 0.1$ M. Therefore,

 $\mu = 1/2 \times (0.2 \ M \times 1^2 + 0.1 \ M \times 2^2) = 0.3 \ M$

Ex/ Calculate (μ) of solution content 0.1 M KNO₃, also another solution content 0.1 M Na₂SO₄

Solution:

$$KNO_{3} \rightarrow K^{+} + NO_{3}^{-}$$

$$0.1 \qquad 0.1 \qquad 0.1$$

$$\mu = 1/2 \ (0.1 \ x1^{2} + 0.1 \ x1^{2}) = \frac{1}{2} (0.2) = 0.1$$

$$Na_{2}SO_{4} \rightarrow 2Na^{+} + SO4^{-}$$

$$0.1 \qquad 2x0.1 \qquad 0.1$$

 $\mu = \frac{1}{2} (2x0.1 \ x1^2 \ + 0.1 \ x2^2) = 0.3$

Ex/ calculate (μ) for solution content 0.05 M KNO₃ and 0.1 M NaSO₄.

$$\begin{split} \mathrm{KNO}_3 \ + \ \mathrm{Na}_2\mathrm{SO4} \ \to \ \mathrm{K}^+ \ \ + \ \mathrm{NO}_3^- + \ \ 2\mathrm{Na}^+ + \ \mathrm{SO}_4^= \\ 0.05 \ \ \ 0.05 \ \ \ 2\mathrm{x}0.1 \ \ \ 0.1 \\ \mu \ = \frac{1}{2}(0.05\ \mathrm{x}1^2 \ + 0.05\ \mathrm{x}1^2 \ + 0.2\ \mathrm{x}1^2 \ + 0.1\ \mathrm{x}2^2) = 0.35 \\ \mathrm{M} = \mu \ - 1 \\ \mathrm{a}_2 \ \ \mathrm{b}_2 \ \ \mathrmb}_2 \ \ \mathrmb_2 \ \ \mathrmb$$

These examples show that the ionic strength of a solution of a strong electrolyte consisting solely of singly charged ions is identical to its total molar salt concentration. The ionic strength is greater than the molar concentration, however, if the solution contains ions with multiple charges (see Table 10-1.(For solutions with ionic strengths of 0.1 M or less, the electrolyte effect is independent of the kind of ions and dependent only on the ionic strength. Thus, the solubility of barium sulfate is the same in aqueous sodium iodide, potassium nitrate, or aluminum chloride provided the concentrations of these species are such that the ionic strengths are identical. Note that this independence with respect to electrolyte

species disappears at high ionic strengths.

Home work:

Calculate μ of solution content 0.03 M ZnCl₂ and 0.02 M Al(OH)₃.

The Activity and activity coefficients

The solubility calculate when used molar conc. The calculation is write only in dilute solutions. Less than 10⁻³M. When the conc. increase over 10⁻² M the calculation is wrong because the ions attractive or formation complex or attraction and formation complex effective the molar conc. can expressing as activity conc. (a)

Chemists use a term called activity, *a*, to account for the effects of electrolytes on chemical equilibria. The activity, or effective concentration, of species X depends on the ionic strength of the medium and is defined by

a= **C**. γ or $a_{\rm X} = [{\rm X}].\gamma_{\rm X}$

Where a_X is the activity of the species X, [X] is its molar concentration, and γ_X is a dimensionless quantity called the **activity coefficient**. The activity coefficient and thus the activity of X vary with ionic strength.

γ: activity coefficient

Debye-Hückel equation, takes the form

$$-\log \gamma_{\rm X} = \frac{0.51 Z_{\rm X}^2 \sqrt{\mu}}{1 + 3.3 \alpha_{\rm X} \sqrt{\mu}}$$

where $\gamma_X = \text{activity coefficient of the species X}$ $Z_X = \text{charge on the species X}$ $\mu = \text{ionic strength of the solution}$ $\alpha_X = \text{effective diameter of the hydrated ion X in nanometers (10⁻⁹ m)}$

When μ is less than 0.01 M, 1 + $\sqrt{\mu} < 1$, and Equation becomes

$-\mathrm{Log}\gamma = 0.51\mathrm{Z}^{2}{}_{\mathrm{X}}\sqrt{\mu}$	γ : activity coefficient
	0.51 : constant of water at 25C ⁰
$-\mathrm{Log}\gamma = 0.51\mathrm{Z}^{+}\mathrm{Z}^{-}\sqrt{\mu}$	Z^+Z^- = positive and negative charges of ppt

This equation is referred to as the Debye-Huckel Limiting Law (DHLL). Thus, in solutions of very low ionic strength ($\mu < 0.01$ M), the DHLL can be used to calculate approximate activity coefficients.

