

Centre of Excellence

Training course

abc-ELECTROCHEMISTRY

Lecturer: Prof. Ilia Iliev

Electrochemistry may be defined as the physical chemistry of equilibria and processes occurring in solutions of electrically charged particles, and on the boundary of such solutions with other phases.

The training course is aimed to define and elucidate some basic notions in electrochemistry.

Lecture course content:

Part I: Conduction of electricity

electric charge and electric current; Electrical potential and electric field; Ohm's law;
Classes of conductors; Contact potential differences; Capacitance

Part II: Ionic solutions

Electroneutrality; Electric field; Ionic strength; Activities; Solutions with extremely low ionic strength;
Solutions with high ionic strength; Equilibria in ionic solutions; pH; Electrochemical activities;
Transfer equilibria

Part III: Electrochemical cells

Cell voltages and currents; Thermodynamics of equilibrium cells; Cells with junctions;
Utility of equilibrium cells

Part IV: Electrodes

Electrode potential; Reference electrodes; Standard electrode potentials; Versions of the Nernst Equation

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Part I

1. Conduction of electricity

1.1. Electric charge and electric current

1.2. Electrical potential and electric field

1.3. Ohm's law

1.4 Classes of conductors

1.5 Mobilities

1.6 Contact potential differences

1.7. Capacitance

1.8 Summary

1. Conduction of electricity

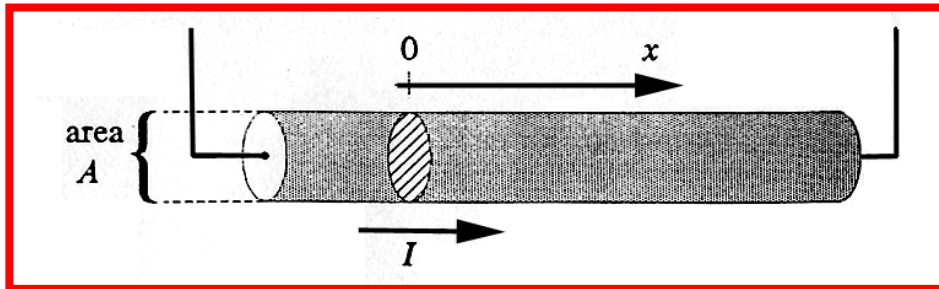
Electrochemistry \Rightarrow coupling **chemical changes** to the **passage of the electricity**

1.1. Electric charge and electric current

Elementary physics - electricity is often treated as a fluid:

- able to flow through **conductors**
- unable to flow through **insulators**

electric charge or **amount of electricity** - **Q** - coulombs (C)



charge dQ crosses at $x = 0$ in the time interval dt

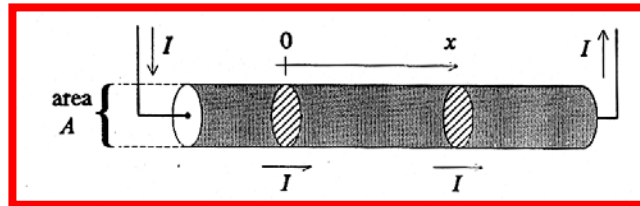
electric current I

$$1:1:1 \quad I = \frac{dQ}{dt} \quad \text{Ampere} \quad (1 \text{ A} = 1 \text{ C} / 1 \text{ s})$$

Current density i

1:1:2 $i = \frac{I}{A}$ Ampere per square meter (Am^{-2})

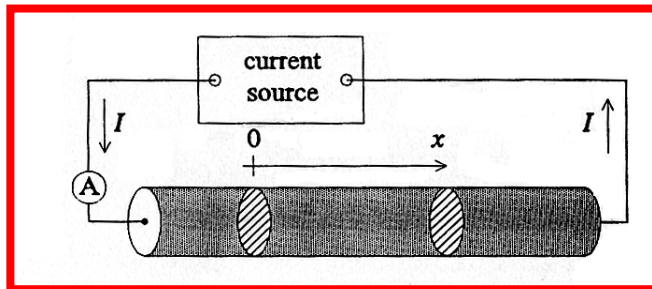
Electricity behaves as **incompressible fluid**



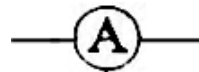
Current I flowing across $x = 0$ plane is equal to that flowing across any plane x

