Dep. of Chem.- Fac. of Science. **South Valley University**

Course of:

Electrochemistry

English Program - الفرقة الرابعة تربية شعبة الكيمياء

أستاذ المقرر

د/ إبراهيم عبدالله إسماعيل حسن

قسم الكيمياء – كلية العلوم بقنا – جامعة جنوب الوادي

Email: **I.Hassan@bath.edu**

[redacted]

حقوق الطبع والنشر:

لا يجوز طبع وبيع هذا الكتاب الا بموافقة المؤلف الكتابية والا سيتعرض من يخالف ذلك للمحاسبة القانونية.

د. ابراهيم عبد الله إسماعيل حسن

[redacted]

[redacted]

بيـــانـــات أساسية

الكلية: التربية

الفرقة: الرابعة

التخصص: كيمياء

عدد الصفحات: 39

القسم التابع له المقرر : قسم الكيمياء بكلية العلوم بقنا

الرموز المستخدمة

فيديو للمشاهدة. 🎞

والدراسة. للقراءة نص 📖

رابط خارجي. 🔗

أسئلة للتفكير والتقييم الذاتي. ❓

أنشطة ومهام. 📋

تواصل عبر مؤتمر الفيديو. 💻

Contents

List of Tables.

List of Figures.

Chapter 1

Electrochemistry

Electrochemistry– concerned with the reactions that involve electrons.

Video 1: Electrochemistry:

https://www.youtube.com/watch?v=f7ssAiyWV2I&t=1s

Electrode potential

Electrochemical cells consist of two electrodes: an anode (the electrode at which the oxidation reaction occurs) and a cathode (the electrode at which the reduction reaction occurs).

$$Zn \leftrightarrow Zn^{2+} + 2e^{-} \quad \text{(oxidation)}$$

$$Cu^{2+} + 2e^{-} \leftrightarrow Cu_{(s)} \quad \text{(reduction)}$$

$$Cu^{++} + Zn_{(s)} \leftrightarrow Cu_{(s)} + Zn^{++}$$

When a metal immersed into its solution; it dissolves acquiring a negative charge.

$$M \underset{Red}{\overset{Ox}{\rightleftharpoons}} M^{z+} + ze$$

Accordingly, a potential will arise on the electrode so if it is connected in an external circuit; a current will pass.

Figure 1: Dissolving of Zn and Dissolving of Cu^{+2}

In these reactions electrons transfer directly from Zinc metal to copper ions without passing through metallic conductor, so it is impossible to obtain electrical energy.

Electrochemical cells

There are two types of electrochemical cells: galvanic ones, which spontaneously produce electrical energy, and electrolytic ones that consume electrical energy.

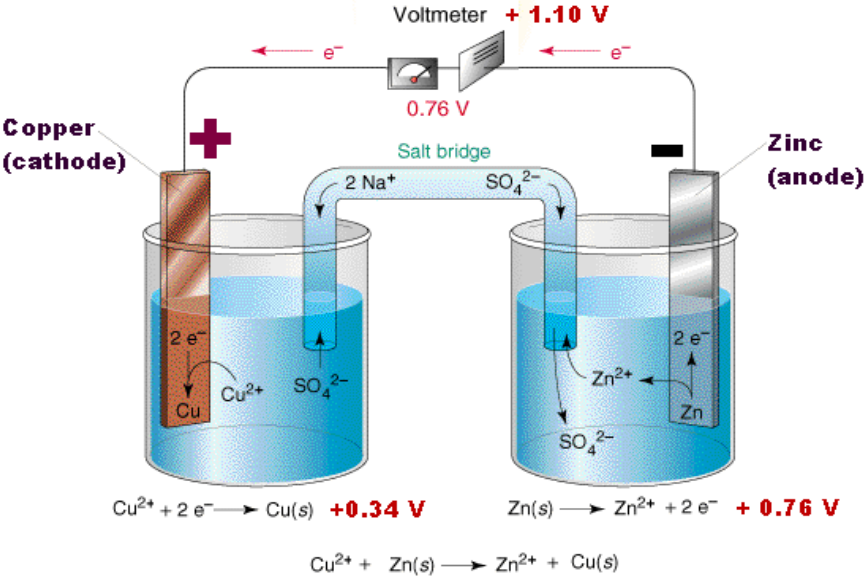


Figure 2: Galvanic Cell of Zn-Cu (Danial cell)

In which an external power supply should be used to pass current through the cell to electrolyse the electrolyte content of ions.

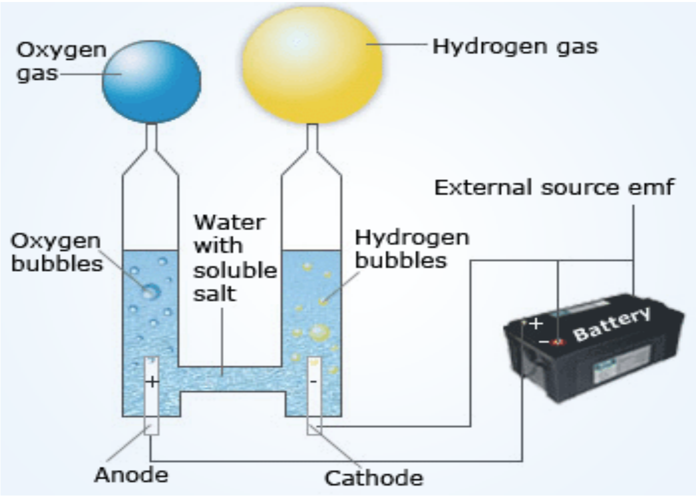


Figure 3: Electrolytic cell for electrolysis of water.

Video 2: Electrochemical cells:

https://www.youtube.com/watch?v=v6HxTu1eQac&t=305s

Origin Electromotive force

Consider a cell represented as:

Metal (a) / Metal (a) ions solution // Metal (b) ions solution / Metal (b)

If the two metal electrodes were connected by a wire, it can be observed the following potential differences:

1. **At connection point between electrodes and wire; this disappears at normal conditions and constant temperature.**
2. **Between metal (a) and solution (a).**
3. **Between metal (b) and solution (b).**
4. **At the junction point between the two solutions (a) and (b) which is the difference in diffusion velocity of ions. This potential can be overcome by using a salt bridge.**

so, the potential of the cell depends only on the potentials of the two electrodes (points 2 and 3).

How does the electrode potential arise?

- **Two factors affect the dissolution of metal in its solution:**

1. **Electric dissolution pressure of the metal ‘P’ which leads to transfer metal ions into solution.**

2. **Osmotic pressure ‘P_s’ which leads to discharge metal ions to precipitate on the electrode.**

The produced positive ions will be close to the electrode surface due to the attraction with the negative charge on the metal surface forming electric double layer (e.d.l).

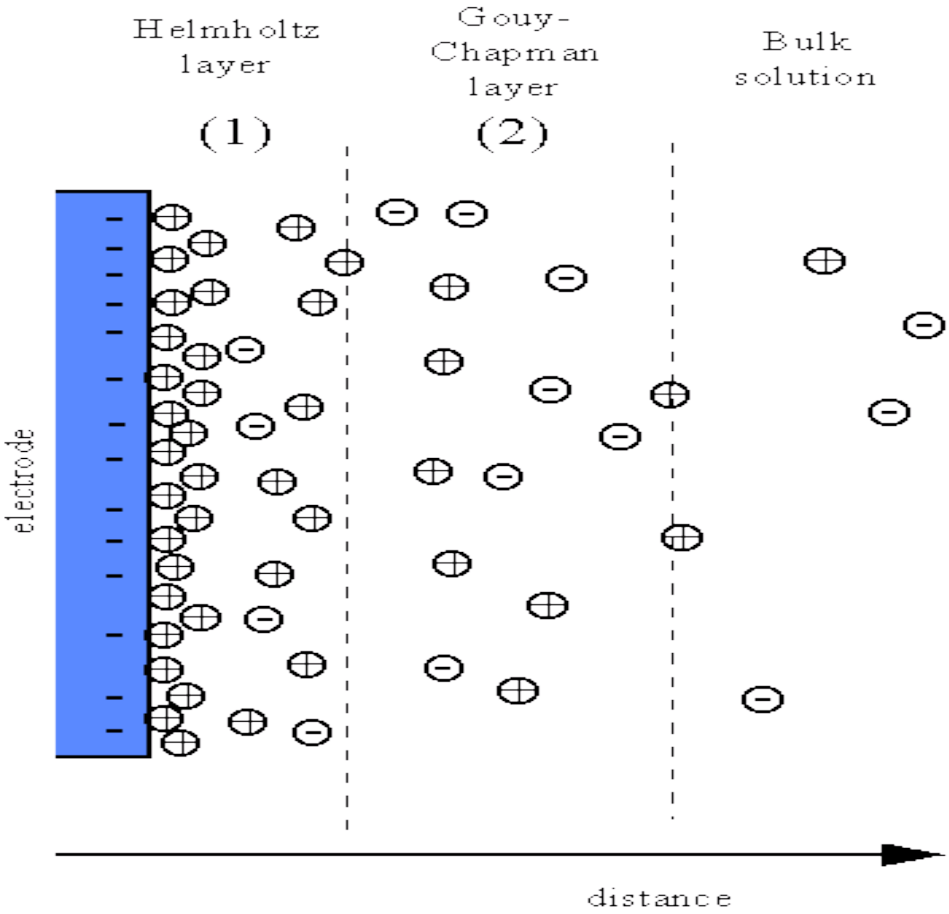


Figure 4: Electric double layer (e.d.l).

- **Osmotic pressure depends on concentration of ions in solution.**

- **Osmotic and electric dissolution pressure depend on the nature of metal.**
  - **Zn…..$P > P_s$**
  - **Cu …..$P_s > P$**
- **The two opposite processes (dissolution and discharge) will continue till reach equilibrium at which the number of dissolved ions equals the number of discharged ions.**
- **$P_{Cu} << P_{Zn}$ and the Osmotic pressure has a considerable effect. So Cu^{++} tend to discharge on Cu electrode which acquires positive charge.**
- **So if it is connected between Zn and Cu Electrodes a current will pass from Zn to Cu cell.**

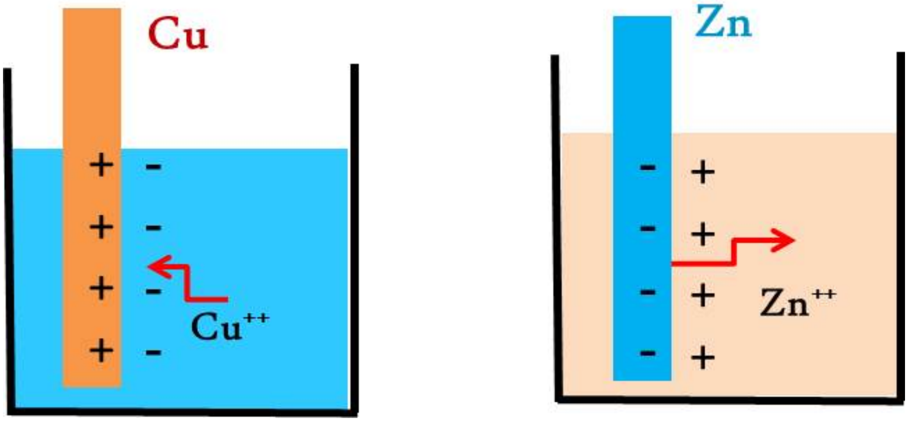


Figure 5: dissolving of Zn and deposition of Cu^{+2} spontaneously.

Single Electrode Potential

- **It is the potential arises between the electrode and its ions solution.**

$$Zn \rightleftharpoons Zn^{++} + 2e^{-}$$

- **It arises from the sum of the oxidation-reduction processes**

- **At Equilibrium the potential difference between metal and its ions depends on:**
- ✓ **Tendency of metal to transfer to its ions in aqueous solution.**
- ✓ **Concentration of metal ions in solution.**
- ✓ **Tendency of metal ions to reduce into its metallic state.**
- **The potential depends on the activity of the metal electrode.**

Zn electrode more negatively charged than H_2 than Cu

Because Zn electrode much active than H_2 than Cu

Standard Electrode Potential

It is the potential of electrode immersed in 1M of its solution.

Gas 1 atm. pressure. Specific potential and can be used as a Reference electrode to measure an electrode potential.

1. Standard Hydrogen Electrode (S.H.E):

Its potential considered as Zero V

1. **Platinum foil.**
2. **Hydrogen gas pressed under 1 atm.**

3. **1M H^+ solution.**
4. **Oxygen capturer.**
5. **Store for H^+ solution.**

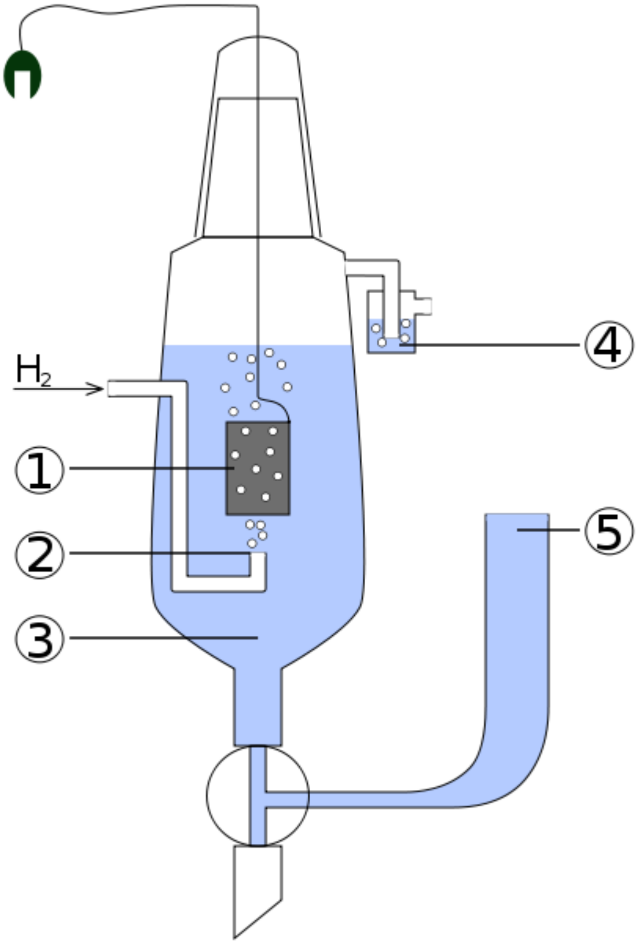


Figure 6: Standard Hydrogen Electrode (S.H.E)

Hydrogen gas tends to transfer into hydrogen ions in solution (Oxidation) and at the same time hydrogen ions tend to gain electrons (Reduction)

$$H_2 \rightleftharpoons 2H^+ + 2e^-$$

2. Calomel Electrode.

1. **Platinum wire.**
2. **Sat KCl.**
3. **Hg + Hg_2Cl_2 + KCl past**
4. **Hg**

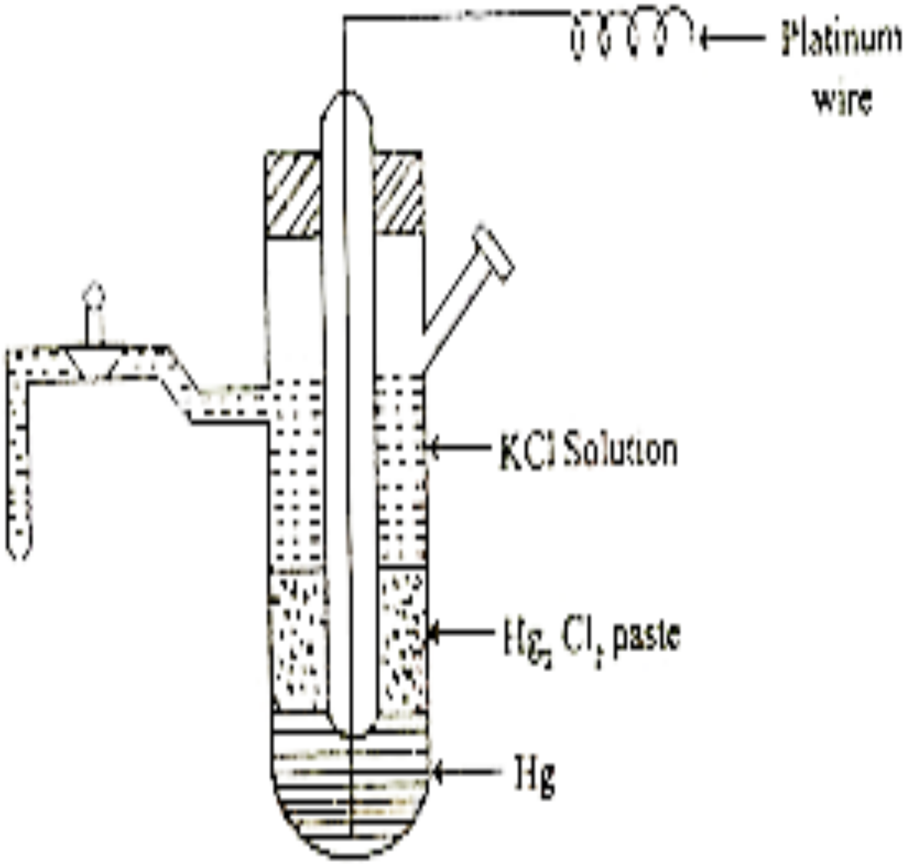


Figure 7: Standard Calomel Electrode.

