

CHAPTER 2:

FUNDAMENTAL CONCEPTS & RELATIONSHIPS

1. Physical units (Review)
2. Faraday's law
3. Efficiencies (Faradaic and Voltaic)
4. Ionic and electronic conduction
5. Ionic conductance, mobility, Kohlrausch's laws
6. Grotthuss transport
7. Strong & weak electrolytes (Arrhenius & Ostwald laws)
8. Some additional fundamentals: Field, Potential, Electrical force,
Poisson's & Laplace's equations
9. Movement of an ion in an electrical field
10. Walden's Laws
11. Debye-Huckel-Onsager theory for strong electrolytes (Overview)
12. Non-aqueous electrolytes.
13. Molten salts, Ionic liquids
14. Heterogeneous media: Maxwell's and Bruggemann's models.
Emulsions, gas evolving electrodes.
15. Conductivity measurements

Review of Few Key Physical Quantities

MECHANICAL

Force: $f = m \times a$ $f = [\text{Dyne or Nt}]$ $m = [\text{gr or Kg}]$ $a = [\text{acceleration, cm/s}^2 \text{ or m/s}^2]$

Work (or energy): $W = F \times S$ $W = [\text{erg; Joule; Watt s; KWH; Cal; BTU}]$

Power: $P = \frac{W}{t}$ $\left[\frac{J}{s} = \text{Watt; KW; HP} \right]$ $746 \text{ W} = 1 \text{ HP}$

ELECTRICAL

Charge: q [cb]

F [1 Faraday = 96,480 cb = 10^5 cb]

Current: $I = [Amp] = \frac{q}{t}$ $\left[\frac{Cb}{s} \right]$

Current density^a $i = \frac{I}{A}$ $\left[\frac{A}{cm^2} \right]$ or $\left[\frac{mA}{cm^2} \right]$ or $\left[\frac{A}{dm^2} \right]$ or $\left[\frac{A}{ft^2}; ASF \right]$

Power = P = V * I [Watt] = [Ampere] x [Volt]

1 HP = 745.7 Watts

Work or Energy = W = P * t = V * I * T

[Joule] = [Watt*S]

[KW*hr]

THERMAL

Thermal energy: Q [cal]

1 cal = 4.18 J

Heat flux $q = \frac{Q}{t}$ $\left[\frac{Cal}{s} \right]$

^a current density units:

$$1 \left[\frac{mA}{cm^2} \right] = \left[1 \frac{mA}{cm^2} \frac{A}{1000 mA} \frac{100 cm^2}{dm^2} \right] = \left[0.1 \frac{A}{dm^2} \right] \sim \left[1 \frac{A}{ft^2}; ASF \right]$$

Few Early Observations

Faraday's Laws:

The quantitative treatment of electrochemical processes was initiated by Faraday.

In 1813, Michael Faraday, a 22 year old bookbinder apprentice joined Davy in his laboratory at the Royal Institute as an assistant. On the basis of experimental observations he formulated in 1834 two laws:

The amount of primary product formed at an electrode by electrolysis is directly proportional to the quantity of electricity

$$w \sim q \quad (= It) \quad \begin{array}{l} w = [\text{gr}] \\ I = [\text{Amp}] \\ i = [\text{A/cm}^2] \\ q = [\text{cb}] \\ t = [\text{sec}] \end{array} \quad [2-1]$$

The amounts of various primary products formed at an electrode by the same quantity of electricity are proportional to their relative molecular, or relative atomic masses divided by the change in their charge numbers for the electrode process.

$$\frac{w}{q} \sim \frac{M}{n} \quad \begin{array}{l} M = \text{At. Wt.} = [\text{gr/gr. Atom}] \\ n = \text{number of e transferred in} \\ \text{electrode rxn [Equiv/Mole]} \end{array} \quad [2-2]$$

Faraday's laws can be combined as

$$\boxed{w = \frac{M I t}{F n}} \quad [2-3]$$

defining the proportionality constant F = Faraday's number. Its numerical value is defined by

$$F = L \cdot e$$

L is the Avogadro-Lochschmidt number and e the electron charge, i.e.

$$1 F = 1 \text{ Faraday} = L \times e = 6.02 \times 10^{23} \times 4.8 \times 10^{-10} (\text{esu}) / 3 \times 10^9 (\text{esu/cb})$$

$$= 96,500 \text{ cb/gr equiv.} = 26.8 \text{ Ahr/gr equiv.}$$

Faraday's Laws

Faraday's Laws provides a relationship between the amount of charge passed to the amount of material reacted in the electrode reaction

① $w \sim q = It$

w - weight

M – Formula weight

q – charge

n – number of electrons

② $\frac{w}{q} = \frac{M}{n}$

I – current

i – current density

t – time

h – deposit thickness

Combine:

$$w \propto \frac{M}{n} It$$

Defining
Faraday's
constant:

$$w = \frac{1}{F} \frac{M}{n} It$$

$$F = 96,480 \text{ cb} = 26.8 \text{ AHr} (=L \cdot e)$$

L – Avogadro No. (6.02×10^{23} [atoms/mole])

e – electron charge (1.6×10^{-19} [cb/electron])

**Deposit
thickness:**

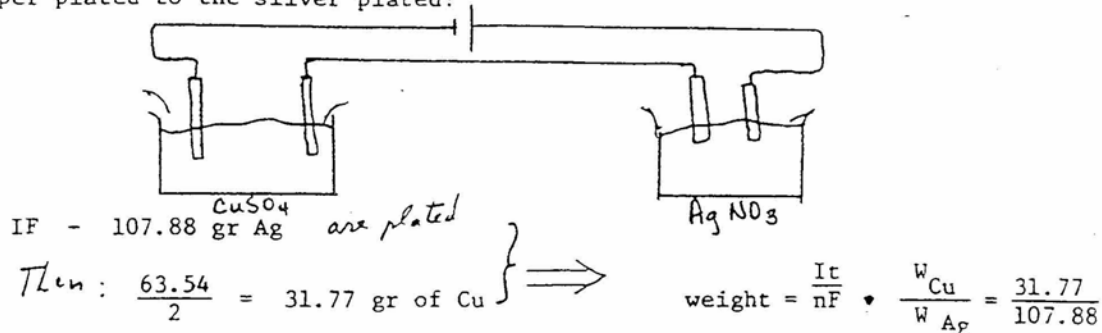
$$h = \frac{1}{F} \frac{M}{n\rho} it$$

Ionic Flux:

$$N = \frac{i}{nF} \quad [\text{M / sec-cm}^2] \text{ or } [\text{gr-ion/sec-cm}^2]$$

example

Copper sulfate and silver nitrate electrolysis cells connected in series and a total current of 0.1 Amp is passed. What is the weight ratio of the copper plated to the silver plated?



The actual weight ratio may be somewhat different! This is because electrochemical reactions (like many other reactions) rarely proceed with 100% efficiency

2. Efficiencies:

Power and Energy input and output from a cell correspond to the current and the voltage:

$$P = V \cdot I$$

or

$$W = V \cdot I \cdot t$$

$$[\text{Watt}] = [\text{Volt}][\text{Ampere}]$$

The overall operating efficiency of the cell is therefore given by

$$\phi_t = \phi_{\text{voltaic}} \cdot \phi_{\text{faradaic}}$$

a) Voltaic Efficiency [ϕ_v]:

The maximum voltaic efficiency of a cell corresponds to its operation at the thermodynamic EMF. This only can take place at equilibrium, i.e. when no current passes. For chemical engineers the situation is not very interesting. Whenever the cell operates, it must deviate from equilibrium due to irreversibilities, and consequently the voltaic efficiency will be less than 100%. This will be further discussed later on, after we have covered thermodynamics and overpotentials.

b) Faradaic, Coulombic, or Current Efficiency

$[\phi_F]$

Deviations from Faraday's laws are expressed in terms of the current efficiency:

$$\phi_F = \text{Fraction of the current which is useful} = \frac{\text{actual product weight}}{\text{theoretical weight calculated according to Faraday's law}} \times 100$$

Many industrial processes are characterized by high efficiency (e.g., Cu refining with 99.999%), however there are some with low efficiencies (e.g., Cr plating with 10% efficiency).

c) Reasons for deviations:

- (1) Recombination of products ($\text{Na} + \text{Cl}_2$)
- (2) Instability of products ($\text{Na} + \text{H}_2\text{O}$)
- (3) Chemical or physical reactions with electrodes or electrolyte ($\text{Cl}_2 + \text{Graphite}$)
- (4) Competing electrode reaction (H_2 or O_2 evolution)

We will discuss later how to avoid some of these pitfalls.

d) Illustration:

An aluminum electrolyzer (cathodic reduction of Al from Al_2O_3 -Kriolyte melt) operates at 100,000 Amperes and 98% cathodic current efficiency.

