University of Baghdad

College of Science

Physical Chemistry (4) / Electrochemistry

Chemistry Department / Third Stage

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Assist .Prof. Dr. Ghadah A. Yiseen

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Electrolysis and Electrical Conductance

Water-soluble substances are distinguished as:

Electrolytes **or** *Nonelectrolytes*

- *Electrolytes* **: Are electrovalent substances that form ions in solution which conduct an electric current.** Sodium chloride, copper (II) sulphate and potassium nitrate are examples of electrolytes.

- *Nonelectrolytes*: Are covalent substances which furnish neutral molecules in solution. ***Their water-solutions do not conduct an electric current***. ***Sugar, alcohol and glycerol are typical nonelectrolytes***.

An electrolyte invariably undergoes chemical decomposition as a result of the passage of electric current through its solution

The phenomenon of decomposition of an electrolyte by passing electric current through its solution is termed → **Electrolysis**

✓ ***The process of electrolysis*** is carried in an apparatus called the ***Electrolytic cell.*** The cell contains water-solution of an electrolyte in which two metallic rods (electrodes) are dipped**.**

- ✓ ***These rods*** are connected to the two terminals of a battery (source of electricity). **The electrode connected to the positive** terminal of the battery attracts the **negative ions (anions)** and is called **anode. The other electrode connected to the negative** end of the battery attracts the **positive ions (cations)** and is called **cathode.**

MECHANISM OF ELECTROLYSIS:

How the electrolysis actually takes place? It is illustrated in the Fig. 1.

- The **cations** migrate to the **cathode** and form a neutral atom by accepting electrons from it
- The **anions** migrate to the **anode** and yield a neutral particle by transfer of electrons to it.
- As a result of ***the loss of electrons by anions*** and ***gain of electrons by cations*** at their respective electrodes ***chemical reaction takes place.***

.

Example:

Let us consider the electrolysis of hydrochloric acid (HCl),
In solution**,** **HCl is ionised**,

$$\mathbf{HCl \longrightarrow H^{+} + Cl^{-}}$$

In the electrolytic cell: **Cl⁻ ions** ***will move toward the anode,***

and **H^{+} ions** ***will move toward the cathode***

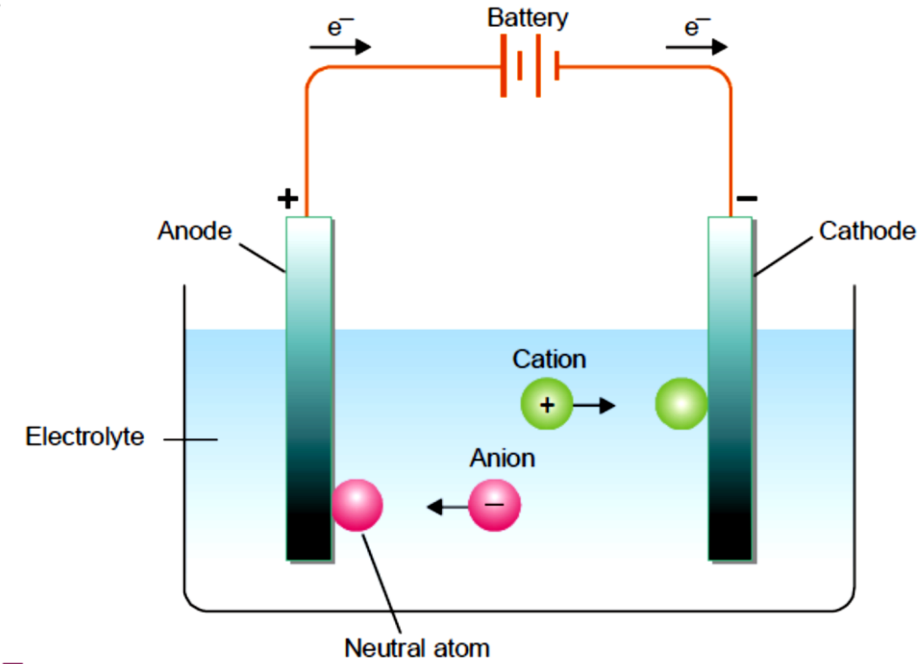
At the electrodes, the following reactions will take place:

At cathode : $H^{+} + e^{-} \longrightarrow H$ ***(Reduction)***

Each **H^{+}** ion picks up an electron from the cathode to become a hydrogen atom.

Pairs of hydrogen atoms then unite to form molecules of hydrogen gas, H_2.

At Anode : $Cl^{-} \longrightarrow Cl + e^{-}$ ***(Oxidation)***



The mechanism of electrolysis

The net effect of the process is ***the decomposition of HCl*** into $\mathbf{H_2}$ and $\mathbf{Cl_2}$ gases.

The overall reaction is :

$$\mathbf{2HCl \longrightarrow H_2 + Cl_2} \qquad \textbf{\textit{(Decomposition)}}$$

ELECTRICAL UNITS:

There are a few electrical units which we should understand before taking up the study of quantitative aspects of electrolysis. These are :

✓ **Coulomb: Is a unit quantity of electricity.**

The electric charge is measured in **Coulombs** (C).

The charge on one **electron** = **-1.602 x 10^{-19} C.**
The charge on ***a proton*** = **+1.602 x 10^{-19} C.**

✓ **Ampere: is a unit rate of flow of electricity. OR, an ampere is a current of one coulomb per second.**

$$\text{current (I)} = \frac{\text{charge (Q)}}{\text{time (t)}}$$

$$1 \text{ Ampere (A)} = \frac{1 \text{ Coulomb (C)}}{1 \text{ second (sec)}}$$

✓ **Volt:** **Is a unit of electromotive force. It is the difference in electrical potential required to send a current of one ampere through a resistance of one ohm.**

$$1 \text{ volt (V)} = \frac{1 \text{ Joule (J)}}{1 \text{ Coulomb (C)}}$$

✓ **Resistance:** **Is the hindrance to the flow of charge, and an *ohm* (Ω) is a unit of electrical resistance.**

CONDUCTANCE OF ELECTROLYTES:

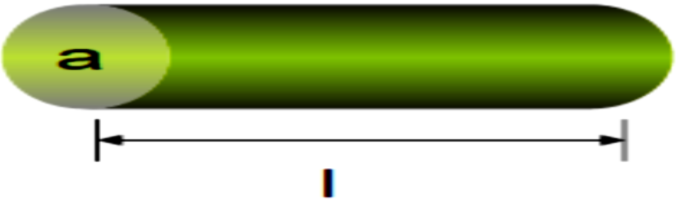
The electrolyte solutions conduct electric currents by movement of the ions to the electrodes*. *The power of electrolytes to conduct electric currents is termed **conductivity or conductance**

Like ***metallic conductors***, ***electrolytes obey Ohm's law:***

$$E = I.\ R \ldots\ldots\ (\text{Ohm law})$$

E = the potential difference

R = the resistance measured in ohms (or Ω).



The resistance R of a conductor is directly proportional to its **length, *l***, and inversely proportional to the area of its **cross-section, *A***.

$$R \propto \frac{l}{A}$$

$$R = \mathbf{r}\frac{\mathbf{l}}{\mathbf{A}} = ohm \ldots\ldots(1)$$

l = the length of the wire in meters (m),

A = the cross-sectional area of the wire in m^2, or cm^2

r = the ***resistivity or specific resistance*** of the material in ***ohm•meter*** (**Ω**. m)

$$r = R\,\frac{A}{L} = ohm\,\frac{\mathrm{cm}^2}{cm} = ohm.cm$$

Conductance of Electrolytes (C):

It is the tendency of a material (solution) to allow the flow of current through it.

It is the reciprocal of resistance. It is unit : ***ohm^{-1} = mho = Siemens.***

ohm^{-1} = mho = Siemens

$$\text{Conductance (C)} = \frac{1}{\text{Resistance (R)}}$$

By substituting, R from equation (1):

$$C = \frac{1}{r}.\frac{A}{L} = \sigma\frac{A}{L} \quad \ldots\ldots..eq.(2)$$

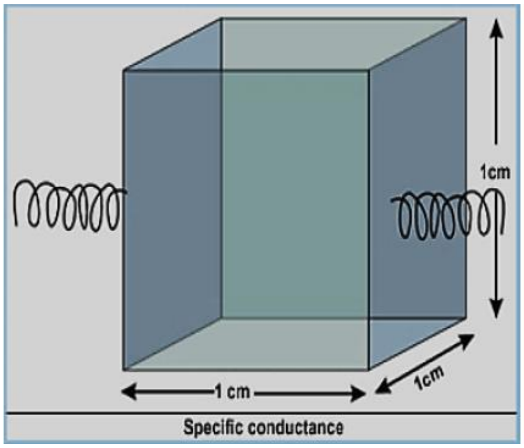
Where:

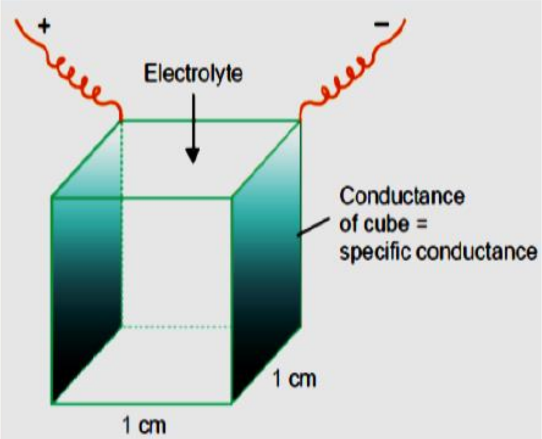
$$\sigma = \frac{1}{r} = specific\ conductance\ (or) conductivity$$

From the equation (2):

$$\sigma = C\,\frac{L}{A}$$

If: $\mathbf{A = 1\ cm^2}$ and $\boldsymbol{l} = \mathbf{1\ cm}$, then $\boldsymbol{\sigma} = C$.





$$\sigma = C$$

Specific conductance or conductivity (σ): ***It is the conductance of a solution occupying 1cm^3 volume.*** It is unit**:** ***ohm^{-1}. cm^{-1} = Siemens. cm^{-1}***

The specific conductance (σ) increases with:

(i) the ionic concentration, (ii) speeds of the ions concerned.

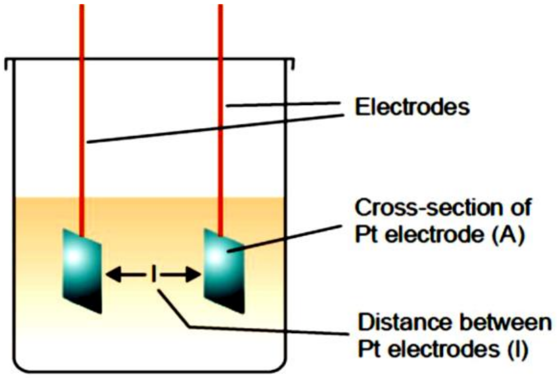
Cell constant (k):

The ratio of the distance between the electrodes,(l) to the cross sectional area, (A) of the electrodes.

$$Cell\ constant\ (k) = \frac{l}{A}$$

$$k = \frac{l}{A} = \frac{R}{r} = \frac{\sigma}{C} = R.\sigma = \frac{1}{C\ .\ r}$$

The unit of is : **k = cm^{-1}**



$$\sigma = C\,\frac{L}{A} = C\,k$$

SOLVED PROBLEM 1.

0.5 Normal solution of a salt placed between two platinum electrodes, **20 cm *apart*** and of area of ***cross-section 4.0 cm*** ^{2} has a ***resistance of 25 ohms***. ***Calculate the cell constant (k) and specific conductance (σ) of the solution?***

Solution:

$$k = \frac{l}{A} = \frac{20}{4} = 5\ cm^{-1}$$

$$\sigma = C\,k = \frac{1}{R}\ x\ k\ = \frac{1}{25}\ x\ 5\ = 0.2\quad ohm^{-1}.\ cm^{-1}$$

SOLVED PROBLEM 2.

The specific conductance (σ) of an N/50 solution of KCl at 25ºC is 0.002765mho. If the resistance (R) of a cell containing this solution is 400 ohms, what is the cell constant (k) ?

Solution:

$$\sigma = C\,k = \frac{1}{R}\ x\ k$$

$$k = \sigma\,R = \ 0.002765\ \ x\ 400\ = 1.106\ cm^{-1}$$

HOMEWORK (1)

The ***specific conducta***nce of N/5 KCl solution at 25°C is **0.002780** $\boldsymbol{Ohm^{-1}.cm^{-1}}$ The resistance of the cell containing this solution is ***500 ohm***. Calculate cell constant?

HOMEWORK (2)

The conductance of N/10 $AgNO_3$ solution taken in a cell with cell constant $0.9555cm^{-1}$ is 0.0099 ohm^{-1}. Calculate the specific conductance?

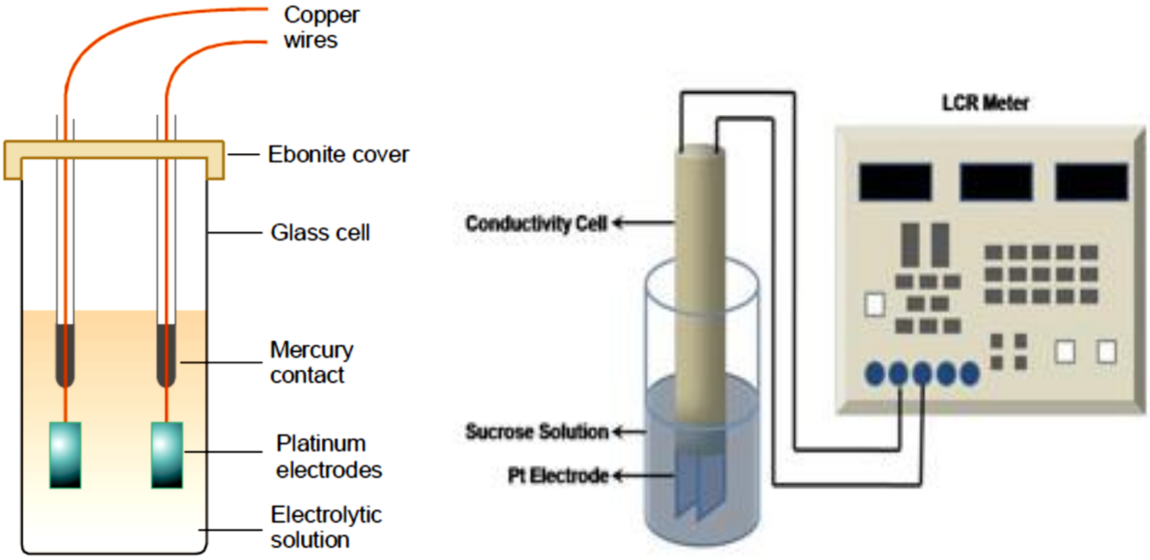
Measurement of Electrolytic Conductance

We know that conductance is the reciprocal of resistance. Therefore it can be determined by measuring the resistance of the electrolytic solution.

The solution whose conductance is to be determined is placed in a special type of cell known as the **conductance cell.**

A simple type of **conductance cell** used in the laboratory is shown in the Figure.

The electrodes fitted in the cell are made of platinum plates coated with platinum black. These are welded to platinum wires fused in two thin glass tubes.



A Conductance cell

To determine the **cell constant (k),** we will use a standard solution of KCl whose **specific conductance** (**σ**) at a given temperature is known:

0.01 N of KCl	**σ= 0.00140877**	**at 25 ºC**
0.1 N of KCl	**σ= 0.0128560**	**at 25 ºC**
1.0 N of KCl	**σ= 0.111342**	**at 25 ºC**

$$\boldsymbol{\sigma = Ck}$$

σ = *observed conductance (C) × cell constant (k)*

EQUIVALENT CONDUCTANCE (Λeq) & MOLAR CONDUCTANCE (Λ_m)

➢ Equivalent conductivity (Λeq)

The conductance of that volume (**V cm^3**) of solution containing one gram-equivalent (1g.eq) of an electrolyte. It is denoted by **Λeq** .

$$\boldsymbol{\Lambda eq = \sigma . \frac{1000}{N}}$$

Units of Λ_{eq}:

$$\Lambda eq = \frac{ohm^{-1}\ cm^{-1}}{eq.cm^{-3}} = ohm^{-1}.eq^{-1}\ cm^2$$

Λeq = Equivalent conductivity.

σ = specific conductance.

N = equivalent concentration.

Molar conductivity (Λ_m)

The conductance of that volume (**V cm^3**) of solution containing one mole-gram (1g.mole) of an electrolyte. It is denoted by **Λ_m** .

$$\Lambda m = \sigma . \frac{1000}{M}$$

Units of **Λ_m**:

$$\Lambda m = \frac{ohm^{-1}\ cm^{-1}}{mol . cm^{-3}} = ohm^{-1} . mol^{-1}\ cm^2$$

Λm = molar conductivity.

σ = specific conductance.

M = Molar concentration.

The relation between equivalent conductance, Λeq & Λ_m Can be given by:

Λ_m = Λ_{eq} x (n) ***equivalent factor of the electrolyte***

n = number of equivalent.