Calomel electrode can be represented as:

$Hg+Hg_2Cl_2$ / KCl

Types of Calomel electrode:

1. **Deci-Normal calomel electrode: contains 0.1 N KCl.**

$Hg + Hg_2Cl_2$ / KCl (0.1N)

E at 25° C = 0.338 V

2. **Normal calomel electrode: contains 1.0 N KCl and represented as:**

$Hg + Hg_2Cl_2$ / KCl (1.0N)

E, at 25° C = 0.281 V

3. **Saturated calomel electrode contains saturated solution of KCl and represented as:**

$Hg + Hg_2Cl_2$ / KCl (sat.)

E, at 25° C = 0.246 V

It can be noticed that the potential values shift to more negative values by increasing chloride ion concentration according to Nernst eq.

C = 0.1N	0.338 V
C = 1 N	0.281 V
C = Sat.	0.246 V

$$E = E^o + 2.303 \frac{RT}{2F} \log [Hg^{++}]$$

Solubility product of Hg_2Cl_2 $K_{sp} = [Hg^{+2}][Cl^{-2}]$

$$E = E^o + 2.303 \frac{RT}{2F} \log \frac{K_{sp}}{[Cl]^{-2}}$$

$$E = E^o + 2.303\frac{RT}{2F}\log K_{sp} - 2.303\frac{RT}{2F}\log [Cl]^{-2}$$

$$E = E'_0 - 0.059 \log [Cl^-]$$

$$E = E'_o - 0.059 \log [Cl^-]$$

The pot. of calomel electrode is also referred to Standard Hydrogen Electrode (SHE).

Ideal reference electrode:

Ideal reference should have the following characters:

1. **Ease of preparation.**
2. **Rapid attainment of reproducible potential value.**
3. **Stable potential with time and solns.**
4. **Stable with temperature.**
5. **Low polarizability.**

Types of Electrodes

1. **Electrodes of first order (1st type): Metal in its ions** **Ag/Ag^+**

$$E_{Ag} = E^o_{Ag} + 0.0591 \log [Ag^+]$$

Metal should be soft, ductile, freely soluble in mercury e.g Ag, Pb, Cu, Cd, Zn, and Hg.

2. Electrodes of second order (2nd type): when the anion concentration is taken into consideration.

$$Ag/AgCl_{(s)}, Cl^-$$

$$E_{Ag} = E^o_{Ag} + 0.0591 \log [Ag^+]$$

The activity of Ag^+ in presence of AgCl depends on activity of Cl^-

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

$$E = E^o + 0.0591 \log K_{AgCl} - 0.0591 \log [Cl-]$$

3. Electrodes of third order (3rd type):

The electrode involves two slightly soluble salts with a common anion as:

$$Pb/PbC_2O_4(s), CaC_2O_4(s), Ca^{++}$$

This electrode can be used to determine Ca^{++} in potentiometric measurements, and its potential depends on $[Pb^{++}]$

$$E = E^o_{Pb} + \frac{0.0591}{2} \log [P^{b++}]$$

$$[Pb^{++}] = \frac{K_{PbC2O4}}{[C_2O_4^{--}]}$$

$$[C_2O_4^{--}] = \frac{K_{CaC2O4}}{[Ca^{++}]}$$

$$E = E^o_{Pb} + \frac{0.0591}{2} \log \frac{K_{PbC2O4}}{K_{CaC2O4}} + \frac{0.0591}{2} \log [Ca^{++}]$$

These types of electrodes can be extended to include inert metals such as Au and Pt, which immersed in a solution containing ions of redox system (e.g. Fe^{+++}/Fe^{++}) expressed by Nernst equation:

$$Fe^{+++} + e \longrightarrow Fe^{++}$$

$$E = E^{o}_{Fe+3/Fe+2} + 0.0591 \log \frac{Fe^{+++}}{Fe^{++}}$$

Measurement of Electrode Potential

by construction of galvanic cell consists of two half-cells, one of standard electrode (S.H.E) and the other half is the electrode under test in its molar ions' solution.

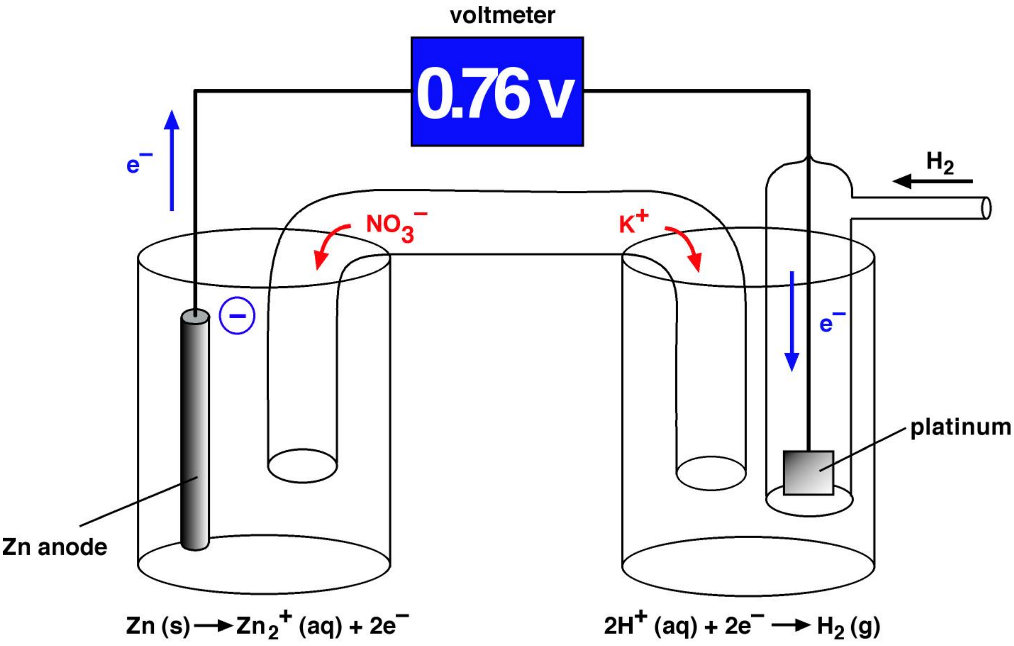


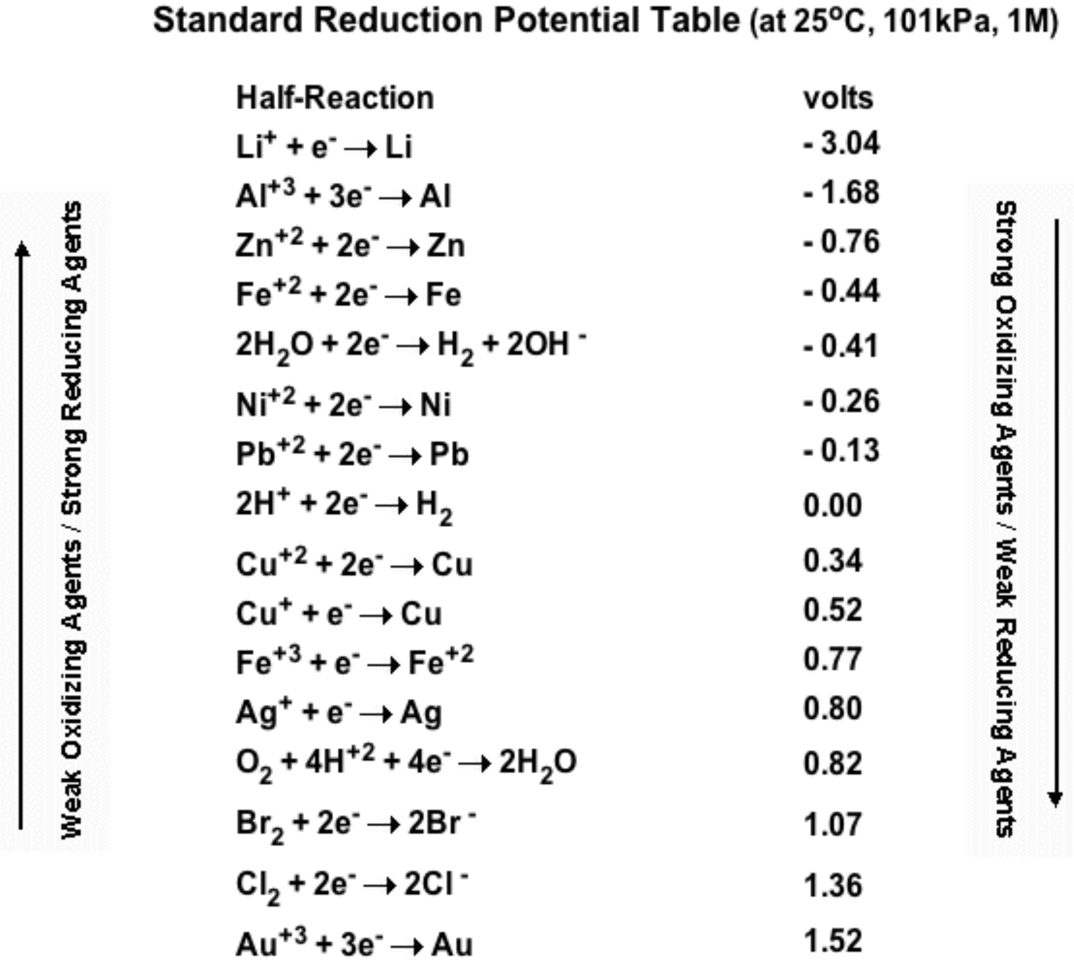
Figure 8: measurement of standard potential of Zn by using Standard Hydrogen Electrode, in a Galvanic cell.

Chapter II

Electromotive Series of the Elements

- **The elements were arranged according to their standard electrode potentials referred to standard hydrogen electrode.**
- **Elements at the top have the most negative potentials (strong reducing agents) and those in the bottom have the most positive potentials (strong oxidizing agents)**

Table 1:



Standard Reduction Potential Table (at 25°C, 101kPa, 1M)

Half-Reaction	volts
$Li^+ + e^- \rightarrow Li$	- 3.04
$Al^{+3} + 3e^- \rightarrow Al$	- 1.68
$Zn^{+2} + 2e^- \rightarrow Zn$	- 0.76
$Fe^{+2} + 2e^- \rightarrow Fe$	- 0.44
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	- 0.41
$Ni^{+2} + 2e^- \rightarrow Ni$	- 0.26
$Pb^{+2} + 2e^- \rightarrow Pb$	- 0.13
$2H^+ + 2e^- \rightarrow H_2$	0.00
$Cu^{+2} + 2e^- \rightarrow Cu$	0.34
$Cu^+ + e^- \rightarrow Cu$	0.52
$Fe^{+3} + e^- \rightarrow Fe^{+2}$	0.77
$Ag^+ + e^- \rightarrow Ag$	0.80
$O_2 + 4H^{+2} + 4e^- \rightarrow 2H_2O$	0.82
$Br_2 + 2e^- \rightarrow 2Br^-$	1.07
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36
$Au^{+3} + 3e^- \rightarrow Au$	1.52

Importance of Electromotive Series

1. **Elements with high negative potentials, at the top, are strong reducing agents and can be easily oxidised.**
2. **Elements with high positive potentials, at the end, are strong oxidising agents and can be easily reduced.**
3. **The reduced form of any element will reduce the oxidized form of any element lie after it in the series.**

Examples:

$$Mg + Cd^{++} \rightleftharpoons Mg^{++} + Cd$$

$$Zn + 2Ag^{+} \rightleftharpoons Zn^{++} + 2Ag$$

$$Zn + Cl_2 \rightleftharpoons Zn^{++} + 2Cl^{-}$$

4. **It can be used to calculate the potentials of the cells as the following example:**

Problems:

Problem 1:

A cell consists of standard Zn half-cell and standard Cu half cell, calculate the potential of the cell?

$$Cu^{++} + 2e \rightleftharpoons Cu \qquad E = +0.34\ V$$

$$Zn^{++} + 2e \rightleftharpoons Zn \qquad E = -0.76\ V$$

Solution:

$$E = E^{+} - E^{-}$$

$$= +0.34 - (-0.76) = +1.10\ V$$

$$Zn + Cu^{++} \rightleftharpoons Zn^{++} + Cu \qquad E = +1.10\ V$$

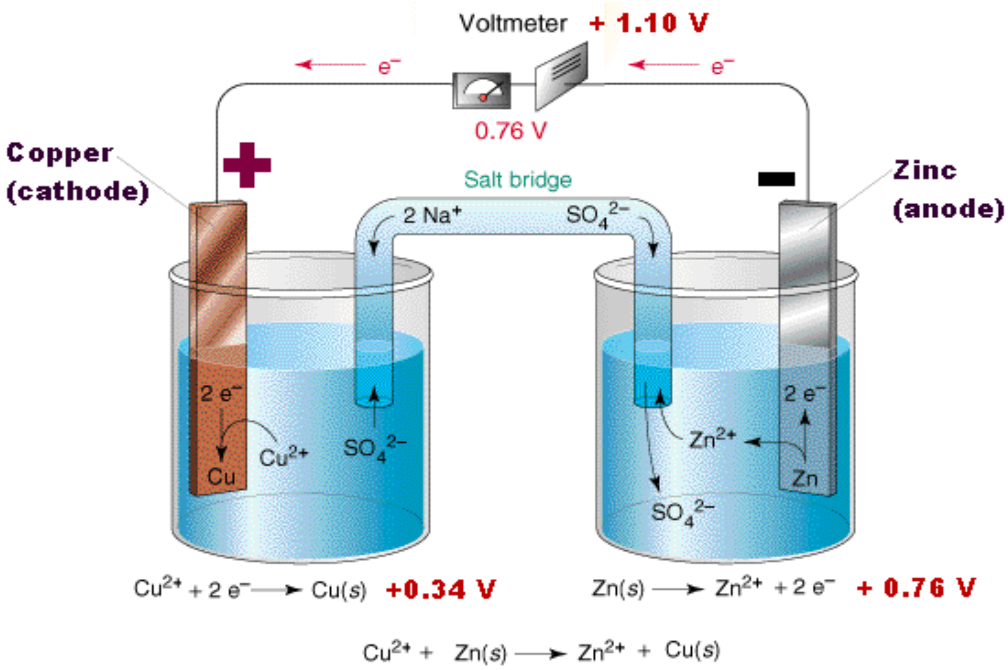


Figure 9: Galvanic Cell of Zn-Cu (Danial cell).

