Electroanalytical methods

Introduction

Reductions and Oxidations

Electrodes, Cells

Half-reactions

Reduction Potentials

The Electrochemical Series

Cell Potentials and Thermodynamic Functions

Equilibrium electrochemistry

1

Books and Monograph Series

1. A. J. Bard, Electroanalytical Chemistry, Marcel Dekker, N.Y. , 1970
2. J. Dvořák, J. Koryta: Elektrochemie, Academia, Praha, 1975
3. J. Zýka et al.: Analytická příručka, 3rd ed. SNTL, Praha, 1979
4. J. Koryta: Iontově selektivní elektrody, Academia, Praha, 1984
5. Ch.M.A.Brett, A.M.O.Brett: Electrochemistry, Oxford, 1993
6. P. Klouda: Moderní analytické metody, P.K., Ostrava, 1994
7. J.O´M. Bockris, A.K.M.Reddy: Modern Electrochemistry 1,2A,2B, Plenum Press, N.Y. 1998
8. K. Markušová: Elektrochemické metódy, PF UPJŠ, Košice, 2003
9. J. Barek, F. Opekar, K. Štulík: Elektroanalytická chemie, Učební texty UK v Praze, 2005 (skripta)
10. J. Wang: Analytical Electrochemistry, VCH Publishers, N.Y., 1st ed., 1984, 2nd ed. 1994, 3rd ed. 2006
11. A. J. Bard, R. L. Faulkner: Electrochemical Methods: Fundamentals and Applications, 2nd ed., Wiley, 2000.
12. F. Scholz: Electroanalytical Methods: Guide to Experiments and Applications, 2nd ed., Springer, 2002.

L. Trnková : Moderní elektrochemické metody, v přípravě

Journals

1. Journal of Electrochemical Society   (J. Electrochem. Soc.)
2. Electrochimica Acta   (Electrochim. Acta)
3. Journal of Electroanalytical Chemistry   (J. Electroanal. Chem.)
4. Bioelectrochemistry (and Bioenergetics)   (Bioelectrochem.)
5. Journal of Applied Electrochemistry   (J. Appl. Electrochem.)
6. Journal of Solid State Electrochemistry   (J. Solid State Electrochem.)
7. Journal of Colloid and Interface Science   (J. Colloid Interface Sci.)
8. Analytical Chemistry   (Anal. Chem.)
9. Electroanalysis
10. Sensors
11. Sensors and Actuators
12. Corrosion Science
13. Langmuir
14. Elektrokhimiya
15. Journal of Physical Chemistry   (J. Phys. Chem.)
16. Biophysical Chemistry   (Biohys. Chem.)

Conferences ISE - *Symposium*

- Recent Advances in Electrochemical Instrumentation and Electrodes
- Electrochemistry meets Biology: Fundamental Aspects of Electrochemistry with Biological Systems
- Advanced Materials Design for Bioelectrochemical Applications: from Biosensors to Biofuel Cells
- Advanced Batteries and Electrochemical Capacitors
- Fuel Cells: Materials, Properties, Performance and Durability
- Physical Modeling and Numerical Simulation of Electrochemical Power Generators
- Cathodic and Anodic Routes to Electrochemical Fabrication
- Electroactive Polymeric and Inorganic Materials
- Corrosion Science and Engineering
- Electrochemical Process Engineering and Technology
- Intermediates and Mechanisms at a Molecular Level
- Photoelectrochemistry, Electrochromism, Electrochemiluminescence
- Physical Electrochemistry: from Fundamentals to Smart Materials and New Catalysts
- Electrochemistry at Liquid-Liquid Interfaces
- General Session

Equilibrium electrochemistry

- Galvanic cell
- Electrolytic cell
- Reduction
- Oxidation
- Half Reactions
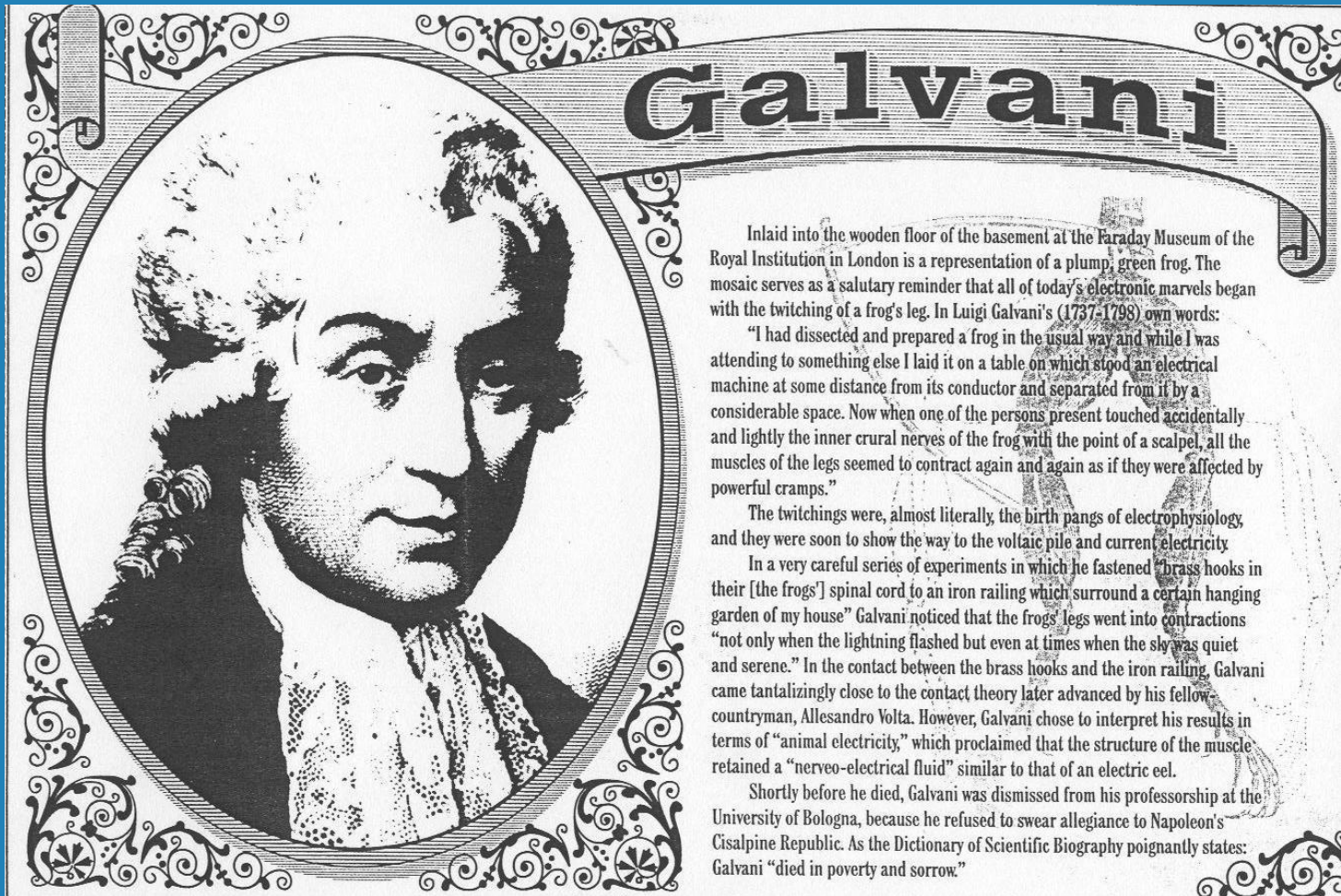- Redox Couple
- Anode
- Cathode
- Standard Electrode Potential

Some Symbols

- **<u>Potential</u>** ....E, φ [V]
- **<u>Potential of Electrolytic cell</u>** ......U, E [V]
- **<u>Current</u>** ....I, i [A]
- **<u>Current density</u>** ....j [A/m^2]
- **<u>Resistance</u>** .... R [Ω] or [S^{-1}]
- **<u>Charge</u>** .... Q, q [C]
- **<u>Conductivity</u>** .... G [S] or [Ω^{-1}]
- **<u>Capacity</u>** .... C [F]
- **<u>Impedance</u>** .... Z [Ω]
- **<u>Permitivity</u>** ....ε_0 [F/m] or ε_r [-]

Introduction

Luigi Galvani, 1791, Bologna

- was born from a union between biochemistry and electricity
Methods of solutions (basic) **Electrochemistry (EC)**

Galvani

Inlaid into the wooden floor of the basement at the Faraday Museum of the Royal Institution in London is a representation of a plump, green frog. The mosaic serves as a salutary reminder that all of today's electronic marvels began with the twitching of a frog's leg. In Luigi Galvani's (1737-1798) own words:

"I had dissected and prepared a frog in the usual way and while I was attending to something else I laid it on a table on which stood an electrical machine at some distance from its conductor and separated from it by a considerable space. Now when one of the persons present touched accidentally and lightly the inner crural nerves of the frog with the point of a scalpel, all the muscles of the legs seemed to contract again and again as if they were affected by powerful cramps."

The twitchings were, almost literally, the birth pangs of electrophysiology, and they were soon to show the way to the voltaic pile and current electricity.

In a very careful series of experiments in which he fastened "brass hooks in their [the frogs'] spinal cord to an iron railing which surround a certain hanging garden of my house" Galvani noticed that the frogs' legs went into contractions "not only when the lightning flashed but even at times when the sky was quiet and serene." In the contact between the brass hooks and the iron railing, Galvani came tantalizingly close to the contact theory later advanced by his fellow-countryman, Allesandro Volta. However, Galvani chose to interpret his results in terms of "animal electricity," which proclaimed that the structure of the muscle retained a "nerveo-electrical fluid" similar to that of an electric eel.

Shortly before he died, Galvani was dismissed from his professorship at the University of Bologna, because he refused to swear allegiance to Napoleon's Cisalpine Republic. As the Dictionary of Scientific Biography poignantly states: Galvani "died in poverty and sorrow."

Introduction

Alessandro Volta, 1800

- silver plate and zinc plate, a pasteboard membrane with salt water , " artificial electric organ"
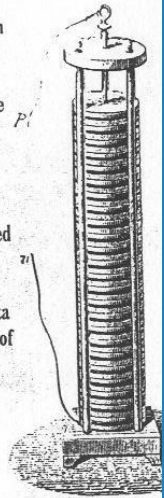

VOLTA

Alessandro Giuseppe Antonio Anastasio Volta (1745-1827) was the great antagonist of Galvani, and his efforts to refute the theory of animal electricity later resulted in his invention of the voltaic pile, the first electric battery. The term volt, a unit of electrical measurement, is named in his honor.

Volta was born in Como, Italy (near Milan). In 1774, he began his first academic position as principal of the state Gymnasium in Como. In 1777, he was appointed Professor of Physics at the University of Pavia. Here he began to repeat Galvani's famous experiments with decapitated frogs. He observed that Galvani had connected brass hooks between the frog's spinal cord and an iron railing. According to Volta's interpretation, the muscle twitches were induced by current flowing between two dissimilar metals connected by the moist flesh of the frog's leg. This led him to develop the first device which demonstrated chemical production of electric current. In 1799, Volta arranged a vertical pile of metal discs (zinc with copper or silver) and separated them from each other with paperboard discs that had been soaked in saline solution. This stack became known as the voltaic pile and was the progenitor for modern alkaline batteries.

In his pursuit of the current generated by his primitive batteries, Volta developed several new devices. He invented the electrophore, a forerunner of the capacitor; the condensatore, a device that detected weak electrical current; and the straw electrometer, a meteorology tool which measured atmospheric electricity.

In 1801, Volta was summoned to Paris to demonstrate his discovery before the Academy of Sciences. Napoleon declared his presentation a triumph, awarded him a gold medal and initiated the annual Volta Prize in his honor. History does not reveal whether he also received the traditional kiss on both cheeks.

The Royal
Society
London

Introduction

Michael Faraday, 1834

– the relation between the amount of electricity consumed and the amount of metal produced in solid form from

Rolls Royce cars

To omit the mention of Humphry Davy from any discussion of Michael Faraday's (1791-1867) contribution to electrochemistry would be to omit an essential element of a key equation.

Davy was Faraday's mentor in his early years of physics and electrochemistry research. For a time, in fact, Faraday extended and developed the research begun by Davy at the Royal Institution in London, where Faraday began his career in 1813 as Davy's Laboratory Assistant. Most of Faraday's early experiments — and published papers — bore the stamp of Davy's involvement.

Faraday achieved scientific prominence of his own for the First Law of Electrochemistry, developed in 1834: "The chemical power of a current of electricity is in direct proportion to the absolute quantity of electricity which passes."

The Second Law of Electrochemistry, also defined by Faraday, states: "Electrochemical equivalents coincide, and are the same, with ordinary chemical equivalents."

The work that led to these two laws also resulted in many of the modern electrochemical terms — electrode, electrolyte, and ion, to name a few — all coined by Faraday.