Calculate the weight of Al produced in a 24 hour operation:

Answer: $\text{Al}^{+3} + 3 e^- \longrightarrow \text{Al}^0$

$$96,500 \text{ cb} = 26.8 \text{ A-Hr} \Rightarrow \frac{27}{3} = 9 \text{ gr Al}$$

$$10^5 \times 24 \text{ A-Hr} \Rightarrow ?$$

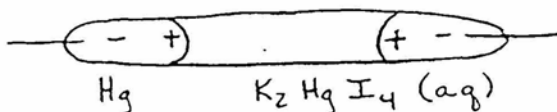
$$W = \frac{9 \times 10^5 \times 24}{26.8} = 8.06 \times 10^5 \text{ gr} = \frac{8.06 \times 10^5}{454 \text{ gr/lb}} = 1,700 \text{ lb Al at 100\% current efficiency}$$

$$W = 1,700 \times 0.88 = 1666 \text{ lb}$$

e) Coulometers:

$$(q = It)$$

Devices which measure charge. In older days they were based on electrochemical reactions which proceed with 100% current efficiency, e.g., Cu, Ag, Hg,



2-5

EFFICIENCIES IN ELECTROCHEMICAL SYSTEMS

- Fraction of *current* or *voltage* which is useful
- Efficiency < 1 or < 100%

	Electricity → Chemicals Plating Battery charging electrolyzer	Chemicals → Electricity Battery discharge
Faradaic } Coulombic } Efficiency Current }	$\frac{\text{Actual Product Wt}}{\text{Theoretical Product Wt}}$	$\frac{\text{Theoretical Product Wt}}{\text{Actual Product Wt}}$
Voltaic Efficiency	$\frac{E^0}{\text{Applied Voltage}}$	$\frac{\text{Applied Voltage}}{E^0}$

Current Efficiency < 1:

Competing reactions (in electrolyte & cell hardware)

Product decomposition

Product recombination

Voltaic Efficiency < 1:

Ohmic overpotential (in cell, electrodes, and external circuitry)

Activation overpotential

Mass transport limitation

Conduction

Metals:

$$R = \rho \frac{l}{A} \quad \rho = \text{resistivity} [\Omega \cdot \text{cm}]$$

Typical metallic resistivity at 20°C:

Ag	$1.6 \times 10^{-6} \Omega \cdot \text{cm}$
Cu	1.7
Al	2.8
Ni	7.8
Fe	10
Hg	96
Carbon (fiber)	4-5000
Graphite	1360

Electrolytes:

$$\kappa = 1/\rho = [\Omega^{-1} \text{cm}^{-1}] = [\text{S/cm}]$$

$$\kappa = f(\text{concentration, } Z, v_i, \text{ composition, } T, \dots)$$

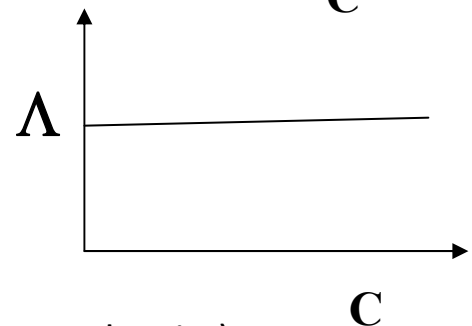
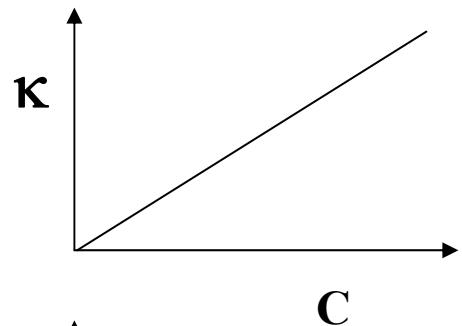
$$\kappa \sim 0.1 - 1 \text{ S/cm} \quad (\sim 10^6 \text{ more resistive than metals!})$$

$$\Lambda \equiv \frac{\kappa}{|Z|C} \quad [\text{S cm}^2 \text{ eq.}^{-1}]$$

$$|Z| \equiv \nu_j z_j = \nu_+ z_+ = \nu_- z_- \quad (\text{"valence"})$$

Implication of limited conductivity:

- Power dissipation (narrow gaps, low current density)
- Non- uniform current distribution
- Structure of water



Ionic and Electronic Conduction:

Current passage, whether it takes place in a metallic conductor through the passage of electrons or in electrolytic solution through the transport of ions, involves the transport of charged species through a medium. The movement of these species is impeded by collisions with the medium and is therefore associated with a certain amount of energy dissipation, expressed as a voltage drop.

Phenomenologically, we can express this through Ohm's law:

$$I = \frac{V}{R}$$

where the resistance, R :

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

defining the resistivity ρ :

$$R = \rho \frac{L}{A}$$

The electrochemical interface:

Electronic conducting phase-ionic conducting phase

- the electrode phase (electronic conducting phase): metal ($\rho \sim 10^{-6} \Omega \text{ cm}$), semiconductor
- the electrolyte phase (ionic conducting phase): ionic solution ($\rho \sim 10^{-6} \Omega \text{ cm}$), molten salt ($\rho \sim 1 \Omega \text{ cm}$), ionic conducting solid ($\rho \sim 5 \Omega \text{ cm}$, 300°C), a plasma

Metals:

In metallic conductors the only charge carriers are electrons in the conduction band and they interact through (a) lattice collisions and (b) collisions with other electrons not in the conduction band.

The voltage drop is related to the current through Ohm's law:

$$V \propto I \quad \text{or} \quad V = R I$$

[volts] = [Ohms] * [Amperes]

The resistance, R, of any electrical conductor, is proportional to its length, L, and

inversely proportional to its cross sectional area, A : $R \propto \frac{L}{A}$

It is therefore possible to write;

$$R = \rho \frac{L}{A}$$

ρ is an intrinsic property of the conductor and called the specific resistance or resistivity ($\Omega \text{ cm}$).

Typical metallic resistivities at 20°C:

$10^{-4} - 10^{-6} \text{ ohm cm}$

Metal	Resistivity ($\mu \Omega \text{ cm}$)
Ag	1.6
Cu	1.7
Al	2.8
Ni	7.8
Fe	10
Hg	96
Carbon (Filament)	4000 – 5000
Graphite	1360

Temperature coefficient $\alpha = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right) [^{\circ}\text{C}^{-1}]$, is positive for metals ($\sim 0.5 \% / ^{\circ}\text{C}$)

and negative for carbon ($\sim -0.05\% / ^{\circ}\text{C}$), and semiconductors..

Electrolytes:

Conduction is by movement of positive and negative ions in the applied field. Because of the very much smaller number of charge carriers, as well as the large resistance offered to the motion of ions (reasonably closely approximated by Stokes resistance for the motion of spheres), the conductivity of electrolytes dissolved in water is very much lower than those of metals. Moderately concentrated solutions, in the range of 1-10 moles/liter have resistivities in the order of $1 < \rho < 10 \Omega \text{ cm}$ at room temperature.

The temperature coefficient of resistivity of electrolytes is negative, and approximately equal and opposite in magnitude of the temperature coefficient of viscosity: $2\text{-}3\%/^{\circ}\text{C}$.

Typical values:

1 N KCl : $10 \Omega \text{ cm}$

1 N CuSO₄: $40 \Omega \text{ cm}$

DI Water: $10^6\text{-}10^8 \Omega \text{ cm}$ ('Megaohm' water)

In electrochemistry we are more concerned with conductance of a solution rather than its resistivity. So we define a new term "Conductivity", κ , such that:

$$\kappa = \frac{1}{\rho} \quad [\Omega^{-1} \text{ cm}^{-1}] \equiv [\text{mho} / \text{cm}] \equiv [S / \text{cm}]$$

Typical conductivity of electrolyte solutions: 0.1 S/cm

This is $\times 10^6$ lower than metals

Thus higher the conductivity, lower is the resistivity and hence the material (or solution) is a better conductor.

It should be noted that typically the conductivity of metals is over 10^6 (a million) times larger than the conductivity of electrolytes. That is why we can often (but not always) neglect the potential drop across metal wires in our calculations involving electrochemical systems.