Activity coefficients have the following properties:

1. The activity coefficient of a species **is a measure of the effectiveness with which that species influences an equilibrium in which it is a participant.** In very dilute solutions in which the ionic strength is minimal, this effectiveness becomes constant, and the activity coefficient is unity. Under these circumstances, the activity and the molar concentration are identical (as are thermodynamic and concentration equilibrium constants). As the ionic strength increases, however, an ion loses some of its effectiveness, and its activity coefficient decreases.

terms of Equations 10-2 and 10-3. At moderate ionic strengths, $\gamma_X < 1$. As the solution approaches infinite dilution, however, $\gamma_X \rightarrow 1$, and thus, $a_X \rightarrow [X]$ while $K'_{sp} \rightarrow K_{sp}$. At high ionic strengths ($\mu > 0.1$ M), activity coefficients often increase and may even become greater than unity. Because interpretation of the behavior of solutions in this region is difficult, we confine our discussion to regions of low or moderate ionic strength (that is, where $\mu \leq 0.1$ M). The variation of typical activity

2. In solutions that are not too concentrated, the activity coefficient for a given species is independent of the nature of the electrolyte and dependent only on the ionic strength.

3. For a given ionic strength, the activity coefficient of an ion decreases more dramatically from unity as the charge on the species increases.

4. The activity coefficient of an uncharged molecule is approximately unity, no matter what the level of ionic strength.

5. At any given ionic strength, the activity coefficients of ions of the same charge are approximately equal. The small variations among ions of the same charge can be correlated with the effective diameter of the hydrated ions.

6. The activity coefficient of a given ion describes its effective behavior in all equilibria in which it participates. For example, at a given ionic strength, a single activity coefficient for cyanide ion describes the influence of that species on any of the following equilibria:

$HCN + H2O \rightarrow$	$H_3O^+ + CN^-$
$Ag^+ + Chr$	AgCN(s)
$Ni^{2+} + 4CN^{-}$	Ni(CN) ₄

Ex/ if BaSO₄ precipitated in a solution containing 0.012M NaCl and 0.02M BaSO₄, calculate the conc. of $[SO_4^{2-}]$ used to precipitate BaSO₄ when using activity and without used it in calculation.: ksp(BaSO₄)=1.1 x 10⁻¹⁰

Solution :

1- Without using activity.
Ksp=
$$[Ba^{++}][SO_4^{=}]$$
 BaSO₄ \leftrightarrow Ba⁺⁺ + SO₄⁼
1.1x10⁻¹⁰ = (0.002) (SO₄⁼)
[SO₄⁼] =(5x 10⁻⁸ M)
2- When using activity
 $\mu = \frac{1}{2}$ (0.012 x1² + 0.012 x1² + 0.002 x2² + 2x0.002 x1²)
= 0.018
-log = 0.51 Z^+Z^- $\sqrt{\mu}$
= 0.51(2x2) $\sqrt{0.018}$
 $\gamma = 0.6$
ksp= (Ba⁺⁺. γ) (SO4⁼. γ)
1.1 x10⁻¹⁰ = (0.002 x0.6)(SO4⁼.0.6)

 $[SO_4^{=}] = 1.39 \text{ x } 10^{-7} \text{ M}$

Compare between the result = $\frac{1.39 \times 10^{-7}}{5 \times 10^{-8}} \approx 3$

Home work :

Cal. the concn of $[Ag^+]$ in saturated solution of Ag_2CrO_4 containing 0.02 M K₂CrO₄, compare the result when using activity and without using it, ksp $(Ag_2CrO_4) = 1x10^{-12}$.