Circuit - usually current flows in a closed path

In a simple circuit, current I has one and the same magnitude everywhere



Current source “pumps the electric fluid”
ammeter



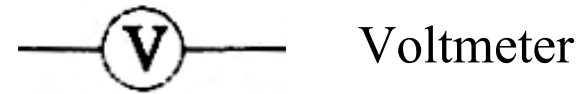
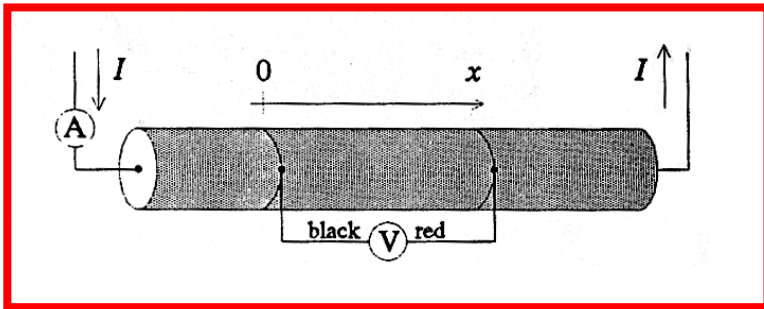
1:1:3 $Q = \int_{t_1}^{t_2} I dt$

Amount of electricity Q passed through the circuit during the **time interval** from $t = t_1$ to $t = t_2$

1.2. Electrical potential and electric field

Electrical potential - Φ – analogue to pressure (measured in Volts - V)

In the electrochemistry is **only possible to measure the *difference*** between two potential values - **electrical potential difference (Voltage) $\Delta\Phi$**



Two leads (not equivalent) -
usually red and black

Voltmeter reads potential difference of $x = x$ plane with respect to $x = 0$ plane

$$1:2:1 \quad \Delta\phi = \phi(x) - \phi(0)$$

For conductor of **uniform composition** and **uniform cross-section** $\Delta\Phi \approx x$

$$1:2:2 \quad \frac{\Delta\phi}{x} = \frac{\phi(x) - \phi(0)}{x} = \text{a negative constant}$$

$$1:2:3 \quad X = - \frac{d\phi}{dx}$$

Electric field strength - V / m

1.3. Ohm's law- fundamental relationship for conduction of electricity

$$1:3:1 \quad i \propto X$$

Current density proportional to the **field strength**

Electrical conductivity - κ

$$1:3:2 \quad i = \kappa X = -\kappa \frac{d\phi}{dx}$$

Characteristic property
of conducting material
(not dependant of geometry)

$$1:3:3 \quad I = -G\Delta\phi$$

or

G - conductance (unit Siemens, S);
(depend on the geometry of the sample)

$$1:3:4 \quad \Delta\phi = -RI$$

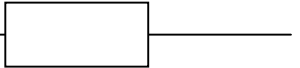
R - resistance (Ohm - Ω)
(depend on the geometry of the sample)

$$1:3:5 \quad G = \frac{1}{R} = \frac{\kappa A}{L} = -\frac{I}{\Delta\phi}$$

conductor with **uniform**
cross-section A and **length L**

$$1:3:6 \quad R = -\frac{\Delta\phi}{I} = -\int \frac{d\phi}{iA(x)} = \int_0^L \frac{dx}{\kappa(x)A(x)}$$

When **conductivity** and/or
cross-section vary along the
length co-ordinate **x**

When current **I** flows through resistor **R**, **energy is dissipated as heat at a rate I^2R** . This quantity has the unit of power - **Watts**. Resistor: 

Electrical quantities and their SI units

| Quantity | | Unit | |
|-----------------|------------|-------------------------|-------------------------------|
| name | symbol | name | symbol |
| current | I | ampere | A |
| current density | i | ampere per square metre | $A\ m^{-2}$ |
| charge | Q | coulomb | $C = A\ s$ |
| charge density | ρ | coulomb per cubic metre | $C\ m^{-3}$ |
| potential | ϕ | volt | $V = J\ C^{-1}$ |
| field strength | X | volt per metre | $V\ m^{-1}$ |
| conductivity | κ | siemens per metre | $S\ m^{-1}$ |
| resistance | R | ohm | $\Omega = S^{-1} = V\ A^{-1}$ |
| conductance | G | siemens | $S = A\ V^{-1}$ |
| permittivity | ϵ | farad per metre | $F\ m^{-1} = C\ V^{-1}m^{-1}$ |
| energy or work | w | joule | $J = V\ C$ |
| power | | watt | $W = J\ s^{-1} = A\ V$ |
| capacitance | C | farad | $F = s\ \Omega^{-1} = S\ s$ |