Problem 2:

$$2Ag^{+} + 2e \rightleftharpoons 2Ag \qquad E = +0.8\ V$$

$$Cu^{++} + 2e \rightleftharpoons Cu \qquad E = +0.34\ V$$

$E = E^{+} - E^{-}$

$= +0.8 - (+0.34) = +0.46\ V$

$Cu + 2Ag^{+} \rightleftharpoons Cu^{++} + 2Ag \qquad E = +0.46\ V$

Problem 3:

2 solutions were mixed into one solution contains 1 M from each of the following: Fe++, Fe+++ and Al+++. Al electrode was immersed in this solution, explain if the following reaction will take place, or no?

$$Al + 3Fe^{+++} \rightleftharpoons Al^{+++} + 3Fe^{++}$$

Where:

$$E^{0}_{Al/Al+++} = -1.66\ V \quad \& \quad E^{0}_{Fe++/Fe+++} = +0.77\ V$$

Solution

By subtracting equation (1) from equation (2) gives:

$$Al^{+++} + 3e \rightleftharpoons 3Al \qquad E^{o} = -1.66\ V \quad \ldots\ldots\ldots 1$$

$$3Fe^{+++} + 3e \rightleftharpoons 3Fe^{++} \qquad E^{o} = +0.77\ V \quad \ldots\ldots\ldots. 2$$

$$Al + 3Fe^{+++} \rightleftharpoons Al^{+++} + 3Fe^{++} \ldots..(3) \qquad E_{cell} = +2.43\ V$$

+ve value means the reaction will take place spontaneously in the same direction as written in eq. 3.

Evolution of H_2 from Molar solutions.

Metals lie before hydrogen in electromotive series can replace and evolve hydrogen from acidic solns. (1M).

i.e all half-cells with negative E^o values and a tendency to loss electrons can reduce hydrogen ions to form hydrogen gas.

$$K/K^+ (-2.93) > Na/Na^+ (-2.71) > Fe/Fe^{++} (-0.44) > H_2/H^+ (0.0).$$

Reaction of metals with water ($[H^+] = 10^{-7}$ M):

Some metals with negative E^o can evolve H_2 from water and others with -ve E^o can't.

How can you prove this fact?

The standard potential of water half-cell was found to be -0.41 V.

Examples:

Example 1: Construction a cell consists of Zn Half-cell and standard half-cell of H_2O. the other half cell consists of H_2(1atm) passing in H_2 electrode and immersed in pure water.

$Zn^{++} + 2e \rightleftharpoons Zn$ E = -0.76 V -ve electrode

$2H^+ + 2e \rightleftharpoons H_2$ E = -0.41 V +ve Electrode

$$E_{cell} = E_+ - E_-$$

$$= -0.41 - (-0.76) = +0.35 \text{ V}$$

$$Zn + 2H^+ \rightleftharpoons Zn^{++} + H_2 \quad E = +0.35 \text{ V}$$

$$\underset{-0.76}{Zn/Zn^{++} (1M)} \quad // \quad \underset{-0.41}{H^+ (10^{-7} M) / H_2 (1 atm) + Pt}$$

Example 2

$Sn^{++} + 2e \rightleftharpoons Sn$ E = -0.14 V +ve Electrode

$2H^{+} + 2e \rightleftharpoons H_2$ E = -0.41 V -ve Electrode

H^{+} (10^{-7} M) / H_2 (1 atm) + Pt // Sn^{++} (1M) / Sn

-0.41 -0.14

Ecell = E^{+} - E^{-}

= -0.14 - (-0.41) = + 0.27 V.

So, $H_2 + Sn^{++} \rightleftharpoons 2H^{+} + Sn$ E = +0.27 V

So, Sn can't replace and evolve H_2 from water.

Position of water half-cell among other half-cells.

K/K^{+} (-2.93) > Na/Na^{+} (-2.71) > Fe/Fe^{++} (-0.44) >

H_2/H^{+} (10-7M, -0.41V) > Sn/Sn^{++} (-0.14) > H_2/H^{+} (0.0)

Chapter III

Reversible and irreversible cells

• Reversible cells

Such as Daniel cell:

$$Zn / Zn^{++}(1M) // Cu^{++}\,(1M) / Cu$$

Zn dissolve to Zn^{++} and Cu^{++} deposited,

$$Zn \rightleftharpoons Zn^{++} + 2e^{-}$$

$$Cu^{++} + 2e \rightleftharpoons Cu$$

$$Zn + CuSO_4 \rightleftharpoons ZnSO_4 + Cu$$

but by-passing equal amount of current in the opposite side; Zn^{++} will deposit and Cu will dissolve.

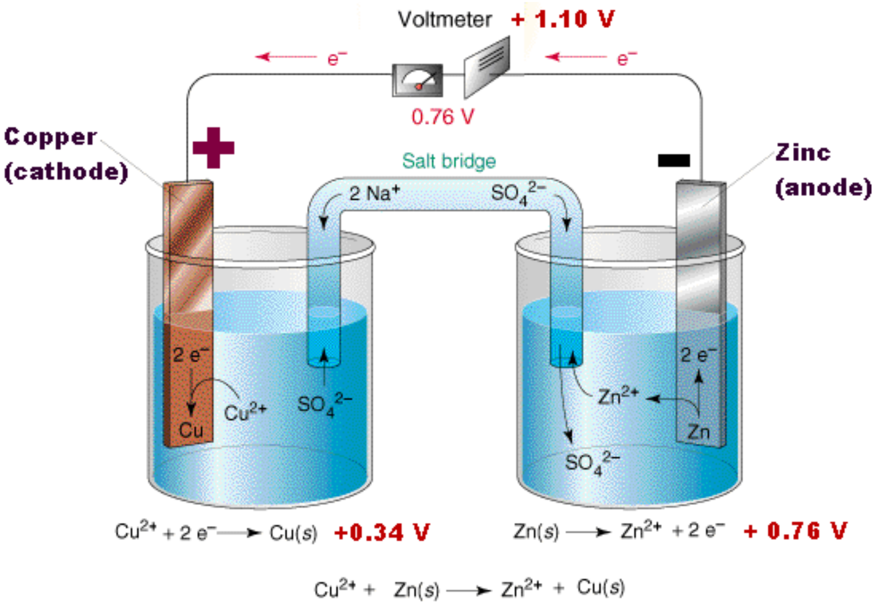


Figure 10: Daniel galvanic cell as an example of reversible electrochemical cell.

• Irreversible cells

$$Zn \,/\, H_2SO_4, aq \,/\, Cu$$

Zn dissolve to Zn^{++} and H_2 evolved,

$$Zn \rightleftharpoons Zn^{++} + 2e^-$$

$$2H^+_{(l)} + 2e \longrightarrow H_{2\,(g)} \uparrow$$

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

$$Cu + H_2SO_4 \xrightarrow{+i} CuSO_4 + H_2$$

- **The maximum electrical work can be obtained from reversible cells according to thermodynamic principles can be expressed as:**

$$W = nEF = -\Delta G$$

$-\Delta G$ is the change in free energy

Effect of concentration on the half cells potentials.

- **Consider a cell consists of Zn half-cell and H_2 half-cell.**

$$\mathrm{Zn} / \mathrm{Zn}^{++}(1\mathrm{M}) // \mathrm{H}^{+}(1\mathrm{M}) / \mathrm{H}_2(1\mathrm{atm}) + \mathrm{Pt}$$

- **If some of Zn^{++} ions were removed and its conc. became less than 1M, while H_2 conc. still constant; the tendency of Zn dissolving will increase.**

e.g

- **Decreasing the conc. of Zn from 1M to 0.1M; the measured potential will decrease (to more –ve side) by 0.03 V.**

$$-0.76-0.03 = -0.79 \text{ V}$$

- **Increasing the conc. of Zn to more than 1M will increase its potential to the positive side; less negative than -0.76 (shifts to more +ve side).**

The relation between electrical potential and concentration of ions ‘Nernst Equation

- **E depends on dissolution pressure and osmotic one.**
- **Metal with diss. Pressure P immersed into its soln. with P_s. Difference between P and Ps is E. conc. of ions is C.**
- **When an electrical current passed reversibly between the electrode and solution till a gram ion of metal was dissolved and the work done in this process is:**

$$W = nEF \ldots\ldots\ldots (1)$$

- **If P_s is changed from P_s to $(P_s - dP_s)$ by decreasing the ions; the potential will decrease from E to E-dE and work will be:**

$$W' = nF(E - dE) \ldots\ldots\ldots (2)$$

So, the work done in the first step is more than that done in the second one, and the decrease of work is given by:

$$W - W' = nEF - nF(E - dE) = nFdE$$

This work equivalent to work needed to transfer a gram ion of solute from one soln (P_s) to another $(P_s - dP_s)$.

Osmotic work is given by VdP_s, where V is the volume of solvent containing gram ion of solute.

$$nFdE = VdP_s \ \ldots\ldots\ldots\ (3)$$

Suppose the solutions are ideal and obey the general law of solutions (gases)

$$P_sV = RT$$

Or

$$V = RT/P_s$$

From eq. 3

$$nFdE = RT.\ dP_s/p_s$$

By integration:

$$\int nFdE = RT\int dPs/p_s$$

$$nFE = RT.\ \ln P_s + constant \ldots\ldots\ldots (4)$$

$$nFE = RT.\ \ln P_s + constant$$

The constant can be determined by taking into consideration that:

If Ps = P, so E = 0

$$0 = RT.\ \ln P + constant$$

$$Constant = -RT \ln P$$

From eq.4

$$nFE = RT.\ \ln P_s + constant$$

$$nFE = RT.\ \ln P_s - RT \ln P$$

$$= RT \ln P_s/P$$

Or

$$E = RT/nF \ln P_s/P \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

If the same electrode was immersed into another soln (C' conc.) and P_s', the pot. E' can be obtained by similar eq.

$$E' = RT/nF \ln P_s'/P \ \ldots\ldots(6)$$

By subtracting eq 6 from 5:

$$E-E' = RT/nF \ln P_s/P \ - \ RT/nF \ln P_s'/P$$

$$E - E' = RT/nF \ln P_s/P_s'$$

Osmotic pressure proportional to conc of ions.

Ps α C & P_s' α C'

$$P_s/P_s' = C/C'$$

$$E - E^{`} = RT/nF \ \ln C/C'$$

If the conc. C' = eq.gm/L then $E' = E^o$ (standard electrde pot.)

$$E = E^o + RT/nF \ \ln C$$

$$\underline{E = E^o + 2.303RT/nF \ \log C}$$

This called Nernst Equation which applied for metallic electrodes.

$$E = E^o + 2.303RT/nF \ \log C$$

If the electrode is non-metal the eq becomes:

$$E = E^o - 2.303RT/nF \ \log C$$

Or in General

$$E = E^o \pm 2.303RT/nF \ \log C$$

The difference in sign in each case (metals and non-metals) depends on the reduced and oxidized forms of elements. Ions of metals are in oxidized form while for non-metals are in reduced form.

Nernst Eq. could be written as:

$$E = E^{o\,+}\, 2.303RT/nF \ \log a$$

Where a is the activity of ions which represents the part of concentration of ions able to reach the electrode surface.

The value of 2.303RT/nF was calculated at 25°C for monovalent ions to be:

$$= 2.303 \times 8.32 \times 298/1 \times 96500 = 0.0591$$

For divalent ions = 0.02955

For Trivalent ions = 0.0197

Accordingly; E of Electrode will shift to more positive or negative side with a value 0.0591 if the concentration of ions increased or decreased to ten times of its initial value.

For divalent and trivalent ions the shifts will become 0.0295 and 0.0197 respectively under such conditions.

By plotting the electrode pot E against log C, a straight line is obtained with slops as it is shown:

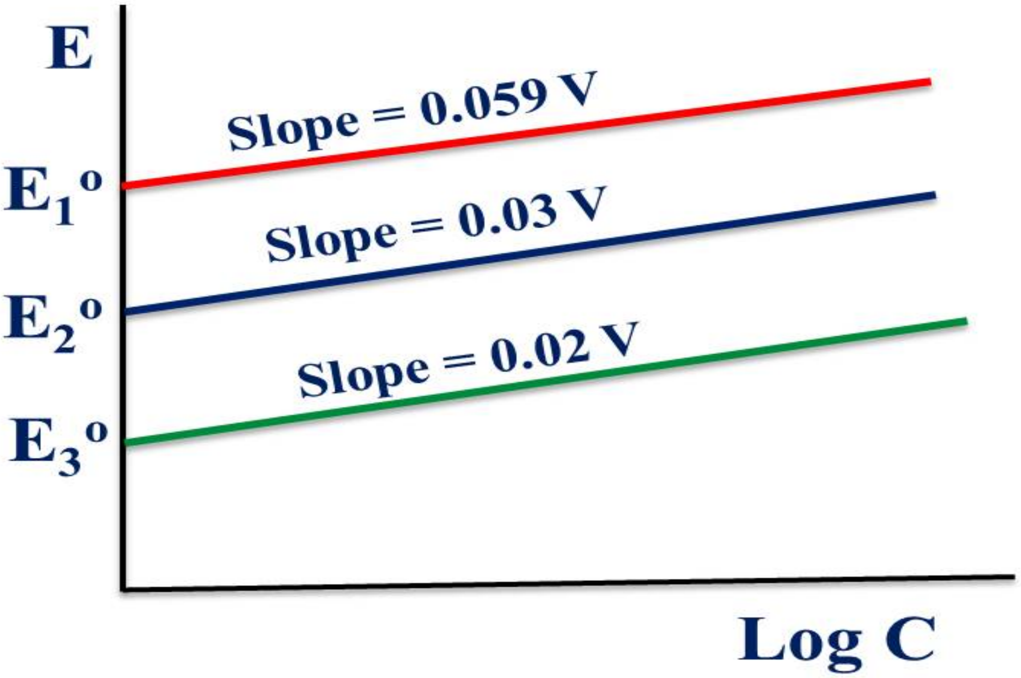


Figure 11: Potential-Concentration relationship diagram, which confirms Nernst Concept.

Chapter IV

Concentration Cells

- **The half-cell potential depends on the concentration of ions.**

Metal (a) / Metal ions soln. a1 // Metal ions soln. a2 / Metal (a)

e direction →

Zn / 0.1M Zn^{++} // 1 M Zn^{++} / Zn

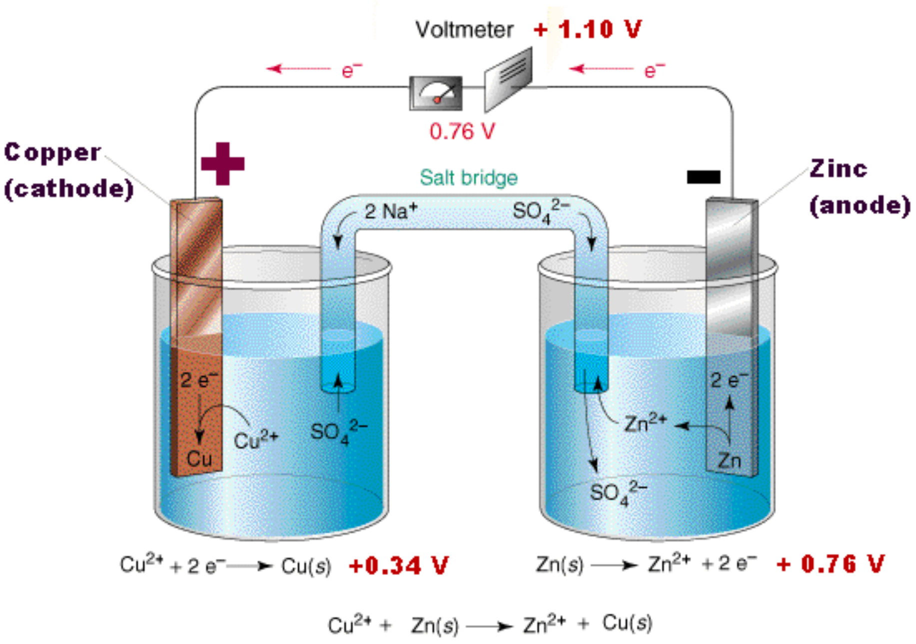


Figure 12: Daniel galvanic cell.

