Electrochemistry Fundamentals

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GERVASIO FIELDS OF SPECIALIZATION: Electrochemistry, power sources (Fuel cells, capacitors, batteries), corrosion, proton conduction, electrocatalysis, heterogeneous catalysis, energy storage.

TEXTBOOK:

ELECTROCHEMISTRY

By

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Chapter 1

Foundations, Definitions and Concepts

Ions, Electrolytes and Electrical Charge

Coulombic Interaction Energy

$$U_{12} = \frac{q_1 \cdot q_2}{4\pi\varepsilon_r\varepsilon_0 r}$$

Ionic Repulsion Energy

$$R_{12} = B/r^n$$

Total Interaction Energy

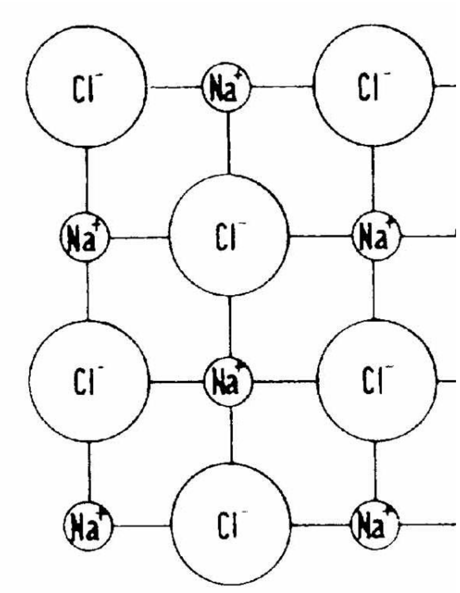
$$E_{12} = U_{12} + R_{12}$$

Total Energy of NaCl

M - Madelung constant (1.75 for NaCl)

L or N_A - Avegadro Number (6.2x1023 mol^{-1})

$$E = \frac{ML|q|^2}{4\pi\varepsilon_0 r}\left(1 - \frac{1}{n}\right)$$

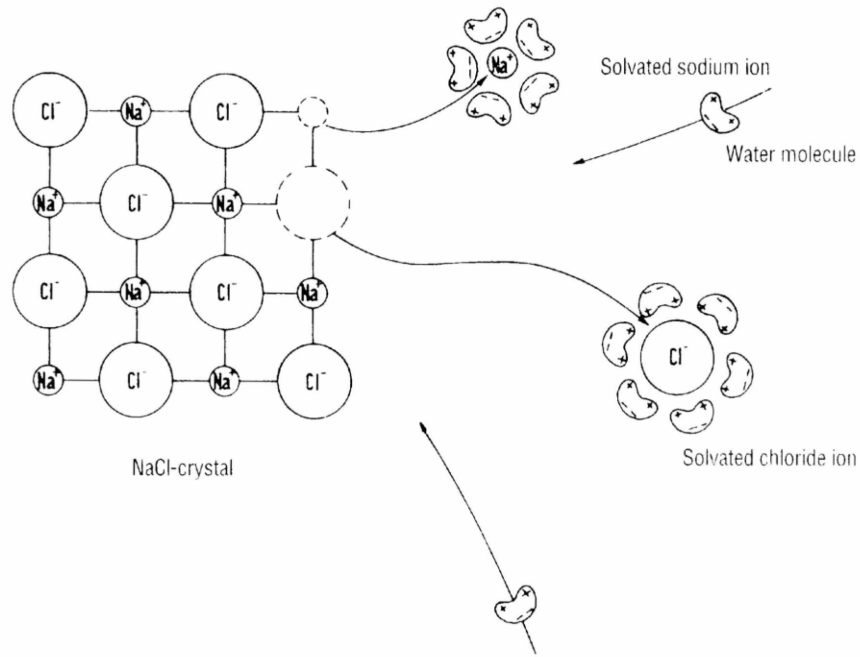


Schematic Diagram
of NaCl Crystal Lattice

Force

$$\mathbf{F} = \partial U / \partial r$$

Salt Crystal Dissolution



Ionic solvation through dissolution of a NaCl crystal in water

- Ionic Attractive Force Reduction
- Solvation (Hydration)