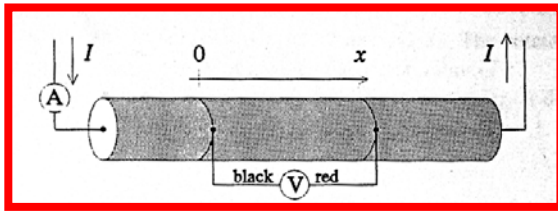
1.4 Classes of conductors - metals and other types of matter - passage of electricity

Insulators - plastics, ceramics, glasses-resist flow of electricity

No clear-cut distinction between **conductors** and **insulators** - continuous range in the abilities of materials to conduct electricity

Electrical conductivity κ of material - measure of how good a particular material conducts electricity - **ranges from 0 (vacuum) to ∞ (superconductors).**

Conductivity of insulators - variable - greatly affected by impurities

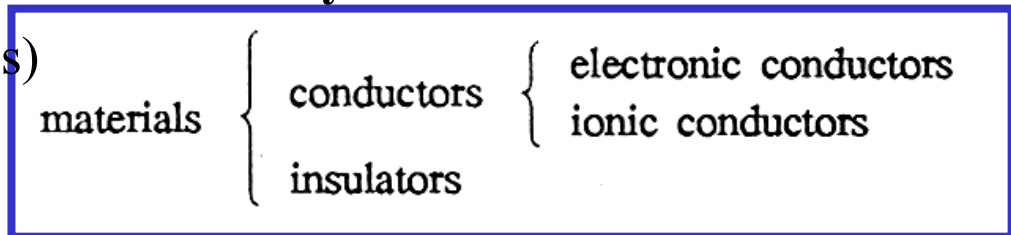


Several **methods for measurements of κ** - *four-terminal method, a.c. impedance method, etc.*

The concept of electricity as “fluid” no longer needed:

Materials are conductors or insulators because of their **chemical structure** and it is the **mobility of electrons** and **other charged chemical species** that are **responsible for the electrical conductivity.**

Nature of the charge carrier(s)



Electrical conductivity of various materials (most at 298 K)

| Material | $\kappa/S\ m^{-1}$ | Charge carriers |
|--------------------------------|----------------------|---------------------|
| superconductors (low temp.) | ∞ | electron pairs |
| Ag | 6.3×10^7 | electrons |
| Cu | 6.0×10^7 | electrons |
| Hg | 1.0×10^6 | electrons |
| C (graphite) | 4×10^4 | pi electrons |
| doped polypyrrole | 6×10^3 | pi electrons |
| molten KCl (at 1043 K) | 217 | K^+ and Cl^- |
| 5.2 M H_2SO_4 (battery acid) | 82 | H^+ and HSO_4^- |
| seawater | 5.2 | cations and anions |
| Ge | 2.2 | electrons and holes |
| 0.10 M KCl | 1.3 | K^+ and Cl^- |
| H_2O | 5.7×10^{-6} | H^+ and OH^- |
| typical glass | 3×10^{-10} | univalent cations |
| $(CF_2)_\infty$ (teflon) | 10^{-15} | ? |
| vacuum and most gases | 0 | |

Electronic conductors - mobile electrons

Metals

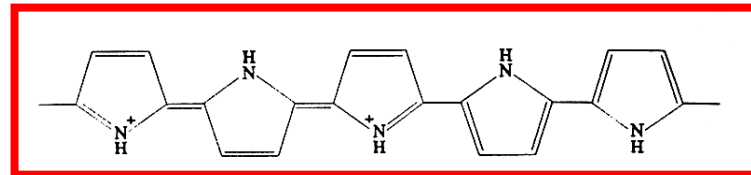
Semi-conductors (PbO_2 , Ag_2S , Ge, etc) -

n-type (excess of electrons) or **p-type** (deficit of electrons) compared with the number required to form the covalent bonds in the semiconductor's crystal lattice

In **p-type** semi-conductors the missing electrons are known as “holes”
Conductivity as being due to the motion of these **positively charged** “holes”.

Intrinsic semiconductors - conduct by both **electron** and “hole” motion.
Pi-electrons - charged carriers in some other materials

- graphite,
- **conductive polymers as polypyrrole**



- **Organic metals** (TTF, TCNQ)

