Quantitative Chemical Analysis

Quantitative chemical analysis, branch of chemistry that deals with the determination of the amount or percentage of one or more constituents of a sample.

A variety of methods is employed for quantitative analyses, which for convenience may be broadly classified as chemical or physical, depending upon which properties are utilized.

Chemical methods depend upon such reactions as precipitation, neutralization, oxidation, or, in general, the formation of a new compound. The major types of strictly chemical methods are known as gravimetric analysis and volumetric, or titrimetric analysis.

Physical methods involve the measurement of some physical property such as density, refractive index, absorption or polarization of light, electromotive force, magnetic susceptibility, and numerous others. An analysis will often require a combination of methods: qualitative for separating desired constituents from a sample and quantitative for measuring the amounts present.

The principles and methods that enables us to measure "how much" is called quantitative analysis. Quantitative chemical analysis measure how much chemical in a sample. The goal of analytical chemist is to use this knowledge of "how much" for greater purpose, such as in scientific investigation, a policy decision, a cost analysis, philosophical satisfaction or myriads other reasons.

Solution Definition

In chemistry, a solution is a special type of homogeneous mixture composed of two or more substances. In such a mixture, a solute is a substance dissolved in another substance, known as a solvent. The solvent is the major component of a solution (the part that does the dissolving). The solute is the minor component of the solution (the part that gets dissolved).

Expression of Concentrations

The SI unit (Systeme International d'Unites) of volume (which has the dimensions length 3) is the cubic meter (m^3). The common unit of volume is liter (L), which is defined as the volume of a cube 0.1 m on each edge. The milliliter (mL; 1 mL= 10^{-3} L) is exactly 1 cm^3. Small scale work especially in biochemistry, often employs microliter (μL; 1 μL = 10^{-6}L) volume.

Concentration signifies **how much** of a substance is contained in **a specified volume/mass.**

Concentration refers to the amount of **solute** that is dissolved in a **solvent**. We normally think of a solute as a solid that is added to a solvent (e.g., adding table salt to water), but the solute could easily exist in another phase. For example, if we add a small amount of ethanol to water, then the ethanol is the solute, and the water is the solvent. If we add a smaller amount of water to a larger amount of ethanol, then the water could be the solute.

Once you have identified the solute and solvent in a solution, you are ready to determine its concentration. Concentration may be expressed several different ways, using **percent composition by mass**, **volume percent**, **mole fraction**, **molarity**, **molality**, or **normality**.

Percent Composition by Mass (%)

This is the mass of the solute divided by the mass of the solution (mass of solute plus mass of solvent), multiplied by 100.
Example:
Determine the percent composition by mass of a 100 g salt solution which contains 20 g salt.
Solution:
20 g NaCl / 100 g solution x 100 = 20% NaCl solution

Example: Seawater has 904ppm of sulfur. What is the mass percent of sulfur in seawater?

Assume one million of grams of seawater. The number of grams of solute in one million grams is 904. This gives

Mass % = (904g/1 x 10^6 g) x 100 = 0.0904%

Mass/mass percentages are the best ways of expressing concentrations for applications in which the physical rather than the chemical properties of the mixture are most important. This is a poor way of expressing concentration for solutions used in chemical reactions because the mole ratio information is buried. We can convert the information to moles using the formula weight if necessary.

Volume Percent (% v/v)
Volume percent or volume/volume percent most often is used when preparing solutions of liquids. Volume percent is defined as:
v/v % = [(volume of solute)/(volume of solution)] x 100%
Note that volume percent is relative to the volume of the solution, not the volume of *solvent*. For example, wine is about 12% v/v ethanol. This means there is 12 ml ethanol for every 100 ml of wine.

Mole Fraction (X)

This is the number of moles of a compound divided by the total number of moles of all chemical species in the solution. Keep in mind, the sum of all mole fractions in a solution always equals 1.
Example: What are the mole fractions of the components of the solution formed when 92 g glycerol is mixed with 90 g water? (molecular weight of water = 18; molecular weight of glycerol = 92)
Solution:
90 g water = 90 g x 1 mol / 18 g = 5 mol water
92 g glycerol = 92 g x 1 mol / 92 g = 1 mol glycerol
total mol = 5 + 1 = 6 mol
x_{water} = 5 mol / 6 mol = 0.833

$x_{glycerol}$ = 1 mol / 6 mol = 0.167
It's a good idea to check your math by making sure the mole fractions add up to 1:
$x_{water} + x_{glycerol}$ = .833 + 0.167 = 1.000

Example 2

Dentist's amalgam is 70% mercury and 30% copper by mass. What is the mole fraction of copper in dentist's amalgam?

Solution

Note that the mole fraction of the components must be 1

Molar mass of Hg = 200.59g/mol; Molar mass of Cu = 63.546g/mol

Assume 100g of amalgam

No of mole of Hg = 70g/200.59 g/mol = 0.35 mol

No of mole of Cu = 30g /63.546g/mol = 0.47mol

By definition mole fraction of each component = no of mole of each component/ total no of moles of the components

$\mathbf{X_{Cu}}$ = 0.47mol / 0.47mol + 0.35mol= 0.47 mol / 0.82 mol = 0.57 mol

For Hg

$\mathbf{X_{Hg}}$ = 0.35mol / 0.82 mol = 0.427 = 0.43

If the mole fraction of the components must be one, then add $\mathbf{X_{Cu}}$ + $\mathbf{X_{Hg}}$ = 0.57 + 0.43 + 1

Molarity (M)

Molarity is probably the most commonly used unit of concentration. It is the number of moles of solute per liter of solution (not necessarily the same as the volume of solvent!).
Example 1:
What is the molarity of a solution made when water is added to 11 g $CaCl_2$ to make 100 mL of solution? (The molecular weight of $CaCl_2$ = 110)
Solution:

Molarity = No of moles/ Volume

No of mole = Mass given / molar mass

Therefore, no of moles of CaCl2 = 11 g $CaCl_2$ / 110 g / mol $CaCl_2$) = 0.10 mol $CaCl_2$
Volume given is in mL, convert to liter

100 mL x 1 L / 1000 mL = 0.10 L
molarity = 0.10 mol / 0.10 L
molarity = 1.0 M

Example 2

A solution contains 5.7 g of potassium nitrate dissolved in enough water to make 233 mL of solution. What is its molarity?

Formula weight or Molar mass of KNO3 = 101.103 g/mol

No of moles of KNO3 = 57g/ 101.103$gmol^-$ = 0.056 mol

M = 0.056mol/ 0.233 L = 0.24 mol/L

Molality (m)

Molality is the number of moles of solute per kilogram of solvent. Because the density of water at 25°C is about 1 kilogram per liter, molality is approximately equal to molarity for dilute aqueous solutions at this temperature. This is a useful approximation, but remember that it is only an approximation and doesn't apply when the solution is at a different temperature, isn't dilute, or uses a solvent other than water. This is useful when the properties of the solvent are being studied rather than the properties of the solute.

Unit = no of moles /kg
Example:

What is the molality of a solution of 10 g NaOH in 500 g water? (Molecular weight of NaOH is 40)
Solution:
No of moles of NaOH = 10 g NaOH / (40 g mol^- of NaOH) = 0.25 mol NaOH
Convert g to Kg = 500 g water x 1 kg / 1000 g = 0.50 kg water
molality = 0.25 mol / 0.50 kg
molality = 0.05 M / kg
molality = 0.50 m

Example 2

100g of amalgam contains 70 g of mercury and 30g of copper. What is the molality of mercury in the amalgam/

m = 0.47mol/ 0. 070kg = 6.7mol/kg = 6.7m

Normality (N)

Normality, N, is similar to molarity, moles of solute per liter of solution. However, instead of the entire solute, the normality is based on the number of moles of the active part of the solute, called a chemical equivalent. For an acid, the chemical equivalent is the number of moles of H^+ ion. For a base, the chemical equivalent is the no of OH^- ions. For oxidation – reduction solution, the chemical equivalent is the number of moles of electron transferred.

N= n x M, where n is the no of moles of proton exchange in a reaction.

N = n mole equivalents / L solution

The normality of HCl, is the same as the molarity of HCl because there is one mole of H^+ ions for every one mole of HCl. The normality of H_2SO_4 is twice the molarity because there are two moles of H^+ per mole of sulfuric acid. Normality has the advantage of giving effective concentration (3M H_2SO_4 is twice as acidic as 3M HCl - this is clear if they are labeled 6N and 3N, respectively.

Formality

The formal concentration refers to the amount of substance dissolved without regard to its actual composition in solution. If a solution is made by diluting 1.00 mol of HBr to 1.00L with water, the formal concentration of HBr is 1.00mole per liter. But the actual concentration of HBr is nearly zero because the HBr molecules have dissociated. Rather than calling the HBr solution 1.00M, it would be more correct to call it 1.00F.

Sometimes used interchangeably with Molarity, in actual sense it is not so. Unless you are fully aware of the chemistry of a particular compound, you rarely know its molarity, but you can know its formal concentration from the amount weighed into a solution by analytical procedure, for this reason, formal concentration is also known as analytical concentration.

F = n formula weight unit/ L solution.

Conversion among Units

1. **Percent Composition to Molarity**

   In order to convert mass percent to molarity or vice versa, you need to know the density of the solution; this gives you a mass of the solution and a mass of solute. Use the density to find the volume of the solution. Use dimensional analysis to convert the mass of the solute to moles. Parts per million and billion can be worked the same way except for the decimal point.

Example

Concentrated hydrochloric acid is 31% hydrochloric acid and 69% water, by mass. If the density of concentrated HCL is 1.16g/mL. What is the Molarity? If the formula weight of HCl is 36.45 g/mol

Assume that 100g of concentrated HCl has 31g of HCL and 69 g of water.

No of moles of HCl = 31g/36.45g/mol = 0.85mol

Density = Mass/ Volume

V = M/D = 100g/ 1.16g/mL = 86.2mL = 0.0862L

Molarity = No of moles / volume = 0.85 mol/0,0826L = 12mol/L == 12M

2. Mole Fraction to Molarity

An aqueous solution of sulfuric acid has a molarity of 18mol/L. If its density is 1.84 g/mL, what is the mole fraction of water in the solution? Formula weight of H2SO4 is 98.08 g/mol

Assume one liter of solution, which has 18 moles of sulfuric acid. The formula weight of sulfuric acid is 98.08 g/mol, so 18 moles of the acid has a mass of 1800g (1756 with two significant figures). Use density to find the mass of the solution.

OR

1 mole = 98.08 g/mol

Therefore 18 moles will have a mass = 18 mol x 98.08 g/mol = 1765.4 rounded to 2 sig. fig. =1800g

D = M/V

M= D x V = 1.85g /mL x 1000mL == 1840 meaning that out of 1840g, 1800g is the mass of sulfuric acid and 40g the mass of water. If the formula weight of water is 18.013 g/mol, we can only have 2mols of water

XH_2O (mole fraction of H_2O) = 2mol/ 18 mol + 2 mol = 0.1 mol

1. Molarity to Molality

An aqueous solution of hydrogen peroxide is 16.9 mol / L, it has a density of 1.196g/mL, what is its molality?

Solution:

Assume one liter of solution, this has 16.9 moles of Hydrogen peroxide. The formula weight of Hydrogen peroxide is 34.015 g/mol.

Mass of the solution = D x V == 1.196g/mL x 1000mL = 1196g

Mass of Hydrogen peroxide in the solution will be

1 mole of H_2O_2 = 34.015g/mol

Therefore, 16.9 mole mass will be == 34.015 g/mol X 16.9 mol = 575g of H_2O_2

If the mixture has 575g of H_2O_2 in 1196 g of solution, 621 will be the mass of water (solvent). The molality is

M == 16.9mol/ 0.621kg (621g converted to kg) = 27.2mol/kg

2. Normality and Formality

What is the normality and formality of concentrated sulfuric acid, 18M?

Answer: Sulfuric acid has two H= in its formula, so one mole solute has two moles of equivalents. Concentrated sulfuric acid has a normality of 36N. The number of gram formula weights for sulfuric is the same as the number of moles of solute, so concentrated sulfuric acid has a formality of 18F.

How to Calculate Dilutions

You dilute a solution whenever you add solvent to a solution. Adding solvent results in a solution of lower concentration. You can calculate the concentration of a solution following a dilution by applying this equation:

$M_iV_i = M_fV_f$

Where M is molarity, V is volume, and the subscripts i and f refer to the initial and final values.

Example:
How many milliliters of 5.5 M NaOH are needed to prepare 300 mL of 1.2 M NaOH?

Solution:
5.5 M x V_1 = 1.2 M x 0.3 L
V_1 = 1.2 M x 0.3 L / 5.5 M
V_1 = 0.065 L
V_1 = 65 mL

Part Per Million (PPM)

Composition is often expressed as parts per million (ppm), parts per billion (ppb) or parts per thousand. The term one part per million, for example indicates that one gram of the substance of interest is present per million grams of total solution or mixture

i.e

$\frac{1\ g\ of\ substance}{1\ x\ 10^6 g\ of\ sample}$ OR $\frac{g\ of\ substance}{g\ of\ sample} 10^{-6}$

ppt = $\frac{g\ of\ substance}{g\ of\ sample} 10^{-3}$ Or $\frac{1\ gram\ of\ substance}{1\ x\ 10^3\ of\ sample}$

ppb = $\frac{\text{g of substance}}{1\ x\ 10^9\ of\ sample}$ Or $\frac{g\ of\ substance}{g\ of\ sample} 10^{-9}$

Examples

1. Convert 1ppm to 1 µg/mL

1 ppm = 1 part of substance / 1 x 10^6 part of solution

= 1 g of X / 1 x 10^6 of solution

= 1 x 10^{-6} / g of solution

= 1µg of X (i.e Substance) / g of solution = µg/ g

If the solution is in water and the density of water is 1 g / mL, then

1 ppm = 1 µg/ mL solution

2. Example 2

A solution contains Cu^{2+} ions at a concentration of 3 X 10^{-4} M. What is the Cu^{2+} concentration in ppm?

Recall1 ppm = 1 µg/ mL solution, but molarity uses moles / L, so the mL need to be converted to L

1 ppm = 1 µg X / mL solution x 10^{-3} L/mL…. converting mL to L

= 1000 µg X / L solution. Note 1000 µg is 1 mg

= mg /L solution

We know that molarity of the solution is in moles /L

**We need to convert moles to mg

moles /L Cu^{2+} = 3 x 10^{-4} M, i. e M is mole/L

Molar mass of Cu = 63.55g / mole

moles /L of Cu^{2+} = 3 x 10^{-4} $\frac{mole}{L}$ x 63.55$\frac{g}{mole}$ = 1.9x 10^{-2} g / L

But we want mg of Cu^{2+}, so convert g to milligram

1000mg = 1g

Thus, 1.9 x 10^{-2} x 1000mg /L = 1.9mg / L, since 1 ppm == 1 mg/ L

Moles / L of Cu^{2+} = 1.9 ppm

How to convert ppm to percent

1% = 1/100

1ppm = 1 / 1,000,000

So 1ppm = 0.0001% i.e 1 / 1,000,000 X 100 = 0.0001%

So to convert ppm to percent, divide the ppm by 10,000

X% = X (ppm)/ 10,000

Example

Find how many percent are in 300ppm.

X (%) = 300ppm 10,000 = 0.03%

Convert 5% to ppm

5/100 x 1,000,000 = 50,000ppm

50.000 ppm/ 10,000 = 5%

Assignments

1. A solution is made by dissolving 12.00 g of benzene C_6H_6 in enough hexane to give 20.0 mL of solution. Find the molarity of the benzene.
2. Commercial concentrated HCl is labelled 37% which you may assume means weight percent. Its density, sometimes called specific gravity is 1.18g/mL. Find a. the molarity of the HCl, b. mass of solution containing 0.100mole of HCl and C. the volume of solution containing 1.00mol of HCl.
3. What quantity of $H_2C_2O_4$. $2H_2O$ (Oxalic acid dihydrate) should be used to prepare 250mL of 150M of the acid.
4. B (a) P is a carcinogen and it was found that the source to human is from air and was determined to be 1ppm. What this concentration is as measured in mg/m^3 in the atmosphere?

References

1. Daniel C. Harris; Quantitative Chemical Analysis, Third Edition. W. H. Freeman and Company, New York
2. G.H Jeffery, J. Bassett, J. Mendham, R.C Denny: VOGEL'S textbook of Quantitative Chemical Analysis. Fifth Edition, Longman Scientific and Technical. John wiley and Sons, Inc., New York

GRAVIMETRIC ANALYSIS METHODS

Gravimetric analysis involves the selective separation of the analyte by precipitation after some form of chemical treatment has been carried out on the substance to be examined, followed by measurement of mass of the precipitate.

e.g. $AgNO_{3(aq)} + NaCl_{(aq)} \rightarrow AgCl_{(s)} + NaNO_{3(aq)}$

Gravimetric is usually time consuming. It however has some advantages which are as follows:

1. It is accurate and precise when using modern analytical balances
2. Possible sources of errors are readily checked since filtrates can be tested for completeness of precipitation and precipitates may be examined for the presence of impurities
3. It is an absolute method, i.e. it involves direct measurement without any form of calibration being required
4. Determination can be carried out with relatively inexpensive apparatus; the most expensive items are a muffle furnace and sometimes platinum crucibles.

Note the following terms below and the difference:

Precipitation

It is the process of conversion of a chemical substance into a solid from a solution by converting the substance into an insoluble form or a super-saturated solution.

Precipitate

When the reaction occurs in a liquid solution, the solid formed is called the precipitate.

Precipitant

The chemical agent that causes the solid to form is called the precipitant.

The following are some examples of commonly Employed Gravimetric Analyses

Substance Analyzed	Precipitate formed	Precipitate weighed	Possible Interferences
Fe	$Fe(OH)_3$	Fe_2O_3	Al, Ti, Cr etc
Ca	CaC_2O_4	$CaCO_3$ or CaO	All metals except alkalis and Mg
Mg	$MgNH_4PO_4$	Mg_2P2O_7	All metals except Alkalis
SO_4^{2-}	$BaSO_4$	$BaSO_4$	NO_3^-, PO_4^{3-}, ClO_3^-
Cl^-	AgCl	AgCl	Br^-, I^-, SCN^-, S^{2-}
PO_4^{3-}	$MgNH_4PO_4$	$Mg_2P_2O_7$	K^+, $C_2O_4^{2-}$, MoO_4^{2-}

Properties of Precipitates and Precipitation Reaction

1. The precipitation reaction undergoes in aqueous solutions or medium in an ionic state.
2. The reaction takes place between ions present in the aqueous solutions, forming the product
3. The products formed at the end of precipitation reaction are the precipitates which are insoluble in aqueous solutions
4. Precipitation reactions are known as ionic reactions since the ions actively take part in the reaction and form the product.
5. These reactions depend on the temperature, concentration of the solution, buffer solution.

Applications of Precipitation Reactions

1. Precipitation reaction helps in determining a particular element present in the given solution.
2. These reactions also monitor the formation of a precipitate when some chemical is added to solutions.
3. They are used for the extraction of magnesium from the seawater.
4. The human body also encounters these reactions existing between antigens and antibodies.

Organic precipitating agents

There are also a large number of organic compounds that are very useful precipitating agents for Metals. Some of these are very selective, and others are very broad in the number of elements they will precipitate. Organic precipitating agents can be designed to selectively target specific ions or compounds, allowing for more efficient separation and purification processes. This is particularly useful in complex mixtures where multiple components need to be separated.

Organic precipitating agents have the advantages of giving precipitates with very low solubility in water a favorable gravimetric factor. Most of them are chelating agents that form slightly soluble, uncharged chelates with the metal ions. A chelating agent is a type of complexing agent that has two or more groups capable of complexing with a metal ion. The complex formed is called a chelate.

CHELATION

A chelating agent is a substance whose molecules can form several bonds to a single metal ion by forming ring structure. An example of a simple chelating agent is ethylenediamine. A single molecule of ethylenediamine can form two bonds to a transition-metal ion such as nickel(II), Ni^{2+}.

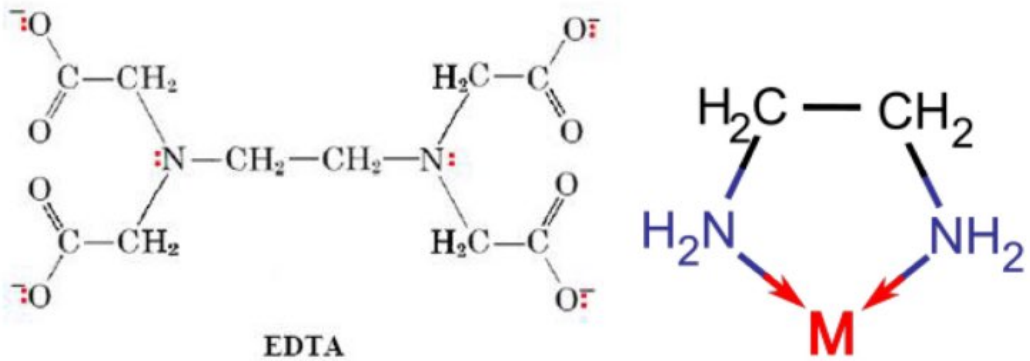
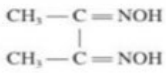
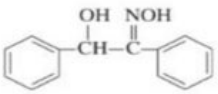
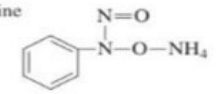
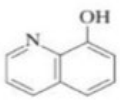
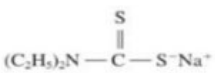


Figure: Ethylenediamine ligand chelating to a metal with two bonds.

Reagent	Structure	Metals Precipitated
Dimethylglyoxime		Ni(II) in NH_3 or buffered HOAc; Pd(II) in HCl ($M^{2+} + 2HR \rightarrow \underline{MR_2} + 2H^+$)
α -Benzoinozime (cupron)		Cu(II) in NH_3 and tartrate; Mo(VI) and W(VI) in H^+ ($M^{2+} + H_2R \rightarrow \underline{MR} + 2H^+$; $M^{2+} = Cu^{2+}$, MoO_2^{+}, WO_2^{2+}) Metal oxide weighed
Ammonium nitrosophenylhydroxylamine (cupferron)		Fe(III), V(V), Ti(IV), Zr(IV), Sn(IV), U(IV) ($M^{n+} + n NH_4R \rightarrow \underline{MR_n} + n NH_4^+$) Metal oxide weighed
8-Hydroxyquinoline (oxine)		Many metals. Useful for Al(III) and Mg(II) ($M^{n+} + nHR \rightarrow \underline{MR_n} + nH^+$)
Sodium diethyldithiocarbamate		Many metals from acid solution ($M^{n+} + n NaR \rightarrow \underline{MRn} + n Na^+$)
Sodium tetraphenylboron	$NaB(C_6H_5)_4$	K^+, Rb^+, Cs^+, Tl^+, Ag^+, Hg(I), Cu(I), NH_4^+, RNH_3^+, $R_2NH_2^+$, R_3NH^+, R_4N^+. Acidic solution ($M^+ + NaR \rightarrow \underline{MR} + Na^+$)
Tetraphenylarsonium chloride	$(C_6H_5)_4AsCl$	$Cr_2O_7^{2-}$, MnO_4^-, ReO_4^-, MoO_4^{2-}, WO_4^{2-}, ClO_4^-, I_3^- Acidic solution ($A^{n-} + n RCl \rightarrow R_nA + n Cl^-$)

Applications of Organic Precipitating Agents

Example of applications of organic precipitating agents are:

1. the Oxine, e.g 8-hydroxyquinoline, which is an organic compound that can act as a precipitating agent for various metal ions, such as aluminum (Al^{3+}), beryllium (Be^{2+}), and iron.

2. Sodium tetraphenylboron (NaTPB) is an organic compound that can act as a precipitating agent for various metal ions, such as potassium (K^+), NH_4^+, rubidium (Rb^+), and cesium (Cs^+).

3. Drug:

Exercises

1. What mass of Ag_2CO_3 is formed from the reaction of $AgNO_3$ with 2.33 g of Na_2CO_3? [Formula mass g/mol: Ag_2CO_3 (275.7); $AgNO_3$ (169.9); Na_2CO_3 (106.0)].

2. Which of the properties below describes product formed from precipitation reaction?

(I) Readily filtered and washed free of contaminants (II) sufficiently high solubility so that no significant loss of the analyte occurs during filtration and washing (III) Unreactive with constituents of the atmosphere (IV) of known composition after it is dried or if necessary ignited

3. The following organic chelating agents form slightly soluble non-ionic products called coordination compounds except:

(I) 8-hydroxyquinoline (II) Dimethylglyoxime (III) Cupferron (IV) Salicylaldoxime

4. A mixture of the 8-hydroxyquinoline complexes of Al and Mg weighed 1.0843 g. When ignited in a furnace open to the air, the mixture decomposed leaving a residue of Al_2O_3 and MgO weighing 0.1344 g. Find the concentration of $Al(C_9H_6NO)_3$ in the original mixture in part per million (ppm). [Formula mass g/mol: Al-8hydroxyquionolate complex (AlQ_3) = 459.43; Mg-8hydroxyquionolate complex (MgQ_2) = 312.61; Al_2O_3 = 101.96; MgO = 40.304].

5. Which of the following is not an organic coordinating agent

(A) Sodium tetraphenylborate (B) sodium borohydride (C) Mandeli acid (D) 1-nitroso-2-naphthol

6. To measure the nickel content in steel, the alloy is dissolved in 12 M HCl and neutralized in the presence of citrate ion, which maintains iron in solution. The slightly basic solution is warmed, and dimethlglyoxime (DMG) was added to precipitate the red DMG-Ni complex quantitatively. The product was filtered, washed and dried at 110 ^{0}C. If 1.1634 g of steel gives 0.1795 g of precipitate, what is the percentage of Ni in the steel? (Formula mass (g/mol): Ni = 58.69; DMG = 116.2; $Ni(DMG)_2$ = 288.91]

7. What is the function of Citrate ion in question 6 above:
(I) Precipitating Agent (II) Redox agent (III) Coordinating agent(IV) Masking agent

8. Ethylenediaminetetracetic acid is an example of:
(A) Monodentate ligand (B) Tetradentate ligand (C) Hexadentate ligand (D) None of the above

9. Magnetite is a mineral having the formula Fe_3O_4. A 1.1324 g sample of a magnetite ore was dissolved in concentrated HCl to give a solution that contained a mixture of Fe^{2+} and Fe^{3+}. Nitric acid was added and the solution was boiled for a few minutes to convert all the iron to Fe^{3+}. The Fe^{3+} was then precipitated as $Fe_2O_3.xH_2O$ by addition of NH_3. After filtration and washing, the residue was ignited at a high temperature to give 0.5394 g of pure Fe_2O_3. Calculate the mass of Fe in (mg) in the sample. (Formula mass (g/mol): Fe_2O_3 = 159.69; Fe = 55.847]

10. Calculate the percentage of Fe in the sample in question 9 above.

11. Differentiate between the following terms below:
(a) Precipitation (b) Precipitate (c) Precipitant

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Gravimetric is usually time-consuming. It however has some advantages which are as follows:

1. It is accurate and precise when using modern analytical balances
2. Possible sources of errors are readily checked since filtrates can be tested for completeness of precipitation and precipitates may be examined for the presence of impurities
3. It is an absolute method, i.e. it involves direct measurement without any form of calibration being required
4. Determination can be carried out with relatively inexpensive apparatus; the most expensive items are a muffle furnace and sometimes platinum crucibles.

Note the following terms below and the difference:

Precipitation

It is the process of conversion of a chemical substance into a solid from a solution by converting the substance into an insoluble form or a super-saturated solution.

Precipitate

When the reaction occurs in a liquid solution, the solid formed is called the precipitate.

Precipitant

The chemical agent that causes the solid to form is called the precipitant.

The following are some examples of commonly Employed Gravimetric Analyses

Substance Analyzed	Precipitate formed	Precipitate weighed	Possible Interferences
Fe	$Fe(OH)_3$	Fe_2O_3	Al, Ti, Cr etc
Ca	CaC_2O_4	$CaCO_3$ or CaO	All metals except alkalis and Mg
Mg	$MgNH_4PO_4$	Mg_2P2O_7	All metals except Alkalis
SO_4^{2-}	$BaSO_4$	$BaSO_4$	NO_3^-, PO_4^{3-}, ClO_3^-
Cl^-	AgCl	AgCl	Br^-, I^-, SCN^-, S^{2-}
PO_4^{3-}	$MgNH_4PO_4$	$Mg_2P_2O_7$	K^+, $C_2O_4^{2-}$, MoO_4^{2-}

Properties of Precipitates and Precipitation Reaction

1. The precipitation reaction undergoes in aqueous solutions or medium in an ionic state.
2. The reaction takes place between ions present in the aqueous solutions, forming the product
3. The products formed at the end of precipitation reaction are the precipitates which are insoluble in aqueous solutions
4. Precipitation reactions are known as ionic reactions since the ions actively take part in the reaction and form the product.
5. These reactions depend on the temperature, concentration of the solution, buffer solution.

Applications of Precipitation Reactions

1. Precipitation reaction helps in determining a particular element present in the given solution.
2. These reactions also monitor the formation of a precipitate when some chemical is added to solutions.
3. They are used for the extraction of magnesium from the seawater.
4. The human body also encounters these reactions existing between antigens and antibodies.

Example 1

1. A 10.00 mL solution containing Cl^- was treated with excess $AgNO_3$ to precipitate 0.436 g of AgCl (FM 143.321). What was the molarity of Cl- in the unknown?

Reaction: $Ag+ \quad + \quad Cl- \quad \rightarrow \quad AgCl_{(s)}$

Solution: mole of AgCl = $\frac{mass}{molar\ mass} = \frac{0.4368 g AgCl}{\frac{143.321 g}{mol} AgCl} = 3.048x10^{-3}$

Note: I mole of AgCl contains 1 mol of Cl^- = 3.048 x 10^{-3} mole

Molarity of Cl^- in the unknown = $\frac{3.048x10^{-3} mole}{0.0100 L} = 0.3048 M$

Organic precipitating agents

There are also a large number of organic compounds that are very useful precipitating agents for Metals. Some of these are very selective, and others are very broad in the number of elements they will precipitate. Organic precipitating agents can be designed to selectively target specific ions or compounds, allowing for more efficient separation and purification processes. This is particularly useful in complex mixtures where multiple components need to be separated.

Organic precipitating agents have the advantages of giving precipitates with very low solubility in water a favorable gravimetric factor. Most of them are chelating agents that form slightly soluble, uncharged chelates with the metal ions. A chelating agent is a type of complexing agent that has two or more groups capable of complexing with a metal ion. The complex formed is called a chelate.

CHELATION

A chelating agent is a substance whose molecules can form several bonds to a single metal ion by forming ring structure. An example of a simple chelating agent is ethylenediamine. A single molecule of ethylenediamine can form two bonds to a transition-metal ion such as nickel(II), Ni^{2+}.

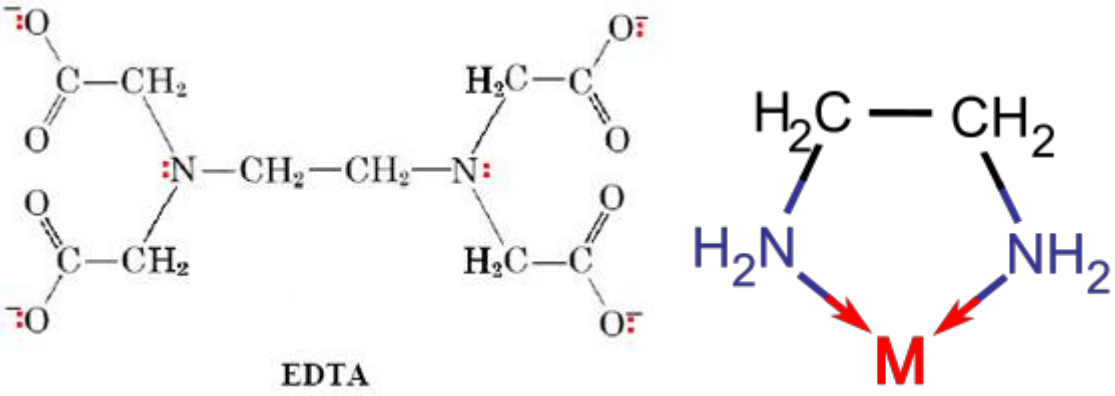
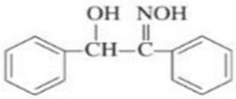
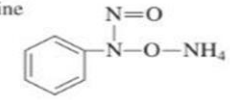
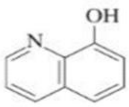


Figure: Ethylenediamine ligand chelating to a metal with two bonds.