But Faraday didn't consider himself an electrochemist; he preferred the title of "natural philosopher" and devoted his life to proving the interconnection of natural forces. His electrochemical research was one outcome of this effort: exploring the connection between the chemical and electrical forces of the voltaic battery. Among Faraday's greatest accomplishments are:

- His discovery of electromagnetic induction and the related development of the first transformer, electric generator, and the electric motor.
- Development of fundamental laws of electromagnetism.
- Discovery of the "Faraday Effect", the rotation of the plane of polarization of light by a magnetic field (which later served as the foundation for the field of magneto-optics).
- Discovery of paramagnetism and diamagnetism

Faraday was also a superb lecturer and initiated two lecture series, the "Friday Evening Discourses" and the "Christmas Lectures" at the Royal Institution. Both series continue to this day Though he arose from very humble beginnings, left school at the age of 12 and was essentially self-taught, Faraday came to be respected as one of the greatest of all scientists.
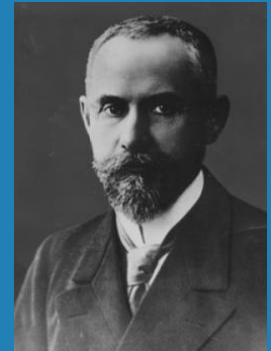
Introduction

pedant **Julius Tafel, 1905** – electric currents passing across metal-solution interfaces could be made to increase exponentially by changing the electric potential
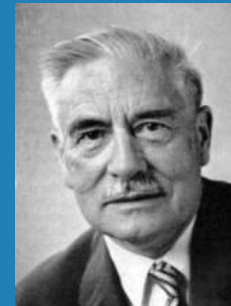
$$v_{thermal} \sim A \; exp \; (-E_a/RT)$$

$$v_{elchem} \sim B \; exp \; (-\alpha EF/RT)$$

application

– the first moon landing in 1969
– electrochemical fuell cells (U.S. space vehicles)
– electrochemical sensors (diabetics)
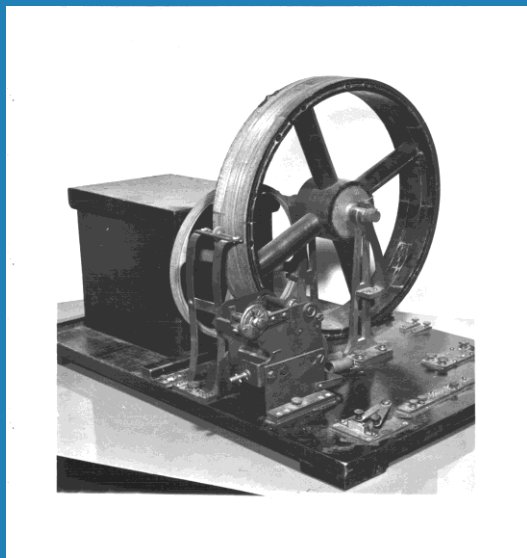– corrosion inhibition (sea oil platform)

Debye and Hückel, 1923 – a credible theory of the properties of ionically conducting solutions

10

Introduction

Jaroslav Heyrovský Nobel Prize 1959

Polarograph, Model 1924

Jaroslav Heyrovsky and Michael Heyrovsky

ZDE PŮSOBIL
V LETECH
1919-1950
PROFESOR
JAROSLAV
HEYROVSKÝ
NOSITEL NOBELOVY
CENY ZA CHEMII

Introduction

ELECTROCHEMICAL   METHODS   (current = 0)

- __Potentiometry__

      direct (pH)

      titration determination of equilibrium

               constants,

               protonation $- pK_a$

               complexation $- pK_{AL}$

Introduction

ELECTROCHEMICAL   METHODS (current $\neq 0$)

- Polarography (d.c., tast, a. c.)

- Pulse Polarography (PP) , voltammetry (PV)

- Differential Pulse Polarography (DPP) , voltammetry (DPV)

- Linear Sweep Voltammetry (LSV)

- Cyclic Voltammetry (CV), Fast CV

- Adsorptive Stripping Voltammetry (AdSV)

- Square Wave Voltammetry (SWV)

- Constant Current Derivative Chronopotentiometric
                    Stripping Analysis (CPSA)

- Coulometry (Coul)

- Elimination Polarography (EP)

- Elimination Voltammetry with Linear Scan (EVLS)

Introduction

Two kinds of EC

| IONIC | ← **EC** → | ELECTRODICS |

**ion – solvent interactions
ion – ion interactions
ion transport
ionic liquids**

**interfacial region
mechanism of electrically
controlled surface reactions**

*the electrode is the stage
the solution is the theater and audience*

e^-

$X^{\pm}$

Introduction

UNCUT METAL - ELECTRONS RANDOM
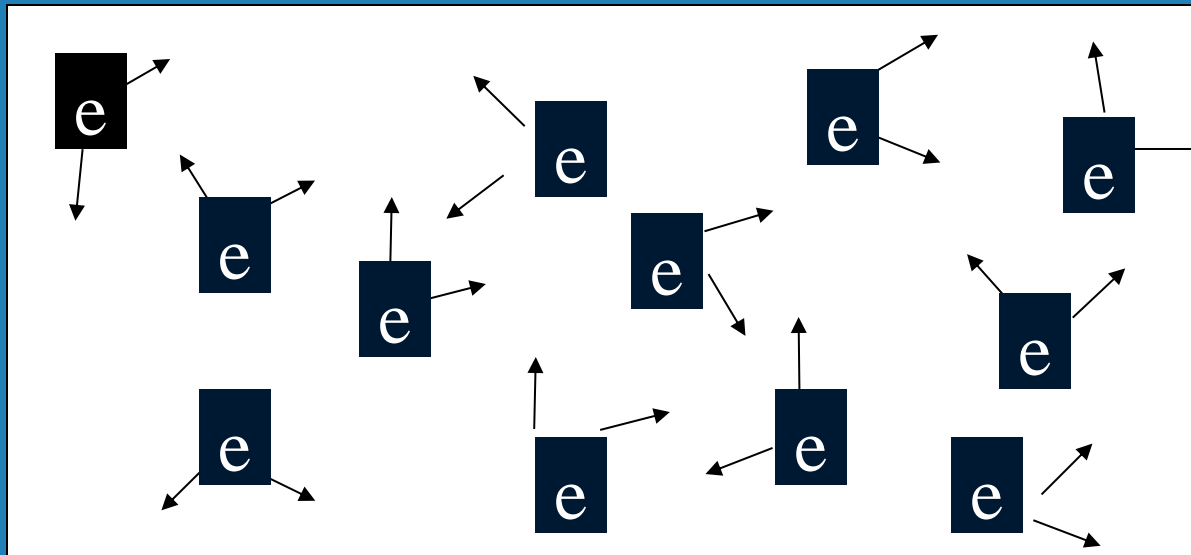
quantal particles

" **electron gas" , Pauli princip (fermiony)**

Fermi-Dirac statistics

Fermi function

Introduction

electron - fermion

Enrico Fermi
(Nobel prize 1938)
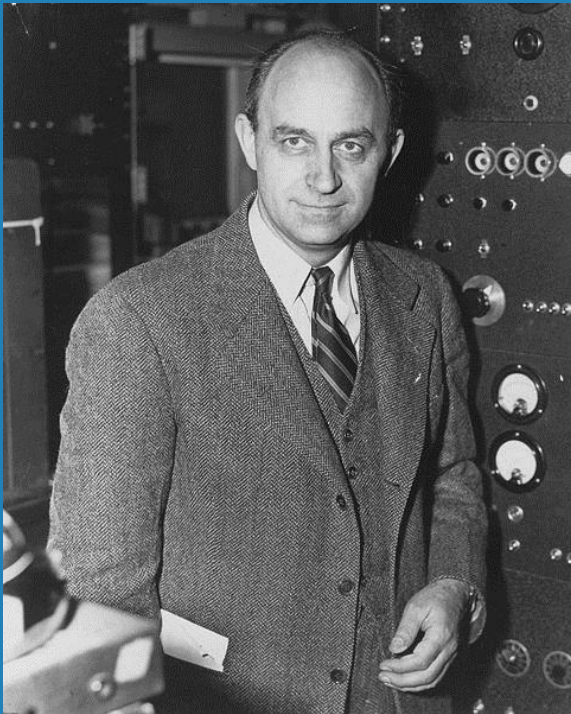
Paul Adrien Maurice Dirac
(Nobel prize 1933)
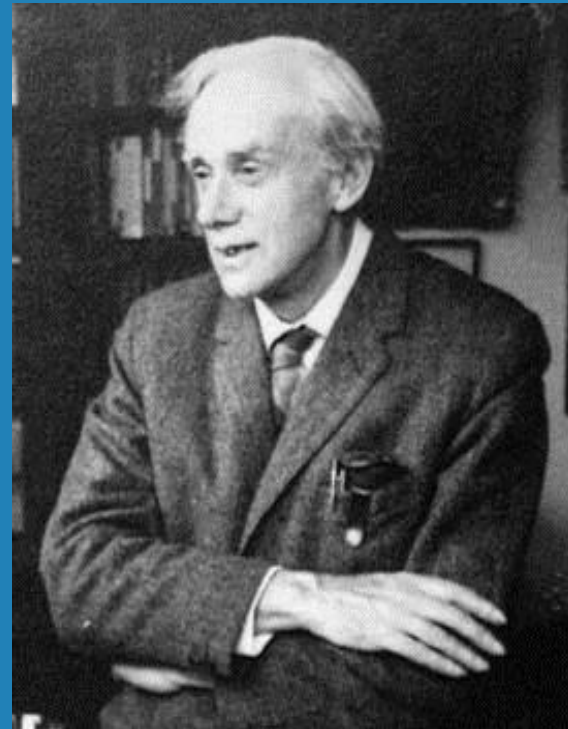
Introduction

Fermi-Dirac statistics is a particular case of particle statistics developed by Enrico Fermi and Paul Dirac that determines the statistical distribution of fermions **over the energy states** for a system in **thermal equilibrium**. In other words, it is a probability of a given energy level to be occupied by a fermion.

Fermions (spin 1/2, 3/2, 5/2 …) are particles which are indistinguishable and obey the Pauli exclusion principle, i.e., no more than one particle may occupy the same quantum state at the same time. **Statistical thermodynamics** is used to describe the behaviour of large numbers of particles. A collection of non-interacting fermions is called a **Fermi gas**.

$$P = \frac{1}{1 + \exp[(E - E_F)/k_B T]}$$

$$E_F \quad versus \quad k_B T$$

Introduction

F-D statistics:

the expected number of particles in states with energy ε_i is:

$$n_i = \frac{g_i}{e^{(\varepsilon_i - \mu)/kT} + 1}$$

where:

n_i is the number of particles in state i,

ε_i is the energy of state i,

g_i is the degeneracy of state i (the number of states with energy ε_i),

μ is the chemical potential (sometimes the Fermi energy E_F is used instead, as a low-temperature approximation),

k is Boltzmann's constant, and

T is absolute temperature.

In the case where μ is the Fermi energy E_F and $g_i = 1$ the function is called the **Fermi function**:

$$F(E) = \frac{1}{e^{(\varepsilon_i - E_F)/kT} + 1}$$

Introduction

$E_F/100 = k_B T$
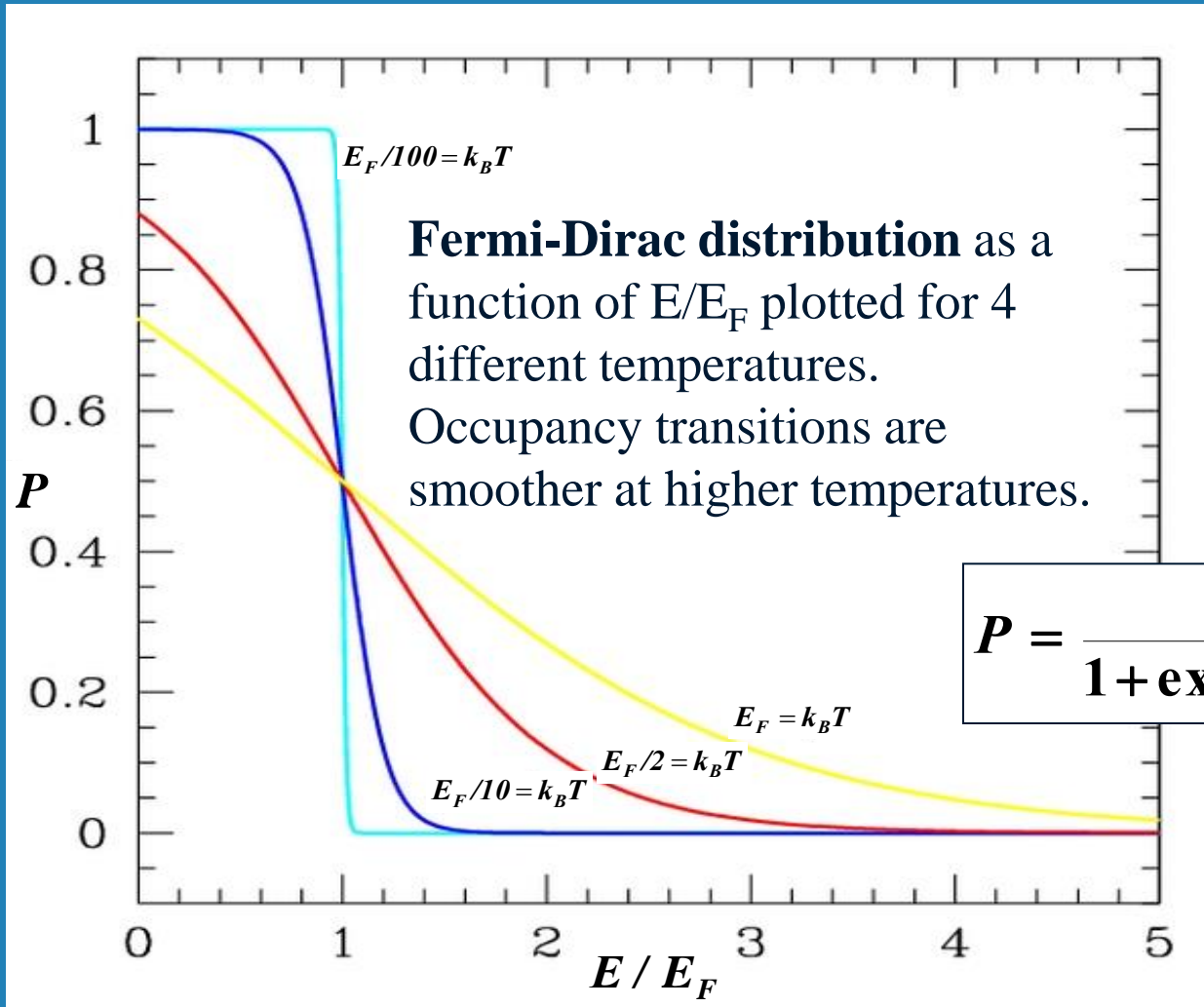
Fermi-Dirac distribution as a function of E/E$_F$ plotted for 4 different temperatures. Occupancy transitions are smoother at higher temperatures.