- **If the metal is divalent:**

$$E_1 = E^o + 2.303 \frac{RT}{2F} \log a_1$$

$$E_2 = E^o + 2.303 \frac{RT}{2F} \log a_2$$

- **The electromotive force of the cell:**

$$E = E_2 - E_1 = 2.303 \frac{RT}{2F} \log \frac{a_2}{a_1}$$

The expression is correct if the cell doesn't involve a junction potential which arises from the concentration gradient which can be neglected by:

- **Velocity of anions = velocity of cations**
- **Use of salt bridge.**

If the cell involves junction potential: electric DL will arise at the junction point between the two solutions causing extra pot.

$$E = E_2 - E_1 + E_3$$

E_3 is the junction pot arises between diluted an concentrated solutions.

E_3 given by:

$$E_3 = \frac{uc - ua}{uc + ua} . 2.303 \frac{RT}{F} \log \frac{a_1}{a_2}$$

a_1 and a_2 are the activities of cations in two solutions uc and ua are the velocities of cations and anions respectively.

So, the cell potential E_t (t = total) is given by:

$$E_t = (2.303\frac{RT}{F}\ \log\frac{a_2}{a_1}) + (\frac{uc - ua}{uc + ua}\ .\ 2.303\frac{RT}{F}\ \log\frac{a_1}{a_2})$$

$$E_t = (2.303\frac{RT}{F}\ \log\frac{a_2}{a_1}) - (\frac{uc - ua}{uc + ua}\ .\ 2.303\frac{RT}{F}\ \log\frac{a_2}{a_1})$$

E_t given by:

$$E_t = (2.303\frac{RT}{F}\ \log\frac{a_2}{a_1})\ (1 - \frac{uc - ua}{uc + ua})$$

$$E_t = (2.303\frac{RT}{F}\ \log\frac{a_2}{a_1})\ (\frac{uc + ua\ -\ uc + ua}{uc + ua})$$

$$E_t = \frac{2\ ua}{uc + ua}\ .\ 2.303\frac{RT}{F}\ \log\frac{a_2}{a_1}$$

From the two values of cell potential in absence and presence of junction potential, the transport number of cations and anions can be calculated by dividing the second equation by the first one:

$$\frac{E_t}{E} = (\frac{2\ ua}{uc + ua}\ .\ 2.303\ \frac{RT}{F}\log\frac{a_2}{a_1}) \Big/ (2.303\ \frac{RT}{F}\ \log\frac{a_2}{a_1})$$

$$\frac{E_t}{E} = \frac{2ua}{ua + uc}$$

Example:

Calculate the potential of the following cell at 18° C:

Ag / $AgNO_3$ (0.1N) // $AgNO_3$ (0.01N) Ag

Where:

Ion transport of nitrate (ua) = 0.528

a_2 (activity coefficient) of $AgNO_3$ (0.1 N) = 0.072

a_1 (activity coefficient) of $AgNO_3$ (0.01 N) = 0.009

Solution:

$$E_t = \frac{2\,ua}{uc + ua} \;.\; 2.303\frac{RT}{F} \;\log\frac{a_2}{a_1}$$

$$E_t = 2 \times 0.528 \times 0.577 \;\log\frac{0.072}{0.009} = 0.55\ V$$

Cells of amalgam electrodes:

Metal dissolves in Mercury as atoms forming amalgam.

If metal amalgam electrode was immersed in solution containing ions of that metal; the potential of the cell depends on:

1. **Concentration of metal ions in the soln.**
2. **Concentration of metal atoms in the amalgam.**

If two amalgam electrodes containing different concentrations of metal in mercury (C_1 & C_2); the produced energy of the formed cell will depend on the work done to transfer the dissolved metal atoms from one amalgam at conc C_1 to the other amalgam with conc C_2.

The potential of such a cell can be driven by:

$$E = 2.303 \frac{RT}{F} \log \frac{C_1}{C_2}$$

Where $C_1 > C_2$

Metal – Metal Oxide electrode

- **When a metal is covered by its oxide, the potential of such system can alter according to Hydrogen concentration.**
- **Hydrogen is in equilibrium with ion in soln.**

$$H_2 \rightleftharpoons 2H^+ + 2e^-$$

- **Also, Oxygen electrode is in equilibrium with OH^- in soln.**

$$O_2 \rightleftharpoons 2O + 4e^- \rightleftharpoons 2O^{--} + 2H_2O \rightleftharpoons 4OH^-$$

- **So, the potential of Oxygen electrode depends on the concentration of hydroxyl ion (OH^-).**

- **$[OH^-]$ depends on $[H^+]$**

$$H_2O \rightleftharpoons OH^- + H^+$$

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

- **So, potential of Oxygen electrode will depend on the hydrogen ion concentration in the soln.**

- **Oxygen electrode can be prepared by the same way as hydrogen one. So, its potential depends also on the partial pressure of oxygen passing through electrode in soln.**
- **Metal – Metal oxide electrode can be considered as oxygen electrode at partial pressure equals the dissociation pressure of oxide.**
- **The potential of metal-metal oxide electrode can be calculated from Nernst eq.**

$$E = E'_0 + 2.303 \frac{RT}{F} \log [H^+]$$

$$E = E'_0 - 2.303 \frac{RT}{F} pH$$

This relation can be driven as the following:

- **Suppose Metal-Oxide is MO and its reaction with hydrogen:**

$$MO + 2H^+ = M^{++} + H_2O$$

$$K = \frac{[M^{++}] [H_2O]}{[MO] [H^+]^2}$$

Suppose that H_2O and MO (solid) present in sufficient amounts and their activities can be considered to equal 1, then:

$$[M^{++}] = K[H^+]^2$$

By multiplying the two sides by $[OH^-]^2$:

$$[M^{++}] [OH^-]^2 = K[H^+]^2 [OH^-]^2$$

$K_{sp(M(OH)2)} = [M^{++}] [OH^-]^2$

$$K_w = [H^+] [OH^-] \quad \cdots\cdots \quad K^2_w = [H^+]^2 [OH^-]^2$$

$$K = \frac{K_{sp}}{K^2_w} \qquad K_{sp} = K.K^2_w$$

By applying Nernst eq.:

$$E = E^o + 2.303\frac{RT}{2F}\log[M^{++}]$$

$$E = E^o + 2.303\frac{RT}{2F}\log K[H^+]^2$$

$$E = E^o + 2.303\frac{RT}{2F}\log K + 2.303\frac{RT}{2F}\log[H^+]^2$$

$$E = E^o + 2.303\frac{RT}{2F}\log\frac{K_{sp}}{K^2_w} + 2.303\frac{RT}{F}\log[H^+]$$

The values E^o, K_{sp}, K_w are constant = $E`_o$

$$E^o + 2.303\frac{RT}{2F}\log\frac{K_{sp}}{K^2_w} = \text{constant} = E`_o$$

$$E = E`_o + 2.303\frac{RT}{F}\log[H^+]$$

$$\boxed{E = E`_o - 0.0591\,pH \qquad \text{at } 25^oC}$$

From the last equation, it can be concluded that, potential of metal-metal oxide doesn't depend on the metal valence.

References:

1. **Joseph Wang, “Analytical Electrochemistry”, Third Edition, SBN:9780471678793, Published by John Wiley & Sons, Inc., Hoboken, New Jersey. Published simultaneously in Canada, 2006.**
2. **V. S. BAGOTSKY “Fundamentals of Electrochemistry”, Second Edition, Published by John Wiley & Sons, Inc., Hoboken, New Jersey Published simultaneously in Canada, 2006.**

Dep. of Chem.- Fac. of Science. **South Valley University**

Course of:

Instrumental Analysis

الفرقة الرابعة تربية شعبة الكيمياء - English Program

اعداد أستاذ المقرر:

د/ إبراهيم عبدالله إسماعيل حسن

قسم الكيمياء – كلية العلوم بقنا – جامعة جنوب الوادي

Email: I.Hassan@bath.edu

WhatsApp:. +1 (416)-948-9468

العام الجامعي

2022 / 2023م

بيـــانـــات أساسية

الكلية: التربية

الفرقة: الرابعة

التخصص: كيمياء

عدد الصفحات: 43

القسم التابع له المقرر : قسم الكيمياء بكلية العلوم بقنا

الرموز المستخدمة

🎞 **فيديو للمشاهدة.**

📖 نص للقراءة والدراسة.

🔗 **رابط خارجي.**

❓ **أسئلة للتفكير والتقييم الذاتي.**

📋 **أنشطة ومهام.**

🖥 **تواصل عبر مؤتمر الفيديو.**

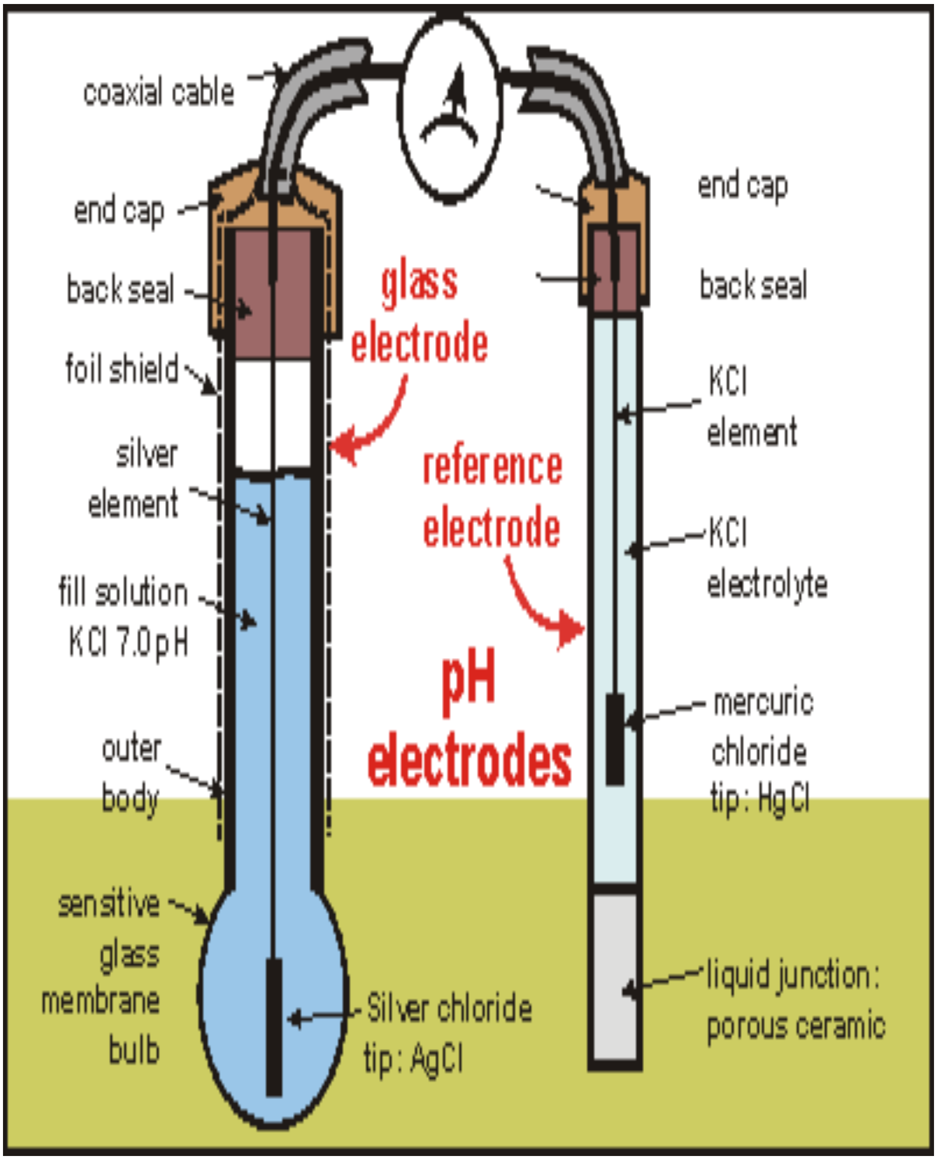
Contents

List of Figures.

List of Videos

Chapter I

Potentiometry



Potentiometry

Determines concentrations by measuring the potential (i.e., voltage) of an electrochemical cell (galvanic cell).

Two electrodes are required:

1. **Indicator Electrode – potential responds to activity of species of interest.**
2. **Reference Electrode – chosen so that its potential is independent of solution composition.**

Electrode potential

When a metal immersed into its solution; it dissolves acquiring a negative charge.

$$M \underset{Red}{\overset{Ox}{\rightleftharpoons}} M^{z+} + ze$$

Accordingly, a potential will arise on the electrode so if it is connected in an external circuit; a current will pass.

Video 1: Potentiometry

https://youtu.be/xH5noYAOGio

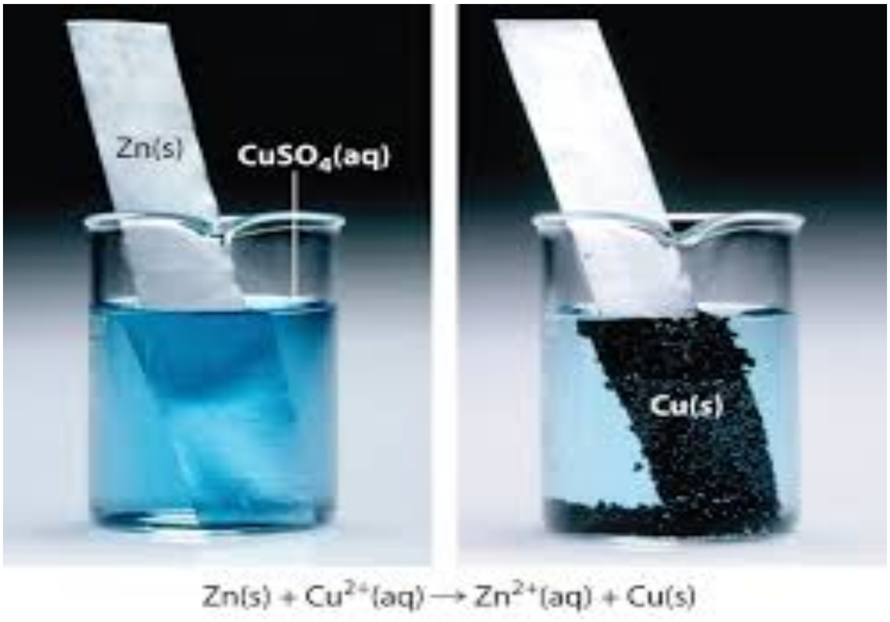


Figure 1: Dissolving of Zn and Dissolving of Cu^{+2}

In these reactions electrons transfer directly from Zinc metal to copper ions without passing through metallic conductor, so it is impossible to obtain electrical energy.

Electrochemical cells

There are two types of electrochemical cells: galvanic ones, which spontaneously produce electrical energy and electrolytic ones that consume electrical energy, in which an external power supply should be used to pass current through the cell to electrolyse the electrolyte content of ions.

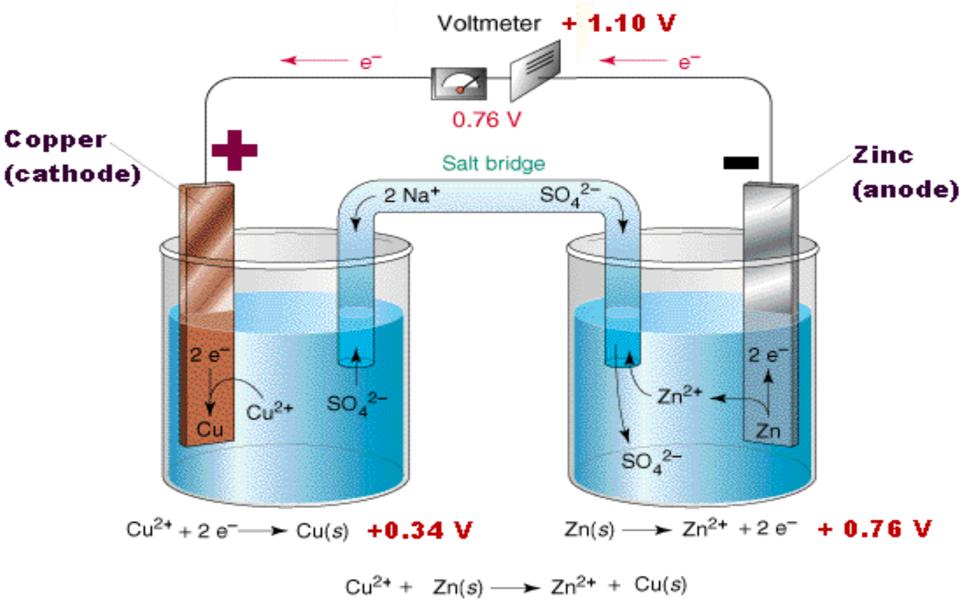


Figure 2.: Galvanic Electrochemical cell (Daniel Cell).