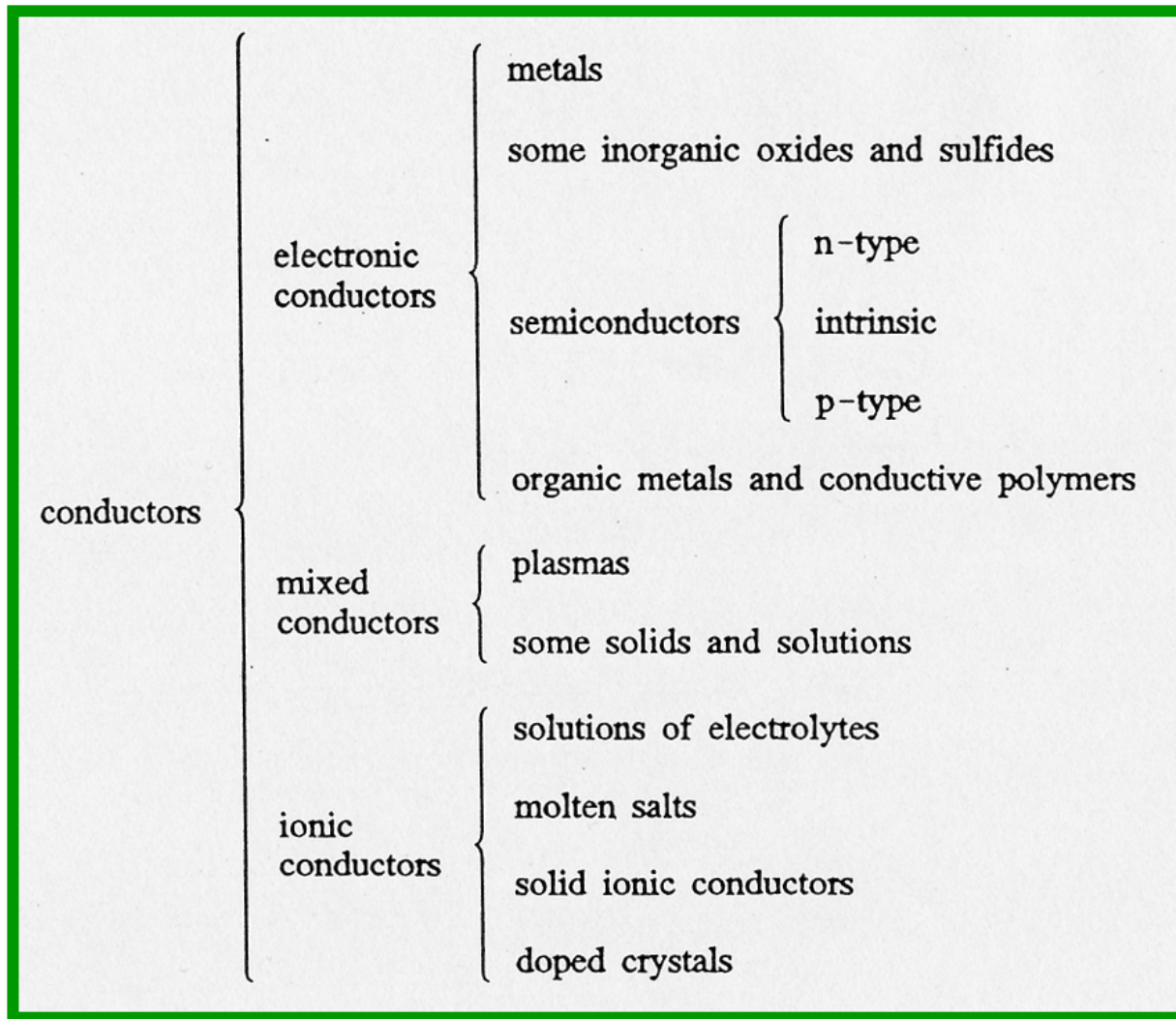
Ionic conductors - motion of **anions** and/or **cations** - solutions of electrolytes (salts, acids and bases) in water and other liquids, molten salts

Solid ionic conductors (“solid electrolytes”) - usually have only one mobile ionic species ($\text{ZrO}_2 - \text{O}^{2-}$, $\text{RuAg}_4\text{I}_5 - \text{Ag}^+$, LaF_3 “doped” by $\text{EuF}_2 - \text{F}^-$).

Crystals of doped LaF_3 have “**fluoride ion holes**” which move exactly as do electron holes in p-type semiconductor.

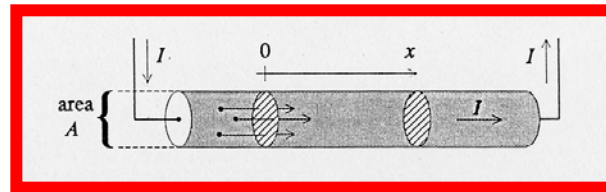
Few materials permit the flow of electricity by both **electronic** and **ionic** conduction: hot gases (**plasmas**); sodium metal dissolved in liquid ammonia (contains Na^+ cations and solvated electrons); hydrogen dissolved in Pd-metal