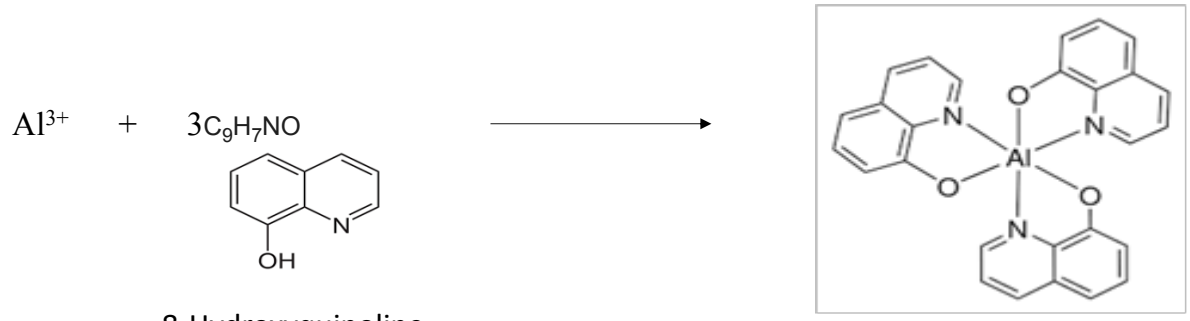
Reagent	Structure	Metals Precipitated
Dimethylglyoxime	$CH_3-C(=NOH)-C(=NOH)-CH_3$	Ni(II) in NH_3 or buffered HOAc; Pd(II) in HCl ($M^{2+} + 2HR \rightarrow \underline{MR_2} + 2H^+$)
α -Benzoinozime (cupron)		Cu(II) in NH_3 and tartrate; Mo(VI) and W(VI) in H^+ ($M^{2+} + H_2R \rightarrow \underline{MR}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

Applications of Organic Precipitating Agents

Example of applications of organic precipitating agents are:

1. the Oxine, e.g 8-hydroxyquinoline, which is an organic compound that can act as a precipitating agent for various metal ions, such as aluminum (Al^{3+}), beryllium (Be^{2+}), and iron.

Tris(8-hydroxyquinolinato)aluminium is the chemical compound with the formula $Al(C_9H_6NO)_3$. It is abbreviated as Alq_3 and it is a coordination complex where aluminium is bonded in a bidentate manner to the conjugate base of three 8-hydroxyquinoline ligands.

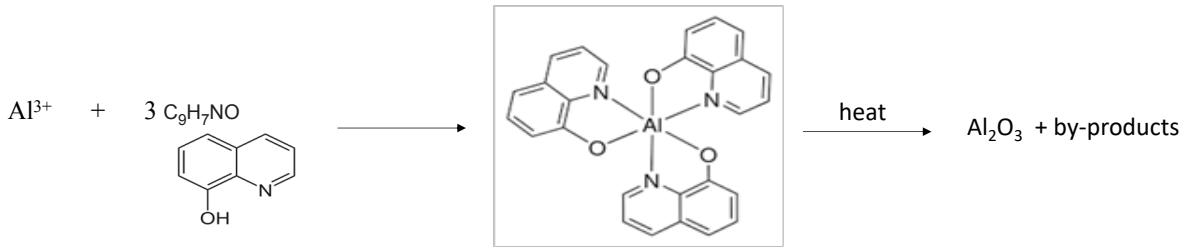


8-Hydroxyquinoline

Tris(8-hydroxyquinolinato)aluminium

Example 2

A solid residue weighing 8.444 g from an aluminium refining process was dissolved in acid to give Al^{3+} in the solution. The solution was treated with 8-hydroxyquinoline to precipitate (8-hydroxyquinoline)3Al which was ignited to give Al_2O_3 weighing 0.8554 g. Find the weight percent of Al in the original mixture.



8-Hydroxyquinoline

Tris(8-hydroxyquinolinato)aluminium

Solution: %Wt Al = $\frac{Mass\ of\ Al}{Mass\ of\ sample}\ x\ 100$

Note: We need to find the mole of Al from the total moles of the product to calculate the mass of Al.

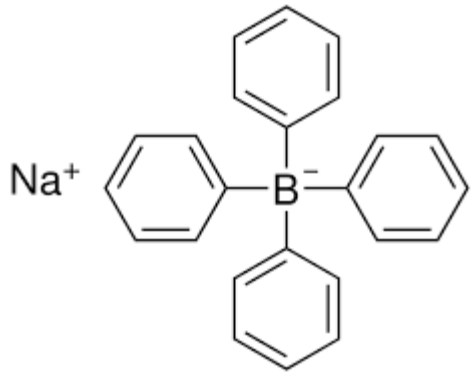
Thus, moles of product = $\frac{Mass\ of\ product}{M.M\ of\ Al2O3} = \frac{0.8854g}{101.961} = 0.008389\ mol\ Al2O3$

Mole of Al in the product = $\frac{2mol\ Al}{mol\ Al2O3}\ x\ 0.008389\ mol\ Al2O3 = 0.01677\ mol\ Al.$

Mass of Al = mole Al x A.M = 0.01677 mol x 26.982 g/mol = 0.4527 g Al.

%wt Al = $\frac{0.4527g\ Al}{8.4448\ g\ unknown} x\ 100 = 5.361\%$

2. Sodium tetraphenylborate (NaTPB) is an organic compound that can act as a precipitating agent for various metal ions, such as potassium (K^+), NH_4^+, rubidium (Rb^+), and caesium (Cs^+). It is a colourless compound that has high solubility in water, ethanol, methanol, and acetone. When an excess of NATPB is added to a solution of a sample containing K^+, the potassium ion is precipitated out as potassium tetraphenylborate and removed by filtration.



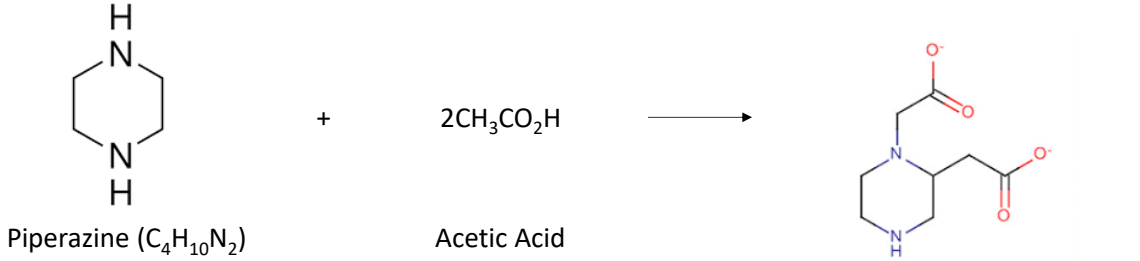
Sodiumtetraphenylborate

3. Drug: In pharmaceuticals, precipitation is used as a method of purification to isolate pure crystalline pharmaceutical intermediate, ingredient, or excipient (additives e.g. sugar or gum used in forming tablets or capsules) after bioprocesses. This purification process extracts a pure form of the crystalline compound after the synthesis and extraction process.

Example 3

Piperazine is an antihelminthic drug that selectively blocks the neuromuscular cholinergic receptors of worms and an oral dose of 4g of piperazine hydrate has been used in the treatment of ascariasis.

The piperazine content of an impure commercial material can be determined by precipitating and weighing piperazine diacetate.



Piperazine ($C_4H_{10}N_2$) (FM = 86.136)

Acetic Acid (FM = 60.052)

Piperazine diacetate (FM = 206.240)

Thus, in an experiment, 0.31226 g of sample was dissolved in 25 mL of acetone, and 1 mL of acetic acid was added. After 5 min, the precipitate was filtered, washed with acetone, dried at 110 0C, and found to be 0.7121 g. Find wt% piperazine in the commercial material.

Solution:

%Wt piperazine = $\frac{Mass\ of\ piperazine}{Mass\ of\ sample}\ x\ 100$

Note: Since we know the mass of the sample to be 0.3126 g, we need to find the mass of piperazine.

But from the equation above, we 1 mole of piperazine diacetate we give 1 mole of piperazine.

So, mole of piperazine diacetate = $\frac{Mass\ of\ piperazine\ diacetate}{FM} = \frac{0.7121\ g}{206.240\ g/mol} =$

$3.453\ x\ 10^{-3}\ mol$

Since 1 mol piperazine diacetate = 1 mol piperazine,

Therefore, 3.453 x 10^{-3} piperazine diacetate = 3.453 x 10^{-3} mol piperazine

Thus, mass of piperazine = 3.453 x 10^{-3} mol piperazine x 86.136 = 0.2974 g

%Wt piperazine = $\frac{0.2974g\ pierazine}{0.3126\ g\ unknown}\ x\ 100 = 95.14\%$

Exercises

1. What mass of Ag_2CO_3 is formed from the reaction of $AgNO_3$ with 2.33 g of Na_2CO_3? [Formula mass g/mol: Ag_2CO_3 (275.7); $AgNO_3$ (169.9); Na_2CO_3 (106.0)].

2. Which of the properties below describes a product formed from a precipitation reaction?

(I) Readily filtered and washed free of contaminants (II) sufficiently high solubility so that no significant loss of the analyte occurs during filtration and washing (III) Unreactive with constituents of the atmosphere (IV) of known composition after it is dried or if necessary ignited

3. The following organic chelating agents form slightly soluble non-ionic products called coordination compounds except:

(I) 8-hydroxyquinoline (II) Dimethylglyoxime (III) Cupferron (IV) Salicylaldoxime

4. A mixture of the 8-hydroxyquinoline complexes of Al and Mg weighed 1.0843 g. When ignited in a furnace open to the air, the mixture decomposed leaving a residue of Al_2O_3 and MgO weighing 0.1344 g. Find the concentration of $Al(C_9H_6NO)_3$ in the original mixture in part per million (ppm). [Formula mass g/mol: Al-8hydroxyquionolate complex (AlQ_3) = 459.43; Mg-8hydroxyquionolate complex (MgQ_2) = 312.61; Al_2O_3 = 101.96; MgO = 40.304].

5. Which of the following is not an organic coordinating agent

(A) Sodium tetraphenylborate (B) sodium borohydride (C) Mandeli acid (D) 1-nitroso-2-naphthol

6. To measure the nickel content in steel, the alloy is dissolved in 12 M HCl and neutralized in the presence of citrate ion, which maintains iron in solution. The slightly basic solution is warmed, and dimethlglyoxime (DMG) was added to precipitate the red DMG-Ni complex quantitatively. The product was filtered, washed and dried at 110 ^{0}C. If 1.1634 g of steel gives 0.1795 g of precipitate, what is the percentage of Ni in the steel? (Formula mass (g/mol): Ni = 58.69; DMG = 116.2; $Ni(DMG)_2$ = 288.91]

7. What is the function of Citrate ion in question 6 above:
(I) Precipitating Agent (II) Redox agent (III) Coordinating agent(IV) Masking agent

8. Ethylenediaminetetracetic acid is an example of:
(A) Monodentate ligand (B) Tetradentate ligand (C) Hexadentate ligand (D) None of the above

9. Magnetite is a mineral having the formula Fe_3O_4. A 1.1324 g sample of a magnetite ore was dissolved in concentrated HCl to give a solution that contained a mixture of Fe^{2+} and Fe^{3+}. Nitric acid was added and the solution was boiled for a few minutes to convert all the iron to Fe^{3+}. The Fe^{3+} was then precipitated as $Fe_2O_3.xH_2O$ by the addition of NH_3. After filtration and washing, the residue was ignited at a high temperature to give 0.5394 g of pure Fe_2O_3. Calculate the mass of Fe in (mg) in the sample. (Formula mass (g/mol): Fe_2O_3 = 159.69; Fe = 55.847]

10. Calculate the percentage of Fe in the sample in question 9 above.

11. Differentiate between the following terms below:
(a) Precipitation (b) Precipitate (c) Precipitant

GENERAL OPERATION AND TOOLS OF THE TRADE

Analytical chemist or scientist use a range of equipment from simple glassware to complex instruments that measure spectroscopic or electrical properties of analytes. It is therefore important to know how to handle the operations in the laboratory. To start with we will deal with Laboratory safety practices.

GENERAL SAFETY RULES IN THE LABORATORY

- The primary safety rule is to do nothing that you or your supervisor/instructor consider to be dangerous
- Do not start any experiment or operation in the lab until a sensible procedures and precautions are in place.
- Before you start your work you should be familiar with safety features and precautions appropriate to your laboratory.
- You should wear goggles or safety glasses with shields at all times in the lab to protect your eyes from liquids and glass, which fly around when least expected.
- Contact lenses are not recommended in the lab because vapors can be trapped between the lens and your eye.
- Use of rubber gloves is necessary when pouring concentrated acids or corrosive chemicals
- Anything in the lab is considered toxic or contaminated hence no eating, drinking, or chewing gum are allow at all in lab
- Organic solvents, conc acids and ammonia should be handle in a fume hold – air flowing into the hood keeps fumes out of the lab and dilutes the fumes before expelling them from the roof.
- Wear a respirator when handling fine powders, which could produce a cloud of dust that might be inhaled.
- Clean up spills immediately to prevent accidental contact by others in the lab.
- Treat spills on your skin first by flooding with water
- Know where to find and how to operate the emergency shower and eye wash in your lab- in case of splashes on your body or in your eyes.
- Know how to operate fire extinguish and an emergency blanket to extinguish burning clothing.
- All chemical containers must be properly labeled to indicate their contents: an unlabeled chemical bottle/container in the lab present an expensive disposal problem because the contents must be analyzed before they can be legally discarded.
- Chemical waste production should be minimized and waste should be dispose in a responsible manner.

- Recycling is a way of reducing chemical wastes hence it is advisable to reuse solvent generated in the lab when possible.

Dress Code for the Lab

1. At all times, students must wear safety goggles with splash protection.
2. Contact lenses may not be worn in the lab. Vapors and toxic fumes may get trapped beneath the contact lenses and harm your eyes.
3. Wear clothes that provide maximum protection and cover most of the skin. Short clothes and sandals are not allowed. Wear clothes that cover your torso and your legs to the knees. **Clothes should be made of natural materials, such as cotton, that do not catch fire as easily as synthetic materials.**
4 You must wear closed-toe shoes.
5. You must wear lab apron or coat to protect your clothes.

Long hair, extremely loose clothing or clothes with long loose sleeves, and dangling jewelry can get caught and become a hazard. Avoid loose clothing and tie long hair back.

Working with Chemicals

Treat all chemicals in the laboratory as though they are hazardous

1. Do not touch, eat, or smell any chemical unless instructed to do so. When instructed to smell a chemical, you need to fan the air above the chemical toward your nose. Do not sniff the chemical directly by bringing it close to your nose. If you do so, the odor may badly irritate your nasal passage.
2. Do not touch your face, eyes, or mouth while in laboratory. If you must do so, first wash your hands.
3. Hold chemical containers away from your body.
4. Carefully check the label on the bottle before using its content. Make sure it is the correct chemical and correct concentration.
5. Do not contaminate chemicals

    a. Never put your spatula to remove solid chemicals from a bottle. If you do so, you will be contaminating the chemical. Instead, pour solid directly into your container by tilting the bottle and rotating it to control the amount dispensed.

    b. If the solid seems to be tightly packed and would not pour off, close the container and then gently tap the bottle with the palm of your hand to loosen up the caked solid.

    c. Never put your medicine dropper into a reagent bottle. If you do so, you will be contaminating the reagent. Instead, pour some liquid into your container, and then use your medicine dropper to take as much as you need from the container.

d. Never return unused chemicals to their original containers. If you do so, you will be contaminating it. Dispose of the leftover in the proper "waste container". Check with your instructor if you are unsure on what to do with the leftover.

6. Do not waste chemicals; do not take more than what is required. Chemicals used in the laboratory are costly.
7. Never move a reagent bottle to your bench. Leave the bottle at its designated area on the supply bench. Take your own container to the reagent bench to dispense the necessary amount of reagent that you will take back to your lab bench.
8. Always hold all reagent bottles at the labels. Wipe any drips that may take place on the other side of the bottle before putting it back. Be sure the bottle is dry before replacing it on the lab bench/shelf.
9. Handle corrosive chemicals with extreme care. When diluting a concentrated acid, you must always add the acid slowly to the water while stirring to avoid spattering and releasing the heat all at once. In other words, ADD ACID TO WATER. Never do the reverse for the result could be quite hazardous.
10. Do not pipette by mouth.
11. Always store chemicals in labeled containers. The etched white part on beakers and flasks is good for applying labels and markings **using pencil.**
12. Handle toxic fumes produced by your experiment under the fume hood. Keep the fume hood sash down as far as possible.
13. Keep flammable liquids away from heat sources and open flames in the fume hood. If a flammable liquid is used in the laboratory, do not use an open flame at all.
14. Never remove chemicals from the laboratory unless under explicit direction of the lab instructor.
15. Alcohol used in lab is chemically denatured. It has been tainted with poison to make it unsuitable for drinking.

Working with Glassware

1. Do not use cracked or chipped glassware. Get replacement from the stockroom.
2. Most accidents in the chemistry labs are due to inserting and removing glass tubes and thermometers from rubber stoppers. Always lubricate the glass tube before inserting it in a rubber stopper and hold it close to the end near the stopper. Protect your hands with a towel when inserting glass tubing. Insert carefully with a gentle twisting motion. Do NOT force it. If not successful, ask for help from the instructor. When inserting a pipette into a pipette suction bulb, hold the pipette near the bulb and gently insert the pipette.

3. Any broken glass must be cleaned up immediately. Follow the instructor's guideline. Do not touch broken glass and do not attempt to clean broken glassware yourself, unless instructed to do so. The instructor will clean up broken glass using dustpan and brush. Broken glass will be placed in a special bin labeled "Broken Glass". Search the floor and lab bench for any small pieces of broken glass.
4. If ground glass stopper is frozen (stuck), report it to your instructor for replacement. If you force the stopper off the bottle, you may experience chemical splash, burn and bodily injury.
5. Do not shake a thermometer. Lay thermometer on a towel to cool, away from the edge of the lab bench. Stoppers: To remove a cork, stopper, or lid, do the following: After picking up the stopper, turn it upside down before placing it on the counter top. This will help avoid contaminating the chemical when the stopper is replaced.

Working with Hot Glassware/ Equipment

1. Heated metals, glassware and cermaics stay hot for a long time. Allow plenty of time for a hot metal to cool before touching it. Since you cannot tell from the appearance of the metal, glass, or ceramics that it is still hot, you should test it by cautiously bringing the back of your hand close to the metal to feel if heat is radiating from it.
2. Handle hot objects like a beaker, evaporating dish, and crucible with the proper pair of tongs. Use the beaker tongs, evaporating dish tongs, and crucible tongs, respectively.
3. Keep your hair, clothing, and hands at a safe distance from the gas burner.
4. Evaporating dishes and crucibles can be heated to very high temperatures. They will crack and shatter if placed hot on the lab bench or come into contact with water. Therefore, they should be placed on wire gauze to cool. Do not place hot evaporating dishes or crucibles on your lab manual.
5. When heating liquid in test tube,
    a. hold the test tube with the test tube holder such that it is pointing along the length of the lab bench. The open end of the test tube should point away from yourself and your neighbors.
    b. move the test tube back and forth through the flame at an angle. Do not heat above the liquid level. A test tube may shatter if the liquid splashes over that hot glass.
6. Do not heat a closed container. Pressure build up may cause the container to explode.
7. Do not allow hot glassware to come in contact with cold water. It will shatter.

Green Chemistry

This is a set of principles intended to change our behaviour to help sustain a habitable planet. Examples of unsustainable behaviour are consumption of a limited resource and careless disposal

of waste. Green chemistry seeks to design chemical products and processes to reduce the use of resources and energy and the generation of hazardous wastes.
It is better to prevent waste production than to dispose it.

THE LABORATORY NOTEBOOK

Purpose of a Laboratory Notebook

A laboratory notebook provides a permanent record of research, ideas, concepts, data, analysis, and/or observations. It is a legal record of your work and may be used as evidence for patent filing, patent protection, or other legal purposes. Documentation and maintenance of your records is a fundamental part of GLP (Good Laboratory Practice) and is essential for the management and protection of intellectual property rights. The proper use of a laboratory notebook will ensure that the progress from conception to reduction to practice can be retraced in a chronological and logical manner, thus providing a solid basis for patent purposes. Moreover, the contents of the laboratory notebook must be able to withstand any challenges to their validity or accuracy

Functions of a lab notebook

The critical function of your lab notebook are to state what you did, what you observed in the lab, and it should supply understanding of your work to a stranger

Basic requirements for a lab notebook

A laboratory notebook should be permanently bound, with sequentially numbered pages. Pages must never be removed or tampered with. A laboratory notebook is a legal document and must be handled accordingly.

Rules for the use of a lab notebook

Complete description of an experiment must be written with sections dealing with purpose, methods, results and conclusions.
It is a good practice to write a balanced chemical equation for every reaction you use. This practice help you understand what you are doing and may point out what you do not understand about what you are doing.
A good lab notebook will allow you or anyone else to duplicate an experiment in the exact manner in which it was first conducted.

- *You must not tear off any portion of your lab notebook.*
- *You must not deface any portion of the record or pages of the lab note book*

- *If you make any mistake: draw a line across the content, state the reason for the cancellation and sign.*

Entries should start at the top of each documentation page. Spaces, which are free of entries, must be crossed out. Do not start a new page until the previous page is full or has been marked so that no additional entries can be made on it. Do not write outside the documentation area. If an entry will be continued on the next page, this should be noted in the spaces provided.

Entries must be made in ink, preferably archival ink. Never use pencils or any non-permanent writing instrument. It is permitted to affix entries, such as raw data tables, folded graphs, or computer printouts to the documentation pages in an appropriate, chronological location. This must be done so that the entry is permanent. Initial both the affixed entry and the notebook page. The purpose of these supplemental entries should be clearly described nearby.

Never attempt to remove, obliterate, blot out or erase entries. Before a page is signed and dated, you may correct an entry by marking with a single line through the specific error and add your initials next to it. It is important that the error is still legible.

Every laboratory notebook page must be signed by the author and countersigned by at least one corroborating witness. This witness should not be directly involved in the documented activities. The witness confirms with their signature and the date that she/he understood the entries and that the activities performed took place on a certain date.

After a page is signed and dated, no further changes, interlineations, deletions, or additions are permitted. If an entry must be corrected subsequently, use a new page and refer to it in your new entry.

The person assigned the laboratory book is responsible for its content and safe keeping. Entries by a third party are not permitted, with the exception of the witness when signing and dating a page.

Immediately enter your work in a clear, concise, structured and legible manner. Entries should be recorded with the intent of an independent person, who is skilled in the art, being able to comprehend and reproduce your results.

Record all experimental work, calculations, sketches, diagrams, and any other related information directly into the notebook.

Retain a consistent language, numbering system, and indication nomenclature throughout the laboratory notebook in order to avoid confusion. Abbreviations must be defined and remain constant throughout the entire book.

Provide figures and equations with numbers or letters and refer to them within the description

Essential Glasswares in the Laboratory

Analytical chemists use a variety of glassware to measure volume in the laboratory. The type of glassware used depends on how exact the volume needs to be. Beakers, dropping pipets, and graduated cylinders are used to measure volumes approximately, typically with errors of several percent. Pipets, burettes and volumetric flasks provide a more accurate/precise means for measuring volume.

Burets

A burette is a precisely manufactured glass tube with graduations enabling you to measure the volume of liquid delivered through the stopcock (the valve) at the bottom. Numbers on burette increase from top to bottom with 0 mL (zero milliliter mark) near the top. A volumetric measurement is made by reading the level before and after draining liquid from the burette and subtracting the first reading from the second.

Tolerance of Class A Burette – most accurate grade at burette

Burette volume (mL)	Smallest Graduation (mL)	Tolerance (mL)
5	0.01	± 0.01
10	0.05 or 0.02	± 0.02
25	0.1	± 0.03
50	0.1	± 0.05
100	0.2	± 0.10

Tolerance of a burette is used to determine the accuracy of the measurements made with the burette. For example, if the initial reading of a 50 mL burette is 0.83 mL and the final reading/level is 27.16 mL, then the volume of solution used is 27.16-0.83 = 26.33 mL. Hence the true volume can be anywhere in the range 26.28-26.58 and still be within the tolerance of ± 0.05mL.

Correct practice to ensure accuracy in the use of a burette

- When reading the liquid level in a burette, your eyes should be at the same height as the top of the liquid to avoid the error of parallax.
- The meniscus of the liquid surface must be considered to determine the actual liquid level.

- Liquid should drain evenly down the wall of a burette. The tendency of liquid to stick to the glass wall is reduced by draining the burette slowly, <20mL/min. If many droplet stick to the wall, clean the burette properly.
- A common burette error is caused by failure to expel the air bubble often found beneath the value. The bubble can be dislodged valve. The bubble can be dislodged by draining the burette for a second or two the value wide open.
- Before filling a burette with fresh solution, rinse it several times with small portions of the new solution, discarding each wash. It is not necessary to fill the burette to the zero-mark level before you start your titration, just note where you started.

Volumetric Flasks

A volumetric flask is calibrated to contain (not to deliver) a particular volume of solution at specified temperature, usually 20^{o}C (or as written on the flask) when the bottom of the meniscus is adjusted to the centre of the mark on the neck of the flask.

Most flask bear the label "TC 20^{o}C" which means to contain at 20^{o}C. Other volumetric glassware, such as burette and pipette bear the label "TD 20^{o}C" which means to deliver at 20^{o}C. Hence the temperature of a volumetric glass ware is relevant to its accuracy because liquid and glass expand with rise in temperature when heated. This is why it is not advisable to dry volumetric flasks inside oven at high temperature.

We use volume flask to prepare solution of known volume not to deliver a liquid of known volume.

Preparation of solution with a volumetric flask

To prepare solution in a volumetric flask, dissolve the desired mass of reagent in the flask swirling with less than the final volume of liquid.

Add more liquid and mix the solution again until complete dissolution. Adjust the final volume with as much liquid as required until the level reached the mark on the neck of the volumetric flask. Then put the cap and hold it firmly in place while inverting the flask several times to complete mixing and to obtain homogeneous solution.

Question: How would you use a volumetric flask to prepare 250.00 mL of 0.150 M K_2SO_4?

Hints: Calculate the amount (g) of K_2SO_4 needed to give the desired concentration in 250 mL flask. Weigh it accurately and follow the above procedure

Problem with Glass Vol. Flask

Glass is notorious for adsorbing traces of chemicals especially cation (metals).

For critical work, acid wash the glassware to replace low concentrations with H^+. To do this, soak already thoroughly cleared vol. glassware in 3-6 M HCl or HMO_3 (in a fume hood) for >1hr, followed by several rinses with distilled water and a final soak in distilled water.

Pipets

Measuring pipette **Transfer pipette** **Pipette filler**

Pipettes are manufactured and calibrated to deliver known volumes of liquid at a specified temperature. There are 2 types: (1) Transfer pipette and (2) Measuring Pipette

A transfer pipette is calibrated to deliver one fixed volume of liquid, as specified on it. The last drop does not drain out of the pipet and should not be blown out. A measuring pipette is calibrated to deliver variable volume of liquid, which is the difference between the initial and final volume, just like in burette. Transfer pipettes are more accurate than measuring pipettes.

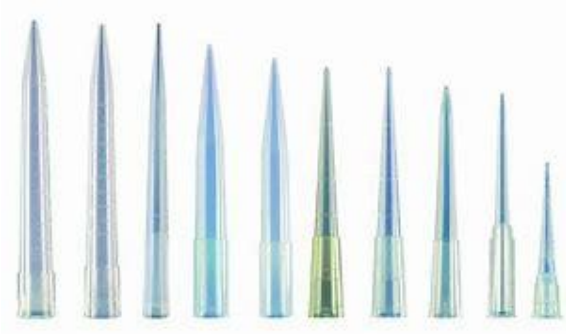
Using a transfer pipette

Using a rubber bulb or other pipet sunction device/filler, NOT YOUR MOUTH, suck liquid up past the calibration mark. It is a good idea to discard one or two pipet volumes of liquid to remove traces of the previous reagent from the pipet. After taking up the third volume past the calibration mark, quickly replace the bulb with your index finger at the end of the pipet. The liquid should still be above the mark after this maneuver. (Gently pressing the pipet against the bottom of the vessel while removing the rubber bulb helps prevent liquid from draping while you put your finger in place).

Wipe the excess liquid off the outside of the pipet with a clean tissue. Touch the tip of the pipet to the side of a beaker and drain the liquid until the bottom of the meniscus just reach the center at the mark. (Touching the beaker wall draws liquid from the pipet without leaving part of a drop hanging from the pipet when the level reaches the calibration mark).

Transfer the pipet to the desired receiving vessel and drain it by gravity while holding the tip against the wall of the vessel. After the pipet stops draining, hold it against the wall for a few more seconds to complete the draining. Do not blow out the last drop. The pipet should be nearly vertical at the end of delivery. Rinse the pipet with distilled water or soak until you are ready to clean it.

Micropipettes



Plastic disposable tips

There are 2 types; adjustable volume and fixed Volume μ Pipet.

A micropipette is used to deliver volumes of 1 to 1000 μL (1 μL = 10^{-6}L). Liquid is containing in a disposable plastic tip, made of poly-propylene, which is stable to most aqueous solutions and many organic solvents except chloroform.

Using a micropipette

To use a micropipette, place a fresh tip tightly on the barrel. Set the desired volume, if it is a transfer pipet, with the knob at the top of the pipet. Depress the plunger to the first stop, which corresponds to the selected volume. Hold the pipet vertically, dip it 3-5 mm into the reagent solution, and slowly release the finger to suck up liquid. Leave the tip in the liquid for a few seconds to allow aspiration of liquid into the tip to go to completion. Withdraw the pipet vertically from the liquid without touching the tip to the wall of the vessel.

To dispense liquid, touch the micropipette tip to the wall of the receiver and gently depress the plunger to the first stop, wait a few second to allow liquid to drain down the tip, and then depress the plunger further to squirt out the last liquid. The method described is known as forward mode. This is good for non-foaming liquid or solution. For foaming solution like protein and surfactant solutions or viscous liquid, the procedure is called reverse mode. In this case: The micropipette plunger is depressed beyond the first stop and excess liquid is taken in. to deliver the correct vol. of liquid, depress the plunger to the first stop and not beyond.

Precaution when working with volume glasswares

1. The volume delivered by any volumetric glassware assumes that the glassware is clean. Hence it is important to clean your volumetric glasswares properly for accuracy in volume

2. When using a pipet or vol. flask, set the liquids level exactly at the calibration mark.
3. Before using a volumetric glassware for your experiment, you should rinse it with several small portions of the solution whose vol. is being measured.

Calibration of Vol. Glassware

Calibration is the process of relating the actual quantity (such as mass, volume, or electric current) to the quantity indicated on the scale of an instrument. Volumetric glassware can be calibrated to measure the vol that is actually contained in or delivered by a particular piece of equipment.

Calibration of vol. glassware is done by measuring the mass of water contained or delivered by a volumetric glassware and the volume of 1g of H_2O at the specified temperature.

True Vol = (weight of water (g)) x (Vol of 1g of H_2O at a specified temperature)

To Calibrate a 25-mL transfer pipet, first weigh an empty weighing bottle, then fill the pipet to the mark with distilled water, drain it carefully into the weighing bottle and cap the bottle to prevent evaporation. Weigh the bottle again to find the mass of water delivered from the pipet.

True volume = (Mass of water (g) x (Vol. of 1g of H_2O at a specified temperature)

Example

An empty weighing bottle has a mass of 10.283 g. After water was added from a 25-mL pipet, the mass was 35.225g. The temperature 23°C. Find the vol of the water delivered by the pipet if 1g of H_2O has a vol of 1.0035 mL at 23°C.

Solution

Mass of water delivered = 35.225 – 10.283 = 24.942 g

True vol. = (24.942g x 1.0035mL/g) = 25.029 mL

Q. A 10mL pipet delivered 10.00g of H_2O at 15°C to a weighing bottle. What is the true volume of the pipet if 1g of H_2O weighed 1.0020 mL/g at 15 °C.

Temp (°C)	Vol. of 1 g of H_2O (mL/g)	Temp (°C)	Vol of 1g of H_2O (mL/g)
10	1.0014	21	1.0031
11	1.0015	22	1.0033
12	1.0016	23	1.0035
13	1.0017	24	1.0038
14	1.0018	25	1.0040
15	1.0020	26	1.0043
16	1.0021	27	1.0046
17	1.0023	28	1.0048
18	1.0025	29	1.0051
19	1.0027	30	1.0054
20	1.0029		

Temperature effect on solution prepared – Thermal Expansion.