The Degree of Ionization (α)

$$\alpha = \frac{\Lambda}{\Lambda \infty}$$

SOLVED PROBLEM

A conductance cell on being filled with a ***0.02N solution of KCl at 25ºC*** showed a ***resistance of 165 ohms***. The ***specific conductance*** of the KCl solution used is ***2.77× 10⁻³ Ohm⁻¹ cm⁻¹***. The same cell containing ***0.01N NaCl*** solution gave an electrical ***resistance of 384 ohms***. Calculate the ***specific and equivalent conductance of the NaCl solution?***

Solution:

$$\sigma = Ck \quad \Longrightarrow \quad \sigma = \frac{k}{R} \quad \Longrightarrow \quad k = \sigma R$$

$$k = 2.77\times 10^{-3}\ Ohm^{-1}\ cm^{-1}\ x165\ Ohm = 0.4455\ cm^{-1}$$

$$\sigma = \frac{k}{R} = 0.4455\ cm^{-1} / 384\ Ohm = 0.001160\ Ohm^{-1}\ cm^{-1}$$

$$\Lambda eq = \sigma.\frac{1000}{N} = \frac{0.001160\ x\ 1000}{0.01} = 116\ ohm^{-1}.eq^{-1}\ cm^{2}$$

And :

$$\Lambda_m \text{ for NaCl} = \Lambda_{eq} \quad x \quad (n)$$

$$= 116\ ohm^{-1}.eq^{-1}\ cm^{2}\ x\ 1 = 116\ ohm^{-1}.mol^{-1}\ cm^{2}$$

Homework 1

Specific conductance of 0.02 N KCl at 298 K is 0.002768 ohm^{-1} cm^{-1} and it has resistance of 500 ohms. An 0.25 N solution of another salt kept in the same cell was found to have resistance of 300 ohms at 298 K. Calculate the cell constant and equivalent conductance of the salt solution?

Homework 2

0.5 N NaCl is placed between two electrodes 1.5 cm apart and having an area of each 3.0 cm^2 offered a resistance of 25 ohms. Calculate the equivalent conductance of NaCl?

Homework 3

The molar conductance of a solution of Aluminum chloride is found to be 130 ohm^{-1} mol^{-1} cm^2 at 298 K. What would be its equivalent conductance at the same temperature?

Homework 4

Explain the difference between molecular and equivalent conductance of a solution. What are the units for the two terms?

ملاحظة

جزء من درجة حل الواجب البيتي تعتمد على :

الترتيب , وضوح الخط (الحل بالقلم الجاف حصرا)واستلامه ضمن المدة المحددة.

STRONG AND WEAK ELECTROLYTES

Electrolytes may be divided into two types :

(*a*) Strong electrolytes

(*b*) Weak electrolytes

➢ *Strong Electrolytes*

A strong electrolyte is a substance that gives a solution in which almost all the molecules are ionized. The solution itself is called **a strong electrolytic solution.** Such solutions are ***good conductors of electricity and have a high value of equivalent conductance even at low concentrations***. The strong electrolytes are:

(1) **The strong acids** *e.g.*, HCl, H_2SO_4, HNO_3, $HClO_4$, HBr and HI.

(2) **The strong bases** *e.g.*, NaOH, KOH, Ca $(OH)_2$, Mg $(OH)_2$, etc.

(3) **The salts.** Practically all salts (NaCl, KCl, etc) are strong electrolytes.

➢ *Weak Electrolytes*

A weak electrolyte is a substance that gives a solution in which only a small proportion of the solute molecules are ionized. Such a solution is called **a weak electrolytic solution that** has low value of equivalent conductance.

The weak electrolytes are :

(1) **The weak acids :** All organic acids such as Acetic acid (CH_3COOH), Sulphurous acid (H_2SO_3).

(2) **The weak bases :** Most organic bases *e.g.*, as Alkyl amines ($C_2H_5NH_2$), NH_4OH are weak electrolytes.

(3) **Salts:** A few salts such as Mercury (II) chloride ($HgCl_2$) and Lead (II) acetate (Pb ($CH_3COO)_2$) are weak electrolytes

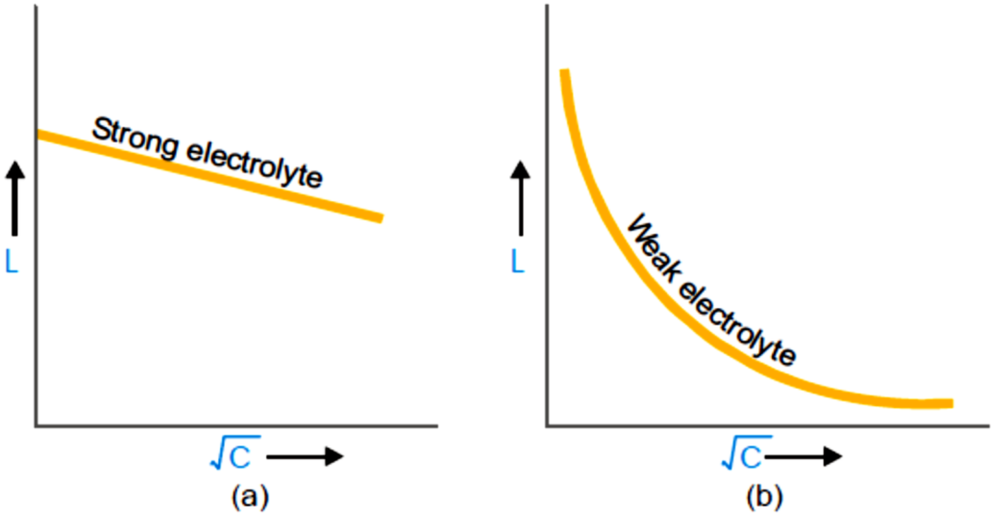
➢ Variation of Equivalent conductance with Concentration

The equivalent conductance Λ_{eq} of a solution does not vary linearly with concentration.

The effect of concentration on equivalent conductance can be studied by plotting Λ_{eq} values against the $\sqrt{C}$ of the concentration.

It has been found that variation of equivalent conductance Λ_{eq} with $\sqrt{C}$ depends upon the nature of electrolyte.

The Figure shows the behavior of strong and weak electrolytes with change of concentration.



- **Strong electrolytes are completely ionized at all concentrations (or dilutions).** ***The increase in equivalent conductance is not due to the increase in the number of current carrying ions. Due to the decrease in forces of attraction between the ions of opposite charges with the decrease in concentration (or increase in dilution).***

At higher concentration*, the forces of attraction between the opposite ions increase ((F* $\propto q_1 q_2 / r^2$***) Coulomb's law). Consequently, it affects the speed of the ions with which they move towards oppositely charged electrodes.***

This phenomenon is called ionic interference. As the solution becomes more and more dilute, the equivalent conductance increases, till it reaches a limitary value. This value is known as ***equivalent conductance at infinite dilution*** **(zero concentration) and is denoted by** $\Lambda\infty$**.**

- **Weak electrolytes have low ionic concentrations and hence interionic forces are negligible.**

Ionic speeds are not affected with decrease in concentration (or increase in dilution). **The increase in equivalent conductance with increasing dilution is due to the increase in the number of current carrier ions. In other words, the increases degree of ionisation (α).** Thus **increase** in equivalent conductance (Λ) in case of a weak electrolyte ***is due to the increase in the number of ions.***

In case of a weak electrolyte (**Λ∞)** ***is the equivalent conductance when ionization is complete***. So, ***the conductance ratio*** (**Λ/ Λ∞)** is **the degree of ionization** (α)

$$\alpha = \frac{\Lambda}{\Lambda_{\propto}}$$

KOHLRAUSCH'S LAW:

The equivalent conductance of an electrolyte at infinite dilution is equal to the sum of the equivalent conductance of the component ions.

KOHLRAUSCH'S LAW expressed mathematically as:

$$\Lambda_\infty = \lambda^a_\infty + \lambda^c_\infty$$

Where:

λ^a_∞ = **The equivalent conductance of the anion at infinite dilution**

λ^c_∞= **The equivalent conductance of the cation at infinite dilution**

Λ_∞ = **the equivalent conductance of electrolyte at infinite dilution (Or the limiting equivalent conductivity)**

Example:

What is the equivalent conductance of NaCl at infinite dilution at 25°C if the equivalent conductance of Na^+ and Cl^- ion is 50.11 ohm^{-1} eq^{-1} cm^2 and 76.34 ohm^{-1} eq^{-1} cm^2 respectively ?

$$\Lambda_\infty = \lambda^a_\infty + \lambda^c_\infty$$

$$\Lambda_\infty = 50.11 + 76.34 = 126.45\ ohm^{-1}\ eq^{-1}\ cm^2$$

This is in conformity with the Kohlrausch's Law.

Applications of Kohlrausch's Law

1) **Determination the limiting conductivities of weak electrolytes Λ_∞**
2) **Determination of degree of ionization (α) of weak electrolyte**
3) **Determination the dissociation constant (K_d) of weak electrolyte**
4) **Determination the Solubility (S) of sparingly soluble salts**

1) *Determination the limiting conductivities of weak electrolytes $\Lambda\infty$*

Q: If the molar conductivities at infinite dilution of *$NaCl$, HCl and CH_3COONa* are *126.4, 426.1 and 91.0 $ohm^{-1}\ cm^2\ mol^{-1}$* respectively, what will be that of acetic acid *(CH_3COOH)*?

Solution:

$$CH_3COONa \quad + \quad HCl \quad = \quad CH_3COOH \quad + \quad NaCl$$

$$\Lambda_\infty(CH_3COONa) + \Lambda_\infty(HCl) = \Lambda_\infty(CH_3COOH) + \Lambda_\infty(NaCl)$$

$$\Lambda_\infty(CH_3COOH) = \Lambda_\infty(CH_3COONa) + \Lambda_\infty(HCl) - \Lambda_\infty(NaCl)$$

$$\Lambda_\infty(CH_3COOH) = 91.0 + 426.1 - 126.4$$

$$= 390.7\ ohm^{-1}\ cm^2\ mol^{-1}$$

2) *Determination of degree of ionization (α) of weak electrolyte*

$$\alpha = \frac{\Lambda eq}{\Lambda\infty} = \frac{\lambda^{a} + \lambda^{c}}{\lambda^{a}_{\infty} + \lambda^{c}_{\infty}}$$

α = ***degree of ionization of weak electrolyte***

Λeq = the equivalent conductance of electrolyte at specific concentration

$\Lambda\infty$ = the equivalent conductance of electrolyte at infinite dilution
(Or the limiting equivalent conductivity)

λ^{a} = the equivalent conductance of the anion at specific concentration

λ^{c} = the equivalent conductance of the cation at specific concentration

λ^{a}_{∞} = the equivalent conductance of the anion at infinite dilution
(Or the limiting ionic equivalent conductivity)

λ^{c}_{∞} = the equivalent conductance of the cation at infinite dilution
(Or the limiting ionic equivalent conductivity)

SOLVED PROBLEM

The equivalent conductance at 18°C of a normal solution of KCl is 98.2 ohm^{-1}eq^{-1} cm^{2} and for infinite dilution at the same temperature 131 ohm^{-1} eq^{-1} cm^{2}. Calculate the degree of dissociation (α) of KCl at this dilution?

Solution:

$$\boldsymbol{\alpha = \frac{\Lambda eq}{\Lambda\infty} = \frac{98.2}{131} = 0.749}$$

3)Determination the dissociation constant (K_d) of weak electrolyte

EX:

$CH_3COOH + H_2O = CH_3COO^- + H_3O^+$

C = 0 0 t=Zero time of reaction

C (1-α) = C α C α t= after specific time

$$Kd = \frac{[CH3COO^-][H3O^+]}{[\mathrm{CH3COOH}]}$$

$$Kd = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\,\alpha^2}{(1-\alpha)}$$

$$\alpha = \frac{\Lambda eq}{\Lambda\infty}$$

$$kd = \frac{C\left[\frac{\Lambda eq}{\Lambda\infty}\right]^2}{1-\left[\frac{\Lambda eq}{\Lambda\infty}\right]}$$

$$K = \frac{\alpha^2 C}{1-\alpha}$$

$$K = \frac{\left(\frac{\Lambda}{\Lambda_o}\right)^2 C}{1 - \frac{\Lambda}{\Lambda_o}} = \frac{\frac{\Lambda^2}{\Lambda^2_o} C}{\frac{\Lambda_o - \Lambda}{\Lambda_o}}$$

$$K = \frac{\Lambda^2 C}{\Lambda_o(\Lambda_o - \Lambda)}$$

SOLVED PROBLEM

The specific conductivity of 0.05 N solution of CH_3COOH at 18 ^0C is $4.4x10^{-4}$ $Ohm^{-1}cm^{-1}$. The ionic equivalent conductivity of H^+ & CH_3COO^- ions at the same temperature are: 310 & 77 Ohm^{-1} eq^{-1} cm^2 respectively . Calculate the dissociation constant (K_d) of CH_3COOH?

Solution:

$$CH_3COOH + H_2O = CH_3COO^- + H_3O^+$$

$$Kd = \frac{[CH3COO^-][H3O^+]}{[CH3COOH]} \quad , \quad Kd = \frac{C\,\alpha^2}{(1-\alpha)} \quad , \quad \alpha = \frac{\Lambda eq}{\Lambda\infty}$$

$$\Lambda eq = \sigma.\frac{1000}{N} = \frac{4.4x10^{-4}x1000}{0.05} = 8.8\ Ohm^{-1}\,eq^{-1}\,cm^2$$

$$\Lambda_\infty = \lambda^a_\infty + \lambda^c_\infty = \lambda_{CH3COO-} + \lambda_{H+} = 77 + 310 = 387\ Ohm^{-1}\,eq^{-1}\,cm^2$$

$$\alpha = \frac{\Lambda eq}{\Lambda\infty} = \frac{8.8}{387} = 0.02274\ Ohm^{-1}\,eq^{-1}\,cm^2$$

$$Kd = \frac{C\,\alpha^2}{(1-\alpha)} = \frac{0.05x(0.02274)^2}{(1-0.02274)} = 2.645x10^{-5}$$

4) Determination the Solubility (S) of sparingly soluble salts

Solubility:

The concentration of a substance in its saturated solution is called as its solubility at a given temperature. It is denoted by letter 'S' it is expressed as *grams per liter or as moles per liter at a given temperature*.

Classification of solids on the basis of solubility:

- **The solids having solubility *greater than 0.1 M* (S>0.1M) *are classified as soluble solids*, e.g. NaCl, Sugar, etc.**

- **The solids having solubility *between 0.01 M and 0.1 M* (0.1M> S>0.01M) *are classified as slightly soluble solids*, e.g. $Ca_3 (PO_4)_2$**

- **The solids having solubility *less than 0.01 M* (S<0.01M) *are classified as sparingly soluble solids*, e.g. $BaSO_4$, AgCl, etc..**

Sparingly Soluble Salts: أملاح شحيحة الذوبان

A certain substance like AgCl, PbSO4, BaSO4, etc…. *have negligible solubility in water at ordinary temperature.* Such substances which are practically insoluble in water are called as sparingly soluble electrolytes. *The amount of such salts getting dissolved is so small that their saturated solution may be regarded as extremely dilute and hence dissolved part can be considered as completely ionized.*

SO:

$$\sigma\ (solution)\ =\ \sigma\ (solute)\ + \sigma\ (H2O)$$

$$\sigma\ (solute)\ =\ \sigma\ (solution) - \sigma\ (H2O)$$

$$S = \frac{\sigma(solute) x\ 1000}{\Lambda\infty}$$

= specific conductance of the solution$\boldsymbol{\sigma}\ (\boldsymbol{solution})$

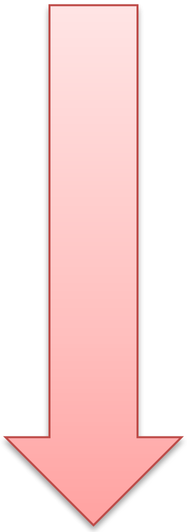
= specific conductance of the solute$\boldsymbol{\sigma}\ (\boldsymbol{solute})$

= specific conductance of $\mathbf{H_2O}\boldsymbol{\sigma}\ (\boldsymbol{H2O})$

S = solubility of the sparingly soluble salt

$\Lambda\infty$ **= the equivalent conductance of electrolyte at infinite dilution**
Or (the limiting equivalent conductivity)

المثال أدناه يوضح آلية الحسابات بالتفصيل



SOLVED PROBLEM

The specific conductance (**σ**) of a **saturated aqueous solution** of AgCl at 25 ^{o}C is **$3.41\text{x}10^{-6}$ Ohm^{-1} cm^{-1}**, and that of the **H_2O** used is **$1.60\text{x}\ 10^{-6}$ Ohm^{-1}cm^{-1}.**

The ionic conductivity (λ) of **Ag^+** ion and **Cl^-** ion at 25 ^{o}C are **61.92 Ohm^{-1}eq^{-1}cm^{2}** and **76.34 Ohm^{-1}eq^{-1}cm^{2} ,** respectively . Calculate the solubility of AgCl in water at 25 ^{o}C?

