



وزارة التعليم العالي والبحث العلمي .  
الجامعة التقنية الشمالية / الكلية التقنية الهندسية - كركوك .  
قسم هندسة البيئة والتلوث .

## الحقيبة الدراسية

- المادة الدراسية / الكيمياء العامة / General Chemistry .
- عدد الساعات / (3) نظري & (2) عملي .
- لغة التدريس / الانكليزية .
- طبيعة المادة / سنوية .
- عدد الاسابيع / (30) اسبوع .
- الفئة المستهدفة / طلبة المرحلة الاولى .
- اهداف المادة / بعد اكمال دراسة المادة سيكون الطالب قادراً على ان :-
  1. يفصل العناصر المكونة لمركب ما ومن ثم تعيين وتقدير كميتها .
  2. يستخدم الآت واجهزة معقدة بنيت اساساً واعتماداً على قياس خاصية معينة لها علاقة بتركيز نموذج ما .
- الوحدات النمطية / ( كل وحدة نمطية تمثل مفردة اسبوع دراسي واحد) .
- المدرس القائم بالتدريس / أ.م. د. جودت حلمي عبدالواحد .

## Chemistry

| Week No.     | Items Detail                                     |
|--------------|--|
| 1 , 2        | Basic concept of qualitative and quantitative.   |
| 3 , 4        | Qualitative at quantitative analytical methods.  |
| 5 , 6        | Chemical equilibrium and solubility products.    |
| 7 , 8        | Stoichiometric calculations.                     |
| 9 , 10 , 11  | Gravimetric methods of analysis.                 |
| 12 , 13      | Reactions of acids, Bases.                       |
| 14 , 15      | Precipitation at reductions.                     |
| 16 , 17      | Oxidation at reduction.                          |
| 18 , 19 , 20 | Complex formation reactions.                     |
| 21 , 22      | Complexes.                                       |
| 23 , 24      | Catalyst used in industry.                       |
| 25 , 26      | Drawing of reaction curves in aqueous solutions. |
| 27 , 28      | Methods and principle of spectrometric analysis. |
| 29 , 30      | Instrumental analysis employed for industry.     |

الاسبوع الاول والثاني  
( الوحدة النمطية )

**Basic concept of qualitative and quantitative analysis**

**مقدمة :-**

**Qualitative analysis is the group of process**

That detect the contents of substances or compounds or elements that founded in composition of some substance or molecule of compounds either in solid state or in solution of some solvent .

Quantitative analysis is the determination of the quantity of contents or elements that founded in the composition of chemical compounds .

**الهدف :** معرفة العمليات التي بواسطتها يتم الكشف عن هوية المواد او المركبات او العناصر الداخلة في تركيب مادة ما او خليط من المواد ثم تقدير كمية المكونات او العناصر .

Compare between the qualitative and quantitative analysis ? .

## Qualitative and Quantitative analysis

Quantitative analysis is the group of process that detected the contents of substances or compounds or elements that founded in composition of some substance or mixture of compounds either in solution of some solvent .

**Note** :- This type of analysis not deals with quantity of this components .

Quantitative analysis is the determination of the quantity of contents or elements that founded in the composition of chemical compounds

Note:qualtitative method for unknown compound prior to quantitative analysis

Quantitative method include :-

- 1- Gravimetric analysis :- is determined the mass of the analyte or that of some compound chemically related to the analyte is determined .

Titrimetric method : is measured the quantity of reagent necessary to react completely with the analyte .

Standard solution :-

We can prepare standard solution by solve weighing quantity of standard substance which have high degree of purity then dilute it in volumetric flask , but if the substance not standard ( don't have high degree of purity ) in this case we can prepare solution of approximate concentration and calibrated with known concentration of primary standard substance .

The properties of chemical standard compounds .

1- Stability .

- a- The compound should not be deliquesce or hygroscopic .
- b- The compound should not undergo to chemical changes upon drying .
- c- The compound should be easily weighable .
- d- Both the solution and compound should be stable in air and in solution .

2- It should have high molecular weight .

3- Solubility : It should solve easily .

4- Toxicity : The compound should have as low as toxicity as possible .

- Some examples of standard compounds .

Acids : (  $\text{KHIO}_3$  ,  $\text{HCl}$  , &  $\text{C}_6\text{H}_5\text{COOH}$  )

Bases :  $\text{MgO}$  ,  $\text{Na}_2\text{CO}_3$

Oxidizing agent :  $\text{KBrO}_3$  ,  $\text{K}_2\text{Cr}_2\text{O}_7$  ,  $\text{I}_2$  ,  $\text{KIO}_3$

Reducing agent :  $\text{K}_4\text{Fe}(\text{CN})_6$  , other substances :  $\text{KCl}$  ,  $\text{NaCl}$

الاسبوع الثالث والرابع

الوحدة النمطية

## Qualitative and quantitative analytical methods

مقدمة :-

### The quantitative methods in clued the following .

A volumetric analysis : is one in which the analysis completed by measuring the volume of a solution of established the concentration needed to react completely with substance being determined . Gravimetric method are based upon the measurement of the weight of analyte or a compound of known composition that contains the analyte .

الهدف : ان يتعرف الطالب على طرق التحليل النوعي والكمي بنوعه الحجمي

والوزني .

امتحان قصير :

Write the types of gravimetric methods them define it ? .

## **Gravimetric methods .**

Gravimetric method of analysis are based upon the measurement of the weight of analyte or of a compound of known composition that contains the analyte . Two types of gravimetric methods :-

### **1- precipitation methods :-**

the analyte ( or a species related to it ) is isolated as a sparingly soluble precipitate that either has a known composition or can be converted to a product of known composition by suitable heat treatment .

### **2- Volatilization methods :-**

The analyte or it's decomposition products are volatilized at a suitable temperature . The volatile product is either collected and weighed , or the weight of the product is determined indirectly from the loss in weight of the sample .

## **" Volumetric Analysis "**

A volumetric analysis is one in which the analysis completed by measuring the volume of a solution of established concentration needed to react completely with the substance being determined . volumetric methods as frequently equivalent in accuracy to gravimetric procedures and are more rapid and convenient . It include the following

1- Titration method .

2- Gas Analysis .

## **Titration Method**

A titration is a process by which a standard solution is slowly added from a buret to a solution of the analyte until the two is judged to be complete. The volume needed to complete the titration is determined from the difference between the initial & final buret readings. The point in a titration where the amount added titrant is chemically equivalent to the amount of analyte in the sample is called the equivalence point .

### **Equivalence points & end points :-**

It should be understood that the equivalence point of titration is a theoretical point that can not be determined experimentally . It can only be estimated by observing some physical change associated with the condition of titration any volume difference between the equivalence point and the end point is small , A common method of detecting end points involves the using of a substance called an indicator which produces an observable physical change in the solution at or near the equivalence point . This change is caused by a large change in the relative concentration of analyte or titrant that occurs in the equivalence . Point region . Typical indicator changes include the appearance or disappearance of a color and the appearance or disappearance of turbidity .

End points are also obtained with instruments that respond to certain properties of the solution that change in a characteristic way during the titration . Among such properties are electric potential , current , and conductance , optical absorbance and refractive index .



### **Standard Solution** :-

The ideal standard solution for a volumetric method should :-

- 1- be sufficiently stable so that its concentration remains unchanged .
- 2- react rapidly with the analyte so that the time required between additions of reagent is minimized .
- 3- react more or less completely with the analyte .
- 4- undergo the selective reaction with the analyte that can be described by a simple balanced equation .

### **Precipitation Titration** :-

The precipitation method is based on titration with the use of reactions accompanied by the formation of sparingly soluble compounds . Although many such reactions are known , only a few of them can be used in volumetric analysis . They must satisfy a number of condition namely :-

- 1- The precipitate must be partially in soluble .
- 2- The precipitation should be rapid .
- 3- The titration should not be distorted appreciably by adsorption effects .
- 4- It should be possible to detect the equivalence point during the titration .

## Chemical equilibrium of stability products introduction :-

Acid : is the substance that give ( H<sup>+</sup> ) ions .

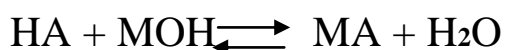
Base : is the substance that taken ( H<sup>+</sup> ) ions .

Suggest that acid is ( HA ) which dissociated in aqueous solution according to the following equation :-



We can refer to base by ( MOH ) which dissociated to given ( M<sup>+</sup> + OH<sup>-</sup> ) ions .

The reaction between acid ( HA ) and base ( MOH ) is :-



The reaction is approximately perfect because .

The dissociation of water molecule is very small .

## Equilibrium constant :-

The chemical reaction is in equilibrium state if the rate of reaction to right equal to rate of reaction to left ( reversible ) .

In this state the concentration of reactants and products coordinate through the equation of equilibrium constant .

For example the equilibrium constant for this reaction is .



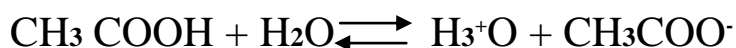
$$K_c = \frac{[\text{D}]^p [\text{E}]^q}{[\text{A}]^m [\text{B}]^n}$$

When p , q m , n is the coefficient of this compound in chemical reaction .

K : Equilibrium constant .

Acid and Base Ionization Constant .

e . g :- for acetic acid



$$K_c = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{H}_2\text{O}][\text{CH}_3\text{COOH}]}$$

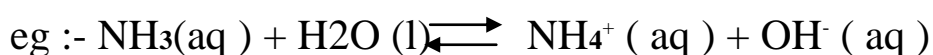
**Note** : the concentration of  $\text{H}_2\text{O}$  is constant there for the multi play of two constant is :-

$$K_i = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$K_i$  : ionization constant for weak electrolyte like

$K_a$  : for weak acid

$K_b$  : for weak base



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$K_b$  : base ionization constant .

Note :-  $\text{p}K_a = -\log K_a$                        $\text{p}K_b = -\log K_b$

PH of hydrogen ion con c .

The pure water dissociated according to the following equation :-



$$K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

∴ the conc. of water is constant .

∴  $K_c \cdot [\text{H}_2\text{O}]^2 = K_w$

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

The conc. Of hydrous & hydroxide ions in water is  $(1 \times 10^{-7}) (1 \times 10^{-7}) = 1 \times 10^{-14}$

e.g.) The conc. Of HCl is ( 0.1 M ),  $[H_3O^+] = 10^{-1}M$  there for  $[HO^-] = 10^{-13} M$ .

$$PH = -\text{Log}^{[H^+]}$$

$$POH = -\text{Log}^{[OH^-]}$$

The following table show the relation between PH & conc. of hydronium and hydroxyl ions :-

|          |            |            |           |           |           |            |            |
|----------|------------|------------|-----------|-----------|-----------|------------|------------|
| $H_3O^+$ | $10^{-1}$  | $10^{-3}$  | $10^{-5}$ | $10^{-7}$ | $10^{-9}$ | $10^{-11}$ | $10^{-13}$ |
| $OH^-$   | $10^{-13}$ | $10^{-11}$ | $10^{-9}$ | $10^{-7}$ | $10^{-5}$ | $10^{-3}$  | $10^{-1}$  |
| PH       | 1          | 3          | 5         | 7         | 9         | 11         | 13         |
| POH      | 13         | 11         | 9         | 7         | 5         | 3          | 1          |

$$PH + POH = 14$$

e.g.) calculate the PH of solution which the conc. Of  $H^+ = 0.0002 M$  ?