Fractional precipitation :-

When added AgNO₃ to solution content [Cl⁻] and [I⁻]

- which ion is precpitate first ?
- the reaction complete or in complete .

It depended upon value of ksp of each ppt. as seen in the following equations :-

- $Ag^+ + Cl^- \leftrightarrow AgCl$, $ksp=10^{-10}$
- $Ag^+ + I^- \leftrightarrow AgI$, $ksp=10^{-16}$
- When ksp of ppt small it needed small conc. of Ag to ppt (1st) when conc. of (Ag⁺) increase the [Cl⁻] ion state to ppt
- AgI first ppt, then AgCl start to ppt. (that depend upon value of ksp).
- To cheak the ppt complete or incomplete used this calculation .

$$\frac{ksp [AgI]}{ksp[AgCl]} = \frac{10^{-16}}{10^{-10}}$$

Or $\frac{[Ag^+][I^-]}{[Ag^+][Cl^-]} = \frac{10^{-16}}{10^{-10}}$
Or $\frac{[I^-]}{[Cl^-]} = \frac{10^{-16}}{1} = \frac{1}{10^6}$ the ppt complete

That mean all [I-] ppt as AgF after finish all ions of [I-] the [Cl-] start to ppt as AgCl.

Another example $\frac{Ksp \ AgI}{ksp \ AgBr} = \frac{[Ag^+][I^-]}{[Ag^+][Br^-]} = \frac{[I^-]}{[Br^-]} = \frac{10^{-16}}{10^{-13}} \quad \therefore \frac{[I^-]}{[Br^-]} = \frac{10^{-3}}{1} = \frac{1}{10^{-3}}$ the ppt not complete

Because the ratio less than million

* it mean (AgBr) start ppt before finishing all ions of $[I^-]$. which mean there will be a mixture of [AgI] and [AgBr] ppt.

Home works 1- What mass (in grams) of Ba(IO₃)₂ (487 g/mol) can be dissolved in 500 mL of water at 25°C?(Answer, 0.178g)

- 2- Calculate the solubility of $Ba(IO_3)_2$ in a solution prepared by mixing 200 mL of 0.0100 M $Ba(NO_3)_2$ with 100 mL of 0.100 M $NaIO_3$.(Answer, S= 3.93 ×10⁻⁶ M)
- 3- Generate the solubility-product expression and Express the solubility-product constant for each substance in terms of its molar solubility *S*. for: *(a) CuBr. (b) La(IO₃)₃. *(c) HgCl₂. (d) Ag₃AsO₄. *(e) PbCl₂.

4- Calculate the molar solubility of Ba(IO₃)₂ in a solution that is 0.0200 M in Ba(NO₃)₂.(answer, S= 1.40×10^{-4} M)

5- Calculate the solubility-product constant for each of the following substances, given that the molar concentrations of their saturated solutions are as indicated:

- (a) AgSeCN (2.0×10^{-8} M; products are Ag⁺¹ and SeCN⁻¹).
- (b) RaSO₄ (6.6×10^{-6} M).
- (c) $Pb(BrO_3)_2 (1.7 \times 10^{-1} \text{ M}).$
- (d) Ce(IO₃)₃ (1.9×10^{-3} M).

Then calculate the solubility of the solutes above for solutions in which the cation concentration is 0.030 M. And Calculate the solubility of the solutes above for solutions in which the anion concentration is 0.030 M.

6- The solubility-product constant for K_2PdCl_6 is 6.0×10^{-6} ($K_2PdCl_6 \longrightarrow 2K^{+1} + PdCl_6^{-2}$).

What is the K^{+1} concentration of a solution prepared by mixing 50.0 mL of 0.200 M KCl with 50.0 mL of

- (a) 0.0800 M PdCl₆ ⁻²?
- (b) 0.160 M PdCl₆ ⁻² ?
- (c) $0.240 \text{ M PdCl}_6^{-2}$?

Chapter (5)

A-Volatilization Gravimetry

Lec.9

The two most common: determining water and carbon dioxide.

* Water is quantitatively distilled from many materials by heating.

*In direct determination water vapor is collected on any of several solid desiccants, and its mass is determined from the mass gain of the desiccant.