Solution:

$$\sigma_{\text{(Solution)}} = \sigma_{\text{(solute)}} + \sigma_{\text{(H2O)}}$$

$$\sigma_{\text{(solute)}} = \sigma_{\text{(Solution)}} - \sigma_{\text{(H2O)}}$$

$$\sigma_{\text{(solute)}} = 3.41\text{x}10^{-6} - 1.60\text{x}\ 10^{-6}$$

⇨ $\sigma_{\text{(solute)}} = 1.81\text{x}10^{-6}\ \text{Ohm}^{-1}\text{cm}^{-1}$

$$\Lambda_\infty = \lambda^{a}_{\infty} + \lambda^{c}_{\infty}$$

$$\Lambda_\infty = 76.34 + 61.92$$

⇨ $\Lambda_\infty = 138.26\ \text{Ohm}^{-1}\text{eq}^{-1}\text{cm}^{2}$

$$= \frac{1.81\text{x}10^{-6} x\ 1000}{138.26} \qquad S = \frac{\sigma(solute) x\ 1000}{\Lambda\infty}$$

⇨ $S = 1.309\text{x}10^{-5}\ \text{eq cm}^{-3}$

Absolute Ionic mobility:

The absolute ionic mobility (U) of an ion is defined as, **the velocity of an ion in centimeter per second(cm.s^{-1}) under a *potential gradient* (Ɛ) of one volt per centimeter(1V.cm^{-1}) . *It is expressed in* $cm^2\,V^{-1}\,sec^{-1}$.**

يتم تعريف الانتقالية الأيونية المطلقة لأيون على أنها سرعة أيون بالسنتيمتر لكل الثانية (cm/s) تحت انحدار جهد يبلغ فولت واحد لكل سنتيمتر (V/cm). ووحدتها سم مربع لكل فولت لكل ثانية ($cm^2\,V^{-1}\,s^{-1}$)

(Potential gradient ($\mathcal{E}$) = applied EMF / distance between (the electrodes))

$$\text{Unit of ionic mobility} = \frac{Unit\ of\ velocity(v)}{Unit\ of\ potential\ gradient(\mathcal{E})} = \frac{cm\ s^{-1}}{V cm^{-1}} =$$

$$cm^2\ V^{-1}\ s^{-1}$$

For example:

Let *the velocity (v)* of the ion at infinite dilution be *G cm s^{-1}* when the distance between the electrodes is *20cm* and the *voltage 100 V*.

Then :

The potential gradient ($\mathcal{E}$) = 100/20 = 5 V cm^{-1}

The ionic mobility = *the velocity (v) / the potential gradient* (Ɛ)

= G *cm s^{-1}* / 5 *V cm^{-1}*

The ionic mobility(U) = (G/5) cm^2 V^{-1} sec^{-1}

- ***It has been found that:***

The ionic conductance (λ) is *directly proportional* to the ionic mobility (U)

$$\lambda_a \ \alpha \ U_a \qquad \text{and} \qquad \lambda_c \ \alpha \ U_c$$

$$\lambda_a = F\,U_a \qquad \text{and} \qquad \lambda_c = F\,U_c$$

Generally: $$\lambda_a = Z_- F\,U_a \qquad \text{and} \qquad \lambda_c = Z_+ F\,U_c$$

Where:

***F* = the proportionality constant.**

Its value is equal to the charge on one gram-equivalent of the ion under the potential gradient of 1 volt / cm. (*F* = 96500 coulomb); or (1 Faraday)

U_a = ionic mobility of anion

U_c = ionic mobility of cation

Z_+ or Z_- = the valence of the ions

$$U_a = \lambda_a / Z_- F \qquad \text{and} \qquad U_c = \lambda_c / Z_+ F$$

Or: $$U_a = \lambda_a / Z_- \, 96500 \qquad \text{and} \qquad U_c = \lambda_c / Z_+ \, 96500$$

While: $$\Lambda = \lambda_a + \lambda_c$$

$$\Lambda = Z_- F\,U_a + Z_+ F\,U_c$$

So: $$\Lambda = F(Z_- U_a + Z_+ U_c)$$

$U^a_\infty = \lambda^a_\infty / Z_- F$ **and** $U^c_\infty = \lambda^c_\infty / Z_+ F$

$U^a_\infty = \lambda^a_\infty / Z_- 96500$ **and** $U^c_\infty = \lambda^c_\infty / Z_+ 96500$

$\lambda^a_\infty = Z_- F U^a_\infty$ **and** $\lambda^c_\infty = Z_- F U^c_\infty$

$$\Lambda_\infty = \lambda^a_\infty + \lambda^c_\infty$$

$$\Lambda_\infty = Z_- F U^a_\infty + Z_+ F U^c_\infty$$

$$\Lambda_\infty = F(Z_- U^a_\infty + Z_+ U^c_\infty)$$

TRANSPORT NUMBERS:

During electrolysis ***the current is carried by the anions and the cations***.

“ **The fraction of the total current carried by the cation or the anion is termed its *Transport number”.***

So; $$t_+ + t_- = 1$$

t_+ = **the transport number of cation**

t_- = **the transport number of anion**

For example:

0.01N solution of NaCl, $t_+ (Na^+) = 0.4$ **and** $t_-(Cl^-) = 0.6$**, so:**

$$t_+ + t_- = 1$$

$$t_+ (Na^+) + t_-(Cl-) = 0.4 + 0.6 = 1$$

The Relationship between the Equivalent Conductance (Λ), Ionic Mobility (U), and the Transport Number (t):

If:

$v+$ = *the speed of migration of the cation*

$v-$ = *the speed of migration of the anion,*

the transport number of cation $\tau_+ = \frac{v_+}{v_+ + v_-} = \frac{U_+}{U_+ + U_-}$

the transport number of anion $\tau_- = \frac{v_-}{v_- + v_+} = \frac{U_-}{U_- + U_+}$

$$\tau_+ = \frac{v_+}{v_+ + v_-} = \frac{U_+}{U_+ + U_-} = \frac{\lambda_+}{\lambda_+ + \lambda_-} = \frac{\lambda_+}{\Lambda}$$

$$\tau_- = \frac{v_-}{v_- + v_+} = \frac{U_-}{U_- + U_+} = \frac{\lambda_-}{\lambda_- + \lambda_+} = \frac{\lambda_-}{\Lambda}$$

$$\lambda_+ = t_+ \Lambda \qquad \text{and} \qquad \lambda_- = t_- \Lambda$$

ملاحظة (3) مهمة جدا : المعادلات السابقة تستخدم في حالة كون المحلول له تركيز معين.

اما في حالة التخفيف الى مالانهاية توضع الاشارة (∞) مع كل رمز كما ذكر أعلاه

SOLVED PROBLEM

At 25°C the ***transport number of*** H^+ ***ion*** in HCl and CH_3COO^- ***ion*** in CH_3COONa are ***0.81 and 0.47*** respectively. The ***equivalent conductance at infinite dilution*** of HCl and CH_3COONa are ***426*** $ohm^{-1}\ cm^2\ eqvt^{-1}$ and ***91.0*** $ohm^{-1}\ cm^2\ eq^{-1}$ respectively. Calculate the ***equivalent conductance of acetic acid*** CH_3COOH ***at infinite dilution?***

Solution

$$\lambda_{H+} = t_+\ \Lambda = t_{H+}\ \Lambda_{HCl} = 0.81 x\ 426 = 345.06\ ohm^{-1}\ cm^2\ eq^{-1}$$

$$\lambda_{CH3COO-} = t_-\ \Lambda = t_{CH3COO-}\ \Lambda_{CH3COONa} = 0.47 x\ 91 = 42.77 ohm^{-1}\ cm^2\ eq^{-1}$$

$$\Lambda_\infty = \lambda^a_\infty + \lambda^c_\infty$$

$$\Lambda_\infty = 42.77 + 345.06 = 387.83\ ohm^{-1}\ cm^2\ eq^{-1}$$

Homework (1):

Calculate the ionic mobility of the cation in an infinitely dilute solution of KBr at 298 K. Given that the transport number of K^+ is 0.48 and the molar conductance of KBr at infinite dilution is 1.52 x l0^{-2} S m^2 mol^{-1}

Homework (2)

Molar conductivities at infinite dilution at 25°C of NH_4Cl, NaOH and NaCl are 129.8, 217.4 & 108.9 Ohm^{-1} cm^2 mol^{-1}. For 0.01 M NH_4OH molar conductance is 9.33 Ohm^{-1} cm^2 mol^{-1}. Calculate ionization constant of NH4OH?

Homework (3)

If the transport number of K^+ is 0.492 in KCl solution. What is the transport number of Cl^- ion ?

.

ملاحظة

جزء من درجة حل الواجب البيتي تعتمد على : الترتيب , وضوح الخط (الحل بالقلم
الجاف حصرا)واستلامه ضمن المدة المحددة.

THE FACTORS AFFECTING THE CONDUCTANCE AND THE IONIC MOBILITY OF ELECTROLYTE SOLUTIONS

1- Temperature: درجة الحرارة

- ***For strong electrolytes*:**

The conductance of a given electrolyte depends on two factors:

(1) ***The number of ions present in unit volume of solution***

(2) ***The speed at which ions move towards the electrodes***

- ***At a given temperature*:**

The first ***factor (1)*** remains the same for a particular electrolyte. Thus the increase in conductance with rise in temperature is due to the influence of ***factor (2). With rise in temperature the viscosity of the solvent (water) decreases which makes the ions to move freely toward the electrodes***.

- ***For weak electrolytes*:**

The influence of temperature on conductance depends upon the value of ***ΔH accompanying the process of ionization***.

If the ionization is exothermic (–ΔH), the degree of ionization is less at higher temperature (Le Chatelier's principle) and conductance decreases. Conversely, ***if the ionization is endothermic (+ΔH), the degree of ionization is more at higher temperature and conductance increases.***

- **Exothermic Reactions**

Exothermic reactions are reactions or processes that release energy, usually in the form of heat or light. In an exothermic reaction, energy is released because the total energy of the products is less than the total energy of the reactants. For this reason, the change in enthalpy, ΔH(-), for an exothermic reaction will always be negative. In the presence of water, a strong acid will dissociate quickly and release heat, so it is an exothermic reaction.

- **Endothermic Reactions**

Endothermic reactions are reactions that require external energy, usually in the form of heat, for the reaction to proceed. Since endothermic reactions draw in heat from their surroundings, they tend to cause their environments to cool down. They are also generally non-spontaneous, since endothermic reactions yield products that are higher in energy than the reactants. As such, the change in enthalpy for an endothermic reaction is always positive ΔH(+). In order to melt the ice cube, heat is required, so the process is endothermic.

2- Nature of electrolyte: طبيعة الالكتروليت

- ***Strong Electrolytes***
- ***Weak Electrolytes***

3- Ionic size & mobility: حجم الايون والانتقالية

- The ***ionic mobility decreases with increase in ion size and hence conductivity also decreases.***

Finally, let us discuss the effect of the hydration shell of associated water molecules formed in aqueous solution on the cation mobility. In dilute aqueous solution, the ion mobility decreases in the order:

$(H+) > (K+) > u(Na+) > u(Li+)$.

This is surprising, since one would expect the Li^+-ions to be smaller than the K^+-ions, for example.

However, in aqueous solution the ions are surrounded by a hydration shell of water molecules, and the number of these water molecules is the larger the higher the surface charge density:

approximately, the hydration shell of Li^+ -consists of 12, that of Na^+ of 8, and that of K^+ of 4 water molecules, rendering the K^+-ion effectively smaller and therefore more mobile in aqueous solution.

4- The nature of solvent and its viscosity: طبيعة المذيب ولزوجته

- The ***ionic mobility is reduced in more viscous solvents***. Hence the conductivity also ***decreases***.

Finally, the ion mobility also depends on temperature, since the viscosity of the solvent and therefore the frictional resistance is decreasing with temperature.

The Walden's rule states that: ***the product of the equivalent conductivity and the viscosity of the solvent for a specific electrolyte at a given temperature is constant*.**

Debye-Huckel Theory

In 1923 Debye and Huckel and in 1926 Onsagar put forward “*the modern theory of strong electrolytes in which account is taken of the electrostatic forces between the ions”.*

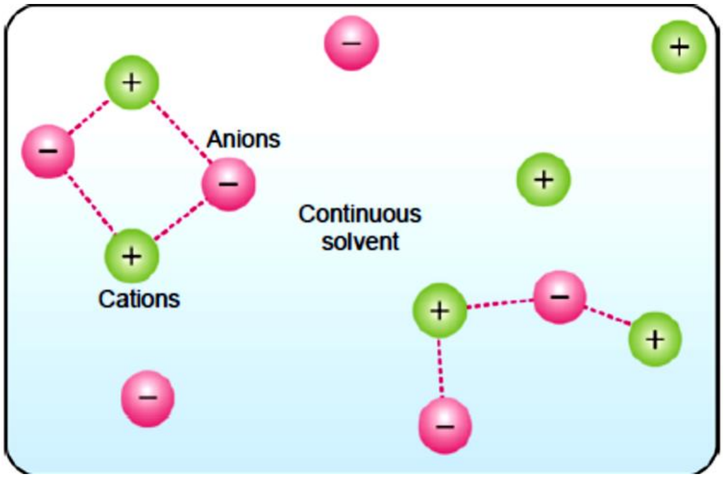
Without going into its mathematical details, a brief outline of the main ideas of the theory is given below:

(1) The strong electrolyte is completely ionized at all dilutions.

(2) Since oppositely charged ions attract each other, it suggests that anions and cations are not uniformly distributed in the solution of an electrolyte but that the cations tend to be found in the vicinity of anions and *vice-versa* *(see the Figure).*

- Though the solution is on the whole neutral, there is in the vicinity of any given ion a predominance of ions of opposite charge which we call as ***counter ions*.**

  The ions are all the time on the move in all directions but on the average, more ***counter ions*** than like *ions* pass by any given ion. ***This spherical haze of opposite charge is called ionic atmosphere*.**



(3) **Decrease in equivalent conductance with increase in concentration is due to fall in mobilities of the ions due to greater inter-ionic effect and *vice-versa.***

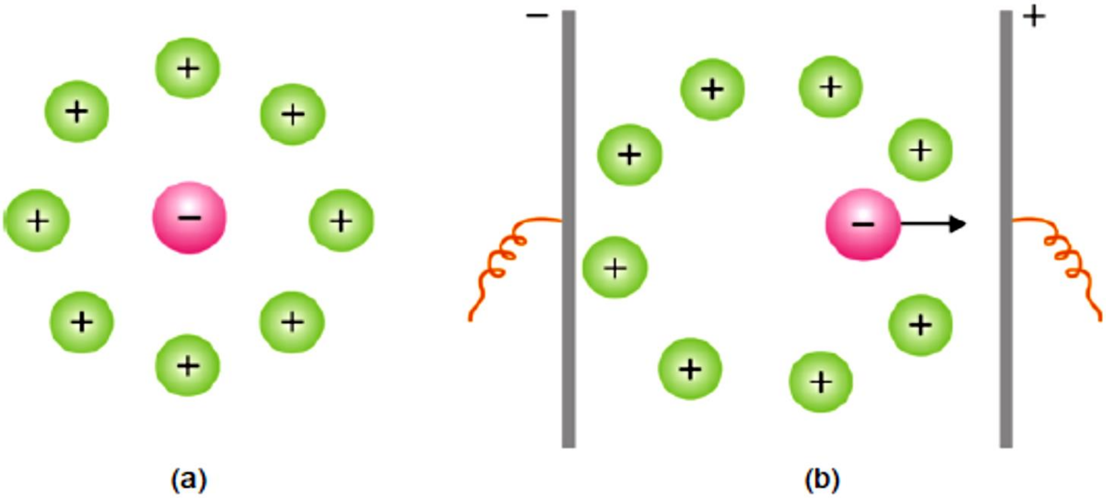
(4) **The ratio $(\Lambda_{eq} / \Lambda\infty)$ does not correctly give the degree of dissociation (α) for strong electrolytes. Due to the complete ionization, (Λ_{eq}) is much less than $(\Lambda\infty)$.**

The deviations from the theory are due to the following reasons:

(1) Asymmetry or Relaxation Effect.

- Imagine a ***central negative ion***. This is surrounded by a number of positively charged ions which form its ***‘ionic atmosphere***.’ ***This atmosphere is symmetrically situated in the absence of any electrical field and the force of attraction exerted by the atmosphere on the central ion is uniform in all directions***. ***(see the fig.(a))*** When an ***electric field is applied***, ***the negative ion moves towards the anode and the positive ionic atmosphere towards the cathode***, ***which leads to destroy the symmetry of the atmosphere about the central negative ion is and it becomes distorted***. ***(see the Fig(b)).***Whereas initially ***the force of attraction exerted by the atmosphere on the central ion was uniform it becomes greater now behind the ion than in front***. As a result of this: ***the negative ion experiences a force which tends to drag it backwards and this slows down its movement in the forward direction***. This behavior is known as:

“Asymmetry Effect”



(a) Symmetrical ionic atmosphere at rest

(b) Asymmetrical ionic atmosphere under the influence of applied field.

