Oxidation and Reduction

Lavoisier

Oxygen discovery – new element, routing of flogiston theory

Burning = binding of oxygen = oxidation

$2\ Mg + O_2 \rightarrow 2\ MgO$
$S + O_2 \rightarrow SO_2$

Reduction = removal of oxygen

$Fe_2O_3 + 3\ C \rightarrow 2\ Fe + 3\ CO$
$CuO + H_2 \rightarrow Cu + H_2O$

Oxidation and Reduction

Concept of oxidation and reduction

Oxidation	Reduction
Loss of electron (from HOMO)	**Gain** of electron (to LUMO)
Incr of oxidation number	Decr of oxidation number

$$\mathbf{Fe^{3+} \leftarrow \quad Fe^{2+} \rightarrow Fe}$$

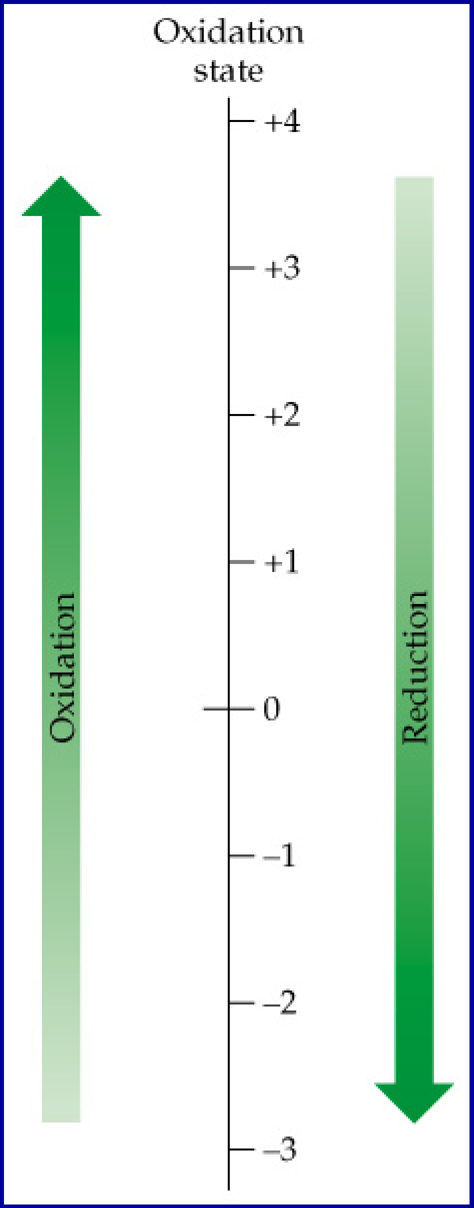
Oxidized form Reduced form

More electrons

Oxidation

Loss of electron

Incr of oxidation number



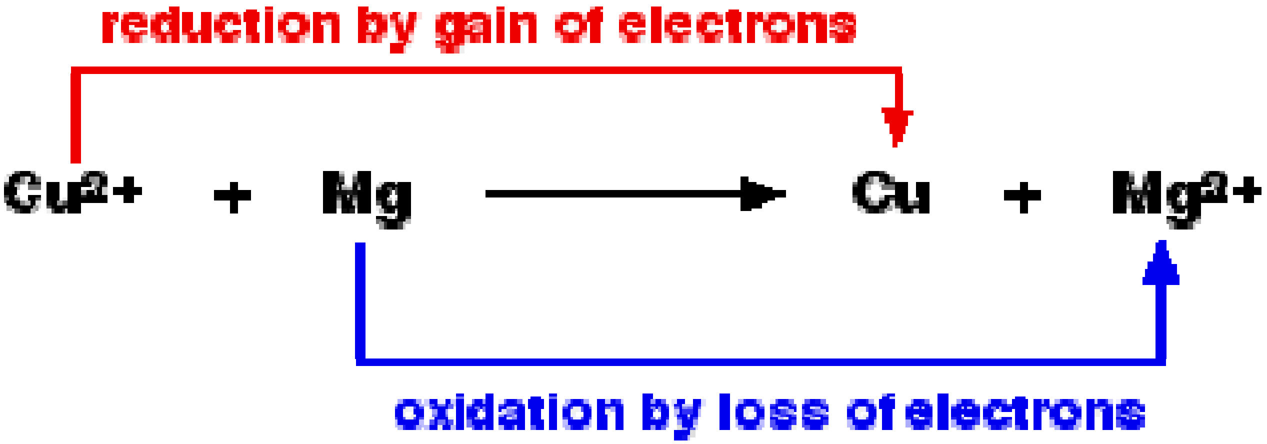
Reduction

Gain of electron

Decr of oxidation numbe

Oxidation and Reduction

Oxidation and reduction must proceed simultaneously

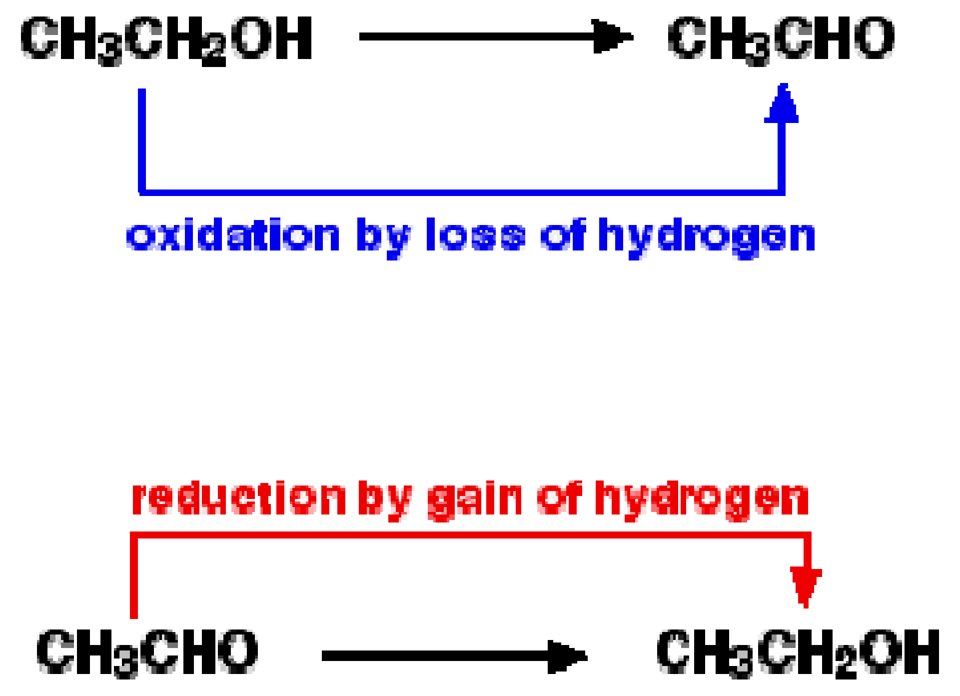


$$Cu^{2+} + Mg \longrightarrow Cu + Mg^{2+}$$

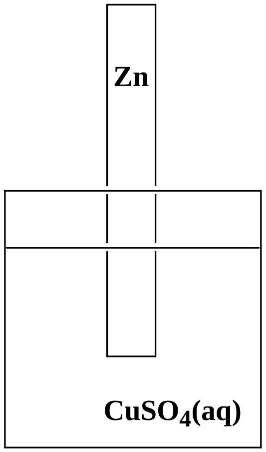
Oxidation and Reduction

Oxidation state of C = –1

Oxidation state of C = +1



Oxidation and Reduction



Half-reactions

Ox $Zn \rightarrow Zn^{2+} + 2\,e^-$

Red $Cu^{2+} + 2\,e^- \rightarrow Cu$

Redox pairs: Zn^{2+}/Zn, Cu^{2+}/Cu

No free electrons in redox reactions.

Oxidation and reduction cannot proceed separately,

Must be simultaneous, electron neutral reactions

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$ **Exchange of 2 electrons**

Redox Pairs

The stronger the reduced form gives up electrons, the weaker oxidized form accepts electrons.