* The indirect method in which the amount of water is determined by the loss of mass of the sample during heating is less satisfactory because it must be assumed that water is the only component that is volatilized.

* determination of the sodium hydrogen carbonate content of antacid tablets



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

$NaHCO_3(aq) + H_2SO_4(aq) \rightarrow CO_2(g) + H_2O(l) + NaHSO_4(aq)$

* Sulfides and sulfites can also be determined by volatilization. Hydrogen sulfide or sulfur dioxide evolved from the sample after treatment with acid is collected in a suitable absorbent.

**Finally, the classical method for the determination of carbon and hydrogen in organic compounds is a gravimetric volatilization procedure in which the combustion products (H_2O and CO_2) are collected selectively on weighed absorbents. The increase in mass serves as the analytical variable.

B-Particle size and Purity of precipitates

1- Characteristics of Ion, colloid and particle

• The particle size of solids formed by precipitation varies enormously. At one extreme are colloidal suspensions, whose tiny particles are invisible to the naked eye (10-7 to 10-4 cm in diameter). Colloidal particles show no tendency to settle from solution and are difficult to filter.

• At the other extreme are particles with dimensions on the order of tenths of a millimeter or greater. The temporary dispersion of such particles in the liquid phase is called a crystalline suspension. The particles of a crystalline suspension tend to settle spontaneously and are easily filtered.

Characteristics	Diameter	Name
Dissolved	$\sim 10^{-8} \text{ cm} (\text{A}^{\circ})$	Ion
Suspended	10 ⁻⁷ ~10 ⁻⁴ cm (nm-µm)	Colloid
Settled from solution (filterable)	>10 ⁻⁴ cm (µm)	Crystalline

• Precipitates consisting of large particles are generally desirable for gravimetric work because these particles are easy to filter and wash free of impurities.

2-Factors That Determine the Particle Size of Precipitates

Precipitate formation has been studied for many years, but the mechanism of the process is still not fully understood. What is certain, however, is that the particle size of a precipitate is influenced by:

* precipitate solubility,

- * temperature,
- * reactant concentrations,
- and the * rate at which reactants are mixed.

The net effect of these variables can be accounted for, at least qualitatively, by assuming that the particle size is related to a single property of the system called **relative supersaturation**, **RSS**, where :
$$RSS = \frac{Q-S}{S}$$

Von Weimarn equation, 1925

Q: the concentration of the solute at any instant

S: the concentration solute **at equilibrium**

A supersaturated solution is one that contains more dissolved solute than that predicted by equilibrium chemistry. The solution is inherently unstable and precipitates solute to reach its equilibrium position. How quickly this process occurs depends, in part, on the value of RSS.

3-Relative supersaturation (RSS)

A **supersaturated solution is an** unstable solution that contains a higher solute concentration than a saturated solution. As excess solute precipitates with time, supersaturation decreases to zero.



-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.

- A supersaturated solution is an unstable solution that contains a higher solute concentration than a saturated solution. As excess solute precipitates with time, supersaturation decreases to zero.

RSS	Process	Result
Large	Nucleation dominate	Smaller particles (colloidal)
Small	Particle growth dominate	Larger Particle (Crystalline)

4- Nucleation and Particle growth

The step of ppt formation

1- Nucleation 2-Particle growth

*Nucleation: The initial formation process in which a minimum number of atoms, ions, or molecules join together to give a stable solid.

Often, these nuclei form on the surface of suspended solid contaminants, such as dust particles

*Particle growth: The subsequent growth after nucleation.

Mechanism of Precipitate Formation

*If nucleation predominates, a precipitate containing a large number of small particles results, and

*if growth predominates, a smaller number of larger particles is produced.

properties of precipitate depends on:

- 1- solubility
- 2- purity
- 3- stability

	Result	Process	RSS
5-	Smaller particles (colloidal)	Nucleation dominate	Large
<u>J-</u>	Larger Particle (Crystalline)	Particle growth dominate	Small

Experimental Control of Particle Size

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

(The lower RSS value the larger particles)

Increase S:

Heating to increase solubility pH adjustment (If the solubility of the precipitate depends on pH) Adding complexing agent

Decrease Q:

Using dilute precipitating solution Adding precipitating agent slowly and stirring Using homogeneous precipitation technique

Lec.10

6-Colloidal Precipitates

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.