Types of conductors



1.5 Mobilities

Electric current I equals the rate dQ/dt at which charge crosses any plane perpendicular to its flow



$$\text{electric current} = \begin{matrix} \text{rate at} \\ \text{which charge} \\ \text{crosses} \\ \text{any plane} \end{matrix} = \begin{matrix} \text{(number of} \\ \text{carriers} \\ \text{per unit} \\ \text{volume)} \end{matrix} \begin{matrix} \text{(cross} \\ \text{sectional} \\ \text{area)} \end{matrix} \begin{matrix} \text{(charge} \\ \text{on each} \\ \text{carrier)} \end{matrix} \begin{matrix} \text{(average} \\ \text{carrier} \\ \text{speed)} \end{matrix}$$

$$1:5:1 \quad I = \frac{dQ}{dt} = (N_A c_i)(A)(Q_i)(v_i)$$

i - identifies particular charge carrier; c_i - its concentration;

Q_i - its charge; v_i - average velocity in the direction of the current;

N_A - Avogadro's constant ($6.0220 \times 10^{23} \text{ mol}^{-1}$) and A - the area .

Electric charge is a **discrete quantity** and is **always encountered in multiples** of the **elementary charge** $Q_e = 1.6022 \times 10^{-19} \text{ C}$.

$Z_i = Q_i/Q_e$ - charge number

$$1:5:2 \quad Q_i = z_i Q_e$$

Experimentally $1:5:3 \quad v_i \propto f_i \propto X \propto \frac{d\phi}{dx}$

The absolute value of the **velocity-to-field ratio** is known as **mobility** u_i ($\text{m}^2\text{V}^{-1}\text{s}^{-1}$) of the carrier but the **direction of motion** depends on the **sign of the charge**.

$$1:5:4 \quad v_i = \pm u_i X = - \frac{z_i}{|z_i|} u_i \frac{d\phi}{dx}$$

The group of the terms $z_i / |z_i|$ takes account for the sign of the carrier's charge

The mobility of an ion in aqueous solution is smaller than the mobility of electrons in metals by factor ca. 10^5 ($\text{Ag} - u_{e^-} = 6.7 \times 10^{-3} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$)

Ion mobilities at extreme dilution in aqueous solution at 298 K

| cation | $u^0/\text{m}^2 \text{ s}^{-1} \text{ V}^{-1}$ | anion | $u^0/\text{m}^2 \text{ s}^{-1} \text{ V}^{-1}$ |
|--------------------------------------|------------------------------------------------|------------------------------------|------------------------------------------------|
| H^+ | 362.5×10^{-9} | OH^- | 204.8×10^{-9} |
| $\text{Co}(\text{NH}_3)_6^{3+}$ | 102.8×10^{-9} | $\text{Fe}(\text{CN})_6^{4-}$ | 114.5×10^{-9} |
| K^+ | 76.2×10^{-9} | $\text{Fe}(\text{CN})_6^{3-}$ | 104.7×10^{-9} |
| NH_4^+ | 76.1×10^{-9} | SO_4^{2-} | 82.7×10^{-9} |
| Ag^+ | 64.2×10^{-9} | Br^- | 81.3×10^{-9} |
| Cu^{2+} | 58.6×10^{-9} | Cl^- | 79.1×10^{-9} |
| Mg^{2+} | 55.0×10^{-9} | NO_3^- | 74.0×10^{-9} |
| Zn^{2+} | 54.7×10^{-9} | CO_3^{2-} | 71.8×10^{-9} |
| Na^+ | 51.9×10^{-9} | ClO_4^- | 69.8×10^{-9} |
| Li^+ | 40.1×10^{-9} | HCO_3^- | 46.1×10^{-9} |
| $(\text{C}_4\text{H}_9)_4\text{N}^+$ | 19.8×10^{-9} | $\text{C}_6\text{H}_5\text{COO}^-$ | 33.5×10^{-9} |

From $1:5:4 \quad v_i = \pm u_i X = -\frac{z_i}{|z_i|} u_i \frac{d\phi}{dx}$

$1:5:2 \quad Q_i = z_i Q_e$

$1:5:1 \quad I = \frac{dQ}{dt} = (N_A c_i)(A)(Q_i)(v_i)$

follows:

$1:5:5 \quad I = -AN_A Q_e |z_i| u_i c_i \frac{d\phi}{dx}$ Valid for conductor containing only one kind of charge carrier

The product $N_A Q_e$ of **Avogadro's constant** and the **elementary charge** is a **fundamental constant** of prime importance in electrochemistry - **Faraday's constant F**:

$$1:5:6 \quad F = N_A Q_e = (6.0220 \times 10^{23} \text{ mol}^{-1})(1.6022 \times 10^{-19} \text{ C}) \\ = 96485 \text{ C mol}^{-1}$$