Zn^{2+}/Zn	Na^{+}/Na
Cu^{2+}/ Cu	F_2/ F^{-}

Redox series:

Na, Zn, Fe,..... Reducing agent = loses electrons

O_2, F_2, Cl_2, I_2, ...Oxidizing agent = accepts electrons

Balancing Redox Equations

Find oxidation states of all atoms in compounds

Find elements changing their oxidation state

Find oxidizing agent(s) and reducing agent(s)

Draw redox half-equations

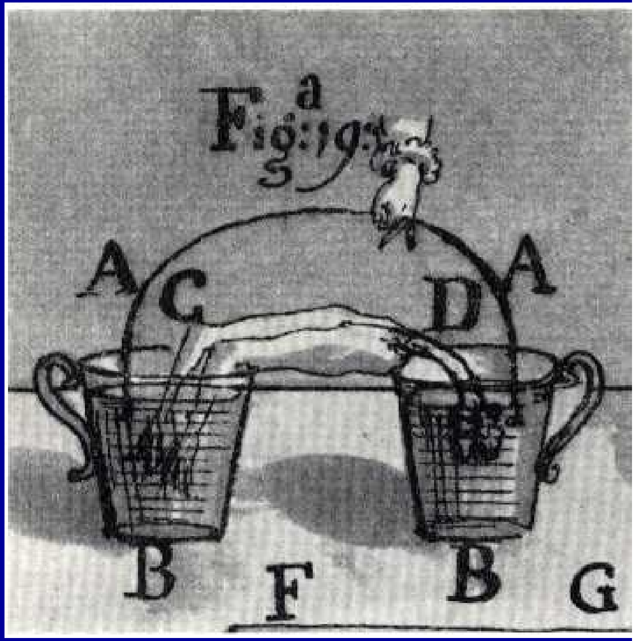
Find total number of electrons needed for **oxidation** and **reduction**

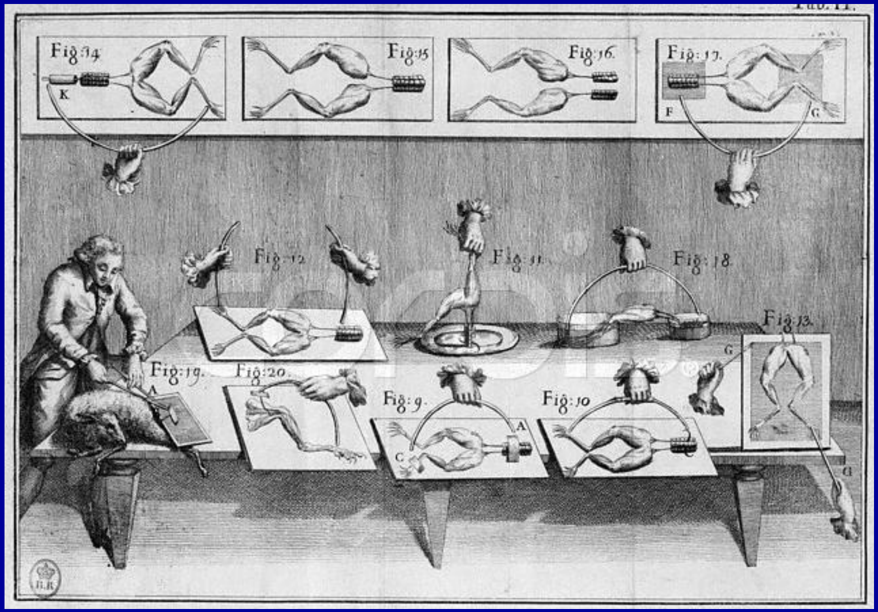
Balance number of electrons – electroneutrality, no free electrons

Balance remaining elements

Animal Electricity

Luigi Galvani
(1737-1798)





Galvanic or Voltaic Cells

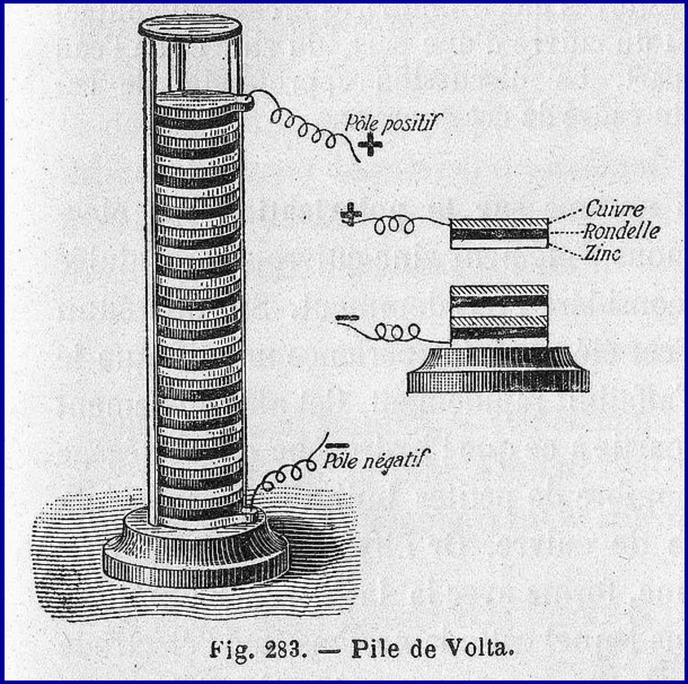


Fig. 283. — Pile de Volta.

Alessandro Volta
(1745-1827)

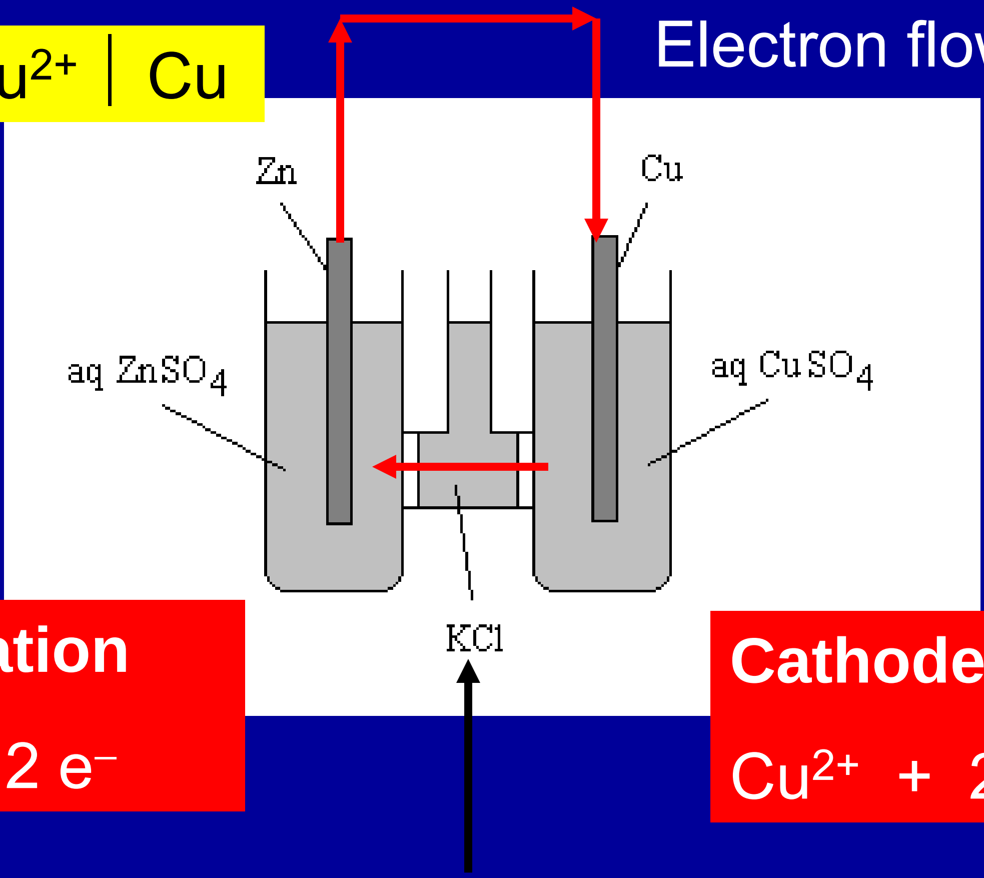
Separation of reduction and oxidation: $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