.

$$[H_3O^+] = 2 \times 10^{-4}$$

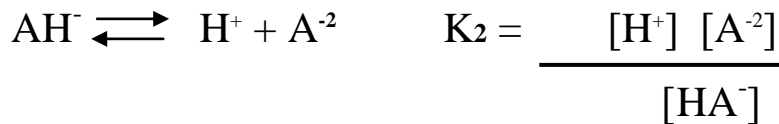
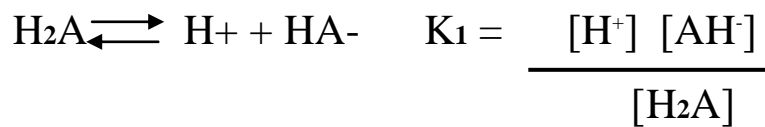
$$PH = -\text{Log} [H^+]$$

$$= -\text{Log} (2 \times 10^{-4})$$

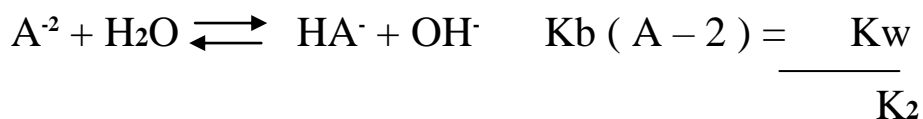
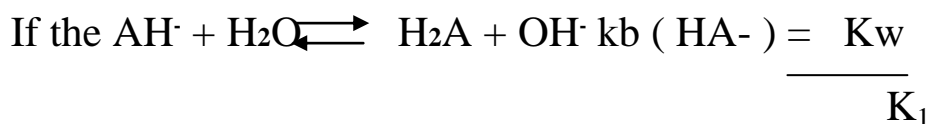
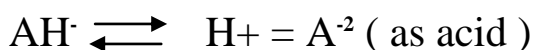
$$= 3.7$$

## Poly portic Acids & Bases :-

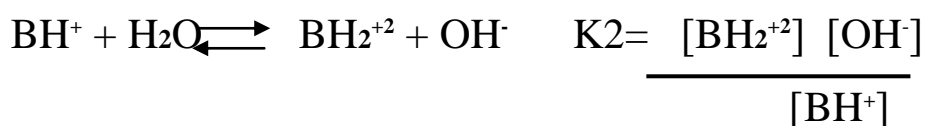
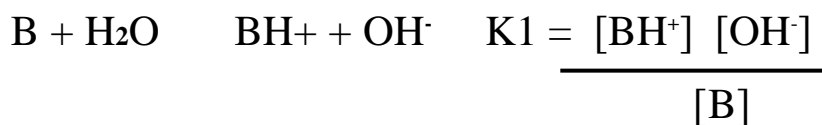
1- Diprotic acids ( H<sub>2</sub>A )



[HA<sup>-</sup>] can react either as acid or base

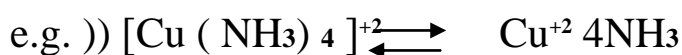


2- Diprotic base (B)



## Dissociation constant of complexion :-

A complexion is one that is in equilibrium with it's constituents these constituents are ordinary simple positive ion , neutral molecule or negative ion .

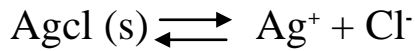


$$K = \frac{[\text{Cu}^{+2}] [\text{NH}_3]^4}{[\text{Cu} (\text{NH}_3)_4]^{+2}}$$

## Solubility product .

The following reaction obtain when we put any solid salt in water like

:-



$$K_c = \frac{[\text{Ag}^+] [\text{Cl}^-]}{[\text{Agcl}]}$$

∞ [Agcl ] is constant because it's solid substance

$$\circ K_c [\text{Agcl(s)}] = [\text{Ag}^+] [\text{Cl}^-]$$

$$K_{sp} [\text{Agcl(s)}] = [\text{Agcl(s)}]$$

K<sub>sp</sub> = solubility product

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

e.g.)) calculat the solubility product if the solubility of Mg (OH )<sub>2</sub> is

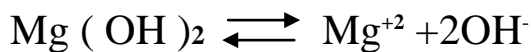
0.0009 gm in 100ml ?

24.3 f.wt

$$\underline{0.009} = 1.54 \times 10^{-4}$$

اولاً : نستخرج الذوبانية المولارية :

58.3



$$[\text{Mg}^{+2}] = 1.54 \times 10^{-3}$$

$$[\text{OH}^-] = 2 \times 1.54 \times 10^{-3}$$

$$3.08 \times 10^{-3} \text{ mol/L}$$

$$K_{sp} = ( 1.54 \times 10^{-3} ) ( 3.03 \times 10^{-3} )^2$$

$$14.6 \times 10^{-9}$$

الاسبوع السابع والثامن

الوحدة النمطية

### **Stoichiometric calculation from chemical equation**

**مقدمة :-**

There are many methods are founded in chemical analysis to calculate the conc. Of solution , each methods depended on the quantity of solution , each methods depended on the quantity of solvent and solute .

**الهدف :-**

ان يكون الطالب قادراً على ان يفهم بعض المفاهيم الاساسية حول طرق حساب تراكيز المواد الكيميائية وحساب الاوزان الجزيئية والاوزان المتكافئة .

**امتحان قصير :-**

Define the mole fraction ?.

## Stoichiometric calculation of chemical analysis .

### Concentration units :-

There are many methods are founded in chemical analysis to calculate the conc. Of solution , each methods depended on the quantity of solvent and solute . The units of conc. Classified into two groups :-

#### 1- **physical methods :-**

- a- gm of solute in liter ( or 1000ml ) of solution .
- b- gm of solute in liter ( or 1000ml ) of solvent .
- c- gm of solute in 100 gm or ( 1000 gm ) of solution .
- d- percentage included .

#### 1- Weighing percentage ( w / w )

Is the percent of weight of solute to weight of solution

$$\frac{\text{Wt . of solute ( gm )}}{\text{Wt . of solution ( gm )}} \times 100$$

#### 2- volume percent of ( v / v )

is the percent of volume of dissolved liquid to volume of solution

$$\frac{\text{v . of solute}}{\text{v . of solution}} \times 100$$

#### 3- percent ( w / v )

is the percent of weight of solute to volume of solvent it expressed by ppm .

$$\text{ppm} = \frac{\text{wt}}{\text{v ( ml) }} \times 10^6$$



## 2- Chemical methods :-

### 1- Molar method

Molar solution : is the solution that contain one mole of solute in liter of solution .

Molarity of solution : Mole of solute in liter of solution .

$$M = \frac{\text{no. moles of solute}}{V(L)} \quad \text{no. of moles} = \frac{Wt}{M.wt}$$

$$M = \frac{Wt}{M.Wt} \times \frac{1000}{V(ml)}$$

The Molarity of 10.62 gm ( Ag NO<sub>3</sub> ) in 500 ml of solution

$$M = \frac{10.62}{170} \times \frac{1000}{50} \quad \begin{array}{l} f.wt. Ag = 108 \\ N = 14 \\ O = 16 \end{array}$$

=0.125

### 2- Molal solution :-

is the solution which contain one mole of solute in 1kgm of solvent .

Modality is the number of moles of solute in 1000gm of solvent

$$m = \frac{\text{no. moles of solut}}{1000gm \text{ of solvent}}$$

### 3- Mole fraction :-

Is the ratio of total moles of solute to total moles of solution

The sum . of mole fraction to solute and solvent = 1

### 4- formality :-

Is the number of formula weights of solute to liter of solution

$$F = \frac{\text{no } f . \text{wt}}{V(L)}$$

$$= \frac{Wt}{f . \text{wt}} \times \frac{1}{V(L)}$$

**5- normality :-**

is the no . of gram equivalent weight of solute to liter of solution

$$N_z = \frac{\text{no} . \text{eq} . \text{wt}}{V(L)}$$

$$\text{no} . \text{eq} \text{ wt} = \frac{\text{wt}}{\text{eq} . \text{wt}}$$

$$N = \frac{\text{wt}}{\text{eq} . \text{wt}} \times \frac{1000}{V(\text{ml})}$$

The relation between Morality & normality is  $nM = N$

When  $n$  : no . of equivalent

$$M = \frac{\text{wt}}{M . \text{wt}} \times \frac{1000}{V(\text{ml})}$$

$$Wt = M . \text{wt} \times v(L) \times M \dots\dots\dots 1$$

$$N = \frac{\text{wt}}{\text{eq} . \text{wt}} \times \frac{1000}{v(\text{ml})}$$

$$Wt = \text{eq} . \text{wt} \times v(L) \times N \dots\dots\dots 2$$

$$\therefore 1 = 2$$

$$M \times v(L) \times M . wt = N \times v(L) \times eq . wt$$

$$M \times M . wt = N \times eq . wt$$

$$M \times M . wt = N \times \frac{M . wt}{n}$$

$$nM = N$$

### **Equivalent weight of compound :-**

Is the weight of compound which accompanied with ( or exchange with ) one weight of hydrogen or eight weight of oxygen .We can calculate the equivalent weight of different compounds when we know the equivalent number of them .

### **The equivalent numbers of compounds**

1- The equivalent no . of Acid

a- mono basic acids :-

e.g.))  $\text{CH}_3 \text{COOH}$  ,  $\text{HCl}$  ,  $\text{HNO}_3$  ,  $\text{HClO}_4$

e.q no . = 1

b- Dibasic acids :-

e.g.))  $\text{H}_2\text{SO}_4$  ,  $\text{H}_2\text{SO}_3$  ,  $\text{H}_2\text{S}$

eq . no . = 2

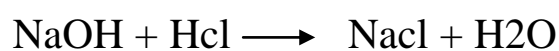
c- Tri basic acids :-

$\text{H}_3\text{PO}_4$

Eq . no . = 3

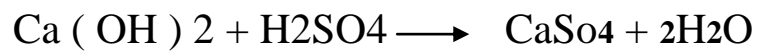
2- The equivalent no. of base

1- Mono basic base



eq . no . = 1

2- Di basic base



eq. no. = 2

$\text{Zn}(\text{OH})_2$  eq. no. = 2

3- The eq. no. of salt

A)  $\text{AgCl}$ ,  $\text{NaCl}$ ,  $\text{AgNO}_3$ ,  $\text{NaNO}_3$  eq. no. = 1

B) salt like  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{BaSO}_4$  eq. no. = 2

الاسبوع التاسع والعاشر والحادي عشر  
الوحدة النمطية

**Principles of quantitative gravimetric analysis**

**مقدمة :-**

Gravimetric methods of analysis are based upon the measurement of the weight of analyte or of a compound of known composition that contains the analyte . Two types of gravimetric methods :-

- 1- Precipitation methods .
- 2- Volatilization methods .

**الهدف :-**

ان يكون الطالب قادراً على ان يقوم بتقدير كمية المكونات او العناصر الداخلة في تركيب المركب الكيميائي او الخليط .

**امتحان قصير :-**

We dissolve the sample of manganite ( 1.542 gm ) and oxidized  $Fe^{+2}$  them precipitate it as  $Fe(OH)_3$  after this we ignition the precipitate which formed  $Fe_2O_3$  ( 1.485 gm ) what is the percentage of  $Fe_3O_4$  in sample ? .

## **Gravimetric methods of analysis :-**

Gravimetric method of analysis are based upon the measurement of the weight of analyte or of a compound of known composition that contains the analyte . Two types of gravimetric methods :-

### 1- **precipitation method** :-

The analyte ( or a species related to it ) is isolated as a sparingly soluble precipitate that either has a known composition or can be converted to a product of known composition by suitable heat treatment .

### 2- **Volatilization methods** :-

The analyte or it's decomposition products are volatilized at a suitable temperature .The volatile product is either collected and weighed , or the weight of the product is determined in directly from the loss in weight of the sample .

## **Properties of precipitates and precipitating reagent :-**

- 1- has a low solubility that losses from this source are negligible .
- 2- is readily filtered and washed free of contaminates .
- 3- is un reactive and of known composition after drying or , if necessary , ignition .