Chemical compounds that are dissociated into ions in solid, liquid or dissolved forms are termed electrolytes

From the dissolution of monovalent electrolytes each ion carries one unit of elementary charge e_0 of magnitude I .602 x 10^{-19} C. Each ion has a "valency", *z,* which is the *charge of the ion.*

For an species $A_{\nu+}B_{\nu-}$ which forms A^{z+} and B^{z-} in solution electroneutrality requires $z_+\nu_+ = z_-\nu_-$ and is termed electrolyte number

Transition from Electronic to Ionic Conductivity in an Electrochemical Cell

If the ions in an electrolyte solution are subjected to an electric field, ***E*,** applied from 2 electrodes in solution then the ions will experience a force, ***F*,** inducing ion motion

$$F = z\, e_o\, E$$

At the negative electrode:

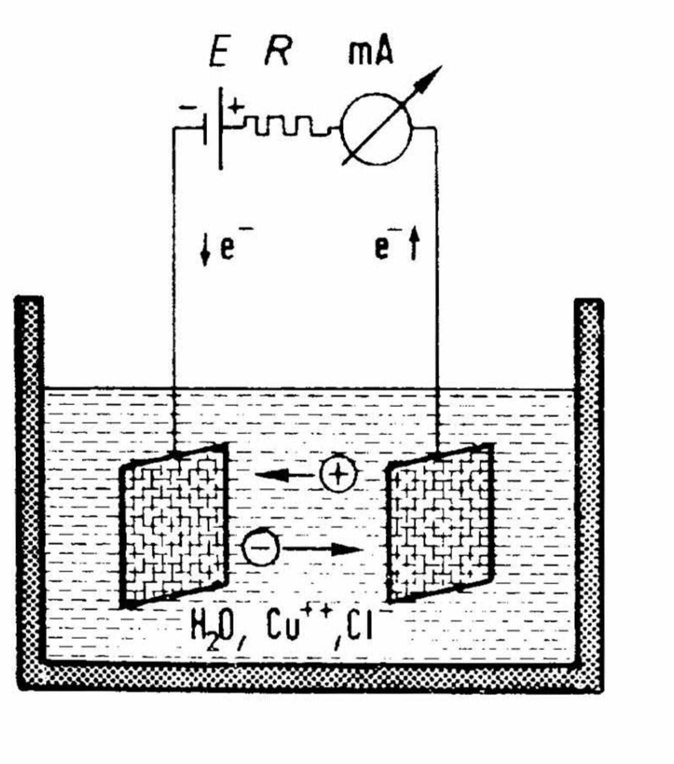
$$Cu^{+2} + 2e^- \rightarrow Cu^0$$

At the positive electrode:

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

Overall Cell Reaction

Electrode– reactions	Cu^{++}	+	$2e^-$	→	Cu^0
	$2Cl^-$			→	$Cl_2 + 2e^-$
Cell reaction	Cu^{++}	+	$2Cl^-$	→	$Cu^0 + Cl_2$



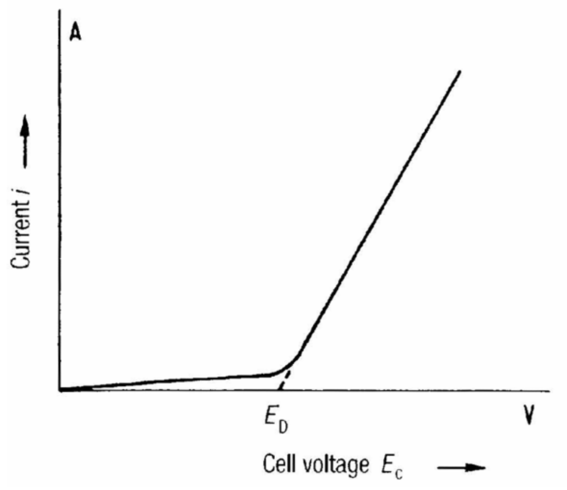
Electrochemical cell for the electrolysis of aqueous $CuCl_2$ solution.