Spontaneous redox reaction produce electric current

Chemicl energy converts to electrical energy

Galvanic Cell (Daniell's)

$Zn \mid Zn^{2+} \mid\mid Cu^{2+} \mid Cu$



Electron flow

Anode – Oxidation

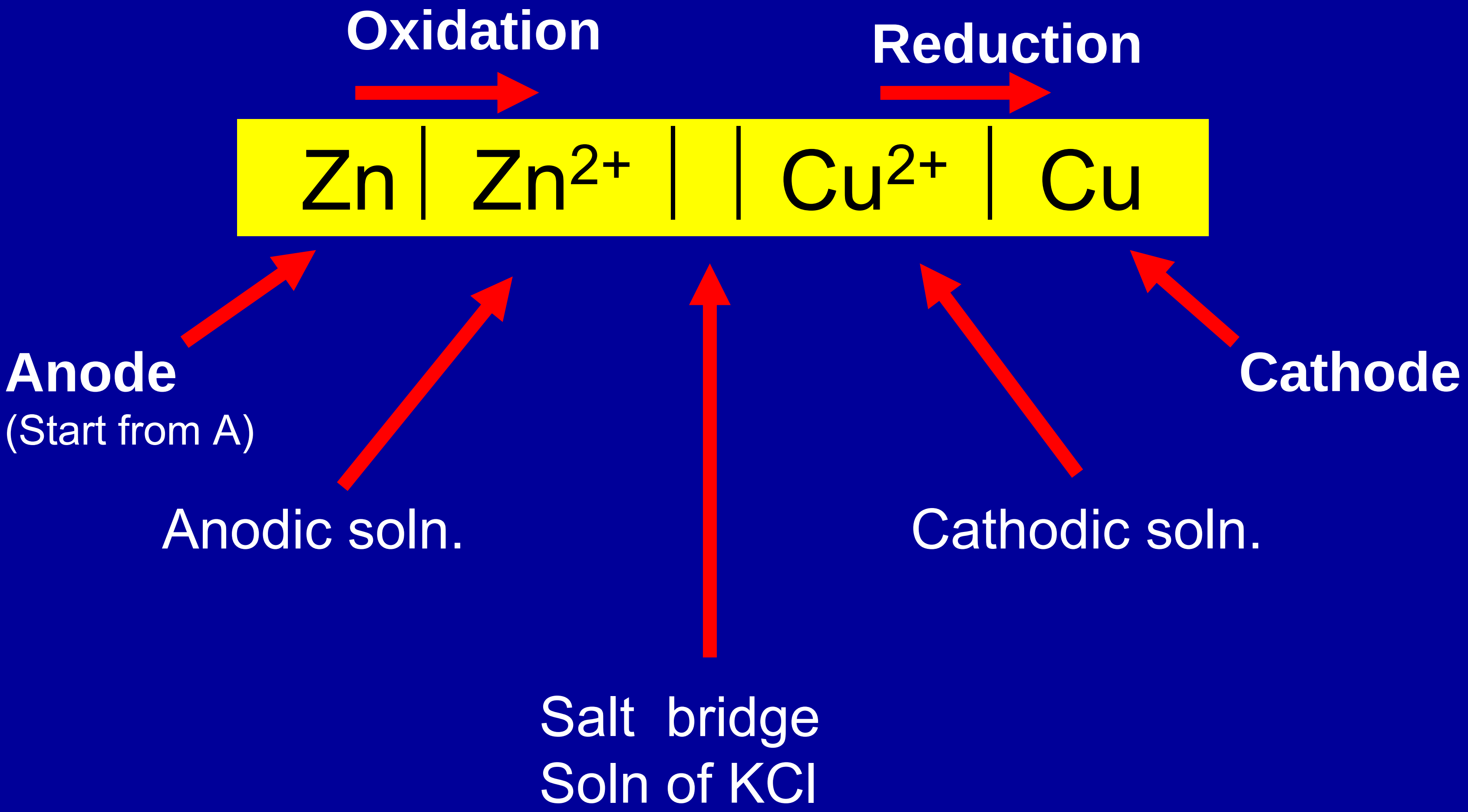
$Zn \rightarrow Zn^{2+} + 2\,e^-$

Cathode – Reduction

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

Salt bridge
Flow of ions, NOT electrons

Cell Schematics



Oxidation

Reduction

$\mathrm{Zn} \,|\, \mathrm{Zn}^{2+} \,||\, \mathrm{Cu}^{2+} \,|\, \mathrm{Cu}$

Anode
(Start from A)

Anodic soln.

Salt bridge
Soln of KCl

Cathodic soln.

Cathode

Electrodes

Anode – Oxidation (A O vowels)

$M \rightarrow M^{n+} + n\,e^-$

$M^{n+} \rightarrow M^{(n+1)+} + e^-$

$2\,X^- \rightarrow X_2 + 2\,e^-$

$4\,OH^- \rightarrow 2\,H_2O + O_2 + 4\,e^-$

$6\,H_2O \rightarrow 4\,H_3O^+ + O_2 + 4\,e^-$

Cathode – Reduction (K R)

$M^{n+} + n\,e^- \rightarrow M$

$M^{(n+1)+} + e^- \rightarrow M^{n+}$

$2\,H_3O^+ + 2\,e^- \rightarrow H_2 + 2\,H_2O$

$2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^-$

Metal Electrodes

Metal immersed in soln of its salt (ions)

$$\mathrm{M} \underset{\text{reduction}}{\overset{\text{oxidation}}{\rightleftarrows}} \mathrm{M}^{n+} + n\,e^{-}$$

Double layer

Potential depends on:

- Type of metal
- Concentration of cation
- Temperature

Nernst equation

$$E_{Zn,Zn^{2+}} = E^{\circ}_{Zn,Zn^{2+}} + \frac{RT}{2F}\ln a_{Zn^{2+}}$$

$E = E^{\circ} + (RT/nF) \ln a(M^{n+})$

Activity

$E = E^{\circ} + (RT/nF) \ln [M^{n+}]$

Concentration

Nernst Equation

Reduction $M^{n+} + n\,e^{-} \rightarrow M$

$$E_{M,M^{n+}} = E^{\circ}_{M,M^{n+}} - \frac{RT}{nF}\ln Q$$

E° = standard **reduction** potential

n = number of exchanged electrons

$Q = [\text{products}] / [\text{educts}] = [M] / [M^{n+}]$

$E = E^{\circ} - (RT/nF)\ \ln\ (1 / [M^{n+}]) = E^{\circ} + (RT/nF)\ \ln\ [M^{n+}]$

Standard Hydrogen Electrode

Potential of one redox pair, E and E^0, cannot be measured directly

Can measure electromotoric force of a cell, potential difference of two redox pairůs