In most careful work, it is necessary to account for expansion of solutions and the glassware with changing temperature. For this purpose you should know the lab temperature when a solution is prepared and when it is used. This is because the conc. of solution is proportional to its density. Water for instance expands by 0.02% per degree near 20 ºC.

Correction for thermal expansion is:

$$\frac{C_i}{d_i} = \frac{C_2}{d_2}$$

Where C_i & d_i are conc. and density at temp T_i and C_2 and d_2 apply at temperature T_2

Example

A 0.03146 M aqueous solution was prepared in winter when the lab temp. was 17 ºC. What is the molarity of the solution on a warm day when the temperature is 25 ºC. Density of water at 17ºC = 0.99878 g/mL and @ 25ºC = 0.99705g/mL.

Since the solution is in water and it is dilute, we assume the thermal expansion of a dilute solution equal to the thermal expansion of water.

Then:

$$\frac{C^1@25^oC}{0.99705g/mL} = \frac{0.03146M}{0.99878gmL}$$

C^1 = 0.03141 M

The conc has decreased by 0.16% on the warm day

Q

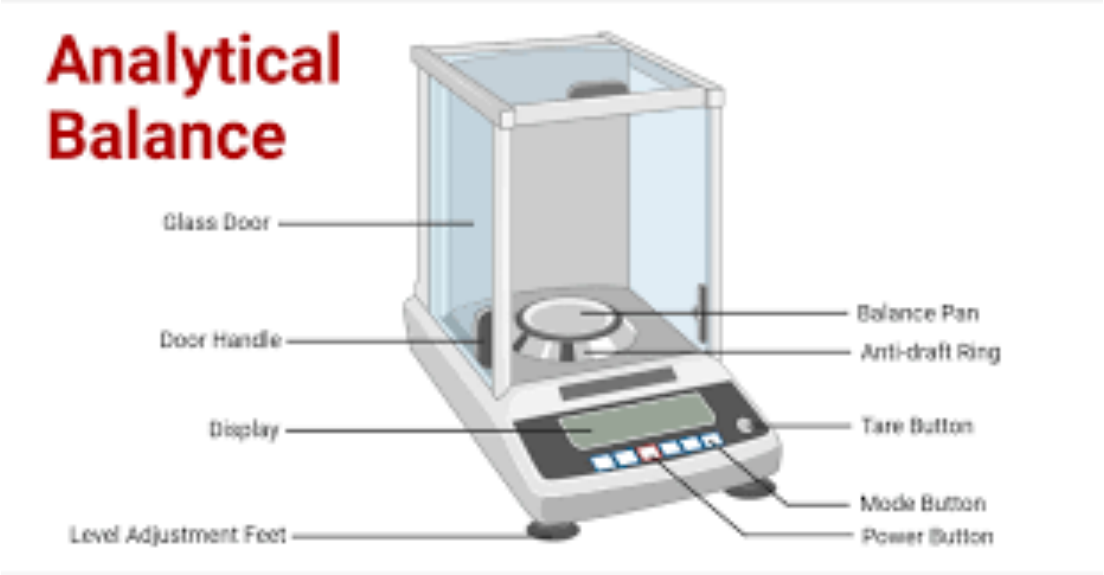
If a solution of 0.050 M solution is prepared at 10 ºC, what would its molarity be at 30ºC? What is the percent change in conc.? [density of water = 0.99970g/mL @ 10ºC and 0.99565g/mL @ 30 ºC.

Desiccator – is a closed chamber containing a drying agent called a desiccant. The lid is greased to make an airtight seal. Desiccant is placed in the bottom beneath of perforated disk. Common desiccants in approximate order of decreasing efficiency are magnesium perchlorate (Mg/)>barium oxide (BaO) = alumina (Al_2O_3) = phosphorous pentoxide (P_4O_{10})>> calcium chloride ($CaCl_2$) = Calcium sulfate ($CaSO_4$) = silica gel (SiO_2). After placing a hot object in the desiccator, leave the lid cracked open for a minute until the object has cooled slightly. This practice prevents the lid from popping open when the air inside warns up. To open a desiccator, slide the lid sideways rather than trying to pull up straight.



Instrumentation for Measuring Mass

An object's mass is measured using a balance. The most common type of balance is an electronic balance in which the balance pan is placed over an electromagnet (Figure below). The sample to be weighed is placed on the sample pan, displacing the pan downward by a force equal to the product of the sample's mass and the acceleration due to gravity. The balance detects this downward movement and generates a counterbalancing force using an electromagnet. The current needed to produce this force is proportional to the object's mass. A typical electronic balance has a capacity of 100–200 g and can measure mass to the nearest ±0.01 to ±1 mg.



Important points in the operation of a laboratory balance

- The mass of a sample is determined by difference.
- **If the material being weighed is not moisture-sensitive**, a clean and dry container is placed on the balance.
- The mass of the container is called the tare. Most balances allow the tare to be automatically adjusted to read a mass of zero.
- The sample is transferred into the container after it has been tared, its mass adjusted to zero,
- then the mass of the sample is measured and noted
- the sample is removed from the container and the container is reweighed without any adjustments to the balance reading
- the sample's mass is determined by subtracting the mass of the container, after the sample has been removed, from the original mass of the sample measured.
- **For samples that absorb moisture from the air**, they are weighed differently. The sample is placed in a covered weighing bottle and their combined mass is determined.

- A portion of the sample is removed, and the weighing bottle and remaining sample are reweighed. The difference between the two masses gives the mass of the transferred sample.

Precautions required for an accurate use of a laboratory balance

Several important precautions help to minimize errors in measuring an object's mass.

- Balances should be placed on heavy surfaces to minimize the effect of vibrations in the surrounding environment and should be maintained in a level position.
- Check to ensure that the liquid balance level, spirit level, is balanced before using a balance
- Analytical balances are sensitive enough that they can measure the mass of a fingerprint. For this reason, materials placed on a balance should normally be handled using tongs or laboratory tissues.
- Volatile liquid samples should be weighed in a covered container to avoid the loss of sample by evaporation.
- Air currents can significantly affect a sample's mass. To avoid air currents, the balance's glass doors should be closed, or the balance's wind shield should be in place.
- A sample that is cooler or warmer than the surrounding air will create convective air currents that adversely affect the measurement of its mass, hence allow sample to equilibrate to the prevailing temperature before measurement of it mass
- A samples dried in an oven should be stored in a desiccator to prevent them from reabsorbing moisture from the atmosphere

CHM 208

Limitation of Analytical Methods

The function of an analyst is to obtain a result as near to the true value as possible by the correct application of the analytical procedure employed. The level of confidence that the analyst may enjoy in his result will be very small unless he has knowledge of the accuracy and precision of the method used as well as being aware of the sources of error which may be introduced.

Classification of Errors

Errors that affect experimental results could be classified as "Determinate/Systematic errors and Random/Indeterminate errors.

Systematic/Determinate Errors

These are errors that can be avoided or whose magnitude can be determined. Examples include:

1. Operational/Personal errors: these could arise from constitutional inability of an individual to make certain observations accurately e.g parallax error, inability to judge colour changes during visual titration, mechanical loss of materials in various steps of analysis, under/over washing of precipitates at correct temperature, insufficient cooling of crucible before weighing, allowing hygroscopic materials to absorb moisture before or during weighing, the use of reagent containing harmful impurities.
2. Instrumental and Reagent errors: these arise from faulty construction of balances, the use of uncalibrated or improperly calibrated weights, graduated glassware and other instruments, the attack of reagents upon glassware, porcelain etc resulting in the introduction of foreign materials, volatilization of platinum at very high temperatures and the use of reagents containing impurities
3. Error of Method: These originate from incorrect sampling and from incompleteness of a reaction. In gravitational analysis, errors such as appreciable solubility of precipitates, co-precipitation, post-precipitation, decomposition etc. In titrimetric analysis, errors such as failure of reaction to proceed to completion, occurrence of induced side reaction etc
4. Additive and proportional Error: E.g of additive error are loss of weight of a crucible in which a precipitate is ignited and error in weight. This error is revealed by taking different weights. The absolute value of a proportional error depends upon the amount of the constituent. The absolute value of an additive error is independent of the amount of the constituent present in the determination. Proportional error may arise from the impurity in a standard substance which leads to an incorrect value for the molarity of a standard solution

Random/ Indeterminate Error

These errors manifest themselves by the slight variations that occur in successive measurements made by the same observer with the greatest care under as nearly identical conditions as possible. They are due to causes over which the analyst has no control.

Accuracy and Precision

Accuracy is defined as ‘the degree to which the result of a measurement conforms to the correct value or a standard’ and essentially refers to how close a measurement is to its agreed value.

Precision is defined as ‘the quality of being exact’ and refers to how close two or more measurements are to each other, regardless of whether those measurements are accurate or not. It is possible for precision measurements to not be accurate.

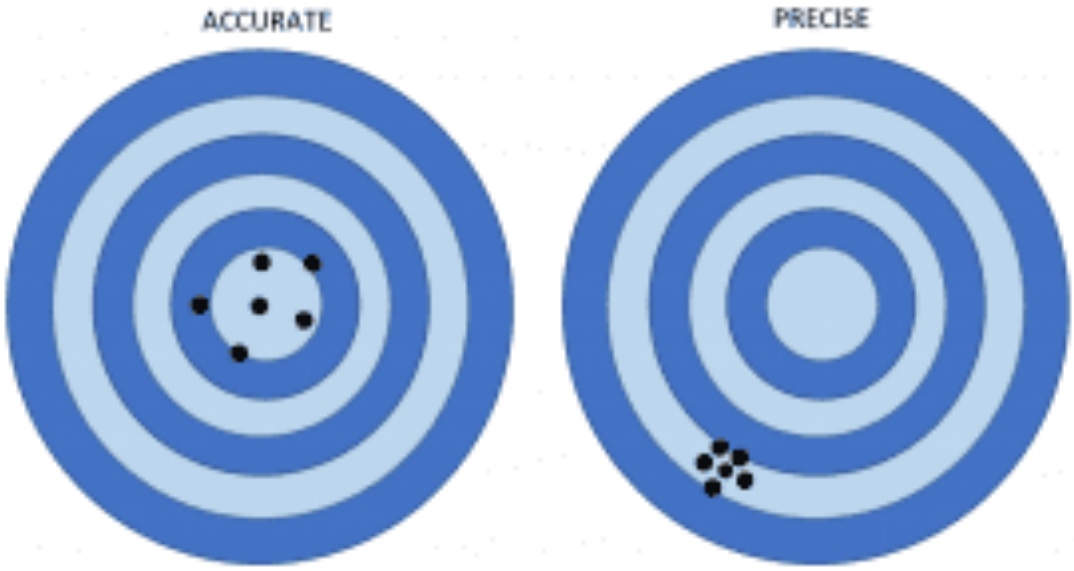
Difference between Accuracy and Precision

Accuracy reflects how close a measurement is to a known or accepted value, while precision reflects how reproducible measurements are, even if they are far from the accepted value. Measurements that are both precise and accurate are repeatable and very close to true values.

Example of the difference between Accuracy and Precision…

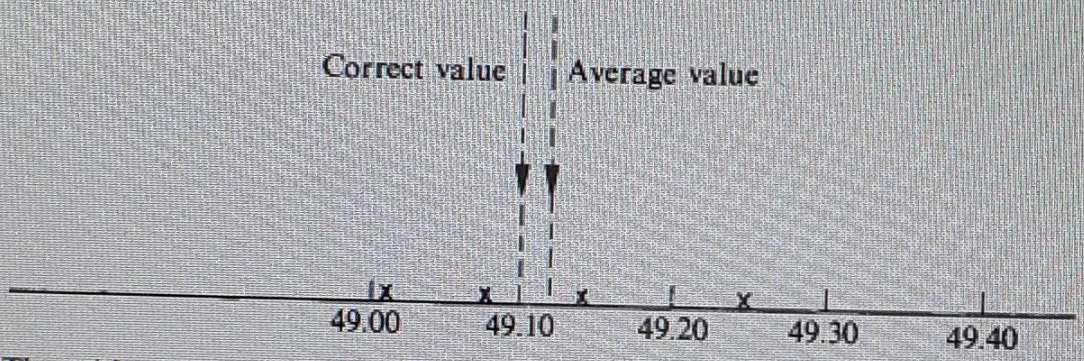
The example of a darts board is often used when talking about the difference between accuracy and precision.

Accurately hitting the target means you are close to the Centre of the target, even if all the marks are on different sides of the Centre. Precisely hitting a target means all the hits are closely spaced, even if they are very far from the Centre of the target.



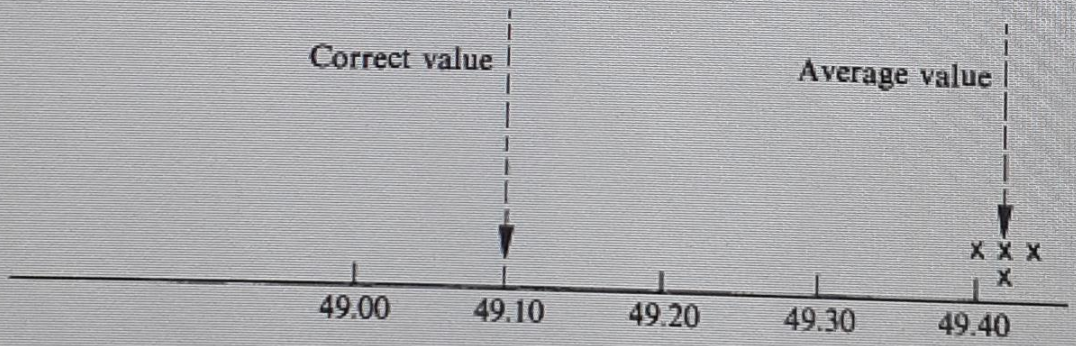
Example 2 that differentiate accuracy from precision

Analyst (1) %A 49.01; 49.25; 49.08; 49.14



The arithmetic mean is 49.12% and the results range from 49.01% to 49.25%.

Analyst (2) %A 49.40; 49.44; 49.42; 49.42



The arithmetic mean is 49.42% and the results range from 49.40% to 49.44%.

We can summarise the results of the analyses as follows.

(*a*) The values obtained by Analyst 1 are accurate (very close to the correct result), but the precision is inferior to the results given by Analyst 2. The values obtained by Analyst 2 are very precise but are not accurate.

(*b*) The results of Analyst 1 face on both sides of the mean value and could be attributed to random errors. It is apparent that there is a constant (systematic) error present in the results of Analyst 2.

Precision was previously described as the reproducibility of a measurement. However, the modern analyst makes a distinction between the terms '**reproducible**' and '**repeatable**'. On further consideration of the above example:

(*c*) If Analyst 2 had made the determinations on the same day in rapid succession, then this would be defined as 'repeatable' analysis. However, if the determinations had been made on separate days when laboratory conditions may vary, this set of results would be defined as '**reproducible**'.

Thus, there is a distinction between a within-run precision (repeatability) and a between-run precision (reproducibility).

Statistics

Statistics is the discipline that concerns the collection, organization, analysis, interpretation, and presentation of data. In applying statistics to a scientific, industrial, or social problem, it is conventional to begin with a statistical population or a statistical model to be studied.

Descriptive Statistics

Descriptive statistics is the term given to the analysis of data that helps describe, show or summarize data in a meaningful way such that, for example, patterns might emerge from the data. Descriptive statistics do not, however, allow us to make conclusions beyond the data we have analyzed or reach conclusions regarding any hypotheses we might have made. They are simply a way to describe our data.

Descriptive statistics are very important because if we simply presented our raw data it would be hard to visualize what the data was showing, especially if there was a lot of it. Descriptive statistics therefore enables us to present the data in a more meaningful way, which allows simpler interpretation of the data. For example, if we had the results of 100 pieces of students' coursework, we may be interested in the overall performance of those students. We would also be interested in the distribution or spread of the marks. Descriptive statistics allow us to do this. Typically, there are two general types of statistic that are used to describe data:

- **Measures of central tendency:** these are ways of describing the central position of a frequency distribution for a group of data. In this case, the frequency distribution is simply the distribution and pattern of marks scored by the 100 students from the lowest to the highest. We can describe this central position using a number of statistics, including the **mode, median, and mean**.
- **Measures of spread:** these are ways of summarizing a group of data by describing how spread out the scores are. For example, the mean score of our 100 students may be 65 out of 100. However, not all students will have scored 65 marks. Rather, their scores will be spread out. Some will be lower and others higher. Measures of spread help us to summarize how spread out these scores are. To describe this spread, a number of statistics are available to us, including the **range, quartiles, absolute deviation, variance and standard deviation.**

Inferential Statistics

We have seen that descriptive statistics provide information about our immediate group of data. For example, we could calculate the mean and standard deviation of the exam marks for the 100 students and this could provide valuable information about this group of 100 students. Any group of data like this, which includes all the data you are interested in, is called a **population**. A

population can be small or large, as long as it includes all the data you are interested in. For example, if you were only interested in the exam marks of 100 students, the 100 students would represent your population. Descriptive statistics are applied to populations, and the properties of populations, like the mean or standard deviation, are called **parameters** as they represent the whole population (i.e., everybody you are interested in).

Often, however, you do not have access to the whole population you are interested in investigating, but only a limited number of data instead. For example, you might be interested in the exam marks of all students in OAU. It is not feasible to measure all exam marks of all students in the whole of the OAU, so, you have to measure a smaller sample **of students (e.g., 100 students), which are used to represent the larger population of all OAU students.**

Inferential statistics are techniques that allow us to use these samples to make generalizations about the populations from which the samples were drawn. It is, therefore, important that the sample accurately represents the population. The process of achieving this is called sampling. Inferential statistics arise out of the fact that sampling naturally incurs sampling error and thus a sample is not expected to perfectly represent the population. The methods of inferential statistics are (1) the estimation of parameter(s) and (2) testing of statistical hypotheses.

Descriptive Statistics

Measures of central tendency help you find the middle, or the average, of a data set. The 3 most common measures of central tendency are the mode, median, and mean.

- **Mode:** the most frequent value.
- **Median:** the middle number in an ordered data set. It is the value above and below which there is an equal number of data points for an odd numbers/values, the median of the even numbers is the average of the two numbers of an ordered set of values.
- **Mean:** the sum of all values divided by the total number of values.

In addition to central tendency, the variability and distribution of your data set is important to understand when performing descriptive statistics. Measures of Variability include Range, Standard Deviation, Variance.

Example, consider the set of data below:

7, 11, 11, 15, 20, 20, 28.

Determine the Median, Mode, Mean, Range, Standard deviation, and Variance.

Solution:

Median = 15

Mode = 11 and 20

Mean = $\bar{X}=\frac{\sum X}{n} = \frac{112}{7} = 16$

Range = 28 – 7 = 21

Data values (x)	Mean ($\bar{x}$)	(x-$\bar{x}$)	$(x-\bar{x})^2$
7	16	-9	81
11	16	-5	25
11	16	-5	25
15	16	-1	1
20	16	4	16
20	16	4	16
28	16	12	144

$\sum x = 112$ $\sum (x-\bar{x})^2 = 308$

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

SD = $\sqrt{\frac{308}{6}} = \sqrt{51.333} = \pm 7.165$

Variance = $S^2 = (7.165)^2 = 51.333$

.

Distributions and central tendency

A data set is a **distribution** of *n* number of scores or values.

Normal distribution

In a normal distribution, data is symmetrically distributed with no skew. Most values cluster around a central region, with values tapering off as they go further away from the center. The mean, mode and median are exactly the same in a normal distribution.

Skewed distributions

In skewed distributions, more values fall on one side of the center than the other, and the mean, median and mode all differ from each other. One side has a more spread out and longer tail with fewer scores at one end than the other. The direction of this tail tells you the side of the skew

In a positively skewed distribution, there's a cluster of lower scores and a spread out tail on the right. In a negatively skewed distribution, there's a cluster of higher scores and a spread out tail on the left.

- Positively skewed distribution
- Negatively skewed distribution

In a positively skewed distribution, mode < median < mean.
In a negatively skewed distribution, mean < median < mode.

Geometric Mean

It is a special type of average where we multiply the numbers together and then take a square root (for the two numbers), cube root (for three numbers) etc.

Example; what is the Geometric mean of 10, 51.2, and 8

Solution:

G .M = $(\prod_i^n xi)$ = $\sqrt[3]{10x\ 51.2\ x8}$ = 16

Thus, G.M = $\sqrt[n]{n1\ X\ n2\ X\ n3\ \ldots\ldots X\ ni}$

Geometric mean is useful when we want to compare things with very different properties.

If we consider a series of n observations arranged in ascending order of magnitude $X_1+X_2 + X_3 + X_4 +\ldots\ldots\ldots X_{n-1} + X_n$ the arithmetic mean (simply mean) is given by

$\bar{X} = \frac{X1+X2 + X3 + X4 +\cdots\ldots\ldots Xn-1 + Xn}{n}$

This spread of values is measured most efficiently by the Standard Deviations defined by

S = $\sqrt{\frac{(x1-\bar{x})^2+(x2-\bar{x})^2+(xn-\bar{x})^2}{n-1}}$

In this equation the denominator (n-1) rather than n, when the number of values is small, this equation may also be written as

S = $\sqrt{\frac{(x-\bar{x})^2}{n-1}}$ the square of the SD is called the Variance.

A further measure of precision, known as the Relative Standard Deviation (R.S.D) is given by

RSD = $\frac{S}{\bar{x}}$

This measure is often expressed as a percentage known as the coefficient of variation (CV)

C.V = $\frac{S}{\bar{x}}$ X $\frac{100}{1}$

Example

Find the mean, median, mode, geometric mean and SD of the following data, 287, 345, 365, 298 and 380

Solution

First arrange in ascending order

287, 298, 345, 365, 380

$\sum X$ = 287 + 298 + 345 + 365 + 380 = 1675 n = 5

$\bar{X} = \sum \frac{X}{n} = \frac{1675}{5}$ = 335

Median = 345, the one at the middle of the data after arranging in ascending order

Mode is the most frequently occurring datum, here all appear singly, no mode

$$SD = \sqrt{\frac{(x-\overline{x})^2}{n-1}} = \sqrt{\frac{(287-335)^2+(298-335)^2+(365-335)^2+(380-335)^2+(345-335)^2}{5-1}}$$

$$= \sqrt{\frac{(-48)^2+(-37)^2+(30)^2+(45)^2(10)^2}{4}} = \sqrt{\frac{6698}{4}} = \sqrt{1674.5} = 40.921$$

It is important to write the mean and standard deviation in the same decimal places mean = 335.0 and SD 40.9.

Geometric mean = $\sqrt[5]{287\ X\ 345X\ 365X298X380}$

$$= \sqrt[5]{4092547389000} = 332.965$$

Range

The range of a spread is the difference between the highest and the lowest values.

The range of 126.2, 127.5, 127.1, 125.9 and 126.4 is

Highest value – lowest value

= 127.5-125.9 = 1.6

Example 2

Analyses of a sample of iron ore gave the following percent value for the iron content; 7.08, 7.21, 7.12, 7.09, 7.16, 7.14, 7.07, 7.14, 7.18, 7.11. Calculate the mean, standard deviation, coefficient of variation for the values.

Solution

Result (x)	(x-$\bar{x}$)	$(x-\bar{x})^2$
7.08	-0.05	0.0025
7.21	0.08	0.0064
7.12	-0.01	0.0001
7.09	-0.04	0.0016
7.16	0.03	0.0009
7.14	0.01	0.0001
7.07	-0.06	0.0036
7.14	0.01	0.0001
7.18	0.05	0.0025
7.11	-0.02	0.0004

$\sum x = 71.30$ $\sum (x-\bar{x})^2 = 0.0182$

$\bar{x}$ = 7.13% SD = $\sqrt{\frac{0.0182}{9}}$ = $\sqrt{0.0020}$ = ± 0.045%

Coefficient of Variation (CV) = $\frac{s}{\bar{x}}$ x 100 =0.63%

The mean of several readings ($\bar{x}$) will make a more reliable estimate of the true mean (μ) than is given by one observation. **The greater the number of measurements (n), the closer will the sample average approach the true mean.**

The standard error of mean S_x is given by

$S_x = \frac{S}{\sqrt{n}}$ in the above example,

$S_x = \pm \frac{0.045}{\sqrt{10}}$ = ± 0.014 and if the measurement is 100

$S_x = \pm \frac{0.045}{\sqrt{100}}$ = ± 0.0045

Hence, the precision of a measurement may be improved by increasing the no of measurement.

Reliability of Results

Statistical figures obtained from a set of results have limited value by themselves. Analysis of the results can be considered in two main categories:

1. The reliability of the result 2. Comparison of the results with the true value or with other sets of data.

The most important consideration is to be able to arrive at a sensible decision as to whether certain results may be rejected.

Example: The following values were obtained for the determination of Cadmium in a sample of dust; 4.3, 4.1, 4.0 and 3.2μgg^{-1}. Should the last value 3.2 be rejected?

Solution

The Q test may be applied to solve this problem

$Q = \frac{|Qustionable\ value - Nearest\ value|}{\text{Largest value - Smallest Value}} = \frac{Gap}{Range}$

Q = |3.2-4.0| / 4.3 – 3.2 i.e Gap / Range = 0.8/1.1 = 0.727

If the calculated Q exceed the Critical value given in the Q table, then, the questionable value may be rejected.

In this example Q calculated is 0.727 and Q critical for the sample size four is 0.831. Hence, the result 3.2 μgg^{-1} should be retained.

If, however, in the above example, three additional measurements were made with the results; 4.3, 4.1, 4.0, 3.2, 4.2, 3.9 and 4.0 μgg^{-1}.

Then,

Q = |3.2 – 3.9| / 4.3 – 3.2 =0.7 / 1.1 = 0.636

The value of Q critical for the sample size seven is 0.570, so rejection of the value 3.2 $\mu g g^{-1}$ is justified. **It should be noted that the value Q has no regard to algebraic sign.**

Confidence Interval

When a small number of observations is made, the value of the standard deviation S, does not by itself give a measure of how close the sample mean $\bar{x}$ might be to the true mean. It is however possible to calculate a confidence interval to estimate the range within which the true mean may be found. The limits of this confidence interval, known as the confidence limits, are given by the expression:

Confidence limits of μ, for n replicate measurements, $\mu = \bar{x} \pm \frac{ts}{\sqrt{n}}$ where t is a parameter that depends upon the number of degrees of freedom and the confidence level required. A table of the values of t at different confidence levels and degrees of freedom will be provided.

Example; The mean $\bar{x}$ of four determinations of the copper content of a sample of an alloy was 8.27 percent with a standard deviation s = 0.17 percent. Calculate the 95% confidence limit for the true value.

From the t-table, the value of t for the 95 percent confidence level with (n-1) i.e, three degree of freedom is 3.18

Hence, from equation of confidence interval, the 95% confidence level

95% (C.L) for $\mu = 8.27 \pm \frac{3.18\ X\ 0.17}{\sqrt{4}}$

$= 8.27 \pm 0.27$ percent

Thus, there is 95 % confidence that the true value of copper content of the alloy lies in the range 8.00 - 8.54 %

Volumetric Methods

(i) Acid-Base Titrations

Definition

Acid base titration is the same as neutralization titration in which we have:

$H^+ + OH \rightarrow H_2O$

- Note that the range in pH change of reaction depends on the concentration of the acid and indicator.

Consider the reaction between H^+ and OH^- to give H_2O

$2H_2O \rightleftharpoons H_3O^+ + OH^-$ or $H_2O \rightleftharpoons H^+ + OH^-$

$$K_{equil} = \frac{[H^+][OH^-]}{H_2O}$$

$$K_w = [H^+][OH^-] \quad ----(2)$$

$$Where: K_w = ion\ product\ consant\ of\ water = 1.0\ x\ 10^{-14}$$

By definition:

$pH = -\log[H^+]$

$Introduce - \log\ in\ eqn\ 2.$

$-\log K_w = -\log[H^+] + -\log[OH^-]$

Therefore $pK_w = pH + pOH$

$$pK_w = -logK_w = -log1.0\ x\ 10^{-14} = 14 = pH + pOH$$

$$i.e. -\log K_w = pK_w = 14$$

INDICATOR FOR ACID BASE TITRATION

Theory of Indicator behaviour

Acid base indicators are fairly high molecular weight weak organic acids or bases, which upon dissociation or association undergo structural changes that give rise to alterations in

color. The indicator is usually added to the solution and visually detect as a color change. The color of the ionized form of the indicator is usually different from the non-ionized form. One form may be colorless, but the other form may be colored.

SYMBOLIC REPRESENTATION OF TYPICAL REACTION OF ACID BASE INDICATOR

Suppose we have an indicator of a weak acid, designated Hln, and assume that the non-ionized form is red while the ionized form is blue thus:

(a) H_2O + Hln ⇌ H_3O^+ + ln^-

Acid color (red) Basic color (blue)

(b) ln^- + H_2O ⇌ lnH^+ + OH^-

Basic color acid color

(Base indicator)

At equilibrium concentrations for each reaction can be calculated thus:

$$k_a = \frac{[H_3O^+][\ ln^-]}{[Hln]} \text{ - ----------(3)}$$

$$k_b = \frac{[lnH^+][OH^-]}{[ln]} \text{ ---------- (4)}$$

Rearranging equations 3 & 4

$$\frac{[\ ln^-]}{[Hln]} = \frac{k}{[H_3O^+]} \text{- ----- (5)}$$

$$\frac{[\ lnH^+]}{[\ ln]} = \frac{k_b}{[OH^-]} \text{- ---------- (6)}$$

But $k_w = [OH^-][H_3O^+]$

$[OH^-] = \frac{k_w}{[H_3O^+]}$ substitute this is equation 6

$$\frac{[\ lnH^+]}{[\ ln]} = \frac{k_b}{\frac{k_w}{[H_3O^+]}} = \frac{k_b[H_3O^+]}{k_w}$$

But k_b and k_w *are constant*

Hence $\frac{[\ln H^+]}{[ln]} = [H_3O^+]$

Hence as $[H_3O^+]$ change there will be a change in concentration of ratio $\frac{[\ln H^+]}{[ln]}$

Similarly, again recall that $k_w = [OH^-][H_3O^+]$

Therefore $[H_3O^+] = k_w/OH^-$

Substitute this in equation 5 and solve as before you will get:

$\frac{[\ \ln^-]}{[Hln]} = [OH^-]$

Hence a change in $[OH^-]$ will result in change of ratio $\frac{[\ \ln^-]}{[Hln]}$

With indicator in which both forms are colored, generally only one color is observed if the ratio of the concentration of the two forms is 10:1; only the color of the more concentrated form is seen. When only the color of the non-ionized form is seen, then

$$\frac{[\ \ln^-]}{[Hln]} = 1/10$$

Hence for $\frac{[\ \ln^-]}{[Hln]} \leq \frac{1}{10}$ acid color predominate

For $\frac{[1_n^-]}{[H1_n]} \leq \frac{10}{1}$ Base color predominate

To evaluate the range of $[H^+]$ concentration needed to effect the color change of indicator we have:

from equation 3 ------$k_a = \frac{[H_3O^+][\ \ln^-]}{[H\ln]}$

$$k_a = [H_3O^+]\frac{1}{10}$$

$[H_3O^+] = 10k_a$ -- (7)

$$for\ full\ basic\ color\ from\ equation\ ,if:$$

$$k_{a=} \frac{[H_3O^+][\quad \ln^-]}{[H\ln]}$$

$[H_3O^+] = \frac{Ka}{10}$ Eqtn 8

Indicator range is given from equations 7 and 8 by taking the negative log of the 2 equations:

- $\log [H_3O^+] = -\log 10k_a \; to \; -\log \frac{k_a}{10}$

- $\log [H_3O^+] = pH = -\log 10 - \log k_a \; to - log10^{-1} - \log k_a$

$$= -1 + pk_a \; to \; (+1) - \log k_a$$

$$pH = -1 + pk_a \; to + 1 + pk_a$$

Therefore $pH\ range = pk_a \pm 1$ which means $pH\ range = 4 \; to \; 6 \; i.e \; 4 - 6$

So the pH in going from one color to the other has changed from $pK_a - 1$ to $pK_a + 1$. This is a pH change of 2, and most indicators require a transition range of about two pH units. During this transition the observed color is a mixture of the two colors. Midway in the transition, the concentrations of the two forms are equal, and pH = pK_a **.** Obviously, then the pK_a of the indicator should be close to the pH of the equivalence point.