(2) Electrophoretic Effect:

- Another factor which acts as a drag and tends to retard the motion of an ion in solution ***is the tendency of the applied field to move the ionic atmosphere (to which solvent molecules are also attached) in a direction opposite to that in which the central ion associated with solvent molecules is moving. Thus the central negative ion moving towards the anode has to make its way through the ionic atmosphere with its associated solvent molecules which is moving in the opposite direction i.e., towards the cathode.*** This causes a retarding influence on the movement of the ion the effect of which is equal to the increase in the viscous resistance of the solvent. By analogy to the resistance acting on the movement of a colloidal particle under an electrical field this effect is called:

Electrophoretic Effect

- **Both the above** ***reasons reduce the velocity of the ion and operate in solutions of strong electrolytes with the result that a value of equivalent conductance (Λeq) lower than the value at infinite dilution ($\Lambda\infty$) is obtained***. **At infinite dilution since the electrical effects are practically absent*, the two values tend to approach each other***.

Debye-Huckel-Onsagar *(D-H-O)* Conductance Equation

Takes these **reasons** into account and for a ***univalent electrolyte supposed to be completely dissociated* is written in the form:**

$$\Lambda_{eq} = \Lambda_{\infty} - (A + B\,\Lambda_{\infty})\sqrt{C}\ \ldots\ldots\ldots(D\text{-}H\text{-}O)$$

Where:

A is the constant of the electrophoretic effect

B is the constant of the asymmetry effect

C is the concentration *in (gm-eq/ litre)*.

***These constants depend only on*:**

1) The nature of the solvent

2) The temperature

And are given by the relationships:

$$A = \frac{82.4}{(DT)^{1/2}\,\eta} \quad \text{and} \quad B = \frac{8.20 \times 10^{5}}{(DT)^{3/2}}$$

D = The ***dielectric constant***

η = The ***coefficient of viscosity of the medium***

T= The ***absolute temperature*** in K.

- ***For H_2O as a solvent at 25°C :***

$D = 78.5$

$\eta \times 10^3 = 8.95$,

$A = 60.20$,

$B = 0.229$.

On substituting these values in the above equation, we have:

$$\Lambda_{eq} = \Lambda_\infty - (60.20 + 0.229\,\Lambda_\infty)\sqrt{C}$$

HOMEWORK (1)

Depending on Debye-Huckel theory, what is/are the effect that tends to retard the mobility of ions in solution?

HOMEWORK (2)

Explain the factors that affecting the conductance of an electrolyte?

HOMEWORK (3)

Write short notes on the Ionic atmosphere?

HOMEWORK (4)

Explain briefly the use of Kohlrausch's law to determine the solubility of a sparingly soluble salt?

HOMEWORK (5)

For $AgNO_3$ in aqueous solution Λ_∞ =133.36 $Ohm^{-1}eq^{-1}$ cm^2, A= 0.5091and B=0.3226 at 25 °C. Using the D-H-O equation calculated Λeq for 0.001N solution at the same temperature?

Do you think $AgNO_{3\ (aq)}$ solution obey D-H-O equation?

ملاحظة

جزء من درجة حل الواجب البيتي تعتمد على : الترتيب , وضوح الخط (الحل بالقلم الجاف حصرا) واستلامه ضمن المدة المحددة

Electrochemistry/ Part two

Learning points

- **Introduction to the concept of energy transfer**
- **Commercially available electro-chemical cells**
- **Understand and recognize electro-chemical equations**
- **Differentiate between Cathode / Anode and Reduction / Oxidation reactions**
- **Introduction to potential difference between cells**

Energy Transfer

Reduction / Oxidation (also called "Redox") reactions, like all other chemical reactions, have an associated enthalpy change. If the reactants are mixed in direct contact, then this enthalpy change (ΔH) would be seen as release of heat. If the reactants are physically separated, but are connected via an external circuit, then an electric current is generated instead.

Applications of Electro-chemistry تطبيقات الكيمياء الكهربائية

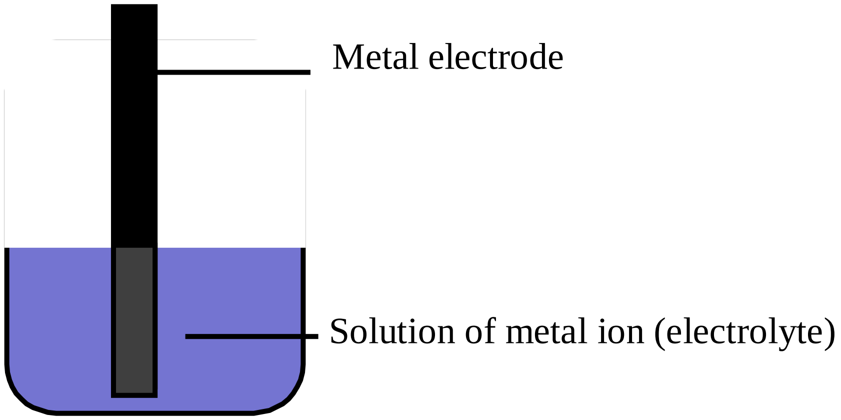
The applications of these reactions range from the lead-acid batteries in cars to torch batteries as seen below.

Electro-chemical Cells الخلايا الكهروكيميائية

An electro-chemical cell is a system consisting of two half-cells in which electrodes dip into an electrolyte. When they are connected electrically into a circuit, a chemical reaction occurs, which either uses or generates an electric current.

❖ Half-cells نصف خلية

Generally half-cells are composed of a metal electrode immersed in the corresponding solution of metal ion as showed in the figure below



❖ Voltaic Cells

- A **voltaic** cell (or "galvanic cell") is an electro-chemical cell in which a **spontaneous reaction** generates an electric **current**.

This type of cell is able to produce an electric current because of a potential difference between the two electrodes.

- An **electrolytic cell** is an electro-chemical cell in which an electric **current drives** an otherwise **non- spontaneous reaction**.

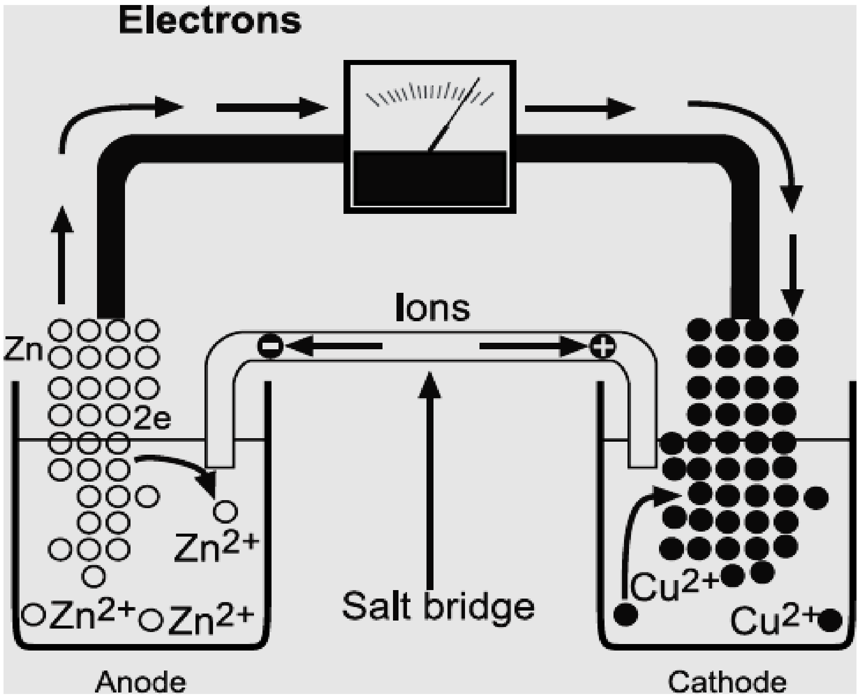
Each half-cell is a portion of the electro-chemical cell in which a half-reaction takes place. A simple half-cell can be made from a metal strip dipped into a solution of its metal ion.

For example:

- The **zinc-zinc ion half-cell consists** of a zinc strip dipped into a solution of zinc sulphate (**$ZnSO_4$**).

- Another simple half-cell consists of a **copper strip dipped into a solution of a copper salt (**$CuSO_4$**)**.

- **In the cell**, two half-cells are connected so that electrons flow from one metal electrode to the other through an external circuit. ***The figure below illustrates what is happening to the atoms in a zinc / copper voltaic cell.***



As long as there is an external circuit, electrons can flow through it from one electrode to the other.

Zinc is a more reactive metal and has a greater tendency to lose electrons than copper. The zinc atoms in the zinc electrode lose electrons to form zinc ions.

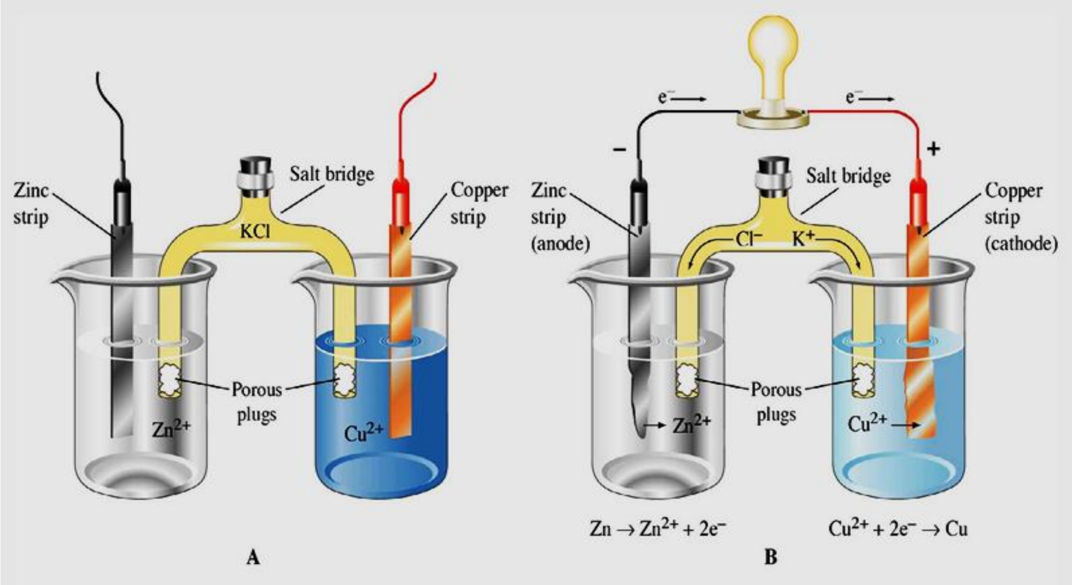
The electrons flow through the external circuit to the copper electrode where copper ions gain the electrons to become copper metal.

The two half-cells must also be connected internally to allow ions to flow between them. Without this internal connection, too much positive charge builds up in the zinc half-cell (and too much negative charge in the copper half-cell) causing the reaction to stop.
Thus, the two half-cells must be connected by a salt bridge.

❖ Salt bridge

- The salt bridge which connects the half cells is usually a tube of an electrolyte in a gel or a piece of filter paper soaked in the electrolyte.

- The salt bridge allows the flow of ions but prevents the mixing of the different solutions that would allow direct reaction of the cell reactants.



The complete electrical circuit

❖ Effect on Electrodes

It is important to note that **the zinc electrode (Zn) gradually gets smaller, as it reacts to form zinc ions (Zn^{2+}) in solution**.
Similarly, the copper electrode (Cu) grows as copper ions (Cu^{2+}) in solution react to form more copper metal (Cu).

❖ Half-cell redox reactions

The two half-cell reactions in the Zn/Cu cell are as follows:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- \qquad \text{(oxidation half- reaction)}$$
$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \qquad \text{(reduction half-reaction)}$$

In the first reaction, electrons are lost by zinc atoms in an oxidation half-reaction.
The electrode at which **oxidation occurs** is **the anode**.

The two half-cell reactions in the Zn/Cu cell are as follows:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$$
$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$$

In the second reaction, electrons are gained by copper ions in a reduction half- reaction.
The electrode at which **reduction occurs** is **the cathode.**

❖ Overall cell reaction

The sum of the two half-reactions can be seen below:

$$Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Cu\ (s)\ \ldots\ldots\ \text{Cell reaction}$$

This is the net reaction that occurs in the electro-chemical cell.

It is called the : ***cell reaction***.

Note that electrons are given up at the anode and thus flow from it to the cathode where reduction occurs.

❖ Anode and Cathode

ANODE: **The anode is the electrode in a voltaic cell which has a negative sign because electrons flow from it.**

CATHODE: **The cathode in a voltaic cell has a positive sign.**

❖ Electro-chemical Cell Notation تدوين(ترميز) الخلايا الكهروكيميائية

It is easier to have a shorthand way of writing out particular electrochemical cells. A cell consisting of the zinc-zinc ion half-cell and the copper-copper ion half-cell, is written:

$$\text{Zn (s)} \mid \text{Zn}^{2+}\text{ (aq)} \parallel \text{Cu}^{2+}\text{ (aq)} \mid \text{Cu(s)}$$

Oxidation half-cell **Reduction half-cell**

The anode (oxidation half-cell) is written on the left.

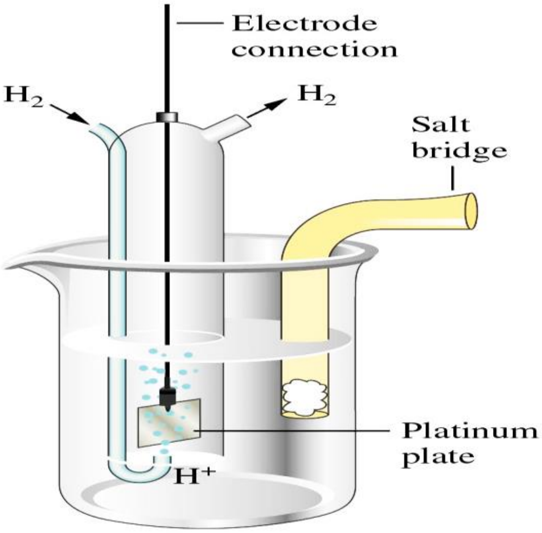
The cathode (reduction half-cell) is written on the right.

Oxidation half reaction,	Reduction half reaction	Net reaction
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

Hydrogen electrode

When the half-cell reaction involves a gas, an inert material such as platinum serves as a terminal and an electrode surface on which the reaction occurs. In a hydrogen electrode, hydrogen bubbles over a platinum plate immersed in an acidic solution.

The anode half-reaction is: $H_2\text{ (g)} \rightarrow 2H^+\text{ (aq)} + 2e^-$



The notation for the hydrogen electrode, written as an anode, is shown below:

$$\mathbf{Pt \mid H_2\,(g) \mid H^+\,(aq) \parallel}$$

To write such an electrode as a cathode, the notation is simply reversed as shown below:

$$\mathbf{\parallel H^+\,(aq) \mid H_2\,(g) \mid Pt}$$

$$\mathbf{Pt \mid H_2\,(g) \mid H^+\,(aq) \parallel H^+\,(aq) \mid H_2\,(g) \mid Pt}$$

Same phase half-cells انصاف الخلايا المتشابهة

Some half cells contain two related substances in solution rather than a metal in a solution of one of its salts.

E.X: → **A mixture of $Br_{2\,(l)}$ and $Br^{-}_{(aq)}$**

E.X: → **A mixture of $Fe^{2+}_{(aq)}$ and $Fe^{3+}_{(aq)}$**

The cell diagram is written with a comma separating them rather than using the vertical bar separator |. However, an inert solid electrode is also needed.

E.X. → **$Br_{2\,(l)}, Br^{-}_{(aq)}$ | Pt**

$$Br_{2\,(l)} + 2e \longrightarrow 2Br^{-}_{(aq)}$$ **(Reduction reaction)**

Electro-Chemical Cell

Sometimes the concentrations of the solutions and the pressure of gases are specified. In the cell notation, these are written in brackets.

For example:

$$\mathbf{Zn\ (s)\ |\ Zn^{2+}\ (1.0\ M)\ ||\ H^{+}\ (aq)\ |\ H_2\ (1.0\ atm)\ |\ Pt}$$

It should be noted that standard conditions are attained for concentrations of 1 mol.dm^{-3} and pressures of 1 atm.

- **Example:**

Give the overall cell reaction for the following electro-chemical cell:

$$\mathbf{Cd(s)\,|\,Cd^{2+}\,(1.0\,M)\,||\,H^{+}\,(aq)\,|\,H_2\,(1.0\,atm)\,|\,Pt}$$

Solution:

The half-cell reactions are:

$$\mathbf{Cd(s) \rightarrow Cd^{2+}\,(aq) + 2e^{-}}$$

$$\mathbf{2H^{+}\,(aq) + 2e- \rightarrow H_2\,(g)}$$

The overall reaction for the electro-chemical cell is therefore:

$$\mathbf{Cd_{(s)} + 2H^{+}_{(aq)} \rightarrow Cd^{2+}_{(aq)} + H_{2\,(g)}}$$

❖ Potential Difference الفرق في الجهد

Potential difference is the difference in electric potential (also referred to as electrical pressure) between two points. This difference in electrical potential can be measured by a voltmeter. The volt (symbol V) is the SI unit of potential difference.

The movement of electrons in electro-chemical cells can be compared to water flowing or being pumped from one point to another. Water moves from a point of high pressure to a point of lower pressure. Thus, a pressure difference is required. The work done in moving the water through a pipe depends on the volume of water and the pressure difference.