Hydrogen Electrode selected as a standard: $E^0(H_2, H^+) = 0$

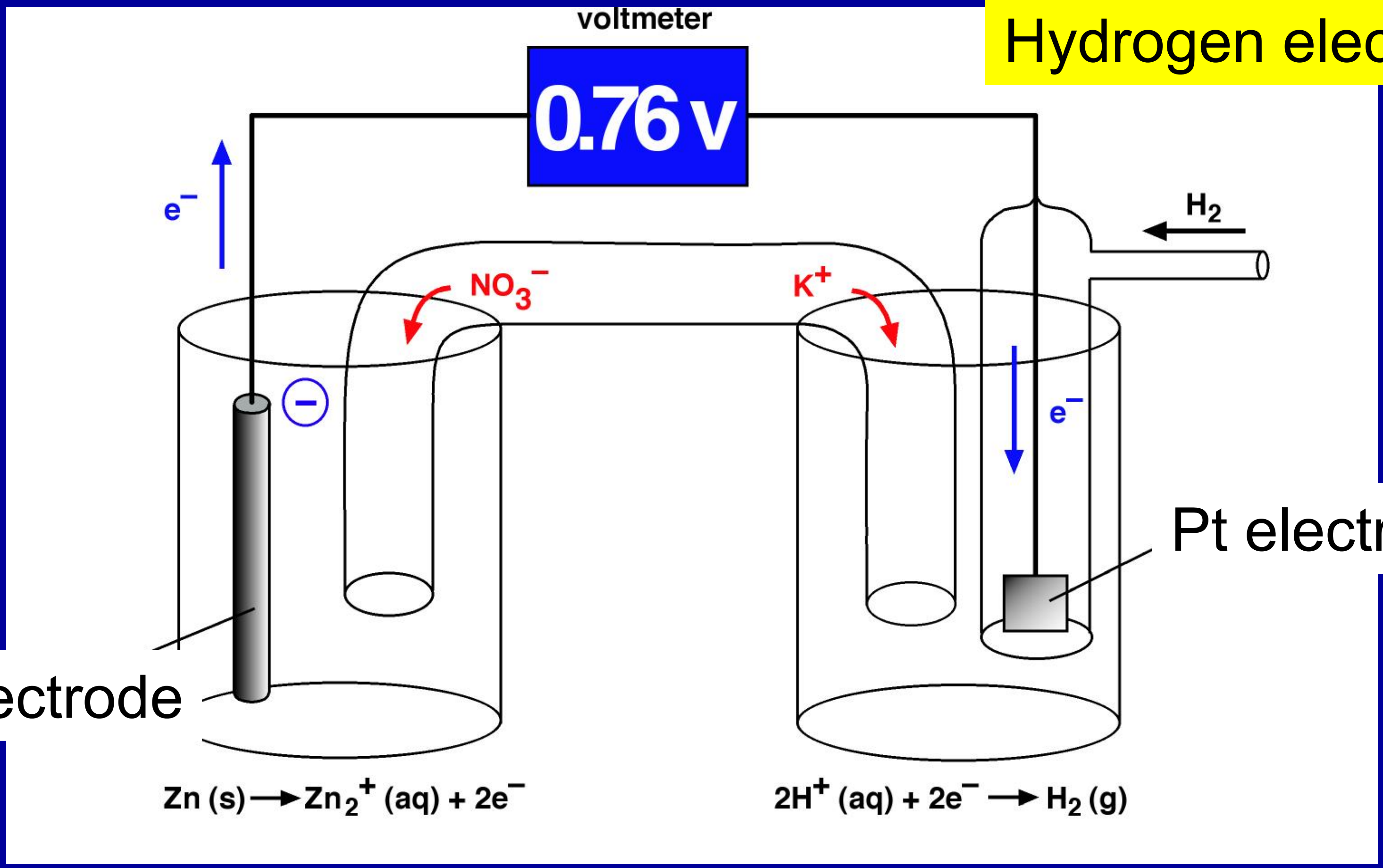
$2\ H_3O^+ + 2\ e^- \leftrightarrows H_2 + 2\ H_2O$

$$E = E^0 - (RT/2F) \ln \{p(H_2) / [H^+]^2\} =$$
$$= E^0 + (RT/2F) \ln \{[H^+]^2 / p(H_2)\}$$

$E^0 = 0$ $[H^+] = 1$ $p(H_2) = p_{H2} / p_0 = 1$ $T = 298\ K$

$E = 0$

Standard Hydrogen Electrode



Hydrogen electrode

Pt electrode

Zn electrode

Electrochemical Series

Standard **reduction** potentials M^{n+} + n e^- → M
(in water at 25 °C)

Redox pair	E^0, V
$2\ OF_2 + 4\ e^- \rightarrow 4\ F^- + O_2$	+3.2
$F_2 + 2\ e^- \rightarrow 2\ F^-$	+2.87
$MnO_4^- + 8\ H^+ + 5\ e^- \rightarrow Mn^{2+} + 4\ H_2O$	+1.51
$Cl_2 + 2\ e^- \rightarrow 2\ Cl^-$	+1.36
$Cu^{2+} + 2\ e^- \rightarrow Cu$	+0.34
$2\ H_3O^+ + 2\ e^- \rightarrow H_2 + 2\ H_2O$	0.00
$Fe^{2+} + 2\ e^- \rightarrow Fe$	–0.44
$Zn^{2+} + 2\ e^- \rightarrow Zn$	–0.76
$Na^+ + e^- \rightarrow Na$	–2.71
$3\ N_2 + 2\ e^- \rightarrow 2\ N_3^-$	–3.6

Standard Reduction Potentials

$F_2 + 2\,e^- \rightarrow 2\,F^-$ $E^0 = +2.87$ V positive E^0

F_2 is a strong oxidation agent →

reaction equil. shifted to right

$2\,F^- \rightarrow F_2 + 2\,e^-$ $E^0 = -2.87$ V

F^- is a weak reduction agent

$Na^+ + e^- \rightarrow Na$ $E^0 = -2.71$ V negative E^0

Na^+ is a weak oxidation agent ←

reaction equil. shifted to left

$Na \rightarrow Na^+ + e^-$ $E^0 = +2.71$ V

Na is a strong reduction agent

Standard Reduction Potentials

Standard Reduction Potentials

$F_2 + 2\,e^- \rightarrow 2\,F^-$ $E^0 = +2.87$ V

(Standard oxidation potential) opposite sign

$2\,F^- \rightarrow F_2 + 2\,e^-$ $E^0 = -2.87$ V

Electromotoric Force

Anode Zn | Zn^{2+} || Cu^{2+} | Cu Cathode

$[M^{n+}] = 1$ M

$E_{Zn} = E^0_{Zn} + (RT/2F) \ln [Zn^{2+}]$ $E_{Cu} = E^0_{Cu} + (RT/2F) \ln [Cu^{2+}]$

convention!!!
$E_{cell} = E(\text{right}) - E(\text{left})$

E_{cell} intensive variable, **not multiplied by n!!!**

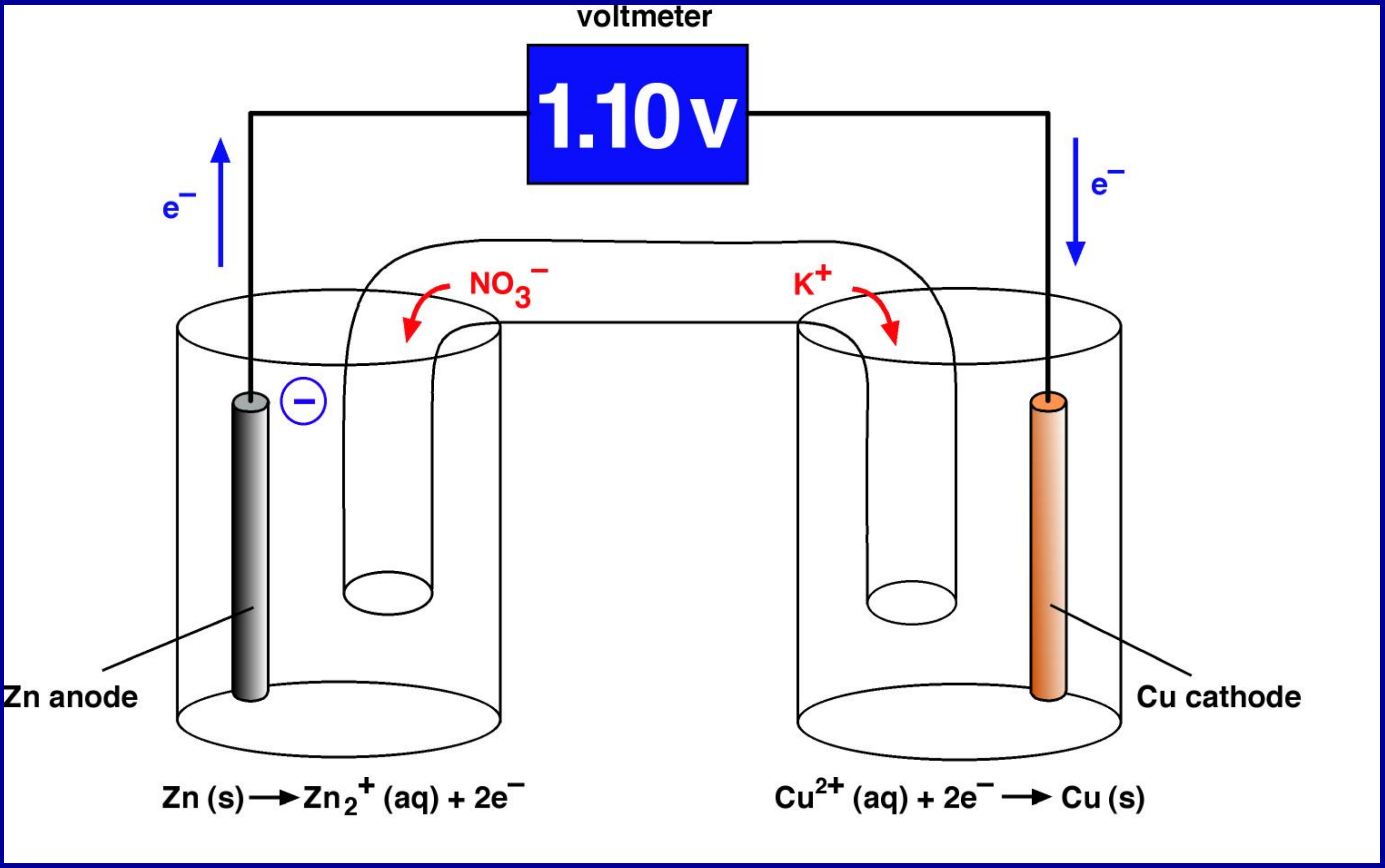
$E_{cell} = E^0_{Cu} - E^0_{Zn} = +0.34 - (-0.76) = +1.10$ V