Importance of Limited Conductivity of Electrolytes:

a. Power dissipation in electrochemical cells $P = I^2 R = I^2 \rho L / A$

- Implications:**
1. Narrow gap between the electrodes problems:
electrode shorting, mechanical strength, chemicals supply.
 2. Low current density ($i = I/A$), often below 100 mA/cm² in industrial processes.
 3. Cooling may be required

Illustration:

Electrochemical machining is a typically high current operation, Assume that the cathode tool and the part are 1 cm apart and a current density of 100 Amp/cm² is applied. The electrolyte is 1 M KCl ($\rho \sim 10 \Omega \text{ cm}$). Calculate the electrolyte flow rate required.

$$P = I^2 R = (100)^2 10 = 10^5 \text{ Watt} = 2.5 \times 10^4 \text{ cal/sec} \quad [1 \text{ Watt} \sim 1/4 \text{ cal/sec}]$$
$$\text{Rate of heating of electrolyte} = 25,000 \text{ }^\circ\text{C/sec}$$

High flow rate is required to remove this heat. Assume inlet electrolyte temp. at 30 °C and outlet at 90 °C:

$$\Delta T = 90^\circ\text{C} - 30^\circ\text{C} = 60^\circ\text{C}$$

$$G = \frac{Q}{\rho C_p \Delta T} = \frac{25,000}{1 \times 1 \times 60} = 400 \text{ cc/s} = 0.4 \text{ L/s} = 24 \text{ L/min}$$

b. Current Distribution:

This is very rarely a problem in metals in which the current is assumed to "fill" the entire conductor. Due to the much higher electrolyte resistance, the current will be distributed in electrochemical systems in such a manner that the voltage balance is maintained. The ohmic drop in the electrolyte is just one component of the many voltage drops associated with electrochemical cells, however often it is very important and most often leads to extremely non-uniform current distribution (the so-called primary distribution). We will later spend time in learning how to evaluate this current distribution in a variety of geometries. Here it will suffice to say that the problem of non-uniform current distribution

is an important one and may lead to inefficient use of electrochemical cells and to serious damages (burned membrane or deposits).

Conductivity is effected by:

- Concentration C
- Number of charges per ion z
- Ionic velocity v
- Temperature T
- Pressure, Magnetic and electric fields (to a much smaller extent)

5. Effect of Concentration

Conductivity is a very strong function of the concentration, since the ions are the charge carriers. In order to reduce his many experimental results to a common basis, Kohlrausch defined (~1880) the equivalent conductivity, Λ , such that it is normalized with respect to concentrations:

$$\Lambda = \frac{k}{C|z|} = \frac{k}{C_{\text{equiv.}}} \quad [cm^2 \text{ eq}^{-1}]$$

where C is the molar concentration in gr moles/cm³; $|z|$ is the "valence" of the salt, (A factor of 1000 is often introduced to convert the concentration from a liter base to a cc).

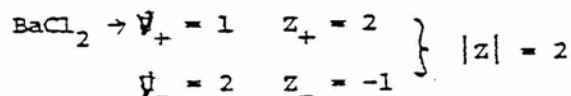
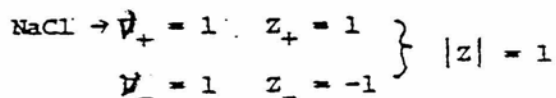
$$C_{\text{eq}} = C|z| = \text{equivalent concentration [gr equivalent/cm}^3]$$

$$\text{also: } |z| = \text{"Valence"} = \nu_+ z_+ = \nu_- z_-$$

where ν_+ , ν_- is the number of cations and anions respectively produced by dissociation of one molecule electrolyte.

z_+ , z_- is the charge number of species (number of proton charges on one ion)

Examples:



by electroneutrality:

$$C = \frac{C_+}{\nu_+} = \frac{C_-}{\nu_-}$$

Therefore:

$$\Lambda = \frac{k}{\nu_+ z_+ c} = \frac{k}{\nu_- z_- c}$$

On the basis of the simplistic resistance model, neglecting higher order interactions one would expect the conductivity to be a linear increasing function of the concentration (charge carriers, or Λ to be const. vs. conc.)

This rarely happens and we often find:

KOH Soln.

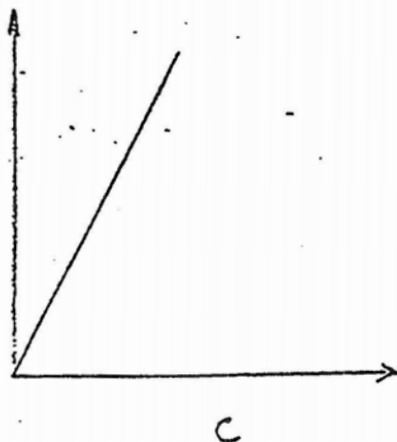
wt %

2.37
5.73
12.8
21
30
42
49

[Ω cm], 25°C

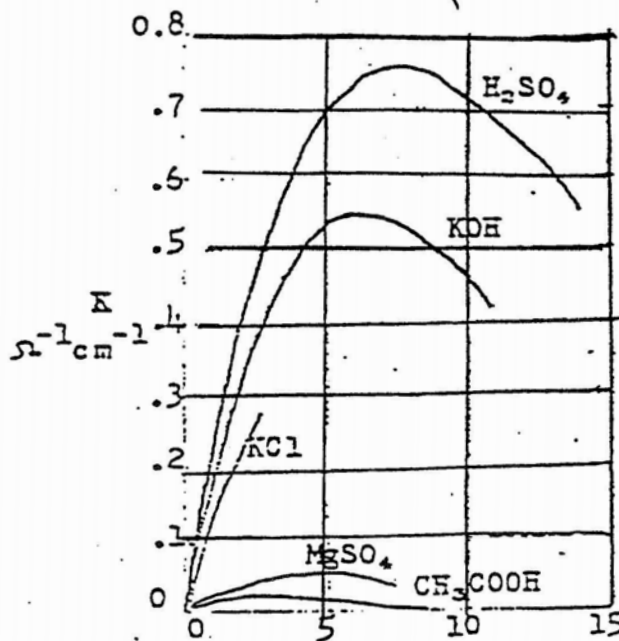
10.6
4.47
2.28
1.01 ← minimum
1.54
1.91
2.55

Ideal



2-14

Real



similarly, one expects to find that Λ does not vary with the concentration (left drawing), whereas in reality the concentration (plotted here as normality, for comparison sake) dependence of the equivalent conductance is quite significant (right).

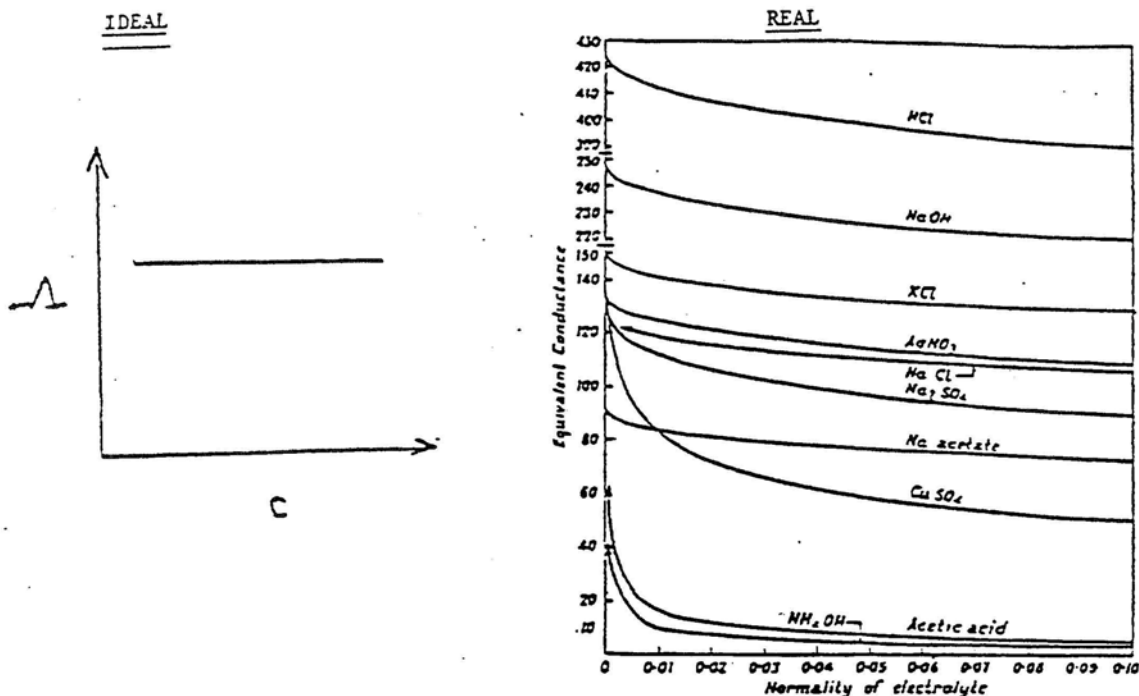


FIG. 6. Concentration dependence of equivalent conductance for aqueous solutions at 25° C.

From: Ref 1 E.C. Potter "Electrochemistry"
Cleaver Hume Press, 1961

The idealized model assumes no interaction of ions or any changes in viscosity due to concentration variations. Later we will see how more sophisticated models will account for some of the anomalies.