## **Gravimetric factor :-**

Gravimetric analysis depended upon weight of two substances :-

- 1- Sample .
- 2- Analyte .

The relationship between two weights [ weight of analyte and weight of substance ] is called gravimetric factor and we can use it to find the percent age or the conc. Of the analyte .

$$\text{Gravimetric factor} = \frac{f . w \text{ of the analyte}}{f . w \text{ of substance}} \times \frac{a}{b}$$

Where a & b are small numbers that have values such that the number of formula weights in the numerator and the denominator are chemically equivalent .

e .g.)):-

We dissolve the sample of manganite ( 1 . 542 gm ) and oxidized  $\text{Fe}^{+2}$  then precipitate it as  $\text{Fe}(\text{OH})_3$  after this we ignition the precipitate which formed  $\text{Fe}_2\text{O}_3$  in sample ? .

$$\begin{aligned} G.f &= \frac{M . wt \text{Fe}_3\text{O}_4}{M . wt \text{Fe}_2\text{O}_3} \times \frac{a}{b} \\ &= \frac{231.55}{159.7} \times \frac{2}{3} \\ &= 0.967 \end{aligned}$$

$$\begin{aligned} Wt \text{Fe}_3\text{O}_4 &= wt \text{ of } \text{Fe}_2\text{O}_3 \times G.f \\ &= 1.485 \times 0.967 \\ &= 1.436 \end{aligned}$$

$$\begin{aligned} \% \text{Fe}_3\text{O}_4 &= \frac{1.436}{1.542} \times 100 \\ &= 93.12\% \end{aligned}$$

### **Mechanism of precipitate formation :-**

Precipitation mechanisms contain nucleation and particle growth . The particle size of a formed precipitate is governed by the extent to which one of these processes predominates over the other .

Nucleation is a process by which some minimum of ions , atoms or molecules ( perhaps as few as four or five ) unite to form a stable second phase most commonly on the surface of suspended solid contaminants such as dust particles . Precipitation then occurs either by additional nucleation or by growth on nuclei ( particle growth ) or by a mixture of the two processes . If nucleation predominates a precipitate containing a large number of small particles results , if growth predominates a smaller number of large particles is produced .

### **Volatilization procedures :-**

The two most common gravimetric methods based on volatilization are those for water and carbon dioxide . Water is quantitatively eliminated from many inorganic samples by ignition . In the direct determination , it is collected on any of several solid desiccants and its mass is determined from the weight gain of the desiccant .

The indirect method based upon the weight loss suffered by the sample as the result of ignition .

Carbonates are decomposed by acids to give carbon dioxide (  $\text{CO}_2$  ) , which is readily evolved from solution by heat as in the direct analysis for water , the weight of carbon dioxide is established from the increase in the weight of a solid absorbent .

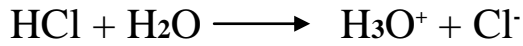


الاسبوع الثاني عشر والثالث عشر  
الوحدة النمطية

**Reaction of acids and bases**

**مقدمة :-**

Acids ionized in water to give hydronium ion which have a positive charge like this example .



Bases are soluble in water which called alkali , aqueous solutions of alkalis are electrolyte .

**الهدف :-**

ان يكون الطالب قادرا على ان يفهم تفاعلات التعادل ولمدى الذي تتفكك به الحوامض في المحلول وظروف الاتزان لمثل هذه التفاعلات .

**امتحان قصير :-**

Calculate the PH for solution prepared by addition of 85ml from NaOH ( 0 . 1 M ) to 75 ml of Hcl ( 0 . 1 M ) ? .

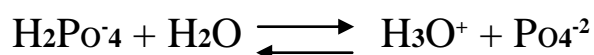
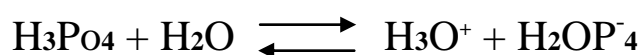
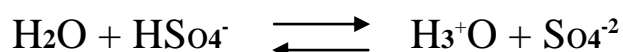
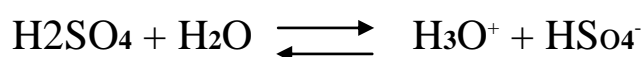
## **Ionization of acids & bases**

**acids ionized in water to give hydronium ion which have a positive**

**charge like this example**  $\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$

**This equation about the ionization of mono basic .**

The ionization of poly basic like  $\text{H}_2\text{SO}_4$  ,  $\text{H}_3\text{PO}_4$  are obtain in two or three steps :-



Bases are soluble in water which called alkali .

Aqueous solutions of alkalis are electrolyte .

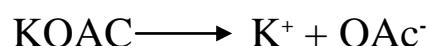
Alkaline and acid solutions are change the colors of indicators .

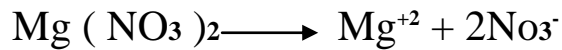
## **Electrolytes .**

Electrolytes are substances that produce ions on dissolving in water .

If dissociation ions is complete , as in the dissolution of a crystal NaCl to give the ions  $\text{Na}^+$  and  $\text{Cl}^-$  , or HCl to give the ions  $\text{H}^+$  and  $\text{Cl}^-$  , the substance is called a strong electrolyte if ionization is in complete .

As in a solution of acetic acid to give a mixture of un dissociated HOAC molecules and  $\text{H}^+$  and  $\text{OAc}^-$  ions , the substance is called a weak electrolyte . Most salts ionize almost completely in water and there fore are strong electrolytes :





PH of Aqueous solution :-

### 1- Strong Acid .

بما ان يكون الحامض قوي اذن يتفكك بدرجة كبيرة فيكون تركيز ايون الهيدورينوم ه نفسه التركيز المولاري للحامض في المحلول .

e.g.)) ∴ calculate the PH for solution at addition of 10ml of

0 . 1 M NaoH to 100ml Hcl ( 0 . 025 M ) ?

$$\text{m . mole of Hcl} = 100 \times 0 . 025$$

$$= 2 . 5$$

$$\text{m . mole of NaOH} = 10 \times 0 . 1$$

$$= 1$$

$$\text{m . mole of Hcl remain} = 2 . 5 - 1$$

$$= 1 . 5$$

$$\text{Total volume} = 100$$

$$+ 10 = 110$$

$$[\text{H}^+] = \frac{1.5}{110}$$

$$= 0 . 014$$

$$0 . 014$$

$$\text{PH} = - \log^{[\text{H}^+]} \Rightarrow \text{PH} = - \log^{0.014}$$

$$= 1 . 86$$

### 2- Strong Base .

calculate the PH , of solution prepared by addition of 85ml from

NaOH ( 0 . 1 M ) to 75 ml of Hcl ( 0 . 1M ) ?

$$\text{m . mole of NaOH} = 85 \times 0 . 1 = 8 . 5$$

$$m . \text{ mole of HCl} = 75 \times 0 . 1 = 7 . 5$$

$$m . \text{ mole of base remain} = 8 . 5 - 7 . 5 = 1$$

$$\text{Total volume} = 85 + 75$$

$$= 160$$

$$\frac{1}{160} \Rightarrow 6.25 \times 10^{-3} M$$

$$POH = -10g^{[OH^-]} \Rightarrow POH = -10g^{6.25 \times 10^{-3}}$$

$$[OH^-] = \quad \quad \quad = 2.21$$

$$PH = 14 - POH$$

$$= 11.79$$

### 3- PH of weak Acid .

The equation which used to calculate the conc. Of hydroinim ion for weak acid is :-

$$[H_3^+O] = \sqrt{Ka . c}$$

Ka : ionization constant of weak acid

C : conc. Of weak acid

e.g.))  $\therefore$  calculate the PH for the solution of 0 . 01M acetic acid if you know that Degree of ionization is 0 . 135 ?

$$\text{Degree of Ionization} = \frac{[H^+]}{[CH_3COOH]}$$

$$[H^+] = 0.135 \times 0.01 = 1.35 \times 10^{-3}$$

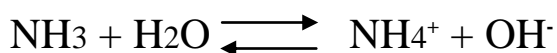
$$PH = -Log^{1.35 \times 10^{-3}}$$

$$= 2.87$$

#### 4- PH of weak base .

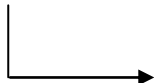
e.g.)) ∴ calculate PH for 0.1M Ammonium Solution

$$K_b = 1.8 \times 10^{-5} =$$



$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$1.8 \times 10^{-5} = \frac{x^2}{0.1 - x}$$



يمكن اهملها لانها صغيرة  $x$

$$x = 1.34 \times 10^{-3}$$

$$POH = 2.87$$

$$PH = 14 - 2.87$$

$$= 11.13$$

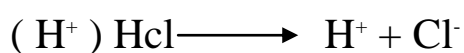
اذن المعادلة العامة لحساب الاس الهيدروجيني PH لمحاليل القواعد الضعيفة :-

$$[OH^-] = \sqrt{K_b \cdot c}$$

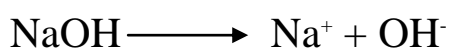
### Theory of Acids and Bases .

#### 1- Arrhenius Definition :-

Acid :- any substance that ionized in water to give hydrogen ions

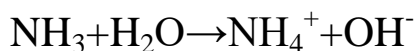


Base :- any substance that ionized in water to give hydroxyl ions



#### 2- Bronsted – Lowry Definition :-

Acid :- a substance that given proton .  $\text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^-$  Bases: a substance that taken proton .



### **Lewis Definition :-**

Acid : a substance that can accept pair of electrons or more to form an a covalent bond , because it containe empty orbital in outer shell . It included the following :-

1-Positive ion like :  $\text{H}^+$  ,  $\text{Ag}^+$  ,  $\text{Cu}^{+2}$  ,  $[\text{Fe}(\text{H}_2\text{O})_6]^{+2}$

2-Molecules that have a central atom with deficiency two electrons .

**Base** : a substance that can donate pair of electrons to from an a covalent bond .

Which included the following :-

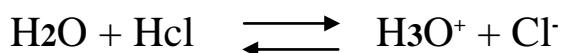
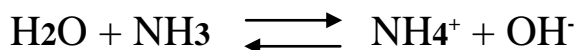
1- Negative ions like :  $\text{CN}^-$  ,  $\text{OH}^-$  :  $\text{H}^-$

2- Us saturated hydrocarbons that container double or triple bond like  $\text{CH}_2=\text{CH}_2$  ,  $\text{CH}\equiv\text{CH}$  .

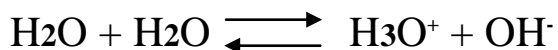
3- Moleclues that have un shared pair of electrons like  $\text{NH}_3$  ,  $\text{H}_2\text{O}$  .

### **Amphoteric substance .**

A substance which can react as acid and base like  $\text{H}_2\text{O}$



$\therefore$   $\text{H}_2\text{O}$  can react as acid & base there for it can react with itself :-



conc. Of the analyte .

الاسبوع الرابع عشر والخامس عشر

الوحدة النمطية

## **Precipitation reactions**

**مقدمة :-**

Precipitation is the formation of a solid in a solution or inside another solid during a chemical reaction or by diffusion in a solid .

**الهدف :-**

ان يكون الطالب قادراً على ان يفهم تفاعلات الترسيب وميكانيكية تكوين الراسب حيث تغير تفاعلات الترسيب مهمة لانها تستخدم في مجالات عديدة مثل ازالة الاملاح من الماء او في صناعة الاصباغ .

**امتحان قصير :-**

**Define the following :-**

Precipitation reaction , Digestion .

## **Precipitation reactions**

Precipitation is the formation of a solid in a solution or inside another solid during a chemical reaction or by diffusion in a solid . When the reaction occurs in a liquid , the solid formed is called the precipitate , and the liquid remaining above the solid is called the supernatant . Powders derived from precipitation have also historically been known as flowers .