When $E_{cell} > 0$ then reaction is spontaneous, producing current

$Zn + Cu^{2+} \leftrightarrows Zn^{2+} + Cu$

Electromotoric Force

E_{cell} [V] = EMS = EMF



$W = q \times E$

E_{cell} and Electric Work W

1 J = work of taking charge of 1 C thru potencial difference of 1 V

$$E_{cell} = \text{cell voltage [V]} = \frac{\text{W, work [J]}}{\text{q, charge [C]}}$$

$E_{čl} > 0$ spontaneous reaction, current does work ($-W$)

$$E_{čl} = \frac{-W}{q} \qquad W = -q\,E_{čl} = -nF\,E_{čl}$$

For p, T = const $\quad W_{max} = \Delta G = -q\,E_{cell} = -n\,F\,E_{cell}$

$$\Delta G = -n\,F\,E_{cell}$$

Free Energy

$$\Delta G^0 = - n F E^0_{cell}$$

Maximum E^0_{cell} is directly proportional to the difference of free energies of reactants and products

Method for measuring ΔG^0 of reactions

Nernst Equation

$$Zn + Cu^{2+} \leftrightarrows Zn^{2+} + Cu$$

$\Delta G = -\, n\, F\, E_{cell}$

$Q = [Zn^{2+}] / [Cu^{2+}]$

$\Delta G = \Delta G^0 + RT \ln (Q)$

$-n\, F\, E_{cell} = -n\, F\, E^0_{cell} + RT \ln (Q)$

$$E_{cell} = E^0{}_{cell} - \frac{RT}{nF} \ln Q$$

Walther Hermann Nernst
(1864-1941)

Nernst Equation

$Zn + Cu^{2+} \leftrightarrows Zn^{2+} + Cu$ $\quad$ $Q = [Zn^{2+}] / [Cu^{2+}]$

$$E_{cell} = E^0{}_{cell} - \frac{RT}{nF} \ln Q$$

$\Delta G = -\, n\, F\, E_{cell}$

When $Q = [Zn^{2+}] / [Cu^{2+}] < K$ then $E_{ell} > 0$

Equilibrium

$Q \rightarrow K$

$$\Delta G^0 = -RT \ln(K)$$

$$\Delta G = \Delta G^0 + RT \ln(K)$$

$\Delta G = 0$ the cell reached equilibrium

$E_{cell} = 0$ battery is empty

$$\Delta G = -n F E_{cell}$$

Electric current flows from anode to cathode

Concentrations change

Cell spontaneously discharges and reaches equilibrium

Free energies in both half-cells become equal

Redox Electrodes

An electrode of inert metal submerged in a solution of oxidized and reduced forms (metal cations, organic compounds,…)

$Fe^{3+} + e \leftrightarrows Fe^{2+}$

$\mathbf{Pt \mid Fe^{3+}, Fe^{2+} \| Ag^{+} \mid Ag}$

$$E_{Fe^{3+},Fe^{2+}} = E^{0}{}_{Fe^{3+},Fe^{2+}} + \frac{RT}{F}\ln\frac{a_{Fe^{3+}}}{a_{Fe^{2+}}}$$

Nernst-Peters equation

$$E_{red,ox} = E^{0}{}_{red,ox} + \frac{RT}{nF}\ln\frac{a_{ox}}{a_{red}}$$

Redox Electrodes

An electrode of inert metal submerged in a solution of oxidized and reduced forms (metal cations, organic compounds,…)

Pt | Cr^{3+}, Cr^{2+}|| Ag^{+} | Ag $Cr^{3+} + e \leftrightarrows Cr^{2+}$

$$E_{cell} = E(right) – E(left)$$

$$= E^0(Ag^+, Ag) – E^0(Cr^{3+}, Cr^{2+})$$

$$= +0.80\ V – (– 0.41\ V) = +1.21\ V$$

$$Ag^+ + Cr^{2+} \rightarrow Ag + Cr^{3+}$$

Redox Electrodes

Equilibrium $E_{cell} = 0$ E(right) = E(left)

$$E^0(Ag^+,Ag) - RT/F \ln 1/[Ag^+]_{eq} =$$
$$E^0(Cr^{3+},Cr^{2+}) - RT/F \ln [Cr^{2+}]_{eq} / [Cr^{3+}]_{eq}$$

$$E^0(Ag^+,Ag) - E^0(Cr^{3+},Cr^{2+}) =$$
$$- RT/F \ln [Cr^{2+}]_{eq} / [Cr^{3+}]_{eq} - RT/F \ln [Ag^+]_{eq}$$

$$\ln [Cr^{3+}]_{eq} / [Cr^{2+}]_{eq} [Ag^+]_{eq} =$$

$$\ln K_{eq} = [E^0(Ag^+,Ag) - E^0(Cr^{3+},Cr^{2+})] F / RT$$

Measurements of equilibrium constants K_{eq}

Concentration Galvanic Cell

Anode

$Ag \rightarrow Ag^{+} + e^{-}$

Cathode

$Ag^{+} + e^{-} \rightarrow Ag$

$E(\text{left}) = E^{0}(Ag^{+},Ag) + (RT/F)\ \ln[Ag^{+}]_{\text{anode}}$

$E(\text{right}) = E^{0}(Ag^{+},Ag) + (RT/F)\ \ln[Ag^{+}]_{\text{cathode}}$

$E_{\text{cell}} = E(\text{right}) - E(\text{left})$

$E_{\text{čl}} = RT/F\ \ln[Ag^{+}]_{\text{cathode}} - RT/F\ \ln[Ag^{+}]_{\text{anode}}$