If Λ is constant with concentration:

$$\Lambda = \frac{\kappa}{zC} = \frac{l}{RAzC}$$

$$R = \left(\frac{l}{A z \Lambda} \right) \frac{1}{C} \quad [\Omega]$$

assuming that geometry is fixed

$$V = IR$$

for constant voltage applications in a fixed geometry cell: $V = IR$, and:

$$I \propto C$$

Later we will see why this is often incorrect.

2-15

Observing the conductivity data Kohlrausch came to two conclusions:

- a) extrapolation to $C=0$ very often gives a finite value
- b) $\Lambda = \Lambda_0 - A C^{1/2}$ holds for dilute solutions of strong electrolytes
(where $A = \text{constant}$)

Hence, if one plots the conductivity data vs. \sqrt{C} one should expect straight lines with finite intercept. This is true for some electrolytes (strong ones) but not all: (not true for weak electrolytes).

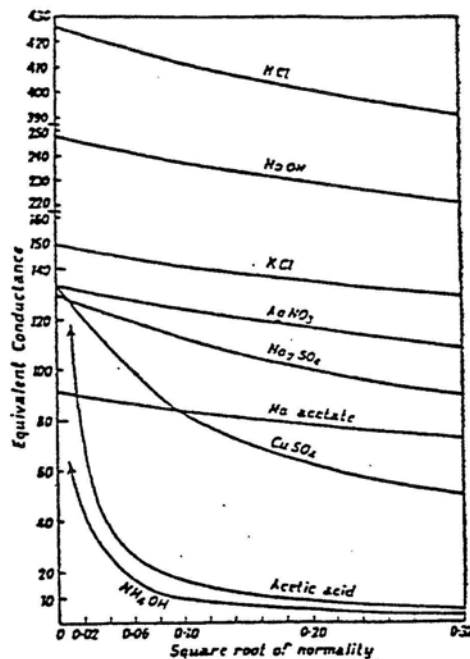


FIG. 7. Kohlrausch square-root law for equivalent conductance of aqueous electrolytes at 25° C.

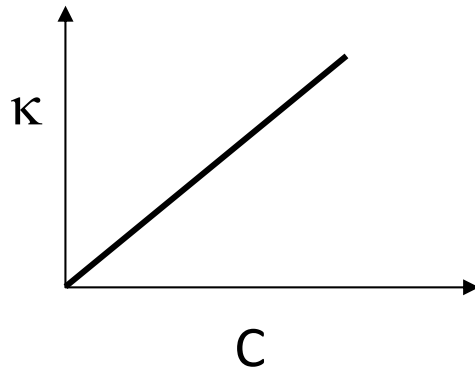
From Ref. 1 - Potter

Kohlrausch introduced the empirical square root dependence, many years before it received theoretical justification by the theory of Debye & Hückel

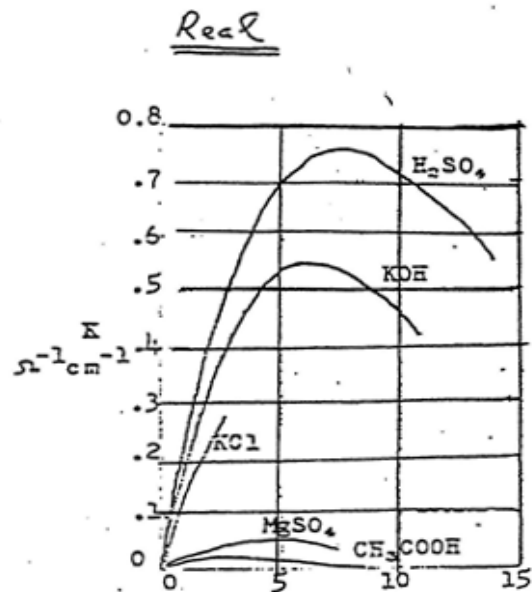
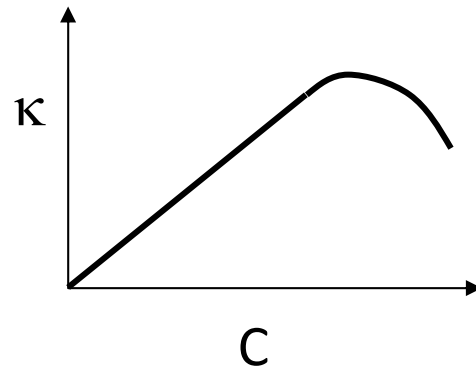
(We shall discuss this theory later).

16

We Expect



We Have



Define Equivalent Conductance:

$$\Lambda = \frac{K}{|z|C} \quad [\text{S cm}^2 \text{ eq}^{-1}]$$

$$|Z| \equiv \nu_j z_j = \nu_+ z_+ = |\nu_- z_-| \quad (\text{"valence"})$$

$$C = [\text{Mole/cc}]$$

$$\Lambda = \frac{K}{|z|C} = \frac{K}{\nu_+ z_+ C} = \frac{K}{|\nu_- z_-| C}$$

IDEAL

REAL

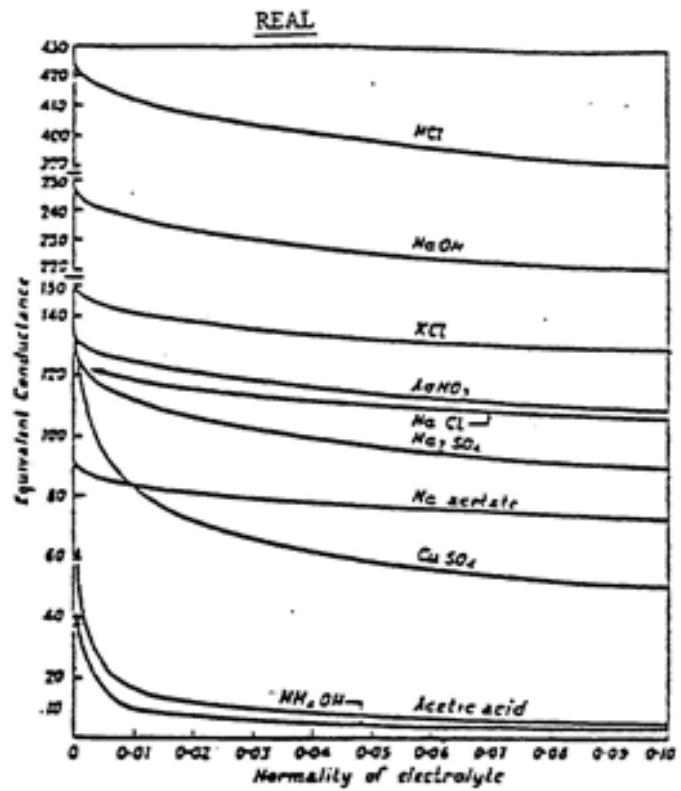
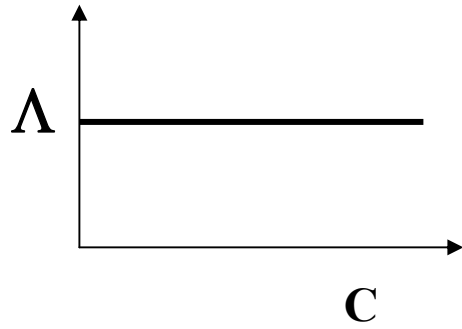


FIG. 6. Concentration dependence of equivalent conductance for aqueous solutions at 25° C.

From: Ref 1 E.C. Potter "Electrochemistry"
Cleaver Hume Press, 1961

Law of Independent Ionic Mobilities

Kohlrausch observed that the equivalent conductivity data at infinite dilution, Λ_0 , exhibited some unusual properties. The difference between equivalent conductivities of different salts with common cation or anion was constant:

salt	Λ_0	Difference	salt	Λ_0	difference
KCl	149.86	23.41	KCl	149.86	4.9
NaCl	126.45		NaNO ₃	144.96	
KNO ₃	144.96	23.41	Cl	126.45	4.9
NaNO ₃	121.55		NaNO ₃	121.55	
KJ	150.32	23.41	LiCl	115.03	4.9
NaJ	126.91		LiNO ₃	110.1	

$$\begin{aligned} \therefore (\lambda_{K^+} + \lambda_{Cl^-}) - (\lambda_{Na^+} + \lambda_{Cl^-}) &= \\ &= \lambda_{K^+} - \lambda_{Na^+} = 23.41 \end{aligned}$$

$$\begin{aligned} \therefore (\lambda_{K^+} + \lambda_{Cl^-}) - (\lambda_{Na^+} + \lambda_{NO_3^-}) &= \\ &= \lambda_{Cl^-} - \lambda_{NO_3^-} = 4.9 \end{aligned}$$

This led Kohlrausch to the conclusion that the individual contribution of each ion to the total conductivity of the solution (at infinite dilution) is specific to the ion, is additive, and is independent of the other ions in the solution.