No change in electron conductor; change in ionic conducting solution

Electrolysis Cells and Galvanic Cells

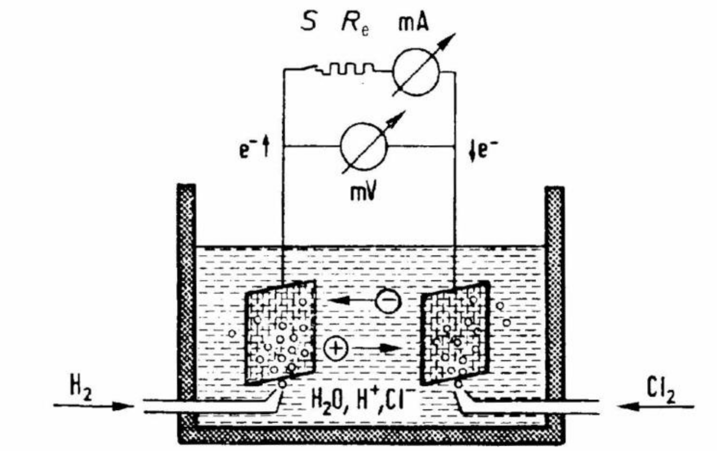
Electrochemical Decomposition of HCl

$$
\begin{array}{lcl}
2\,Cl^- & \rightarrow & Cl_2 + 2\,e^- \\
2\,H_3O^+ + 2\,e^- & \rightarrow & H_2 + 2\,H_2O \\
\hline
2\,HCl & \rightarrow & H_2 + Cl_2
\end{array}
$$



Electrolysis current as a function of the cell Voltage E_C.. E_D is the decomposition voltage

- Cell Voltage $\Delta V = V_{anode} - V_{cathode}$
- Electromotive Force EMF $E_0 = lim_{t\rightarrow 0}\, \Delta V$
- Decomposition Voltage $E_D \approx E_0$



Galvanic cell based on the H_2/Cl_2 reaction

Electrolysis Cells vs Galvanic Cells

Cathode: Reduction Reaction

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$
$$Cu^{2+} + 2e^- \rightarrow Cu^0$$

Anode: Oxidation Reaction

$$2Cl^- \rightarrow Cl_2 + 2e^-$$
$$2H_2O + H_2 \rightarrow 2H_3O^+ + 2e^-$$

For a galvanic cell:

$$E_0 = iR_i + iR_e = iR_i + \Delta V$$
$$E = E_0 - iR_i$$

The power output P of the cell :

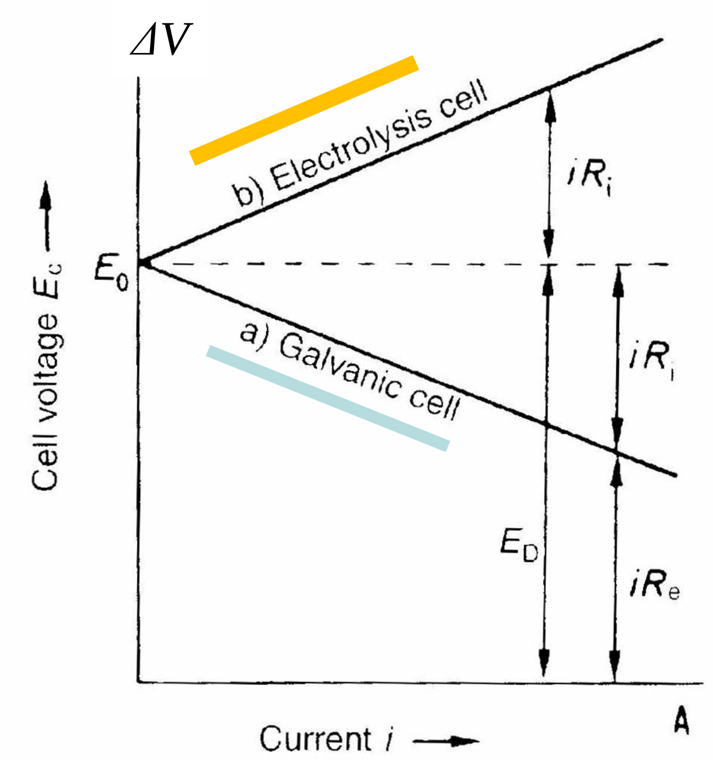
$$P = i\,\Delta V = i\,(E_0 - iR_i)$$

For an electrolysis cell:

$$E = E_0 + iR_i$$

The power appied to the cell, P :

$$P = i\,\Delta V = i\,(E_0 + iR_i)$$



Schematic variation of cell voltage ***Ec*** against load current ***i*** for
(a) a galvanic cell:
(b) an electrolvsis cell.

Faraday's Laws

- The mass of material converted by the total charge passing between ionic and electronic conductors must be proportional to this charge

$$m = \text{const.}Q = \text{const.}i_e t$$

For oxidation or reduction of 1 mol:

$$Q_m = Le_0 = 96{,}485 \text{ C} = F$$

where …
L is Avagadro's number
e_0 is the charge on an electron

$$1 \text{ C} = M / (F z) = 107.88/(96{,}485 \times 1) = 1.118 \text{ mg of Ag}$$

which is basis of silver Coulometer

- The ratio of the masses of material converted at the two electrodes will be proportional to the ratio of the ion-equivalents, M_i / z_i, of the participating materials

$$m_1/m_2 = (M_1/z_1)/(M_2/z_2).$$

where M_i is the formula weight of species i, z_i is its valency and M_i / z_i is the molar mass of an ion-equivalent of species i

Coulometry

Basic Formulation:

$$Q = \frac{m}{M/zF}$$

where
m is mass deposited,
M is formula weight,
note: m/M is moles
z is charge per equivalent,
F is Faraday's constant

- **Silver Coulometer:**

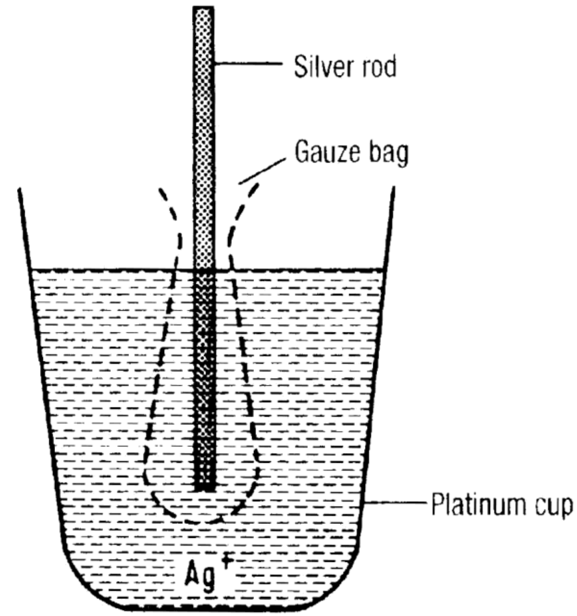
Passing 1 Coulomb deposits 1.118 mg of silver

Platinum Crucible (cathode): $Ag^{+} + e^{-} \rightarrow Ag^{0}$

Silver Rod (anode): $Ag^{0} \rightarrow Ag^{+} + e^{-}$

or the number of Coulomb is the mass plated / 1/118 mg of Ag

Q [C] = m [mg]/1.118



Schematic diagram of a silver coulometer for determination of the total quantity of electricity passed

- **Gas Combustion Coulometer:**

The mixture of O_2 and H2 is determined volumetrically where 1 mole is 22.4 liter

Cathode: $2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}$

Anode: $2OH^{-} \rightarrow H_2O + 1/2O_2 + 2e^{-}$

Overall: $H_2O \rightarrow H_2 + 1/2O_2$

Ion Conduction
Chapter 2