$$E_{cell} = \frac{RT}{F}\ln\frac{[Ag^{+}]_{cathode}}{[Ag^{+}]_{anode}}$$

$E_{\text{cell}} > 0$

$E_{\text{cell}} = 0$

$E_{\text{cell}} < 0$

Types of Cells

Galvanic

Spontaneous redox reaction produces electric current

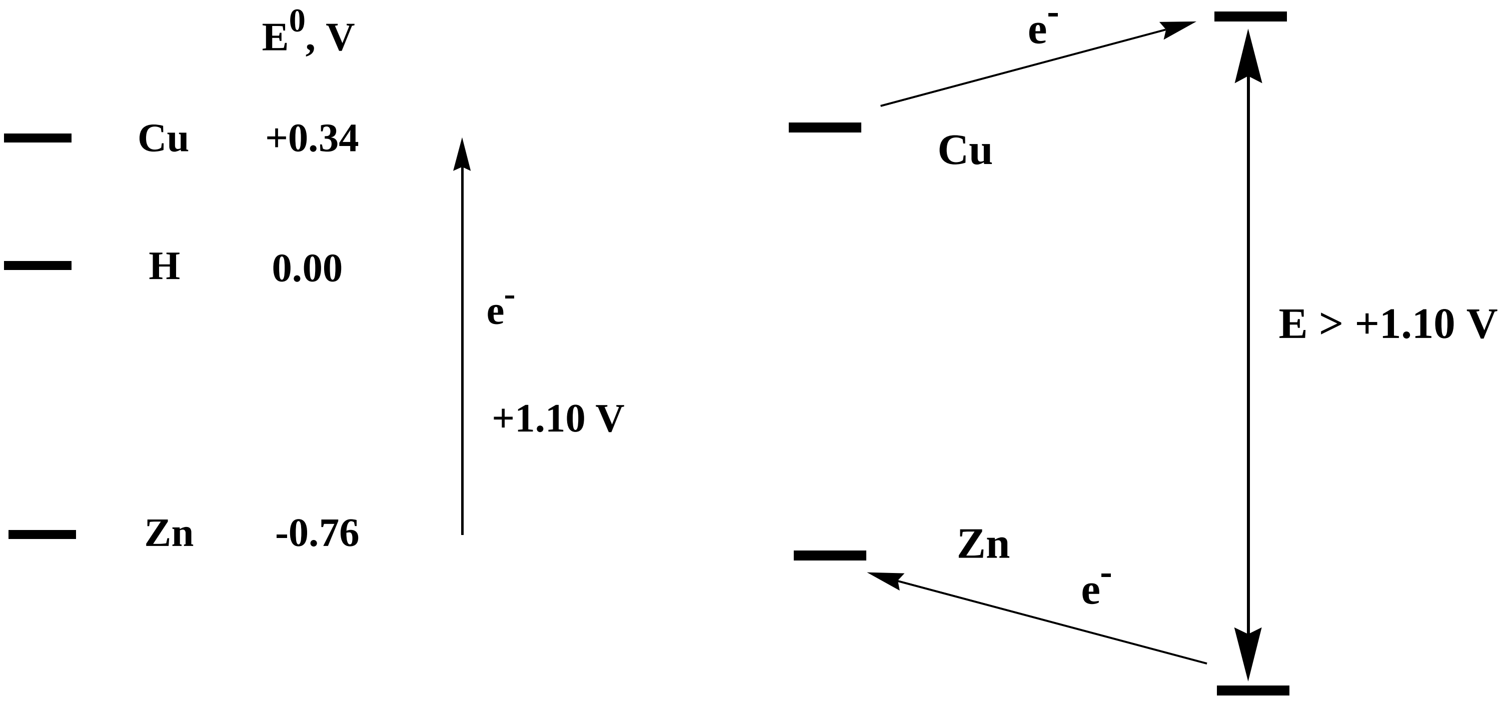
$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

Electrolytic

Non-spontaneous redox reaction can be driven by added electric work

$$Zn^{2+} + Cu \rightarrow Zn + Cu^{2+}$$

Galvanic and Electrolytic Cells



$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

$Zn^{2+} + Cu \rightarrow Zn + Cu^{2+}$

Electrodes

Anode – Oxidation (AO)	**Cathode – Reduction (K R)**
Galvanic cell –	Galvanic cell +
$\mathrm{Zn} \rightarrow \mathrm{Zn}^{2+} + 2\ e^{-}$	$\mathrm{Cu}^{2+} + 2\ e^{-} \rightarrow \mathrm{Cu}$
Electrons produced	Electrons consumed
Electrolytic cell +	Electrolytic cell –
$\mathrm{Cu} \rightarrow \mathrm{Cu}^{2+} + 2\ e^{-}$	$\mathrm{Zn}^{2+} + 2\ e^{-} \rightarrow \mathrm{Zn}$
$2\ \mathrm{Br}^{-} \rightarrow \mathrm{Br}_2 + 2\ e^{-}$	$\mathrm{Ag}^{+} + e^{-} \rightarrow \mathrm{Ag}$

Electrolysis

Electrolyte: aqueous solutions, melts

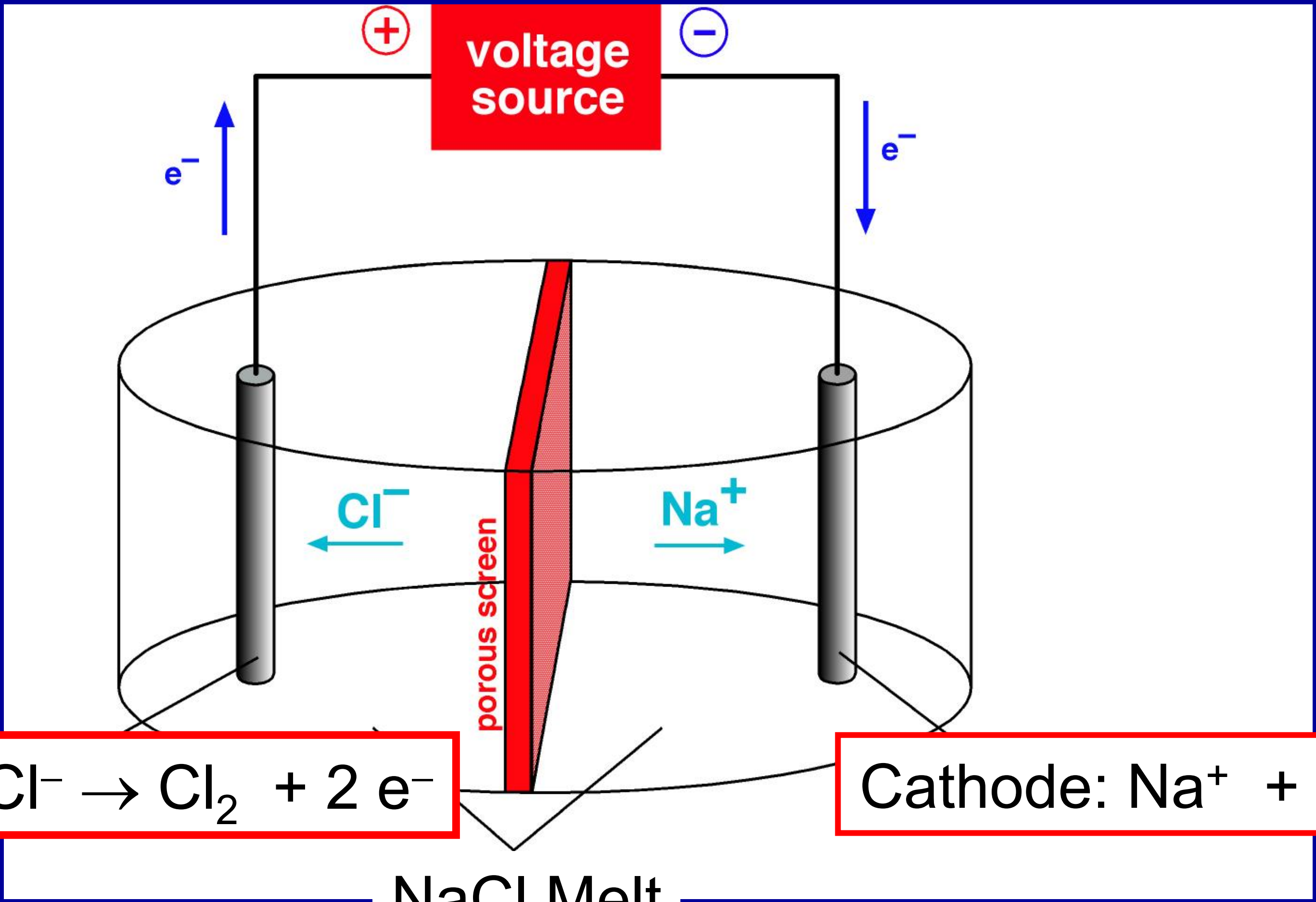
Electrodes: inert Pt, C, Ti, Hg, Fe,....