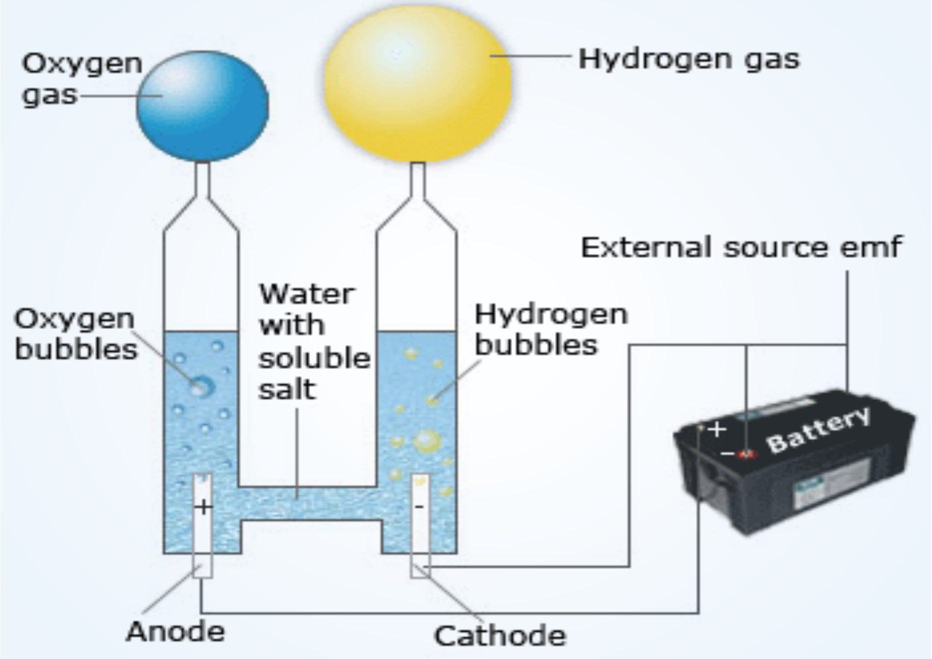


Figure 3.: Electrolytic Electrochemical cell

In Potentiometry, it should be differentiated between two concepts:

1) **Potentiometric Systems – measure potential of a galvanic cell (produces electricity spontaneously).**
2) **Voltametric Systems – control potential & usually measure current in an electrolytic cell (consumes power to cause an electrochemical reaction to occur).**

pH measurements

pH Electrode

$K_w = [H^+] [OH^-] = 10^{-14}$ pH = - log $[H^+]$

Neutral Solution $[H^+] = 10^{-7}$ M

pH = - log $10^{-7} = 7$

Strong Base: $[H^+] = K_w / [OH^-] = 10^{-14} / 1 = 10^{-14}$ pH = 14

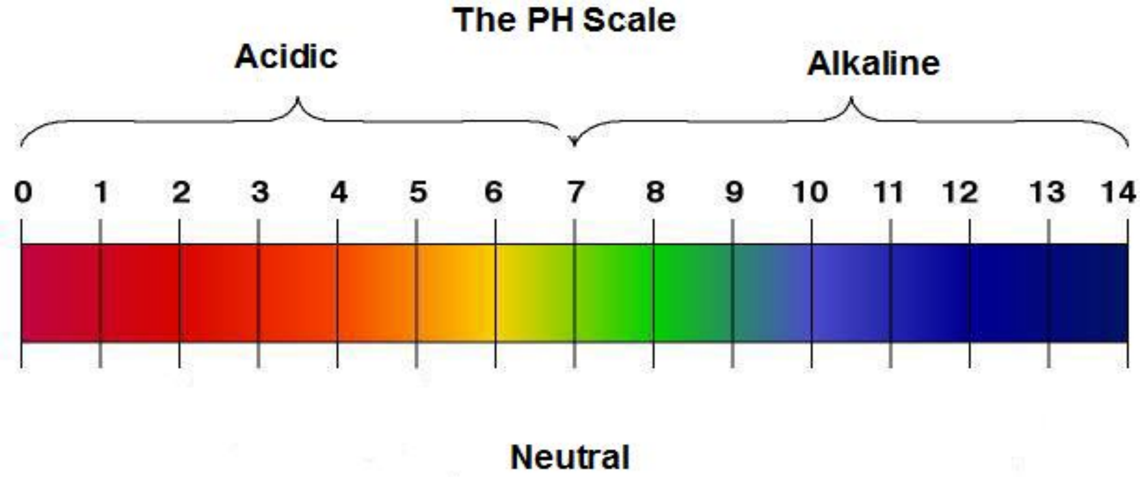


Figure 4.: The pH Scale

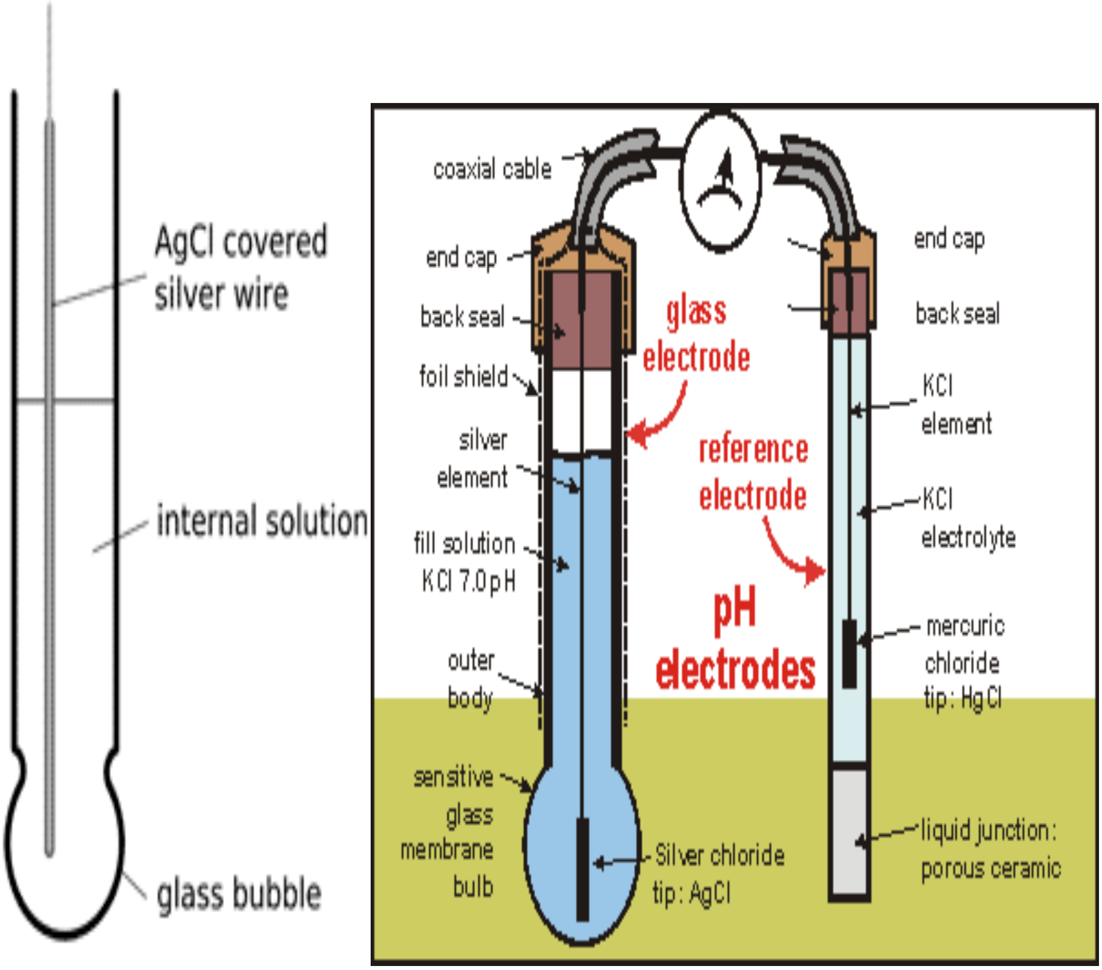


Figure 5.: The pH electrode separated from reference electrode

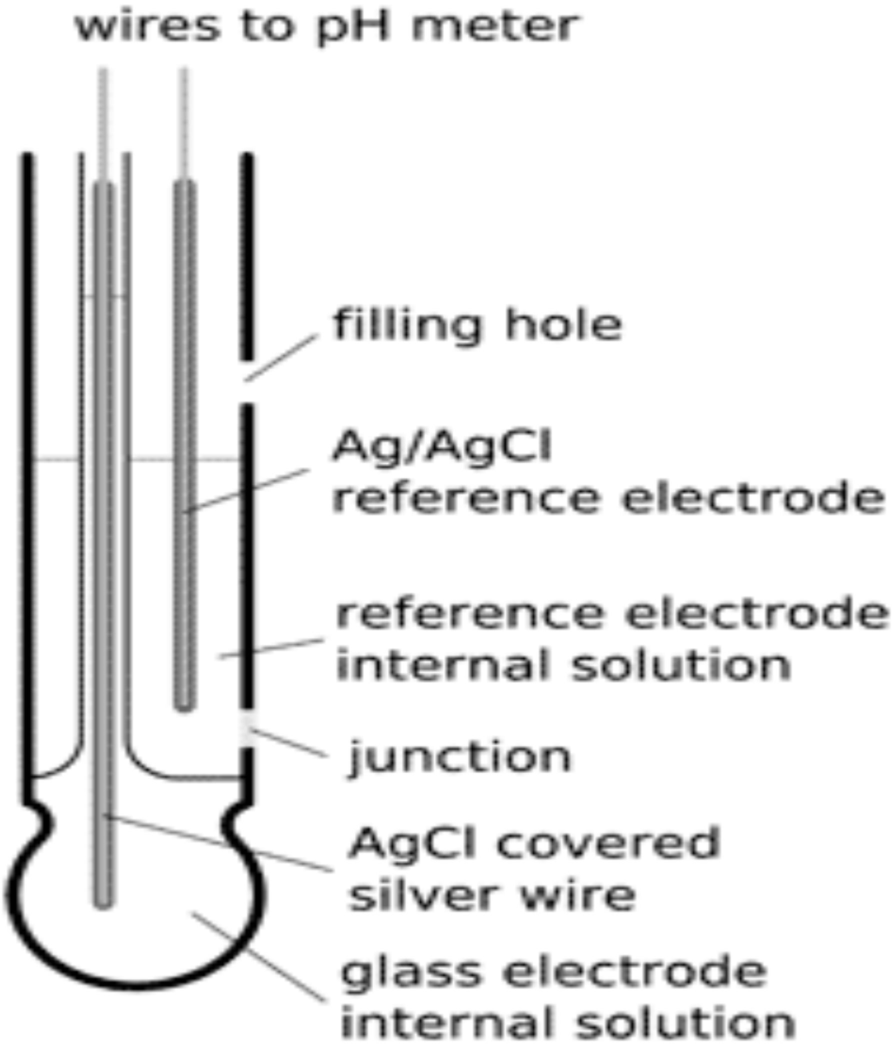


Figure 6.: The pH electrode combined with reference electrode

Video 2: pH electrode1: 🎞

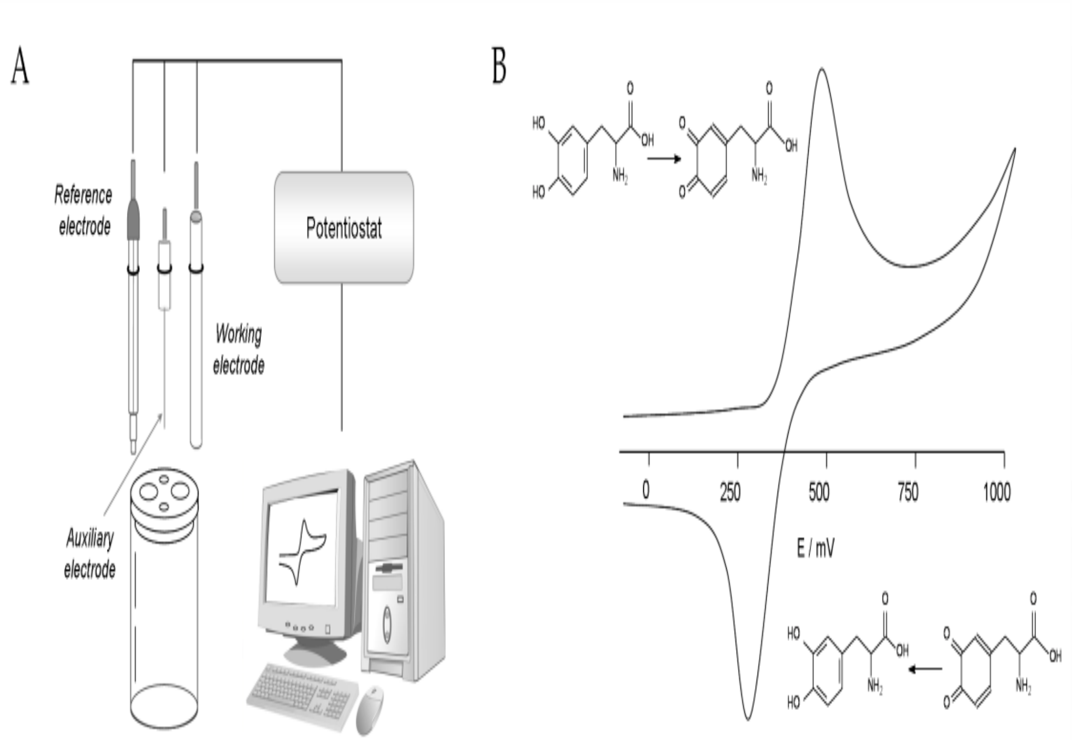
https://youtu.be/4jvremiDpRI

Video 3: pH electrode2 🎞

https://youtu.be/rxWnKKz1YJo

Chapter II

Voltammetry



Voltammetry

is a name given to a wide range of methods that study the composition of a solution by looking at current–potential relationships. It is essentially an electrolysis on microscale, using a micro working electrode (e.g., a platinum wire).

Voltametric Systems – scanning a potential slowly and the current is measured as a function in the applied potential in an electrolytic cell. The recorded results give a plot of current versus applied potential called voltammogram.

- ☐ **Voltammetry techniques measure current as a function of applied potential under conditions that promote polarization of a working electrode.**
- ☐ **Polarography: Invented by J. Heyrovsky (Nobel Prize 1959). Differs from voltammetry in that it employs a dropping mercury electrode (DME) to continuously renew the electrode surface.**
- ☐ **Amperometry: current proportional to analyte concentration is monitored at a fixed potential.**

The Voltametric cell – An electrolytic cell

Consists of three electrodes:

1. **Micro working electrode:**
2. **Auxiliary (Counter) electrode.**
3. **Reference electrode.**

Working electrode including mercury, platinum, gold, silver, and carbon. Because mercury is a liquid, the working electrode is often a drop suspended from the end of a capillary tube.