Therefore, we can write:

$$\Lambda_0 = \lambda_+^0 + \lambda_-^0$$

where λ_+^0, λ_-^0 are the equivalent ionic conductivities or limiting ionic conductivities.

Using this technique, tables of limiting ionic conductivities have been prepared, from which the conductivities of various salts can be obtained by simple addition. It turns out, and we will see later why, that there is a correlation between the solvated ionic radii and the limiting ionic conductivities.

Table 2-1: Equivalent ionic conductivities and solvated ionic radii

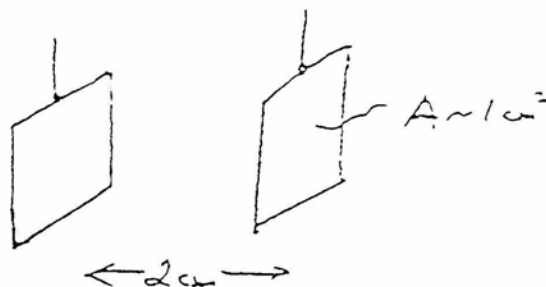
ION	λ [$\text{ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$]	Radius [Å] (<i>solvated ionic radius</i>)
Li^+	39	2.36
Na^+	50	1.8
K^+	73	1.21
Rb^+	78	
Cs^+	73	
Ag^+	62	1.455
Mg^{++}	53	1.725
SO_4^{--}	79.6	1.15
Cl^-	76	1.2
I^-	77	1.16
NO_3^-	71.4	1.37
H^+	350	0.25 (Grothuss Mechanism)
OH^-	200	0.44 (Grothuss Mechanism)
All other ions:	~ 50	~ 1.5

It should be recognized that these values are valid only for infinitely dilute solutions, and appropriate corrections should be introduced for concentrated solutions. For $C < 1\text{M}$, the limiting values provide however a valuable estimate. Close examination of the conductivity data reveals that with the exception of a H^+ and OH^- all values fall within the narrow range of $40\text{--}80 \text{ ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$. For estimating purposes it is very useful and sufficient to remember one average value of 50. Similarly, a value of 350 should be remembered for H^+ and 200 for OH^- . These three numbers permit us to perform simple yet extremely useful rough calculations without having to resort to handbook values.

Illustration:

Calculate the voltage required to pass a current of 10 mA between two parallel electrodes 2 cm apart, each having a surface area of 1 cm². The electrolyte is 0.1 N NaOH.

Solution:



$$\Lambda = 50 + 200 = 250$$

$$\kappa = 10^{-3} \Lambda C = 25 \times 10^{-3} [\text{cm}^{-1} \text{cm}^{-1}]$$

$$\rho = \frac{1}{\kappa} = 40 \Omega \text{cm}$$

$$R = \frac{\rho l}{A} = 40 \left(\frac{2}{1} \right) = 80 \Omega$$

$$V = IR = 0.01 \times 80 = .8 \text{ V}$$

(We have neglected here effects due to non-uniform current distribution leading to a considerable lower voltage. On the other hand, we also neglected electrode kinetic effects and concentration variations which would lead to a higher voltage. We will learn as the course progresses to account for all these effects.)

II. Hydration of Ions

The reason for relatively narrow range of the ionic conductivities of all ions (with the exception of H⁺ and OH⁻) is that the conductivity determining factor, as we shall later discover by simple analysis, is their ionic radius. It turns out that the variations in the solvated ionic radii are considerably smaller than variations in crystallographic radii.

ion	λ°	relative hydration
Li^{+}	38.69	14
Na^{+}	50.11	8.4
K^{+}	73.52	5.4

Despite the fact that Li^{+} is the smallest and lightest ion its ionic conductance is the lowest! This is because the ions are hydrated.

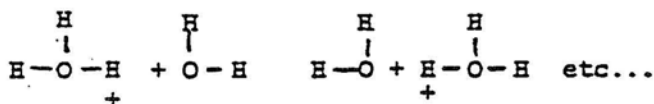


The smaller the ion the closer is the central charge to the surface, the greater the electric field and the greater the attraction to water dipoles.

8. Abnormal Conductivity of Proton and Hydroxyl Ions

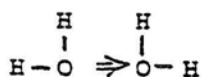
The proton and hydroxyl ions exhibit abnormally high conductivities of 350 and 200 respectively. We have stated before that conductivity is intimately related to the ease with which the charge carriers can move inside the medium. The abnormally high conductivity values of the proton and the hydroxyl cannot however be explained in terms of a smaller ionic radius and a different conduction mechanism, superimposed on the regular ionic movement must be assumed.

The Grotthuss transport mechanism based on a chain-type transfer of the proton between neighboring water molecules provides such a possible mechanism:



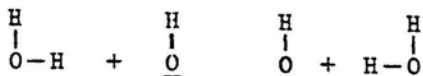
transport of bond rather than of the proton!

This step may be followed by a rotation of the donor water molecule such that it is again in position to accept another proton.



Hence, the proton transport in water is equivalent to the much simpler and faster process of water molecules rotation, one which requires less energy.

The hydroxyl transport mechanism is a similar process of proton transport:



These mechanisms are active only in hydroxyl containing solvents such as water or alcohols.

Ice exhibits a second anomaly of even a much higher conductivity. When water freezes the conductivity jumps by a factor of about 50 over that of water at 0 °C. A possible explanation is a quantum mechanical tunneling of protons across the rigid ice structure.

9. Conductivities of Weak and Strong Electrolytes

From: A.R. Denaro "Elementary Electrochemistry" Butterworth, 1971

Although two or three attempts were made during the nineteenth century to account for the origins of the ions in electrolyte solutions, it was not until 1887, when Arrhenius proposed his theory of ionisation, that any degree of success was achieved.

Arrhenius suggested that in a solution of an electrolyte, ions

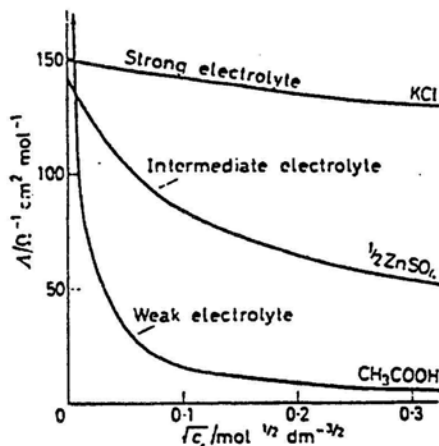
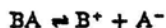


Figure 4. Variation of molar conductivity with \sqrt{c}

are always present in equilibrium with un-ionised molecules. Thus for a binary electrolyte, BA, there exists the equilibrium



As the dilution increases, the equilibrium is displaced towards the right and more ionisation occurs until, at infinite dilution, ionisation is complete. Λ^∞ , which is the limiting molar conductivity at infinite dilution should be a measure of the total number of ions which can be produced and Λ , at any other concentration

2-21

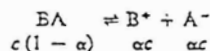
ELECTROLYTIC CONDUCTION

α , should be a measure of the number of ions present at that particular concentration. If the speeds of the ions do not change with concentration, then the ratio of Λ to Λ_0^∞ will be equal to the degree of ionisation

$$\text{Arrhenius} \rightarrow \frac{\Lambda}{\Lambda_0^\infty} = \alpha \quad (2.9)$$

where α is the fraction of the solute molecules which have ionised.

Weak Electrolytes
Ostwald (1888) applied the equilibrium law to the ionisation of an electrolyte. Consider a binary electrolyte, BA, providing the ions B^+ and A^- in solution where the concentration of BA is c . Suppose a fraction α of the BA ionises so that the concentration of un-ionised BA is $c(1 - \alpha)$ and the concentration of B^+ and A^- ions is αc for each ion



The equilibrium law states that

$$\frac{[B^+][A^-]}{[BA]} = k \quad (2.10)$$

where k is a constant and the terms in square brackets represent concentrations. Substituting for the concentration terms in (2.10)

$$\text{Ostwald} \rightarrow \frac{\alpha c \cdot \alpha c}{c(1 - \alpha)} = k$$

or

$$\frac{\alpha^2 c}{(1 - \alpha)} = k = \frac{\Lambda^2 c}{\Lambda_0^2 (1 - \frac{\Lambda}{\Lambda_0})} \quad (2.11)$$

This relationship is known as Ostwald's dilution law.