There are 3 major types of acid base titrations

(i) Strong acid vs strong base

(ii) Strong acid vs weak base

(iii) Weak acid vs. strong base

Choice of an Indicator for an acid-base titration

An indicator for an acid base titration must fulfil two main conditions:

- ✓ It must undergo a readily detectable color change for the addition of a very small quantity of titrant
- ✓ The color change must occur at (or very close to) the equivalence point.

The Table below shows the list of indicators suitable for different types of acid-base titrations.

ype of Titration	Suitable Indicator
Strong acid-strong base	Any indicator-methyl orange, bromothymol blue, phenolphthalein etc
Weak acid-strong base	Phenolphthalein
Strong acid-weak base	Methyl orange, bromothymol blue
Weak acid-weak base	None (titration curve has no vertical section at equivalence point so the first condition above is not satisfied)

TITRATION CURVES

Titration curve for acid-base reactions is a plot of pH (or pOH) against milliliters of titrant. It is a plot showing the change in pH of the solution in the conical flask as the reagent is added from the burette.

(a) Strong acid Vs. strong base

Note that bcause it is a strong acid-base reaction, ionization is complete and the reaction can be simplified as: H^+ (aq) + OH^- (aq) $\longrightarrow$ H_2O (l)

<u>100 mL of 0.1 M HCl Vs 100 mL of 0.1M NaOH</u>

Assume initially (zero/no titration): $pH = -\log 10^{-1} = 1$
$At\ 90\%\ titration, HCl\ left = 10\%$

$$\Rightarrow pH = -log\frac{10}{100}\ x\ 0.1 = -log10^{-2} = \underline{2}$$

$at\ 99\%\ titration, HCl\ left\ = 1\%$

$$\Rightarrow pH = -log\frac{1\ x\ 0.1}{100} = -log10^{-3} = 3$$

$at\ 99.9\%\ titration, HCl$ left $= 0.1\%$

$$\Rightarrow pH = -log\frac{0.1\ x\ 0.1}{100} = -log10^{-4} = 4$$

$if\ 100.1ml\ of\ NaOH\ is\ used\ \Rightarrow 0.1ml$ of NaOH was in excess

$$\Rightarrow pOH = -log\ \frac{0.1}{100}\ x\ \frac{0.1}{1} = 4$$

Recall that pH + pOH = 14

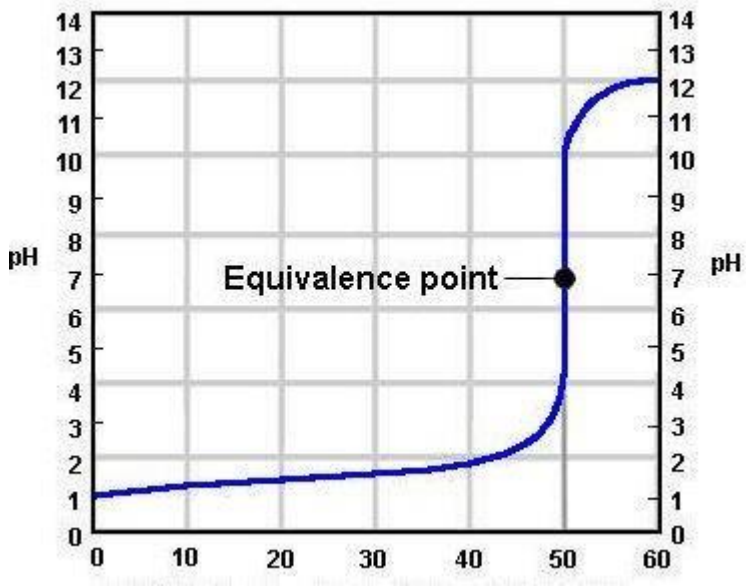
Therefore $pH = 14 - 4 = 10$

$$Hence\ pH = 1\ (initially\ 0\ mL)$$

$$pH = 2\ (90\ mL)$$

$$pH = 4\ (99.9\ mL)$$

Below is an example of titration curve of a strong base added to a strong acid of same molarity (e.g. using mL 0.1M NaOH added to 50 mL 0.1 M HCl)



mL 0.1M NaOH added

*Note that the pH range is (4-10) which is so large that all the indicators can usually be used to follow the titration (**Any indicator will do)**

Titration curve for a Weak acid vs. strong base e.g. Acetic acid vs Sodium hydroxide

0.1 M 100 mL Acetic acid vs 0.1M 100 mL NaOH

$HOAC + NaOH = NaOAC + H_2O$

Note that acetic acid (HOAC or CH_3COOH) is a weak acid hence ionization is incomplete.

- The initial pH cannot be 1

  1. Hence consider the K_{ac} $HOAC = H^+ + OAC^-$

  $K_{AC} = \frac{[H^+][OAC^-]}{[HOAC]} = 1.75\ x\ 10^{-5}$ (K_a $for\ acetic\ acid$)

  $let\ [H^+]\ and\ [OAC^-]\ be\ taken\ to\ be\ x\ respectively \Rightarrow [HOAC]) = c - x$ at equilibrium

  But x <<< c

  $$Therefore\ c - x = c$$

  $$K_{ac} = \frac{x^2}{c}$$

  $$1.75\ x\ 10^{-5} = \frac{x^2}{0.1}$$

  $x = \sqrt{1.75\ x10^{-6}} = 0.00132$

  $$pH = -\log 0.00132$$

  $$= 2.878 = 2.88\ at\ initial\ stage$$

  2. $But\ at\ mid\ point$ 50/50

  $$[OAC^-] = [HOAC]$$

$$\Rightarrow pH = pK_a - log\frac{[acid]}{[salt]}$$

$$pH = pK_a - log\frac{[50]}{[50]}$$

$$But\ pK_a = -logK_a = -\log 1.75\ x\ 10^{-5}$$

$$pH = -log 1.75\ x\ 10^{5} - \log 1$$

$$pH = 4.757\ at\ the\ mid\ pt$$

3. The point of abrupt change in pH starts from where we add 0.1 mL of free HOAC to 0.1 mL of free NaOH.

If 99.9 mL of NaOH was added we have 0.1 mL free HOAC

$$\Rightarrow 99.9\ mL\ of\ HOAC\ must\ have\ been\ added.$$

$$\Rightarrow pH = -logK_a - \log\frac{0.1}{99.9}$$

$$\Rightarrow pH = pK_a + 3$$

$$pH = 7.77 \approx 8: \Rightarrow the\ point\ at\ which\ the\ abrupt\ change\ in\ pH\ starts.$$

$$4.\ Suppose\ we\ have\ 0.1mL\ free\ NaOH \Rightarrow we\ have\ 0.1\%\ NaOH\ left$$

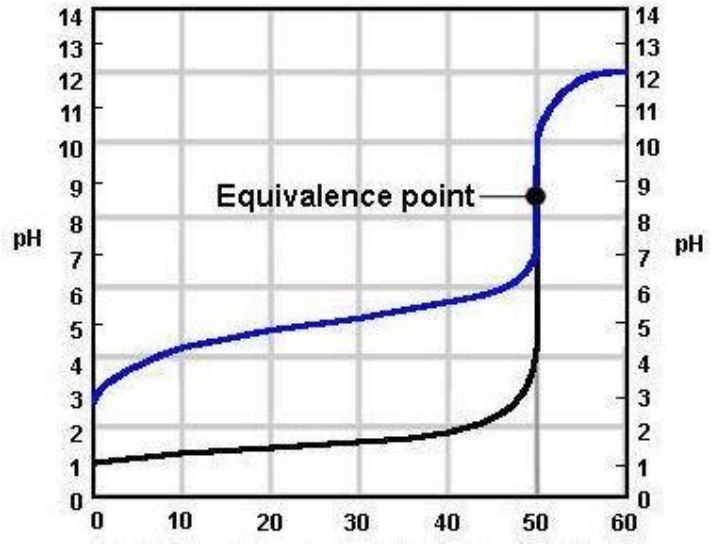
$$\Rightarrow pOH = -\log\frac{0.1}{100}\ x\ \frac{0.1}{1} = 4$$

$$pOH = 4,$$

$$pH = 14 - 4 = 10$$

pH range is 8-10 hence limited number of indicator can be used to follow the titration.

Below Is the Titration curve of a weak acid vs strong base:



Volume (mL) of 0.1M NaOH to the acid

*Note from the curve that the pH range is narrow (8-10) hence limited number of indicators can be used to follow the titration. Likely indicator = phenolphthalein.

Strong acid Vs. weak base e.g. HCl Vs. NH_4OH

$$pK_{(NH_4OH)=1.85\ x\ 10^{-5}}$$

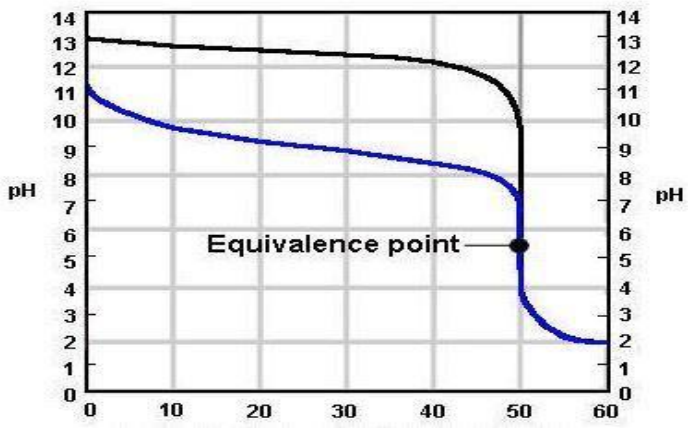
$$[OH] = \sqrt{K_{base}C_{base}}$$

$$pH = 14 - pOH$$

The abrupt pH range at transition state is 4.0 - 6.74 which falls in the acid region.
Because the pH transition range is narrow, hence choice of indicator is restricted.

- Another disadvantage of this is that the end point cannot be sharp/satisfactory, hence we can have titration error.
- This is the case with Kjedah analysis method of N2 determination. In which case instead of titrating weak base NH4SO4with strong acid, we dissolve in strong acid and back titrate with strong base.

The indicators that can follow this reaction are: methyl orange & methyl red. Below is the titration curve for titration involving strong acid vs weak base:



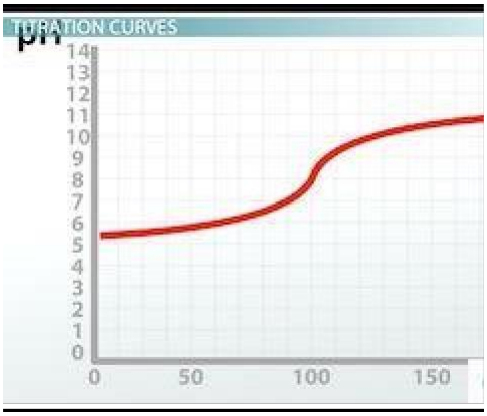
mL of 0.1M of NH_4OH

*Note from the curve that the pH range is narrow (4-6.74) hence limited number of indicators can be used to follow the titration.

Weak Acid vs weak base e.g. CH_3COOH vs NH_4OH

In this case, the pH change in the region of the equivalence-point is very much less than sharp than in the previous examples and there is no vertical section in the curve. Therefore, the equivalence point depends on the relative strengths of the weak base and the weak acid being used which both have $K_a = K_b$ giving an equivalence point of

pH = 7. Hence it is difficult to monitor the end point and therefore no indicator can be used to detect the end point.



Titration curve for weak acid vs weak base

(ii) REDOX TITRATION / OXIDATION REDUCTION TITRATION

- This is defined as volumetric analyses based on titration with reducing or oxidizing agents.
- It is a reduction-oxidation reaction (commonly called a redox reaction) that occurs between a reducing agent and an oxidizing agent
- $OX_1 + Red_2 = Red_1 + OX_2$
- OX_1 is reduced to Red_1
- Red_2 is oxidized to OX_2, where:

  OX_1 = Oxidizing agent

  Red_1 = Reducing agent
- The reducing and oxidizing tendency of a substance will depend on its oxidation state (Valency) and its structure.
- Oxidation implies loss of electron(s)) e.g $Fe^{2+} - e^- \rightarrow Fe^{3+}$
- while reduction implies gain of e^- e.g. $Fe^{3+} + e^- \rightarrow Fe^{2+}$
- An oxidizing agent is therefore an e^- acceptor (Fe^{3+} in the case of the example from above) and a reducing agent is an e- donor (Fe^{2+} in the case of the example from above)

Guide to balancing redox reaction:

- ✓ **the reduction oxidation reaction can be broken down into two half-reactions and overall reaction;**

- ✓ **to balance a reduction-oxidation reaction each half-reaction is first balanced (balance atoms and electrons);**
- ✓ **there must be a net gain or loss of zero electrons in the overall reaction;**
- ✓ **to achieve bullet three above, multiply one or both of the half-reactions by an appropriate factor or factors so that when they are added, the electrons cancel; and**
- ✓ **addition of the balanced half-reactions gives an overall reaction**

Read-up details of Balancing of redox Reactions with specific examples by consulting your CHM 101 note

DETECTION OF END POINT

- End point can be detected by measuring the potential of the solution with an electrode.
- This is then plotted against the volume of titrant used
- As in other titration however, it is more convenient to use visual indicator.

3 Methods exists for Visual Indicators

1. STARCH INDICATOR

- This is used for titration involving iodine. Starch forms a complex with I_2 (a very dark blue color). The color reaction is sensitive to a very small amount of iodine.

In titrations of reducing reagents with iodine, the solution remain colourless up to equivalence point a fraction of a drop of excess titrant turns the solution to a definite blue.

REDOX INDICATORS

- Starch and self-indication methods do not depend on the half-reaction potentials of the solution. The examples of these 2 methods of visual indications are few.
- Most types of redox titration are detected using redox indicators

- Redox indicators are highly coloured dyes that are weak reducing or oxidizing agents that can be reduced or oxidized.
- The colors of the oxidized or reduced forms are different.
- The oxidation state of the indicator and hence its color depends on the potential of the solution at a given point in the titration.
- For the indicator, a half reaction and the Nernst equation can be written thus:-

  $OX_{ind} + ne^- = Red_{ind}$

  $E_{ind} = E_{ind}^{o} - \frac{0.059}{n} \log \frac{[Red_{ind}]}{[OX_{ind}]}$
- The half potentials of the solution during the titration determines E_{lnd} and hence $\frac{[Red_{ind}]}{[OX_{ind}]}$
- As with acid-base indicators the potential must change from $^{10}/_{1}$ to $^{1}/_{10}$ in order for a sharp color change to be seen.
- A potential change ΔE equal to $2\ x\ \frac{(0.059)}{n}$ V is required

If n for the indicator is equal to 1 then a 0.12V change is required. If E^0_{ind} is near the equivalence point potential of the titration, where there is a rapid change in potential in excess of 0.12 V, then the colour change occurs at equivalence point.

- The table below lists some of the common redox indicators:

Indicator	Colour at Reduced Form	Colour at Oxidized form	Solution and E^o(V)
Nitroferroin	Red	Pale Blue	1M H_2SO_4 1.23
Ferroin	Red	PaleBlue	IM H_2SO_4 1.06
Methylene blue	Blue	Colorless	1Macid 0.53
Diphenyl Amine	Colorless	Violet	1M H_2SO_4 0.76

SELF INDICATOR

- If the titrant is highly colored then this colour may be used to detect the end point.
- e.g 0.02M solution of $KMNO_4$ is deep purple.
- A dilute solution of $KMNO_4$ is pink. During titration with $KMnO_4$ the purple colour of MnO_4^- is removed because it is reduced to Mn^{2+}.
- $MnO_4^- + 5e \rightarrow Mn^{2+}$
- As soon as the titration is complete, a fraction of a drop of excess MnO_4^- solution imparts a definite pink colour to the solution indicating that the reaction is complete.
- $KMnO_4$ cannot be used as primary standard because:

(i) It is not stable

(ii) It is not in pure form

(iii) It can undergo auto-catalysis in the presence of light to give MnO_2, hence should be kept in dark bottle.

- It is standardize by Oxalic acid as a primary standard
- Titration should be carried out while hot to get a sharp end point.
- In any event re-standardization every one to two weeks is a precautionary measure.

$H_2C_2O_4 + 2MnO_4^- + 16H^+ \rightarrow Mn^{2+} + 10CO_2 + 8H_2O$

- **Application:**

ESTIMATION OF IRION IN AN ORE BY TITRATION WITH $KMNO_4$

3. Titration with a standard oxidant

- A known weight of the iron ore is digested with acid e.g H_2SO_4 but not HCl.
- The resulting solution is made up to the mark in a graduated flask
- An aliquot portion of the solution is taken
- This is subjected to a suitable reduction procedure
- It is then titrated with standard $KMnO_4$ solution
- HCl is not use in the digestion because MnO_4^- will oxidize HCl to $Cl_2(g)$
- The form an of $Cl_{2(g)}$ is however inhibited in the presence of Zimmermann Reinhard solution of (Mn^{2+}/H_3PO_4) by decreasing the potential of manganese III/manganese II couple.
- Hence the Mn^{2+} reduces the potential of the manganese III/ Manganese II couple sufficiently so that the permanganate will not oxidize the chloride.
- The phosphoric acid (H_3PO_4) in Reinhart reagent forms a stable complex with manganese (III)
- In addition, it complexes with the iron (III) produced in the titration.
- This prevents the intense yellow color of iron (III) chloride complexes from interfering with the end point.
- Hence the end point is sharper and can be easily reached.

OXIDIZING AGENTS

1. Read up $KMnO_4$

2. $K_2Cr_2O_7$ (Potassium dichromate)

- This is a slightly weaker oxidizing agent than $KMnO_4$

- The great advantage of this reagent is its:

(i) Availability as a primary (1^o) std.

(ii) In most cases solution need not be standardized

(iii) In titration of iron (II) standardizing Potassium Chromate against electrolytic iron is preferable

(iv) Oxidation of chloride ion is not a problem with dichromate.

(v) However, the formal potential of $Cr_2O_7^{2-}/Cr^{3+}$ couple is reduced from 1.33V to 1.00V in 1M HCl.

(vi) Phosphoric acid must be added to reduce the potential of the Fe^{3+}/Fe^{2+} couple.

- Hence a sharper end point is reached.

IODIMETRIC TITRATION

- It is a direct method of iodine determination. Iodine is a moderately "strong oxidizing" agent and it can be used to titrate reducing agent
- Titrations with I_2 are called iodimetric methods. These titrations are performed usually in neutral or mildly alkaline (pH8) to weekly acid solution.
- If the pH is too alkali I_2 will disproportionate to hypoiodate and iodide:
- $I_2 + 2OH^- \rightarrow IO^- + I^- + H_2O$
- The 3 reasons for keeping the solution from becoming strongly acidic are:-

(i) The starch used for the detection of end point tends to decompose in strong acid hence the end point is affected.

(ii) The reducing power of several reducing agents is increased in neutral solution.

(iii) I^- produced in the reaction tends to be oxidized by dissolved oxygen in acid solution. $4I^- + O_2 + 4H^+ \rightarrow 2I_2 + 2H_2O$

The important uses of iodimetric titration are determination of :-

(i) H_2S

$$H_2S + I_2 \rightarrow 5 + 2I^- + 2H^+(acid\ in\ solution)$$

(ii) SO_3^{2-}

$$SO_3^{2-} + I_2 + H_2O \rightarrow SO_4^{2-} + 2I^- + 2H^+ \ (acid\ in\ solution)$$

(iii) Sn^{2+}

$$Sn^{2+} + I_2 \rightarrow Sn^{4+} + 2I^-$$

(iv) AS(III)

$$H_2ASO_3^- + I_2 + H_2O \rightarrow HASO_4^{2-} + 2I^- + 3H^+ \ (pH8)$$

(v) N_2H_4

$$N_2H_4 + 2I_2 \rightarrow N_2 + 4H^+ + 4I^-$$

Other examples are

(i) **Determination of dichromate**

$$Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O \ \ldots\ldots\ldots\ldots\ldots *$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} x3$$

$$3I_2 + 6S_2O_3^{2-} \rightarrow 6I^- + 3S_4O_6^{2-} \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .. **$$

Equation * + **

$$Cr_2O_7^{2-} + 6I^- + 14H^+ + 3I_2 + 6S_2O_3^{2-} \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O + 6I^- + 3S_4O_6^{2-}$$

$$Cr_2O_7^{2-} + 14H^+ + 6S_2O_3^{2-} \rightarrow 2Cr^{3+} + 7H_2O + 3S_4O_6^{2-}$$

$mole\ ratio$:- $\frac{Cr_2O_7^{2-}}{S_2O_3^{2-}}$ = 1/6

(ii) **Determination of iodate**

$$IO_3^- + 6I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} \; x\; 3$$

$$3I_2 + 6S_2O_3^{2-} \rightarrow 6I^- + 3S_4O_6^{2-}$$

$$[IO_3^- + 6I^- + 6H^+ + 3I_2 + 6S_2O_3^{2-} \rightarrow 3I_2 + 3H_2O + 6I^- + 3S_4O_6^{2-}]$$

$$IO_3^- + 6H^+ + 6S_2O_3^{2-} \rightarrow 3H_2O + 3S_4O_6^{2-}$$

$$\frac{IO_3^-}{S_2O_3^{2-}} = \frac{1}{6}$$

3. In the estimation of copper:-

$$2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$$

$$I_2 + S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

$$\frac{Cu^{2+}}{S_2O_3^{2-}} = \frac{1}{1}$$

- **The end point for iodometric titration is detected by the use of starch**.
- The disappearance of blue starch – I_2 color indicate the end point
- The oxidizing agent ($Cr_2O_7^{2-}$) is not titrated directly with thiosulphate because strong oxidizing agents oxidize thio-sulphate to higher oxidation states than that of tetrathionate $S_4O_6^{2-}$ (eg. To SO_4^{2-}) and the reaction got at the end point is not stoichiometric.

Exercise

A 0.200 mg of sample containing copper is analysed iodometrically. Copper is reduced to copper (I) by iodide in the process according to the equation:

$2Cu^{2+} + 4I^{-} \rightarrow 2CuI + I_2$

Calculate the percentage of copper in the sample if 20.0 mL of 0.10 M $Na_2S_2O_3$ is required for the titration of the I_2 that was liberated.

Ans = 63.5%

(Hint: $I_2 + 2S_2O^{2-} \rightarrow 2I^{-} + S_4O^{2-}$ **)**
3 6

- **Karl Fischer titration can be used in direct determination of water in a wide variety of organic substances e.g**
- Alcohols
- Unsaturated Hydrocarbons
- Acids
- Acids anhydrides
- Esters

- Ethers
- Amines
- Sulfides
- Nitroso and nitro compounds
- Certain substances interfere during the titration, they include:-

1. active carbonyl compounds that forms acetals or ketals with methanol
2. Mercaptans
3. Some amines that react with iodine
4. Oxidizing substances that oxide the iodide from the reaction to convert it back to iodine.

- Karl-Fischer reagent is useful for the determination of substances that consume or liberated a stoichiometric amount of H_2O in a chemical reaction.
- It has been used widely in functional group determination in organic compounds.
- Alcohol can be determined by the esterification of acetic acid to give the ester and
-

$$\text{water (BF}_3\text{ catalysed) CH}_3\text{CO}_2\text{H} + \text{ROH} \xrightarrow{BF_3} \text{CH}_3\text{COOR} + \text{H}_2\text{O}$$

- Carboxylic acid are determined by the same reaction using excess methanol

IODIMETRIC TITRATION IN THE DETERMINATION OF VITAMIN C

CONTENT OF VITAMIN C TABLET

- 100mg of Vitamin C tablet is weighed and dissolve in distilled water ($10cm^3$), $5cm^3$ of 6M HCl and $5cm^3$ of CCl_4
- This is titrated with iodate 0.025M KIO_3 solution .
- Watch the iodine color developed in the organic layer – shake vigorously.
- Continue the titration until the violet color in the organic layer just disappears.
- This leaves a very faint yellow color of ICl in the organic layer.
- Repeat the experiment for 4-6 times

- Then calculate the percentage ascorbic acid in the tablet using IO_3^- as a strong oxidizing agents.
- In the presence of 3-9M HCl medium, oxidation goes on in stages thus:
- $IO_3^- + 6H^+ + 6e^- \rightarrow I^- + 3H_2O$
- $IO_3^- + 6H^+ + 6I^- \rightarrow 3I_2 + 3H_2O$
- $IO_3^- + 6H^+ + 2I_2 \rightarrow 5I^- + 3H_2O$
- At the beginning of such titration iodine is produced and as more titrant is added, oxidation proceeds to iodine mono-chloride, and the dark colour of the solution gradually disappears.
- Effective half equation is:-
- $IO_3^- + 6H^+ + Cl^- + 4e^- = ICl + 3H_2O$
- The reducing agent used for this reaction is ascorbic acid (Vit C) which reacts as follows:
- $C_6H_8O_6 \rightarrow C_6H_6O_6 + 2H^+ + 2e$ x 2
- $2C_6H_8O_6 \rightarrow 2C_6H_6O_6 + 4H^+ + 4e^-$
- $IO_3^- + 6H^+ + Cl^- + 4e^- \rightarrow ICl + 3H_2O$
- $the\ overall\ rxn\ is$:
- $2C_6H_8O_6 + IO_3^- + 6H^+ + Cl^- \rightarrow 2C_6H_6O_6 + 4H^+ + ICl + 3H_2O$
- $2C_6H_8O_6 + IO_3^- + 6H^+ + Cl^- \rightarrow ICl + 2C_6H_6O_6 + 3H_2O + 4H^+$
- $mole\ ratio = \frac{nC6H8O6}{nIO_3^-} = \frac{2}{1}$

Precipitation and Complexometric Titration

Precipitation Titration

Precipitation titration is a type of titration which involves the formation of precipitate during the titration technique. In precipitation titration, the titrant reacts with the analyte and forms an insoluble substance called a precipitate. It continues till the last amount of analyte is consumed.

E.g. to determine the Cl^- ion content in a solution, silver nitrate ($AgNO_3$) solution is titrated against the chloride solution to give a white solid silver chloride precipitate AgCl(s) as indicated in the net ionic equation:

$NaCl_{(aq)} + AgNO_{3\,(aq)} \longrightarrow AgCl_{(s)} + NaNO_{3(aq)}$

$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$.

Thus, the quantity of silver ion used to the equivalence point is equal to the amount of chloride ion originally present.

Classification of Complexometric titration

- Direct titration: In this method, the metal ions in the sample are titrated directly with a chelating agent, such as EDTA. ...
- Back titration: ...
- Replacement (displacement) titration: ...
- Alkalimetric titration:

Types of Precipitation Titration

(i) Mohr's method

This method is used to determine chlorides in a neutral solution. Mohr titration is defined as the type of titration that helps in determining the Chloride ion (Cl^-) concentration when it is titrated against silver nitrate ($AgNO_3$). When we add silver nitrate ($AgNO_3$) to a chloride solution it forms Silver Chloride (AgCl) precipitates. When all the chloride ions are precipitated, the endpoint is reached.

Silver ions Ag^+ that are left in the solution will react with the Chromate ion $(CrO_4)^{2-}$ of the indicator Potassium chromate K_2CrO_4 to form a red-brown precipitate of silver chromate Ag_2CrO_4 that indicates theendpoint.

$$2Ag^+(aq) + (CrO_4)^{2-}(aq) \rightarrow Ag_2CrO_4(s)$$

So, by this method chloride ion concentration can be determined in any source like seawater, sewage, etc.

Summary

- Karl Friedrich Mohr was the scientist who introduced this method.
- **Titrant** - 0.1 N $AgNO_3$ (Silver nitrate)
- **Analyte** – 0.1 N NaCl (Sodium chloride)
- **Indicator** – 5% K_2CrO_4 (Potassium chromate)

Principle:

$NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$ $\quad Ksp[AgCl]= 1.2X\ 10^{-10}$

$K_2CrO_4 + AgNO_3 \longrightarrow Ag_2CrO_4 + 2KNO_3$ $\quad Ksp[AgCrO_4]= 1.7X\ 10^{-12}$

- Chlorides and bromides are used as analytes in this method.

- The pH range in Mohr's method is 6.5-7.5

Disadvantage

- Cannot be used when the solution is acidic as chromate ions are protonated to form chromic acid.
- Ag+ ions cannot precipitate with chromic acid.

Example:

An excess amount of 0.0500 $molL^{-1}$ solution of silver nitrate is added to 50.0 mL of a solution containing an unknown concentration of chloride ions. Some amount of potassium chromate is added and used as an indicator. The endpoint of the titration is marked by the formation of silver chromate ions according to the reaction:

$2Ag+(aq) + CrO_4^{2-}(aq) \longrightarrow Ag_2CrO_{4(s)}$

The average titre value after 5 repeated experiments is 18.50 mL. Calculate the concentration of chloride in $molL^{-1}$.

Solution:

Assuming the salt is NaCl(s)

$NaCl_{(s)} + AgNO_{3\,(aq)} \longrightarrow AgCl_{(s)} + NaNO_{3(aq)}$

$Na^+_{(aq)} + Cl^-_{(aq)} + Ag^+_{(aq)} + NO_3^-{}_{(aq)} \longrightarrow Ag^+_{(aq)} + Cl^-_{\,(aq)} + Na^+_{(aq)} + NO_3^-{}_{(aq)}$

Hence, $n(Cl^-) = n(Ag^+)$ $\quad (1:1)$

$n(Ag^+) = 0.05\ M \times 18.50/1000\ L = 9.25 \times 10^{-4}$ mol.

$n(Cl^-) = 9.25 \times 10^{-4}$ mol

Therefore, $n[Cl^-] = 9.25 \times 10^{-4} / 0.05L = 0.0185\ molL^{-1}$.

(ii) Volhard's method (Back titration method)

This method involves the titration of bromides, iodides, and chlorides, in an acidic medium. The chloride in the solution is converted to silver chloride when reacted with excess silver nitrate solution. The leftover silver nitrate is estimated against potassium thiocyanate solution. When all thiocyanate consumes all the silver, the excess of thiocyanate is made to react with an indicator. It gives a red colour on reacting with ferric ammonium sulfate indicator and a ferrous thiocyanate complex is formed.

If analyte contains chloride anions, the reaction will be as follows.

To titrate Ag+; determination of Cl- involves a back titration

First, Cl- is precipitated by excess AgNO3

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

In the presence of Fe3+, excess Ag+ is titrated with KSCN

$$Ag^+ (aq) + SCN^- (aq) \rightarrow AgSCN(s)$$

When Ag+ has been consumed, a red complex forms

$$Fe3^+ (aq) + SCN^- (aq) \rightarrow [FeSCN]^{2+}(aq)$$

(Note: Titration with NaSCN determines n(Ag+) in excess.)

Therefore, $n(Cl^-) = n(Ag^+)$ reacted

$n(Ag^+)$ reacted = $n(Ag^+)$ initial - $n(Ag^+)$ excess

This method is preferred over Mohr's method in an acidic solution.

Summary:

- Volhard Method is a **back titration/ indirect titration** and a precipitation titration that depends on the formation of colored complex ions (colored solution) at the endpoint.
- The titration is performed only in an acidic medium using nitric acid (HNO_3).
- Fe^{3+} ion from ferric alum (Ferric ammonium sulfate) $NH_4Fe(SO_4)_2$. $12H_2O$ acts as an indicator in this practical.
- Brick red color is observed at the endpoint.

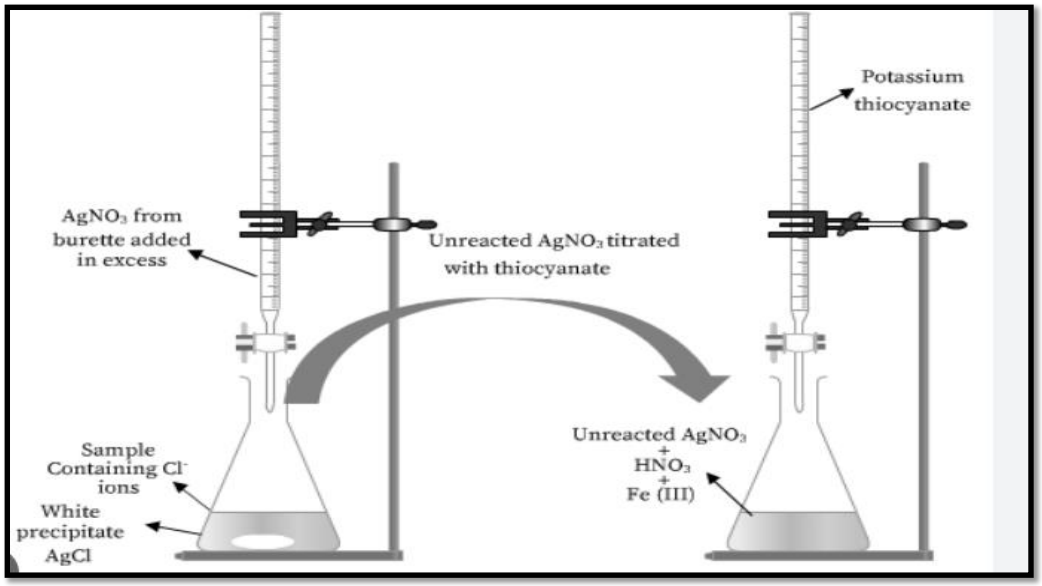
➠ **Titrant**- AgNO3, Potassium thiocyanate (KSCN)/ Ammonium thiocyanate (NH_4SCN)

➠ **Analyte** – 0.1 N NaCl/NaBr/NaI (Sodium chloride, Sodium bromide, sodium iodide)

➠ **Indicator** – (Ferric ammonium sulfate) $NH_4Fe(SO_4)_2$. $12H_2O$ /Iron alum.