### **Methods of precipitation :-**

Natural methods of precipitation include settling or sedimentation , where a solid forms over a period of time due to ambient forces like gravity or centrifugation . During chemical reactions . Precipitation may also occur particularly if an insoluble substance is introduced into a solution and the density happens to be greater ( otherwise the precipitate would float or form a suspension ) . With soluble substances , precipitation is accelerated once the solution becomes supersaturated . In solids , precipitation occurs if the concentration of one solid is above the solubility limit in the host solid , due to e . g . rapid quenching or ion implantation , and the temperature is high enough that diffusion can lead to segregation into precipitates. precipitation in solids is routinely used to synthesize nano clusters . An important stage of the precipitation process is the onset of nucleation . The creation of a hypothetical solid particle includes the formation of an interface , which requires some energy based on the relative surface energy of the solid and the solution . If this energy is



not available , and no suitable nucleation surface is available , super saturation occurs .

## **The operations of precipitation analysis**

### **Dissolution of sample .**

We dissolve the sample by using suitable solvent like H<sub>2</sub>O , acid or base

### **Digestion.**

Digestion , or precipitate ageing

, happens when a freshly – formed precipitate is left , usually at a higher , in the solution from which it is precipitated . It underlying digestion is called outward ripening .

### **Filtration .**

We can not use the filter paper for some precipitate which can reduce it like AgCl because its burned the filter paper then reduce the precipitate . We can use filter paper and crucible for precipitate which contain big crystals .

### **Washing .**

We washed the precipitate for many times to remove the solution & the suspended solid .

### **Drying and ignition .**

We must dry the wet precipitate before weighing it at temperature ( 110 – 150°C ) which remove the adsorbent water from some

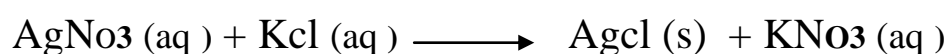
precipitate . Some times we need the ignition at high temperature to remove the adsorbant water from precipitate like ferric oxides .

### **Application :-**

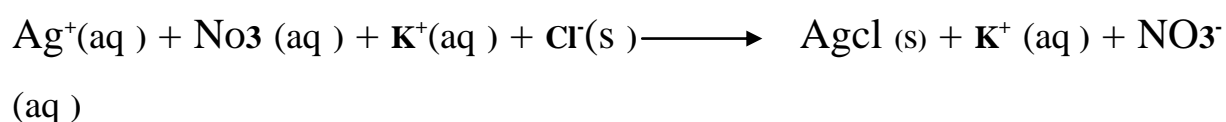
Precipitation reactions can be used for making pigments , removing salts from water in water treatment , and in classical qualitative inorganic analysis . Precipitation is also useful to isolate the products of a reaction during workup . Ideally . The product of the reaction is insoluble in the reaction solvent . Thus , it precipitates as it is formed , preferably forming pure crystals . Precipitation from a solid solution is also a useful way to strengthen alloys , this process is known as solid solution strengthening .

### **Re presentation using chemical equations :-**

An example of a precipitation reaction : Aqueous silver nitrate (  $\text{AgNO}_3$  ) is added to a solution containing potassium chloride (  $\text{KCl}$  ) and the precipitation of a white solid , silver chloride is observed

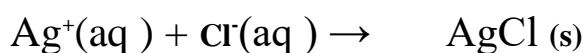


The silver chloride (  $\text{AgCl}$  ) has formed as a solid , which is observed as a precipitate . This reaction can be written emphasizing the dissociated ions in a combined solution . This is known as the ionic equation



A final way to represent a precipitate reaction is known as a net ionic reaction . In this case , any spectator ions ( those which do not

contribute to the reaction ) are left out of the formula completely .  
 This simplifies the above equations to the following :



### **Cation sensitivity** .

Precipitate formation is useful in the detection of the type of cation in salt . To do this , an alkali first reacts with the unknown salt to produce a precipitate which is the hydroxide of the unknown salt . To identify the action , the color of the precipitate and its solubility in excess are noted . Similar processes are often used to separate chemically similar elements , such as the Alkali earth metals . tem premature .

e.g.)) Is the precipitate of Agcl formed in the addition of 3mg AgNo3 and 2mg Nacl to 250 ml H2O ?

$$170\text{gm/mole} \quad K_{\text{sp}} = 10^{-10}$$

$$\begin{aligned} \text{m . mole AgNo}_3 &= 3\text{mg} / 170 \text{ mg} / \text{m . mole} \\ &= 0 . 0177 \text{ m . mole} \end{aligned}$$

$$[\text{AgNo}_3] = 0 . 0177 \text{ m . mole} / 250 \text{ ml} = 7 \times 10^{-5} \text{ M}$$

$$7 \times 10^{-5} = [\text{Ag}^+]$$

$$\begin{aligned} \text{m . mole Nacl} &= 2\text{mg} / 58 . 5\text{mg} / \text{m . mole} \\ &= 0 . 0342 \end{aligned}$$

$$[\text{Nacl}] = 0 . 0342 / 250 = 1 . 4 \times 10^{-4}$$

$$= 1 . 4 \times 10^{-4} = [\text{Cl}^-]$$

$$\begin{aligned} [\text{Ag}^+][\text{Cl}^-] &= (7 \times 10^{-5})(1 . 4 \times 10^{-4}) \\ &= 10^{-8} \end{aligned}$$

$$K_{sp} = 10^{-10}$$

$$10^{-10} < 10^{-8}$$

∴ The precipitate is formed

الاسبوع السادس عشر والسابع عشر  
الوحدة النمطية

**Oxidation and reduction**

**مقدمة :-**

In an oxidation / reduction reaction , electrons are transferred from one reactant to an other . A substance which tends to extract electrons from other species is called an oxidizing agent or an oxidant . A reagent that

readily donates electrons to another species is called reducing agent or reluctant .

**الهدف :-**

ان يكون الطالب قادرا على ان يفهم تفاعلات الاكسدة والاختزال المصحوبة بتغير الحالة التاكسدية لمادتين , حيث تحصل هذه التغيرات نتيجة لانتقال اليكترون او اكثر من ذرة ايون الى اخرى .

**امتحان قصير :-**

Define the Galvanic and Electrolytic cell ? .

## The Oxidation / Reduction Equilibrium

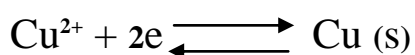
### Oxidation / Reduction processes .

In an oxidation / reduction reaction , electrons are transferred from one reactant to another . A substance that has a strong affinity for electrons and thus tends to extract them from other species is called an oxidizing agent or an oxidant . A reducing agent , or reluctant , is a reagent that readily donates electrons to another species  $Ce^{+4} + Fe^{+2} = Ce^{+3} + Fe^{+3}$

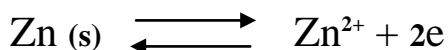
### Oxidation / Reduction in Electro chemical cells .

Most oxidation / reduction reaction can be carried out in two ways , In the first , the oxidant and reluctant are brought together in a medium where in the reacting molecules , atoms , or ion approach one another closely enough so that a direct trans for of electrons can take place . In the second , the reactants are made apart of an electro chemical cell in which the two half – reactions are physically separated , electron transfer then takes place via a metallic conductor of electricity .

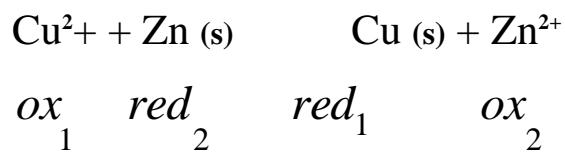
As an example of the first method , metallic zinc can be oxidized to zinc ions by immersing a piece of the metal in a solution containing copper sulfate . Copper (II) ions migrate to the surface of the zinc and are reduced :



While a chemically equivalent quantity of zinc is oxidized :



The equation for the over all process is obtained by adding the equations for the two half – reactions :

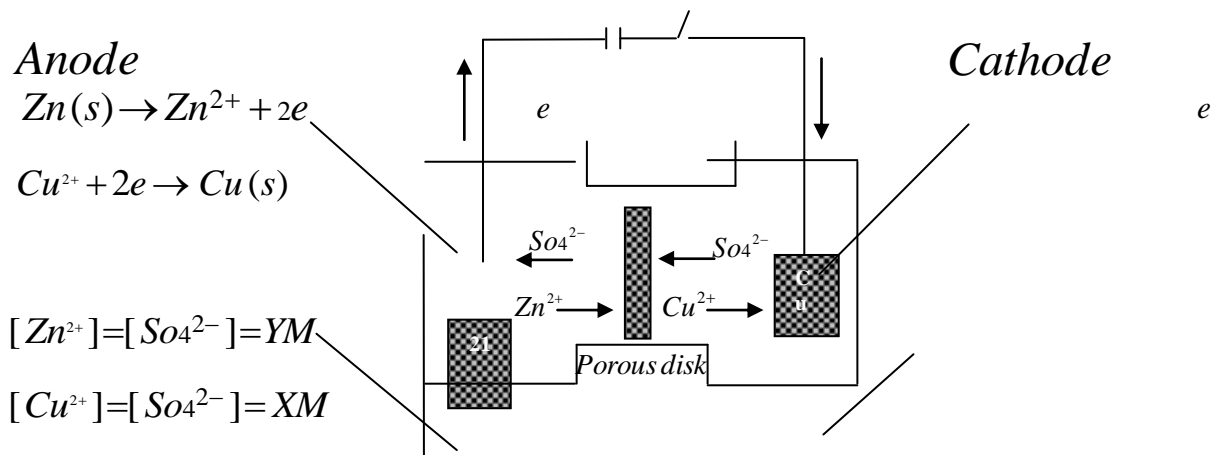


### **Electro chemical cells .**

A cell consists of a pair of conductors or electrodes , usually metallic , each of which immersed in an electrolyte . when the electrodes are connected by an external . Conductor and a passage of current ensure , a chemical oxidation – reduction at the surface of electrodes occurs .

### **Galvanic of Electrolytic cells .**

Electro chemical cells are classified as galvanic ( or voltaic ) when they act a source of electrical power and electrolytic when they consume electrical\_energy . Many cells can be converted form one mode to the other . For example , the cell in figure ( i ) is a galvanic cell that develops a potential of roughly IV . It could operate as an electrolytic cell , however a potential some what greater then IV were incur pirated .



### The schematic Representation of cell .

The cell in figure (1) can be represented as  $Zn / ZnSO_4 (yM) / CuSO_4 (xM) / Cu$ . Where  $yM$  is the molar conc. Of the  $ZnSO_4$  and  $xM$  is the molar conc. Of the  $CuSO_4$ . An alternative way of describing this cell is

$Zn / Zn^{2+} (yM) / Cu^{2+} (xM) / Cu$ .

### The Definition of electrode potential .

The potential of an electro chemical cell involving a carefully defined reference electrode .

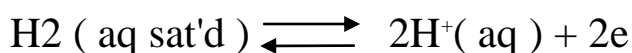
Like :  $Cu^{2+} + 2e \rightleftharpoons Cu (s)$       Electrode potential  
 $(v)$   
 $+ 0.334$

### The standard Hydrogen Electrode .

The hydrogen electrode can serve as an anode or cathode depending upon the half – cell with which it is coupled . Hydrogen is oxidized to hydrogen ions when the electrode acts as an anode , The reverse occurs when it acts as a cathode . The purpose of the gas stream shown in figure (2) is to ensure that the solution is



continuously saturated with molecular hydrogen . Thus , when a hydrogen electrode operates as an anode , the half-cell process is the sum of two reactions :



The over all reaction is

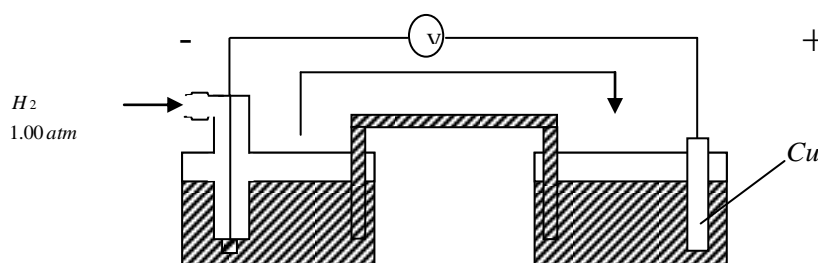
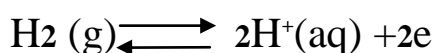
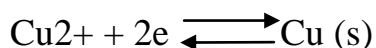


Figure (2)

The definition of electrode potential for the half – reaction



### The effect of concentration on electrode potentials .

#### The nernst equation .

Consider the generalized reversible half – reaction .