$E_F = k_B T$

$E_F/2 = k_B T$

$E_F/10 = k_B T$

$$P = \frac{1}{1 + \exp[(E - E_F)/k_B T]}$$

P

E / E_F
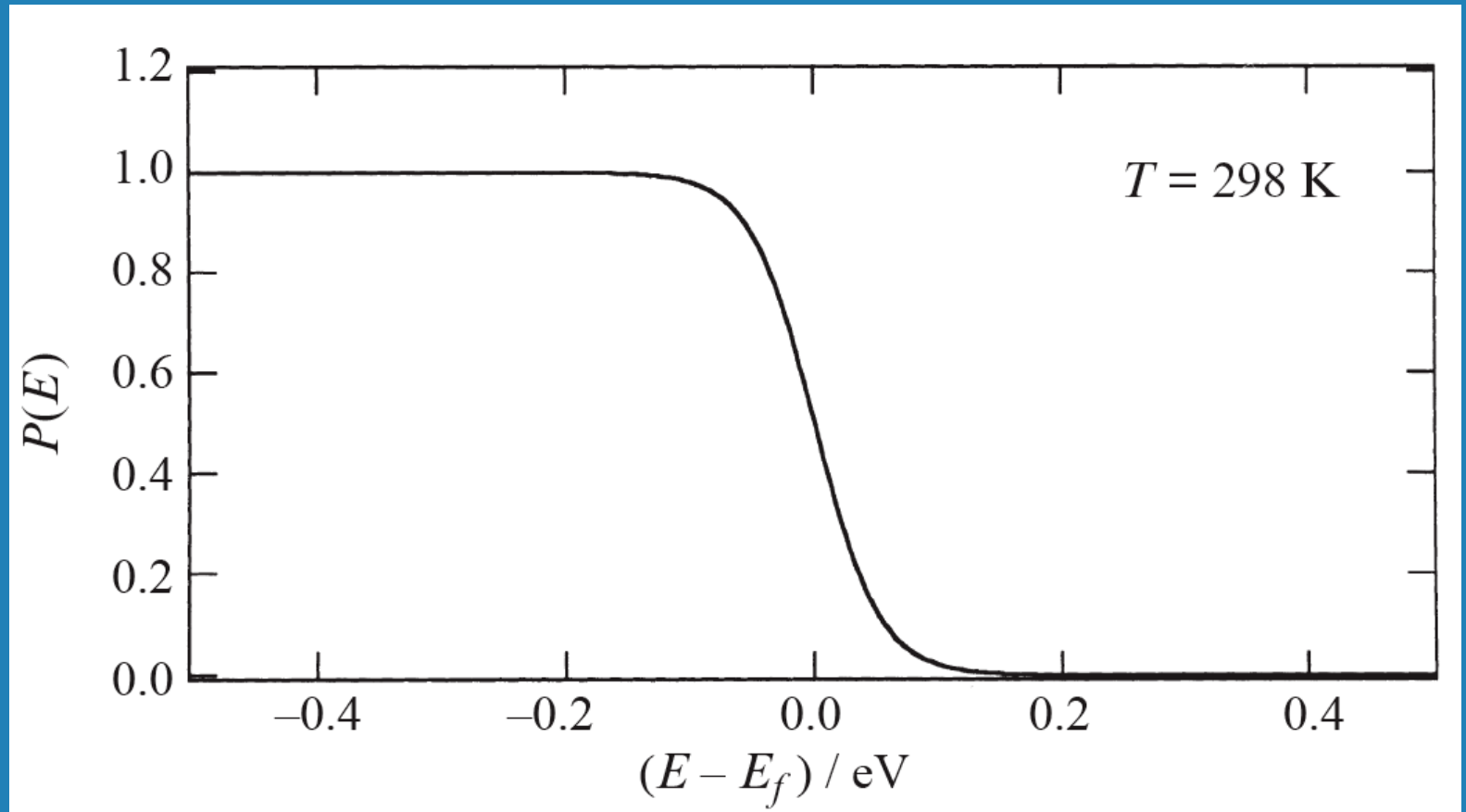
Introduction

The Fermi-Dirac distribution function

Introduction
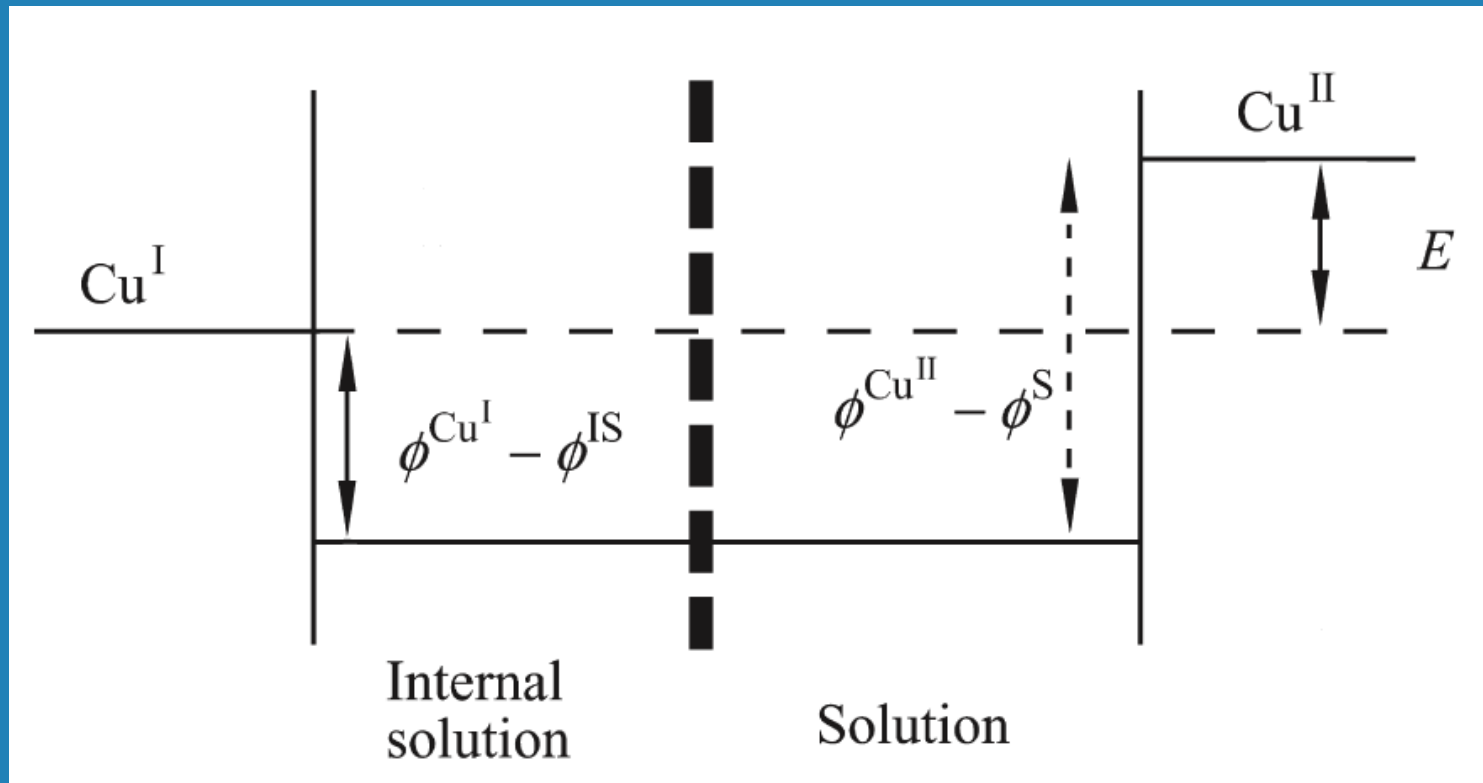
Schematic representation of the potential distribution in a cell. For clarity, the potential in the metal M and in the reference electrode is not shown

Introduction
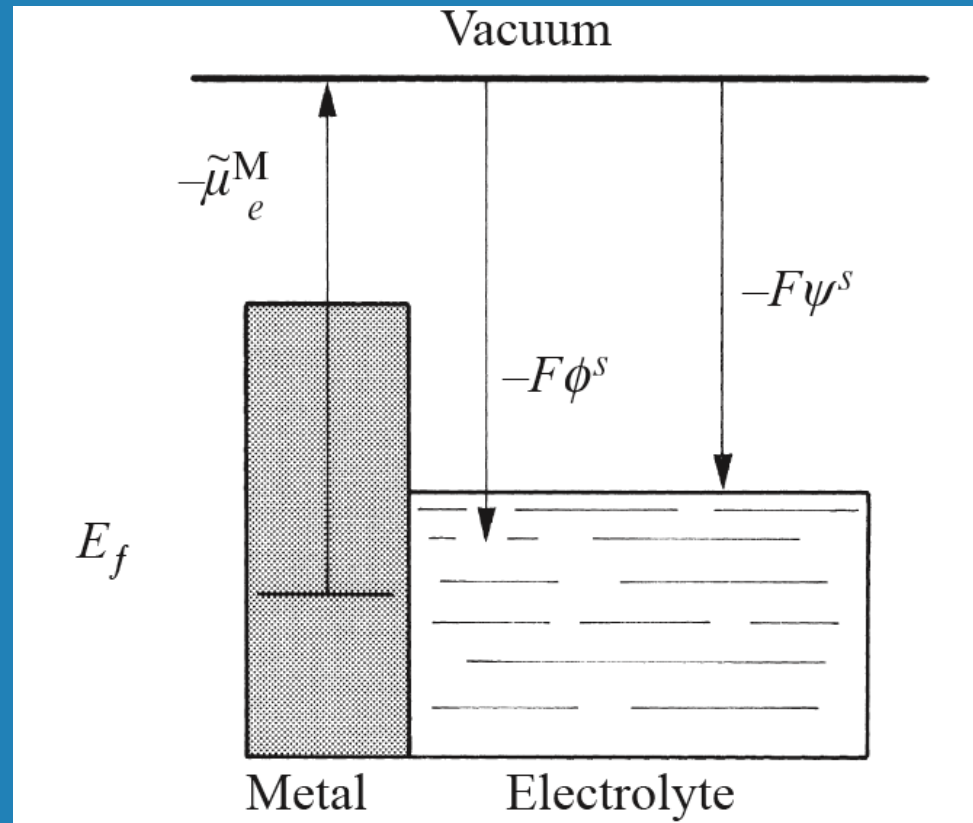
Energy diagram of the metal | electrolyte interface

