

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, 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: Bruggemann's equation. 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: $I = [\text{Amp}] = \frac{q}{t}$ $\left[\frac{\text{Cb}}{s} \right]$

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

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

^a current density units:

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

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

$$\textcircled{1} \quad w \sim q = It$$

w - weight

M – Formula weight

q – charge

n – number of electrons

$$\textcircled{2} \quad \frac{w}{q} \propto \frac{M}{n}$$

I – current

i – current density

t – time

h – deposit thickness

Combine:

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

Defining
Faraday's
constant:

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

$$F = 96,480 \text{ cb} = 26.8 \text{ Ahr} (=L^*e)$$

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:

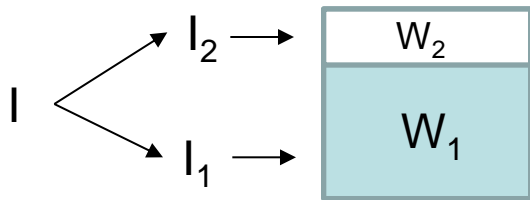
$$N = \frac{i}{nF}$$

[M / sec-cm²] or
[gr-ion/sec-cm²]

EFFICIENCIES IN ELECTROCHEMICAL SYSTEMS

Fraction of *current* or *voltage* which is useful

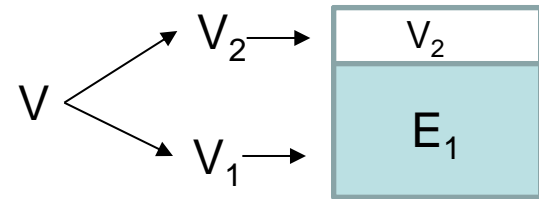
Efficiency < 1 or < 100%



$$\varepsilon_F = \frac{I_1}{I_T} = \frac{I_1}{I_1 + I_2} = \frac{W_1}{W_1 + W_2} = \frac{W_1}{W_{Theoretical}}$$

Current Efficiency < 1:

- Competing reactions
- Product decomposition
- Product recombination



$$\varepsilon_V = \frac{V_1}{V_T} = \frac{V_1}{V_1 + V_2}$$

Voltaic Efficiency < 1:

- Ohmic overpotential
- Activation overpotential
- Mass transport limitation

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
- Product decomposition
- Product recombination

Voltaic Efficiency < 1:

- Ohmic overpotential
- 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:

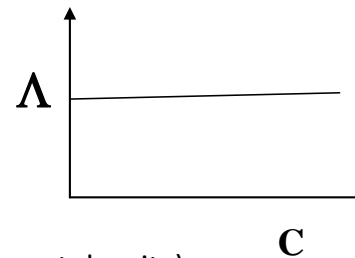
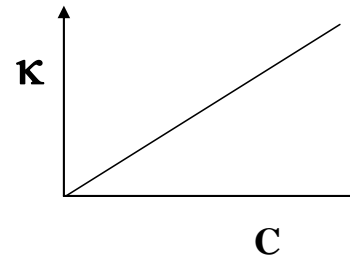
$$\kappa = 1/\rho = [\Omega^{-1} \text{cm}^{-1}] = [\text{S/cm}]$$

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

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

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

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



Implication of limited conductivity:

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

Define Equivalent Conductance:

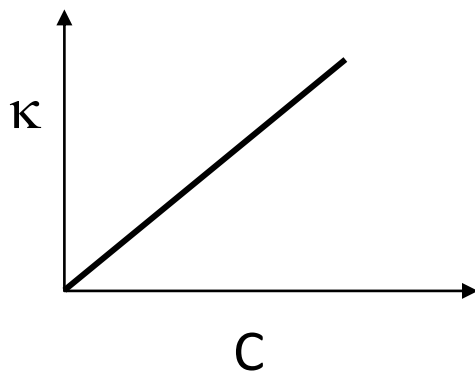
$$\Lambda = \frac{K}{|z|C} \quad [\text{S cm}^2 \text{ eq.}^{-1}]$$

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

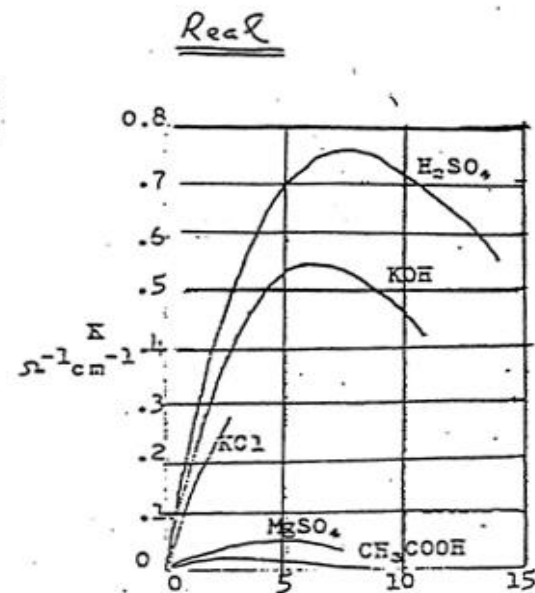
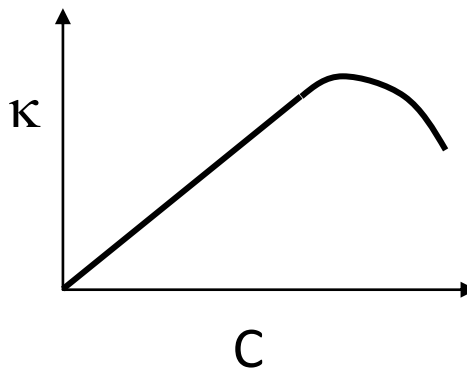
$$C = [\text{Mole/cc}]$$