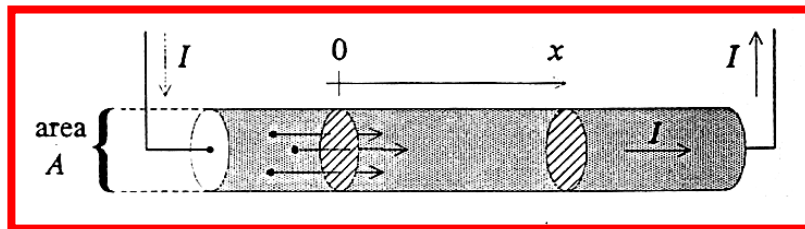
Faraday constant is a rather large number and that has important economic and scientific repercussions (electrochemical manufacture of aluminium, electrochemical methods of analysis, etc)

For conductors with several kinds of charge carriers:

$$1:5:7 \quad I = -AF \frac{d\phi}{dx} \sum_i |z_i| u_i c_i \quad \text{or} \quad i = -F \frac{d\phi}{dx} \sum_i |z_i| u_i c_i$$

For anions and for cations **each one of the three terms** $|z_i|$, u_i and c_i is positive

Although **anions** and **cations** move in **opposite direction** both motions correspond to electric charge moving in the same direction as the **cations**.



When there is a **single charge carrier** that is **negative**, as with electrons in metals, the **direction of current flow is opposite to the direction of the motion of the carrier**.

The fraction of the total current carried by one particular charge carrier is known as the **transport number** of these species t_i :

$$1:5:8 \quad t_i = \frac{|z_i| u_i c_i}{\sum_i |z_i| u_i c_i} \quad \left(\sum_i t_i = 1 \right)$$

Ion motion caused by electric field is known as migration

From:

$$1:3:2 \quad i = \kappa X = -\kappa \frac{d\phi}{dx}$$

$$1:5:7 \quad i = -F \frac{d\phi}{dx} \sum_i |z_i| u_i c_i$$

is obtained:

$$1:5:9 \quad \kappa = F \sum_i |z_i| u_i c_i$$

Equivalent ionic conductivity and molar ionic conductivity

$$1:5:10 \quad |z_i| F u_i \quad \text{and} \quad F u_i$$

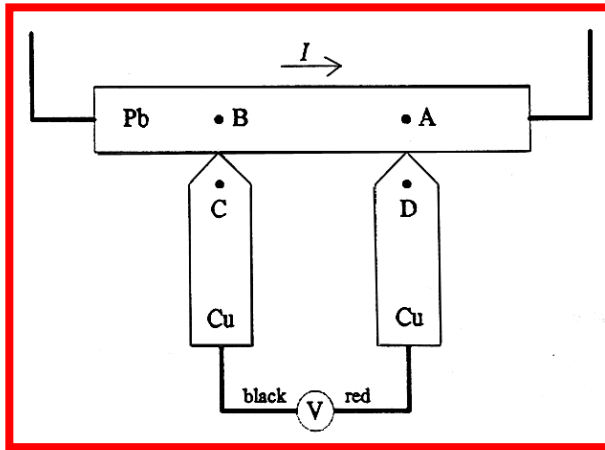
In a solution that contains only one kind of anion ($\mathbf{i} = -$) and one kind of cation ($\mathbf{i} = +$) the **electroneutrality relationship** requires that

$$z_+ c_+ = -z_- c_-$$

It can be defined the equivalent conductance Λ of this solution by:

$$1:5:11 \quad \Lambda = \frac{\kappa}{z_+ c_+} = - \frac{\kappa}{z_- c_-} = F(u_+ + u_-)$$

1.6 Contact potential differences



$$\Delta\phi = \phi_a - \phi_b$$

Actually the voltmeter can measure the potential difference ΔE between its own terminals (usually made of copper) - it is the potential difference between points **D** and **C** -

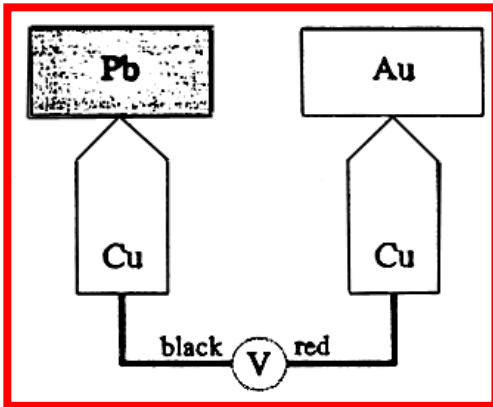
$$\Delta E = \phi_D - \phi_C.$$

Retaining the symbol $\Delta\phi$ to mean the potential difference **A** and **B** we obtain:

$$\begin{aligned} 1:6:1 \quad \Delta E &= (\phi_D - \phi_A) + (\phi_A - \phi_B) + (\phi_B - \phi_C) \\ &= \Delta\phi - (\phi_A - \phi_D) + (\phi_B - \phi_C) \end{aligned}$$