A , B , B , C , D : formulas for species .

e : electron

a , b , c , d and n : the number of moles of participants involved in the half – cell process .

It can be shown that the electrode potential for this process is :-

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[C]^c [D]^d \dots}{[A]^a [B]^b \dots}$$

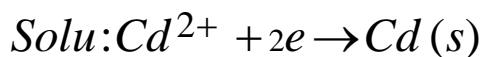
Where :  $E^\circ$  = a constant called the standard electrode potential which change characteristic for each half – cell reaction

- R : The gas constant , 8 , 314 KJ<sup>-1</sup> mol<sup>-1</sup>
- T : Temperature in K
- N : Number of electrons
- F : Faraday = 96485 coulombs
- Ln : natural logarithm = 2 . 303 log for temperature 25C<sup>o</sup> the using equation is
- 

$$E = E^\circ - \frac{0.0592}{n} \log \frac{[C]^c [D]^d \dots}{[A]^a [B]^b \dots}$$

e.g.1)):-

calculate potential of a cadmium electrode immersed in a 0 . 0100 M Cd<sup>2+</sup> solution if you know that  $E^\circ = -0.403V$



←

$$E = E^\circ - \frac{0.0592}{2} \log \frac{1}{[Cd^{2+}]}$$

$$= -0.403 - \frac{0.592}{2} \log \frac{1}{0.0100}$$

$$= -0.403 - \frac{0.0592}{2} \log 100$$

$$= -0.403 - \frac{0.0592}{2} \times 2 = -0.462V$$

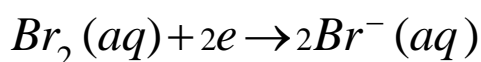
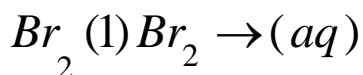
e.g.2):-

Calculate the potential of a platinum electrode immersed in a solution Prepared by saturating 0.0100M KBr with Br<sub>2</sub>.

The pertinent half – reaction is



Note that the symbol ( l ) in this half – reaction indicates that liquid Br<sub>2</sub> is present in excess and that the aqueous solution of KBr is at all times saturated with Br<sub>2</sub> , then by definition , the activity of Br<sub>2</sub> is constant and assigned a value of 1.00 The overall process can be considered the sum of the two equilibrium



$$E = 1.065 - \frac{0.0592}{2} \log \frac{[\text{Br}^-]^2}{1.00}$$

$$= 1.065 - \frac{0.0592}{2} \log \frac{(1.00 \times 10^{-2})^2}{1.00}$$

$$= 1.056 - \frac{0.0592}{2} (-4.00) = 1.183V$$

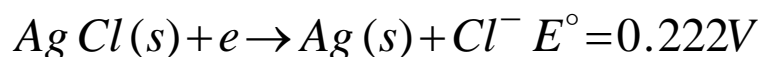
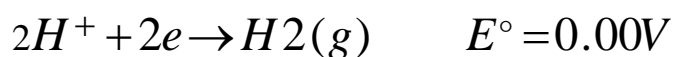
### The calculation of cell potentials .

The potential of a cell , be it galvanic or electrolytic , is the difference between the electrode potential of the cathode and that of the anode :-

$$E_{cell} = E_{Cathode} - E_{anode}$$

e.g.3)):-

Calculate the theoretical potential for the cell Ag / Agcl ( sat'd ) Hcl ( 0 . 0200 M ) / H2 ( 0 . 800 atm ) , pt

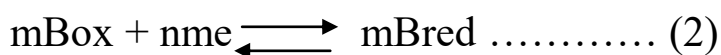
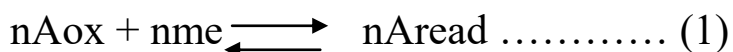


$$E_{Agcl} = 0.222 - \frac{0.0592}{1} \log 0.0200 = 0.323V$$

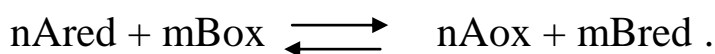
$$E_{pt.H_2} = 0.000 - \frac{0.0592}{2} \log \frac{0.800}{(0.0200)^2} = -0.098V$$

$$E_{Cell} = -0.098 - 0.323 = -0.421V$$

### **The calculation of Equilibrium constants for oxidation / Reduction Reactions from standard Electrode Potential :**



Subtraction of the first equation from the second yields



When this system is in equilibrium :-

$$E_A = E_B$$

$$E_A^\circ - \frac{0.0592}{nm} \log \frac{[A_{red}]^n}{[A_{ox}]^n} = E_B^\circ - \frac{0.0592}{nm} \log \frac{[B_{red}]^m}{[B_{ox}]^m}$$

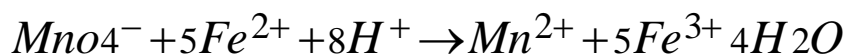
Which re arranges to

$$E_B^\circ - E_A^\circ = \frac{0.0592}{nm} \log \frac{[A_{ox}]^n [B_{red}]^m}{[A_{red}]^n [B_{ox}]^m} = \frac{0.0592}{nm} \log K_{eq}$$

$$\text{Then } \log k_{eq} = \frac{nm(E_B^\circ - E_A^\circ)}{0.0592}$$

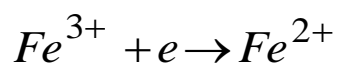
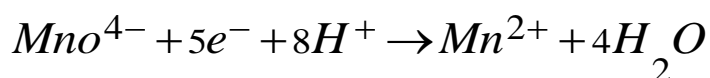
e.g.4):-

Calculate the equilibrium constant for the reaction



$$E^\circ MnO_4 = +1.51V \quad E^\circ Fe^{3+} = +0.771V$$

solu ) :-



ملاحظة :- عند ضرب المعادلة بـ 5 لا يؤثر على قيمة

$$E_{Fe^{3+}} = E_{MnO_4^-}$$

$$E^\circ_{Fe^{3+}} - \frac{0.0592}{3} \log \frac{[Fe^{2+}]^5}{[Fe^{3+}]^5} = E^\circ_{MnO_4^-} - \frac{0.0592}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

$$\frac{0.0592}{5} \log \frac{[Mn^{2+}][Fe^{3+}]^5}{[MnO_4^-][Fe^{2+}]^5[H^+]^8} = \frac{0.0592}{5} \log keq = E^\circ_{MnO_4^-} - E^\circ_{Fe^{3+}}$$

$$\log keq = \frac{5(1.51 - 0.771)}{0.0592} = 62.52 = 62.5$$

$$keq = 10^{0.52} \times 10^{62} = 3 \times 10^{62}$$

الاسبوع الثامن عشر والتاسع عشر والعشرون  
الوحدة النمطية

**Complex formation reactions**

**مقدمة :-**

A complex is an ion or molecule formed by reaction between two or more ions or molecules capable of independent existence .

**الهدف :-**

ان يكون الطالب قادراً على ان يفهم التفاعلات المتضمنة تكوين المعقدات وانواع الليكاندات المكونة لهذه المعقدات .

**امتحان قصير :-**

What is the types of Ligand with examples ? .

## Complex formation reaction

### Introduction :-

A complex is an ion or molecule formed by reaction between two or more ions or molecules capable of independent existence . The most important complication reactions from an analytic cell point of view are those in which one reactant is a metal ion and the other an ion or molecule possessing an atom with an unshared pair of electrons . The electron – pair donor ion or molecule , called a ligands , are  $\text{H}_2\text{O}$  ,  $\text{NH}_3$  ,  $\text{Cl}^-$  , and the amino acid glycine (  $\text{H}_2\text{NCH}_2\text{COOH}$  ) .

A metal ion can usually form a bond with more than one donor atom . The maximum depends on the coordination number . The number of electron pairs the mutation can accept , it depends also on the number and location of the unshared electron pairs on the legend . Coordination numbers and geometries for some metal ions in aqueous solution are listed in the following table .

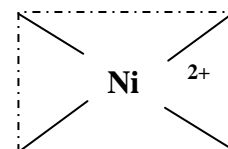


| Metalion | Usual Coordination Number in Aqueous solution | Usual Geometry |
|----------|---|----------------|
|----------|---|----------------|

Ag ( I )  
 Cu ( II ) , Ni ( II ) 4 or 6 , depending

2 linear  
 4 planer

- Ag<sup>+</sup> -

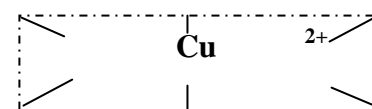
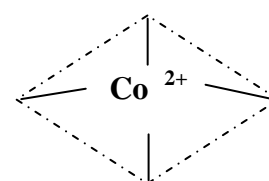


Or

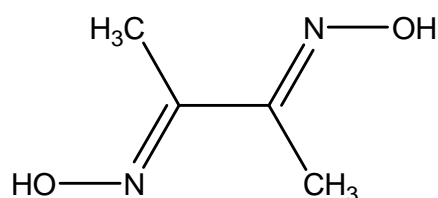
Fe ( II ) , Ni ( III )  
 Co ( III )

6

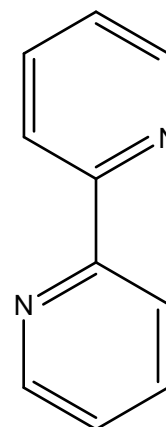
4 Tetrahedral  
 Octahedral



Ligands that provide one pair of electrons to a bond are called unidentate , or condensate , examples are NH<sub>3</sub> , Br<sup>-</sup> , SCN<sup>-</sup> and CH<sub>3</sub>CN . Those that are capable of bonding to a metal ion by two or more electron pairs are multidentate , or polydentate . Multidentate ligands are also called cheats , Examples of chelae legends are .



Dimethyl glyoxime  
 (DMG)

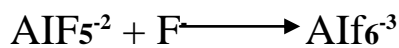
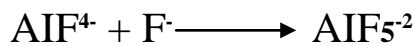
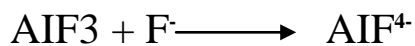
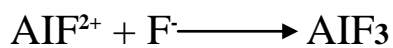
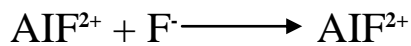
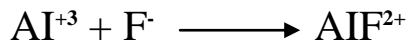


bipyridine  
 ( Bipy )

In those compounds the sites of coordination to metal ions are either nitrogen or oxygen .