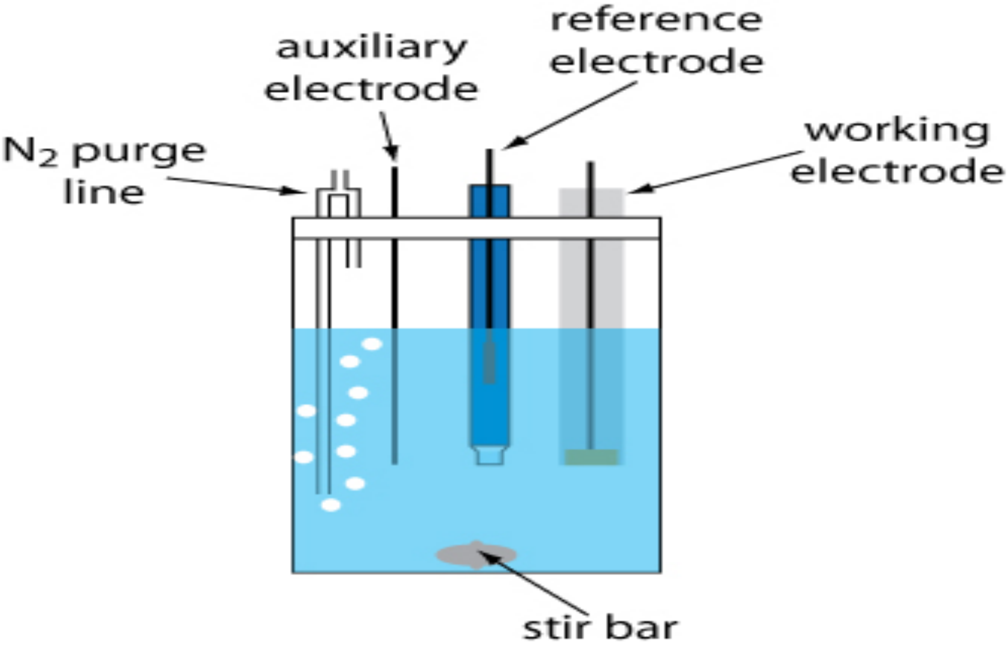


Figure 7.: The Voltametric cell

Figure 8.: The Voltametric cell; vital picture.

Voltammetry is one of the techniques which electrochemists employ to investigate electrolysis mechanisms. There are numerous forms of voltammetry:

1. **Potential step**
2. **Linear sweep**
3. **Cyclic voltammetry**

Cyclic Voltammetry

- **Cyclic voltammetry (CV) is one of the most widely used electroanalytical methods because of its ability to study and characterize redox systems from macroscopic scales down to nanoelectrodes**
- **In CV the potential scans run from the starting potential to the end potential, then reverse from the end potential back to the starting potential.**

The essential elements needed for an electrolysis measurement are:

1. **The electrode: This is usually made of an inert metal (such as Gold or Platinum)**
2. **The solvent: This usually has a high dielectric constant (eg water or acetonitrile) to enable the electrolyte to dissolve and aid the passage of current.**
3. **An electrolyte: is usually added in to allow the current to pass.**
4. **The reactant: Typically, in low concentration 10^{-3} M**

The waveform, and the resulting I-E curve is shown in Figure 8.

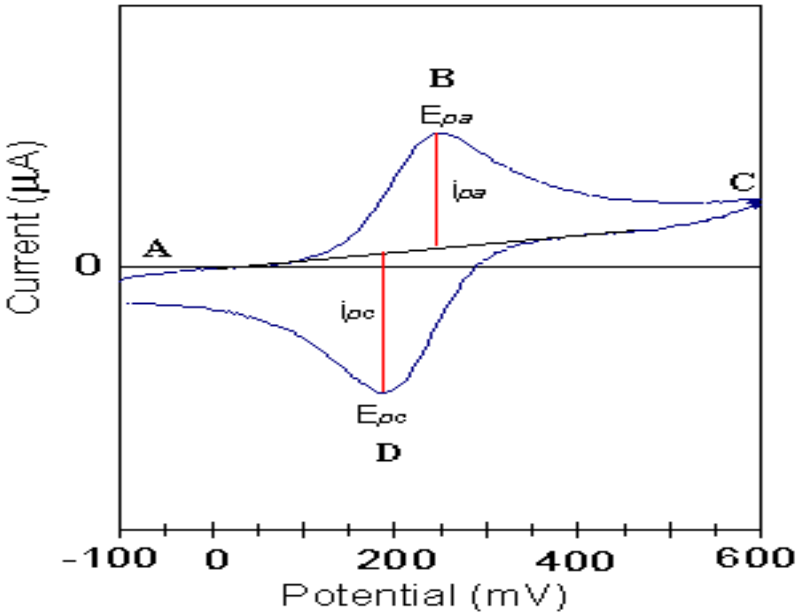


Figure 9.: The Cyclic-Voltammogram

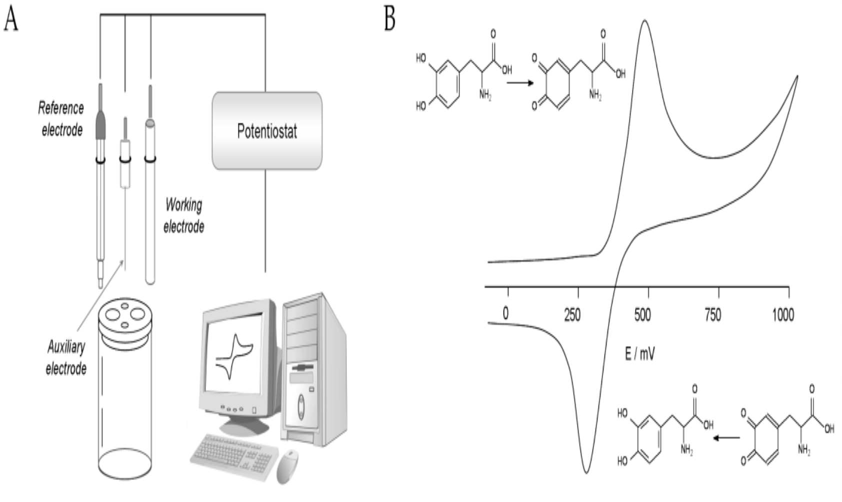


Figure 10.: A: The Cyclic-Voltammetry set. B: Redox reactions shown in Cyclic-Voltammogram.

Advantages of CV

- **Can determine mechanisms and kinetics of redox reactions.**

Stripping Analysis

Mercury working electrode

1. **Hanging mercury drop electrode (HMDE): A drop of Hg suspended from the end of a capillary tube extruded by rotating a micrometer screw that pushes the mercury from a reservoir through a narrow capillary tube.**
2. **Dropping mercury electrode (DME): drops form at the end of the capillary tube because of gravity. Unlike the HMDE, the mercury drop of a DME grows continuously.**

The Voltametric cell – HDME

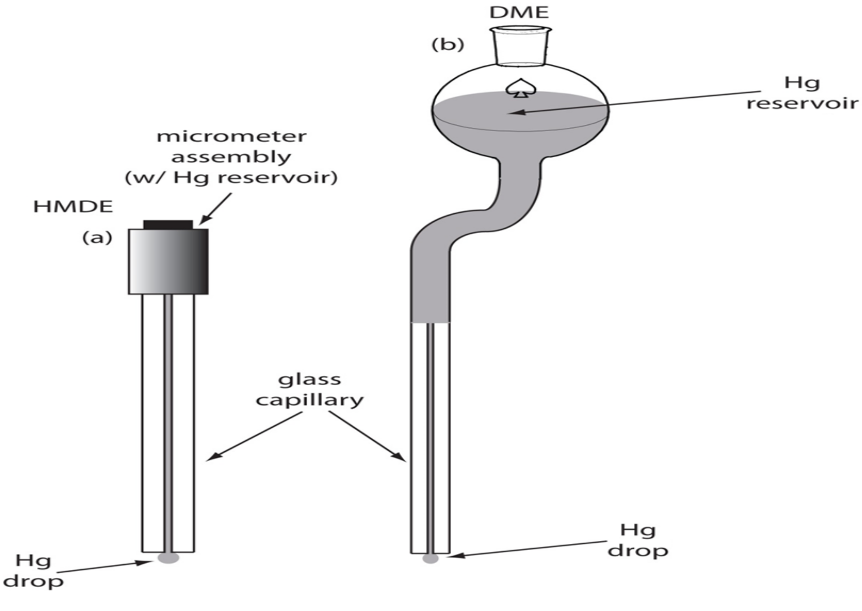


Figure 11.: The HMDE a d DME for Stripping Analysis.

Stripping Analysis

- **The analyte is electrochemicaly deposited on the working electrode.**
- **The polarity of the working electrode is reversed, and the analyte ‘stripped’ from the electrode.**
- **During this step, the current is monitored.**
- **The more easily oxidized substances are removed first.**
- **The integrated area under each peak is proportional to the amount of that species present.**

The Voltametric cell – Stripping Analysis vs HDME

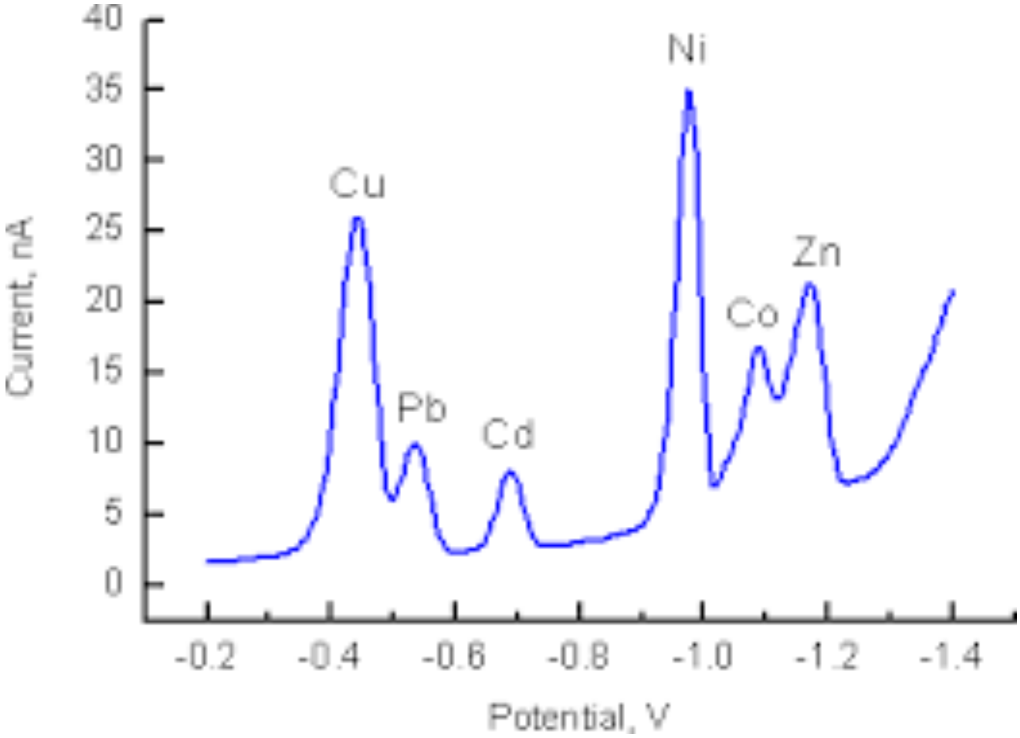


Figure 12: The Voltametric cell – Stripping Analysis vs HDME.

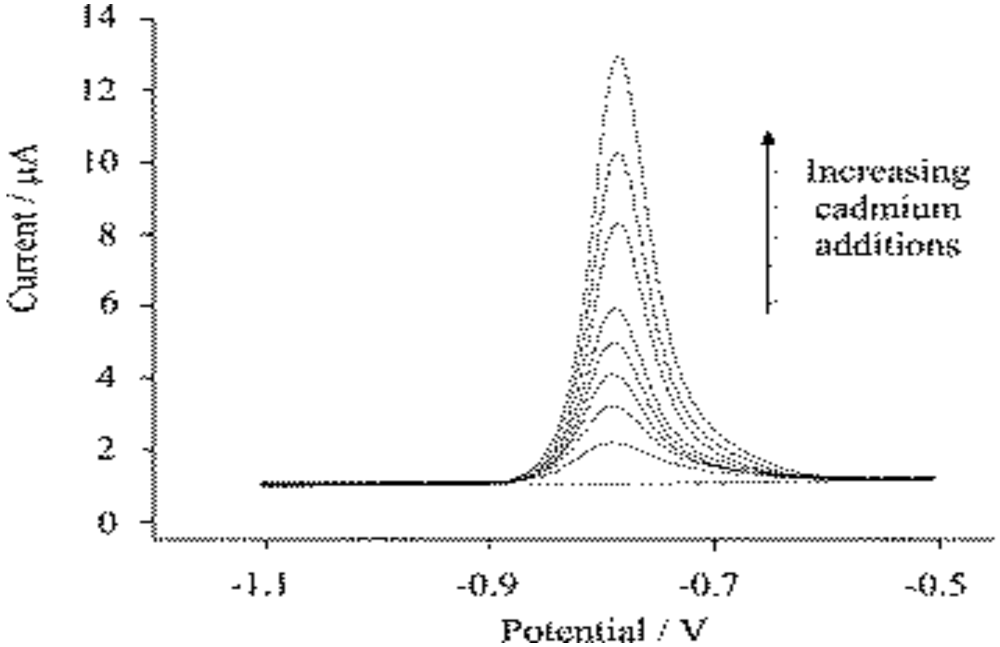


Figure 13.: The Anodic stripping peaks for added Cd^{+2} cell – Stripping Analysis vs HDME.

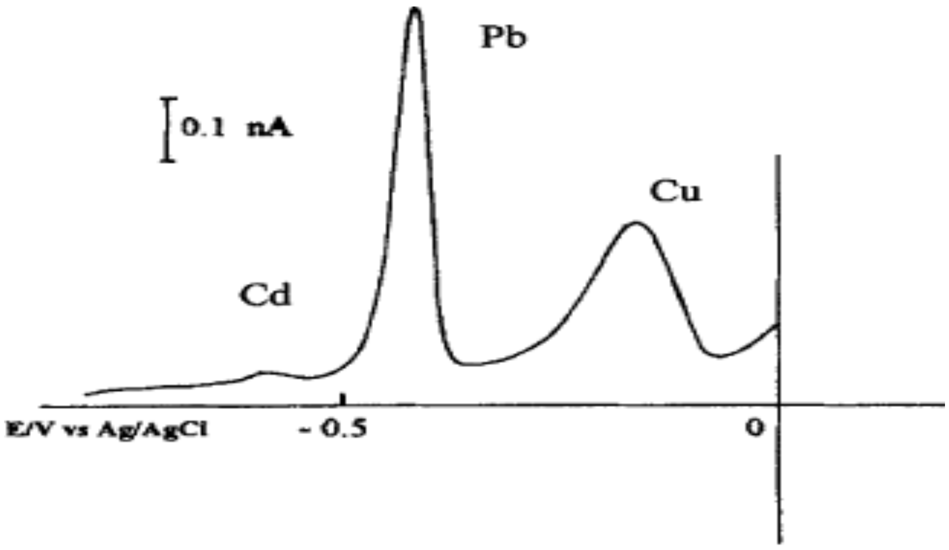


Figure 14.: The Anodic stripping voltammogram recorded at a mercury microelectrode in a pore-water sample acidified at pH = 2. Scan rate 50 mV s^{-1}.

Chapter III

Conductometry

Conductometry

This is a method of analysis based on measuring electrolytic conductance.

Conductance:

Is the ability of the medium to carry the electric current.

Electric current passes through metallic conductors, e.g. wires of iron or copper in the form of electron flow.

While

- **Conduction of electricity through an electrolyte solution involves migration of positively charged species towards the cathode and negatively charged ones towards the anode, i.e. current is carried**

- **by all ions present in solution.**
- **The conductance of the solution is a reciprocal of its resistance and has the units of Ohm^{-1}.**
- **The SI unit of conductivity is S/m (Siemens/meter).**
- **More generally encountered is the traditional unit of µS/cm.**

- **Conductivity is measured by using conductometer.**

Figure 15.: Different versions of conductometer.

Figure 16.: Different versions of conductometer.