Electric Potential

Before an electro-chemical cell is connected, a redox reaction is ready to take place but cannot yet proceed. At the anode, the oxidation half-reaction is ready to produce surplus electrons, so there is a high electric potential. At the cathode, the reduction half- equation is ready to use up surplus electrons, so there is a low electric potential.

Redox couples أزدواج أكسدة اختزال

Note that each redox half reaction must always refer to a pair of species; the reduced form and the oxidized form.

The reduction potential of the redox couple is a measure of how easily the oxidized species accepts an electron to change to the reduced species.

The oxidation potential is a measure of how easily the reduced form donates an electron to change to the oxidized form. It is the negative of the reduction potential for the reverse reaction.

For example:

The reaction ($Zn \rightarrow Zn^{2+} + 2e$) happens easily.

Whereas,

The reaction ($Zn^{2+} + 2e \rightarrow Zn$) does not happen easily.

Therefore, the following redox equilibrium lies well to the left as follows:

$$Zn^{2+} + 2e \longleftrightarrow Zn$$

Potential Difference

The difference in electric potential between the two half-cells gives the overall cell voltage. If the two half-cells are connected by a wire and a voltmeter, the potential difference can be measured.

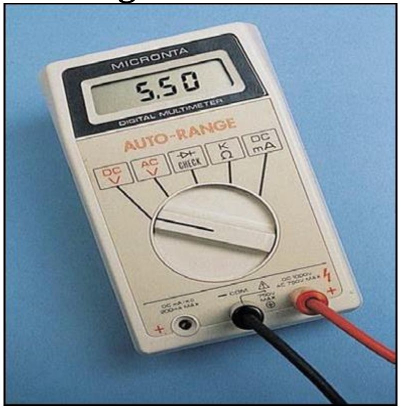
Electro-motive Force (emf)

Normally the potential difference (voltage) measured across the electrodes is less than the maximum possible voltage of the cell. This is because the actual flow of electrons reduces the electrical pressure. Thus, a cell voltage has its maximum value when no current flows.

Electro-motive Force: Ecell

The maximum potential difference between the electrodes of a voltaic cell is referred to as the electro- motive force (also called emf) of the cell, or Ecell. It can be measured by an electronic digital voltmeter, which draws negligible current.

A digital voltmeter



Potential Difference

Potential difference is a measure of the capacity of the cell to do work by moving electric charge through that potential difference. The amount of work that can be done is directly related to the enthalpy ΔH for the redox reaction (strictly ΔG, the free energy change which also incorporates entropy S).

Electrical work

The amount of work done in moving an electrical charge through a conductor from a point of high electrical potential (or high electrical pressure) to one of lower electrical potential is dependent on:

- **The amount of charge,**
- **The potential difference**

Potential difference

By definition, **Electrical Work [J] = Charge [C] × Potential Difference [V].**

Therefore, one volt is equivalent to one joule of energy per coulomb of charge. In other words,

1V = 1J / 1C

Faraday constant

We know that ***the charge of one electron is*** 1.60×10^{-19} ***C.***

Thus,

The charge carried by one mole of electrons will be $= N \times e$

$$= 6.02 \times 10^{23} \times 1.60 \times 10^{-19}$$

= 96500 Coulombs

N= ***Avogadro no.***

e = ***the charge of one electron***

We note that [96500 C] is also called [1 Faraday]

The Faraday constant (F) is the amount of charge in one mole of electrons.

In moving one mole of electrons through a circuit, the value of the work done by an electro-chemical cell is the product of the Faraday constant (referred to as F) by the potential difference between the electrodes as shown below:

Work [J] = – F [C] × Potential Difference [V]

Electromotive Force

We can now write an expression for the maximum work attainable by an electro-chemical cell. Let "n" be the number of electrons transferred in the overall electrochemical cell reaction. **The maximum work (W_{max}) for molar amounts of reactants is given by the following formula:**

$$W_{max} = - n \times F \times E_{cell}$$

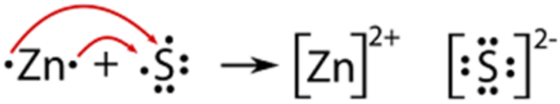
Electrochemistry

Redox Reactions

A redox reaction involves a transfer of electrons from one species to another. This results in a **change in oxidation number**.

Oxidation reaction (reducing agent)= loss of electrons
Reduction reaction (oxidizing agent)= gain of electrons
[These reactions must occur together]

Consider the reaction of elemental zinc and sulfur to form zinc sulfide:



Reaction between zinc and sulfur

Zinc (Zn) **is losing electrons in the reaction and is thus oxidized to the zinc cation,**

Sulfur (S) **is gaining electrons and is thus reduced to the sulfide anion.**

Oxidation reaction = loss of electrons
Reduction reaction = gain of electrons

Zn= Reducing agent ; S = Oxidizing agent

$$\underbrace{Zn \rightarrow Zn^{2+} + 2e^-}_{\text{Oxidation}}$$

$$\underbrace{S + 2e^- \rightarrow S^{2-}}_{\text{Reduction}}$$

$$\textbf{oxidation} = \text{increase in oxidation number}$$
$$\textbf{reduction} = \text{decrease in oxidation number}$$

$$\textbf{Reductant (reducing agent)} = \text{species that is oxidized}$$
$$\textbf{Oxidant (oxidizing agent)} = \text{species that is reduced}$$

Balancing Simple Redox Reactions

In a redox reaction both ***the mass*** and ***the charge*** must be balanced

Example: (net ionic equation)

$$\mathbf{Al_{(s)} + Ni^{2+}{}_{(aq)} \rightarrow Al^{3+}{}_{(aq)} + Ni_{(s)}}$$

Balanced by mass, but *not* by charge

What do we do?

1. Divide reaction into two half-reactions and add e^- to each half-reaction to balance the charge.

The two half-reactions correspond to reduction and oxidation

$$\mathbf{Al_{(s)} \rightarrow Al^{3+}{}_{(aq)} + 3e^-}$$

$$\mathbf{Ni^{2+}{}_{(aq)} + 2e^- \rightarrow Ni_{(s)}}$$

2. Multiply to get same number of e^- in each reaction:

(number of e^- lost must equal number of e^- gained)

$$\mathbf{2\,[Al_{(s)} \rightarrow Al^{3+}{}_{(aq)} + 3e^-\,]}$$

$$\mathbf{3\,[Ni^{2+}{}_{(aq)} + 2e^- \rightarrow Ni_{(s)}\,]}$$

3. Cancel e^- to get the balanced net ionic reaction:

$$\mathbf{2\,Al_{(s)} \rightarrow 2\,Al^{3+}{}_{(aq)} + 6\,e^-}$$

$$\mathbf{3\,Ni^{2+}{}_{(aq)} + 6\,e^- \rightarrow 3\,Ni_{(s)}}$$

$$\mathbf{2\,Al_{(s)} + 3\,Ni^{2+}{}_{(aq)} \rightarrow 2\,Al^{3+}{}_{(aq)} + 3\,Ni_{(s)}}$$

If a redox reaction can be split into half reactions it becomes possible to build a device, called an electrochemical cell, that has separate compartments (cells) for the oxidant and reductant. This physically prevents them from contacting each other and reacting, but allows for charge transfer in the form of electrons through an external circuit and in the form of counter ions in a salt bridge that connects the cells.

Electrolytic Cells

Voltaic cells are driven by a spontaneous chemical reaction that produces an electric current through an outside circuit. These cells are important because they are the basis for the batteries that fuel modern society. But they are not the only kind of electrochemical cell. The reverse reaction in each case is non-spontaneous and requires electrical energy to occur.

The general form of the reaction can be written as:

Spontaneous →

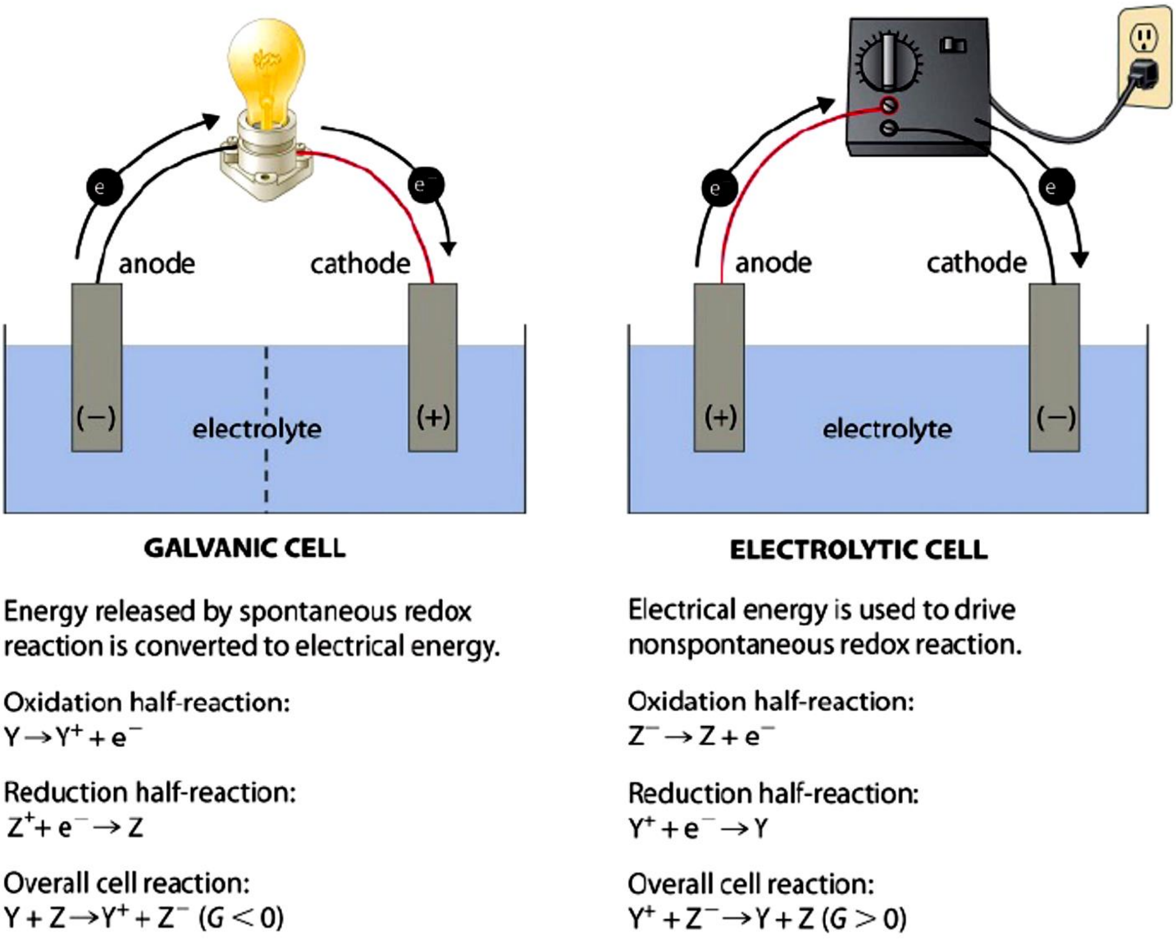
[Reactants ⇔ Products + Electrical Energy]

← Non spontaneous

It is possible to construct a cell that does work on a chemical system by driving an electric current through the system. **These cells are called electrolytic cells**. ***Electrolytic cells, like galvanic cells, are composed of two half-cells; one is a reduction half-cell, the other is an oxidation half-cell***. The direction of electron flow in electrolytic cells, however, may be reversed from the direction of spontaneous electron flow in galvanic cells, but the definition of both cathode and anode remain the same, where reduction takes place at the cathode and oxidation occurs at the anode.

Electrolytic cells are very similar to **voltaic (galvanic) cells** in the sense that both require a salt bridge, both have a cathode and anode side, and both have a consistent flow of electrons from the anode to the cathode.

The main differences between the two electrochemical cells are outlined below:



GALVANIC CELL

Energy released by spontaneous redox reaction is converted to electrical energy.

Oxidation half-reaction:
$Y \rightarrow Y^{+} + e^{-}$

Reduction half-reaction:
$Z^{+} + e^{-} \rightarrow Z$

Overall cell reaction:
$Y + Z \rightarrow Y^{+} + Z^{-}$ $(G < 0)$

ELECTROLYTIC CELL

Electrical energy is used to drive nonspontaneous redox reaction.

Oxidation half-reaction:
$Z^{-} \rightarrow Z + e^{-}$

Reduction half-reaction:
$Y^{+} + e^{-} \rightarrow Y$

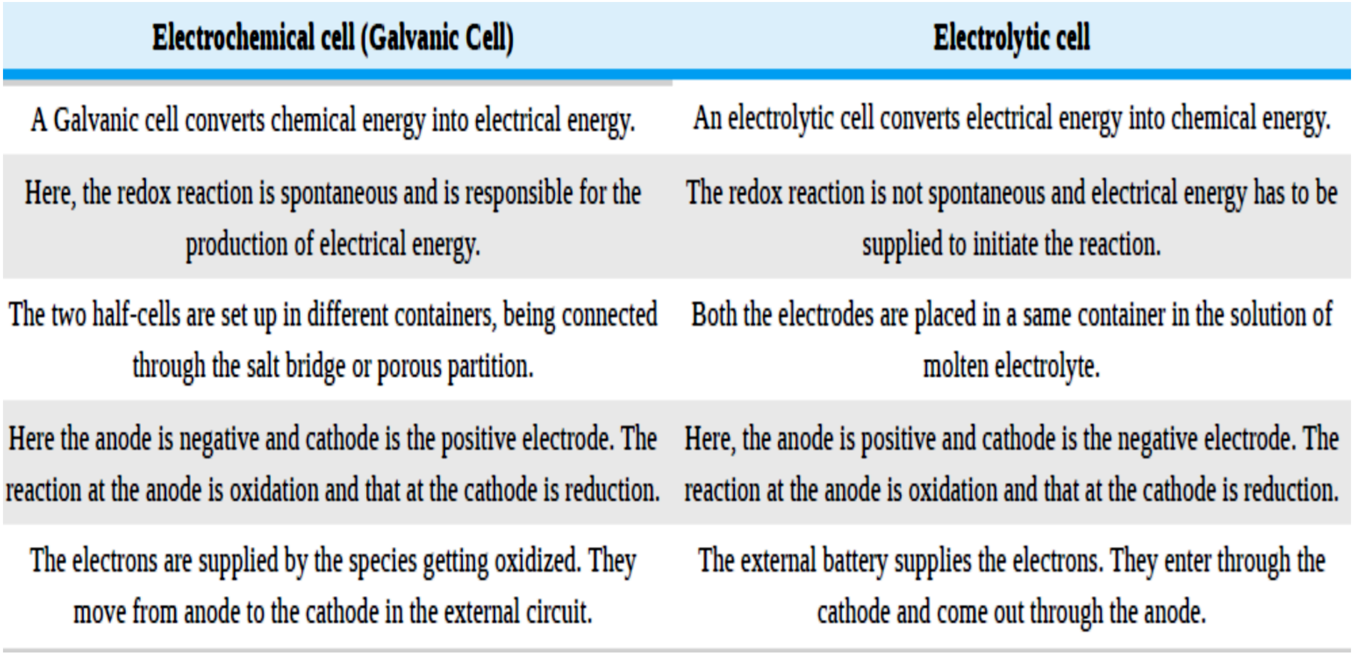
Overall cell reaction:
$Y^{+} + Z^{-} \rightarrow Y + Z$ $(G > 0)$

Figure 1**: Electrochemical Cells.**

- ***A galvanic cell (left)*** transforms the energy released by a spontaneous redox reaction into electrical energy that can be used to perform work. The oxidative and reductive half-reactions usually occur in separate compartments that are connected by an external electrical circuit; in addition, a second connection that allows ions to flow between the compartments (shown here as a vertical dashed line to represent a porous barrier) is necessary to maintain electrical neutrality. The potential difference between the electrodes (voltage) causes electrons to flow from the reductant to the oxidant through the external circuit, generating an electric current.

- ***In an electrolytic cell (right),*** an external source of electrical energy is used to generate a potential difference between the electrodes that forces electrons to flow, driving a nonspontaneous redox reaction; only a single compartment is employed in most applications. In both kinds of electrochemical cells, the anode is the electrode at which the oxidation half-reaction occurs, and the cathode is the electrode at which the reduction half-reaction occurs.

Properties of Galvanic and Electrochemical Cells



Electrochemical cell (Galvanic Cell)	Electrolytic cell
A Galvanic cell converts chemical energy into electrical energy.	An electrolytic cell converts electrical energy into chemical energy.
Here, the redox reaction is spontaneous and is responsible for the production of electrical energy.	The redox reaction is not spontaneous and electrical energy has to be supplied to initiate the reaction.
The two half-cells are set up in different containers, being connected through the salt bridge or porous partition.	Both the electrodes are placed in a same container in the solution of molten electrolyte.
Here the anode is negative and cathode is the positive electrode. The reaction at the anode is oxidation and that at the cathode is reduction.	Here, the anode is positive and cathode is the negative electrode. The reaction at the anode is oxidation and that at the cathode is reduction.
The electrons are supplied by the species getting oxidized. They move from anode to the cathode in the external circuit.	The external battery supplies the electrons. They enter through the cathode and come out through the anode.