### EQUILBRIA WITH UNIDENTATE LIGANDS

Complexes form stepwise . Thus , the complication of Al<sup>3+</sup> ion with fluoride ions involves a series of equilibrium :



Complexation reactions are usually expressed as complex formation . Therefore , complexation equilibrium constants are expressed as stability , or formation constants . For the formation of the first two aluminum fluoride complexes the equilibrium expressions are .

$$\frac{[\text{AlF}^{2+}]}{[\text{Al}^{3+}][\text{F}^-]} = K_1 = 1.3 \times 10^6$$

$$\frac{[\text{AlF}_2^+]}{[\text{AlF}^{2+}][\text{F}^-]} = K_2 = 1.0 \times 10^5$$

Similar expressions for K<sub>3</sub> , K<sub>4</sub> and K<sub>5</sub> have values of 7600 , 1000 and 25 . For the last stage

$$\frac{[\text{AlF}_6^{3-}]}{[\text{AlF}_5^{2-}][\text{F}^-]} = K_6 = 2.5$$

$K_1, K_2, \dots, K_6$  are stepwise formation constants .  
 ( The numerical values quoted here are for complication in solutions  
 with an ionic strength of 0.5 ).

The overall formation constant , which is the equilibrium expression  
 for the overall formation reaction  $Al^{3+} + 6F^- \rightleftharpoons AlF_6^{3-}$  is written

$$K_{eq} = \frac{[AlF_6^{3-}]}{[Al^{3+}][F^-]^6} = 6.3 \times 10^{19}$$

The relation between stepwise and overall formation constants is

$$\beta_1 = K_1, \beta_2 = K_1 K_2, \beta_3 = K_1 K_2 K_3 \text{ and } \dots \text{ soon } . \quad \text{Thus}$$

$$\beta_6 = K_1 K_2 \dots K_6$$

e.g.))

Determine the values of  $\beta_x$  for the tetra amine complex of  $Zn^{2+}$  the  
 values of  $K_1, K_2, K_3$  and  $K_4$  are 210 , 310 , 200 and 160 so :-

$$\beta_4 = K_1 K_2 K_3 K_4 = 2.1 \times 10^9$$

$$\text{similarly } \beta_2 = K_1 K_2 = 6.5 \times 10^4$$

For  $Ag^+$  the values of  $K_1$  and  $K_2$  are  $2 \times 10^3$  and  $7.9 \times 10^3$

$$\beta_2 = K_1 K_2 = 1.6 \times 10^7, \text{ and } \beta_1 = 2 \times 10^3$$

## Analytical Applications of unidentate ligands .

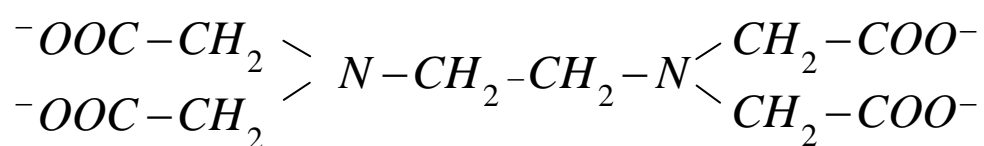
The Analytical used of unidentate Ligands is currently limited to only a few titration . The most important are the titration of cyanide with silver to form  $\text{Ag}(\text{CN})_2$  , the titration of  $\text{Hg}^{2+}$  ,  $\text{Cu}^{2+}$  and  $\text{Ni}(\text{CN})_4^{2-}$  . Because all steps of these complexes are highly stable , stepwise formation does not affect their analytical usefulness .

## Multidentate Ligands .

### Ethylene diamante tetra acetic Acid ( EDTA ) .

Of the many multi dentate Legends that have been investigated as analytical tartans over the past 35 years . The most important is ethylene diamante tetra acetic acid ( EDTA ) often written  $\text{H}_4\text{Y}$  . The tetra basic anion of this acid  $\text{Y}^{4-}$  forms complexes with virtually all metalions .

Are expressed as stability , or formation constants . For the formation of the first two aluminum fluoride complexes the equilibrium expressions are



EDTA

Ethylene diamante tetra acetic acid

الاسبوع الحادي والعشرين والثاني والعشرين

الوحدة النمطية

## Complexes

**مقدمة :-**

A coordination complex or metal complex , is a structure consist ion of a central atom or ion ( usually metallic ) bonded to a surrounding array of molecules or anions ( Ligands , complexing agents )

**الهدف :-**

ان يكون الطالب قادراً على ان يتعرف على المعقدات الكيميائية ( تركيبها , الشكل الهندسي , الازومرات , الازومرات الفراغية ) واصنافها وبعض التطبيقات حول هذه المعقدات .

**امتحان قصير :-**

Enumerate the classification of coordination complexes ? .

## **Coordination complex .**

A coordination complex or metal complex , is a structure consisting of a central atom or ion ( usually metallic ) , bonded to a surrounding array of molecules or anion ( Ligands , complexing agents ) .

Coordination refers to the " coordinate covalent bonds " between the ligands and the central atom .

## **Structure of coordination complexes .**

The ions or molecules surrounding the central atom are called ligands . Ligands are generally bound to central atom by a coordinate covalent bond .

## **Geometry .**

In coordination chemistry , a structure is first described by its coordination number , the number of ligands attached to the metal . coordination numbers are normally between two and nine . The number of bonds depends on the size , charge and electron configuration of the metal ion and the ligands . Metal ions may have more than one coordination number . Typically the chemistry of complexes is dominated by interactions between s and p molecular orbitals of the ligand and the d orbitals of the metal ions . The most observed geometries are listed below .

- 1- Linear for two . Coordination .
- 2- Trigonal planar for three . Coordination .
- 3- Tetrahedral or square planar for four . Coordination .
- 4- Trigonal bipyramidal or square pyramidal for five . Coordinate – ion .

5- Octahedral or trigonal prismatic for six . Coordination .

6- Pentagonal bipyramidal for seven . Coordination .

7- Square anti prismatic for eight . Coordination .

8- Tri – capped octahedral prismatic for nine coordination .

### **Iso merism** .

The arrangement of the ligands is fixed for a given complex but in some cases it is mutable by a reaction that forms another stable isomer .

### **Streo isomerism** .

Streo isomerism occurs with the same bonds in different orientations relative to one another stereoisomerism can be classified into :-

Cis – trans

Cis – trans isomerism occurs in octahedral and square planar complexes . When two ligands are mutually adjacent they are said to be cis , when opposite each other , trans .

### **Classification** .

The coordination complexes can be classified according to the nature of the ligands :-

1- Classical : Ligands in classical coordination chemistry bind to metals . almost exclusively , via their " lone pairs " of electrons residing on the main group atoms of the ligand . Typical ligands are  $\text{H}_2\text{O}$  ,  $\text{Cl}^-$  ,  $\text{CN}^-$  . e.g.)  $[\text{Co}(\text{EDTA})]^-$  ,  $[\text{Co}(\text{NH}_3)_6]^{3+}$

2- Organometallic chemistry : Ligands are organic ( alkenes , alkynes , alkyls ) as well as .

" organic like " ligands such as phosphates , hydride and co .  
e.g.)) ( C<sub>5</sub>H<sub>5</sub> ) Fe ( CO )<sub>2</sub> CH<sub>3</sub> .

3- Bioinorganic chemistry : Ligands are those provided by nature .  
especially in clouding the side chaise of amino acid , and many  
cofactors such as , and porphyrins

e.g.)) hemoglobin

### **Application of coordination compounds .**

- 1- They are used in photography . i . e . Ag Br forms soluble complex with sodium thiosulfate in photography .
- 2- K [ Ag ( CN )<sub>2</sub> ] is used for gold plating .
- 3- Some legends oxidize Co<sup>2+</sup> to Co<sup>3+</sup> ion .
- 4- EDTA is used for estimation of Ca<sup>2+</sup> and Mg<sup>2+</sup> in hard water .
- 5- Silver and gold are extracted by treating zinc with their cyanide complexes .



الاسبوع الثالث والعشرون والرابع والعشرون

الوحدة النمطية

### **Catalyst used in industry**

#### **Catalyst** .

Catalyst , substance that can cause a change in the rate of a chemical reaction without it self being consumed in the reaction . The changing of the reaction rate by use of a catalyst of is called catalysis . substances that in crease the rate of reaction are called positive catalysts or , simply , catalysts , while substances that decrease the rate of reaction are called negative catalysts or inhibitors .

#### **Mechanism of catalysis** .

Catalysts work by changing the a activation energy for a reaction , i . e . the minimum energy needed for the reaction to occur . This is a accomplished by providing a new mechanism or reaction path through which the reaction can proceed . When the new reaction path has a lower activation energy , the reaction rate is increased the reaction is said to be. Catalyzed if activation energy for the new path is higher the reaction rate is decreased and the reaction is said to be inhibited . inhibitors can provide an interesting challenge to the chemist . For example , because oxygen is an inhibitor of free radical reactions , many of which are impotent in the synthesis of polymers , such reactions mute be per formed in an oxygen . Free environment .

e.g.))

A blanket of nitrogen gas .

In some reactions one of the reaction products is a catalyst for the reaction. This phenomenon is called self-catalysis or autocatalysis. An example is the reaction of permanganate ion with oxalic acid to form carbon dioxide and manganous ion, in which the manganous ion acts as an autocatalyst. Such reactions are potentially dangerous since the reaction rate may increase to the point of explosion.

Some substances that are not themselves catalysts increase the activity of a catalyst when added with it to some reaction, such substances are called promoters. Alumina is a promoter for iron when it is used to catalyze the reaction of hydrogen and nitrogen to form ammonia. Substances that react with catalysts to reduce or eliminate this effect are called poisons.

## **Types and importance of catalysts .**

### **Enzymes : Natural Catalysts .**

Enzymes are the commonest and most efficient of the catalysts found in nature . Most of the chemical reactions that occur in the human body and in other living things are high – energy reactions that would occur slowly . If at all with out the catalysis provided by enzymes . For example in the absence of catalysis it takes several weeks for starch to hydrolyze to glucose a trace of the enzyme ptyalin , found in human saliva accelerates the reaction so that starches can be digested . some enzymes increase reaction rates by a factor of one billion or more .

Enzymes are generally specific catalysts that is , they catalyze only one reaction of one particular reactant ( called its substrate ).Usually the enzyme and its substrate have complementary structures and can bond together to form a complex that is more reactive due to the presence of functional groups in the enzyme . Which stabilize the transition state of the reaction or lower the activation energy . The toxicity of certain substances ( e.g. carbon monoxide and the nerve gases ) is due to their inhibition of life – sustaining catalytic reactions in the body .

### **Laboratory and industrial catalysts .**

Catalysis is also important in chemical Laboratories and in industry . Some reactions occur faster in the presence of a small amount of an acid or base and are said to be acid catalyzed or base catalyzed . For example the hydrolysis of esters is catalyzed by the presence of a

small amount of base in this reaction it is the hydroxide ion ,  $\text{OH}^-$  , that reacts with the ester , and the concentration of the hydroxide ion is greatly increased over that of pure water by the presence of the base . Although some of the hydroxide ions provided by the base are used up in the first part of the reaction , they are regenerated in a later step from water molecules , the net amount of hydroxide ion present is the same at the beginning and end of the reaction . So the base is thought of as a catalyst and not as reactant .

Finely divided metals are often used as catalysts . they adsorb the reactants into their surfaces . Where the reaction can occur more readily for e.g . hydrogen and oxygen gases can be mixed without reacting to form water , but if a small amount of powdered platinum is added to the gas mixture the gases react rapidly . Hydrogenation reactions e.g . the formation of hard cooking fats from vegetable oils , are catalyzed by finely divided metals or metal oxides . The commercial preparation of sulfuric acid and nitric acid also depends on such surface catalysis . Other commonly used surface catalysts , in addition to platinum , are copper , Iron , nickel , palladium , rhodium , ruthenium , silica gel ( silicon dioxide ) and vanadium oxide

الاسبوع الخامس والعشرون والسادس والعشرون  
الوحدة النمطية

**Drawing of titration curves of aqueous solutions**

**مقدمة :-**

To know the change in the PH of solution during the titration we drawing the titration curve which is represent the relation between PH of solution and the volume of titrant .