Salt melts:

Cathode: $Ag^+ + e^- \rightarrow Ag$

Anode: $2\ Br^- \rightarrow Br_2 + 2\ e^-$

Electrolysis of NaCl Melt

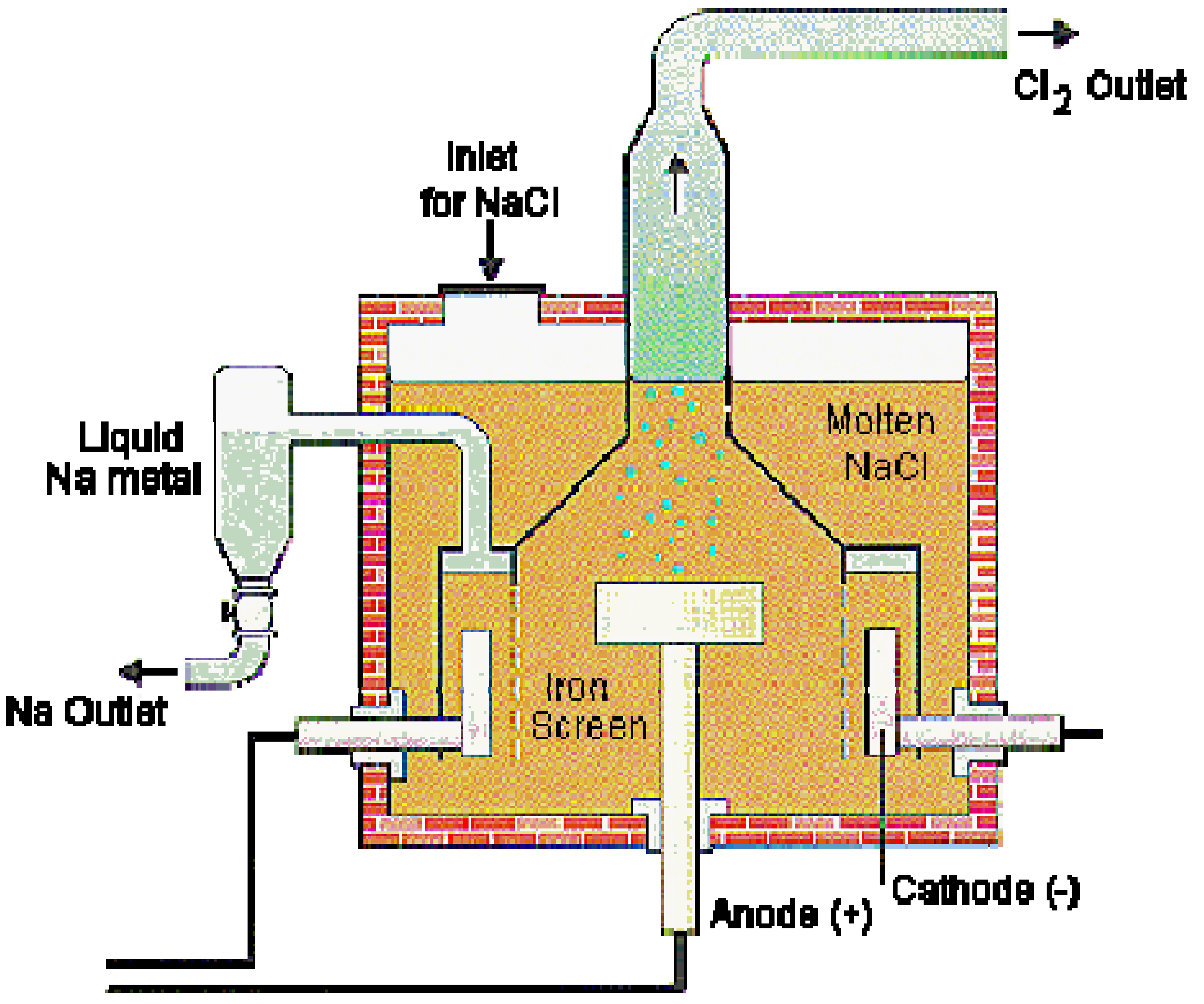


Anode: 2 $Cl^- \rightarrow Cl_2$ + 2 e^-

Cathode: Na^+ + $e^- \rightarrow$ Na

NaCl Melt

Electrolysis of NaCl Melt



Electrolysis of Aqueous Solutions

Aqueous solutions of salts:

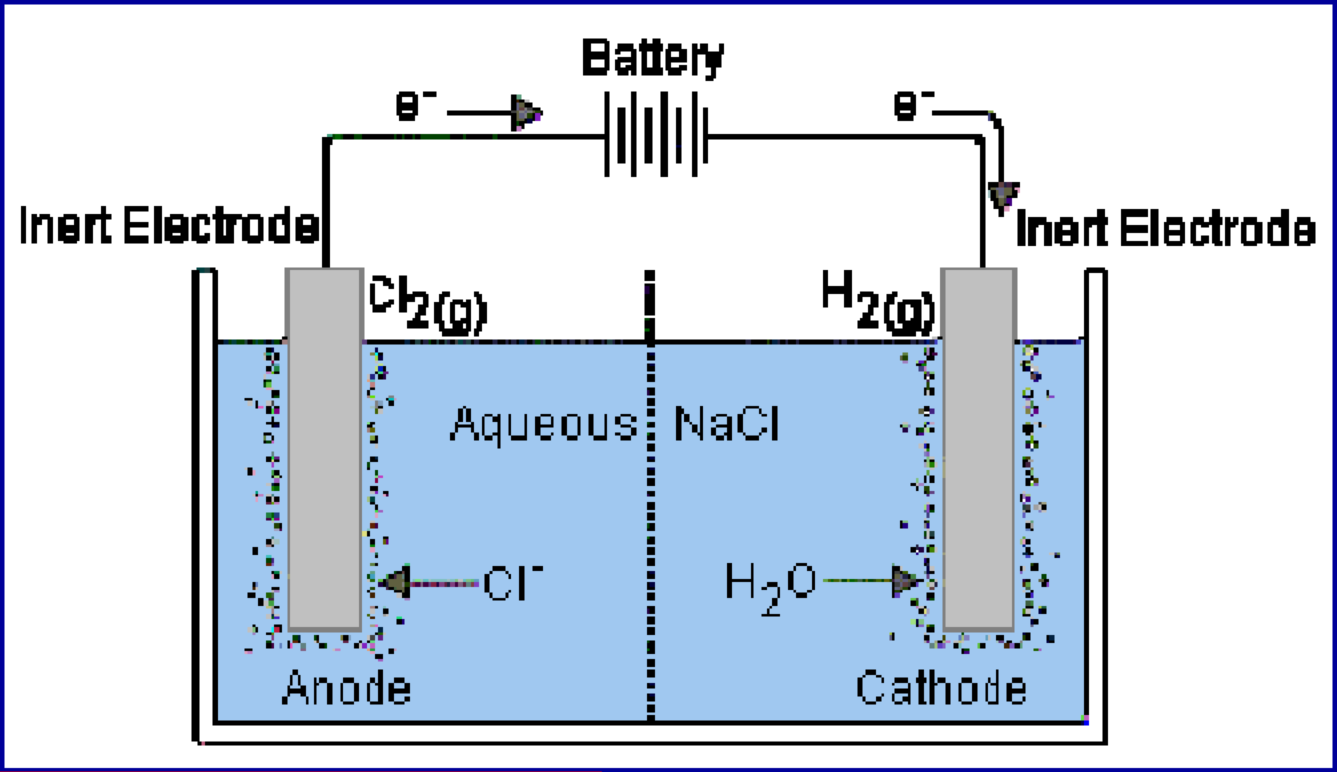
Electrode reactions: solvent or salt ions