Construction Electrolytic Cells:

To explain what happens in an electrolytic cell let us examine ***the decomposition of molten sodium chloride*** ***$NaCl_{(l)}$*** into **Na metal** and **Cl_2 gas**. The reaction is written below:

$$2NaCl_{(l)} \rightleftharpoons 2\,Na_{(s)} + Cl_{2\,(g)}$$

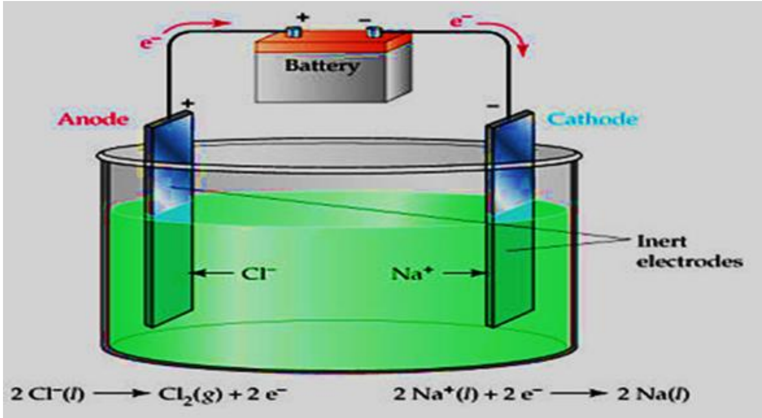
If molten $NaCl_{(l)}$ is placed into the container and inert electrodes of $C(s)$ are inserted, attached to the positive and negative terminals of a battery, an electrolytic reaction will occur.

1- Electrons from the negative terminal travel to the cathode and are used to reduce sodium ions into sodium atoms. The sodium will plate onto the cathode as it forms. The sodium ion are migrating towards the cathode.

$$Na^{+} + e^{-} \rightleftharpoons Na_{(s)} \ldots\ldots\ldots\ldots\ldots(2)$$

2- The negative Chlorine ions migrate towards the anode and release electrons as they oxidize to form chlorine atoms. The chlorine atoms will combine together to form chlorine gas which will bubble away.

$$2Cl^{-} \rightleftharpoons Cl_{2(g)} + 2e^{-} \ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$



3- Note that the site of oxidation is still the anode and the site of reduction is still the cathode. Anode has the positive charged and the cathode has a negative charged.

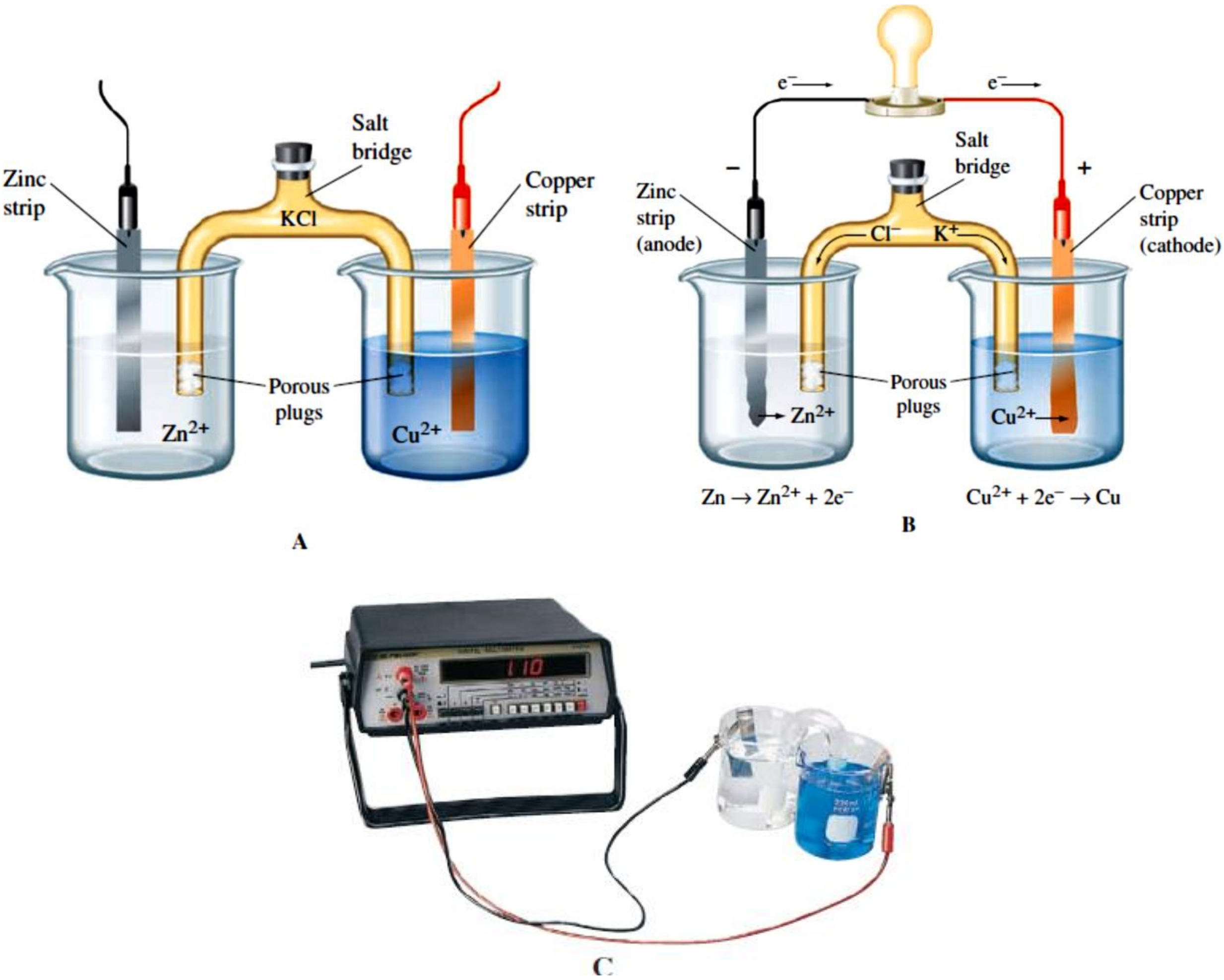
4- The conditions under which the electrolytic cell operates are very important. The substance that is the strongest reducing agent (the substance with the highest standard reduction potential value) will undergo oxidation. The substance that is the strongest oxidizing agent will be reduced.

- ## Construction of Voltaic Cells

In a voltaic cell, two half-cells are connected in such a way that electrons flow from one metal electrode to another through an external circuit, and ions flow from one half-cell to another through an internal cell connection. As long as there is an external circuit, electrons can flow through it from one electrode to another. Because zinc tends to lose electrons more readily than copper, zinc atoms in the zinc electrode lose electrons to produce zinc ions. These electrons flow through the external circuit to the copper electrode, where they react with the copper ions in that half-cell to deposit copper metal atoms. The net result is that zinc metal reacts with copper ions to produce zinc ions and copper metal, and electric current flows through the external circuit.

The two half-cells must be connected internally to allow ions to flow between them. As zinc ions continue to be produced, the zinc ion solution begins to build up a positive charge.

Similarly, as copper ions plate out as copper, the solution builds up a negative charge. The half-cell reactions will stop unless positive ions can move from the zinc half-cell to the copper half-cell, and negative ions from the copper half-cell can move to the zinc half-cell. It is necessary that these ion flows occur without mixing of the zinc ion and copper ion solutions. If copper ion were to come in contact with the zinc metal, for example, direct reaction would occur without an electric current being generated. The voltage would drop, and the battery would run down quickly.



A zinc–copper voltaic cell (Battery)

(A) A zinc-electrode and a copper-electrode, without an external circuit; there is no cell reaction.

(B) When the two electrodes are connected by an external circuit (with a light bulb), chemical reaction occurs.

(C) A similar cell, with the bulb replaced by a voltmeter. Note the blue color of Cu^{2+} (aq).

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \qquad \text{(oxidation half-reaction)}$$

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \qquad \text{(reduction half-reaction)}$$

The first half-reaction, in which a species loses electrons, is the oxidation half reaction. The electrode at which oxidation occurs is called the anode.

The second half reaction, in which a species gains electrons, is the reduction half-reaction. The electrode at which reduction occurs is called the cathode.

These definitions of anode and cathode hold for all electrochemical cells, including electrolytic cells.

Note that the sum of the two half-reactions is the net reaction that occurs in the voltaic cell; it is called the cell reaction.

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

Once you know which electrode is the anode and which the cathode is, you can determine the direction of electron flow in the external portion of the circuit. Electrons are given up by the anode (from the oxidation half-reaction) and thus flow from it, whereas electrons are used up by the cathode (by the reduction half-reaction) and so flow into this electrode. The anode in a voltaic cell has a negative sign, because electrons flow from it. The cathode in a voltaic cell has a positive sign.

Electrode Signs:

Electrolytic Cell	Volatic or Galvanic Cell
E.m.f. is applied to cell	**E.m.f. is generated by cell**

	Electrolytic cell		**Voltaic or Galvanic cell**	
	Anode	**Cathode**	**Anode**	**Cathode**
Sign	+	-	-	+
Electron flow	***Out***	***in***	***Out***	***in***
Half-reaction	***Oxidation***	***reduction***	***Oxidation***	***reduction***

- **Standard Cell Potentials and Standard Electrode Potentials**

A cell potential is a measure of the driving force of the cell reaction. This reaction occurs in the cell as separate half-reactions: an oxidation half-reaction and a reduction half-reaction. The general forms of these half-reactions are:

$$\text{Reduced species} \longrightarrow \text{oxidized species} + ne^- \qquad \text{(oxidation/anode)}$$

$$\text{Oxidized species} + ne^- \longrightarrow \text{reduced species} \qquad \text{(reduction/cathode)}$$

$$E_{\text{cell}} = \text{oxidation potential} + \text{reduction potential}$$

A reduction potential is a measure of the tendency for an oxidized species to gain electrons in the reduction half-reaction (in other words, a measure of the ability of the species to act as an oxidizing agent).

$$\mathbf{E^o_{cell} = E^o_{ox.} + E^o_{red.}}$$

Comparing Strengths of Oxidants and Reductants

- The following table lists (below) the standard potentials for a wide variety of chemical substances that allow us to compare the oxidative and reductive strengths of a variety of substances
- The half-reaction for the standard hydrogen electrode lies halfway down on the table are:

- All species that lie above hydrogen in the table are **stronger oxidizing agent** than H^+, and all those that lie below it are **weaker oxidizing agent**

- All species that lie below H_2 are **stronger reducing agent** than H_2, and those that lie above H_2 are **weaker reducing agent**

$$\text{Oxidized species} + ne^- \longrightarrow \text{reduced species}$$

$$\text{Reduced species} \longrightarrow \text{oxidized species} + ne^-$$

Very Important half-cell reactions to build electrochemical cells (Batteries)

TABLE 18.1 Standard Reduction Potentials at 25°C*

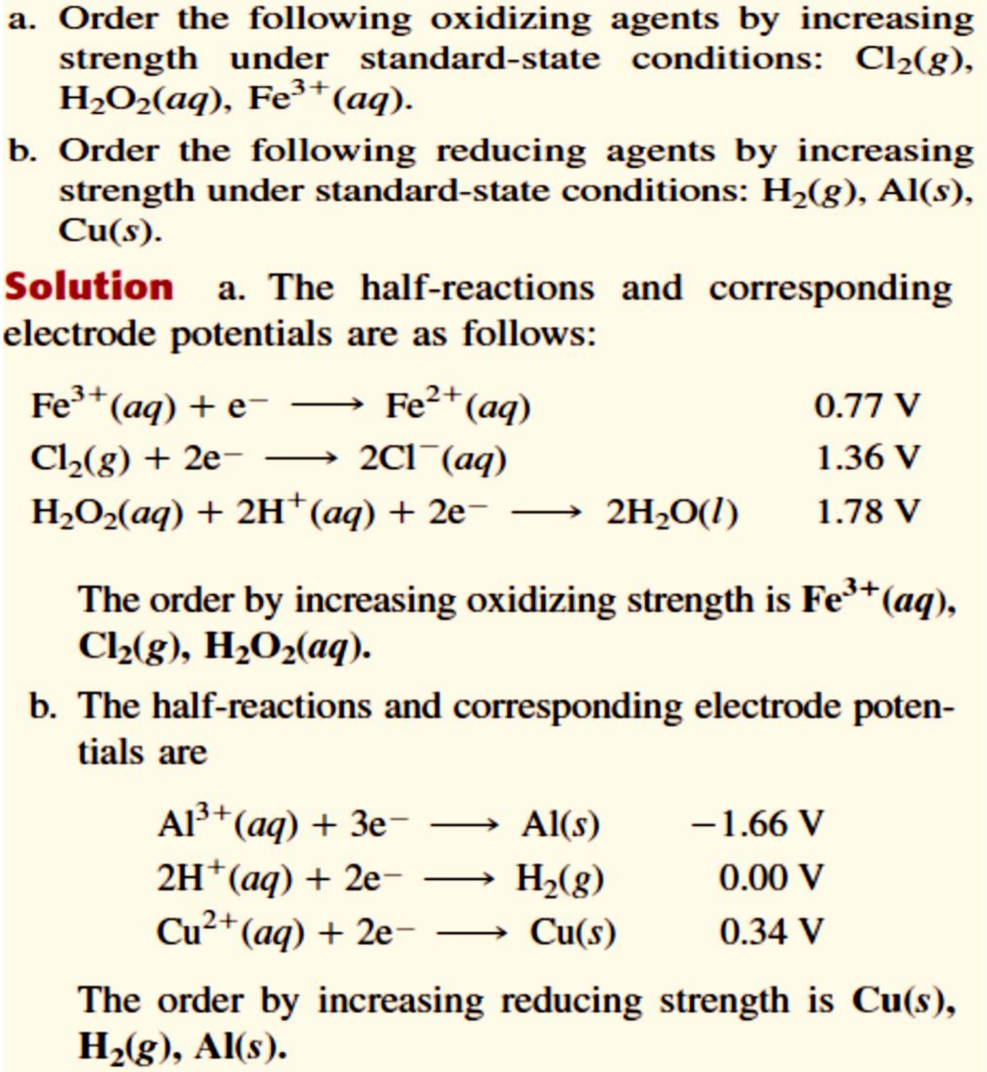
Increasing strength as oxidizing agent

Half-Reaction	$E°$(V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O(l)$	+2.07
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O(l)$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$	+1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$	+1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O(l)$	+0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O(l)$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	−1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05

Increasing strength as reducing agent

Example

Determining the Relative Strengths of Oxidizing and Reducing Agents:



a. Order the following oxidizing agents by increasing strength under standard-state conditions: $Cl_2(g)$, $H_2O_2(aq)$, $Fe^{3+}(aq)$.

b. Order the following reducing agents by increasing strength under standard-state conditions: $H_2(g)$, $Al(s)$, $Cu(s)$.