**الهدف :-**

- ان يكون الطالب قادراً على ان يعين منحنى التسجع بطريقتين :-
1. الطريقة الحسابية :- من خلال حساب الاس الهيدروجيني من الكميات المضافة سواء كانت للحامض وللقاعد .
  2. الطريقة العملية :- وفيها يقاس الاس الهيدروجيني ( PH ) عملياً باستخدام مقياس خاص يبين قيمة الهيدروجين . ( PH . meter ) .

**امتحان قصير :-**

Draw the titration curve for ( 50 ml ) of ammonia ( 0 . 1M ) with 0 . 1M HCl if you know that  $pK_b = 4 . 74$   
a / before any addition of Acid b/ after addition of 10ml acid c/ after addition of 50 ml acid d/ after addition of 70 ml acid .

## Titration curves .

لمعرفة التغير الحاصل في الـ PH الهيدروجيني ( PH ) للمحلول في اثناء عملية التسجج يرسم ما يعرف بمنحنى التسحيح :- وهو عبارة عن رسم بياني يمثل العلاقة بين الـ PH الهيدروجيني للمحلول مع حجم المادة المضافة في عملية التسحيح .

### 1- Titration of strong Acid with strong base :-

Calculate the PH of 20ml . 0 . 05 N Hcl . Then calculate the difference of PH in the addition of 5 , 19 , 20 , 25 ml of 0 . 05 N NaOH . & what the suitable indicator to obtain the equivalence point ? .

سوف يتم حساب الـ PH الهيدروجيني في مناطق مختلفة قبل نقطة التكافؤ وعندها وبعد نقطة التكافؤ .

a . قبل اضافة القاعدة ( before addition Base ) .

$$\begin{aligned} PH &= -\log[H^+] && \text{يوجد هنا فقط الحامض وبما ان الحامض قوي .} \\ &= -\log^{0.05} \\ &= 1.3 \end{aligned}$$

b . 5 ml عند اضافة ( 5 ml ) .

$$m . \text{ mole of Acid} = 20 \times 0 . 05 = 1 .$$

$$m . \text{ mole of base} = 5 \times 0 . 05 = 0 . 25$$

$$m . \text{ mole of Acid remaine} = 1 - 0 . 25 = 0 . 75$$

$$[H^+] = \frac{0.75}{25} = 0.03$$

$$PH = -\log^{0.03}$$

C. عند اضافة 20 ml من NaOH ( 0 . 05N ) سوف نجد في هذه الحالة تفاعل كمية الحامض الموجودة مع جميع القاعدة المضافة ويتكون ملح كلوريد الصوديوم المتأين ويصبح الـ PH = 7

$$m . \text{ mole of acid} = 0 . 05 \times 20 = 1$$

$$m . \text{ mole of base} = 0 . 05 \times 20 = 1$$

$$[ H^+ ] = [ OH^- ] = 1 \times 10^{-7}$$

$$\therefore PH = 7$$

d . عند اضافة 20 . 1

$$m . \text{ mole of Acid} = 1$$

$$m . \text{ mole of base} = 0 . 05 \times 20 . 1 = 1 . 005$$

$$m . \text{ mole of base remaine} = 1 . 005 - 1 = 0 . 005$$

$$[ OH^- ] = \frac{0.005}{40.1} = 1.25 \times 10^{-4} \\ = 0.00125$$

$$POH = -\log^{[OH^-]} \\ = -\log^{1.25 \times 10^{-4}} \\ = 3.9 \\ PH = 14 - 3.9 \\ = 10.1$$

e . عند اضافة 25 ml

$$m . \text{ mole of Acid} = 1$$

$$m . \text{ mole of base} = 25 \times 0 . 025 = 1 . 25$$

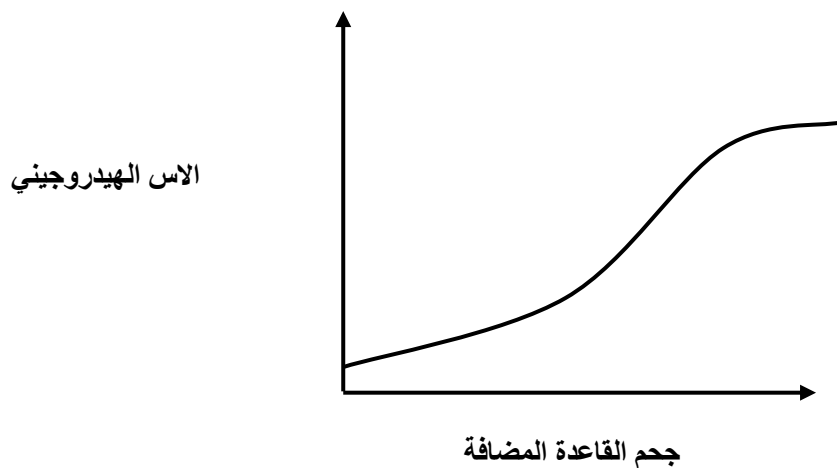
$$m . \text{ mole of base remaine} = 1 . 25 - 1 = 0 . 25$$

$$[OH^-] = \frac{0.25}{45} = 0.0056$$

$$POH = -\log 0.0056 = 2.25$$

$$PH = 14 - 2.25 = 11.75$$

نلاحظ من النتائج السابقة انه عند اضافة كميات من القاعدة عند نقطة التكافؤ وبالقرب منها نجد ان التغير في الـ PH يكون بين 3.9 , 7 , 10.1 اي يمكن استخدام دلائل تعمل في المدى من 3.9 الى 10.1 قبل المثيل البرتقالي والمثيل الاحمر والفينونفثالين بأخطاء بسيطة يمكن التغاضي عنها



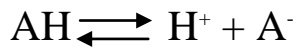
2- Weak Acid – strong Base



Calculate and Draw the titration curve of HOAC Ionization constant  $= 2 \times 10^{-4}$  and the conc. Is 0.1M in the titration with NaOH 0.1 M . then write the suitable indicator ? .

نفرض ان التسجع يحصل 100 مل من الحامض .

1- PH . before add .



$$\begin{aligned} [H^+] &= \sqrt{Ka \cdot c} \\ &= \sqrt{2 \times 10^{-4} \times 0.1} \\ &= 0.0045 \end{aligned}$$

$$PH = -\log^{0.0045}$$

$$PH = 2.35$$

2- PH عند اضافة 99.9 مل

$$m . \text{ mole of Acid} = 100 \times 0.1 = 10$$

$$m . \text{ mole of base} = 0.1 \times 99.9 = 9.99$$

$$m . \text{ mole of Acid remained} = 10 - 9.99$$

$$= 0.01$$

$$[H^+] = \frac{\text{عدد مليمولات الحامض} \times \text{ثابت التاين}}{\text{عدد مليمولات الملح}}$$

$$= \frac{2 \times 10^{-4} \cdot 0.01}{9.99}$$

$$= 2 \times 10^{-6}$$

$$PH = 6.7$$

وهكذا نستخرج قيم PH بعد الاضافات حتى نقطة التكافؤ .

3- عند نقطة التكافؤ عند اضافة 100 ml من 0.1N (NaOH)

بما ان الملح مشتق من قاعدة قوية وحامض ضعيف اذن يطبق القانون التالي :-

$$[OH^-] = \sqrt{\frac{K_w \cdot C_o}{K_a}}$$

$C^\circ$  :

تركيز الملح ويستخرج ما يلي

$$100 \times 0.1 = \frac{10}{200} = 0.05$$

$$[OH^-] = \sqrt{\frac{K_w \cdot C_o}{K_a}}$$

$C_o$  : تركيز الملح يستخرج :

$$100 \times 0.1 = \frac{10}{200} = 0.05$$

$$[OH^-] = \sqrt{\frac{1 \times 10^{-4} \times 0.05}{2 \times 10^{-4}}} = 0.00000158 (.58 \times 10^{-6})$$

$$POH = 5.8$$

$$PH = 8.2$$

بعد نقطة التكافؤ

عند اضافة 100 . 1-4

$$m . \text{ mole of Acid} = 10$$

$$m . \text{ mole of base} = 100 . 1 \times 0 . 1 = 10 . 01$$

$$m . \text{ mole of excess base} = 10 . 01 - 10 = 0 . 01$$

$$[OH^-] = \frac{0.01}{200.1} = 4.9 \times 10^{-5} \quad POH = 4.3$$

$$PH = 14 - 4.3 = 9.7$$

بتغير الـ PH من 7.9 الى 8.2 , 9.7 اي في مدى 6.7 - 9.7 ثم يمكن اختيار دليل يعمل في هذا المدى للحصول على تقدير صحيح لنقطة التكافؤ ومن امثلة هذه الدلائل الاحمر المتعادل والذي يعمل في مدى 6.8 - 8 من وحدات الـ PH .

### 3- Titration of weak base with strong Acid .

e.g.)) Derive the Titration curve for ( 50 ml ) of ammonia of ( 0 .

1 ) M with 0 . 1 M Hcl if you Know that  $pKb = 4 . 74$

- before any addition of acid .
- after addition of 10 ml acid .
- after addition of 50 ml acid .
- after addition of 70 ml acid .

1. قبل اضافة الحامض ( HCl ) محلول يحتوي فقط على قاعدة ضعيفة .

$$pOH = \frac{1}{2} ( PKb - \log^{[NH_4 OH]} )$$

$$= \frac{1}{2} ( 4.74 - \log^{0.1} )$$

$$= 2.87$$

$$PH = 14 - 2.87 \Rightarrow 11.13$$

2. بعد اضافة ( 10 ml ) من 0 . 1 M Hcl .

$$m . \text{ moles ( HCl ) added} = 0 . 1 \times 10 = 1$$

$$m . \text{ moles ( NaOH ) initial} = 0 . 1 \times 50 \text{ ( salt ) formed} = 5$$

$$m . \text{ mole of NaOH remained} = 5 - 1 = 4 \text{ m. mole}$$

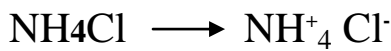
$POH = PKb - \log m . \text{ mole of base remained} + \log m . \text{ moles of salt}$

$$= 4.74 - \log^4 + \log^1$$

$$= 4 . 138$$

$$PH = 9 . 86$$

بعد اضافة 50ml من 0.1 M HCl ( نقطة التكافؤ ) عند نقطة التكافؤ ( القاعدة تتحول بالكامل الى ملح )



no . of m . mole ( Hcl ) added = 0 . 1 × 50 = 5 m . mole of salt

$$[salt] = \frac{5}{100} = 0.05$$

$$PH = \frac{1}{2} ( pkw - pkb - \log^{[salt]} )$$

$$= \frac{1}{2} ( 14 - 4.74 - \log^{0.05} )$$

$$= 5.28$$

بعد اضافة 70 ml من 0.1 HCl يمكن تعيين الـ PH من حساب تركيز ايونات  $[H^+]$  للزائدة .

Total no . of mole ( Hcl ) = 0 . 1 × 70 = 7

initial no . of m .mole ( NH<sub>4</sub>OH ) = 0 . 1 × 50 = 5

No . of m . mole ( acid ) remain = 7 - 5 = 2

$$[H^+] = \frac{2}{120} = 0.0166$$

$$PH = -\log^{0.0166}$$
$$= 1.77$$

الاسبوع السابع والعشرون والثامن والعشرون

## Methods and principles of spectrophotometer analysis

مقدمة :-

Spectroscopy include studies with light and other types of electro magnetic radiation , such as x – rays , ultra violet , infrared , microwave and radio frequency radiation .

الهدف :-

ان يكون الطالب قادراً على ان يقوم بقياس الامتصاصية للمادة المراد تحليلها على امتداد

الاطوال

الموجية المرئية وغير المرئية ذات الاطوال الموجية القصيرة والطويلة .