Introduction
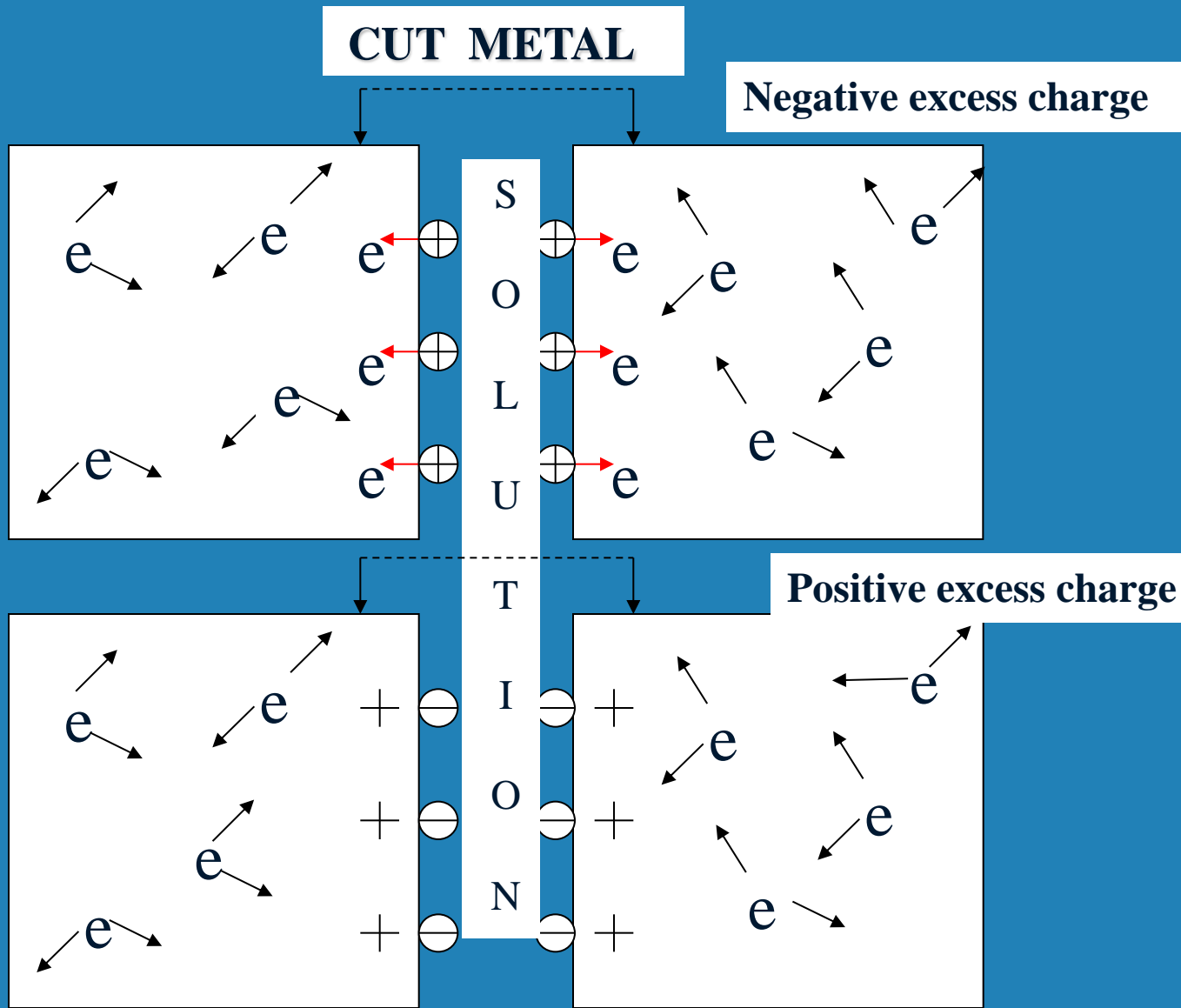
Introduction

the fundamental act in EC

One phase contains electrons

e - - - - - → ⊕

Other phase contains ions

Introduction

reduction   *oxidation*

power supply

2e   2e

pumping electrons into Pt plate

electrons flow back to the power source

H_2 I_2

$2H^+$ $2I^-$

Pt   Rh

$HI \rightleftharpoons H^+ + I^-$
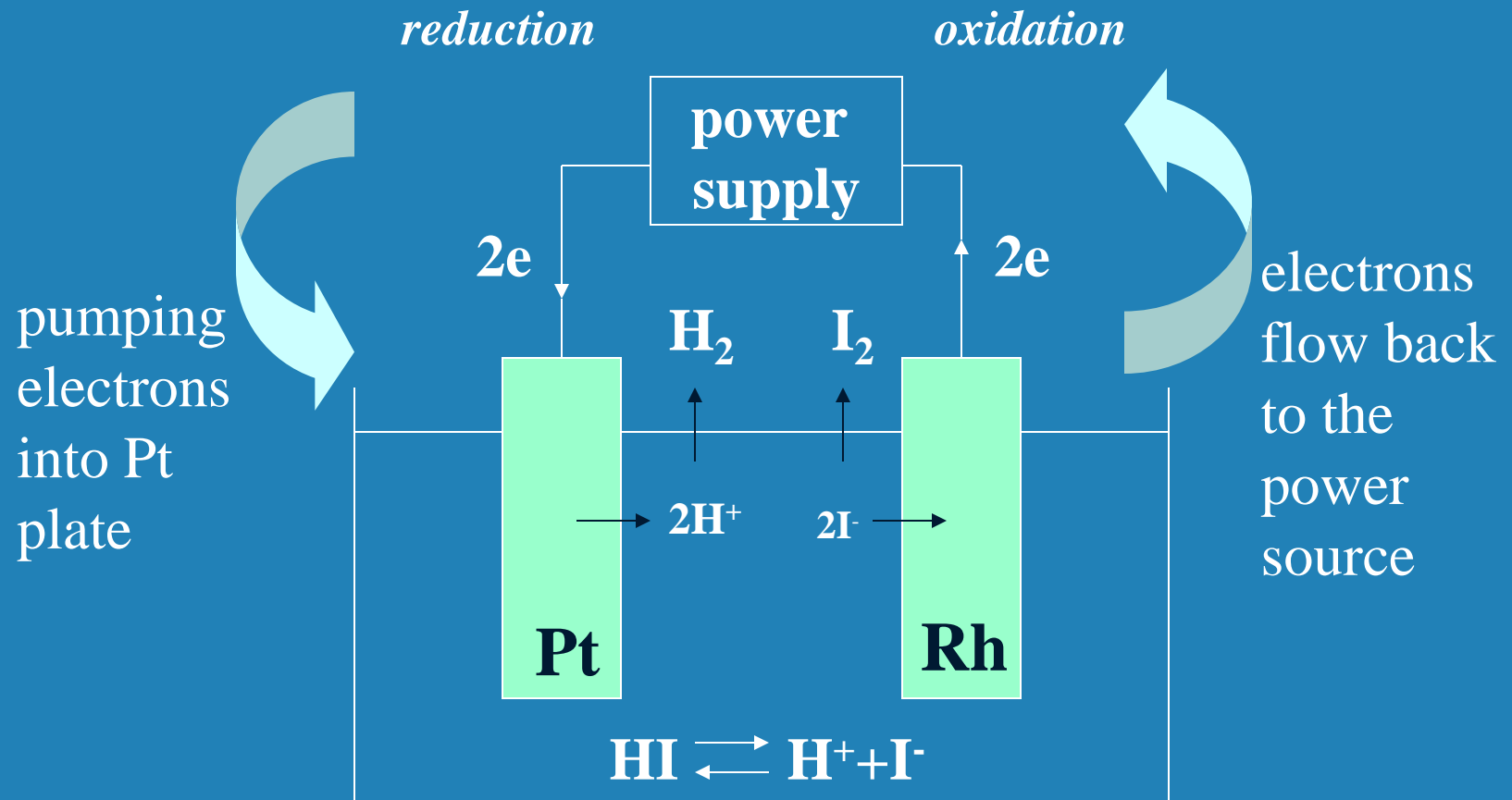
electrochemical reactor

Introduction

$$HI \rightleftharpoons H^+ + I^-$$

$$2HI \xrightarrow{\text{in solution}} 2H^+ (aq) + 2I^- (aq)$$

$$2H^+ (aq) + 2e \xrightarrow{\text{at Pt electrode}} H_2 (g)$$

$$2I^- (aq) \xrightarrow{\text{at Rh electrode}} I_2 (g) + 2e$$

net reaction $\quad 2HI \longrightarrow H_2 (g) + I_2 (g)$

CHEMICAL REACTION

$$H \text{---} I \xrightarrow[\text{collisional activation}]{\text{thermal}} \begin{matrix} H \cdots I \\ \vdots \quad \vdots \\ H \cdots I \end{matrix} \xrightarrow{\text{bond breaking}} \begin{matrix} H & I \\ | & | \\ H & I \\ \hline H_2 & + & I_2 \end{matrix}$$

Introduction

$$HI\ (g) \xrightarrow{\text{water}} H^+\ (aq)\ +\ I^-\ (aq)$$
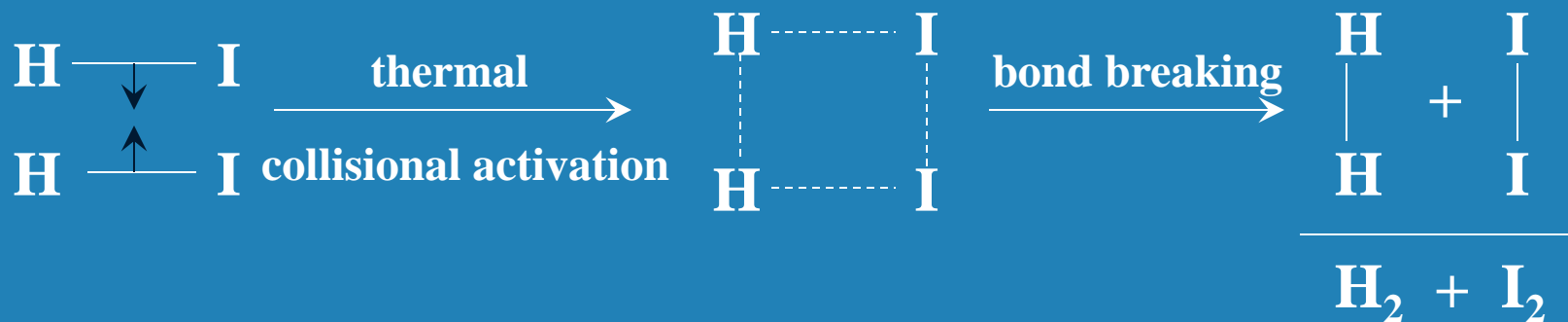
accepts electrons from metal

donates electrons to metal

ELECTROCHEMICAL (ELECTRIC) REACTION

$H_2\ (g)$

$I_2\ (g)$

Introduction

Standard Hydrogen Electrode
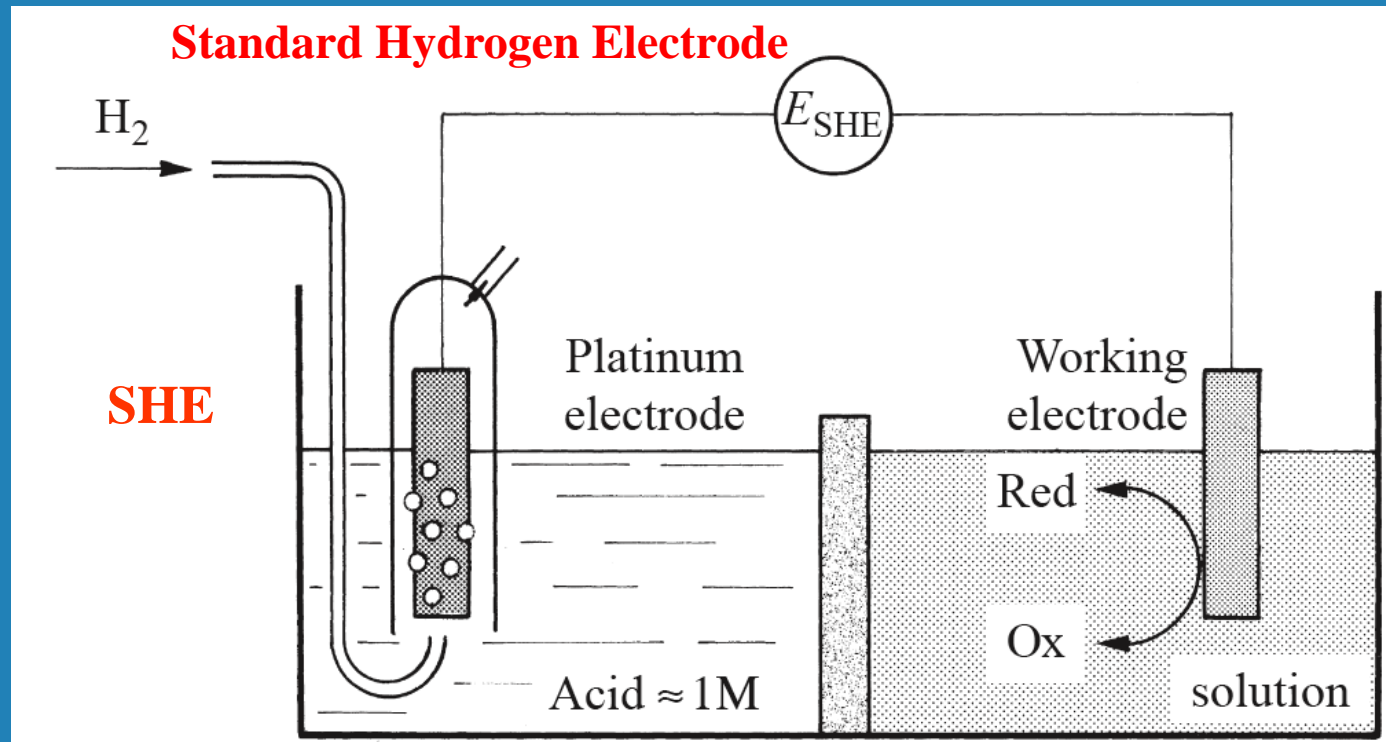
Electrochemical cell for measuring the electrode potential on the **SHE** scale. A salt bridge is an ionic conductor introduced to physically separate the two solutions, but keeping at the same time their inner potentials equal or almost equal

Introduction
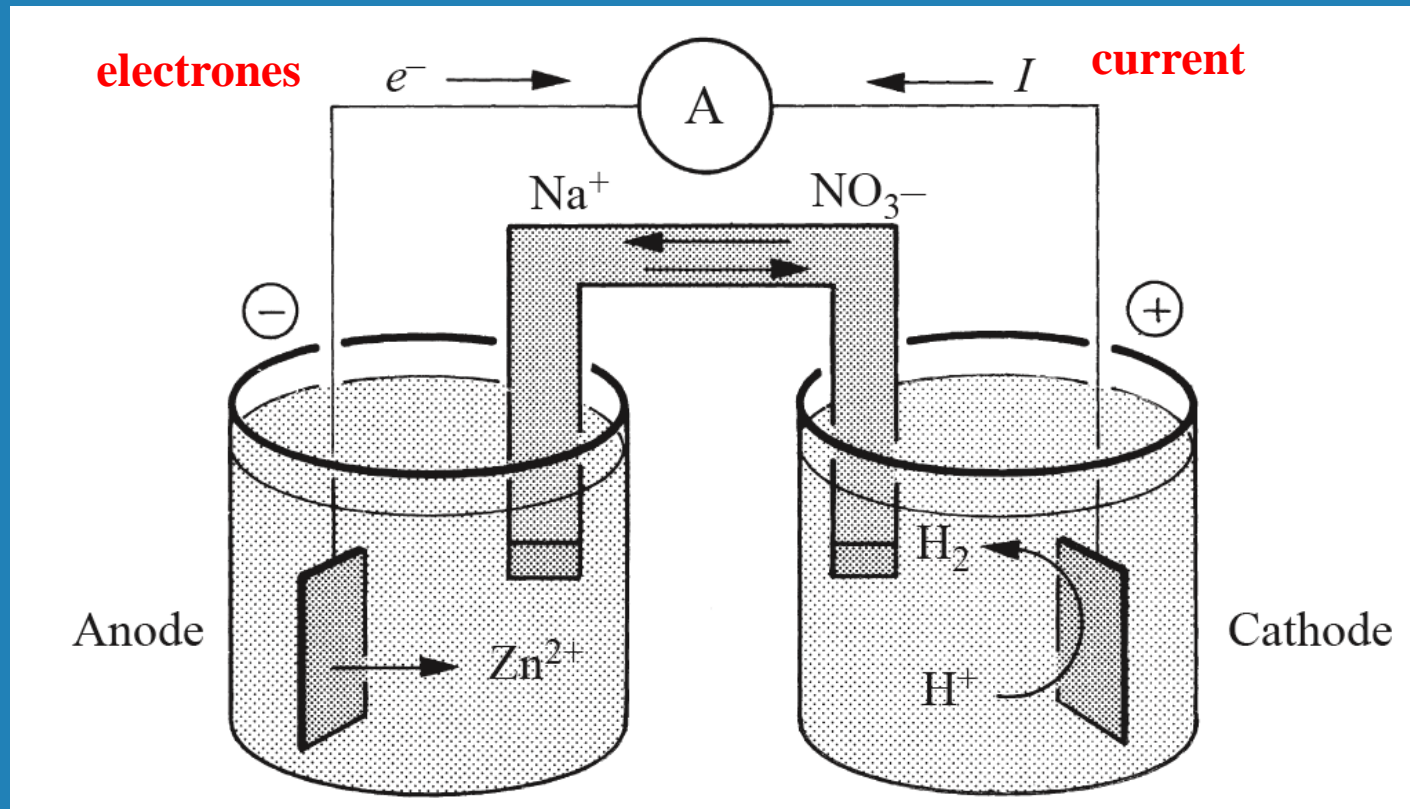
Electrochemical <u>dissolution of zinc</u>. The beaker on the left and the salt bridge are filled with a solution of sodium nitrate, and the beaker on the right is filled with nitric acid

Introduction

Optically Transparent Thin Layer Electrode

OTTLE

UV-VIS

Minigrid Working electrode **WE**

RE

Reference Electrode

Counter Electrode

CE
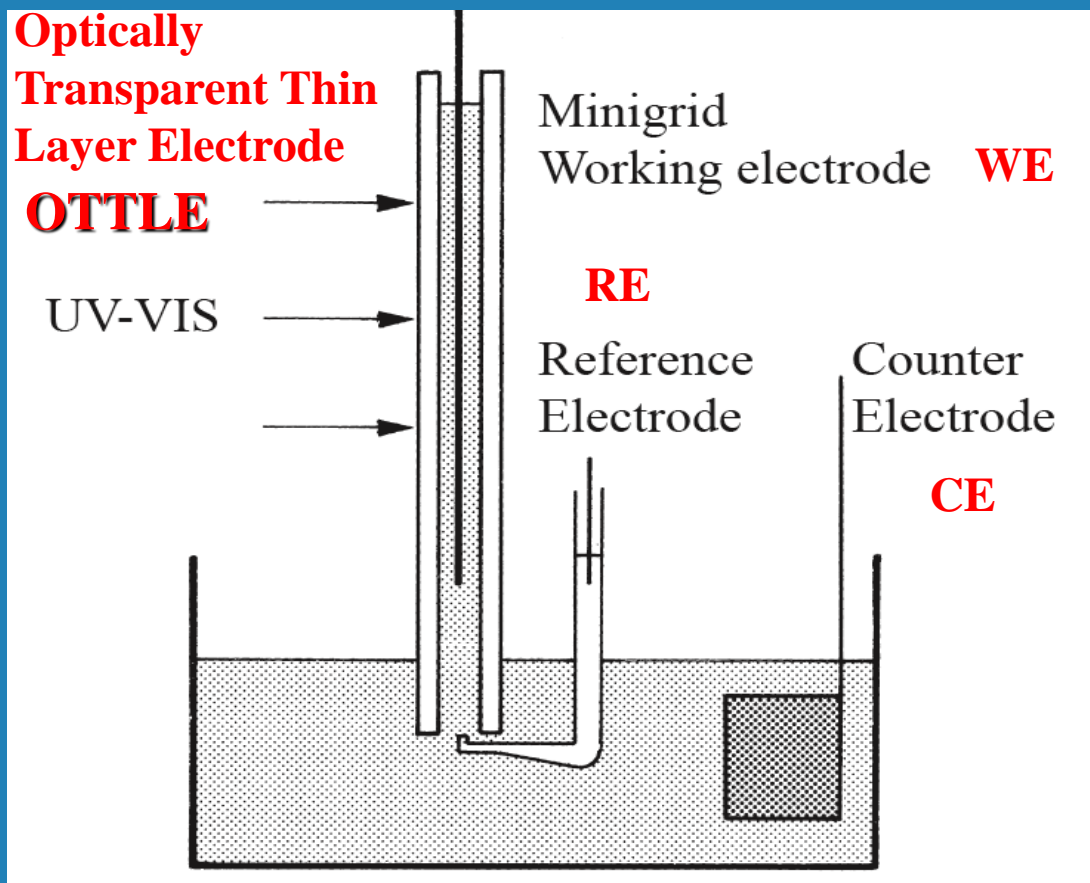
Diagram of an OTTLE electrode. The working electrode is a fine metallic grid placed in a UV-VIS cell with a short optical path

Lead acid battery

Schematic representation of the working principle of a lead acid accumulator

sulphation!