METHODOLOGY

- Procedure for determination of chloride ion concentration by titration (Volhard's Method)
- Fill the burette with 0.1 M potassium thiocyanate solution and adjust the zero.
- Measure 10 ml of the sample and pour it into a conical flask.
- Add 1 ml of ferric ammonium sulfate solution as an indicator.
- Using the potassium thiocyanate (KSCN) solution, titrate the unreacted silver ions.
- Because of the ferric thiocyanate complex, the endpoint is the appearance of a dark red color.
- Repeat the titration three times to get an accurate result.
- Calculate the moles of potassium thiocyanate used.



Example:

50.0 mL of a solution containing an unknown concentration of chloride ions is added to 50.00 mL of 0.0500 molL-1 solution of silver nitrate. The precipitate is filtered, and the filtrate is titrated with 0.0200 molL-1 solution of sodium thiocyanate (NaSCN). The reaction is represented by the equation: $Ag^+_{(aq)} + SCN^-_{(aq)} \longrightarrow AgSCN_{(s)}$

The average titre volume after 3 repeated experiments is 25.00 mL. Calculate the concentration of Cl^- ion in the solution (in $molL^{-1}$).

Solution

$n(Ag+)_{initial} = 0.05 \times 0.05 = 0.0025 \text{ mol} = 2.5 \times 10^{-3} \text{ mol}$

$n(SCN^-) = 0.02 \times 25/1000 = 0.0005 \text{ mol} = n(Ag+)_{excess}$

$n(Ag+)_{excess} = 0.0005 \text{ mol}.$

$n(Ag+)_{reacted} = 0.0025 - 0.0005 = 2 \times 10^{-3} \text{ mol}$

Therefore, $n(Cl^-) = 2 \times 10^{-3} \text{ mol}$

$[Cl-] = 2 \times 10^{-3} \text{ mol}/0.05 \text{ L} = 0.0400 \text{ mol}^{-1}$.

(iii) Fajan's method

This method uses the reaction between the precipitate formed and the indicator. The indicator used is dichlorofluorescein which acts as an anion in solution. In a chloride solution, due to excess chloride ions, they form the primary layer of the precipitate. The second layer is formed by the cations of sodium. The reaction ends with the silver ion in excess. Therefore, the positively charged silver ion becomes the primary layer and attracts indicators to form a second layer. The colour of the indicator signals the end of the reaction.

Summary:

- K. Fajan introduced this method.
- In this titration adsorption indicators are used which are mainly dyes.
- At the endpoint the indicator is adsorbed by the precipitate, and during the process of adsorption, a change occurs in the indicator which leads to the formation of substances of different colour.
- **Titrant** - 0.1 N $AgNO_3$ (Silver nitrate)
- **Analyte** – 0.1 N NaCl/NaBr/NaI (Sodium chloride, Sodium bromide, sodium iodide)
- **Indicator** – Fluorescein, Eosin and Rhodamine dyes
- Fajan's method is used to determine – Chlorides, Bromides and Iodides.

Complexometric Titration

The complexometric titration is where an undissociated complex is formed at an equivalence point. It is greater than the precipitation titrations, and there will be no error due to co-precipitations.

$Hg^{2+} + 2SCN^- \rightarrow Hg(SCN)_2$.

$Ag^+ + 2CN^- \rightarrow [Ag(CN)_2]^-$

Key points

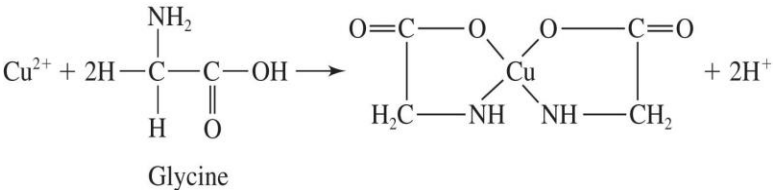
- The technique involves titrating metal ions with a complexing agent or chelating agent (Ligand)
- Ligands (or complexing agents or chelating agents) can be any electron donating entity, which has the ability to bind to the metal ion and produce a complex ion, Ex: H_2O, NH_3 , Cl^- , Br^- , I -…….
- The number of covalent bonds that a cation tends to form with electron donors is its coordination number.
- Typical values for coordination numbers are two, four, and six.
- The species formed as a result of coordination can be electrically positive, neutral, or negative.
- Ethylenediaminetetraacetic acid (EDTA or H4Y) is an aminocarboxylic acid.
- Its fully deprotonated form ($Y4^-$) has six binding sites (four negatively charged carboxylate groups and two tertiary amino groups) that can donate six pairs of electrons to a metal ion.

The resulting metal-ligand complex, in which EDTA forms a cage-like structure around the metal ion, is very stable.

- The actual number of coordination sites depends on the size of the metal ion, however, all metal–EDTA complexes have a 1:1 stoichiometry.

What is a Chelate?

A chelate is produced when a metal ion coordinates with two or more donor groups of a single ligand to form a five- or six-membered heterocyclic ring. The copper complex of glycine, is an example. In this complex, copper bonds to both the oxygen of the carboxyl group and the nitrogen of the amine group.



Classification of Ligands

(1) Unidentate ligand: A ligand that has a single donor group, such as ammonia, is called unidentate (single-toothed)

(2) Bidentate ligand: a ligand that has two groups available for covalent bonding e.g. glycine

(3) Tridentate: the ligand is attached to metal at 3 sites e.g. diethylenetriamine

(4) tetradentate ligand: the ligand is attached to a metal at 4 sites e.g. triethylenetetramine.

Others include pentadentate and hexadentate (EDTA) ligands. Another important complex type is formed between metal ions and cyclic organic compounds, known as macrocycles. These molecules contain nine or more atoms in the cycle and include at least three heteroatoms, usually oxygen, nitrogen or sulfur.

Complexation Equilibria

Complexation reactions involve a metal-ion M reacting with a ligand L to form a complex ML.

$M + L \leftrightarrow ML$

Complexation reactions occur in a stepwise fashion and additional reactions:

$$ML + L \leftrightarrow ML_2$$

$ML_2 + L \leftrightarrow ML_3$ and so on

The symbol βn designates the overall formation constant. Except for the first step, the overall formation constants are products of the Stepwise formation constants for the individual steps leading to the product.

$$M + L \rightleftharpoons ML \qquad \beta_1 = \frac{[ML]}{[M][L]} = K_1$$

$$M + 2L \rightleftharpoons ML_2 \qquad \beta_2 = \frac{[ML_2]}{[M][L]^2} = K_1K_2$$

$$M + 3L \rightleftharpoons ML_3 \qquad \beta_3 = \frac{[ML_3]}{[M][L]^3} = K_1K_2K_3$$

$$\vdots \qquad\qquad \vdots$$

$$M + nL \rightleftharpoons ML_n \qquad \beta_n = \frac{[ML_n]}{[M][L]^n} = K_1K_2 \cdots K_n$$

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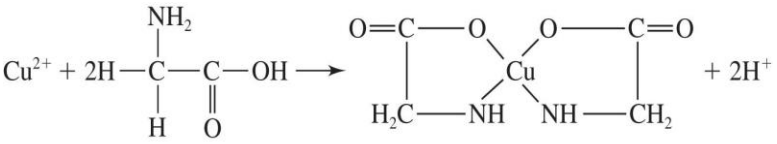

Glycine

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Others include pentadentate and hexadentate (EDTA) ligands. Another important complex type is formed between metal ions and cyclic organic compounds, known as macrocycles. These molecules contain nine or more atoms in the cycle and include at least three heteroatoms, usually oxygen, nitrogen or sulfur.

EDTA (Ethylenediaminetetraacetic Acid)

(Hexadentate Ligand)

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Complexation reactions involve a metal-ion M reacting with a ligand L to form a complex ML.

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The symbol βn designates the overall formation constant. Except for the first step, the overall formation constants are products of the Stepwise formation constants for the individual steps leading to the product.

$$\mathrm{M} + \mathrm{L} \rightleftharpoons \mathrm{ML} \qquad \beta_1 = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]} = K_1$$

$$\mathrm{M} + 2\mathrm{L} \rightleftharpoons \mathrm{ML}_2 \qquad \beta_2 = \frac{[\mathrm{ML}_2]}{[\mathrm{M}][\mathrm{L}]^2} = K_1K_2$$

$$\mathrm{M} + 3\mathrm{L} \rightleftharpoons \mathrm{ML}_3 \qquad \beta_3 = \frac{[\mathrm{ML}_3]}{[\mathrm{M}][\mathrm{L}]^3} = K_1K_2K_3$$

$$\vdots \qquad\qquad \vdots$$

$$\mathrm{M} + n\mathrm{L} \rightleftharpoons \mathrm{ML}_n \qquad \beta_n = \frac{[\mathrm{ML}_n]}{[\mathrm{M}][\mathrm{L}]^n} = K_1K_2 \cdots K_n$$

Unidentate ligands are added in a series of steps as shown above. With multidentate ligands, the maximum coordination number (C.N.) of the cation may be satisfied with only one or a few added ligands. e.g. Cu(II), with a maximum C.N of 4, can form complexes with ammonia that have the formulas $Cu(NH3)^{2+}$, $Cu(NH3)_2{}^{2+}$, $Cu(NH3)_3{}^{2+}$, and $Cu(NH3)_4{}^{2+}$

With the bidentate ligand glycine (gly), the only complexes that form are $Cu(gly)^{2+}$ and $Cu(gly)_2{}^{2+}$

For a given species like the free metal M, we can calculate an alpha value (α), which is the fraction of the total metal concentration in that form. Thus, α_M is the fraction of the total metal present at equilibrium in the free metal form α_{ML} is the fraction in the ML form, and so on. The alpha values are given by

$$\alpha_{\mathrm{M}} = \frac{1}{1 + \beta_1[\mathrm{L}] + \beta_2[\mathrm{L}]^2 + \beta_3[\mathrm{L}]^3 + \cdots + \beta_n[\mathrm{L}]^n}$$

$$\alpha_{\mathrm{ML}} = \frac{\beta_1[\mathrm{L}]}{1 + \beta_1[\mathrm{L}] + \beta_2[\mathrm{L}]^2 + \beta_3[\mathrm{L}]^3 + \cdots + \beta_n[\mathrm{L}]^n}$$

$$\alpha_{\mathrm{ML}_2} = \frac{\beta_2[\mathrm{L}]^2}{1 + \beta_1[\mathrm{L}] + \beta_2[\mathrm{L}]^2 + \beta_3[\mathrm{L}]^3 + \cdots + \beta_n[\mathrm{L}]^n}$$

$$\alpha_{\mathrm{ML}_n} = \frac{\beta_n[\mathrm{L}]^n}{1 + \beta_1[\mathrm{L}] + \beta_2[\mathrm{L}]^2 + \beta_3[\mathrm{L}]^3 + \cdots + \beta_n[\mathrm{L}]^n}$$

For example, the basic form of EDTA (Y^{4-}) reacts with most metal ions to form a 1:1 complex.

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

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

Fraction (α) of the most basic form of EDTA (Y^{4-}) is defined by the H^+ concentration and acid-base equilibrium constants.

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[EDTA]} \Rightarrow \alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[H_6Y^{2+}]+[H_5Y^{+}]+[H_4Y]+[H_3Y^{-}]+[H_2Y^{2-}]+[HY^{3-}]+[Y^{4-}]}$$

where [EDTA] is the total concentration of all free EDTA species in solution

α_{Y4-} is depended on the pH of the solution

Table: Values of $\alpha_{Y^{4-}}$ for EDTA at 20 ^{0}C and μ = 0.10 M

pH	$\alpha_{Y^{4-}}$
0	1.3×10^{-23}
1	1.4×10^{-18}
2	2.6×10^{-14}
3	2.1×10^{-11}
4	3.0×10^{-9}
5	2.9×10^{-7}
6	1.8×10^{-5}
7	3.8×10^{-4}
8	4.2×10^{-3}
9	0.041
10	0.30
11	0.81
12	0.98
13	1.00
14	1.00

The concentration of Y^{4-} and the total concentration of EDTA is solution [EDTA] are related as follows:

$$[Y^{4-}] = \alpha_{y4-}[EDTA]$$

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

$$K_f' = K = K_f \alpha_{Y^{4-}} = \frac{[MY^{n-4}]}{[M^{n+}][EDTA]}$$

At fixed pH **condition, formation constant (K'_f)** could be calculated.

Example:

Calculate the molar Y^{4-} concentration in a 0.0200M EDTA solution buffered to a pH of 10.00

$$[Y^{4-}] = \alpha_{y4-}[EDTA]$$

$$= 0.3 \times 0.0200 = 0.0060 \text{ M}$$

Example

Calculate the equilibrium concentration of Ni^{2+} in a solution with an analytical NiY^{2-} concentration of 0.0150M at pH 8.0 ($K_f = 4.2 \times 10^{18}$) .

$$\underset{0.015-x}{NiY^{2-}} \rightleftharpoons \underset{x}{Ni^{2+}} + \overbrace{\underset{x}{(Y^{4-} + HY^{3-} + H_2Y^{2-} + H_3Y^{-} + H_4Y)}}^{EDTA}$$

$$K_f' = K = K_f \alpha_{Y^{4-}} = \frac{[MY^{n-4}]}{[M^{n+}][EDTA]}$$

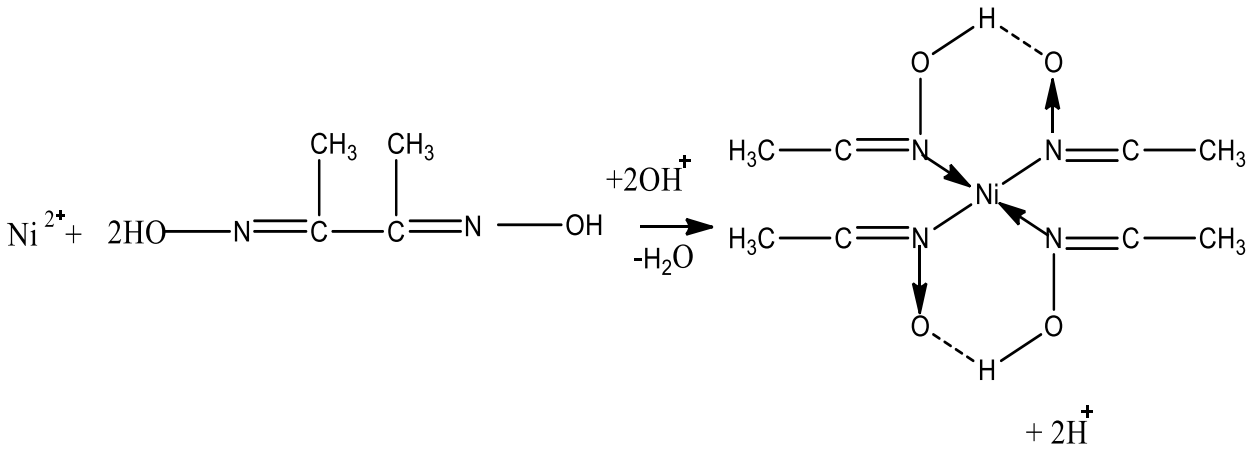
$K'_f = 4.2 \times 10^{18} \times 4.2 \times 10^{-3} = 0.015/x^2$

$= 1.76 \times 10^{15} = 0.015/x^2$

$x = [Ni^{2+}] = \sqrt{(0.015 / 1.76 \times 10^{15})} = 2.9 \times 10^{-9}$ M

The Formation of Insoluble Species

The addition of ligands to a metal ion, however, may result in insoluble species, such as the familiar nickel-dimethylglyoxime precipitate.



In many cases, the intermediate complexes in the stepwise formation scheme may be sparingly soluble, whereas the addition of more ligand molecules may result in soluble species. For example, adding Cl- to Ag+ results in the insoluble AgCl precipitate. The addition of a large excess of Cl^- produces soluble species $AgCl_2$ -, $AgCl_3^{-2}$, and $AgCl_4^{-3}$

For a sparingly soluble salt M_xA_y in a saturated solution,

$M_xA_{y(s)} \leftrightarrow xM^{y+}_{(aq)} + yA^{x-}_{(aq)}$ $\quad Ksp = [M^{y+}]^x[A^{x-}]^y$

Hence, for BiI_3, the solubility product is written, $Ksp = [Bi^{3+}][I-]^3$.

Thus, the formation of soluble complexes can be used to control the concentration of free metal ions in solution and thus control their reactivity. For example, we can prevent a metal ion from precipitating or taking part in another reaction by forming a stable complex, which decreases the free metal-ion concentration.

The control of solubility by complex formation is also used to achieve the separation of one metal ion from another. If the ligand is capable of protonation, as discussed in the next section, even more control can be accomplished by a combination of complexation and pH adjustment

Exercises:

(1) Calculate the silver ion concentration in terms of pAg during the titration of 50.00 mL of 0.05000 M NaCL with 0.1000 M AgNO3 after the addition of the following volume of reagent: (a) in the preequivalent point at 10.00 mL (b) at the equivalence point (25.00 mL) (c) after the equivalence point at 26.00 mL. For AgCl, Ksp = 1.82×10^{-10}.

(2) Calculate the molar Y4- concentration in a 0.0200 M EDTA solution buffered to a pH of 10.0. (at pH 10.00 $\alpha_4 = 0.35$).

(3) To measure the nickel content in steel, the alloy is dissolved in 12 M HCl and neutralized in the presence of citrate ion, which maintains iron in solution. The slightly basic solution is warmed, and dimethlglyoxime (DMG) was added to precipitate the red DMG-Ni complex quantitatively. The product was filtered, washed and dried at 110 ^{0}C. If 1.1634 g of steel gives 0.1795 g of precipitate, what is the percentage of Ni in the steel? (Formula mass (g/mol): Ni = 58.69; DMG = 116.2; $Ni(DMG)_2$ = 288.91].

Electrogravimetric and Coulometric Methods

- For a cell to do any useful work or for an electrolysis to occur, a significant current must flow.
- Whenever current flows, three factors act to decrease the output voltage of a galvanic cell or to increase the applied voltage needed for electrolysis.
- These factors are
  - *ohmic potential,*
  - *concentration polarization (overpotential), and*
  - *Kinetic polarizaton (overpotential)*

Coulometry and Electrogravimetry

- A potential is applied forcing a nonspontaneous chemical reaction to take place
- How much voltage should be applied?
- $E_{applied} = E_{back} + iR$
  - E_{back} = voltage require to cancel out the normal forward reaction (galvanic cell reaction)
  - iR = iR drop. The work applied to force the nonspontaneous reaction to take place. R is the cell resistance
- $E_{back} = E_{reversible\ (galvanic)} +$ Overvoltage

- Overvoltage: it is the extra potential that must be applied beyond what we predict from the Nernst equation

Ohmic Potential

- The voltage needed to force current (ions) to flow through the cell is called the ohmic potential and is given by Ohm's law:

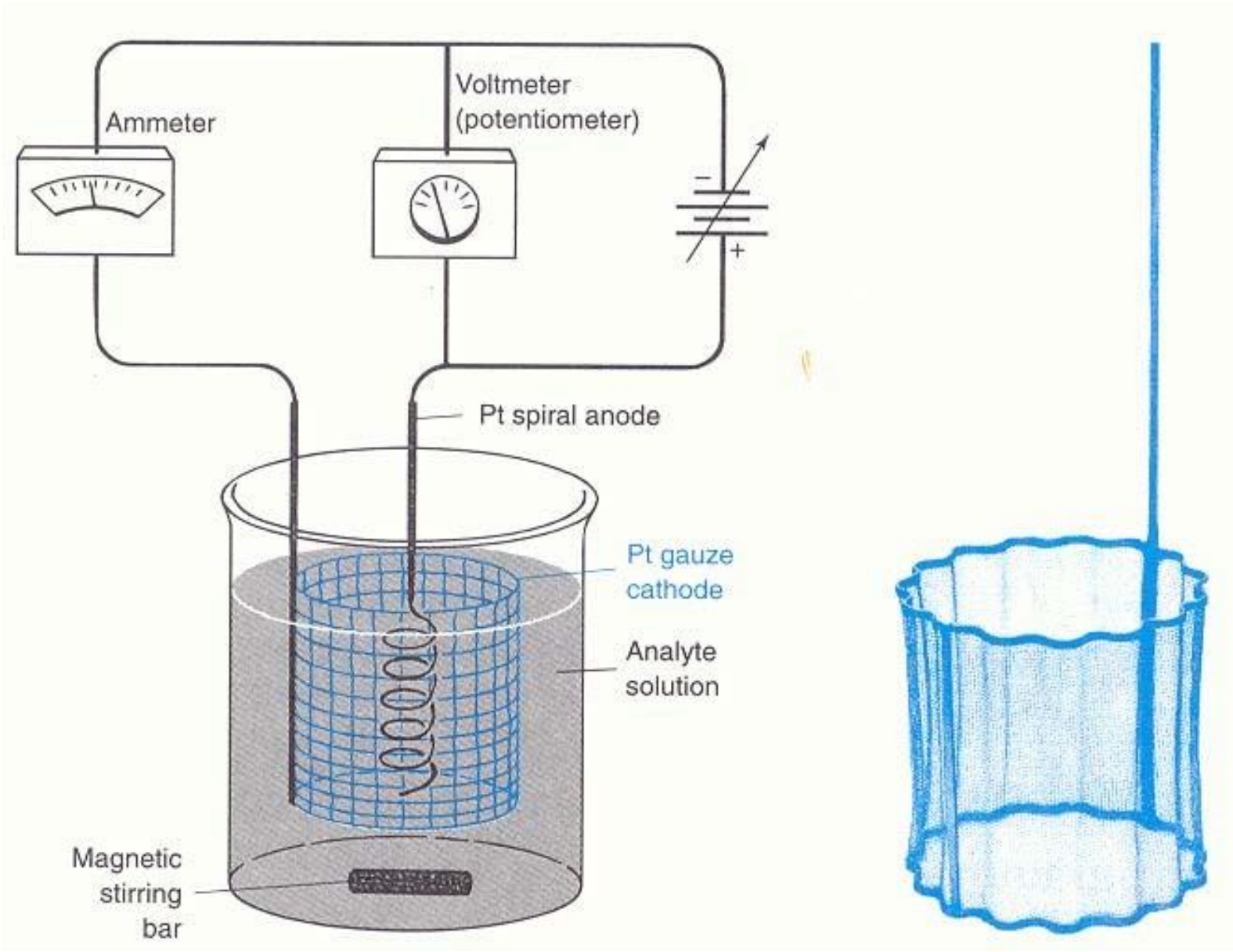
$$E_{ohmic} = IR$$

where I is the current and *R* is the resistance of the cell.

- In a galvanic cell at equilibrium, there is no ohmic potential because I = 0.
- If a current is drawn from the cell, the cell voltage decreases because part of the free energy released by the chemical reaction is needed to overcome the resistance of the cell itself.
- The voltage applied to an electrolysis cell must be great enough to provide the free energy for the chemical reaction and to overcome the cell resistance.
- In the absence of any other effects, *the voltage of a galvanic cell is decreased by IR, and the magnitude of the applied voltage in an electrolysis must be increased by* IR in order for current to flow.

Electrogravimetry

- In an electrogravimetric analysis, the analyte is quantitatively deposited as a solid on the cathode or anode.
  - The mass of the electrode directly measures the amount of analyte.
  - Not always practical because numerous materials can be reduced or oxidized and still not plated out on an electrode.
- Electrogravimetry can be conducted with or without a controlled potential
- When no control
- A fixed potential is set and the electrodeposition is carried out
- The starting potential must be initially high to ensure complete deposition
- The deposition will slow down as the reaction proceeds


Ammeter
Voltmeter
(potentiometer)
−
+
Pt spiral anode
Pt gauze
cathode
Analyte
solution
Magnetic
stirring
bar

- In practice, there may be other electroactive species that interfere by codeposition with the desired analyte.

- Even the solvent (water) is electroactive, since it decomposes to $H_2 + \frac{1}{2} O_2$ at a sufficiently high voltage.

- Although these gases are liberated from the solution, their presence at the electrode surface interferes with deposition of solids.

- Because of these complications, control of the electrode potential is an important feature of a successful electrogravimetric analysis.

Examples on electrogravimetry

- Cu: is deposited from acidic solution using a Pt cathode
- Ni : is deposited from a basic solution
- Zn: is deposited from acidic citrate solution
- Some metals can be deposited as metal complexes e.g., Ag, Cd, Au
- Some metals are deposited as oxides on the anode e.g.,
- Pb^{2+} as PbO_2 and Mn^{2+} as MnO_2

Coulometric Methods of Analysis

•Potentiometry: Electrochemical cells under static conditions

•Coulometry, electrogravimetry, voltammetry: Electrochemical cells under dynamic methods (current passes through the cell)

•Coulometry: an electrochemical method based on the measurement of the quantity of electricity (in coulombs) needed to convert the analyte quantitatively to a different oxidation state

•A potential is applied from an external source forcing a nonspontaneous chemical reaction to take place :Electrolytic method

- measured quantity and the mass of analyte can be computed from known physical constants : standardization is not usually necessary
- as accurate as gravimetric and volumetric procedures
- faster and more convenient than gravimetric measurements

Example: In a mixture solution of Zn^{2+} and Cu^{2+}, convert all Cu^{2+} to Cu metal and leave Zn^{2+} in the solution.

- Hold the working electrode (e.g. Cu) potential at a certain value (positive than that for Zn reduction)

- $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Units for Quantity of Electricity

- The quantity of electricity or charge is measured in units of coulombs (C).
- A coulomb is the quantity of charge transported in one second by a constant current of one ampere.
- Thus, for a constant current of I amperes for t seconds, the charge in coulombs Q is given by the expression

$$Q = It$$

- For a variable current i, the charge is given by

$$Q = \int_0^t i \, dt$$

$$n_A = \frac{Q}{nF}$$

Faraday's law relates the number of moles of the analyte n_A to the charge

n = #moles of electrons transferred in the half-cell rxn

F = Faradays constant = 96487 C mol-1 n_A = number of moles of analyte

Types of Coulometric Methods:

1. Controlled potential coulometry:
2. Controlled current coulometry:

Fundamental requirement for both methods is 100% current efficiency

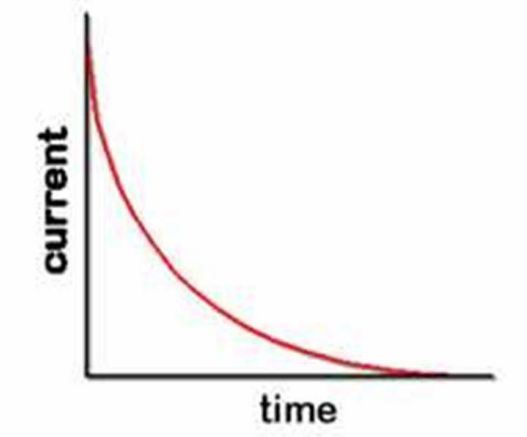
- all e^- go to participate in the desired electrochemical process
- If not, then takes more current □ over-estimate amount of analyte

• Current efficiency of 100% does not, however, imply that the analyte must necessarily participate directly in the electrontransfer process at the electrode. Indeed,more often than not, the analyte participates, at least in part, in a reaction that is secondary to the electrode reaction.

1) Controlled potential (Potentiostatic) coulometry):

- The working electrode will be kept at constant potential that analyte's quantitative reduction or oxidation occurs without simultaneously reducing or oxidizing other species in the solution
- The current flowing through the cell is proportional to the analyte's concentration. As the reactants are consumed, the current decreases. When the reaction is complete,the current is negligible.
- The quantity of electricity is usually measured with an electronic integrator.

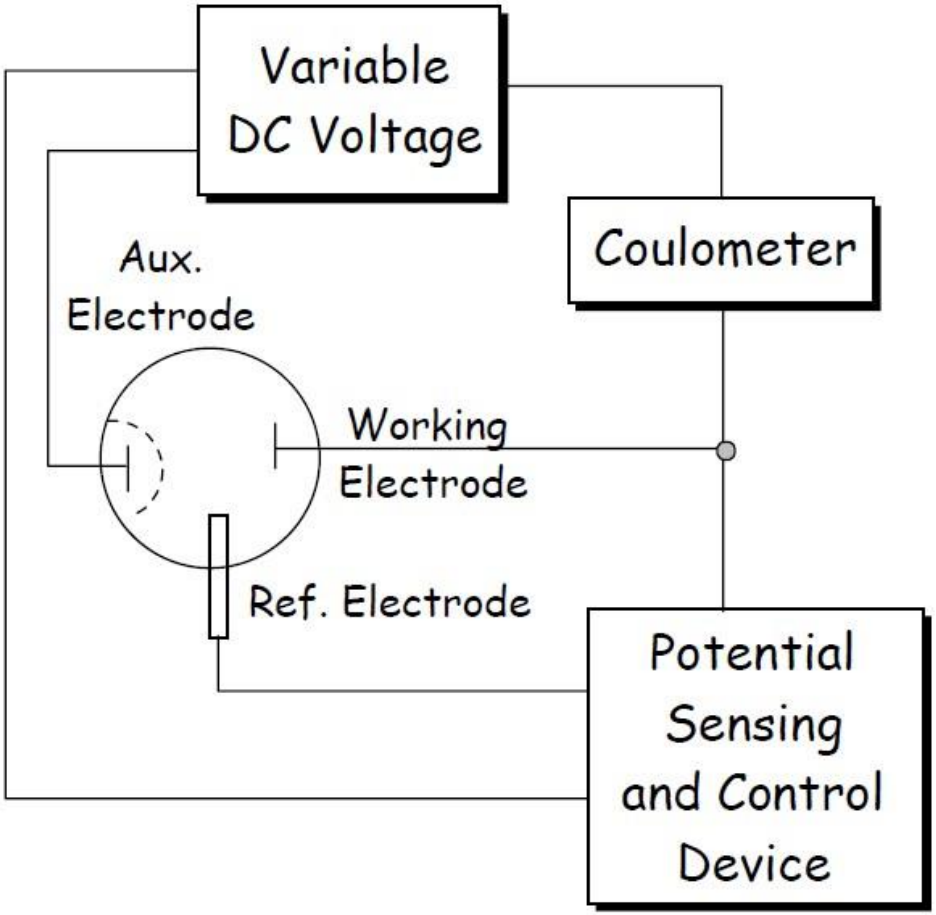
The area under the curve equals the number of coulombs used.



Controlled potential coulometry

- An analysis of this kind has all the advantages of an electrogravimetric method, but it is not necessary to weigh a product. The technique can therefore be applied to systems that yield deposits with poor physical properties as well as to reactions that yield no solid product at all. For example, arsenic may be determined coulometrically by the electrolytic oxidation of arsenous acid (H3AsO3,) to arsenic acid (H3As04) at a platinum anode. Similarly, the analytical conversion of iron(lI) to iron(lII) can be accomplished with suitable control of the anode potential.
- controlled-potential coulometry is carried out in
  - small-volume electrochemical cells,
  - using electrodes with large surface areas
  - with high stirring rates.