Solution a. The half-reactions and corresponding electrode potentials are as follows:

$$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq) \qquad 0.77\ V$$

$$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq) \qquad 1.36\ V$$

$$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O(l) \qquad 1.78\ V$$

The order by increasing oxidizing strength is **$Fe^{3+}(aq)$, $Cl_2(g)$, $H_2O_2(aq)$.**

b. The half-reactions and corresponding electrode potentials are

$$Al^{3+}(aq) + 3e^- \longrightarrow Al(s) \qquad -1.66\ V$$

$$2H^+(aq) + 2e^- \longrightarrow H_2(g) \qquad 0.00\ V$$

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \qquad 0.34\ V$$

The order by increasing reducing strength is **$Cu(s)$, $H_2(g)$, $Al(s)$.**

Example:

Determine the overall cell reaction and E°cell of a galvanic cell made of a Cd electrode in a 1.0 M $Cd(NO_3)_2$ solution and a Pb electrode in a 1.0 M $Pb(NO_3)_2$ solution . If the reduction half-reactions and standard electrode potentials are:

$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$, $E° = -0.13$ V

$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$, $E° = -0.40$ V

Solution:

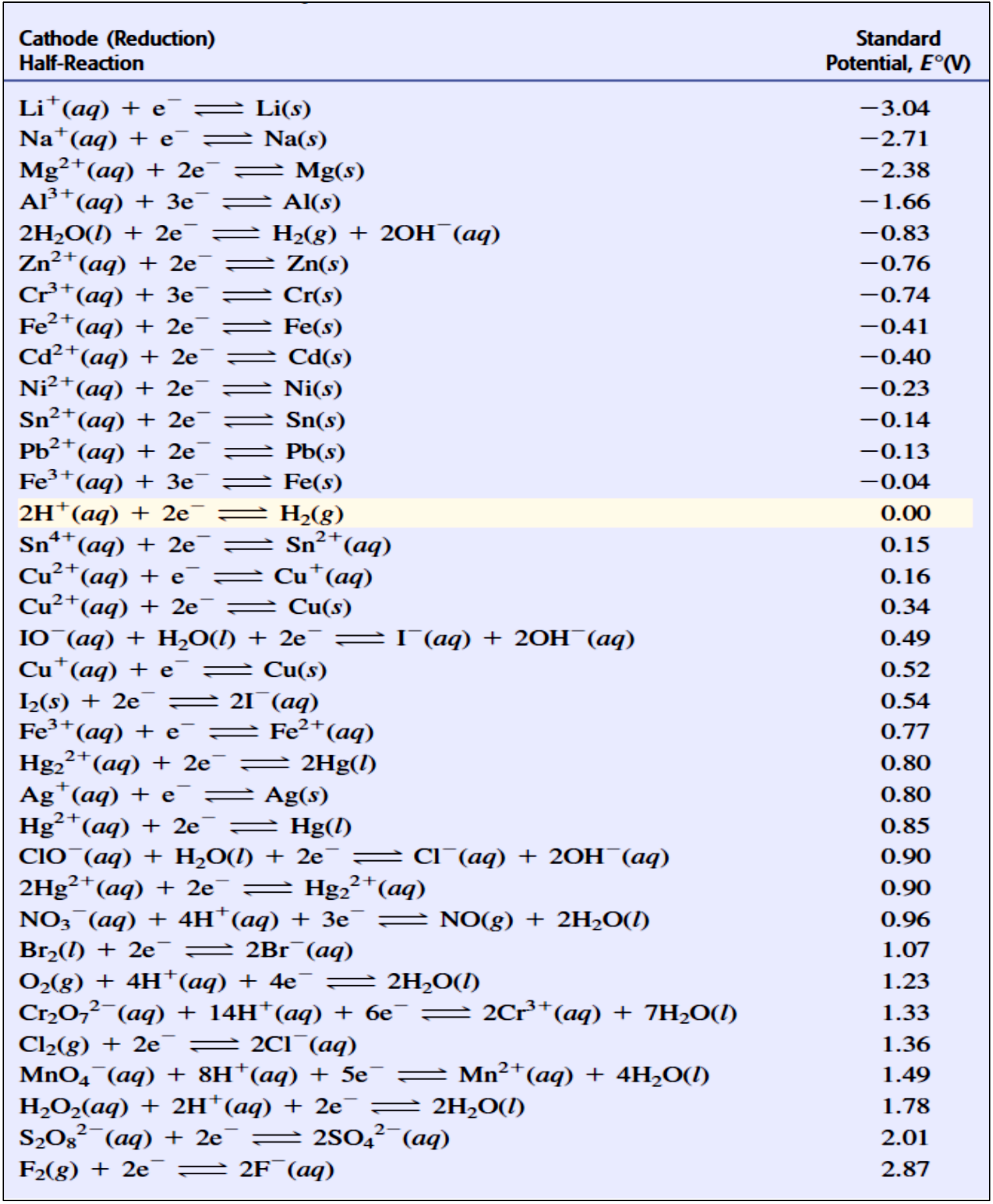
Depending on the standard electrode potentials, ***Pb will therefore go as a reduction reaction (as oxidizing agent) ,*** and ***Cd will go as an oxidation reaction(reducing agent):***

$$Pb^{2+} + Cd_{(s)} \longrightarrow Pb(s) + Cd^{2+}$$

$$E_{cell} = E_{ox} + E_{red}$$

$$E_{cell} = 0.40 + (-0.13) = 0.27v$$

Electrochemical series of electrodes reduction-potential



Cathode (Reduction) Half-Reaction	Standard Potential, $E°$(V)
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	-3.04
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	-2.38
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	-1.66
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	-0.83
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	-0.76
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	-0.74
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.41
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	-0.40
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	-0.23
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	-0.14
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	-0.13
$Fe^{3+}(aq) + 3e^- \rightleftharpoons Fe(s)$	-0.04
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	0.15
$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	0.16
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	0.34
$IO^-(aq) + H_2O(l) + 2e^- \rightleftharpoons I^-(aq) + 2OH^-(aq)$	0.49
$Cu^+(aq) + e^- \rightleftharpoons Cu(s)$	0.52
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	0.54
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	0.77
$Hg_2{}^{2+}(aq) + 2e^- \rightleftharpoons 2Hg(l)$	0.80
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	0.80
$Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg(l)$	0.85
$ClO^-(aq) + H_2O(l) + 2e^- \rightleftharpoons Cl^-(aq) + 2OH^-(aq)$	0.90
$2Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg_2{}^{2+}(aq)$	0.90
$NO_3{}^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	0.96
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	1.07
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	1.23
$Cr_2O_7{}^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	1.36
$MnO_4{}^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	1.49
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	1.78
$S_2O_8{}^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4{}^{2-}(aq)$	2.01
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	2.87

Equilibrium Constants from Cell Potentials

Some of the most important results of electrochemistry are **the relationships among cell potential, free-energy change, and equilibrium constant.** Recall that the **free energy change ΔG for a reaction equals the maximum useful work of the reaction:**

$$\Delta G = w_{max} \;.......(1)$$

***For a voltaic cell*, this work is *the electrical work*:**

$$W_{max} = -nFE_{cell} \;......... (2)$$

Where:

n = The number of moles of electrons transferred in a reaction

So; when **the reactants and products are in their standard states**:

$$\Delta G^o = -nFE^o_{cell} \;........(3)$$

With this equation, ***cell potential (E) measurements become an important source of thermodynamic information***. Alternatively, thermodynamic data can be used to calculate **cell potentials**.

The measurement of cell potentials gives you yet another way to obtain **equilibrium constants (K):**

$$\Delta G^\circ = -RT \ln K \;........ (4)$$

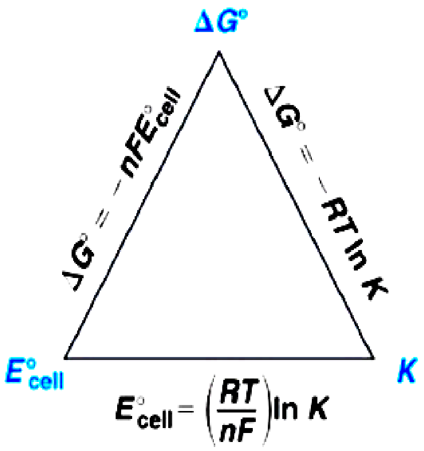
Combining eq.(3) with eq.(4) , we will obtain eq.(5) :

$$nFE^{\circ}_{\text{cell}} = RT \ln K \qquad \text{........ (5)}$$

Or:

$$E^{\circ}_{\text{cell}} = \frac{RT}{nF}\ln K = \frac{2.303\,RT}{nF}\log K$$

> *This formula is typically written using the common logarithm (base 10) function as it is shown here. The factor 2.303 allows for conversion between the common logarithm and base e logarithm (2.303 log x = ln x).*

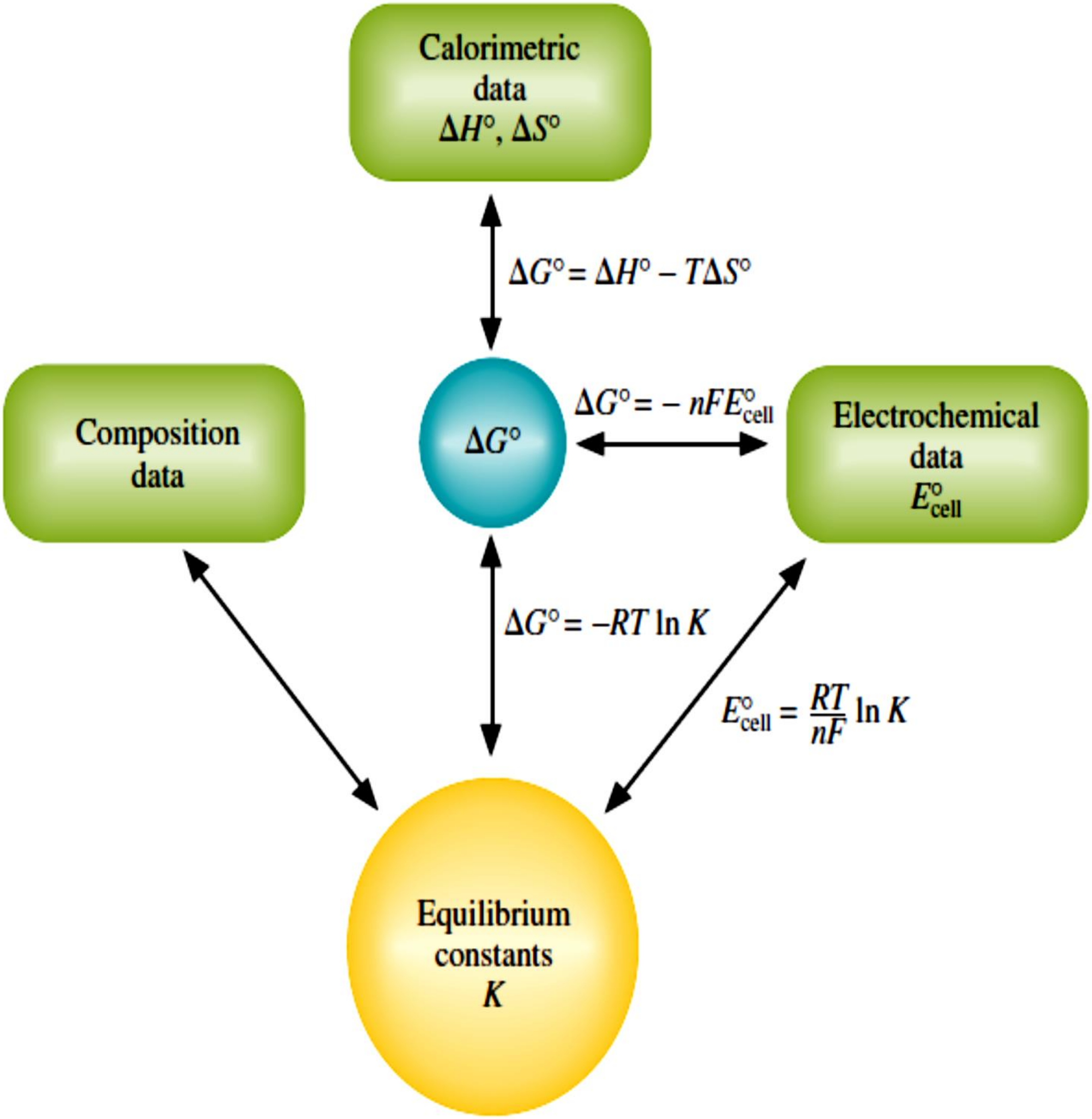


ΔG°	E°_{cell}	K	Direction of Reaction
<0	>0	>1	Spontaneous in forward direction
>0	<0	<1	Spontaneous in reverse direction
0	0	1	No net reaction: system at equilibrium

E > 0, ΔG <0 …….Spontaneous reaction

E<0 , ΔG > 0 ………Non-Spontaneous reaction

E=0 , ΔG=0 …….. Equilibrium reaction


Calorimetric data $\Delta H^\circ, \Delta S^\circ$
$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
Composition data
ΔG°
$\Delta G^\circ = -nFE^\circ_{\text{cell}}$
Electrochemical data E°_{cell}
$\Delta G^\circ = -RT \ln K$
$E^\circ_{\text{cell}} = \frac{RT}{nF} \ln K$
Equilibrium constants K

Example:

Using standard electrode potentials, calculate the standard free-energy change at 25ºC for the reaction:

$$Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$$

If: E^o $Zn^{2+}/Zn = -0.76V$; E^o $Ag^+/Ag = 0.8V$

Solution:

$$\begin{array}{rcl} Zn(s) & \longrightarrow & Zn^{2+}(aq) + 2e^- \\ 2Ag^+(aq) + 2e^- & \longrightarrow & 2Ag(s) \\ \hline Zn(s) + 2Ag^+(aq) & \longrightarrow & Zn^{2+}(aq) + 2Ag(s) \end{array}$$

$$E^o_{cell} = E^o_{ox} + E^o_{red}$$

$$E^o_{cell} = 0.76 + 0.8 = 1.56V$$

$$\Delta G^o = -nFE^o_{cell}$$

$\Delta G^o = -2 \times 96500 \times 1.56 = 3.01 \times 10^5$ J *spontaneous reaction*

Exercise (1) :

What is ΔG^o at 25ºC for the reaction:

$$Sn^{2+}(aq) + 2Hg^{2+}(aq) \longrightarrow Sn^{4+}(aq) + Hg_2{}^{2+}(aq)$$

For data of electrodes reduction-potential {use the table of electrochemical series of previous lecture or from above}.

Exercise (1) :

What is ΔG^o at 25°C for the reaction:

$$Sn^{2+}(aq) + 2Hg^{2+}(aq) \longrightarrow Sn^{4+}(aq) + Hg_2^{2+}(aq)$$

For data of electrodes reduction-potential {use the table of electrochemical series of previous lecture or from above}.

Solution:

$$Sn^{2+} \longrightarrow Sn^{4+} + 2e$$

$$2Hg^{2+} + 2e \longrightarrow Hg_2^{2+}$$

$$Sn^{2+} + 2Hg^{2+} \longrightarrow Sn^{4+} + Hg_2^{2+}$$

$$Hg^{2+}/Hg_2^{2+} = 0.90v; \qquad Sn^{4+}/Sn^{2+} = 0.15v$$

$$E^o_{cell} = E^o_{ox} + E^o_{red}$$

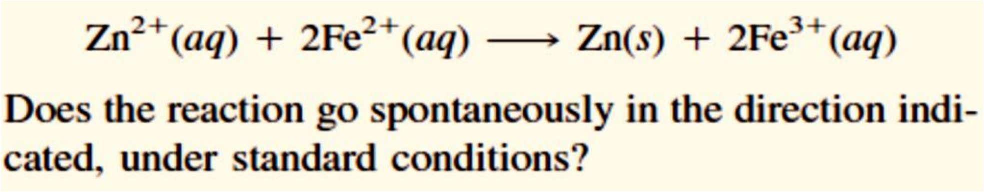
$$E^o_{cell} = - 0.15 + 0.8 = 0.75V$$

$$\Delta G^o = -nFE^o_{cell} \ ; \ \Delta G^o = - 2x96500x\ 0.75 = - 1.44750 \times 10^5\ J$$

$$\Delta G^o < 0 \ \ \textit{spontaneous reaction}$$

EXAMPLE:

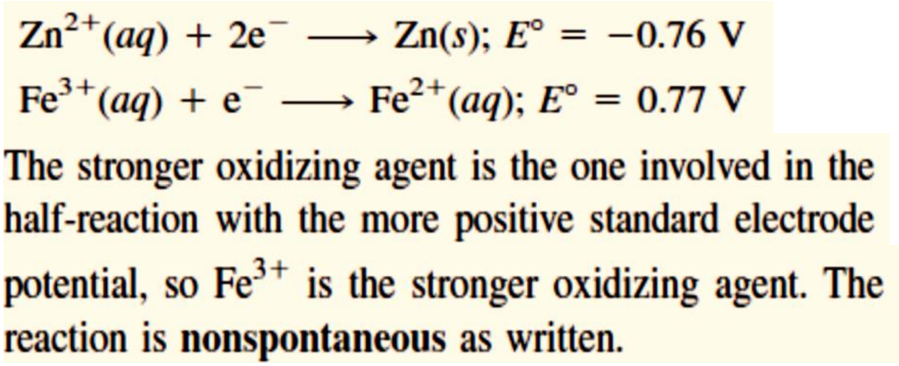
Consider the reaction:



$$Zn^{2+}(aq) + 2Fe^{2+}(aq) \longrightarrow Zn(s) + 2Fe^{3+}(aq)$$

Does the reaction go spontaneously in the direction indicated, under standard conditions?

The corresponding standard electrode potentials are:



$Zn^{2+}(aq) + 2e^{-} \longrightarrow Zn(s); E° = -0.76\ V$

$Fe^{3+}(aq) + e^{-} \longrightarrow Fe^{2+}(aq); E° = 0.77\ V$

The stronger oxidizing agent is the one involved in the half-reaction with the more positive standard electrode potential, so Fe^{3+} is the stronger oxidizing agent. The reaction is **nonspontaneous** as written.

Or:

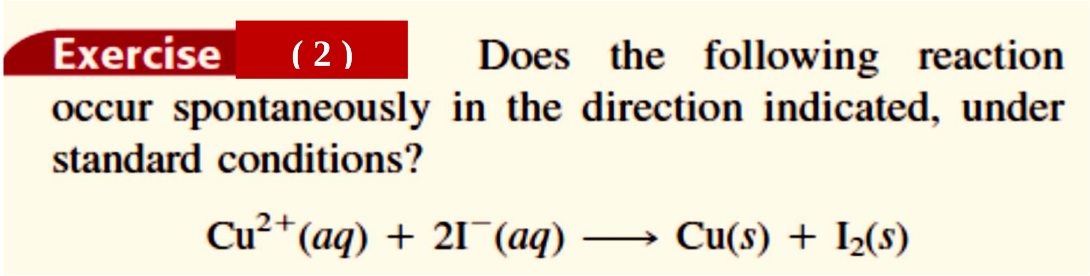
$$E^{o}_{cell} = E^{o}_{ox} + E^{o}_{red}$$

$$E^{o}_{cell} = -0.77v + (-0.76v) = -1.53v$$

$$\Delta G^{o} = -nFE^{o}_{cell}$$

$$\Delta G^{o} = -2x\ 96500x\ (-1.53v) = +295290J$$ **Non spontaneous**

$$\Delta G^{o} > 0$$



Exercise (2) Does the following reaction occur spontaneously in the direction indicated, under standard conditions?

$$Cu^{2+}(aq) + 2I^{-}(aq) \longrightarrow Cu(s) + I_2(s)$$

Nernst Equation

Recall that the free-energy change, ΔG, is related to the standard free-energy change, ΔGº, by the following equation:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Here **Q** is the thermodynamic reaction quotient. The reaction quotient has the form of the equilibrium constant.