Contact potential difference or contact voltage is named a term such as $(\phi_A - \phi_D)$ which represents the **difference** in electric potentials **between neighbouring points** in pieces of **two dissimilar metals** that are **in contact** and between which **no current flows**. The term $(\phi_B - \phi_C)$ is also contact potential difference between Pb and Cu.

There is no reason to suppose that $(\phi_B - \phi_C)$ will differ from $(\phi_A - \phi_D)$ and, if we take them to be equal, representing each by $\Delta\phi_{\text{Pb/Cu}}$, we see from 1:6:1 that $\Delta E = \Delta\phi$.



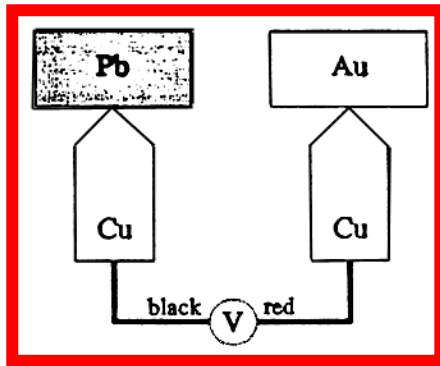
The situation is different when the voltmeter is attached to **samples of two distinct metals** (e.g. Pb and Au). There are now no grounds for assuming that the contact voltages cancel, so that the voltmeter reading ΔE certainly does not equal $\phi_{Au} - \phi_{Pb}$ in this case.

$$\Delta E \neq \phi_{Au} - \phi_{Pb}$$

General principle: it is not possible to measure the difference in the electrical potential between two points, **unless this two points are located in the same phase, or in distinct phases of similar composition.**

This is **true** not only **for electronic conductors** but also **for ionic conductors.**

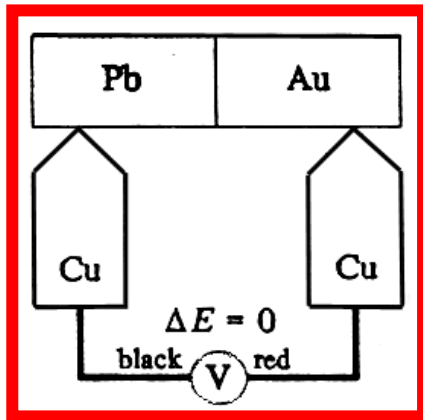
The situation is worse in the case of ionic conductors: **a potential difference can not be measured directly between two points in ionic conductors**, even if their chemical compositions are similar. This is because an “**ionic voltmeter**” has yet to be invented - in this case must be used electronic voltmeter coupled to the ionic conductor(s) through a pair of electrodes.



It is accepted that there are **definite electric potentials** ϕ_{Au} and ϕ_{Pb} inside Au and Pb blocks in the figure (though we may have no way to measure them) and the **difference between these potentials** is given by:

$$1:6:2 \quad \phi_{Au} - \phi_{Pb} = \Delta E + \Delta\phi_{Au/Cu} - \Delta\phi_{Pb/Cu}$$

Where the two $\Delta\phi$ terms are the **contact voltages**.

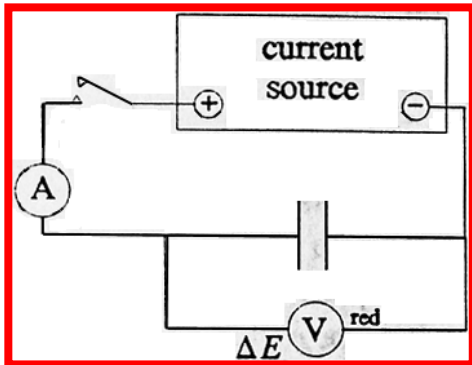


When **Pb and Au blocks are brought into contact** the voltmeter soon reads zero. Apparently the electrons distribute themselves between the four pieces of metal until the **potential difference between Au and Pb itself becomes contact voltage** given by

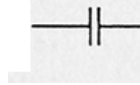
$$1:6:3 \quad \Delta\phi_{Au/Pb} = \Delta\phi_{Au/Cu} - \Delta\phi_{Pb/Cu}$$

According to the term which will be introduced in the next lecture we can say that the **“electrochemical activity” of the electrons is now one and the same in all four pieces of metals.**

1.7. Capacitance



Capacitor - pair of (parallel) conducting plates separated by a narrow gap containing air or some other insulator.