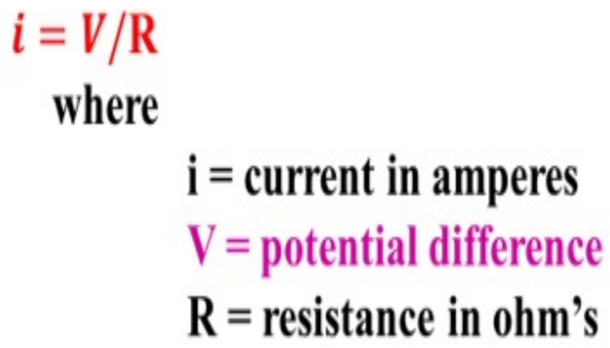
Figure 17.: conductometer.

Total conductance of the solution is directly proportional to the sum of the number individual ion contributions.

Video 4: Conductometry 🎞

https://youtu.be/rxWnKKz1YJo

The magnitude of conductometric titration is based on ohm's law.



$i = V/R$

where

i = current in amperes

V = potential difference

R = resistance in ohm's

G = 1/R

Where G is the conductance of the solution.

Factors Affecting Conductivity

1. **Nature of ions**
2. **Concentrations of ions**
3. **Temperature**
4. **The size of the electrodes**

1. **Nature of ions**

The velocity by which ions move towards the electrodes carrying the electric current varies according to their nature:

i.e. size, molecular weight, and number of charges.

2. **The ions concentration:**

- **The electrical conductance of a solution is a summation of contribution from all ions present.**
- **It depends on the number of ions of solution.**
- **As the number of ions increases, the conductance of the solution increases.**

3. **Temperature**

- **The conductance increases by increasing the temperature of the solution.**
- **An increase of temperature by 1ºC is accompanied by 2 % increase in conductance.**
- **The measurements must be carried out at a constant temperature.**

4. The size of the electrodes:

Conductance is directly proportional to the cross-sectional area A of the electrode, and inversely proportional to the length L between the two electrodes.

$$G \propto \frac{A}{L}$$

The conductance of electrolyte solution can be calculated from:

$$G = K\frac{A}{L}$$

Where G is the conductivity, K is the specific conductivity, A is the cross-sectional area of the electrode, L the length between the two electrodes.

Specific conductivity: -

- ✓ **It is the conductance of a cube of liquid with one centimeter on a side.**

$$K = G\frac{L}{A}$$

- ✓ **Units are 1/Ohm.cm or $\mathrm{Ohm}^{-1}\mathrm{cm}^{-1}$ or siemens/cm.**
- ✓ **L/A is known by the cell constant, K, is a constant value for specific solution.**

Equivalent conductivity: -

It is defined as the conductance of one gram equivalent of solute contained between electrodes spaced one centimeter apart.

Instruments used in conductometric determination:

To carry out conductometric measurement it is necessary to measure the resistance of the solution and the conductance is 1/R

The instrument consists of two parts:

1. **Conductance cell: in which the solution to be measured is filled or placed.**

2. **Conductivity bridge: to measure the resistance and then converts it to conductivity unit.**

1. Conductivity Cell:

Which consists of:

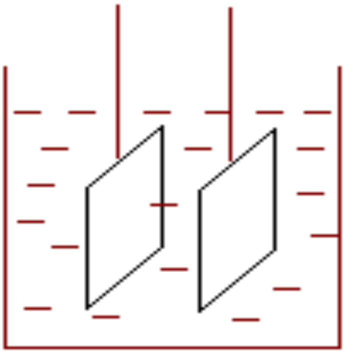


Figure 18.: Basic conductivity cell.

A. Electrodes

Two parallel platinized Platinum foil electrodes or Platinum. black with electrodeposited porous Platinum film which increases the surface area of the electrodes and further reduces faradaic polarization.

B. The cell contains the solution under investigation.

- **The solution should be diluted to avoid the faradaic polarization.**
- **The temperature should be stable to avoid its effect on conductance measurements.**

2.Wheatstone bridge:

- **R_1, R_2 and R_3 are known.**
- **R_2 are variable**
- **V_G is galvanometer employed to indicate an absence of current between D and B, that happened when the voltage between the two points equals zero.**
- **The conductance cell contains the solution replaces the R_x to be measured.**

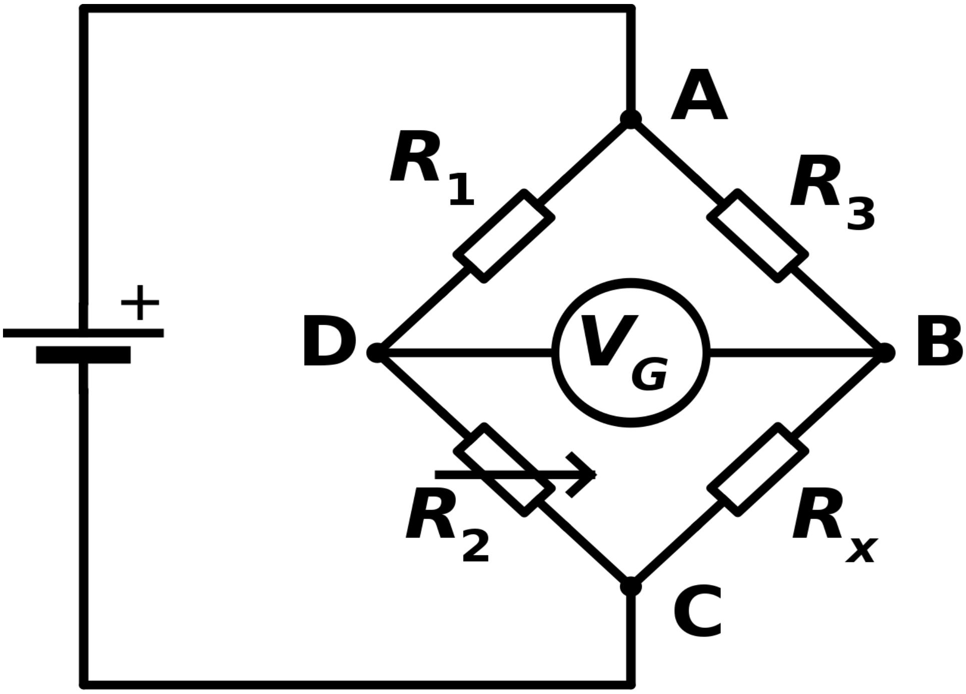


Figure 19.: Wheatstone bridge

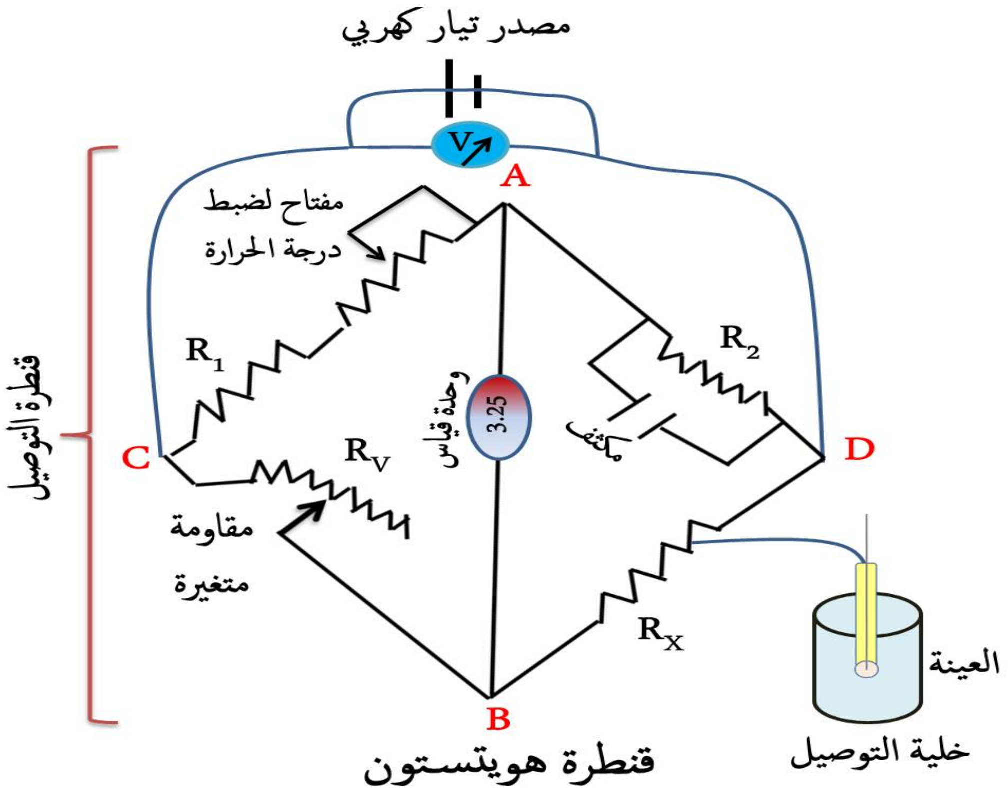


Figure 20.: Wheatstone bridge 2

- **When the current at V_G equals zero that means a Balance achieved at which:**

$$\frac{R_2}{R_1} = \frac{R_x}{R_3}$$

So,

$$R_x = R_3 \frac{R_2}{R_1}$$

$$G = \frac{1}{R_x}$$

APPLICATIONS OF CONDUCTOMETRY

It can be used for the determination of:-

- **Solubility of sparingly soluble salts**
- **Ionic product of water**
- **Basicity of organic acids**
- **Salinity of sea water**
- **Chemical equilibrium in ionic reactions**

CONDUCTOMETRIC TITRATIONS:

- **The determination of end point of a titration by means of conductivity measurements are known as conductometric titrations.**

Video 5: Conductometric Titration

https://youtu.be/MopNOn1IRUw

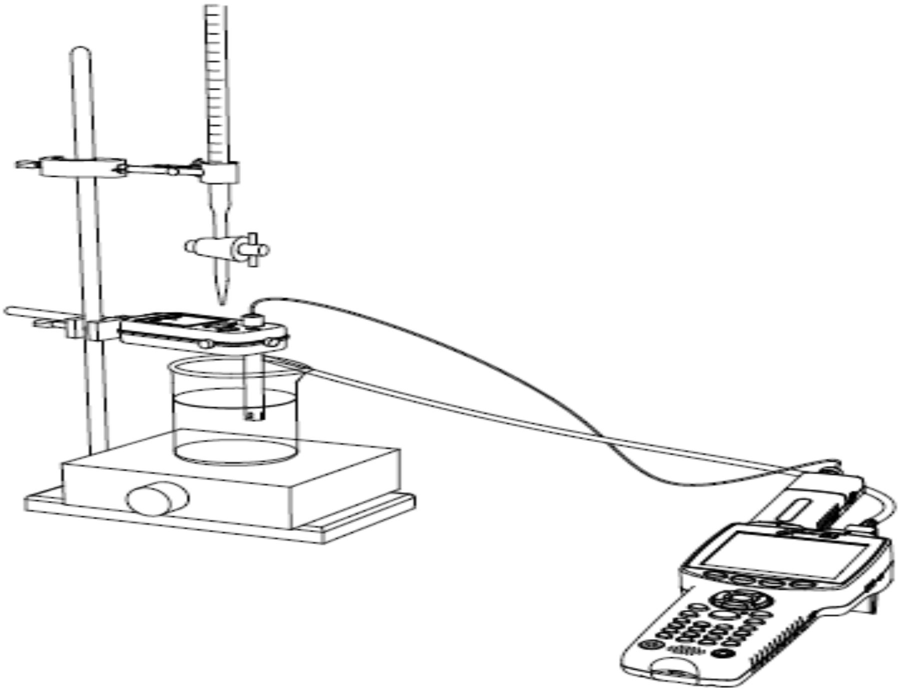


Figure 21.: Conductometric titration set.

Types of conductometric titrations:

- **Acid-base titration**
- **Precipitation titration**
- **Replacement titration**
- **Redox (oxidation-reduction) titration**
- **Complexometric titration**

ACID-BASE TITRATIONS

- **Titration of strong acid:**

(a) with strong base

e.g. HCl with NaOH

(b) with weak base

e.g. HCl with NH_4OH

(a) HCl vs NaOH

(b) HCl vs NH_4OH

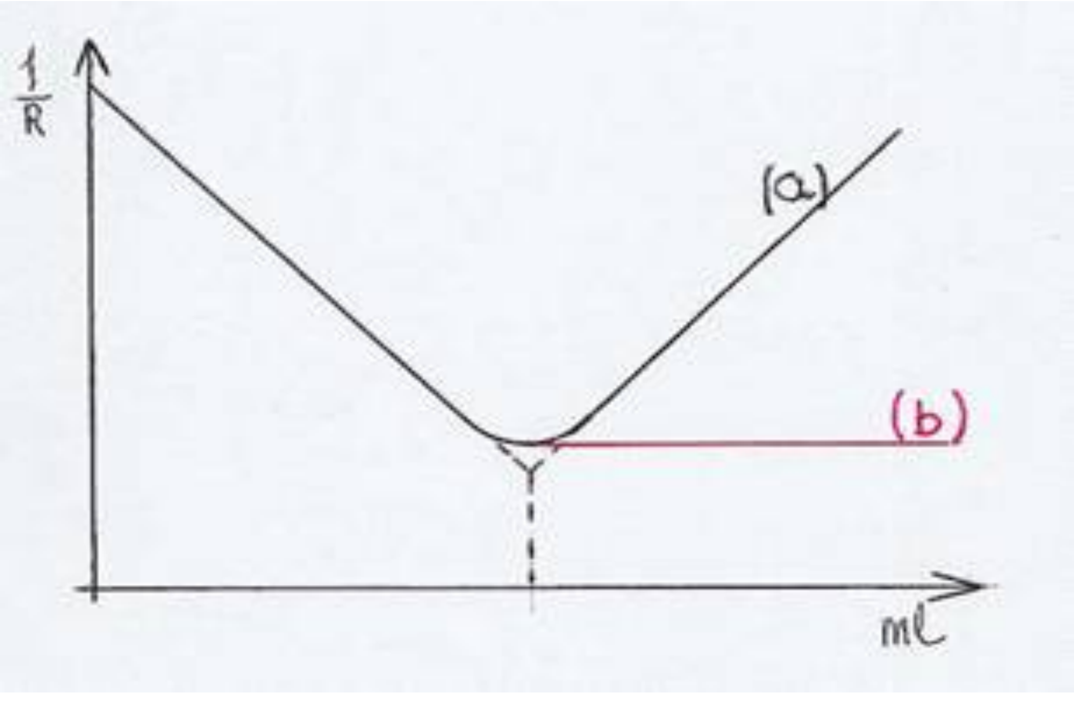
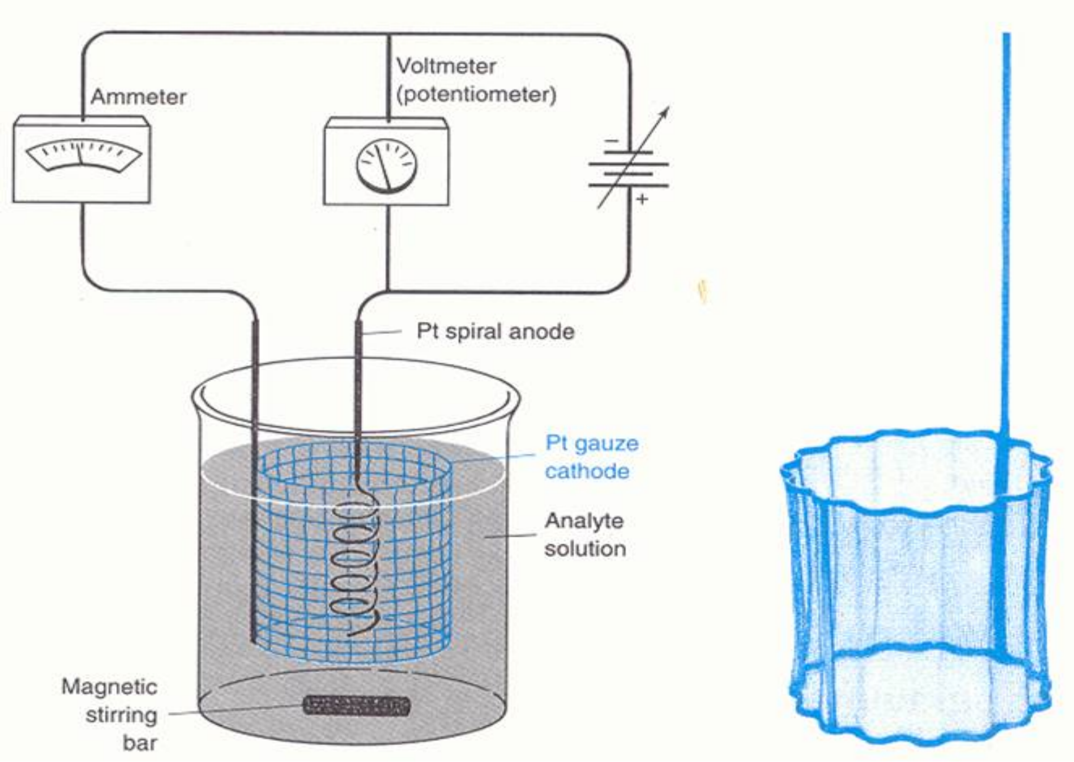


Figure 22.: Conductometric titration curves of (a) HCl vs NaOH (b) HCl vs NH_4OH

.