(When liquid starts to thicken and become solid, it coagulates)

(agglomeration: a large group of many different things collected or brought together)

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**.

Adsorption: A process in which a substance (gas, liquid, or solid) is held on the surface of a solid.

Absorption: A process in which a substance within the pores of a solid.

Attached directly to the solid surface is *the primary adsorption layer*, which consists mainly of adsorbed silver ions. Surrounding the charged particle is a layer of solution, called *the counter-ion layer*, which contains sufficient excess of negative ions (principally nitrate) to just balance the charge on the surface of the particle. • These layers constitute an electric double layer that imparts stability to the colloidal

• These layers constitute an electric double layer that imparts stability to the colloidal suspension. As colloidal particles approach one another, this double layer exerts an electrostatic repulsive force that prevents particles from colliding and adhering.



Figure shows a colloidal silver chloride (AgCl) suspended in a solution of excess $AgNO_3$



- 1. lower line (AB) un sat. Solution
- 2. Between (AB) and (CD) sat. solution
- 3. Above (CD) super sat. solution.

7-Coagulation of Colloids

A coagulated colloid * The upper portion of Figure 12-3 depicts two silver chloride particles and their counter- ion layers as they approach each other in the concentrated silver nitrate just considered. Note that the effective charge on the particles prevents them from approaching one another more closely than about 2d1—a distance that is too great for coagulation to occur.



Figure 12-3 The electrical double layer of a colloid consists of a layer of charge adsorbed on the surface of the particle (the primary adsorption layer) and a layer of opposite charge (the counterion layer) in the solution surrounding the particle. Increasing the electrolyte concentration has the effect of decreasing the volume of the counter-ion layer, thereby increasing the chances for coagulation.

* As shown in the lower part of Figure 12-3, in the more dilute silver nitrate solution, the two particles can approach within 2*d2 of one another*. Ultimately, as the concentration of silver nitrate is further decreased, the distance between particles becomes small enough for the forces of agglomeration to take effect And a coagulated precipitate to appear. Figure 12-3 The electrical double layer of a colloid consists of a layer of charge adsorbed on the surface of the particle (the primary adsorption layer) and a layer of opposite charge (the counter-ion layer) in the solution surrounding the particle. Increasing the electrolyte concentration has the

effect of decreasing the volume of the counter-ion layer, thereby increasing the chances for coagulation. 13/35



A coagulated colloid

Coagulation of a colloidal suspension can often be brought about by a short period of *heating*, particularly if accompanied *by stirring*.

Heating decreases the number of adsorbed ions and thus the thickness, *of the double layer. The particles may* also gain enough kinetic energy at the higher temperature to overcome the barrier to close approach imposed by the double layer.

An even more effective way to coagulate a colloid is to increase the electrolyte concentration of the solution. If we add a suitable ionic compound to a colloidal suspension, the concentration of counter-ions increases in the vicinity of each particle. As a result, the volume of solution that contains sufficient counter-ions to balance the charge of the primary adsorption layer decreases.

8-Peptization of Colloids

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., HNO₃, NH₄NO₃, to avoid peptization.

9-Peptization of Colloids

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.

10-Crystalline Precipitates

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

 \Box 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.

 $\hfill\square$ 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.

11-Coprecipitation

Coprecipitation:

A process in which normally soluble compounds are carried out of solution by a precipitate. It may resulted in **impurities** within the desired precipitates.

Co precipitated impurities may cause either negative or positive errors.

There are four types of co-precipitation:

surface adsorption, mixed-crystal formation, occlusion, and mechanical entrapment.

A- 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

- 1- Washing a coagulated colloid with a solution containing a volatile electrolyte
- 2- Digestion: during this process, water is expelled from the solid to give a denser mass that has a smaller specific surface area for adsorption.
- 3- 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.



B- 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 or MgKPO₄ in MgNH₄PO₄ or MnS in CdS



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

Problem solving:

- Change to another more selective precipitating agent
- Reprecipitation

C-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.)