2V

$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$

Pb H_2O PbO$_2$

− HSO_4^- ←   +

H^+ →

PbSO$_4$ PbSO$_4$

oxidation   **reduction**

$Pb + HSO_4^- \rightleftarrows PbSO_4 + H^+ + 2e^-$ $PbO_2 + 3H^+ + HSO_4^- + 2e^- \rightleftarrows PbSO_4 + 2H_2O$

$$Pb + 2H_2SO_4 + PbO_2 \rightleftarrows PbSO_4 + 2H_2O + PbSO_4$$
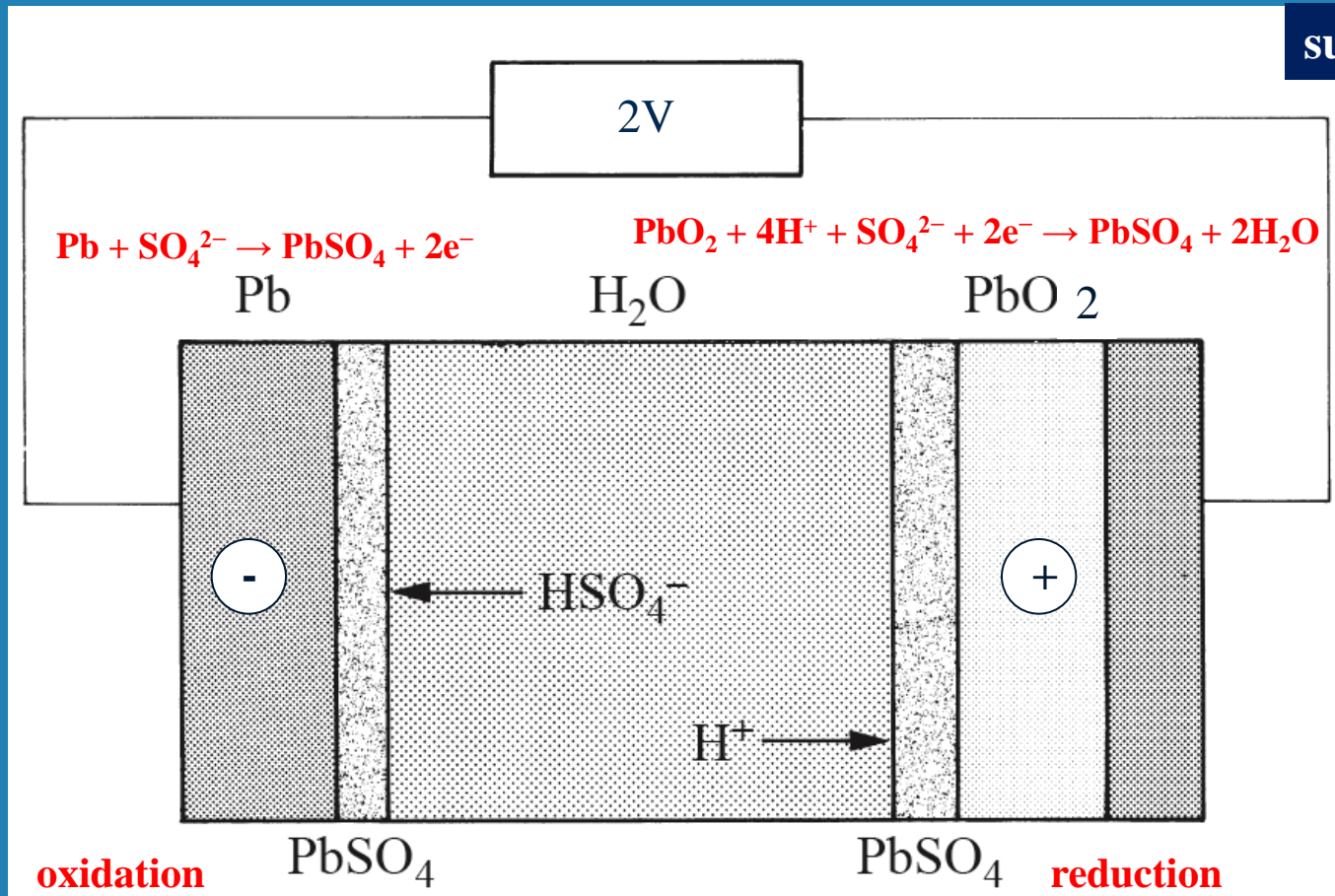
charging

Schema of electron transfer at an electrode

Voltmeter

0.460

Salt Bridge [KNO₃(aq)]

Wire

e-

NO₃⁻

K+

Salt Bridge

Cu

Ag

Anode

Cathode

NO₃⁻

Cu²⁺

Ag⁺

Flow of Electrons

Graphic by Shamsher Singh

Cell Diagram

anode

cathode

$Ag_{(s)}$ | $Ag^+_{(aq)}$ || $Cu^{2+}_{(aq)}$ | $Cu_{(s)}$

half-cell
(oxidation)

salt
bridge

half-cell
(reduction)

Graphic by Shamsher Singh
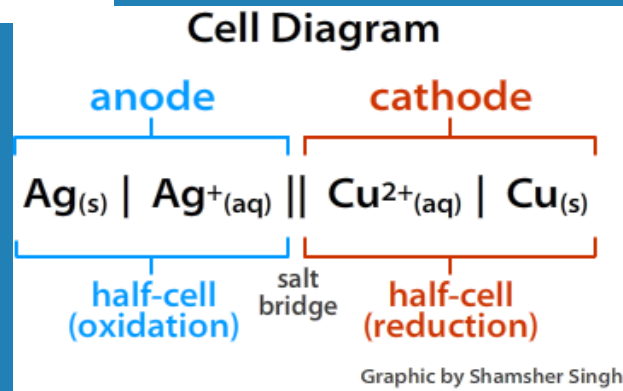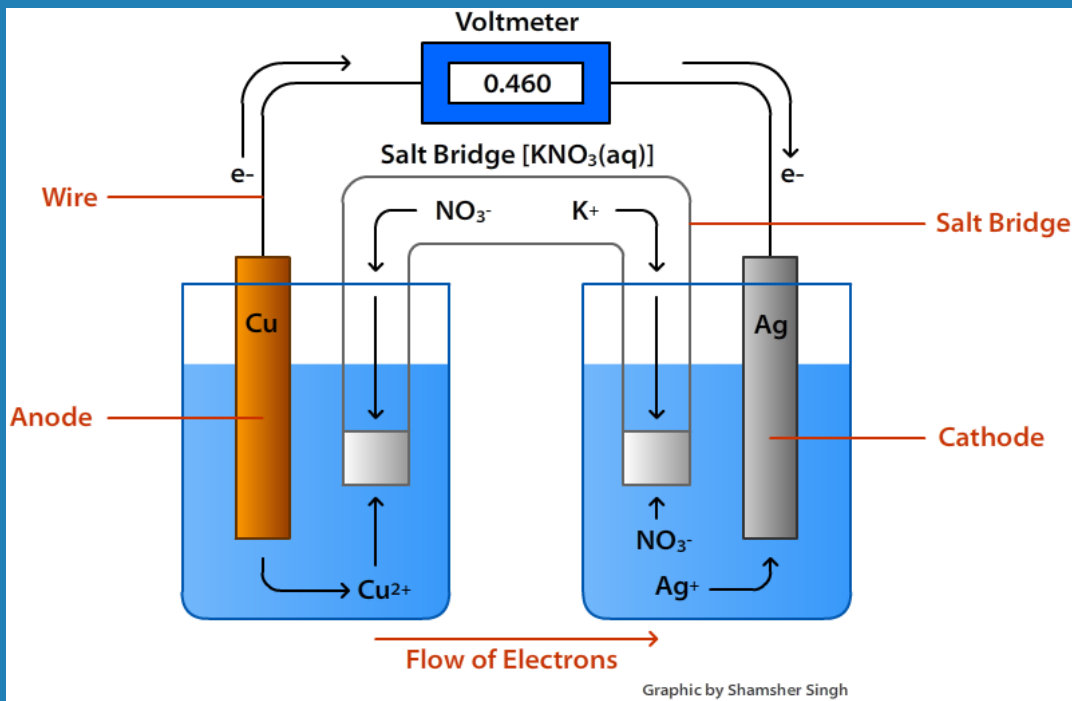
Lithium metal and ion battery

Schematic diagram of the principle of Li battery and Li ion battery

Lithium metal battery

Li/Si — Li metal — Anode — Electrolyte — Li^+ — Li^+ Li^+ Li^+ Li^+ — MnO_2 — Cathode

LiCl/KCl

Lithium ion battery

Li/C — Anode — Li^+ Li^+ Li^+ Li^+ — Li^+ — Li^+ Li^+ Li^+ Li^+ — metal oxid — Cathode

Li salt in organic solvent

Fuel cell

REACTION

Anode $: 2H_2 + 2O^{-2} \rightarrow 2H_2O + 4e^-$

Cathode $: O_2 + 4e^- \rightarrow 2O^{-2}$

Overall Cell $: 2H_2 + O_2 \rightarrow 2H_2O$
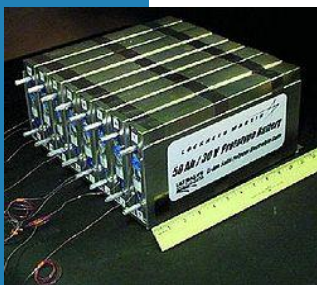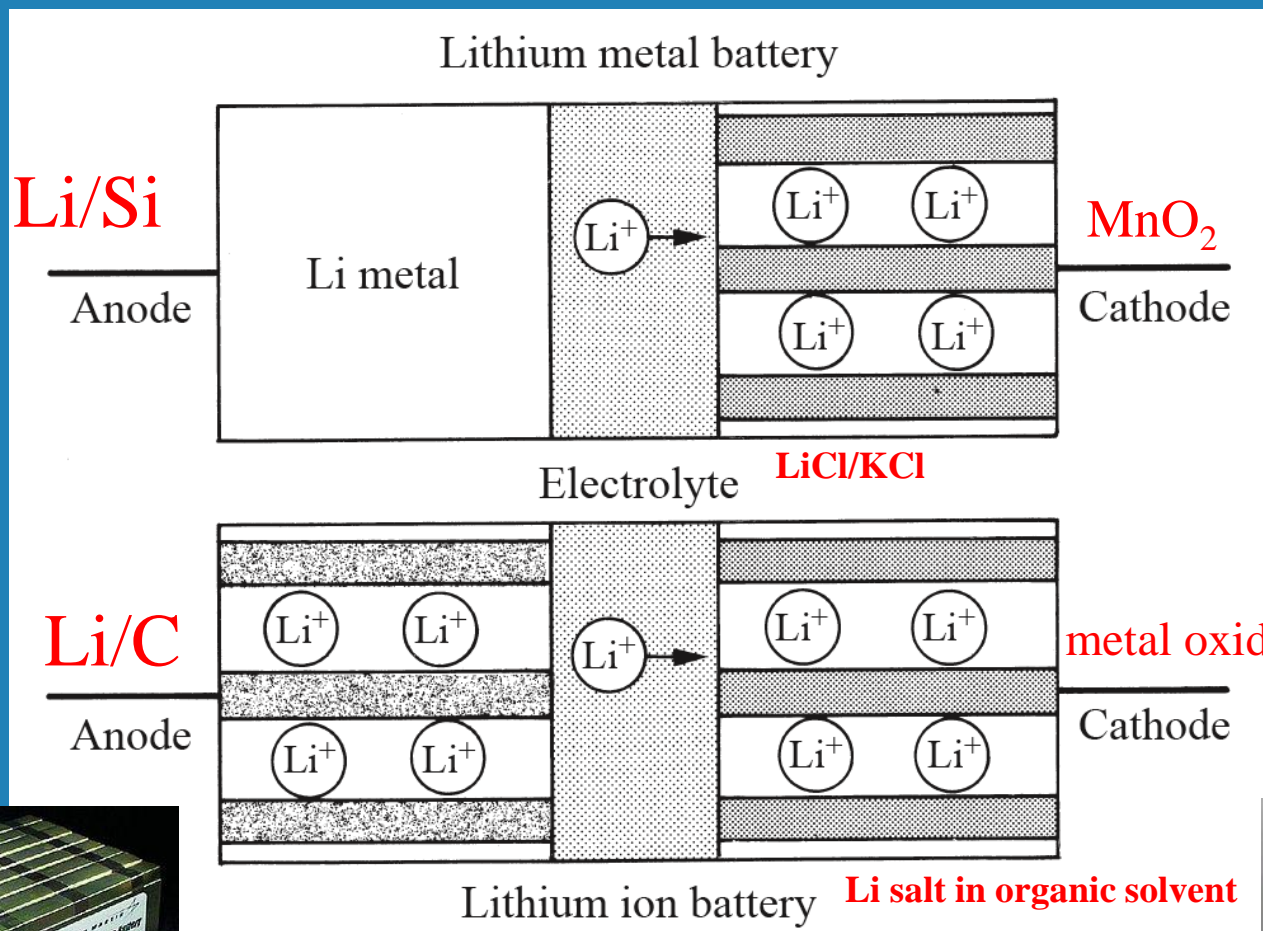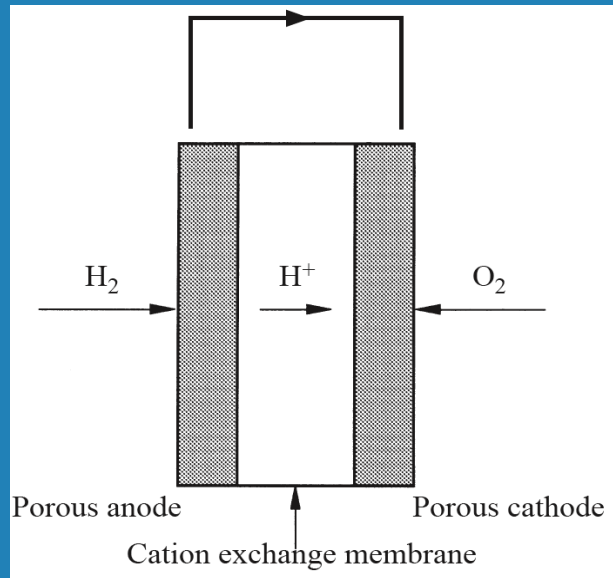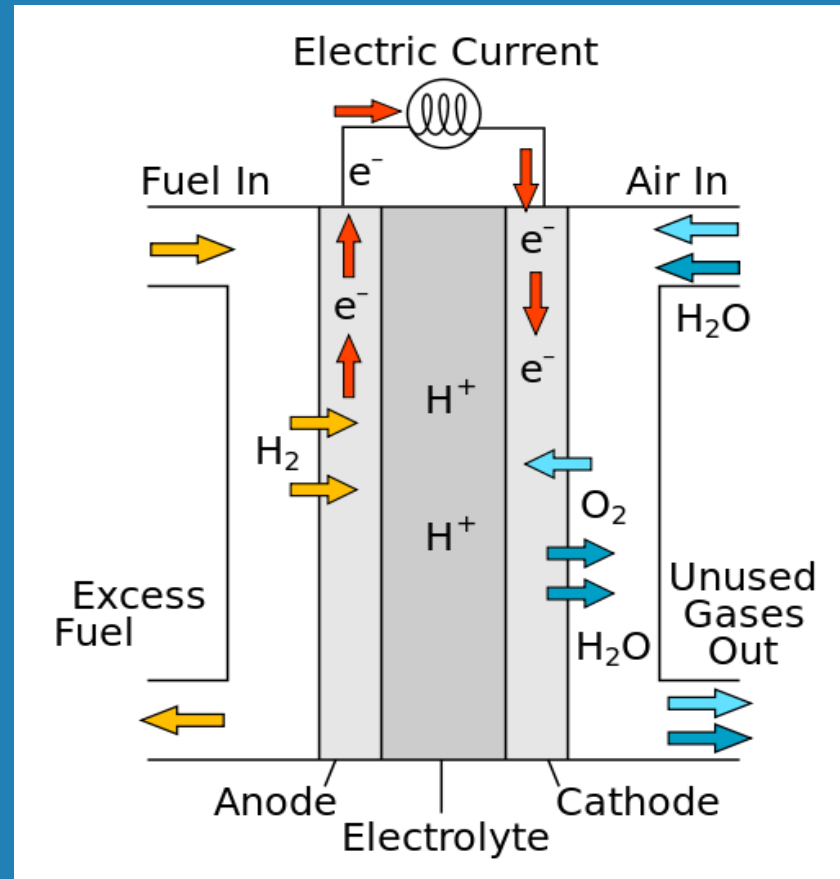
Hydrogen and oxygen are introduced via the <u>porous electrodes</u>. The electrochemical reactions happen at the <u>electrode | membrane interface</u> (oxidation of hydrogen into protons at the anode, reduction of oxygen and the production of water at the cathode).