Chapter IV

Electrogravimetry



Electrogravimetry:

is an electroanalytical method used to separate and quantify ions of a substance, usually a metal.

- **In this process, the analyte solution is electrolyzed.**
- **Electrochemical reduction causes the analyte to be deposited on the cathode.**

- **The cathode is weighed before and after the experiment.**
- **The weight difference is used to calculate the amount of analyte in the original solution.**
- **Controlling the potential of the electrode is important to ensure that only the metal being analyzed will be deposited on the electrode.**

- **This method employs two or three electrodes, just as in voltammetry.**
- **Either a constant current or a constant potential is applied to the pre-weighed working electrode.**

- **After the assayed substance has been completely removed from the solution by the electrochemical reaction, the working electrode is removed, rinsed, dried, and weighed.**
- **The increased mass of the electrode due to the presence of the reaction product is used to calculate the initial concentration of the analyte.**

- **If only one component in the solution can react to form a deposit on the electrode, constant-current electrogravimetry is the preferred method.**
- **In constant-potential electrogravimetry, the potential at the working electrode is controlled so that only a single electrochemical reaction can occur.**

- **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.**

Instrumentation:

- **The apparatus for an analytical electro deposition, without cathode potential control, consists of a suitable cell and direct current supply.**
- **The voltage applied to the cell is controlled by the variable resistance.**

- **The voltage is then maintained at about the initial level until the deposition complete.**
- **A current meter and a voltmeter indicate the approximate current and voltage.**

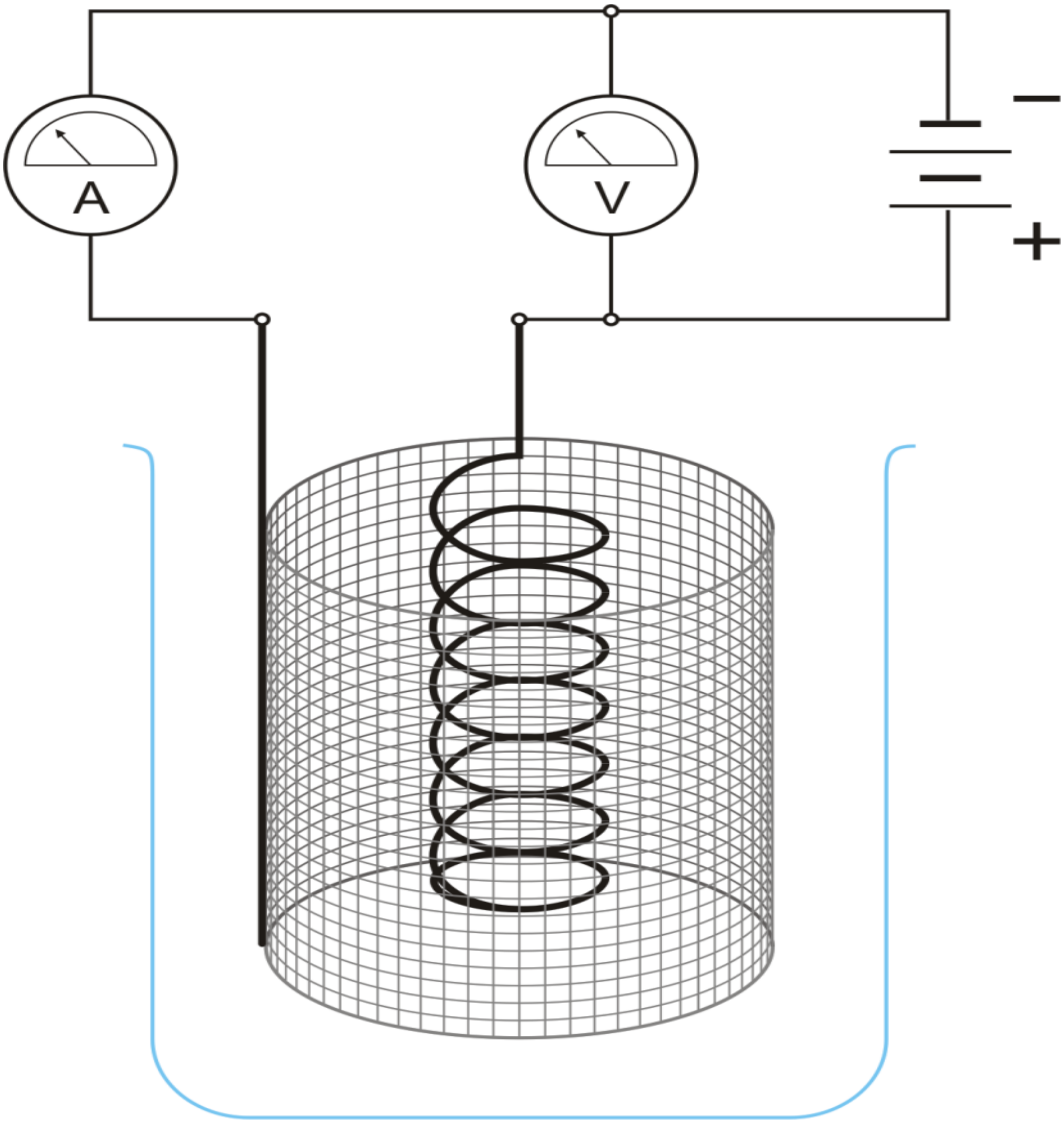


Figure 23.: electrogravimetry measurement set.

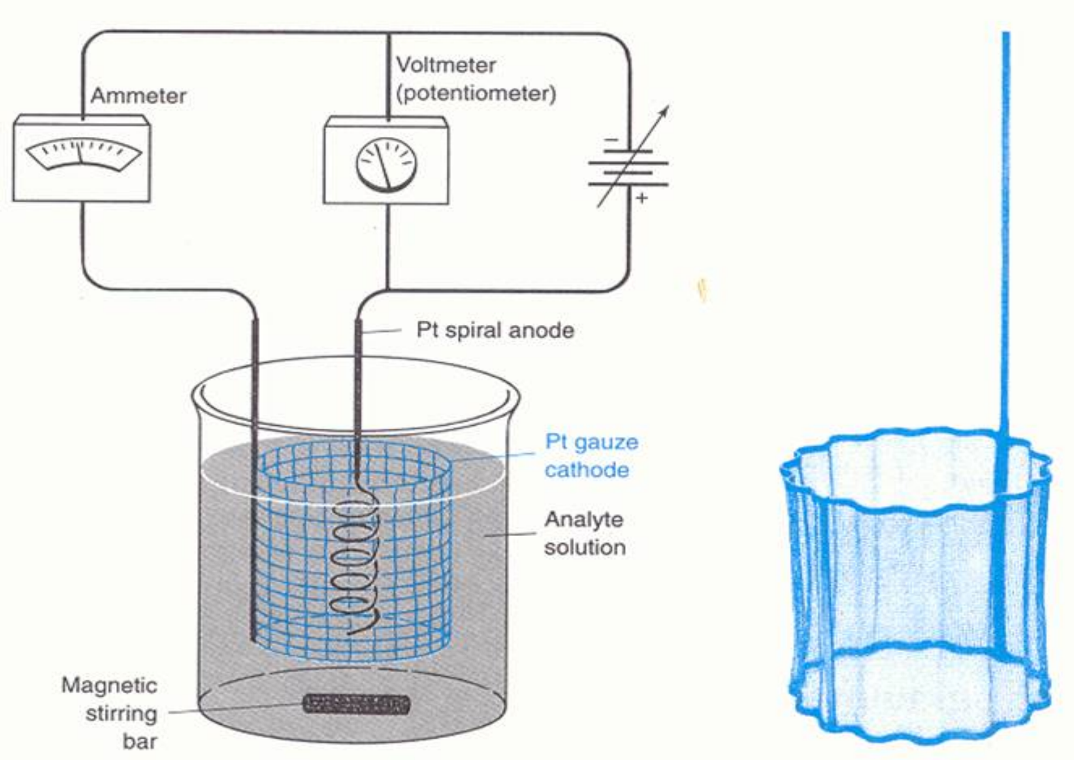


Figure 24.: electrogravimetry measurement set, after separation the precipitate.

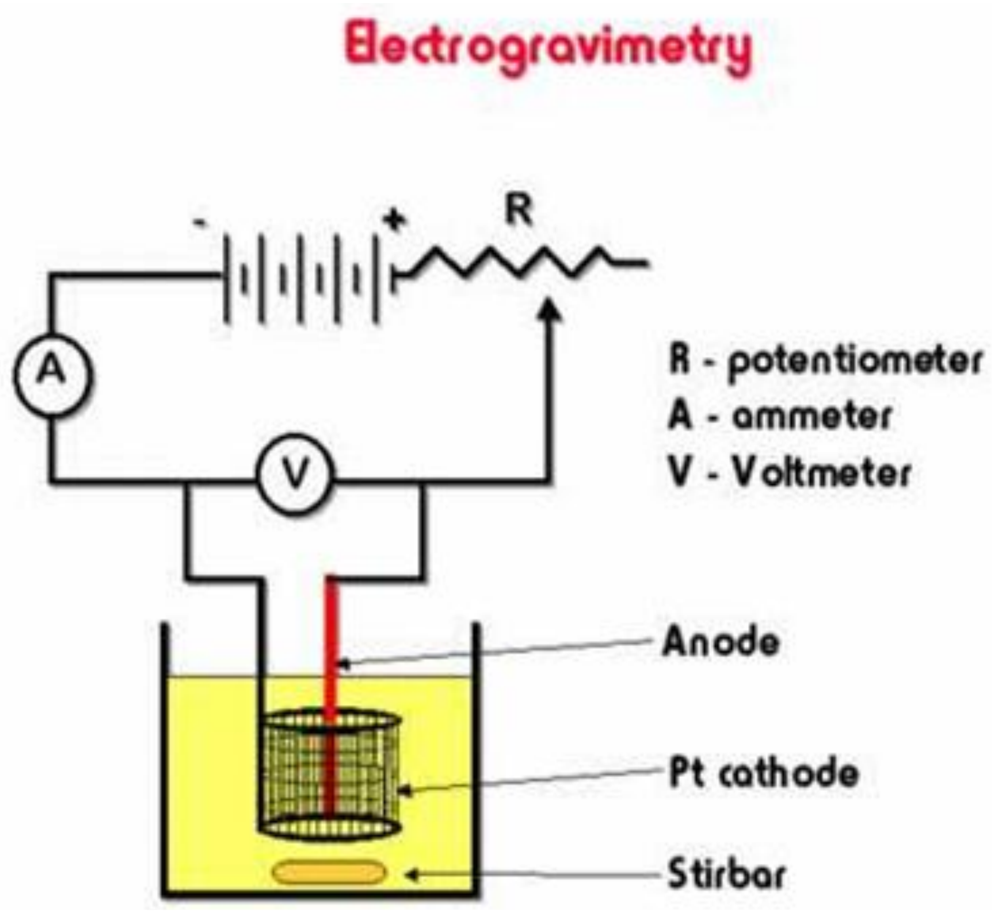


Figure 25.: electrogravimetry measurement apparatus.

Video 6: Electrogravimetry:

https://youtu.be/BJKAt-eeLRg

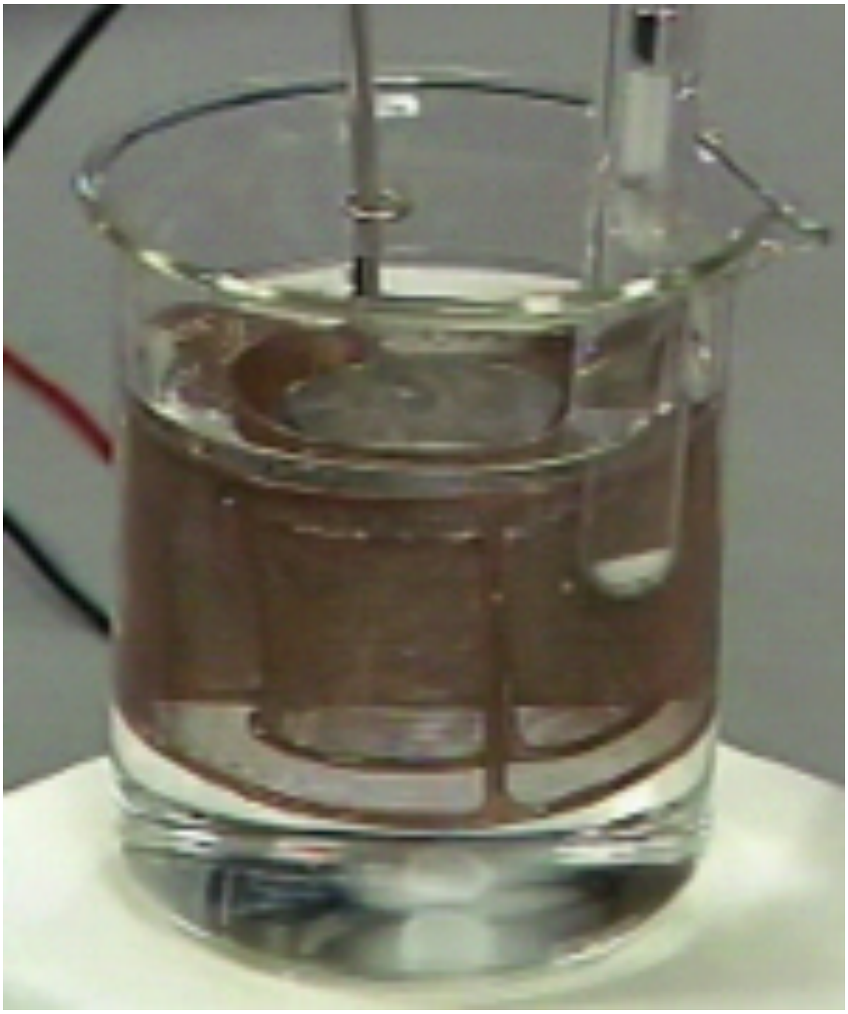


Figure 26.: electrogravimetry measurement set, real picture.

Applications:

- ☐ **It is used for the determination of concentration of chemical elements very accurately and precisely in quantitative analysis.**
- ☐ **In a mixed solution, the different species are separated by selectively plating on and removing out.**

- ☐ **It is used in electrochemical methods for removing interferences.**

Co-deposition

- **In practice, there may be other electroactive species that interfere by co-deposition 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, controlling 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

References:

1. **Joseph Wang, “Analytical Electrochemistry”, Third Edition, SBN:9780471678793, Published by John Wiley & Sons, Inc., Hoboken, New Jersey. Published simultaneously in Canada, 2006.**
2. **V. S. BAGOTSKY “Fundamentals of Electrochemistry”, Second Edition, Published by John Wiley & Sons, Inc., Hoboken, New Jersey Published simultaneously in Canada, 2006.**