Instrumentation:



•The instrumentation for potentiostatic coulometry consists of an:

•electrolysis cell,

•a potentiostat and

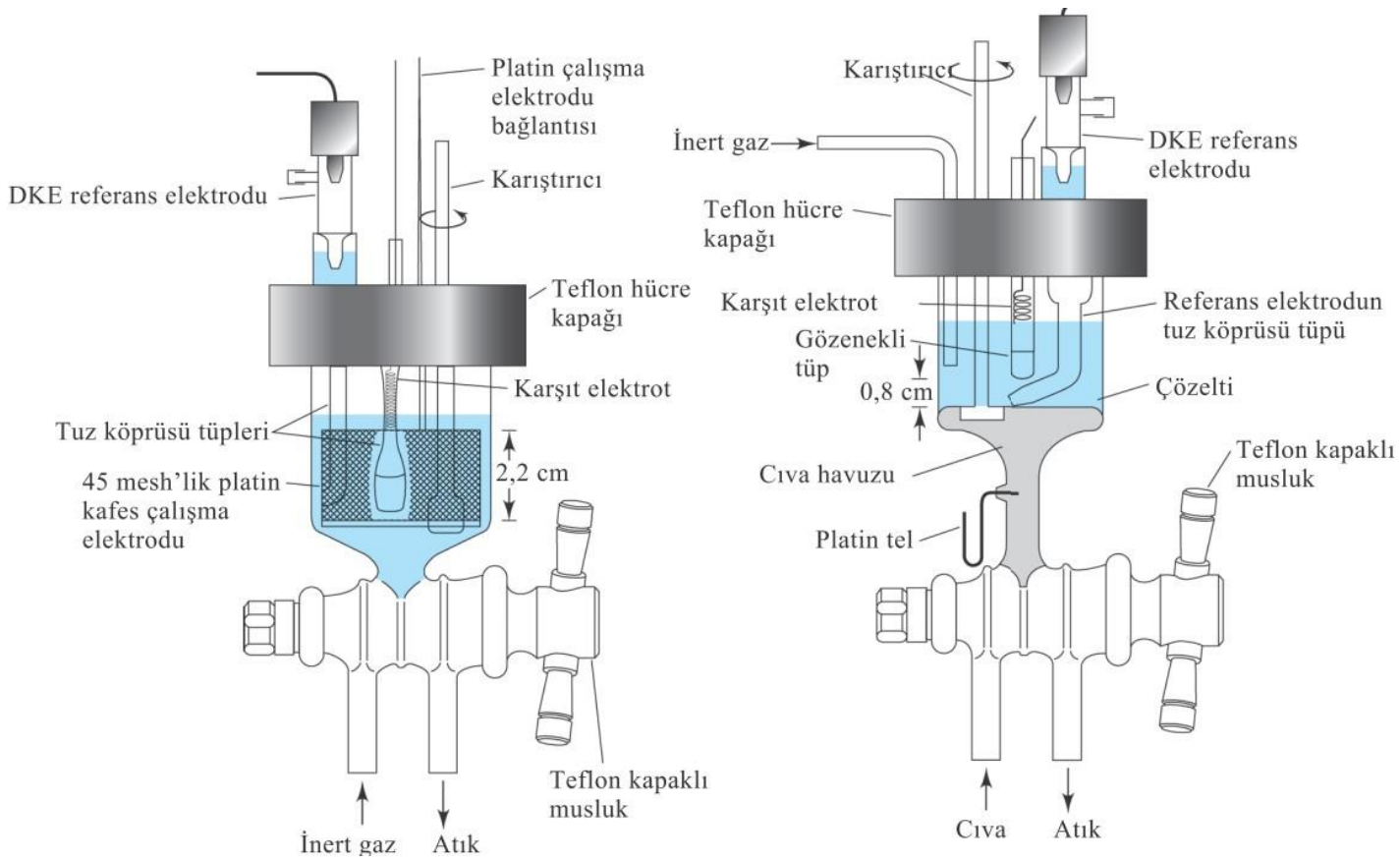
•an electronic integrator for determining the charge consumed.

 Potentiostat is an electronic device that maintains the potential of a working electrode at a constant level with a feedback circuitry which adjust the potential of the variable DC voltage source to maintain E_w - E_{ref} constant

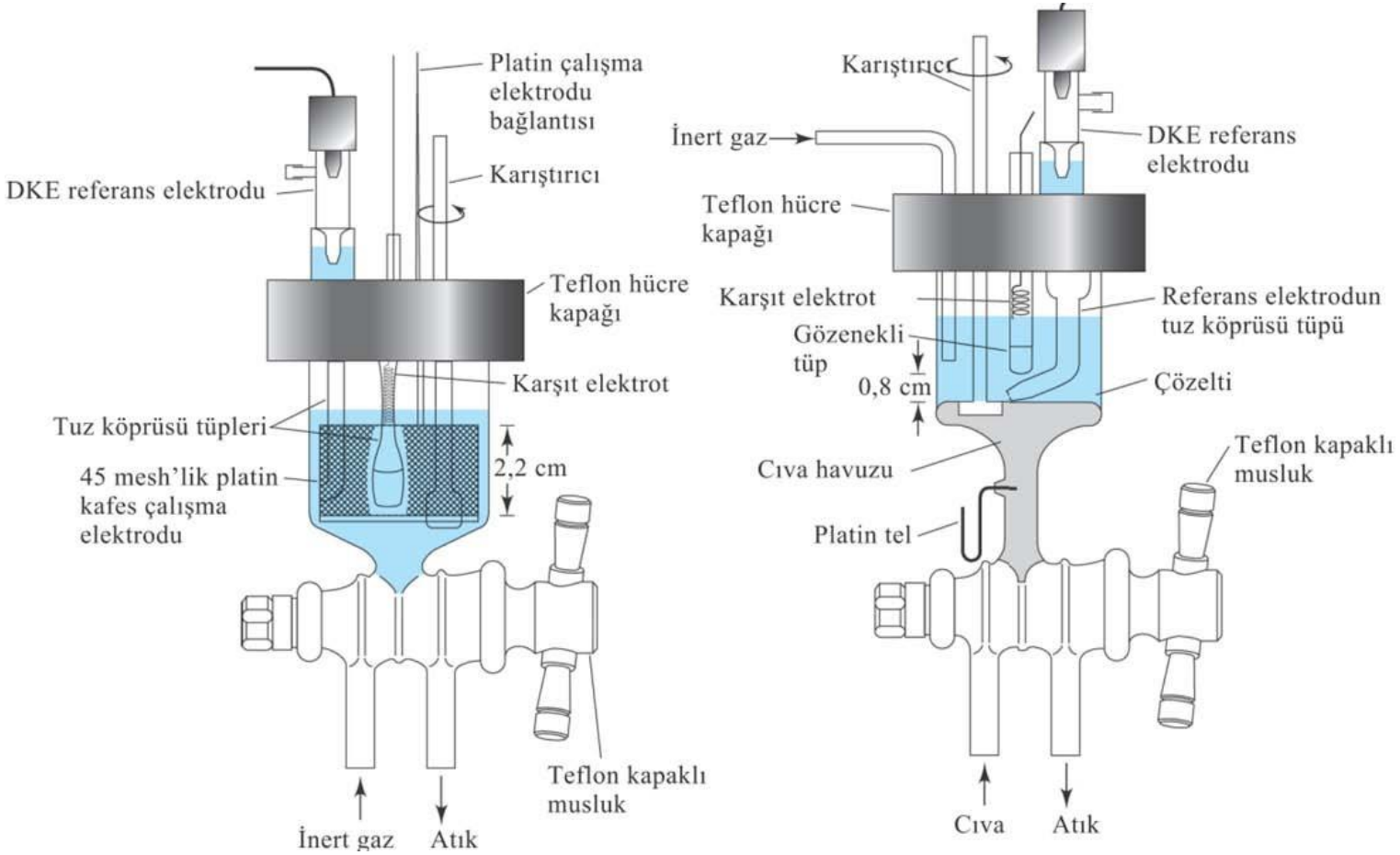
Working electrode is where the electrolysis takes place. E_w is fixed vs the E_{ref} • Two types of working electrodes are commonly used:

- a Pt electrode manufactured from platinum-gauze and fashioned into a cylindrical tube, and
- an Hg pool electrode

- electrolysis cell, consisted of three-electrode system: working electrode, counter (auxilary) electrode, reference electr.



Ref. electrode is often either SCE or Ag/AgCl connected to bulk solution by a salt bridge



- Auxiliary electrode is part of the other half-cell and it is often made from the same material as the working electrode

- Usually separated from the solution in contact with the working electrode to prevent reaction between species produced at Aux. Electr. and species in the bulk of solution

- The auxiliary electrode, which is often a Pt wire, is separated by a salt bridge from the solution containing the analyte.

- This is necessary to prevent electrolysis products generated at the auxiliary electrode from reacting with the analyte and interfering in the analysis.

- A saturated calomel or Ag/AgCI electrode serves as the reference electrode.

- A means of determining the total charge passed during electrolysis. One method is to monitor the current as a function of time and determine the area under the curve.

- Modern instruments, however, use electronic integration to monitor charge as a function of time. The total charge can be read directly from a digital readout or from a plot of charge versus time

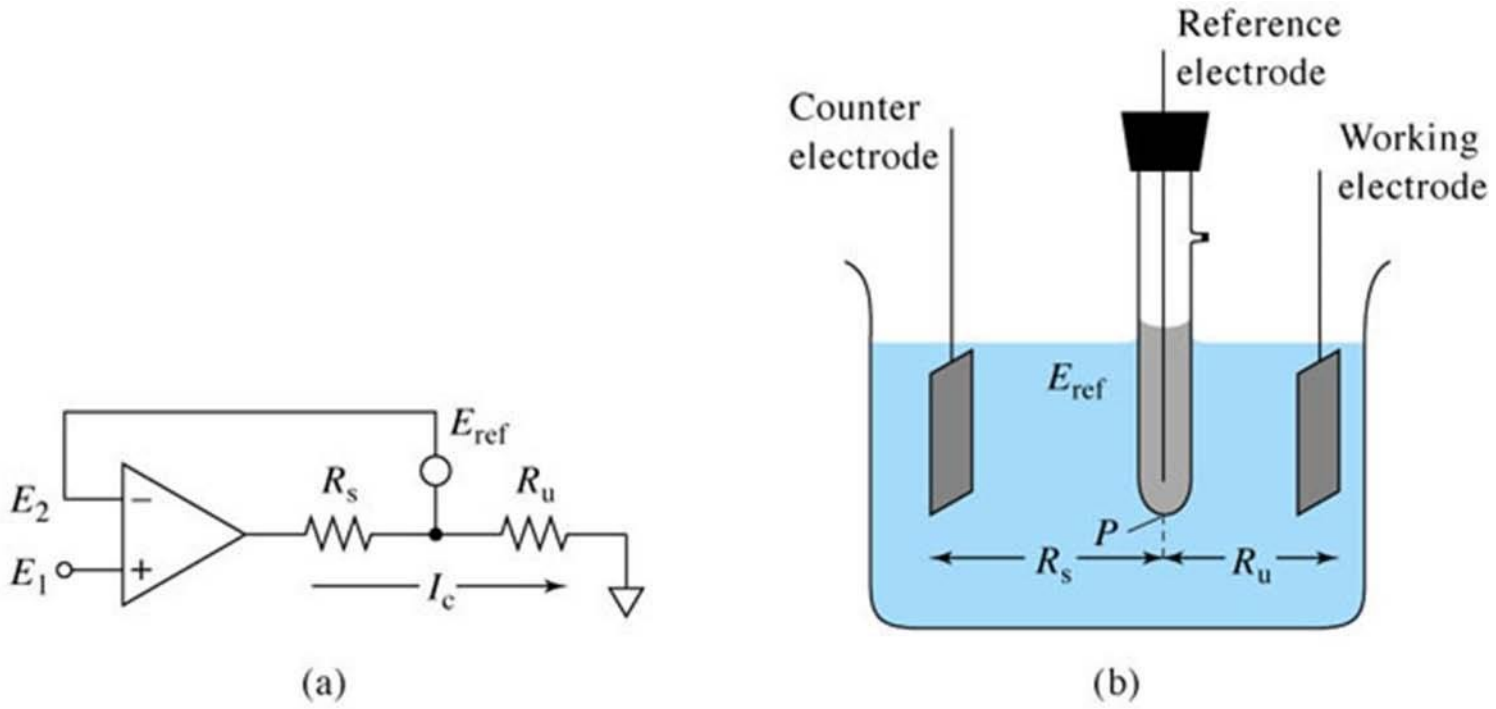


FIGURE 24-6 Schematic of a system for controlled-potential coulometry.
(a) Equivalent circuit. (b)Resistances within the cell. The cell current *Ic* passes to the integrator readout module, which provides a number proportional to the total quantity of charge that passes through the cell.

R_s: cell resistance between counter electrode and tip of the reference electrode R_u: uncompansated cell resistance between the ref. Elec. And working electr.

Controlled-Current (amperostatic) Coulometry:

- The current is kept constant until an indicator signals completion of the analytical reaction.
- The quantity of charge required to attain the end point is calculated from the magnitude of the current and the time of its passage. Q=i x t

- Controlled-current coulometry, also known as amperostatic coulometry or coulometric titrimetry
  - When called coulometric titration, electrons serve as the titrant.
  - An example is the titration of halides by silver ions produced at a silver anode.
- The current in a coulometric titration is carefully maintained at a constant and accurately known level by means of an amperostat.

- Controlled-current coulometry, has two advantages over controlled-potential coulometry.
  - First, using a constant current leads to more rapid analysis since the current does not decrease over time. Thus, a typical analysis time for controlled current coulometry is less than 10 min, as opposed to approximately 30-60 min for controlled-potential coulometry.
  - Second, with a constant current the total charge is simply the product of current and time. A method for integrating the current-time curve, therefore, is not necessary.

Experimental problems with constant current coulometry

1) as electrolysis occurs the analyte's concentration and, therefore, the current due to its oxidation or reduction steadily decreases.
   - To maintain a constant current the cell potential must change until another oxidation or reduction reaction can occur at the working electrode.
   - Unless the system is carefully designed, these secondary reactions will produce a current efficiency of less than 100%.

- Second problem is the need for a method of determining when the analyte has been exhaustively electrolyzed.
  – In controlled-potential coulometry this is signaled by a decrease in the current to a constant background or residual current.

- In controlled-current coulometry, a constant current continues to flow even when the analyte has been completely oxidized or reduced. A suitable means of determining the end-point of the reaction, is needed. Most of the end-point detection methods applicable to volumetricanalysis

are equally satisfactory here. Visual observations of color changes of indicators, as well as potentiometric, amperometric, and photometric measurements have all been used successfully.

Instrumentation

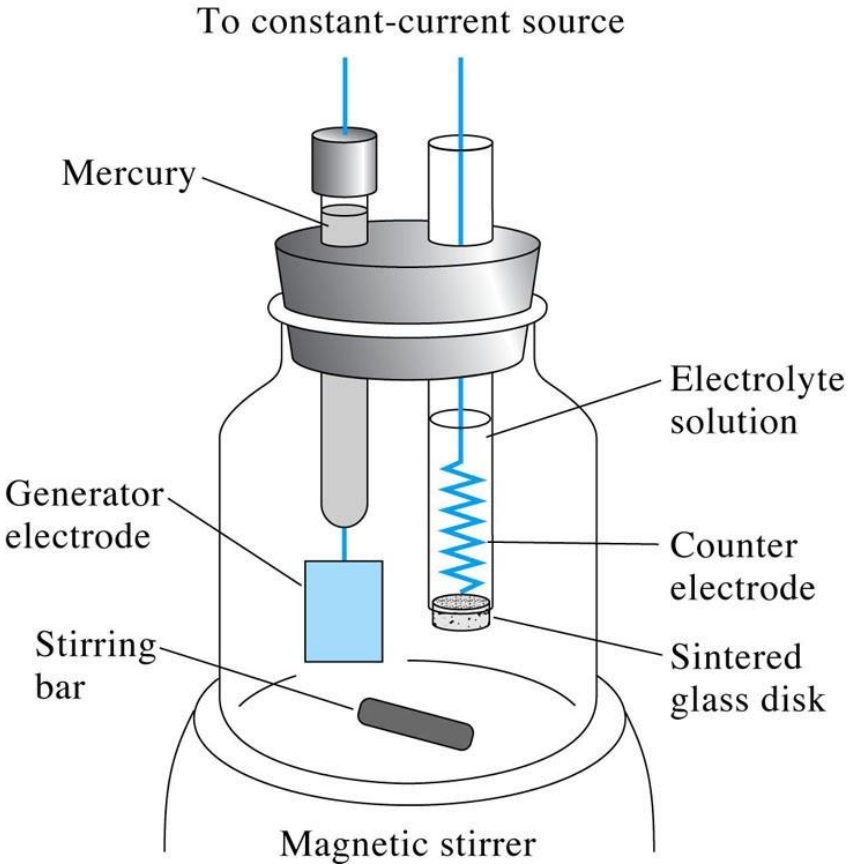
- Controlled-current coulometry normally is carried out using a amperostat and an electrochemical cell consisting of a working electrode and a counter electrode.

- The working electrode is constructed from Pt, is also called the generator electrode since it is where the mediator reacts to generate the species reacting with the analyte.

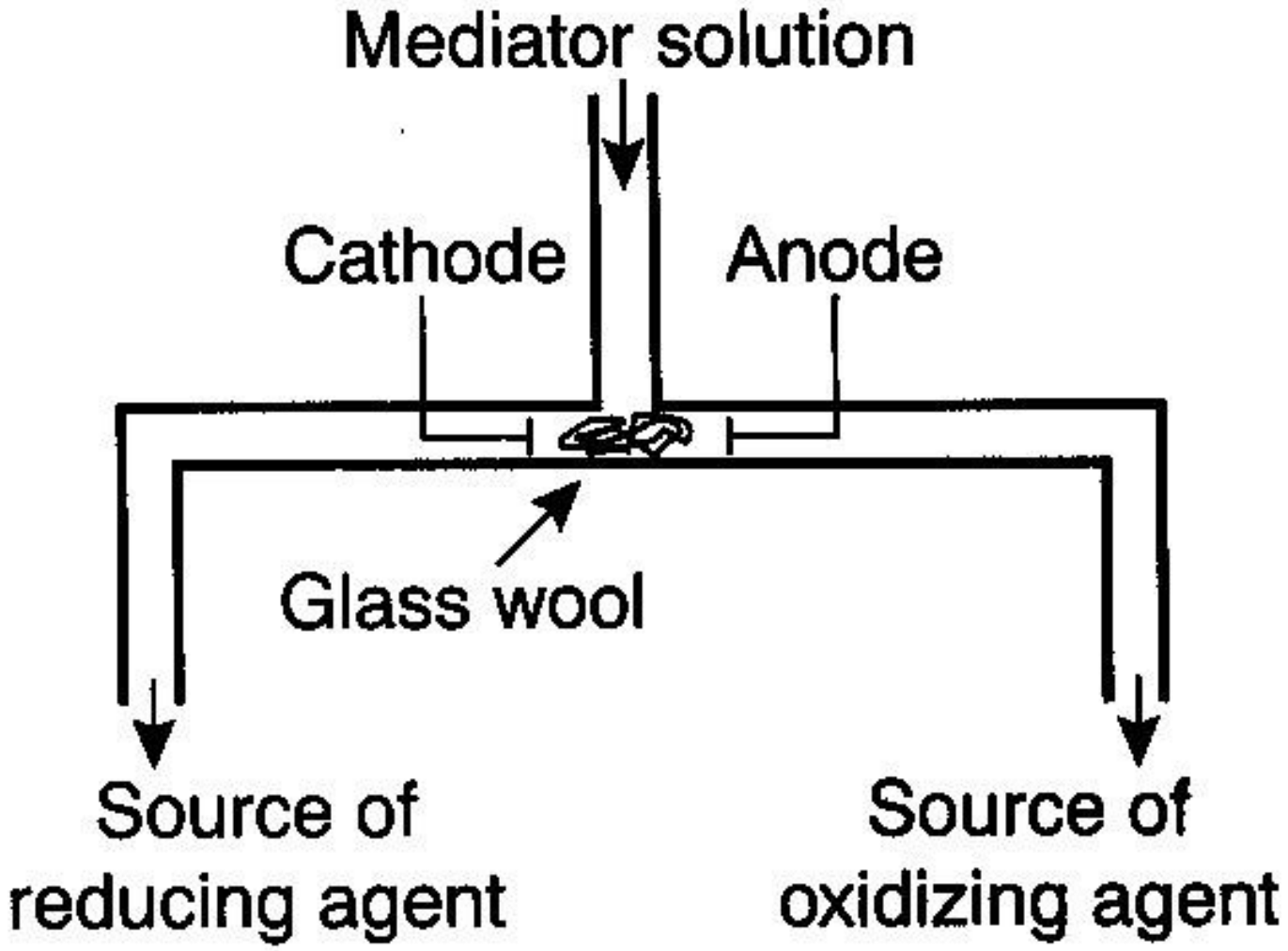
  Should have a large surface area

- The counter electrode is isolated from the analytical solution by a salt bridge or porous frit to prevent its electrolysis products from reacting with the analyte.

  Method for the external generation of oxidizing and reducing



agents in coulomtric titration



- The other necessary instrumental component for controlled-current coulometry is an accurate clock for measuring the electrolysis time, t_e, and a switch for starting and stopping the electrolysis.

- Analog clocks can read time to the nearest ±0.01 s, but the need to frequently stop and start the electrolysis near the end point leads to a net uncertainty of ±0.1 s.
- Digital clocks provide a more accurate measurement of time, with errors of ±1 ms being possible.
- The switch must control the flow of current and the clock, so that an accurate determination of the electrolysis time is possible.

Applications of Coulometric Titrations:

a) Can be used for Acid-Base Titrations

b.) Can be used for Complexation Titrations (EDTA)

c.) Can be used for Redox Titrations

$$Ce^{3+} \leftrightarrow Ce^{4+} + e^-$$

$$Ce^{4+} + Fe^{2+} \leftrightarrow Ce^{3+} + Fe^{3+}$$

Comparison of *Coulometric and Volumetric Titrations*

- Both require a detectable end point and are subject to a titration error as a consequence
- regarding the apparatus and solutions employed:
  - The timer and switch correspond closely to the buret, the switch performing the same function as a stopcock.
- Coulometry, advantages is the elimination of problems associated with the preparation, standardization, and storage of standard solutions. (instability of Br, Cl and Ti)

- With coulometry, by proper choice of current, microquantities of a substance can be introduced with ease and accuracy
- the coulometric method adapts easily to automatic titrations, because current can be controlled quite easily.

Coulometric titrations are subject to five potential sources of error:

(1) variation in the current during electrolysis,

(2) departure of the process from 100% current efficiency,

(3) error in the current measurement,

(4) Error in the measurement of time, and

(5) titration error due to the difference between the equivalence point and the end point.

The last of these difficulties is common to volumetric methods as well. For situations in which the indicator error is the limiting factor, the' two methods are likely to have comparable reliability.

Quantitative calculations:Example 1

- The purity of a sample of $Na_2S_2O_3$ was determined by a coulometric redox titration using I^- as a mediator, and 1_3^- as the "titrant“. A sample weighing 0.1342 g is transferred to a 100-mL volumetric flask and diluted to volume with distilled water. A 10.00-mL portion is transferred to an electrochemical cell along with 25 ml, of 1 M KI, 75 mL of a pH 7.0 phosphate buffer, and several drops of a starch indicator solution. Electrolysis at a constant current of 36.45 mA required 221.8 s to reach the starch indicator end point. Determine the purity of the sample.

From Table 11.9 we see that the coulometric titration of $S_2O_3^{2-}$ with I_3^- is

$$2S_2O_3^{2-}(aq) + I_3^-(aq) \rightleftharpoons S_4O_6^{2-}(aq) + 3I^-(aq)$$

Oxidizing $S_2O_3^{2-}$ to $S_4O_6^{2-}$ requires one electron per $S_2O_3^{2-}$ ($n = 1$). Combining equations 11.23 and 11.24, and making an appropriate substitution for moles of $Na_2S_2O_3$ gives

$$\frac{nF(\text{g } Na_2S_2O_3)}{\text{FW } Na_2S_2O_3} = it_e$$

Solving for the grams of $Na_2S_2O_3$ gives

$$\text{g } Na_2S_2O_3 = \frac{it_e(\text{FW } Na_2S_2O_3)}{nF}$$

$$= \frac{(0.03645 \text{ A})(221.8 \text{ s})(158.1 \text{ g/mol})}{(1 \text{ mol } e^-)(96487 \text{ C/mol } e^-)} = 0.01325 \text{ g } Na_2S_2O_3$$

This represents the amount of $Na_2S_2O_3$ in a 10.00-mL portion of a 100-m sample, thus 0.1325 g of $Na_2S_2O_3$ is present in the original sample. The puri of the sample, therefore, is

$$\frac{0.1325 \text{ g } Na_2S_2O_3}{0.1342\text{-g sample}} \times 100 = 98.73\% \text{ w/w } Na_2S_2O_3$$

Note that the calculation is worked as if $S_2O_3^{2-}$ is oxidized directly at t working electrode instead of in solution.

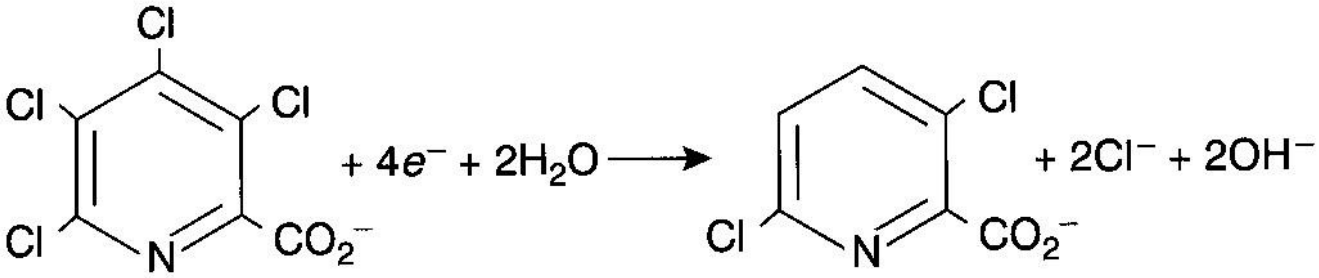
Example 2

- A 0.3619-g sample of tetrachloropicolinic acid, $C_6HNO_2CI_4$, is dissolved in distilled water, transferred to a 1000-ml, volumetric flask, and diluted to volume. An exhaustive controlled-potential electrolysis of a 10.00-mL portion of this solution at a spongy silver cathode requires 5.374 C of charge. What is the value of *n* for this reduction reaction?

The 10.00-mL portion of sample contains 3.619 mg, or 1.39×10^{-5} mol of tetrachloropicolinic acid. Solving equation 11.23 for n and making appropriate substitutions gives

$$n = \frac{Q}{FN} = \frac{5.374\ \text{C}}{(96478\ \text{C/mol}\ e^-)(1.39 \times 10^{-5}\ \text{mol}\ C_6HNO_2Cl_4)} = 4.01$$

Thus, reducing a molecule of tetrachloropicolinic acid requires four electrons. The overall reaction, which results in the selective formation of 3,6-dichloropicolinic acid, is



Potentiometric Methods

Introduction:

1.) *Potentiometric Methods:* based on measurements of the potential of electrochemical cells in the absence of appreciable currents (i ☞ 0)

2.) *Basic Components:*

a) reference electrode: gives reference for potential measurement

b) indicator electrode: where species of interest is measured

c) salt bridge

d) potential measuring device

A reference electrode is a half-cell with an accurately known electrode potential, E_{ref}, that is independent of the concentration of the analyte or any other ions in solution. The indicator electrode, which is immersed in a solution of the analyte, must be an electroactive species which can donate or accept electron(s), It develops a potential, E_{ind}, that depends on the activity of the analyte. Most indicator electrodes are highly selective in their responses. The salt bridge is the third component of a potentiometric cell, it prevents the components of the analyte solution from mixing with those of the reference electrode. At each end od the salt bridge in an electrochemical cell, a potential develops across the liq. Junction. The two potentials tends to cancel each other. If the mobilities of the cations and anions in the bridge solution are about the same. The net junction across the bridge, E_j, is therefore less thank a few mV and may be neglected in most cases. The potential of a cell is there given by :

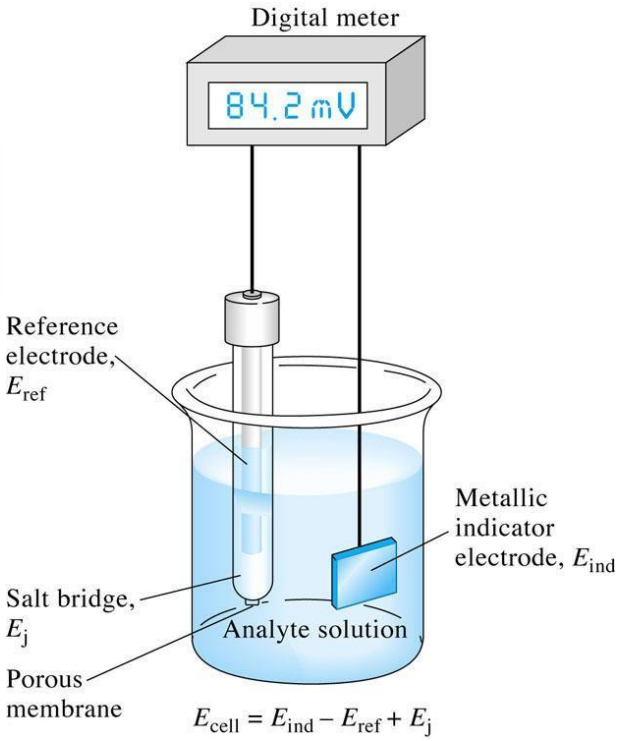
$$E_{cell} = E_{ind} - E_{ref} + E_j$$

reference electrode | salt bridge | analyte solution | indicator electrode

E_{ref} E_j E_{ind}

$$E_{cell} = (E_{ind} - E_{ref}) + E_j$$

For most electroanalytical methods, the junction potential is small enough to be neglected.



A cell for potentiometric determinations

Reference Electrodes:

Need one electrode of system to act as a reference against which potential measurements can be made → relative comparison.

Desired Characteristics:

a) known or fixed potential, E_{ref}
b) constant response (even when there is a net current in the cell)
c) insensitive to composition of solution under study
d) obeys Nernst Equation
e) reversible
f) rugged and easy to assemble
g) Always treated as the left-hand electrode

Common Reference Electrodes used in Potentiometry

i) Calomel Electrodes (Hg in contact with Hg_2Cl_2 & KCl)
ii) Silver/Silver Chloride Electrode

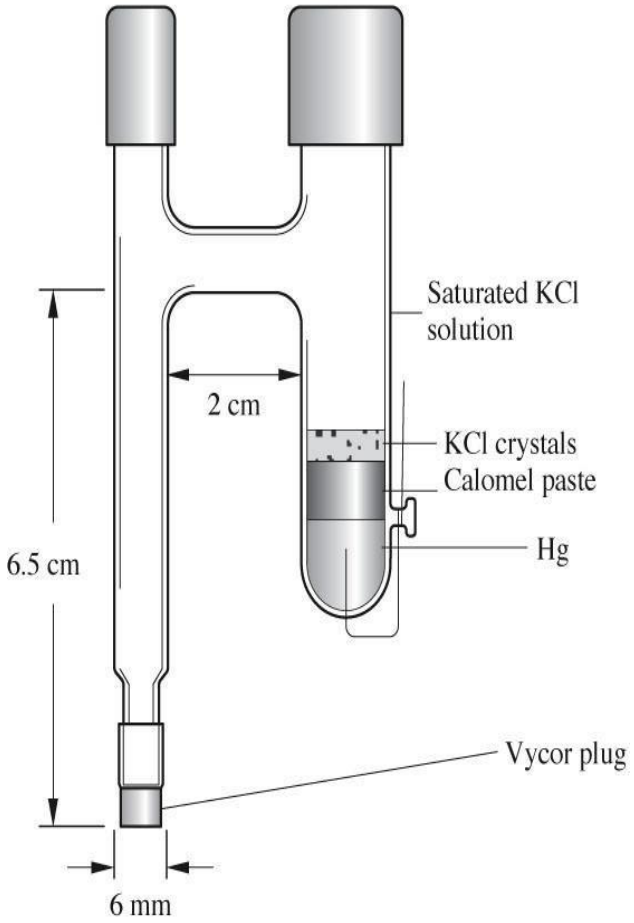
Saturated Calomel Electrode (SCE)

½ cell repr.: $Hg|Hg_2Cl_2$ (satd), KCl (xM)||

½ cell react: $Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-(aq)$

Note: response is dependent on $[Cl^-]$, x, the molar conc. of KCl which can be 0.1 M, 1.0 M or saturated. Thus, the KCl concentration must be specified in describing the electrode. When the KCl conc. is saturated the electrode is referred to as saturated calomel electrode (SCE) and its $[Cl^-]$ does not change if some liq evaporates.