Fuel cell
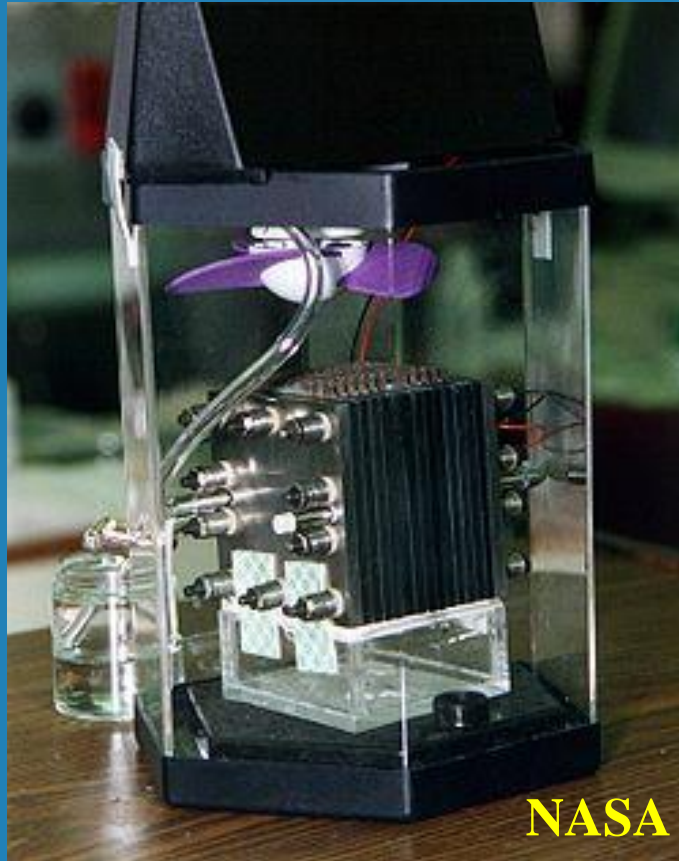
Demonstration model of a direct-methanol fuel cell. The actual fuel cell stack is the layered cube shape in the center of the image

NASA
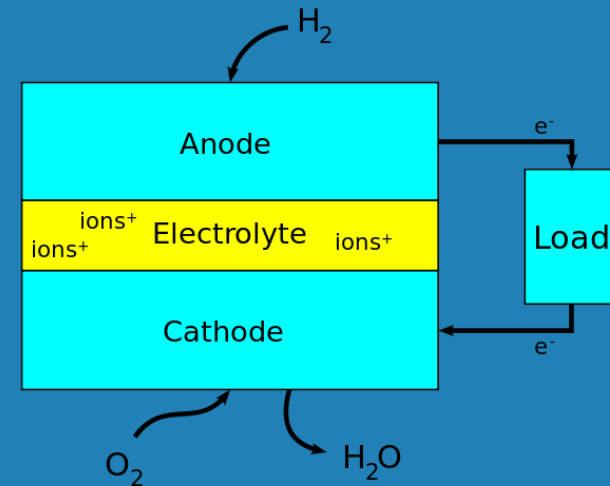
Alcaline fuel cells (AFC)
Phosphoric acid fuel cells (PAFC)
Solid oxide fuel cells (SOFC)
Molten carbonate fuel cells (MCFC)
Polymer electrolyte membrane fuel cells (PEMFC)
Proton exchange membrane fuel cells (PEMFC)

Two Practical Cells

Carbon rod (cathode)
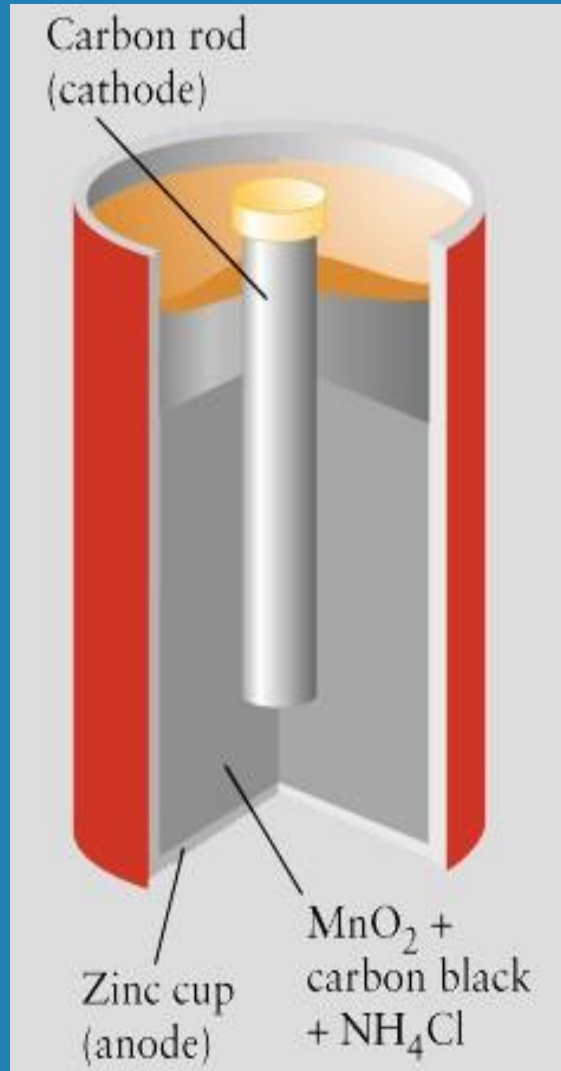
ℒ At left is a <u>primary</u> cell (used once only).

ℒ At right is a <u>secondary</u> cell (may be re-charged)

Zinc cup (anode)