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

We Expect



We Have



IDEAL

REAL

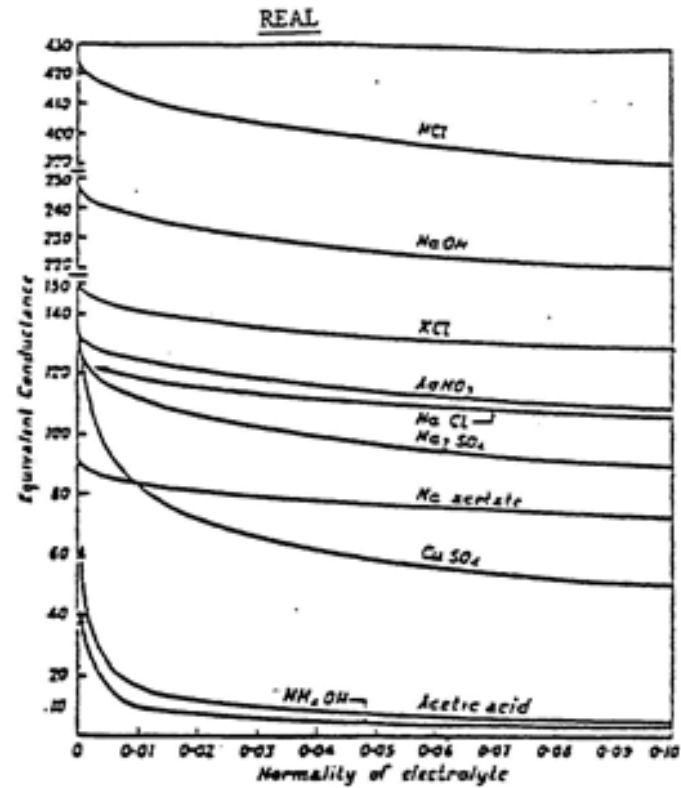
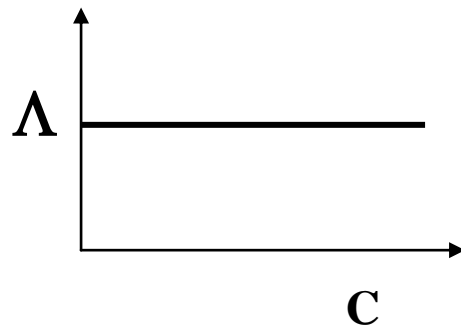
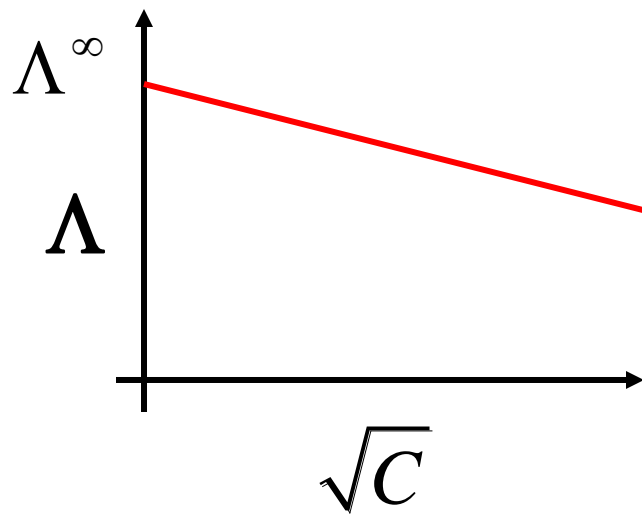


FIG. 6. Concentration dependence of equivalent conductance for aqueous solutions at 25° C.