- widely used, due to ease of preparation
- equilibriation due to temperature change is slow
- leakage of KCl into sample, mercury contamination
- less common than once they were
- still preferred for some certain applications



A typical SCE

Silver/Silver Chloride Electrode

- most widely used reference electrode system
- Ag electrode immersed in KCl solution saturated with AgCl

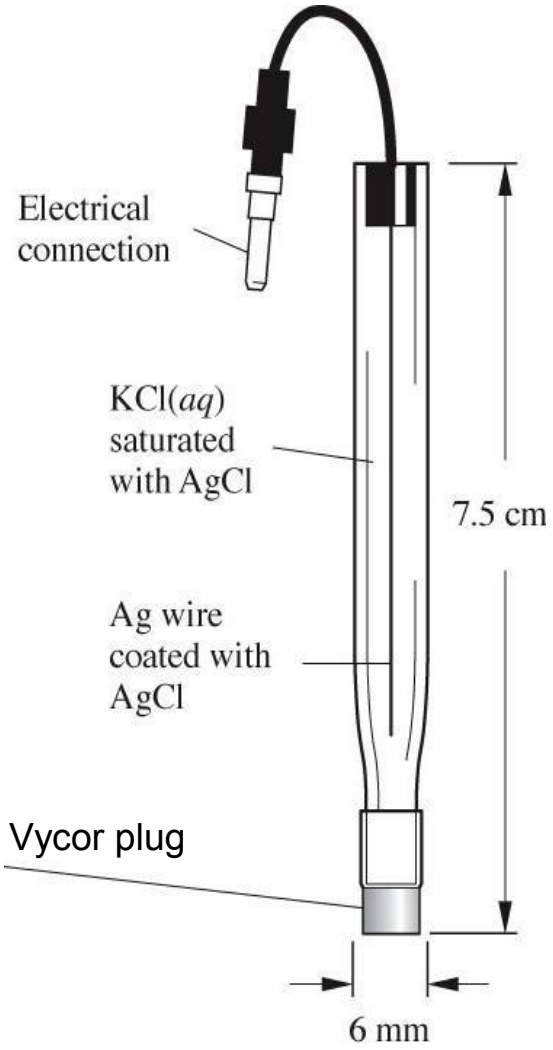
½ cell repr. : Ag | AgCl (satd) $\rightleftharpoons$ KCl (xM)||

½ cell reaction: $AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$

Advantage – one advantage over SCE is that Ag/AgCl electrode can be used at temperatures > 60°C

Disadvantage – Ag reacts with more ions, - plugging of the junction between electrode (Ag) and analyte soln.

- **Precautions in the Use of Reference Electrodes**
- need to keep level of solution in reference electrode above the level in analyte solution (to prevent reaction of Ag/Hg with analyte) - need to prevent flow of analyte solution into reference electrode - **can result in plugging of electrode at junction leading to erratic behavior second salt bridge (non-interfering electrolyte: KNO_3 , $NaSO_4$)**



Indicator Electrodes:

- An indicator electrode Detects or Responds to Presence of Analyte of interest.

An Ideal indicator electrode responds *rapidly and reproducibly* to changes in the concentration of an analyte ion (or groups of analyte ions) in solution.

There are three common types of indicator electrodes:

a) Metallic Indicator Electrodes – these include:

Electrodes of the First Kind

Electrodes of the Second Kind

Electrodes of the Third Kind

Metalic Redox Indicators

b) Membrane Indicator Electrodes which includes:

Crystalline Membrane Electrodes

Non-crystalline Membrane Electrodes

c) Ion selective Electrode (field effect transistor) ISFET

Metallic Indicator Electrode (Four Main Types)

a) Metallic Electrodes of the First Kind: can be describe as a pure metal electrode that is in direct equilibrium with its cation in the solution and can be represented as:

$$X^{n+}(aq) + ne^- \rightleftharpoons X(s)$$

Attributes. i. Involves single reaction *ii.* Detection of cathode derived from the metal used in the electrode *iii.* Example: use of copper electrode to detect Cu^{2+} in solution

½ reaction: $Cu^{2+} + 2e^- = Cu\ (s)$

E_{ind} gives direct measure of Cu^{2+}:

since $a_{Cu(s)} = 1$: $E_{ind} = E^o_{Cu} - (0.0592/2) \log a_{Cu(s)}/a_{Cu}2+$

or using $pCu = -\log a_{Cu}2_+$: $E_{ind} = E^o_{Cu} - (0.0592/2) \log 1/a_{Cu}2+$

$E_{ind} = E^o_{Cu} - (0.0592/2)\ pCu$

Problems with Metallic Electrodes of the First Kind:

- Electrode of the first kind is not very popular because…

— metallic indicator electrodes are not very selective and respond not only to their own cations but also to other more easily reduced cations. – Many metal electrodes can be used only in neutral or basic solutions because they dissolve in the presence of acids

— Easily oxidized, can be used only when analyte solutions are deaerated to remove oxygen

— Certain hard metals (Fe, Cr, Co, Ni) do not provide reproducible potentials

• Limited electrodes are:

— Ag/Ag+ and Hg/Hg2+ in neutral solutions and Cu/Cu2+, Zn/Zn2+, Cd/Cd2+, Bi/Bi3+, Tl/Tl+, and Pb/Pb2+ in deaerated solutions.

b) Metallic Electrodes of the Second Kind:
Metal electrode respond to the activities of anions that form sparingly soluble precipitates or stable complexes.

i. Example: Detection of Cl^- with Ag electrode

½ reaction: $AgCl(s) + e^- = Ag(s) + Cl^-$ $E^O = 0.222$ V

E_{ind} gives direct measure of Cl^-:

$E_{ind} = E^o - (0.0592/1) \log a_{Ag(s)}\, a_{Cl^-}/a_{AgCl(s)}$ *since* $a_{Ag(s)}$ *and* $a_{AgCl(s)} = 1$ *&* $E^o = 0.222$ *V:*

$$E_{ind} = 0.222 - (0.0592/1) \log a_{Cl^-}$$

c) Metallic Electrodes of the Third Kind:
i. Metal electrodes responds to a different cation *ii.* Linked to cation by an intermediate reaction

- *Already saw detection of EDTA by Hg electrode (2^{nd} Kind)*
- Can be made to detect other cations that bind to EDTA → affecting a_{Y4-}

d) Metallic Redox Indicators

i. Electrodes made from inert metals (Pt, Au, Pd) often serve as indicator electrodes for oxidation-reduction systems.

ii. Electrode acts as e^- source/sink for electrons transferred from a redox system in the solution

Example: Detection of Ce^{3+} with Pt electrode

½ reaction: $Ce^{4+} + e^- = Ce^{3+}$

E_{ind} responds to Ce^{4+}: $E_{ind} = E^o - (0.0592/1) \log a_{Ce3+}/a_{Ce4+}$

Thus, a platinum electrode can serve as the indicator electrode in a titration in which Ce(IV) serves as the standard reagent.

Problems:

- electron-transfer processes at inert electrodes are frequently not reversible
- do not respond predictably to ½ reactions in tables

Membrane Indicator Electrodes

Electrodes based on determination of cations or anions by the selective adsorption of these ions to a membrane surface

-Often called Ion Selective Electrodes (ISE) or pIon Electrodes, because the data obtained from them are usually presented as p-functions, (pH, pCa, pNO_3) - The general mechanism by which an

ion selective potential develops in these devices depends on the *nature of the membrane* and is entirely different from the source of potential in metallic indicator electrodes.

- We have seen that the potential of a *metallic electrode* arises from the tendency of an *oxidation-reduction reaction to occur at an electrode surface*.
- In membrane electrodes, in contrast, the observed potential is a kind of *junction potential that develops across a membrane* that separates the analyte solution from a reference solution.

Ideally, an ion selective electrode (ISE) should respond to only one target ion in solution without any interference by the presence of other ions in the test solution. In practice, there is always some level of interferences by other ions in the solution. For example, Na^+ interferes with H^+ when using pH meter. The operation of ISE devices does not depend on redox processes. The key feature of an ISE is a thin selective membrane across which only the target ion can migrate. Other ions cannot cross the membrane. The difference in concentration of the solution inside the electrode and the test solution (outside the electrode) produce a voltage difference across the membrane. The membrane contains a binding agent called ionophore, which assists the target ion to transport across the membrane. The membrane divides the electrode inner reference solution which contains a low concentration of the target ion ion species and the (outer) test/analyte solution containing a higher concentration of the target ion. Ion selective membranes are usually made of hydrophobic organic polymer impregnated with ionophore,

which act as a polydentate ligand for the target ion it possesses a large non-polar structure to pull the ion into the membrane. The aqueous filling solution inside the electrode contains the target ion at low conc.

Examples of ionophore: calcimycin as Ca^{2+} ionophore and valinomycin as K^{+} ionophore.

The electric potential difference (voltage) across the membrane is measured in the presence of of a reference electrode, usually Ag/AgCl reference electrode. If the conc. of the target ion in the unknown solution changes, the voltage changes in proportion to the change in the concentration. Hence, with the use of a calibration curve, the voltage tells us the conc of the target ion in the analyte solution.

The potential difference is governed by the equation:

$$E = constant + \frac{RT}{nF} Ln\, \mathcal{A}i \quad = constant + \frac{0.05916}{n} \log \mathcal{A}i$$

$$E = constant + \frac{0.05916}{n} \log \gamma[i]$$

$$\mathcal{A}i = \gamma[i]$$

Where n is the charge on the ion, $\mathcal{A}i$ is the activity of ion i which does not equal to [i] (concentration of ion i), γ is the activity coefficient. However, when the ionic strength, which is a measure of the total conc of ions in solution is very low, the activity coefficient approaches unity and the two become equal. Also, if a constant ionic strength is maintained in all the standard solution for calibration curve and the unknown solution, the activity can be replaced with conc. This can be accomplished by addition of measured excess of inert electrolyte like total ionic strength adjustment buffer (TISAB).

Hence, $E = constant + \frac{0.05916}{n}\log[i]$.

A plot of E against log [i] will produce a linear plot of slope = $\frac{0.05916}{n}$. If the target ion is an anion, n will be negative and the slope will be negative and if n is positive the slope will be positive.

Desired properties of ISE's

* *minimal solubility*

– membrane will not dissolve in solution during measurement

– Many membranes are formed from large molecules or molecular aggregates: silica glasses, polymeric resin, low solubility inorganic compounds (AgX) can be used as membranes

* *need some electrical conductivity*

– Generally, this conduction takes the form of migration of singly charged ions within the membrane.

* *selective reactivity with the analyte*

Three types of binding are encountered: ion-exchange, crystallization and complexation. The former two are the more common, and we will largely focus on these types of bindings.

pH glass Electrode

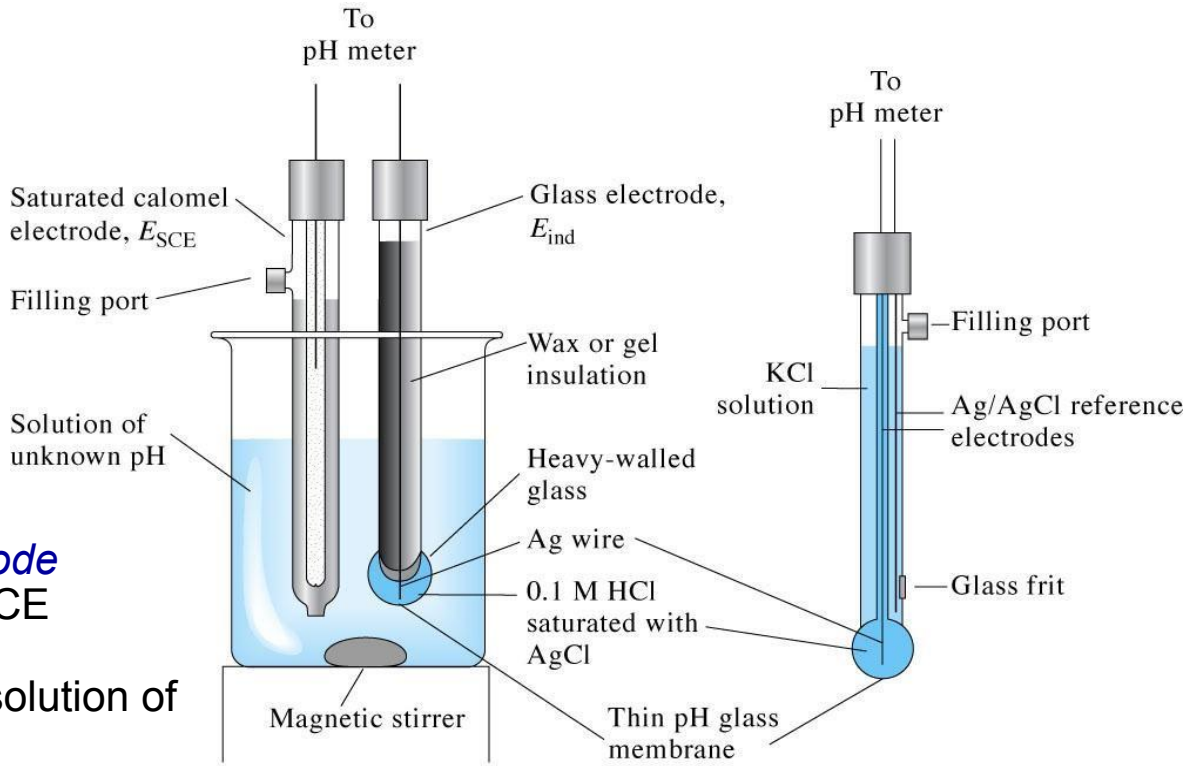
i. most common example of an ISE

- based on use of glass membrane that preferentially binds H^+
- Two reference electrodes here
- one SCE- outside of membrane
- one Ag/AgCl - inside membrane

pH sensing element is glass tip of Ag/AgCl electrode

ii. Typical pH electrode system is shown

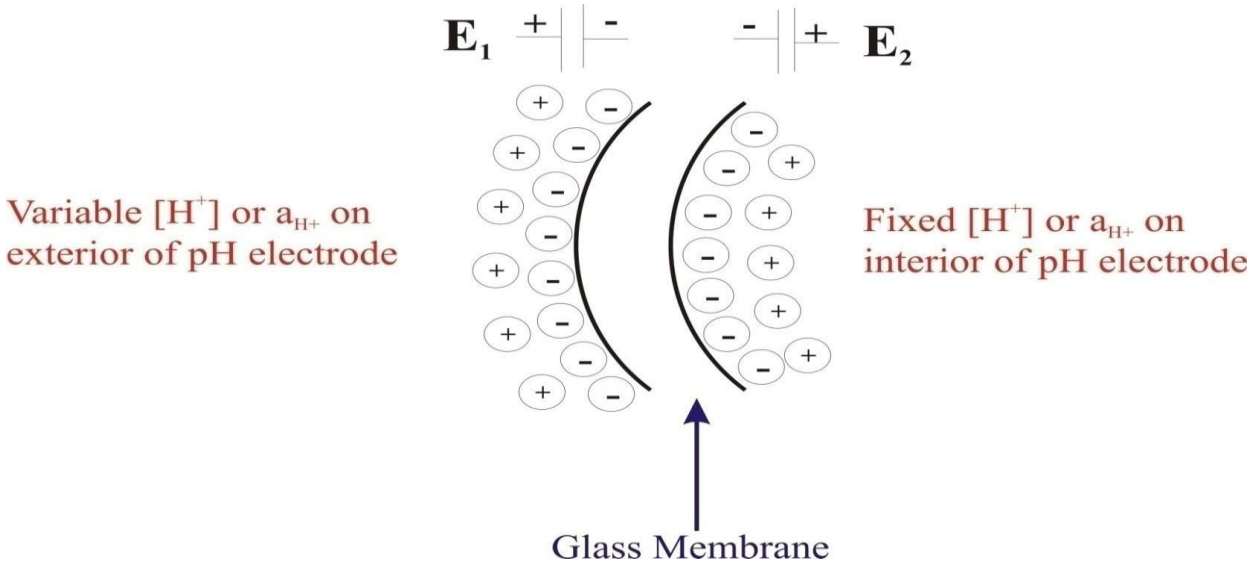
(*b)Combination probe* consisting of both an indicator and a Ag/AgCl ref. electrode.



(a) *Glass electrode* (indicator) and SCE (reference) immersed in a solution of unknown pH.

pH is determined by formation of boundary potential across glass membrane

Whenever there is a charge imbalance across any material, there is an electrical potential across the material:
– the concentration of protons inside the membrane is constant, and the concentration outside is determined by the concentration, or activity, of the protons in the analyte solution. – This concentration difference produces the potential difference that we measure with a pH meter.
- At each membrane-solvent interface, a small local potential develops due to the preferential adsorption of H^+ onto the glass surface.

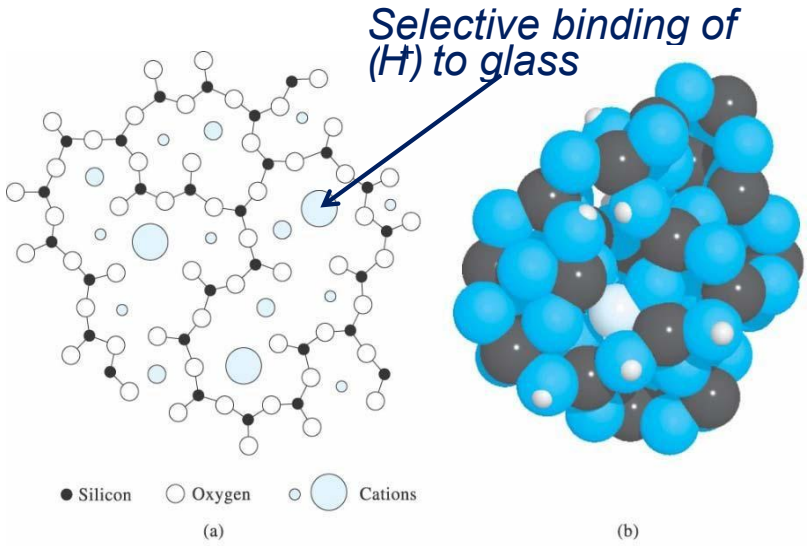


The Composition and Structure of Glass Membranes

- Glass composition affects the sensitivity of membranes to protons and other cations

  - Corning 015 glass, which has been widely used for membranes, consists of approximately 22% Na_2O, 6% CaO, and 72% Si02• This membrane is specific in its response toward hydrogen ions up to a pH of about 9. At higher pH values, however, the glass becomes somewhat responsive to sodium, as well as to other singly charged cations

- Other glass formulations are now in use in which sodium and calcium ions are replaced to various degrees by barium and lithium ions. These membranes have superior selectivity at high pH.



Cross-sectional view of a silicate glass membrane structure. Each silicon atom is shown as being bonded to three oxygen atoms in the plane of the paper. In addition, each is bonded to another oxygen above or below the plane. Thus, the glass consists of an infinite three-dimensional network of SiO, - groups in which each silicon is bonded to four oxygens and each oxygen is shared by two silicons. Within the interstices of this structure are sufficient cations to balance the negative charge of the silicate groups. Singly charged cations, such as sodium and lithium, are mobile in the lattice and are responsible for electrical conduction within the membrane.

Potentiometric pH Measurement with the Glass Electrode

The glass/calomel electrode system is a remarkably versatile tool for the measurement of pH under many conditions.

However, there are distinct limitations to the electrode:

1. The alkaline error
2. The acid error
3. Dehydration
4. Errors in low ionic strength solutions
5. Variation in junction potential
6. Error in the pH of the standard buffer
7. Errors resulting from temperature changes

The operational definition of pH:

➢ The operational definition of pH, endorsed by the National Institute of Standards and Technology (NIST) and IUPAC, is based on the direct calibration of the meter with carefully prescribed standard buffers followed by potentiometric determination of the pH of unknown solutions.

$$pH_s = \frac{E_s - K}{0.0592}$$

where E_S is the cell potential when the electrodes are immersed in the buffer. If the cell potential is E_U when the electrodes are immersed in a solution of unknown pH, we have

$$pH_U = \frac{E_u - K}{0.0592}$$

$$pH_U = pH_S - \frac{(E_U - E_S)}{0.0592}$$

Introduction to Electroanalytical Chemistry!

(chapter 13--ECA)

Potentiometry: measure voltage of galvanic cell--and relate E_{cell} to concentration/activity of given analyte

E_{cell} related to "desire" for electrons to flow-between two electrodes--working and reference but no reactions actually take place!!

Amperometric/Voltammetric: Apply external voltage to electrochemical cell (electrolyte cell) and measure current response---if current flows---reduction reaction takes place at one electrode, and oxidation at other!!

Can also use both methods as detection systems for titrations---using chelating agents, or redox titrants!

All electrochemistry is based on Redox reactions (Ox + ne- <----> Red)!-species gains electrons (reduction) and species lose electrons (oxidation)

Electric charge-(q) is measured in coulombs (C)

a single charge has 1.602×10^{-19} C ; 1 mole of charge has $(1.602 \times 10^{-19}\ C) \times (6.022 \times 10^{23}\ mol^{-1}) = 9.649 \times 10^{4}$ C/mol = F = **Faraday's** constant!

Faraday's law: moles reacted = q/nF ; n = number of electrons in reaction!
or q = nF(moles reacted)

Current is proportional to moles reacted for electrochemical reaction:

current = amperes = 1 C/sec ;

What would be current required to reduce $Sn^{+4} + 2\ e^{-} \text{----}> Sn^{+2}$ at a platinum electrode as a rate of 4.24 mmol/h?
What would be rate per second? $4.24 / 3600 = 1.18 \times 10^{-6}$ mol/sec
current = C/s = q/sec = $(1.18 \times 10^{-6}$ mol/sec) x n x F (C/mol) =
= 0.227 A (amps)

Voltage and work----

Electrical potential difference---difference in charge between two points!---this potential difference is a measure of the work required to bring (move) electrons from one point to the other!----
has units of Volts (V)
and work done or needed to be done has units of Joules (J)

joules (work) = E (volts) x q (charge)

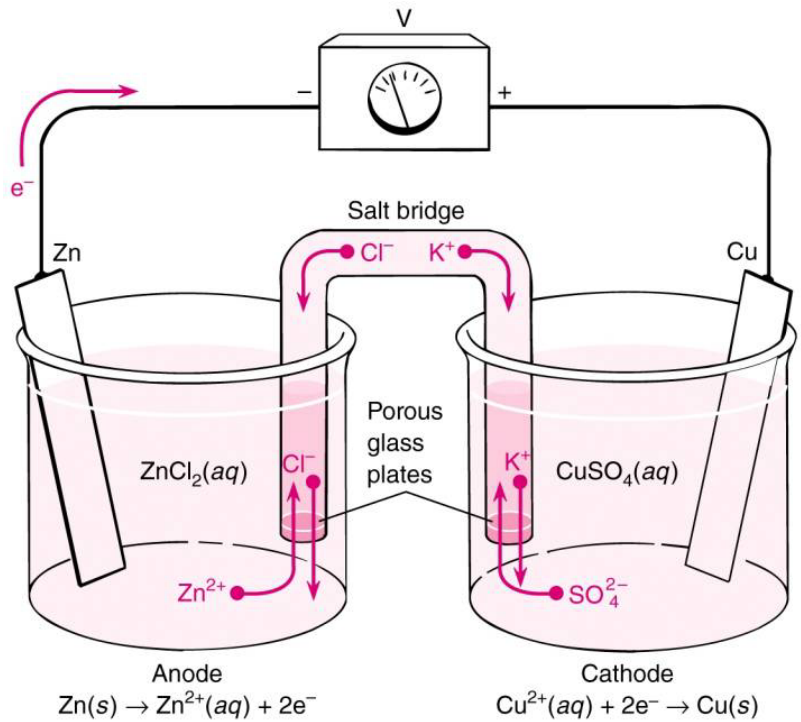
One joule of energy is used to move one coulomb of charge between two points that differ by 1 volt!

therefore-- 1 volt = joules/C

In potentiometry---we measure the desire for charge to flow from one electrode to another (we don't actually let the charge flow)---charge will only want to flow if there is a voltage difference!

… and more definitions

- Cathode: surface where electrons are donated to atoms or molecules, where reduction occurs
- Anode: surface where electrons are accepted from atoms or molecules, where oxidation occurs
- Electrochemical Cell: reduction at a cathode and oxidation at an anode are separated into two compartments connected by an external circuit so that electrons will flow (current) through the circuit
- Galvanic Cell: a battery, electrochemical cell that has spontaneous electron flow, capable of doing work



$$Cu^{+2} + 2e^- \rightarrow Cu(s)$$

$$Zn(s) \rightarrow Zn^{+2} + 2e^-$$

n=2

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

Cell Potential, Current Flow

- Cell Potential, E_{cell}

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

std. reduction potentials

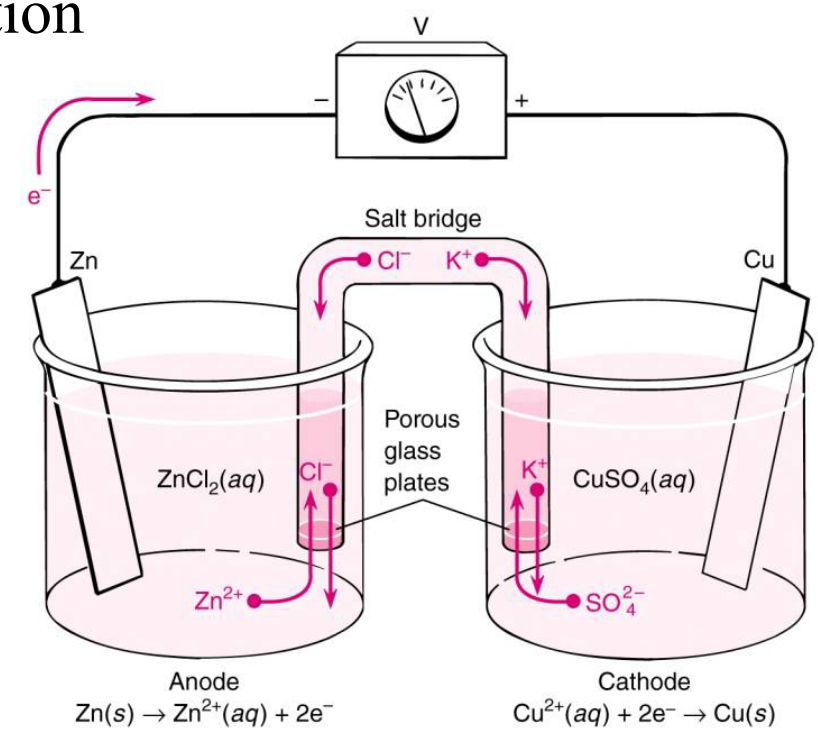
$$Cu^{+2} + 2e^- \rightarrow Cu(s) \qquad E_{cu}{}^0 = 0.339$$

$$Zn(s) \rightarrow Zn^{+2} + 2e^- \qquad -E_{zn}{}^0 = 0.762$$

$$Cu^{+2} + Zn(s) \rightarrow Zn^{+2} + Cu(s)$$

cell rxn

$$E_{cell} = 1.101\,\text{V}$$



- If the cell potential is positive the cell is galvanic.
- Current will flow spontaneously.
- Cell line notation

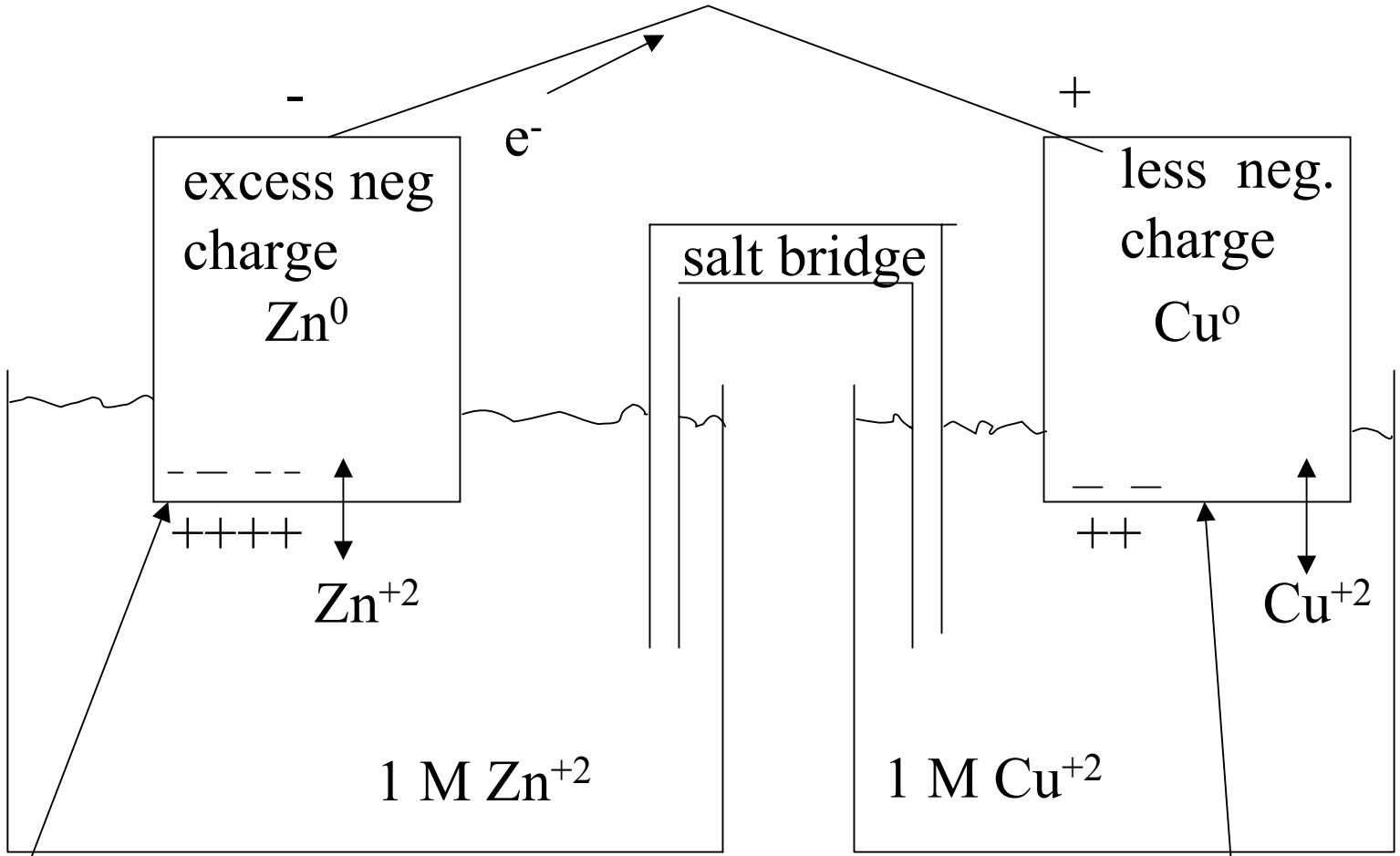
| phase boundary

$$Zn(s)|Zn^{+2}||Cu^{+2}|Cu(s)$$

anode cathode

|| salt bridge

What does E^0 value for each half-cell reaction really mean?



electrical potential difference at interface-- magnitude depends on equil. const for $Zn+2e^- <---> Zn^o$

potential at this interface-- due to $Cu^{+2} +2e^- <—> Cu^o$

Thermodynamic Free Energy

- Laws of Thermodynamics define the work done by a system as Gibbs Free Energy

$Q = (a_{Cu}{}^{o} a_{Zn}{}^{+2}) / (a_{Cu}{}^{+2}\, a_{Zn}{}^{o})$

$F = 9.65 \times 10^{+4}$ C/mol

E^{o}_{cell}

$$\Delta G \equiv \Delta H - T \cdot \Delta S$$

$$\Delta G = \Delta G^{0} + RT \ln(Q)$$

$$\Delta G \equiv work = E \cdot q$$

$$\Delta G = -nFE_{cell}$$

Nernst Equation:

$$E_{cell} = E^{0} - \frac{RT}{nF} \ln Q$$

$$E_{cell} = E^{0} - \frac{0.0592}{n} \log Q$$

at standard conditions:

$$\Delta G^{0} = -nFE^{0}_{cell}$$

R (in joules/^{o}K-mol)
2.3-ln--> log conv.; 25^{o}C

- exothermic reactions (spontaneous) e.g. galvanic: $\Delta G<0$ when $E_{cell}>0$
- endothermic reactions (not spontaneous): $\Delta G>0$ $E_{cell}<0$

actual conc. or activities of species present

E^0 relationship to K for overall electrochemical cell rxn

- Q= product to reactant ratio:
  - in Zn/Cu electrode system-- soluble species at the anode divided by the soluble species at the cathode
- At equilibrium:
  - no current flow
  - $E_{cell} = 0$
  - Q = K (equilibrium constant)
- Calculated (or measured) E^0_{cell} $=E^0_{cathode} - E^0_{anode}$
  - can be used to predict

$$\Delta G = \Delta G^0 + RT\ln(Q)$$

$$\Delta G = 0 = \Delta G^0 + RT\ln(K)$$

$$\Delta G^0 = -RT\ln(K)$$

$$\Delta G^0 = -nFE^0_{cell}$$

E^o_{cell} → $\boxed{E^0 = \frac{RT}{nF}\ln(K)}$ ← equilib. const. for rxn:

$Zn^o + Cu^{+2} <----> Zn^{+2} + Cu^o$

E^O values for half-cell rxns--written as reduction reactions!