If the values of α derived from conductance measurements are correct, then substitution in the left-hand side of eqn. (2.11) should give a constant. Values for acetic acid are given in Table 3. Similar results are obtained for other weak electrolytes and it would appear that the Arrhenius theory is satisfactory for

for weak electrolytes (only for which Ostwald's law holds);

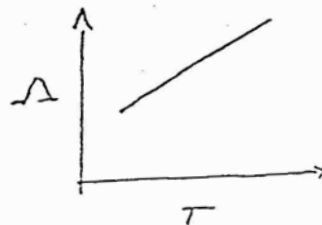
$$(1 - \alpha) \approx 1 \quad k = \frac{\Lambda^2}{\Lambda_0^2} c = \alpha^2 c$$

10. Temperature Effects

(a) Dilute Solutions:

$$\Lambda \approx \Lambda_{ref} (1 + \beta \Delta T)$$

$$\beta \sim 0.02 \quad \text{for } \pm 10^\circ \text{C}$$

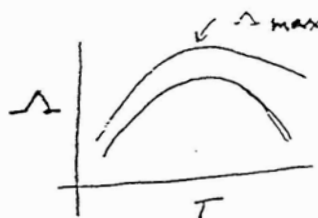


(b) Conc. Solutions

$$\Lambda_{max}$$

$$K_2SO_4 \sim 100^\circ \text{C}$$

$$KCl \sim 280^\circ \text{C}$$



*Pressure - small influence on

*Wien Effect - strong field

2-22

*Frequency - Debye-Falkenhagen Effect

MATH REVIEW

Tensors (general representation of a parameter)

Rank – ‘dimensionality’ or qualities

Scalars – only magnitude, no direction (rank = 0)

Vectors – magnitude + direction (rank = 1, 2, or 3)

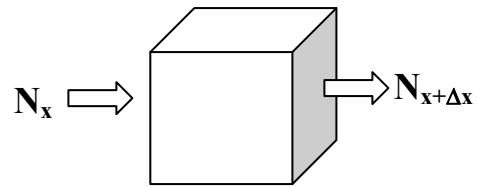
Gradient

$\nabla \Phi$ short hand notation for: $\vec{\nabla} \Phi \equiv \vec{i} \frac{d\Phi}{dx} + \vec{j} \frac{d\Phi}{dy} + \vec{k} \frac{d\Phi}{dz}$

gradient of a scalar (Φ) is a vector

Divergence

$$\nabla \bullet \vec{N}_j = \frac{\partial N_x}{\partial x} + \frac{\partial N_y}{\partial y} + \frac{\partial N_z}{\partial z}$$



Net flux out of a differential volume element. Divergence is the negative of convergence. Divergence of a vector is a scalar. Used often to perform mass balance in the electrolyte.

Material Balance (on any volume element)

$$\frac{\partial C_j}{\partial t} = - \nabla \bullet \vec{N}_j + R_j$$

Rate of accumulation of specie j in a volume element	=	Net flux in of Specie j	+	Rate of generation of specie j (e.g., by homogenous reaction)
--	---	----------------------------	---	---

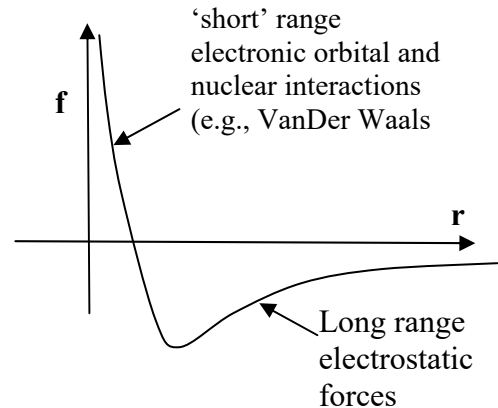
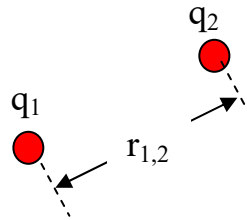
Difference

$$\Delta \Phi = \Phi_i - \Phi_j$$

Electrostatics Review

Force (coulombic)

$$\vec{f} = \frac{q_i q_j}{4\pi \epsilon r_{i,j}^2}$$



f – force between bodies [dyne or N].

q – charge on a body [cb]

r - distance

ϵ – permittivity [cb/(V m)]

ϵ_0 – permittivity of vacuum [= 8.85×10^{-14} cb/(V cm)]

$\epsilon / \epsilon_0 = \Delta$ = Dielectric constant (for water = 78.3)

If q_i and q_j same sign, $f > 0$ (repulsion)

If q_i and q_j different sign, $f < 0$ (attraction)

Coulomb's law is sometimes represented as:

$$\vec{f} = k_C \frac{q_i q_j}{r_{i,j}^2}$$

where:

$$k_C = \frac{1}{4\pi\epsilon_0} \approx 8.988 \times 10^9 \frac{\text{N m}^2}{\text{C}^2} \text{ (also } \frac{\text{m}}{\text{F}} \text{)} \text{ is the } \mathbf{\text{electrostatic constant}},$$

or **Coulomb force constant**, and

$$\epsilon_0 \approx 8.854 \times 10^{-12} \frac{\text{C}^2}{\text{N m}} \text{ (also } \frac{\text{F m}}{} \text{)} \text{ is the } \mathbf{\text{permittivity of free space}}, \text{ also}$$

called electric constant, an important physical constant.

In cgs units, the unit charge, **esu of charge** or statcoulomb, is defined so that this Coulomb force constant is 1.

Units:

$$\text{MKS: } [N] = \frac{[cb]^2}{[\frac{cb}{Vm}][m]^2} = \frac{[V][m][cb]}{[m]^2} = \frac{[V][cb]}{[m]} = \frac{[J]}{[m]} = \frac{[N][m]}{[m]} = [N]$$

$$\text{CGS:} \quad [Dyne] = \frac{[esu]^2}{[cm]^2} \quad [esu] \equiv [cm][Dyne]^{1/2} \quad 1 \text{ esu} = 3.3356 \times 10^{-10} \text{ C}$$

ESU or Statcoulomb

The **statcoulomb (statC)** or **franklin (Fr)** or **electrostatic unit of charge (esu)** is the physical unit for electrical charge used in the centimetre-gram-second (cgs) electrostatic system of units. The SI system of units uses the coulomb (C) instead. The conversion is

$$1 \text{ statC} = 0.1 \text{ Am/c} \approx 3.33564 \times 10^{-10} \text{ C}$$

The **conversion factor** ($\approx 3.33564 \times 10^{-10}$) is equal to **10** divided by the numerical value of the speed of light, c , expressed in cm/s.

Field (electrostatic)

Region where forces are present. Forces can be gravitational, magnetic, electrostatic, etc. We sense the field by putting in the region a test charge (or body) and measure the forces (if any) acting on it.

$$\boxed{\vec{E} = \frac{f}{q_i} = \sum_j \frac{q_j}{4\pi\epsilon r_j^2}} \quad \begin{array}{l} \text{E – electric field [V/m] or [N/Cb] (or [V/cm])} \\ \text{or [dyne/esu]} \end{array}$$

Potential

$$\boxed{-\nabla\Phi = \vec{E}}$$

Φ = **electrostatic potential [V]** (Similar to elevation lines in a topographical map, or temperature isoclines in a region.)

$$P[\text{Power, Watt}] = V[\text{Volt}]I[A]$$

$$W[\text{Energy, Work, J}] = q[cb]V[\text{Volt}] = ItV$$

$$[V] = \frac{[J]}{[cb]} = \frac{[Watt][s]}{[A][s]} = \frac{[Watt]}{[A]} = \frac{[V][A]}{[A]}$$

Poisson's Equation (Gauss's Law)

Gauss's law:

Net electric flux out of an enclosed space is proportional to the net charge within this space

Poisson's Eqn. (Fundamental Law)

$$\nabla \bullet (\epsilon E) = \rho_e \text{ (Density of free charge)}$$

$$-\nabla \bullet (\epsilon \nabla \Phi) = F \sum_j z_j C_j$$

$$\nabla^2 \Phi = -\frac{F}{\epsilon} \sum_j z_j C_j \quad \text{however,} \quad \frac{F}{\epsilon} \approx \frac{10^5}{10^{-13}} = 10^{18} \left[\frac{V \text{ cm}}{\text{equiv.}} \right]$$

Laplace's 's Equation

$$\boxed{\boxed{\nabla^2 \Phi = 0}}$$


Holds when we have electroneutrality. Alternatively, when we deviate slightly from electro neutrality – we get very high potentials $[\Phi]$

Movement of an Ion in an Electric Field

Electrical force

$$F_e = -qE = e z \frac{d\Phi}{dx}$$

$$E = -\nabla\Phi = -\frac{d\Phi}{dx}$$



Electric field
(Volt/cm)

Drag force

$$F_D = 6 \pi \mu r v$$

Units:

MKS: $[N] = [cb] \left[\frac{V}{m} \right] = [cb] \left[\frac{N}{cb} \right]$ $[ez] = [cb] = [\text{cb/unit charge}][\# \text{ of unit charges}]$

CGS: $[\text{dyne}] = [\text{esu}] [\text{dyne/esu}]$

Steady-state:

$$F_e = F_D \quad \Rightarrow \quad e z \frac{d\Phi}{dx} = 6 \pi \mu r v$$

$$v_j = \frac{e z_j}{6 \pi \mu r} \frac{d\Phi}{dx}$$

(~10⁻³ cm/sec under a field of 1 V/cm)

$$\left[\frac{m}{s}\right] = \frac{[cb / charge][\#charges]}{\left[\frac{kg}{m \bullet s}\right]} \left[\frac{V}{m}\right] = \frac{[cb][V][s]}{[kg][m]} = \frac{[J][s]}{[kg][m]} = \frac{[J]}{[Kg]} \left[\frac{m}{s}\right] = \frac{[N][m]}{[N][s]}$$

Define “Mobility” (= velocity per unit field *or* unit force):

$$U_j^R = \frac{v_j}{\left(d\Phi/dx\right)} = \frac{e z_j}{6 \pi \mu r}$$

(Relative mobility = velocity/unit electric field)
= velocity / volt/cm = [cm²/ V sec]

$$\frac{\left[\frac{m}{s}\right]}{\left[\frac{V}{m}\right]} = \frac{[m]^2}{[V][s]} = \frac{[cb][\#]}{\left[\frac{kg}{m \bullet s}\right][m]} = \frac{[cb][s]}{[kg]} = \frac{[J/V][s]}{[kg]} = \frac{[N \cdot m][s]}{[V][Kg]} = \frac{[Kg][m/s^2][m][s]}{[V][Kg]}$$

$$U_j = \frac{v_j}{z_j F \left(\frac{d\Phi}{dx} \right)} = \frac{e}{6 \pi \mu r F}$$

(Absolute mobility = velocity/(force/mol)
= velocity / Nt / M = [cm² M/ Joule sec]
2-30

$$\frac{\left[\frac{m}{s}\right]}{[N/mol]} = \frac{[cb]}{\left[\frac{kg}{m \bullet s}\right][m][cb/mol]} = \frac{[s][mol]}{[kg]} = \frac{[s][mol]}{\left[\frac{N}{m/s^2}\right]} = \frac{[s][mol][m]}{[N][s]^2} = \frac{[m][mol]}{[J/m][s]} = \frac{[m]^2[mol]}{[J][s]}$$

$$\text{Force/mole} = z_j F \left(\frac{d\Phi}{dx} \right) = [eq/mol][cb/eq] \left[\frac{V}{m} \right] = \frac{[J]}{[m][mol]} = \left[\frac{N \cdot m}{m \cdot mol} \right] = [N/mol]$$

The Current Density

$i = ?$

$$\text{charge/ion} = z_j F \quad [(\text{eq./mole}) (\text{cb/eq}) = \text{cb/mole}]$$

$$\text{Conc. of charge} = c_j z_j F \quad [(\text{mole/cm}^3) (\text{cb/mole}) = \text{cb/cm}^3]$$

$$\text{Current density} = i = \sum c_j z_j F v_j \quad [\text{cb}/(\text{sec cm}^2) = \text{A/cm}^2]$$

$$\text{Ionic velocity} = v_j = u_j z_j F \nabla \Phi \quad \Longleftarrow \quad u_j = \frac{v_j}{z_j F \nabla \Phi}$$

$$\rightarrow i = F^2 \sum_j z_j^2 u_j C_j \nabla \Phi$$

Ohm's Law

$$I = -\frac{\Delta \Phi}{R} = -\frac{\Delta \Phi}{\rho \frac{\Delta L}{A}} = -\frac{\Delta \Phi A}{\rho \Delta L} = -\kappa \frac{\Delta \Phi A}{\Delta L}$$

$$\rightarrow i = \frac{I}{A} = -\kappa \frac{\Delta \Phi}{\Delta L} = -\kappa \nabla \Phi$$

$$\kappa = F^2 \sum_j z_j^2 u_j C_j$$

$$\lambda_j = F^2 z_j u_j \quad D_j = RT u_j \quad [cm^2/s]$$

$$\kappa = \sum_j \lambda_j z_j C_j$$

Walden “Rules”

$$\Lambda \mu = \text{const.}$$

1. Any Temp.
2. Any Solvent

Conductivity:

$$\kappa = F^2 \sum_{j=1,n} z_j^2 u_j C_j = \sum_{j=1,n} \lambda_j z_j C_j \quad \lambda_j = F^2 z_j u_j$$

Tying the macroscopic property to molecular features

Conduction in Heterogeneous Media

So far we have discussed homogeneous electrolytes, i.e., single phase with a constant conductivity. However, in certain applications, we may encounter, heterogeneous electrolytes, consisting of multiple phases with different conductivities. Examples include:

- Bubbles due to gas evolving electrodes, or due to air agitation
- Electrolytes containing particulates, or a dispersed phase, e.g., fluidized electrode
- Blood (contains white and red blood cells)

When a dispersed phase is present, which has a lesser or no conductivity, current lines will be forced to go, at least partially, around the particles, causing 'bunching' of the current lines leading to increased resistance and lower conductivity. (See Figure below).

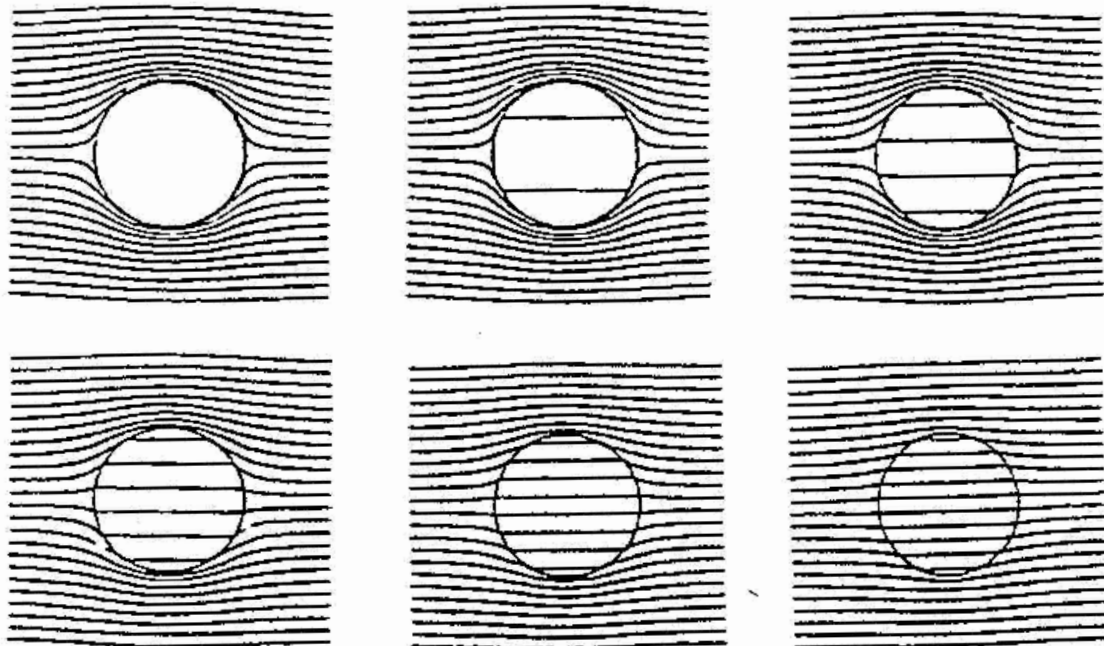
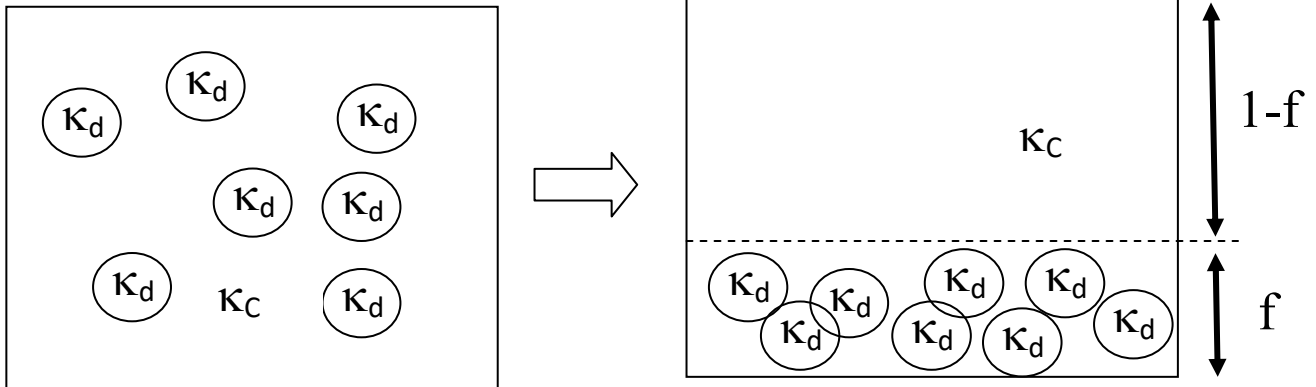


FIG. 1:3. Lines of current flow around spheres placed in a uniform field. The approximate ratios of the conductances of sphere to medium from left to right, top, 0, 0.02, 0.08 and bottom, 0.18, 0.35, 0.6.