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



$$\Lambda = \Lambda^\infty - A\sqrt{C}$$

Debye-Huckel and Onsager

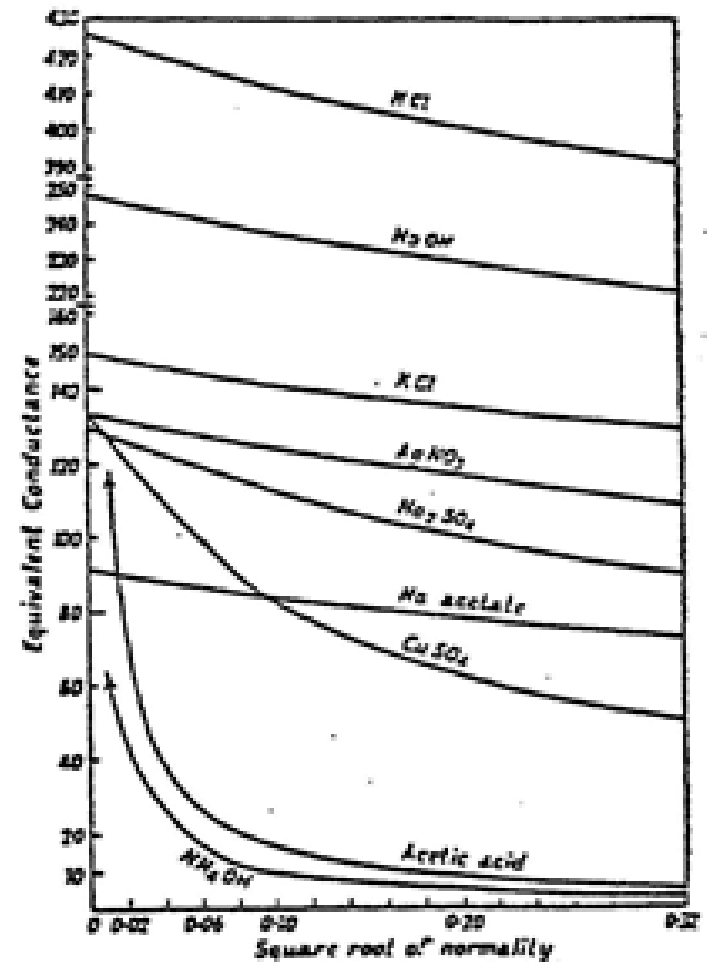


FIG. 7. Kohlrausch square-root law for equivalent conductance of aqueous electrolytes at 25°C.

Law of Independent Ionic Mobilities (Kohlrausch)

salt	Λ_0	Difference	salt	Λ_0	difference
KCl	149.86	23.41	KCl	149.86	4.9
NaCl	126.45		KNO ₃	144.96	
KNO ₃	144.96	23.41	NaCl	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	

$$\lambda_+ + \lambda_- = \Lambda^o$$

Equivalent ionic conductivities and solvated ionic radii

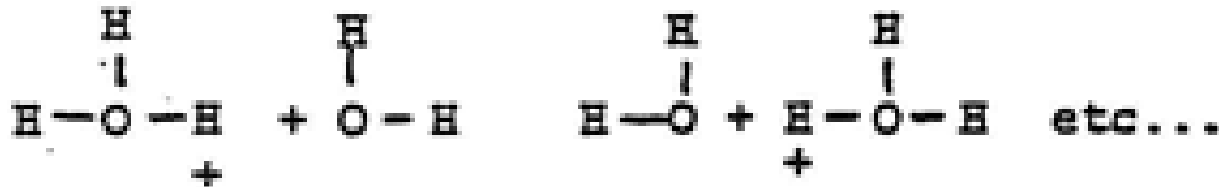
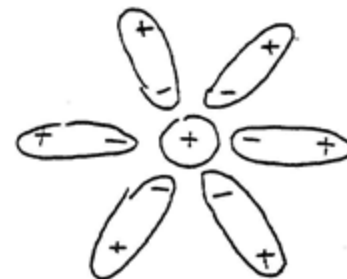
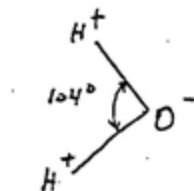
ION	λ [ohm ⁻¹ cm ² eq ⁻¹]	
Li ⁺	39	
Na ⁺	50	
K ⁺	73	
Rb ⁺	78	
Cs ⁺	73	
Ag ⁺	62	
Mg ⁺⁺	53	
SO ₄ ⁻	79.6	
Cl ⁻	76	
I ⁻	77	
NO ₃ ⁻	71.4	
H ⁺	350	
OH ⁻	200	
All other ions:	~ 50	

Equivalent ionic conductivities and solvated ionic radii

ION	λ [ohm ⁻¹ cm ² eq ⁻¹]	Radius [Å] (solvated ionic)
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

Implications:

- Structure of water
- Hydration of ions
- Abnormal conductivity of H^+ and OH^-



Grotthus transport mechanism



Hydroxyl

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)

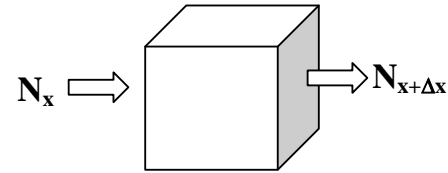
Gradient

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

gradient of a scalar ($\nabla \Phi$) 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)
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Difference

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