MnO_2 + carbon black + NH_4Cl

Separator

Anode grid

Cathode grid
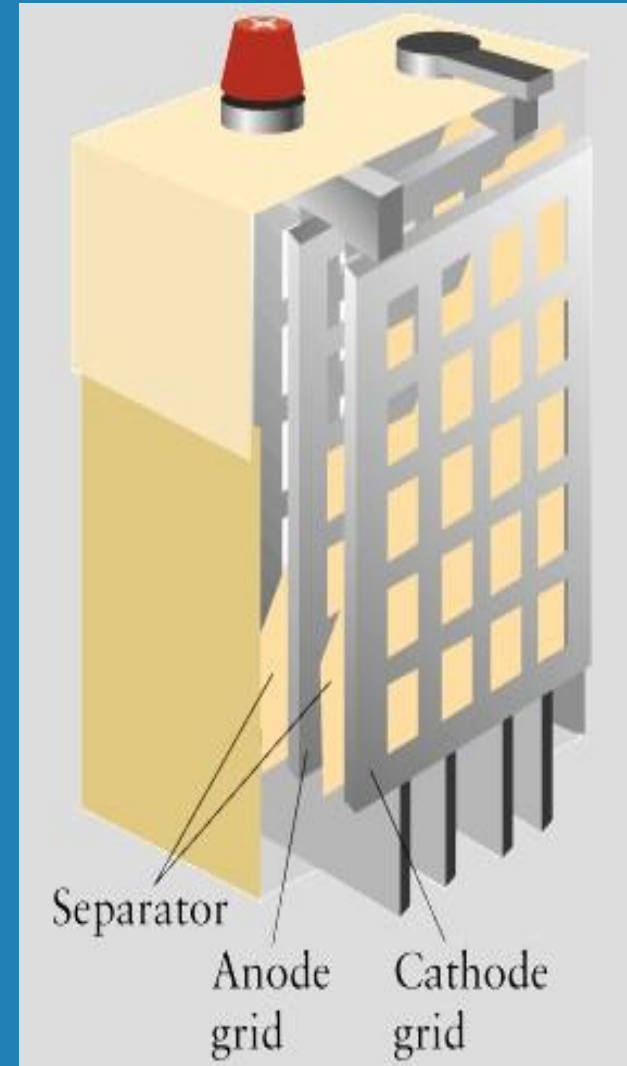
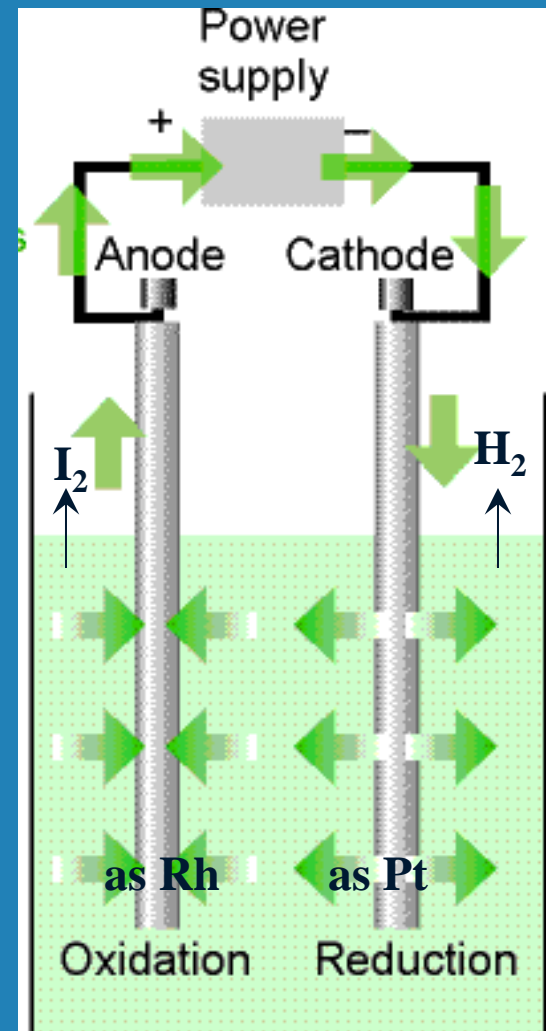# Reactions at electrodes
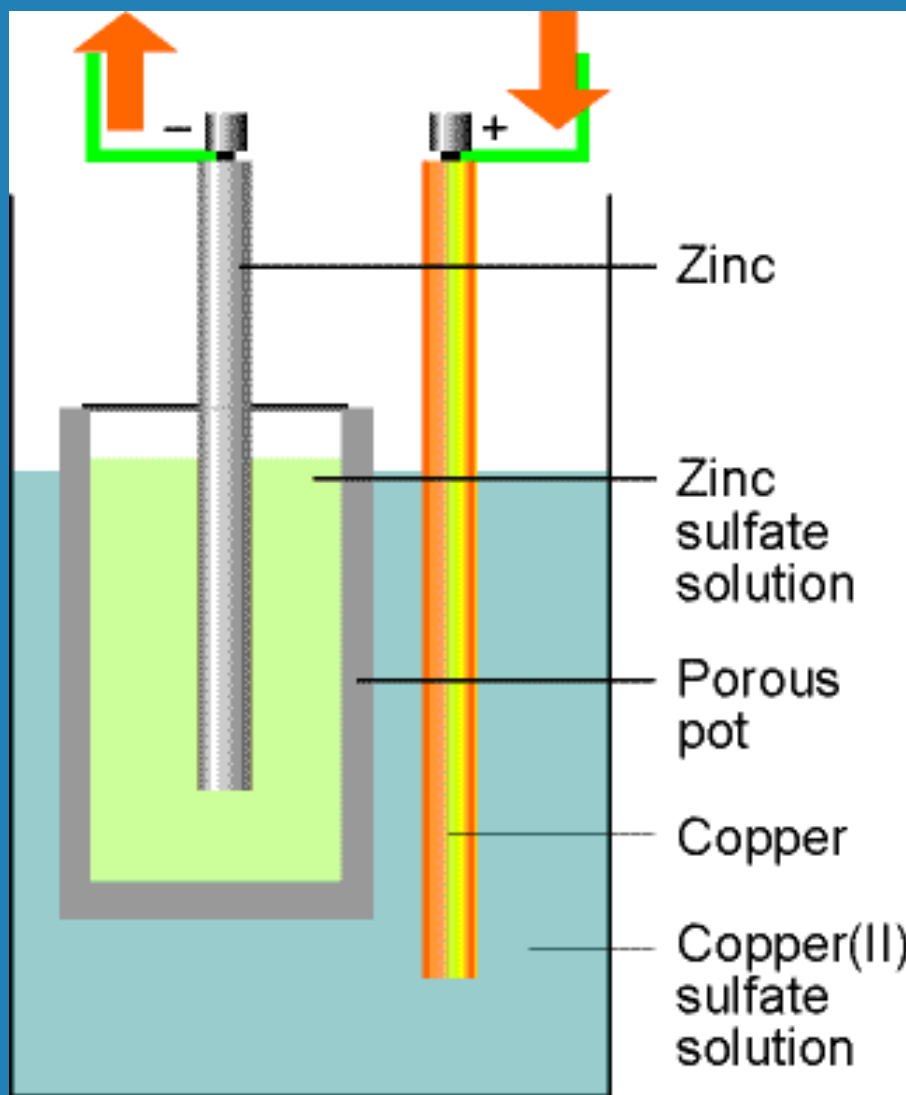
Galvanic cell X Electrolytic cell
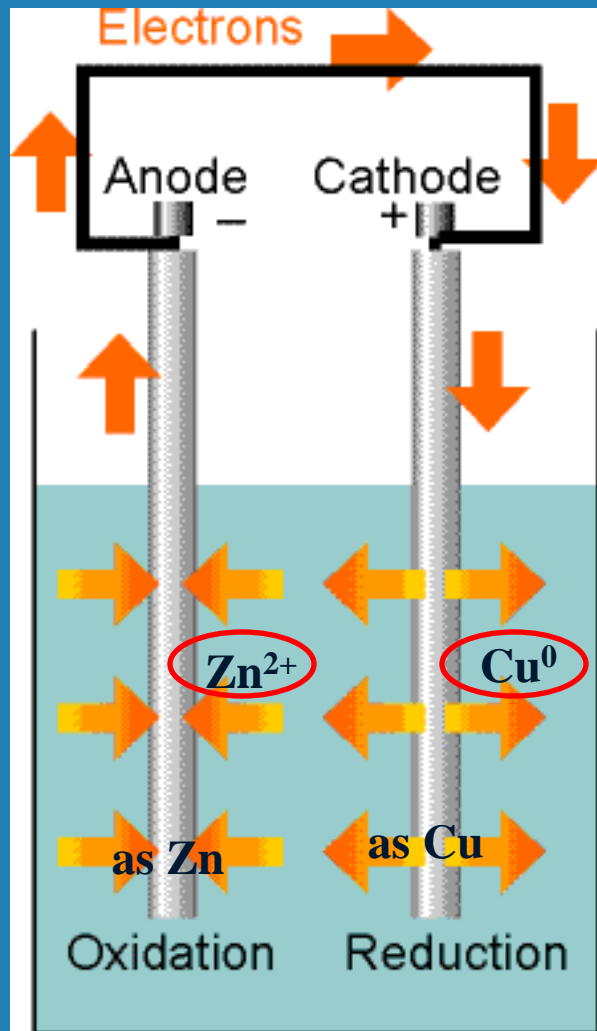
ᴪ Left: **Galvanic cell.** Electrons are deposited on the anode (so it is neg) and collected from the cathode (so it is positive)
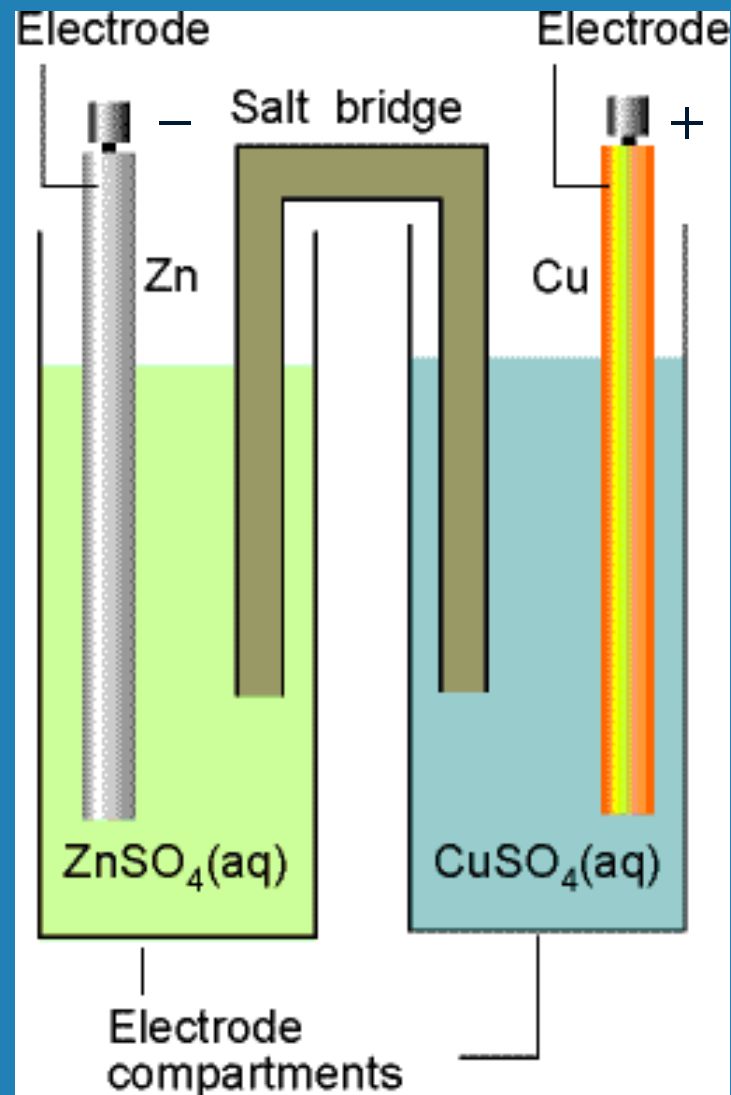
ᴪ Right: **Electrolytic cell.** Electrons are forced out of the anode (positive) and into the cathode (negative)

Two Versions of the Daniell Cell

Zinc

Zinc sulfate solution

Porous pot

Copper

Copper(II) sulfate solution

Electrode

Electrode

Salt bridge

Zn

Cu

$ZnSO_4(aq)$

$CuSO_4(aq)$

Electrode compartments

GC with conversion

GC without conversion

Constructing a Daniell Cell

KCl or 10%KNO$_3$

Cell Notation

Daniell cell

ß In the version of the Daniell cell with the porous pot there is a liquid junction (diffusion or liquid potential). This is denoted as $Zn(s)|ZnSO_4(aq):CuSO_4(aq)|Cu(s)$

ß When the liquid junction potential has been essentially eliminated by use of a salt bridge the Daniell cell is denoted as $Zn(s)|ZnSO_4(aq)||CuSO_4(aq)|Cu(s)$

ß Other punctuation in cell notations includes a comma to separate two species present in the same phase.
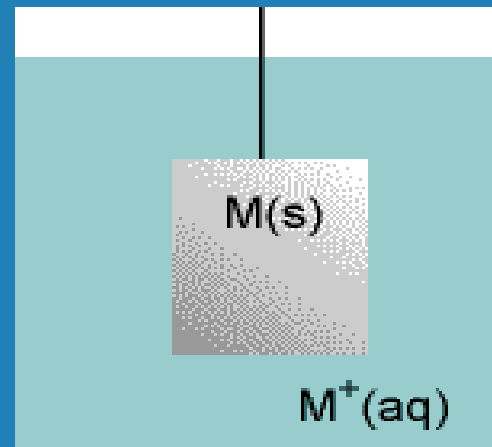
Redox reactions and electrode processes

https://learnnext.com/CBSE-Class-XI-Chemistry/Lesson-Redox-Reactions-And-Electrode--Processes.htm
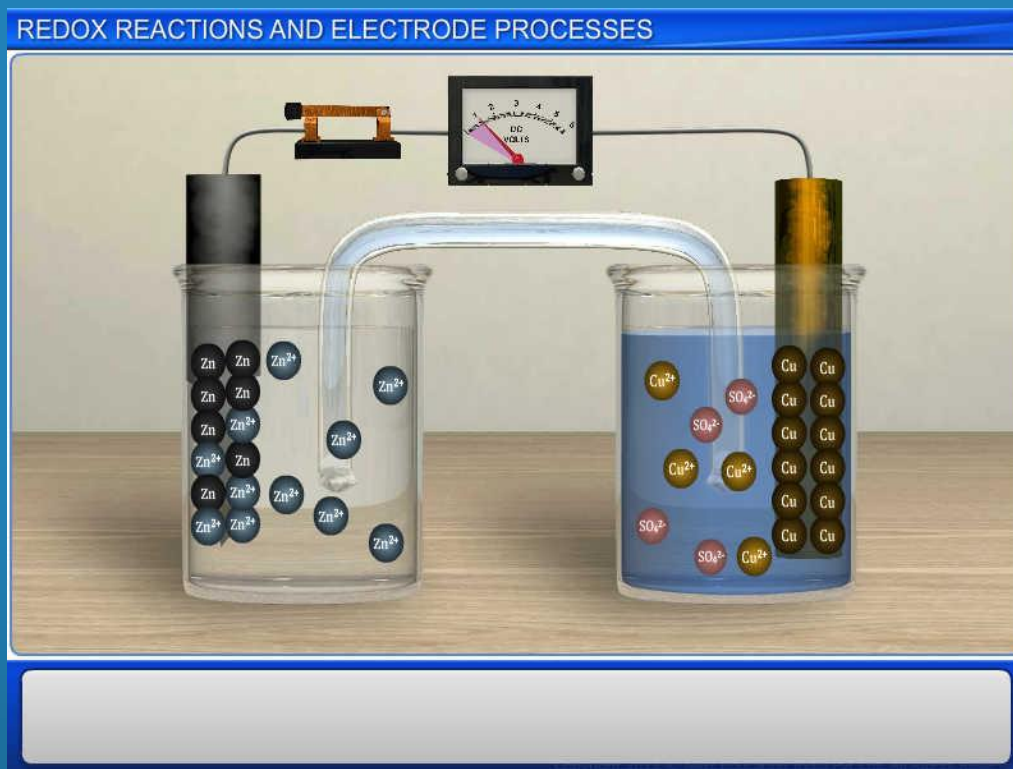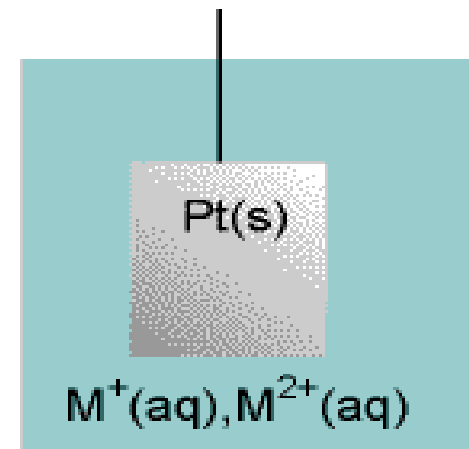
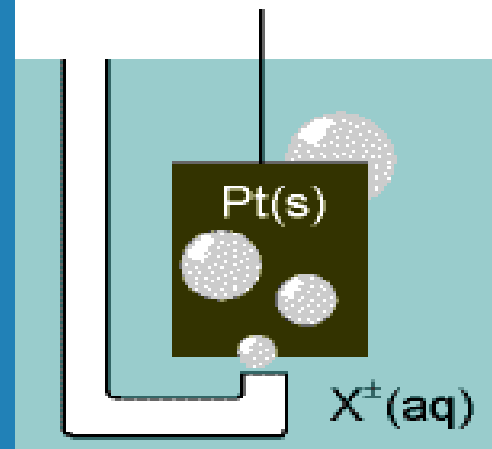# Types of Electrodes

- ♌ (a) metal/metal ion electrode
- ♌ (b) metal/ insoluble salt electrode
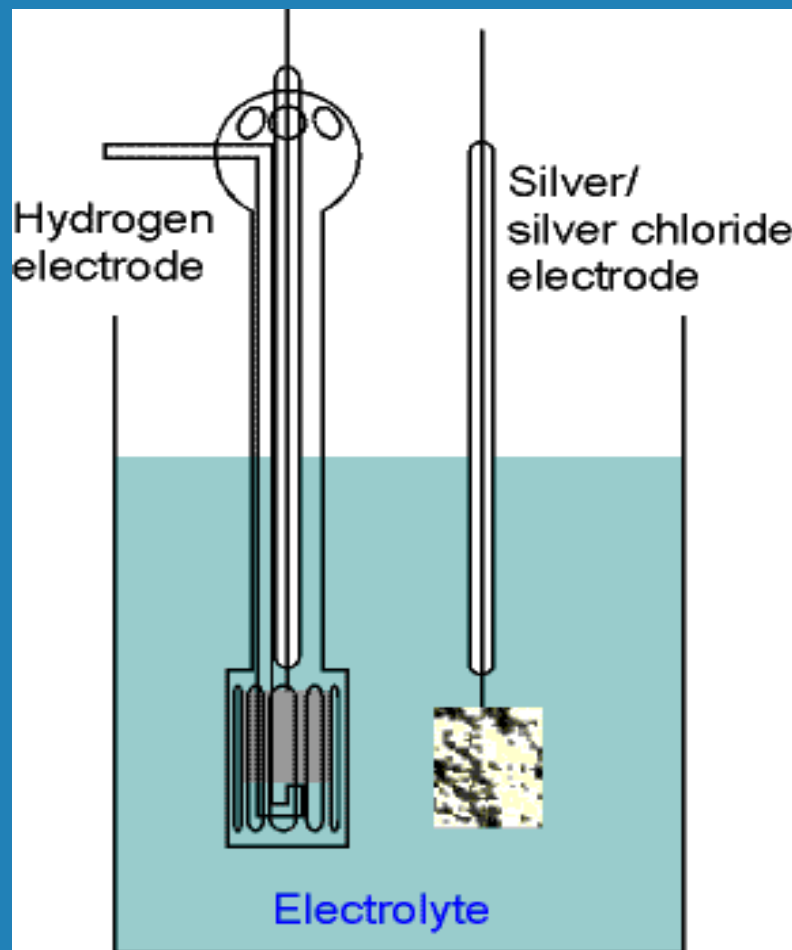- ♌ (c) gas electrode
- ♌ (d) redox electrode