This topic is particularly of interest to biologists who studied extensively such media. A good reference is K.S Cole, "Membranes, ions and impulses", University of California Press, 1968.

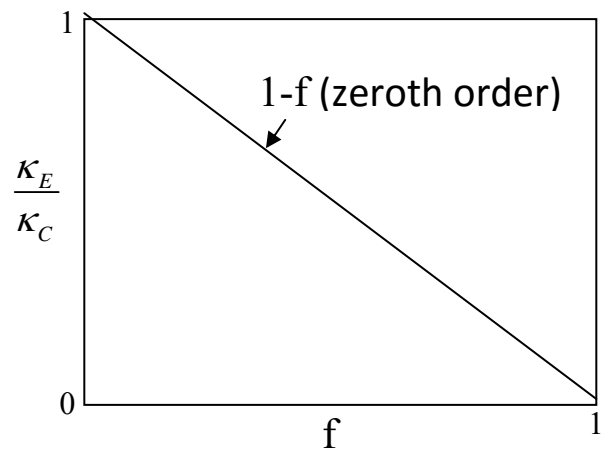
Analysis is typically based on representing the heterogeneous system in terms of an equivalent homogeneous system having a single 'equivalent' or 'effective' conductivity, K_e .

Zeroth order Approximation



$$f \equiv \frac{V_d}{V_d + V_C}$$

κ_e = Effective or equivalent conductivity



Maxwell derived for a dilute dispersed phase with conductivity κ_d in a continuous phase with conductivity κ_c :

$$\frac{\frac{\kappa_e}{\kappa_c} - 1}{\frac{\kappa_e}{\kappa_c} + 2} = f \frac{\frac{\kappa_d}{\kappa_c} - 1}{\frac{\kappa_d}{\kappa_c} + 2}$$

When the dispersed phase is completely non-conductive, e.g., gas bubbles; $\kappa_d=0$ and,

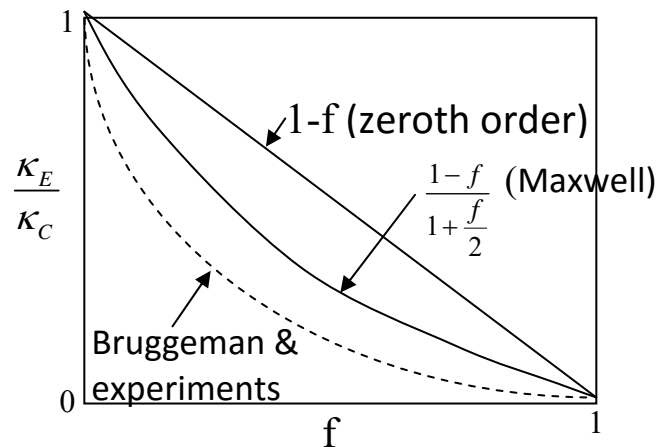
$$\frac{\kappa_e}{\kappa_C} = \frac{1-f}{1+\frac{f}{2}}$$

Bruggeman extended the treatment to concentrated dispersions. He considered the effect of compression of additional lines due to the presence of additional particles, considering the previous case (Maxwell) as a continuum. Bruggeman's equation is an excellent model for dispersed phases ("Effective Medium Theory"):

$$\frac{\frac{\kappa_e}{\kappa_C} - \frac{\kappa_d}{\kappa_C}}{\left(\frac{\kappa_e}{\kappa_C}\right)^{1/3} - \left(1 - \frac{\kappa_d}{\kappa_C}\right)} = 1 - f$$

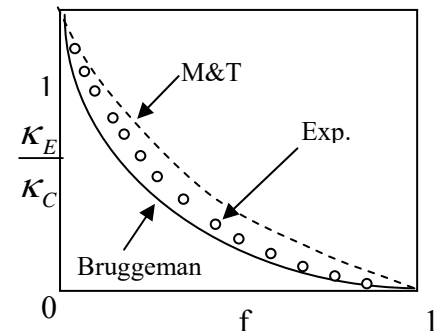
For $\kappa_d=0$, we have,

$$\frac{\kappa_e}{\kappa_C} = (1-f)^2$$



Emulsions:

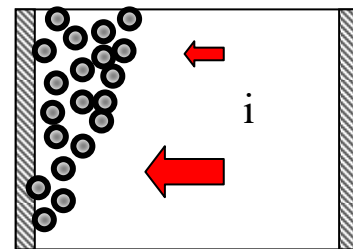
Meredith and Tobias, J. Electrochem. Soc. 108 (3) 286 (1961)



Gas Evolution:

On vertical electrodes: Charles W. Tobias, J. Electrochem. Soc. 106 (9) 286 (1959)

Here due to accumulating bubbles 'cloud' towards the top of the interelectrode gap, the current distribution is no longer uniform.



Electrolyte Conductivity Measurements

Early D.C. measurements of electrolyte conductivities indicated that Ohm's law is not obeyed. This, of course, was an artifact due to non-reversible polarization at the electrodes. Nowadays, AC Wheatston bridges in the audio range (1-4 K Cycle) with capacitance compensation are used for simple and accurate conductivity determination.

Measure Resistance:

$$R = \left[\frac{V}{I} \right] = \rho \frac{l}{A} = \frac{1}{\kappa} \frac{l}{A}$$

Issues:

- A. What are: l, A?
- B. Measure without generating concentration variations

A. What are l, A?

No need to know. Calibrate and determine cell constant, C_K .

$$C_K \equiv \frac{l}{A}$$

Procedure:

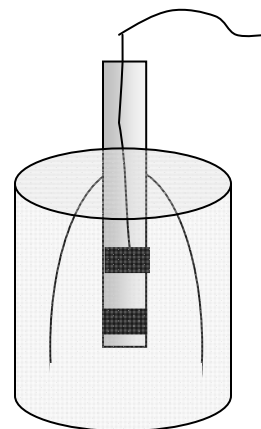
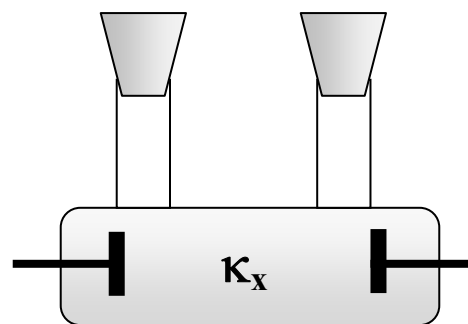
Prepare a known conductivity κ_{ref} solution e.g., 0.1 M NaCl:

Fill cell with known solution and measure R_{ref} .

$$R_{\text{ref}} = \frac{V}{I}$$

$$R_{\text{ref}} = \frac{1}{\kappa_{\text{ref}}} \frac{l}{A} = \frac{1}{\kappa_{\text{ref}}} C_K$$

$$C_K = R_{\text{ref}} \kappa_{\text{ref}}$$



Typically, commercial cells have a known (pre-calibrated) cell constant. The customer can select a cell to fit application

Calculate:

$$C_K = R_{Ref} \kappa_{Ref}$$

Replace solution in cell with unknown and measure R_x :

$$R_x = \frac{V_x}{I_x}$$

Calculate:

$$\kappa_x = \frac{C_K}{R_x}$$

Implied assumption: The current distribution does not change between standard and sample. This is a valid assumption because the measurement is conducted under conditions when there are no concentration variations and no Faradaic electrode reaction takes place. Under these conditions 'Primary distribution' prevails which, as we shall see later, depends only on the cell geometry. Obviously, the latter does not change.

How do we conduct the measurement such that there are no concentration variations and no net Faradaic reaction?

Either of two methods:

Very high frequency AC ($> \text{MHz}$)

Zero current measurement (Wheatstone Bridge):

At all times:

$$\frac{I_x R_x}{I_2 R_2} = \frac{I_3 R_3}{I_4 R_4}$$

At Balance (Galv=I=0)

$$\frac{R_x}{R_2} = \frac{R_3}{R_4} = \frac{L_3}{L_4}$$