$F_{2(g)} + 2\ e^- \ <----------> \ 2\ F^-$	2.890 V
$MnO_4^- + 8\ H^+ + 5\ e^- <------> Mn^{+2} + 4\ H_2O$	1.507
$Ag^+ + e^- \ <----------> \ Ag^o$	0.799
$Cu^{+2} + 2\ e^- \ <---------> \ Cu^0$	0.339
$AgCl + e^- \ <---------> \ Ag^0 + Cl^-$	0.222
$2H^+ + 2\ e^- \ <----------> \ H_{2(g)}$	0.000
$Zn^{+2} + 2\ e^- \ <----------> \ Zn^o$	-0.762

species at top of table are strong oxidizing agents (more easily reduced; species at bottom are strong reducing agents---(easily oxidized)

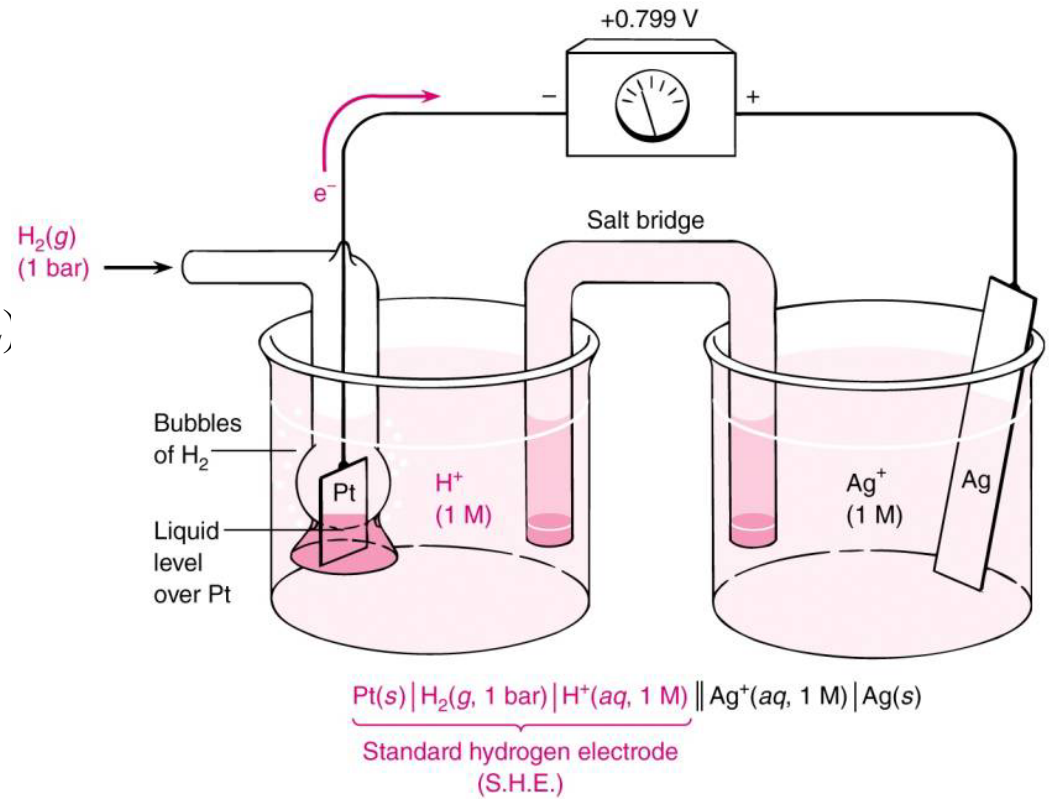
Measuring E^0

- Standard potentials means all conditions are "standard":

  a_i=1; 25 ºC; 1 atm
- The anode: 1 atm H_2 (g) is bubbled over Pt electrode, H_2 is oxidized (NHE)
  - standard half-reactions are written as reductions (cathodic)
  - $H^+ + e^- \rightarrow 1/2\ H_2$ (g)
- The cathode: the reduction of some metal M^+ (activity=1)
  - metal precipitates on the electrode
  - $Ag^+ + e^- \rightarrow Ag(s)$
- <u>Assumption</u>: concentration of all analytes (H^+, M^+) remain constant

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

$$E^0_{cell} = 0.799\ \text{V} = E^0_{cathode} - 0$$



•Standard Hydrogen Electrode, S.H.E. (or NHE) E^0=0.0 V (by convention)

•Ag^+, Ag(s) standard reduction potential equals the measured E_{cell}, E^0=0.799 V

If we know E^0 values---we can always calculate the E_{elect} for each of the two half-cell electrodes; Use Nernst equation for each half cell reaction!

for general 1/2 cell rxn: $Ox + ne^- \text{<----> } Red$

$E_{elect} = E^o - 0.0592 \log (a_{prod}/a_{react}) = \mathbf{E^0 + 0.0592 \log (a_{ox}/a_{red})}$

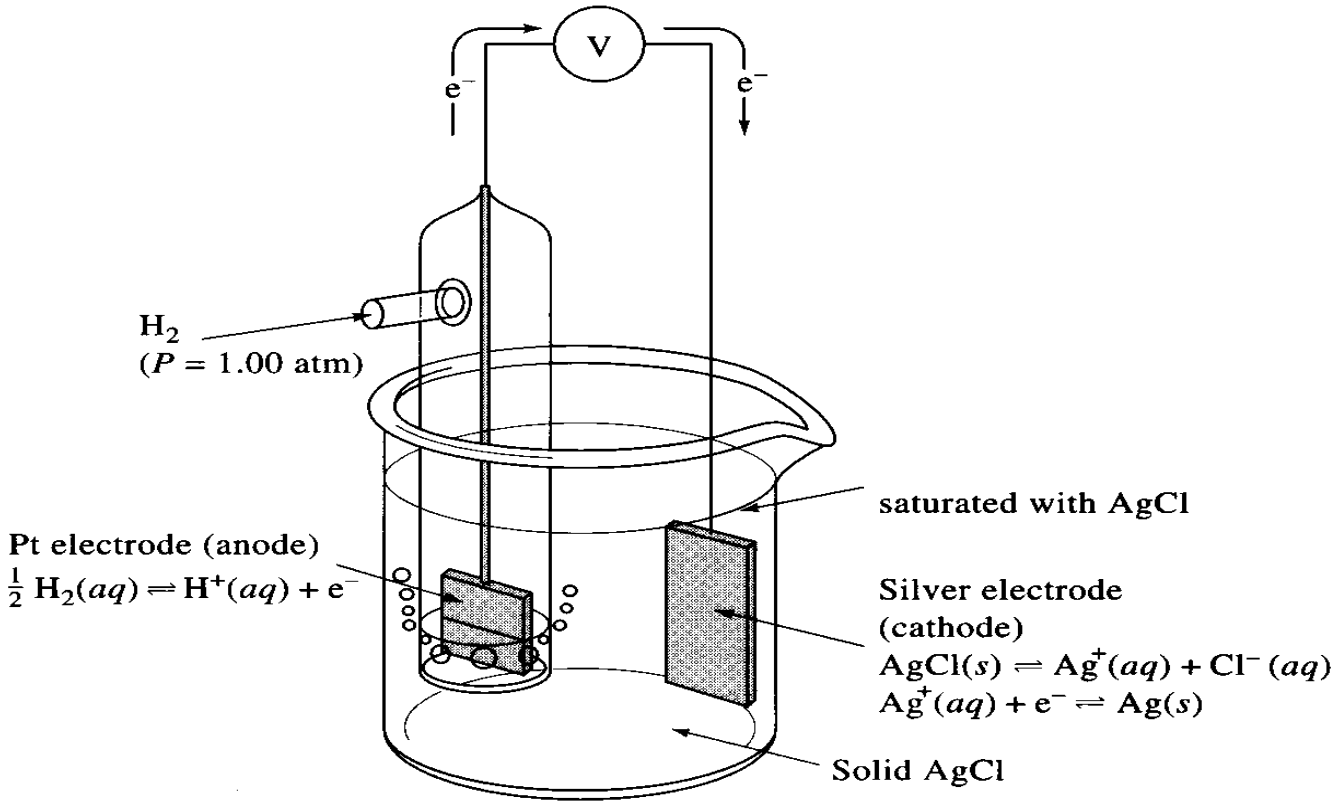
Then to calculate cell potential---

$E_{cell} = E_{cath} - E_{anode}$ (use Nernst equation to calculate potential of each electrode)

What is E_{cell} for following galvanic cell:

Pt, H_2 (1 atm) / H^+ (a=0.1 M), Cl^- (a=0.1M), $AgCl_{(s)}$ /Ag

$E_{cell} = E_{right} - E_{left} = E_{cath} - E_{anode} = E_{Ag/AgC} - E_{H^+/H2(pt)}$



Pt, H_2 (1 atm) / H^+ (a=0.1 M), Cl^- (a=0.1M), $AgCl_{(s)}$ /Ag

$E_{Ag/AgCl} = E^o_{Ag/AgCl} + 0.0592 \log (a_{AgCl(s)} / a_{Cl^-} a_{Ago})$

$= 0.222 \text{ V} + 0.0592 \log (1 / 0.1\ (1))$ unit activity (solids)!

$= 0.222 \text{ V} + 0.0592 \log (10) = 0.281 \text{ V or } 281 \text{ mV}$

$E_{H+/H2} = E^o_{H+/H2} + (0.0592/2) \log (a_{H^+}^2 / P_{H2})$

$= 0.000 \text{ V} + 0.0592 \log (0.1 / 1)$

$= -0.0592 \text{ V}$

2 values from
$2\ H^+ + 2e^- <-->H_{2--}$
but these cancel out because of how you treat exponents in log term!

Therefore: E_{cell} = 0.281 V - (-0.059 V) = 0.340 V or 340 mV

What would be E_{cell} if you had 0.001 M HCl (assume activities= [ ])?

$E_{Ag/AgCl} = 0.222 + 0.0592 \log (1 / 0.001\ (1)) = 0.400$ V or 400 mV

$E_{H+/H2} = 0.000 + 0.0592 \log (0.001 / 1) = -0.178$ V or - 178 mV

$E_{cell} = 0.400 - (-0.178) = 0.578$ V

note that as pH increases in this cell---voltage gets more positive---Indeed, this S.H.E/sample, AgCl(s)/Ag cell was the cell used by **Roger Bates** at NBS (now NIST) to assign the pH ($-\log a_{H+}$) in the buffer standards that we now use to calibrate pH electrodes!

He added constant amount of NaCl salt to each potential buffer ---so that the $E_{Ag/AgCl}$ would not change very much---(he also calculated activity coeff. for chloride so he could plug in the true activity of chloride ion for potential of Ag/AgCl electrode

$E_{cell} = E_{Ag/AgCl} - (E^{0}_{SHE} + 0.0592 \log (a_{H}^{+}) - 0.0592 \log (P_{H2(g)}))$

$\log (a_{H}^{+}) = (E_{cell} - E_{Ag/AgCl}) / 0.0592$

E^0 values--for given redox reactions---and be calculated based on simultaneous equilibrium reactions----true for **Electrodes of Second Kind** (e.g., Ag/AgCl); **Electrode of first kind** (M/M^{n+}) in solution that is saturated with insoluble salt of M^{n+}.

potential of elect. of 1st kind $E_{elect} = E^o_{Mn+/M(o)} + (0.0592/n) \log(a_{Mn+})$

$Ag/AgCl_{(s)}$ $\quad Ag \not\rightleftharpoons Ag^+ + Cl^- <------> AgCl_{(s)}$

$E_{Ag} = E^o_{Ag+/Ag(o)} + 0.0592 \log (a_{Ag+}/a_{Ag(o)}) = 0.799\ V + 0.0592 \log (a_{Ag+})$

but $K_{sp}^{(AgCl)} = a_{Ag+}\, a_{Cl-}$; $a_{Ag+} = K_{sp}/a_{Cl-}$ $\quad K_{sp} = 1.8 \times 10^{-10}$

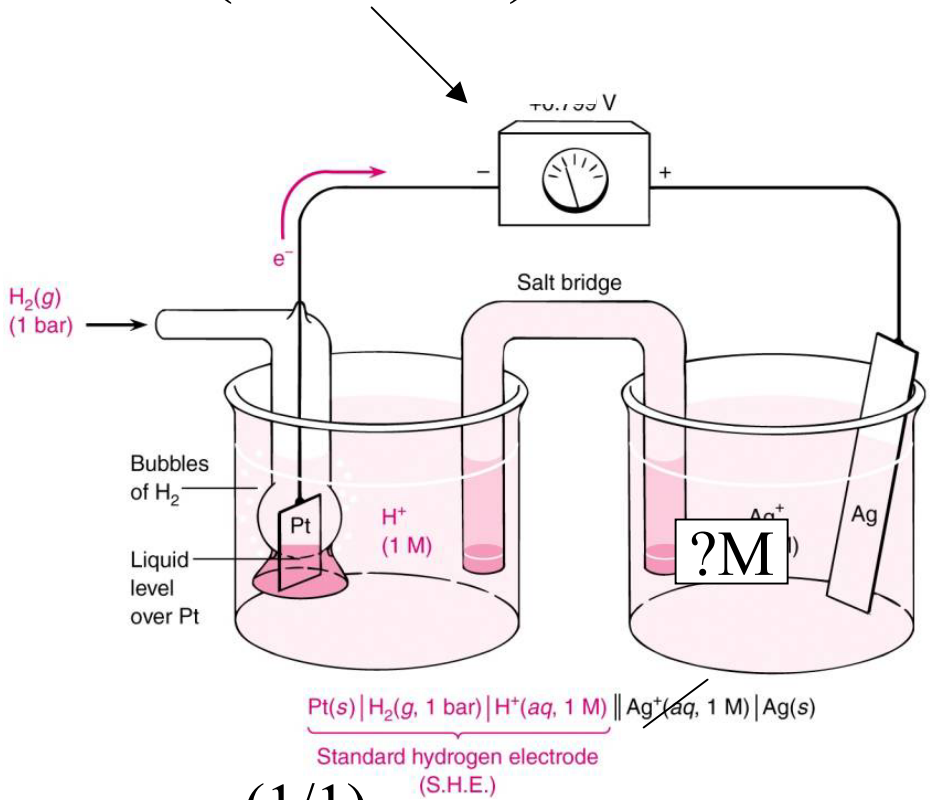
$E_{Ag} = 0.799 + 0.0592 \log (K_{sp}/a_{Cl}^-)$

$E_{Ag/AgCl} = 0.799 + 0.0592 \log K_{sp} - 0.0592 \log a_{Cl-}$

$E_{Ag/AgCl} = 0.222 - 0.0592 \log a_{Cl-}$ $\quad$ elect. responds to Cl^-

Determining Analyte Concentration from measured E_{cell} value (0.682 V)

- Left: Anode, oxidation of H_2
  - S.H.E. standard conditions
  - E_A=0.0 V
- Right: Cathode, reduction of Ag^+, unknown concentration
  - E^0=0.799 V (at standard conditions)
- $E_{cell}=E_C-E_A$ = 0.682 V
  - initial cell voltage measured
  - What is $[Ag^+]$ (assume activity equals concentration)



$0.682 = E_{Ag} - E_{SHE}$

(1/1)

$= (0.799 + 0.0592 \log a_{Ag+}) - (0.000 + 0.0592 \log (a_{H+} / P_{H2})$

Therefore: $\log a_{Ag+} = (0.682 - 0.799) /0.0592$

$a_{Ag+} = 0.0106$ M

In potentiomtric methods---we always use galvanic cell in which one of the electrodes has constant half-cell potential (called **reference electrode**).

The second electrode is called the **working** or **indicator** electrode!

We don't really care whether the cell potential is + or - --and we don't really care which electrode would be anode and which would be cathode if the galvanic cell were to discharge!!
Who cares?---we are only using the E_{cell} value to detect some analyte species, or indirectly detect some analyte (via titration, etc.).

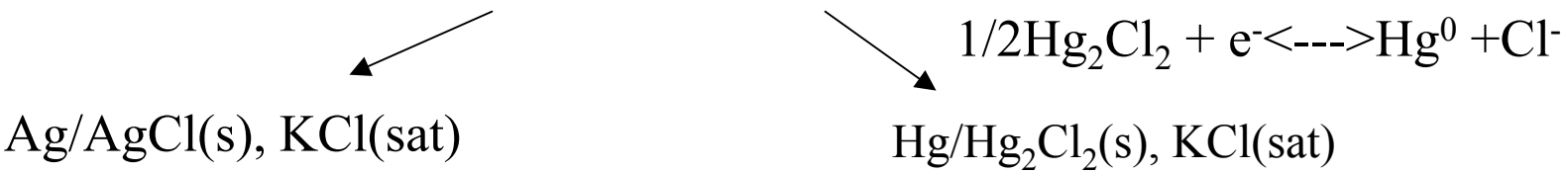
We never let cell discharge---we measure voltage under essentially zero current conditions---so there is no real cathode or anode!!
Hence---$E_{cell} = E_{ind} - E_{ref} = E_{working} - E_{ref} = E_{+} - E_{-}$

+ and - here refer to which jack in meter you connect to !

Types of Electrodes

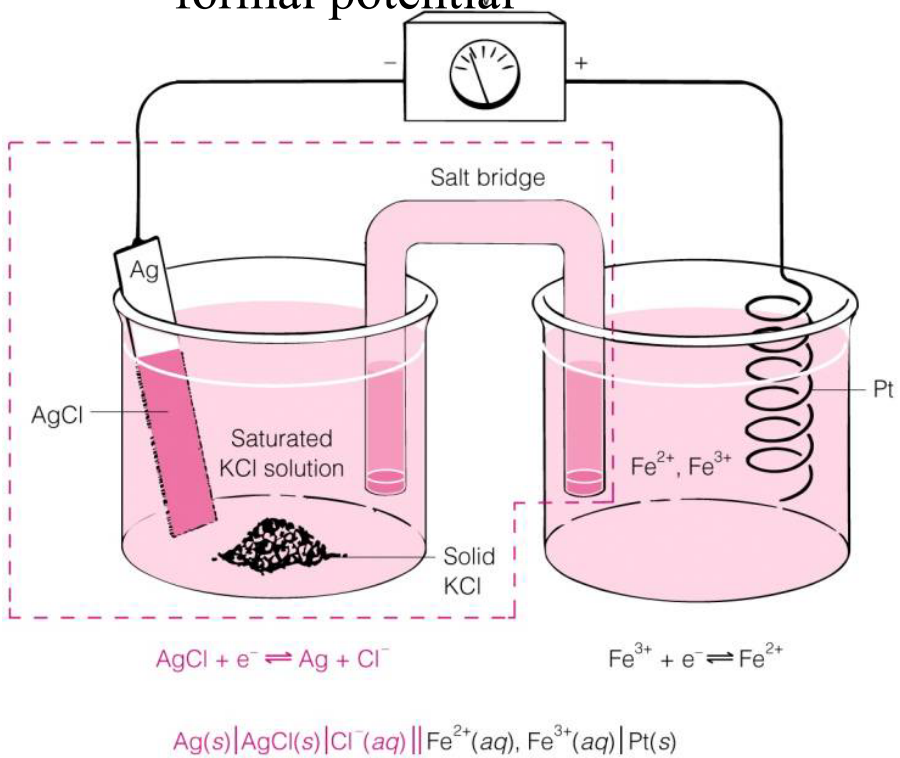
- **Indicator Electrode/Working Electrode**: sensitive to analyte concentration/activity---gives the analytical signal
  - Inert metal Pt (or Au) are typically used to measure redox potentials (ox + ne^- <-----> red); $E_{elect.} = E^o_{ox/red} + (0.0592/n) \log (a_{ox} / a_{red})$
  - Such electrodes also used in voltammetry and amperometry, where analyte comes to surface and is either oxidized or reduced (controlled by potential applied to electrode (electrolytic cell)!
  - electrodes of **first kind** (e.g., Ag^0 to measure silver ion activity, Cu^0 to monitor copper ion activity via potentiometry!
  - **Ion-Selective Membrane Electrodes**----pH, K^+, Ca^{+2}, etc.

- **Reference Electrodes:** electrode with a known stable, half-cell potential, completes the electrochemical cell so the analyte can be measured at the indicator or working electrode-- E_{ref} not affected by sample composition!
  - Examples: 1) S.H.E., 2) Ag/AgCl 3) Calomel



Ag/AgCl Reference Electrode

- formal potential



$$AgCl\ (s) + e^- \rightarrow Ag\ (s) + Cl^-$$
$$E^0 = 0.222\ V$$

Silver chloride salt is spread onto the Ag (metal) electrode as a paste.
Increased contact speeds up the response of the electrode

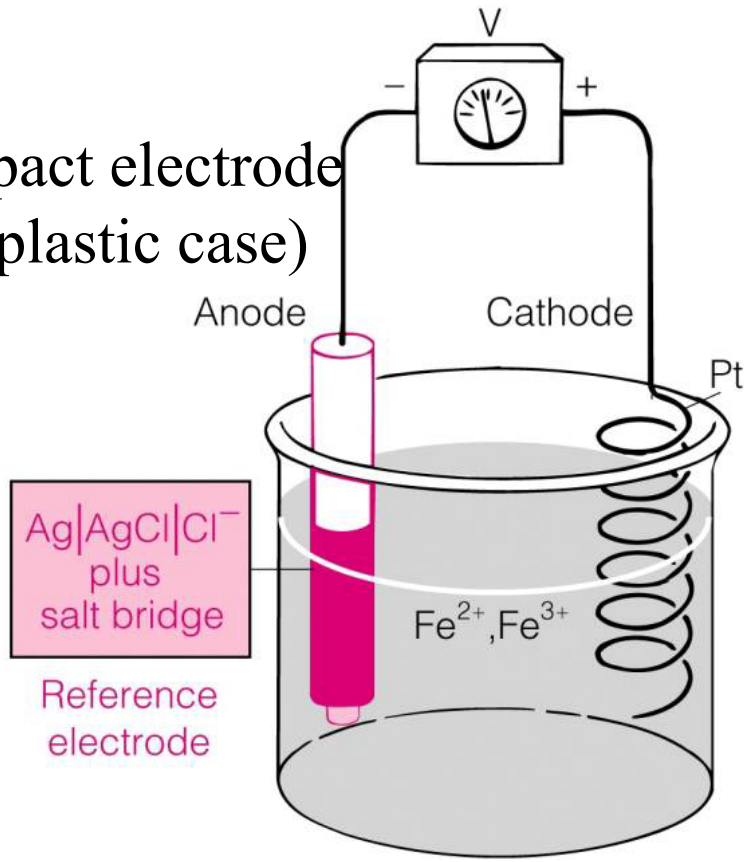
$K_{sp}^{AgCl} = 1.8 \times 10^{-10}$
KCl(sat, 25C)=26.22 wt%
=3.518 M
E_{ref}(KCl, sat)=0.197 V

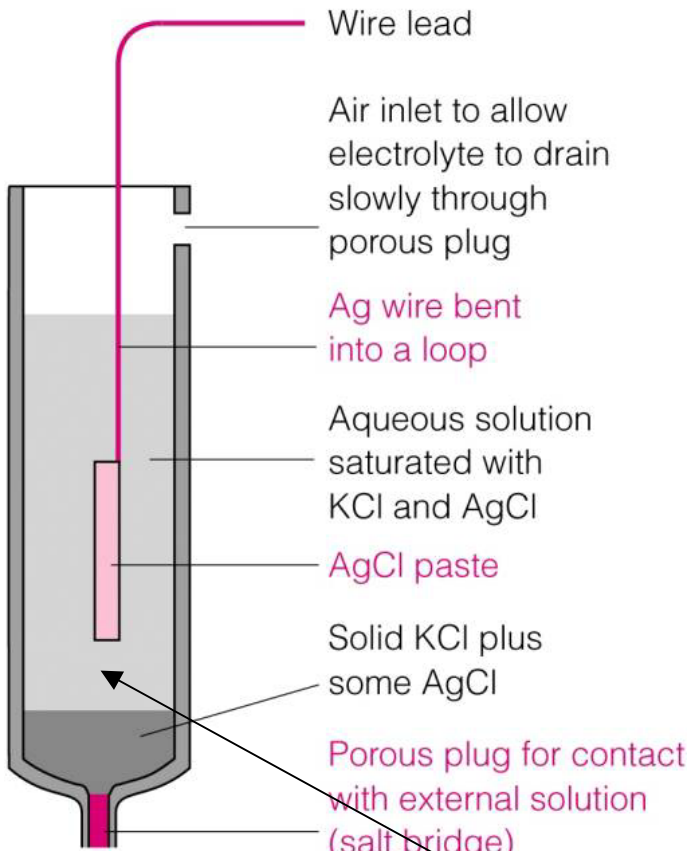
KCl saturated solution
$[Cl^-]$ is constant

formal potential

Compact Electrodes

Compact electrode
(in a plastic case)





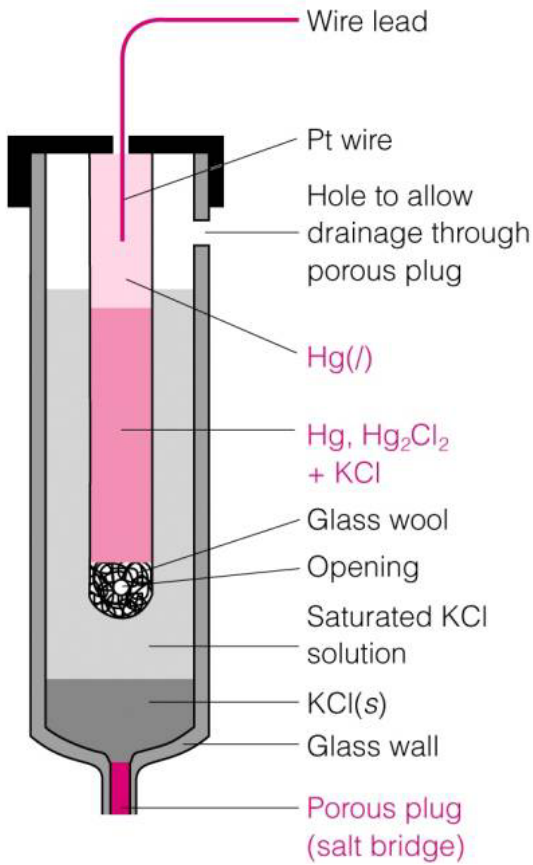
fixed!

salt bridge essential
allows flow of K^+ (or Cl^-) out
maintains electroneutrality

$$E_{ref} = E^o_{Ag/AgCl} - 0.0592 \log a_{Cl^-}$$

Calomel Reference Electrode

- Calomel electrode uses Hg
- Abbreviated, S.C.E. (when electrolyte is Sat'd KCl)
  - Disadvantage, Hg is toxic
  - Advantage, Hg is a liquid, fast response, and easy to clean (Hg, contaminate salts precipitate out)



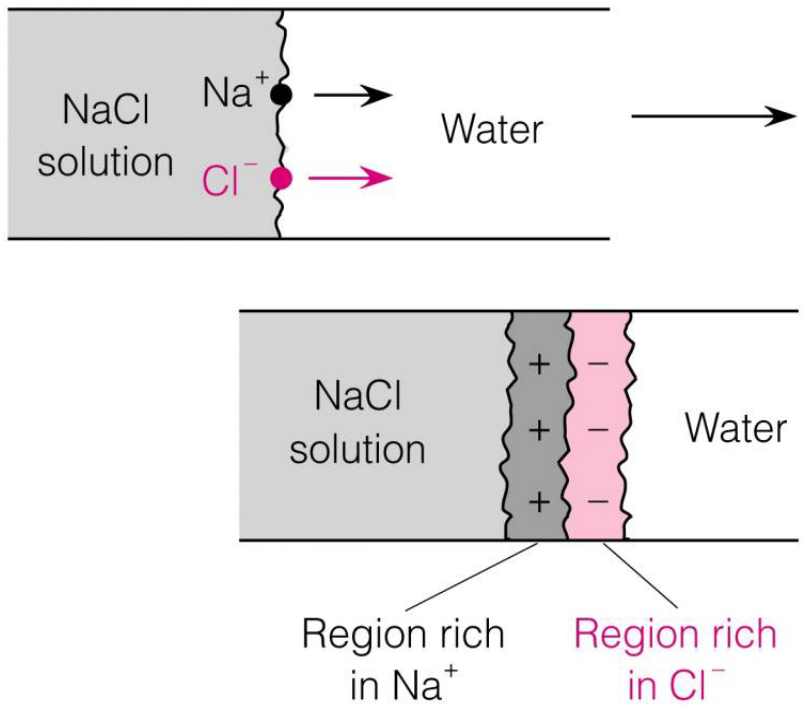
$1/2Hg_2Cl_2 + e^- \rightarrow Hg_{(l)} + Cl^-$ $E^0=0.268$ V

$Hg\ (l)|Hg_2Cl_2(sat'd),KCl\ (x\ M)||$

$E_{ref}(Hg/Hg_2Cl_{2(s)}, KCl\ (sat'd)=0.241$ V

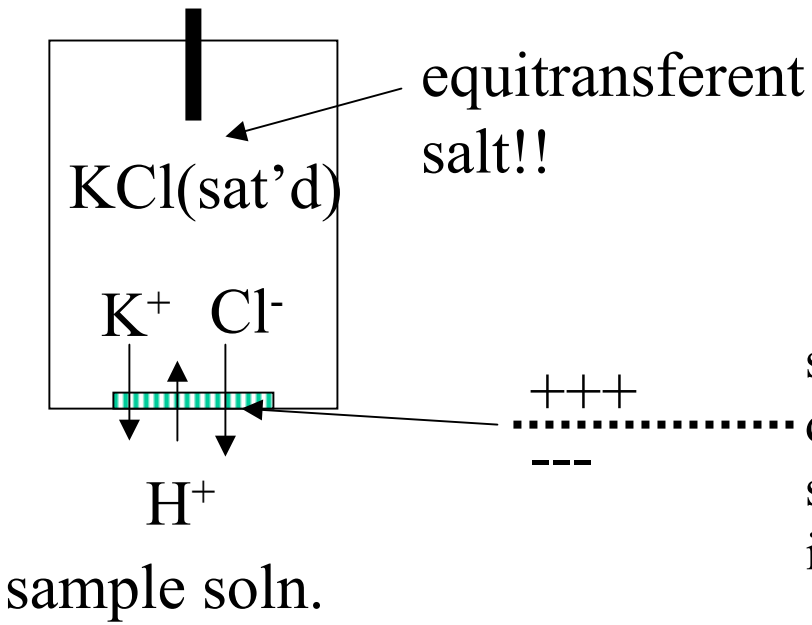
Boundary Layers and Junction Potentials

- Ions diffuse from a region of high ionic strength to a region of lower ionic strength
- Ions will migrate (diffuse) at different rates, depending on their relative charge and size, (z/r)
- Creates regions with higher net negative charge and regions of higher net positive charge at the interface (or junction)
- The difference in local charge represents some work (ΔG free energy), or chemical potential, called a junction potential



All reference electrodes that have their own electrolyte to keep the ion activity constant to yield a fixed half-cell potential----have one additional potential that is not considered when calculating voltage via the Nernst eqn.!

This is call Liquid Junction Potential (E_j)!
It occurs that the interface between the electrolyte solution of the reference electrode, and the sample solution!---
It is due to the different mobilities (diffusion rates) of ions that the interface of the two solutions!



we will ignore junction potentials---but they can cause large errors when sample is very acidic or basic to to high mobility of H^+ and OH^- !!

small voltage difference between solutions due to different rates of ionic diffusion

<u>double junction reference electrodes</u>!---used when you want to prevent leakage of KCl (if you were measuring K^+ or Cl^----would not want these species to leak into sample and change conc.)