(a) M(s) — $M^+(aq)$

(b) M(s), MX(s) — $X^-(aq)$

(c) Pt(s) — $X^\pm(aq)$

(d) Pt(s) — $M^+(aq), M^{2+}(aq)$
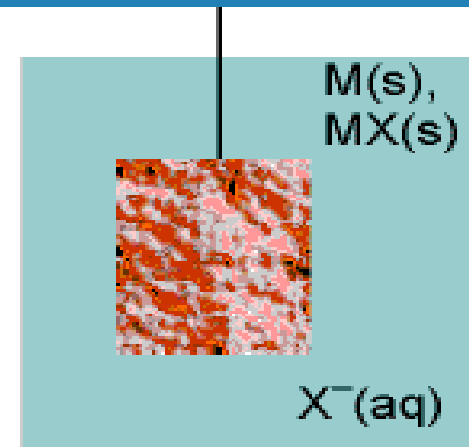
Types of Electrode

Electrode type	Designation	Half reaction
Metal/metal ion	$M(s)/M^+(aq)$	$M^+(aq) + e = M(s)$
Gas	$Pt(s)/X_2(g)/X^+(aq)$	$X^+(aq) + e = 1/2\, X_2(g)$
	$Pt(s)/X_2(g)/X^-(aq)$	$1/2X_2(g) + e = X^-(aq)$
Metal/insol. salt	$M(s)/MX(s)/X^-(aq)$	$MX(s) + e = M(s) + X^-(aq)$
Redox	M^{2+}/M^+	$M^{2+}(aq) + e = M^+(s)$

Cells with a Common Electrolyte

Hydrogen electrode

Silver/ silver chloride electrode

Electrolyte

b a cell in which the anode is a hydrogen electrode and the cathode is a silver-silver chloride

b electrode is denoted

$Pt|H_2(g)|H^+(aq), Cl^-(aq) | AgCl(s)|Ag(s)$

$Pt|H_2(g)|HCl(aq)|AgCl (s)|Ag(s)$
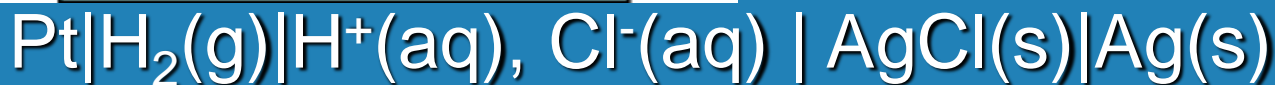
Varieties of Cell

The two basic types:

concentration cells and chemical cells

ᴏ Concentration cells are:

ᴏ **electrolyte** concentration cells, where the electrode compartments are identical except for the concentrations of the electrolytes,

ᴏ **electrode** concentration cells, in which the electrodes themselves have different concentrations, such as amalgams or gas electrodes at different pressures.

ᴏ Most cells are chemical cells.

The Cell Potential

E is <u>intensive</u>

$\Delta_r G < 0,$
$E > 0$

$\Delta_r G > 0,$
$E < 0$

$\Delta_r G = 0,$
$E = 0$

Gibbs energy, G

Extent of reaction, ξ
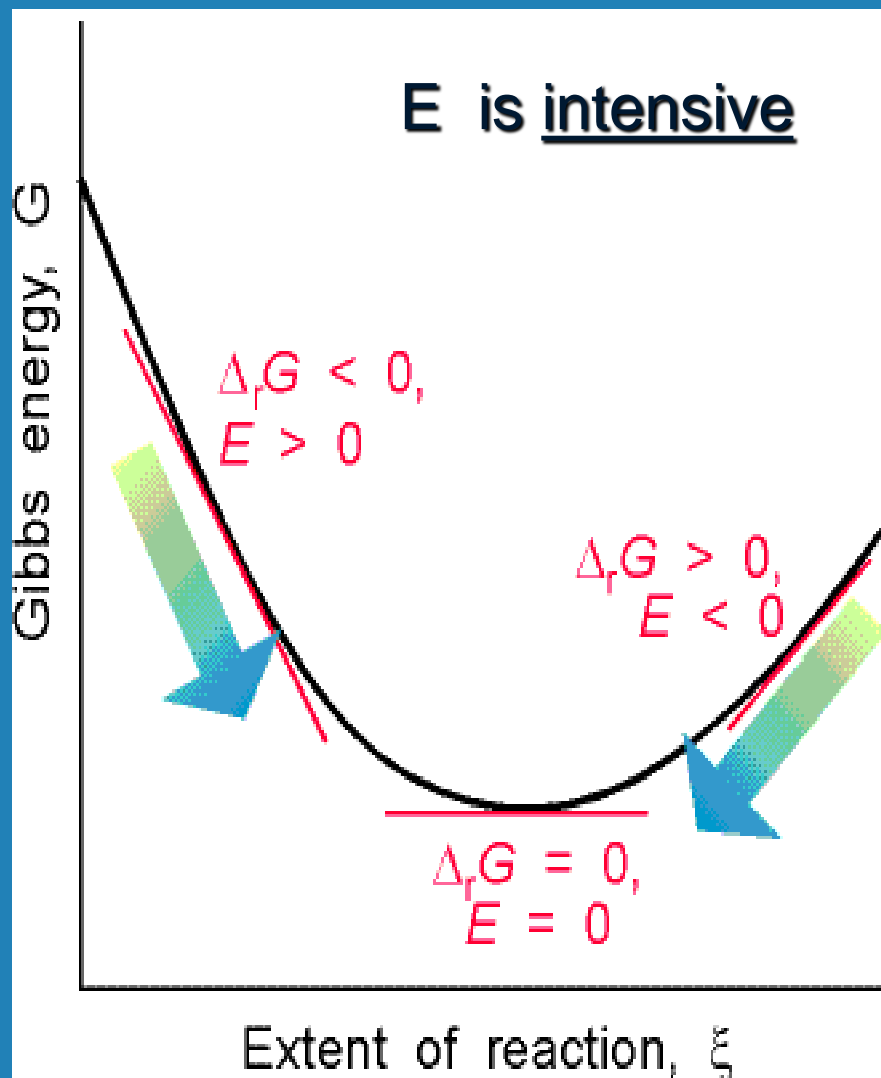
- Since w = ΔG = - work output, and since electrical work output = (charge) x (voltage) = nFE ,
- ΔG = - nFE

ΔG…….Gibbs energy
n……….number of electrons
F ………Faraday constant
E……….potential

- A spontaneous reaction has a negative ΔG and a positive E

The Nernst Equation

ß Substituting $\Delta G = -nFE$ into

$$\Delta G = \Delta G^o + RT \ln Q \qquad \text{gives}$$

reaction $A+B=C+D$

$$Q = a_C a_D / a_A a_B$$

$$-nFE = -nFE^o + RT \ln Q$$

or

$$E = E^o - (RT/nF) \ln Q \qquad \textbf{NERNST EQUATION}$$
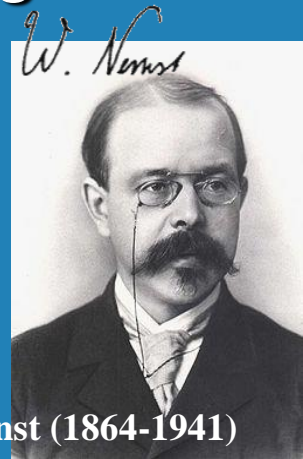
ß At 25°C……… $RT/F = 0.02569 \text{ V} = 25.69 \text{ mV}$

ß A practical form of the Nernst equation is

$$E = E^o - (25.69 \text{ mV}/n) \ln Q$$

ß At equilibrium, $E = 0$ and $Q = K$, so
$$\ln K = nFE^o/RT \qquad E^o = RT \ln K /nF$$

ß At 25°C……… $\ln K = nE^o/(25.69 \text{ mV})$

Walther Hermann Nernst (1864-1941)

Concentration Cells

ß A <u>concentration cell</u> derives its potential from the difference in concentration between the right and left sides.

M|M⁺(aq, L)||M⁺(aq, R)|M

ß The cell reaction is M⁺(aq, R) - M⁺(aq, L)

ß **Using the Nernst equation,** $E = E^o - (RT/nF) \ln Q$

ß $E^o = 0$! *(Do you see why?)*

ß $Q = a_L/a_R$

ß So for a conc. cell, $E = - (RT/nF) \ln (a_L/a_R)$

Standard Electrode Potentials

E^o_{cell}

E^o_{cell} x E^o

ℬ E^o_{cell} can be found from $\Delta_r G^o$ using the equation $\Delta_r G^o = -nFE^o$

(or in general, $\Delta_r G = -nFE$)

ℬ But E^o_{cell} can also be found from values of E^o for the two electrodes involved.

ℬ Standard electrode potentials are given in Tables

ℬ Since it is impossible to measure the potential of one electrode alone, these are all relative to hydrogen standard electrode

$$E^o_{cell} = E^o_R - E^o_L$$

E and Spontaneity

ß $E^o > 0$ goes with K > 1, which indicates a spontaneous reaction

ß However, <u>the direction of a reaction can sometimes be reversed by judicious manipulation of the concentrations of product and reactant species</u>. (That is, by altering $Q = a_C a_D / a_A a_B$ from reaction A+B=C+D)

ß Any given reaction proceeds left to right when E $>$ 0 (not E^o!)

The Electrochemical Series

ß A species with a low standard reduction potential has a thermodynamic tendency to reduce a species with a high standard reduction potential.

- More briefly, <u>low reduces high (LRH)</u>.

- Equivalently, <u>high oxidizes low (HOL)</u>.

ß This is the basis for the **activity series** of metals.

ß Other couples can also be fitted into the activity series.

Activity Series of Metals

increasing reactivity ↑

Metal	Property
potassium / **sodium**	React violently (strongly) with cold water
calcium	React slowly with cold water
magnesium / **aluminum** / **zinc** / **chromium**	React very slowly with steam but quite reactive in acid
iron / **nickel** / **tin** / **lead**	React moderately with high levels of acid < HYDROGEN comes here
copper / **silver** / **platinum** / **gold**	Unreactive in acid Noble metals

The Hydrogen Electrode and pH

ß The potential of a hydrogen electrode is directly proportional to the pH of the solution. Consider the calomel-hydrogen cell

$$Hg(l)| \ Hg_2Cl_2(s)| \ Cl^-(aq)|| \ H^+(aq)|H_2(g)|Pt$$

for which the cell reaction is

$$Hg_2Cl_2(s) + H_2(g) = 2 \ Hg(l) + \ 2 \ Cl^-(aq) + \ 2 \ H^+(aq)$$

ß If the $H_2(g)$ is at standard pressure and the chloride ion activity is constant and incorporated into $E^{o\prime}$, the Nernst equation becomes $E = E^{o\prime} - (RT/2F) \ ln \ a(H^+)^2$

$= E = E^{o\prime} - (RT/2F) \ 2ln \ a(H^+) = E^{o\prime} + (RT \ ln \ 10/F) \ pH$

$= E^{o\prime} + (59.15 \ mV) \ pH$

$$pH = -log \ a(H^+)$$

ß So the pH can be determined from the cell potential.

Thermodynamic Functions and E's

◦ Because of the relationship

$$\Delta_r G = - nF\Delta E$$

$$\Delta_r G^o = - nF\Delta E^o$$

◦ It is possible to obtain the thermodynamic value of the standard reaction Gibbs energy by measuring cell potentials.

$$- \Delta_r G = nF\Delta E = RT \ln K - RT \ln Q$$

$$\Delta E = (RT/nF) \ln K - RT/nF \ln Q$$

$$\Delta E^o$$

ß E^o's for two half-reactions can be <u>combined</u> directly as long as <u>the number of electrons is the same</u> in each half-reaction and the electrons cancel out when the half-reactions are combined.

ß E^o's <u>cannot be directly combined</u> for half-reactions in which <u>the electrons do not cancel out.</u>

- For instance, E^o for $Cu^{2+}|Cu^+$ cannot be found by directly combining E^o's for $Cu^{2+}|Cu$ and $Cu^+|Cu$.

ß In these cases, E^o's may be converted to $\triangle G^o$'s for and the $\triangle G^o$'s for then <u>directly combined</u>.

Other Thermodynamic Values - $\Delta_r H^o$

Enthalpy

 b The van't Hoff equation may be modified to give $\Delta_r H^o$ if E^o is measured at two different temperatures.

- Substitute $-\Delta_r G^o / RT$ for ln K

- Substitute $-nFE^o$ for $\Delta_r G^o$

  – or do it in one step by replacing nFE^o / RT for ln K

    van't Hoff reaction isobar

$$\left(\frac{\partial \ln K}{\partial T} \right) = \frac{\Delta_r H^0}{RT^2}$$

Entropy

$$\Delta_r G^0 = \Delta_r H^0 - T\Delta_r S^0$$

ℬ With expressions for both $\Delta_r G^o$ and $\Delta_r H^o$ the entropy can also be obtained.

ℬ $\Delta_r S^o$ is given by the relation

$$\Delta_r S^0 = nF\frac{E^0(T_2) - E^0(T_1)}{T_2 - T_1}$$

Exercise

ß **Is the equilibrium constant for the displacement of copper by zinc greater or smaller than 1? Calculate the equilibrium constant for this reaction.**

ß Solution: For this cell reaction,

R : $Cu^{2+} + 2e = Cu$ $E^o_R = +0.34$ V

L : $Zn^{2+} + 2e = Zn$ $E^o_L = -0.76$ V

$E^o_{cell} = E^o_R - E^o_L = +0.34$ v $- (-0.76$ v$) = +1.10$ V

Since E^o is positive, the reaction is spontaneous, and K>1.

$\ln K = n\, E^o/(25.69$ mV$) = 2\,(1100$ mV$)/(25.69$ mV$)$

K = 1.554 * 10^{37}