You can apply this equation to a **voltaic cell**. In that case, the concentrations and gas pressures are those that exist in the cell at a particular instant.

If you substitute:

$$\Delta G = -nFE_{\text{cell}} \quad \text{and} \quad \Delta G^\circ = -nFE^\circ_{\text{cell}}$$

We will obtain:

$$-nFE_{\text{cell}} = -nFE^\circ_{\text{cell}} + RT \ln Q$$

This result rearranges to give **the Nernst equation**, **an equation relating the cell potential to its standard cell potential and the reaction quotient**.

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q \qquad \text{or} \qquad E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303\,RT}{nF} \log Q$$

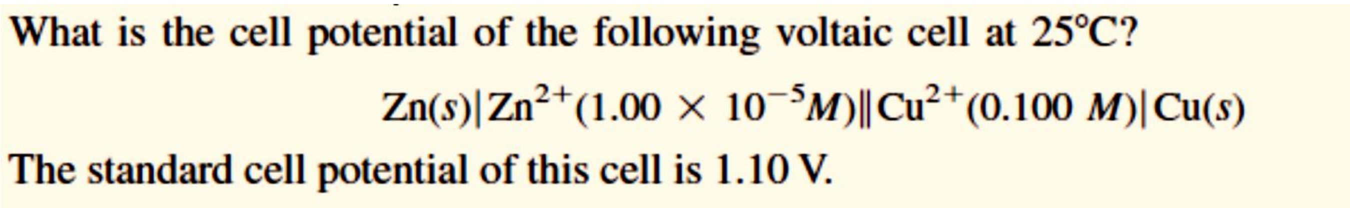
Or:

$$\mathbf{E}_{\text{cell}} = \mathbf{E}^{\mathbf{o}}_{\text{cell}} - \frac{2.303RT}{nF} \log \frac{(Products)}{(reactants)}$$

If: ***R=8.314 JK^{-1} mol^{-1}; T = 298 K ; F=96500 C***

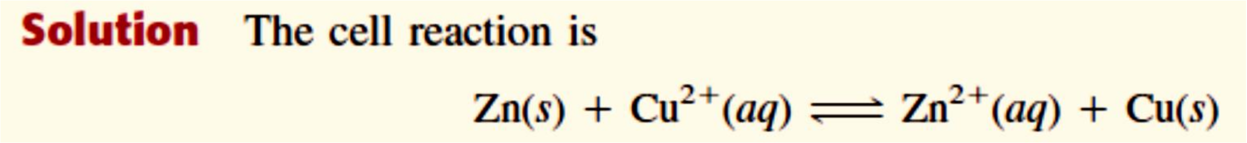
$$\mathbf{E}_{\text{cell}} = \mathbf{E}^{\mathbf{o}}_{\text{cell}} - \frac{0.0591}{n} \log \frac{(Products)}{(reactants)}$$

EXAMPLE :


What is the cell potential of the following voltaic cell at 25°C?

$$\mathrm{Zn}(s)|\mathrm{Zn}^{2+}(1.00 \times 10^{-5} M)\|\mathrm{Cu}^{2+}(0.100\ M)|\mathrm{Cu}(s)$$

The standard cell potential of this cell is 1.10 V.


Solution The cell reaction is

$$\mathrm{Zn}(s) + \mathrm{Cu}^{2+}(aq) \rightleftharpoons \mathrm{Zn}^{2+}(aq) + \mathrm{Cu}(s)$$

$$E_{cell} = E^{o}{}_{cell} - \frac{2.303RT}{nF} \log \frac{(Products)}{(reactants)}$$

$$E_{cell} = E^{o}{}_{cell} - \frac{0.0591}{n} \log \frac{(Products)}{(reactants)}$$

$$E_{cell} = 1.10v - \frac{0.0591}{2} \log \frac{[\ Zn^{2+}\ ]}{[Cu^{2+}\ ]}$$

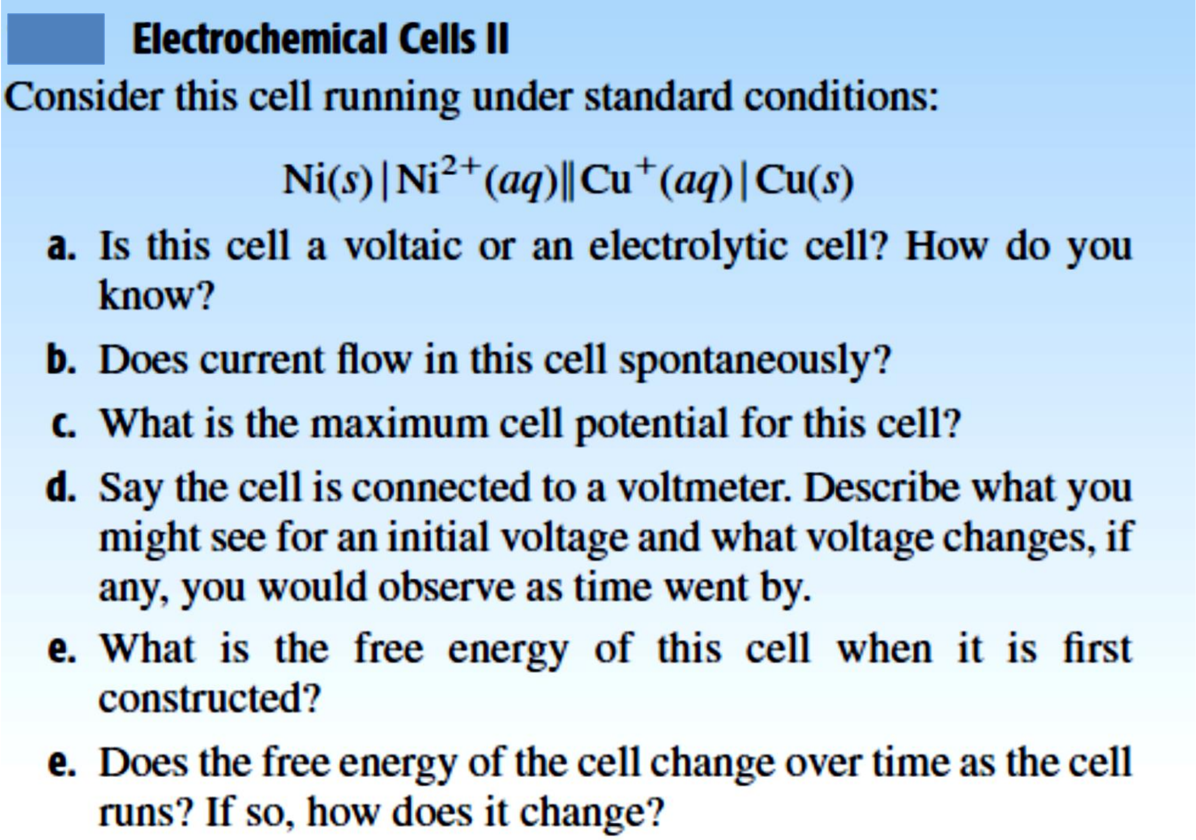
$$E_{cell} = 1.10v - \frac{0.0591}{2} \log \frac{[\ 1x10^{-5}\ M\ ]}{[0.1M\ ]}$$

E_{cell} = 1.10v – (-1.12)= 1.22v the cell potential

ΔG = ???

Is the reaction spontaneous or non-spontaneous reaction? why?

EXERCIS (3)



Electrochemical Cells II

Consider this cell running under standard conditions:

$$\mathrm{Ni}(s)\,|\,\mathrm{Ni}^{2+}(aq)\,\|\,\mathrm{Cu}^{+}(aq)\,|\,\mathrm{Cu}(s)$$

a. Is this cell a voltaic or an electrolytic cell? How do you know?

b. Does current flow in this cell spontaneously?

c. What is the maximum cell potential for this cell?

d. Say the cell is connected to a voltmeter. Describe what you might see for an initial voltage and what voltage changes, if any, you would observe as time went by.

e. What is the free energy of this cell when it is first constructed?

e. Does the free energy of the cell change over time as the cell runs? If so, how does it change?

All Exercises for your training not a Homework

Q1- Specific conductance of **0.02 N KCl** at 298 K is **0.002768 ohm^{-1} cm^{-1}** and it has resistance of **500 ohms**. An 0.25 N solution of another salt kept in the same cell was found to have resistance of **300 ohms** at 298 K. ***Calculate the cell constant and equivalent conductance of the salt solution?***

- **For KCl:** **σ =Ck , σ =k/R , k= σR = 0.002768x500= 1.384 cm^{-1}**
- **For Salt: σ =k/R = 1.384/300= 0.004613 Ω^{-1}cm^{-1}**

Λ= σ 1000/N = 0.004613 Ω^{-1}cm^{-1} x 1000/ 0.25N = ?? Ω^{-1}cm^{2} eq^{-1}

Q2- **Specific conductance** of **0.1 N** solution of an electrolyte is **0.02 ohm^{-1}cm^{-1}**. Calculate its **equivalent conductance(Λeq)?**

Q3 - 0.5 N NaCl is placed between two electrodes 1.5 cm apart and having an area of each 3.0 cm^2 offered a resistance of 25.0 ohms. Calculate the equivalent conductance?

σ =Ck , C=1/R = 1/25= 0.04 Ω^{-1} , k=l/A = 1.5/3=0.5 cm^{-1}

σ = 0.04 Ω^{-1}x 0.5 cm^{-1} = 0.02 Ω^{-1}cm^{-1} ,

Λ= σ 1000/N =(0.02 Ω^{-1}cm^{-1} x 1000/ 0.5N)= 40 Ω^{-1}cm^{2} eq^{-1}

Q4- The resistance of 0.1 N solution of an electrolyte in a cell of cell constant 0.84 cm^{-1} is 60 ohm. Calculate the resistivity (r) of the cell?

R= r (l/A) , k=l/A , R=rk , r=R/k , r= 60/0.84= 71.43 Ω cm^{-1}

Q5- 0.5 N solution of a salt surrounding two platinum electrodes 2.1 cm apart and 2.4 cm^2 in area was found to offer a resistance of 250 ohms. Calculate the equivalent conductance (Λeq) of the solution?

Solution:

Q6- The resistance of a N/100 solution of an electrolyte was found to be 210 ohm at 25°C. Calculate the equivalent conductance of the solution at 25°C.
(Cell constant = 0.88)
Solution:

Q7- In a particular cell, 0.01 M solution of KCl gave a resistance of 15.0 ohms at 298 K while 0.01 M solutions of HCl gave a resistance of *51.4 ohm* at the same temperature. If the specific conductance of 0.01 M KCl is 0.1409 S cm^{-1} at 298 K, calculate the cell constant, specific conductance and equivalent conductance of the HCl solution?

Solution:

Q8- The molecular conductance at infinite dilution of KCl is **130.1**. The **transport number**, **t-** for the chloride ion(**Cl^-**) in very dilute solution is **0.505. Calculate the mobilities** in **cm sec^{-1}** of potassium **K^+** and chloride **Cl^- ions**?

Solution:

$$\lambda Cl^{-1} = \Lambda_\infty \text{ x } \tau\text{-}$$

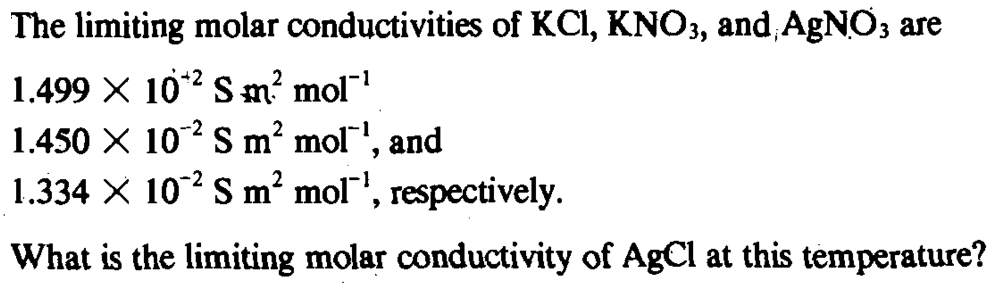
$$\lambda Cl^{-1} = 130.1\text{x } 0.505 = 65.7005$$

$$UCl^{-1} = \lambda Cl^{-1} / Z\text{- } F$$

$$UCl^{-1} = 65.7005 / 96500 = 0.000681 cm^2 V^{-1} sec^{-1}$$

$$UK^+ = 0.000667 \text{ } cm^2 V^{-1} sec^{-1}$$

Q 9



The limiting molar conductivities of KCl, KNO_3, and $AgNO_3$ are

1.499×10^{-2} S m^2 mol^{-1}

1.450×10^{-2} S m^2 mol^{-1}, and

1.334×10^{-2} S m^2 mol^{-1}, respectively.

What is the limiting molar conductivity of AgCl at this temperature?

Solution:

$$KCl + AgNO_3 = KNO_3 + AgCl$$

$$\Lambda_\infty KCl + \Lambda_\infty AgNO_3 = \Lambda_\infty KNO_3 + \Lambda_\infty AgCl$$

$$1.499X10^{-2} + 1.334X10^{-2} - 1.450X10^{-2} = \Lambda_\infty AgCl$$

$$\Lambda_\infty AgCl = ??? \ \Omega^{-1} cm^2 eq^{-1}$$

Q10- Calculate **the ionic mobility** of the cation in an infinitely dilute solution of KBr at 298K. Given that the **transport number** of K^+ is **0.48** and the **molar conductance** of KBr at infinite dilution is **$1.52x10^{-2}$ Sm^2mol^{-1}** ?

$$\lambda + = \Lambda_\infty \text{ x } \tau_+$$

$$U + = \lambda + / Z_+F$$

$$U_+ = 0.48 \text{ x } 1.52X10^{-2}/ 1x96500 = 7.6x10^{-8}\ m^2\ V^{-1}\ sec^{-1}$$

Q11- The equivalent conductance of ammonium chloride(NH_4Cl) at infinite dilution is **149.7 ohm^{-1} cm^2 eq^{-1}**; for sodium hydroxide (NaOH) it is **247.8 ohm^{-1} cm^2 eq^{-1}**; and for sodium chloride(NaCl) is **126.45 ohm^{-1} cm^2 eq^{-1}** at 25°C. Calculate the equivalent conductance for ammonium hydroxide (NH_4OH) in ohm^{-1} cm^2 eq^{-1} at infinite dilution at the same temperature?

Solution:

CHOOSE THE RIGHT ANSWER FOR EACH OF THE FOLLOWING:

Q1- Specific conductance is the conductance of

a) one centimeter cube of solution of an electrolyte
b) one centimeter cube of a solid electrolyte
c) one gram of the solution of an electrolyte
d) one gram of the solid electrolyte

Q2- The units of specific conductance are

(a) ohm cm (b) ohm cm^{-1} (c) ohm^{-1} cm (d) ohm^{-1} cm^{-1}

Q3- As temperature increases, the molar conductivity

- **a) Increases**
- b) Decreases
- c) Tends to zero
- d) Remains constant

Q4- Which of the following is ionic mobility independent of?

- **a) Size of ion**
- **b) Charge on ion**
- **c) Distance of separation between the electrodes**
- **d) Concentration of electrolyte**

Q5- What is the value of the cell constant when the conductance of an electrolytic solution is equal to its conductivity?

0 1 10 100

Q6- Which of the following scientists stated that the equivalent conductivity of an electrolyte at infinite dilution is equal to the sum of the conductances of the ions and cations?

a) Svante Arrhenius
b) Friedrich Kohlrausch
c) Hermann Kolbe
d) Antoine Lavoisier

Q7- Which of the following statements is correct with respect to electrolytic solutions?

a) Its conductance increases with dilution
b) Its conductance decreases with dilution
c) Its conductivity increases with dilution
d) Its equivalent conductance decreases with dilution

Q8- Which of the following conditions are satisfied when the electrolytic solutions are infinitely dilute?

a) Electrolyte is 100% dissociated
b) Interionic effects increase
c) Conductance is infinite at infinite dilution
d) Molecules continue to exist in solution

Q9- Which of the following is ionic mobility independent of?

a) Size of ion
b) Charge on ion
c) Distance of separation between the electrodes
d) Concentration of electrolyte

Q10- The highest electrical conductivity of the following aqueous solutions is of:

(a) 0.1 M acetic acid
(b) 0.1 M chloroacetic acid
(c) 0.1 M fluoroacetic acid
(d) 0.1 M difluoroacetic acid

???????????????????????????

Q11- Select the incorrect statement about the chemical activity at electrodes during electrolysis.

(a) Anions give up electrons (b) Cations take up electrons
(c) Oxidation occurs at the anode **(d) Proton transfer occurs in the reactions**

Q12- “On progressive dilution, specific conductance(σ)of an electrolyte decreases but equivalent conductance increases (Λ)” Discuss.

Q14- Using the plot of molar conductance (Λm) versus concentration of the solution (C), discuss how the molar conductance at infinite dilution of the solution can be obtained?