D- Mechanical Entrapment:

A type of co-precipitation in which co-precipitated physically trap a *pocket of solution* within a precipitate during rapid precipitate formation.

Problem solving: Digestion

Mixed-crystal formation may occur in both colloidal and crystalline precipitates, but occlusion and mechanical entrapment are confined to crystalline precipitates.



<u>12-Drying and Ignition of Precipitates</u>

*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.

Post precipitation

Special type of contamination occurs when separate two ions or more with one precipitate under same condition .

Ex/

 (Ca^{++}, Mg^{++}) with $C_2O_4^{=} \rightarrow CaC_2O_4$ (1st ppt), MgC_2O_4(2nd ppt)

Depended upon value of ksp of each one

Note :

When 1st ppt appearance its can used as nuclei to 2nd ppt.

To prevent this kind of conta. You can filterate CaC_2O_4 after one hour, after time the 2^{nd} ppt MgC₂O₄ can appear without contamination

Applications of gravimetric methods

1- Inorganic Precipitating Agents TABLE 12-2

Some Inorganic Precipitating Agents

Precipitating Agent	Element Precipitated*				
NH ₃ (aq)	Be (BeO), Al (Al ₂ O ₃), Sc (Sc ₂ O ₃), Cr (Cr ₂ O ₃) \dagger , Fe (Fe ₂ O ₃),				
	Ga (Ga ₂ O ₃), Zr (ZrO ₂), In (In ₂ O ₃), Sn (SnO ₂), U (U ₃ O ₈)				
H ₂ S	Cu (CuO) \dagger , Zn (ZnO or ZnSO ₄), Ge (GeO ₂), As (As ₂ O ₃ or As ₂ O ₅),				
	Mo (MoO ₃), Sn (SnO ₂) \uparrow , Sb (Sb ₂ O ₃), or Sb ₂ O ₅), Bi (Bi ₂ S ₃)				
(NH ₄) ₂ S	Hg (HgS), Co (Co ₃ O ₄)				
(NH ₄) ₂ HPO ₄	Mg (Mg ₂ P ₂ O ₇), Al (AlPO ₄), Mn (Mn ₂ P ₂ O ₇), Zn (Zn ₂ P ₂ O ₇),				
	Zr (Zr ₂ P ₂ O ₇), Cd (Cd ₂ P ₂ O ₇), Bi (BiPO ₄)				
H ₂ SO ₄	Li, Mn, Sr, Cd, Pb, Ba (all as sulfates)				
H ₂ PtCl ₆	K (K ₂ PtCl ₆ or Pt), Rb (Rb ₂ PtCl ₆), Cs (Cs ₂ PtCl ₆)				
$H_2C_2O_4$	Ca (CaO), Sr (SrO), Th (ThO ₂)				
(NH ₄) ₂ MoO ₄	Cd (CdMoO ₄)†, Pb (<u>PbMoO₄</u>)				
HCI	Ag (AgCl), Hg (Hg2Cl2), Na (as NaCl from butyl alcohol), Si (SiO2)				
AgNO ₃	Cl (AgCl), Br (<u>AgBr</u>), I(<u>AgI</u>)				
$(NH_4)_2CO_3$	Bi (Bi ₂ O ₃)				
NH ₄ SCN	Cu [Cu ₂ (SCN) ₂]				
NaHCO ₃	Ru, Os, Ir (precipitated as hydrous oxides, reduced with H ₂ to metallic state)				
HNO3	Sn (SnO ₂)				
H ₅ IO ₆	Hg $[Hg_5(IO_6)_2]$				
NaCl, Pb(NO ₃) ₂	F (PbClF)				
BaCl ₂	SO_4^{2-} (BaSO ₄)				
MgCl ₂ , NH ₄ Cl	$PO_4^{3-}(Mg_2P_2O_7)$				

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	
$SO_2 + H_2NOH$	Te	
H ₂ NOH	Se	
$H_2C_2O_4$	Au	
H ₂	Re, Ir	
HCOOH	Pt	
NaNO ₂	Au	
SnCl ₂	Hg	
Electrolytic	Co, Ni, Cu, Zn	
reduction	Ag, In, Sn, Sb,	
	Cd, Re, Bi	