Despite the non-conducting gap a current will flow when the switch is closed.

Electricity passes into the **left-hand plate** and out from the **right-hand plate**, so that **charges accumulate on their surface**.

As a result the plates develop a potential difference ΔE . The amount of stored charge is proportional to it:

$$1:7:1 \quad \int I dt = Q \propto \Delta E$$

The proportionality constant linking Q and ΔE is negative and its absolute value is known as **capacitance** C of the gap.

$$1:7:2 \quad Q = -C\Delta E$$

Capacitance is measured in units of **coulombs per volt** or **farads**. ($1 \text{ F} = 1 \text{ C} / 1 \text{ V}$)

A capacitor can be used as a **current integrator** because the voltage across it is proportional to the integral of the current that has past “through” it:

$$1:7:3 \quad \Delta E = -\frac{Q}{C} = -\frac{1}{C} \int_0^t I dt$$

if the capacitor was uncharged a time $t = 0$.

Capacitors store energy, the amount of stored energy is

$$Q^2/2 C = -Q\Delta E/2$$

The capacitance of the **parallel-plate capacitor** can be calculated from the formula

$$1:7:4 \quad -\frac{Q}{\Delta E} = C = \frac{\epsilon A}{L}$$

A is the cross-section area of the gap and L is its width.

The coefficient ϵ is known as **permittivity** (Fm^{-1}) of the **insulator that occupies the gap**.

The ratio of the **permittivity** ϵ of a material to the **permittivity** ϵ_0 of a vacuum is known as the **relative permittivity** or **dielectric constant** of the material. This ratio, $\epsilon_r = \epsilon / \epsilon_0$ always exceeds unity

Permittivity of various materials

| Material | $10^{12} \epsilon/F \text{ m}^{-1}$ | Material | $10^{12} \epsilon/F \text{ m}^{-1}$ |
|---------------------------------------|-------------------------------------|-----------------------------------------|-------------------------------------|
| vacuum (ϵ_0) | 8.85419 | neoprene | 58 |
| $\text{N}_2(\text{g})$ | 8.85905 | $\text{ClC}_2\text{H}_4\text{Cl}(\ell)$ | 91.7 |
| teflon(s), $(\text{CF}_2)_\infty$ | 18 | $\text{CH}_3\text{OH}(\ell)$ | 288.9 |
| $\text{CCl}_4(\ell)$ | 19.7 | $\text{C}_6\text{H}_5\text{NO}_2(\ell)$ | 308.3 |
| polyethene(s) | 20 | $\text{CH}_3\text{CN}(\ell)$ | 332 |
| mylar(s) [†] | 28 | $\text{H}_2\text{O}(\ell)$ | 695.4 |
| $\text{SiO}_2(\text{s})$ | 38.1 | $\text{HCONH}_2(\ell)$ | 933 |
| typical glass(s) | 44 | $\text{TiO}_2(\text{s})$ | ≤ 1500 |
| $\text{C}_6\text{H}_5\text{Cl}(\ell)$ | 49.8 | $\text{BaTiO}_3(\text{s})$ | ≤ 110000 |

[†] poly(ethylene glycol terephthalate), $(\text{CH}_2 \cdot \text{OOC} \cdot \text{C}_6\text{H}_4 \cdot \text{COO} \cdot \text{CH}_2)_\infty$

1.8 Summary

Electricity flows either by electron motion or ion motion (or simultaneous motion of both of them); in both cases the intensity of the flow, the current density, is proportional to the electric field strength

$$1:9:1 \quad i = \kappa X = -\kappa \frac{d\phi}{dx}$$

The proportionality constant κ is the conductivity of the material being determined by the concentration of charge carriers and their mobilities:

$$1:9:2 \quad \kappa = F \sum_i |z_i| u_i c_i$$

Equation 1:9:1 is form of Ohm's law; another is:

$$1:9:3 \quad \Delta E = -RI$$

Which relates the potential difference across a resistor to the current flowing through it. Whereas resistors dissipate energy, capacitors restore it. The voltage across a capacitor changes as current flows to it, accordance with the equation

$$1:9:4 \quad \frac{d}{dt} \Delta E = -\frac{I}{C}$$

The capacitance C depend on the dimensions of the gap in the capacitor and on the permittivity of the insulator that fills it