امتحان قصير :-

Enumerate the properties of electromagnetic radiation ? .

## **Spectroscopic Methods of Analysis**

Spectroscopy include studies with light and other types of electromagnetic radiation , such as x – ray , ultraviolet , infrared , microwave , and radio – frequency radiation .

### **Properties of electromagnetic radiation .**

Electromagnetic radiation is a type of energy that is transmitted through space at enormous velocities .

### **Wave parameters**

Wave length ( $\lambda$ ) : is the linear distance between successive maxima or minima of a wave

frequency ( $\gamma$ ) : is the number of oscillations of the field per second .

Velocity : is the multiplication of the frequency in waves per second by the wave length in centimeters =  $v_i = \nu \lambda_i$  cm/sec. In a vacuum , the velocity of radiation propagation becomes independent of wave length and is at its maximum .

**Note** : the rate of radiation is less in a medium containing matter because the electromagnetic field of the radiation interacts with the electrons in the atoms or molecules of the medium .

Wave number  $\sigma$  : is the reciprocal of the wavelength in centimeters

$$\sigma = \frac{1}{\lambda} .$$

**Note** : The wave length coordinate with frequency and velocity by this relation  $\lambda \nu = c$

- **The particle properties of radiation .**
- **The energy of electromagnetic radiation .**

The electromagnetic radiation is made up of packets of energy called photons ( or quanta ) . The energy of a photon depends upon the frequency of the radiation and is given by .

$$E = h\nu .$$

Where h is Planck's constant (  $6.63 \times 10^{-34}$  J . S )

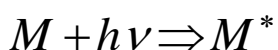
$$\therefore \lambda\nu = c$$

$$\therefore E = \frac{hc}{\lambda} = hc\sigma$$

### **Absorption of radiation .**

Absorption is a process in which a chemical species in a transparent selectively attenuate ( decreases the intensity of ) certain frequencies of electro magnetic radiation .

Atom , ion or molecule has a ground state , at room temperature most particles exist in their ground state . when a photon of radiation passes near an particle , absorption becomes probable if the energy of the photon matches exactly the energy difference between the ground state and one of the higher energy of the photon is transferred to the atom ion or molecule , converting it to the higher energy state which is termed an excited state .



### **Laws of photometry .**

When the parallel radiation which have intensity (P) passed through a layer of solution with a thickness dx and a concentration c the intensity of the radiation is attenuated from  $P^\circ$  to p (-dp) .

$$- dp \propto pc dx .$$

$$- dp = Kpcdx .$$

the integration of equation between  $x = 0$  to  $x = b$

$$\text{when } x = 0 \quad p_0 = p$$

$$\int_{p_0}^p \frac{dp}{p} = -kc \int_{x=0}^{x=b} dx$$

$$\ln \frac{p}{p_0} = -kcb$$

$$\ln \frac{p_0}{p} = 0.4343 kcb$$

$$\log \frac{p_0}{p} = abc = A \quad (1)$$

This relation ship named Lambert – Beer law

Equation

$p_0$  = Intensity of incident light .

$p$  = Intensity of transmitted light .

$\frac{p}{p_0}$  = Transmittance .

$c$  : concentration mole / L

$a$  : molar absorptivity ( $L \cdot mol^{-1} \cdot cm^{-1}$ )

$b$  : sample path length ( Cm )

$k$  : constant

$A$  : absorbance

We can also write this equation like :

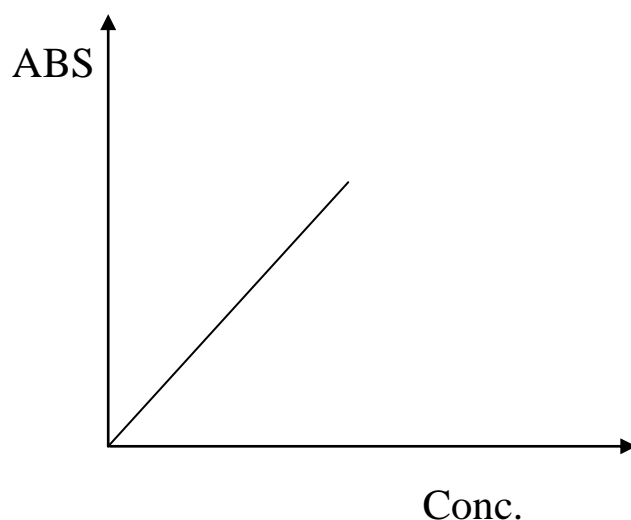
$$P = P_0 \cdot 10^{-abc} \quad (2)$$

Where (  $K$  ) is a constant , which depends on



- 1) The nature of the solute .
- 2) The wave length of the light .
- 3) The nature of the medium .
- 4) The length of the absorbing layers .

**Note** : The relation ship between absorbance and conc. Is linear .



**The Application of Beer's law to Mixtures .**

Beer's law also applies to solutions containing more than one kind of absorbing substance . Provided no interaction occurs among the various species , the total absorbance for a multi component system is

.

$$A_{total} = A_1 + A_2 + \dots + A_n.$$

$$= a_1 b c_1 + a_2 b c_2 + \dots + a_n b c_n$$

**Chemical Deviation .**

The deviations from Beer's Law are frequently encountered as a consequence of association , dissociation , or reaction of the absorbing species with the solvent .

يعزى الى حدود التحسس للآلات والى تأثيرات التوازن الكيميائي غير المتماثل وعادة ينطبق

القانون على التراكيز التي تتراوح بين  $(10^{-2} - 10^{-7} M)$

e.g.)) In one experiment we calculate the transmittance which are 50 % what is the absorbance under the same condition ? .

$$T = \frac{p}{p_0} = \frac{50}{100}$$

$$\log \frac{p_0}{p} =$$

$$\log \frac{100}{50} \Rightarrow A = 0.301$$

الاسبوع التاسع والعشر والثلاثون  
الوحدة النمطية

**Instrumental analysis employed for industry**

**مقدمة :-**

Instrumental analysis include the following

- 1- Analysis by Electrode position .
- 2- Potentio metric titration .
- 3- Atomic Absorption .
- 4- Chromatography .
- 5- Spectro Scopic .

**الهدف :-**

ان يكون الطالب قادراً على ان يقوم بقياس بعض الحوامض التي ترتبط نوعياً بصورة مباشرة او غير مباشرة مع تركيز المادة المراد تحليلها كميّاً كخواصها الكيميائية .

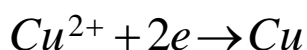
**امتحان قصير :-**

What is the specific chromatographic methods ? .

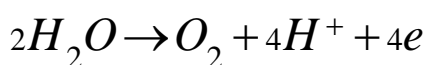
## Instrumental Analysis

### Analysis by Electrode position .

In electrode position the quantity of current passed is not measured . Electrolysis is allowed to proceed until the sought . For substance is quantitatively deposited on the electrode in pure form , at which time the increase in weight of the electrode is directly related to the amount of substance present . The method works best for metals such as copper , nickel or silver . when a solution containing copper sulfate is electrolyzed between two platinum electrodes , the reaction at the cathode is .



And the reaction at the anode is



The copper metal plates out on the surface of the platinum cathode . If electrolysis is continued to quantitative depletion of the copper in solution , the amount originally present can be found directly by determining the increase in weight of the cathode . This is a classical method of analysis for copper or silver .

The potential required to carry out an electrode position can be calculated from the expression .

$$E_{app} = E_{anode} - E_{cathode} + iR + w$$

Were  $E_{app}$  is the potential to be applied ,  $E_{anode}$  and  $E_{cathode}$  are potentials for the couples involved at the two electrodes  $iR$  is potential drop caused by resistance of the cell solution between the two electrodes . and  $w$  is the over potential .

## **Potentiometer Titrations .**

Potentiometer titrations can be carried out with all types of chemical reactions ( redox , acid – base , complexation , and precipitation ) and with all three types of indicator electrodes ( active metal ion , inert and membrane ) . For some titrations suitable indicators are not available , or indicators are unsuitable because the solution to be analyzed is colored or turbid . In these situations the titration can often be followed by monitoring the concentration of a species potentiometrically . The PH during an acid – base titration can be followed with a PH meter and a reference electrode – PH electrode pair , or the potential during a redox titration monitored with a potentiometer or voltmeter and reference electrode – platinum electrode pair . A plot of PH or potential against volume of titrant added then makes possible precise location of the end. point .

## **Atomic Absorption .**

Atomic Absorption methods measure the amount of energy ( in the form of photons of light , and thus a change in the wave length ) absorbed by the sample . Specifically . a detector measures the wave lengths of light transmitted by the sample ( the " after " wave length ) and compares them to the wave lengths , which originally passed through the sample ( the " before " wave length ) . A signal processor then integrates the changes in wave length , which appear in the readout as peaks of energy absorption at discrete wave lengths . Atomic Absorption analysis involves measuring the absorption of light by vaporized ground state atoms and relating the absorption to

concentration . The incident light beam is attenuated by atomic vapor absorption according to Beer's Law . The process of Atomic Absorption spectroscopy ( AAs ) involves two steps :-

- 1- Atomization of the sample .
- 2- The absorption of radiation from a light source by the free atoms .

The sample solution is dispersed into a fine spray , the spray is then desolvated into salt particles in the flame and the particles are subsequently vaporized into neutral atoms , ionic species and molecular species . All of these conversion processes occur in geometrically definable regions in the flame . It is therefore important to set the instrument parameters such that the light from the source ( typically a hollow – cathode lamp ) is directed through the region of the flame that contains the maximum number of neutral atoms . The light produced by the hollow – cathode lamp is emitted from excited atoms of the same element which is to be determined . Therefore the radiant energy corresponds directly to the wavelength which is absorbable by the atomized sample . This method provides both sensitivity and selectivity since other elements in the sample will not generally absorb the chosen wavelength and thus , will not interfere with the measurement . To reduce background interference , the wavelength of interest is isolated by a monochromator placed between the sample and the detector .

## **Chromatography .**

### **Introduction .**

Chromatography is a separations method that relies on differences in partitioning behavior between a flowing mobile phase and a stationary phase to separate the components in a mixture . A column ( or other support for TLC ) holds the stationary phase and the mobile phase carries the sample through it . Sample components that partition strongly into the stationary phase spend a greater amount of time in the column and are separated from components that stay predominantly in the mobile phase and pass through the column faster . As the components elute from the column they can be quantified by a detector and / or collected for further analysis . An analytical instrument can be combined with a separation method for one – line analysis . Examples of such " hyphenated techniques " include gas and liquid chromatography with mass spectrometry ( GC – MS and LC – MS ) . Fourier – transform infrared spectroscopy ( GC – FTIR ) and diode – array UV – VIS absorption spectroscopy ( HPLC – UV – VIS ) .

### **Specific chromatographic methods .**

#### **Gas chromatography ( GC ) .**

Applied to volatile organic compounds . The mobile phase is a gas and the stationary phase is usually a liquid on a solid support or sometimes a solid adsorbent .

### **High – performance liquid chromatography ( HPLC ) .**

A variation of liquid chromatography that utilizes high – pressure pumps to increase the efficiency of the separation .

### **Liquid chromatography .**

Used to separate analytes in solution including metal ions and organic compounds . The mobile phase is a solvent and the stationary phase is a liquid on a solid support , a solid , or an ion – exchange resin .

### **Size – exclusion chromatography ( SEC ) .**

Also called gel – permeation chromatography ( GPC ) , the mobile phase is a solvent and the stationary phase is a packing of porous particles .

### **Thin – layer chromatography ( TLC ) .**

A simple and rapid method to monitor the extent of a reaction or to check the purity of organic compounds . The mobile phase is a solvent and the stationary phase is a solid adsorbent on a flat support .