Water:
Cathodic reduction $2\ H_2O + 2\ e^{-} \rightarrow H_2 + 2\ OH^{-}$ $E^0 = -0.83\ V$

Metals with reduction potencial $E^0 < -0.83\ V$ cannot be reduced at cathode: Al, Mg, Na, K, Li

Anodic oxidation $6\ H_2O \rightarrow 4\ H_3O^{+} + O_2 + 4\ e^{-}$ $E^0 = +1.23\ V$
Ions with $E^0 > 1.23\ V$ cannot be oxidized at anode : F^{-}, Mn^{2+}/MnO_4^{-}

Electrolysis of Aqueous Solutions



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

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

Faraday's Law

Michael Faraday
(1791-1867)

1 F = charge of 1 mole of electrons = N_A e
= 6.022 10^{23} mol^{-1} 1.602 10^{-19} C

1 F = 96487 C mol^{-1}

Charge of 1 F precipitates 1/n mol of ions M^{n+}

I = q / t   1 A = 1C per 1s

Charge passed: q = I t
Number of moles of e: n(e) = q / F = I t / F
Number of moles of ions M^{n+}: n(M) = I t / n F
Mass of metal: m(M) = n(M) A_r = A_r I t / n F

$$\boxed{m = \frac{MIt}{nF}}$$

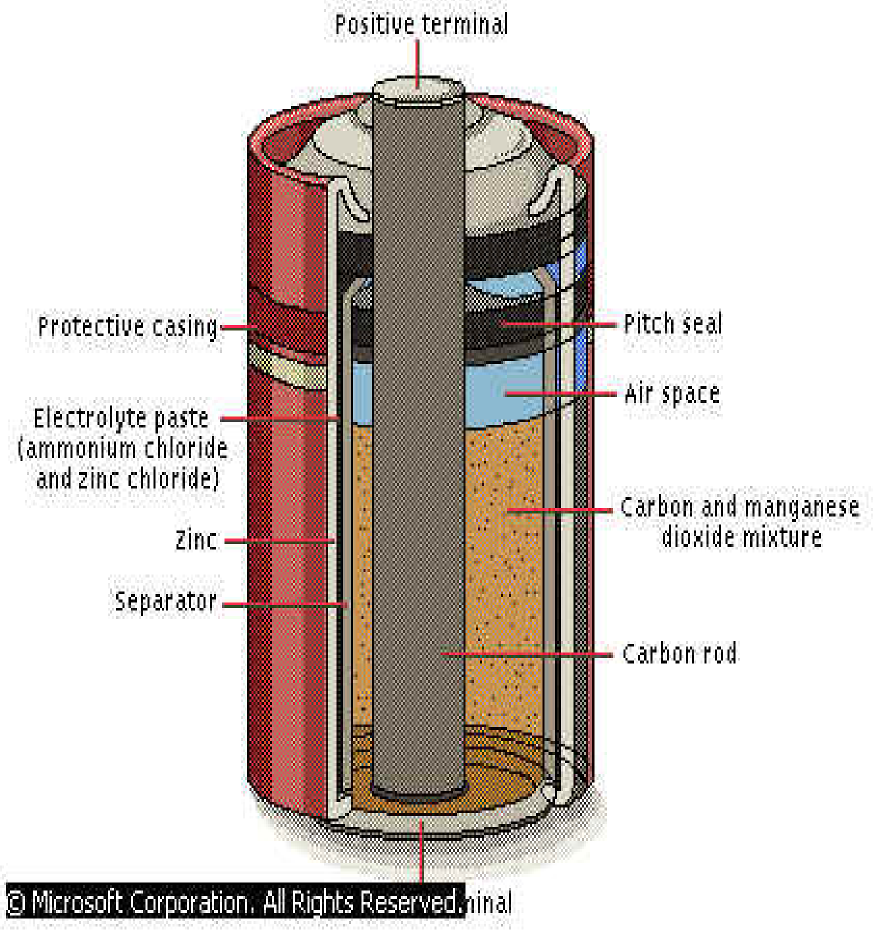
Electrochemical Power Sources

Primary Power Sources = cannot be recharged

Leclanche, dry cell, 1.5 V

$$Zn \rightarrow Zn^{2+} + 2\,e^{-}$$

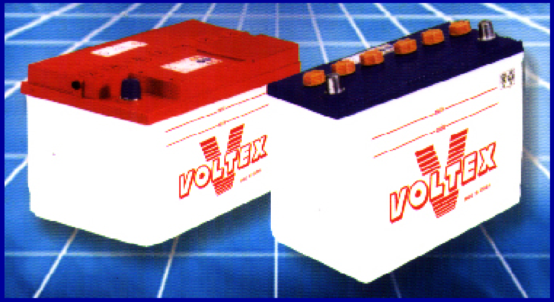
$$2\,MnO_2 + 2\,H_2O + 2\,e^{-} \rightarrow 2\,MnO(OH) + 2\,OH^{-}$$



Electrochemical Power Sources

Secondary Power Sources = rechargable

NiCd, 1.3 V
$Cd + 2\,OH^{-} \rightarrow Cd(OH)_2 + 2\,e^{-}$
$2\,NiO(OH) + 2\,H_2O + 2\,e^{-} \rightarrow 2\,Ni(OH)_2 + 2\,OH^{-}$



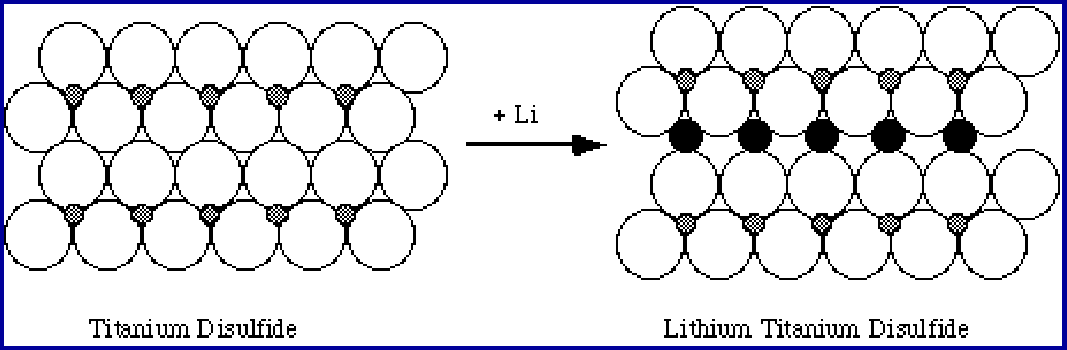
Lead battery, 2.04 V
$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2\,e^{-}$
$PbO_2 + SO_4^{2-} + 4\,H_3O^{+} + 2\,e^{-} \rightarrow PbSO_4 + 6\,H_2O$
Discharge = diluting H_2SO_4

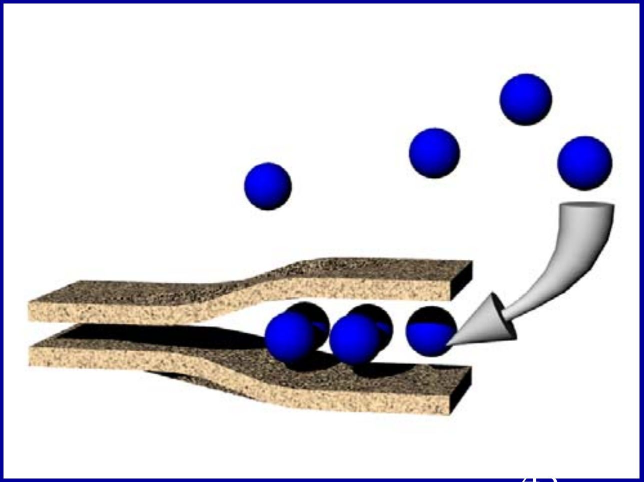
Electrochemical Power Sources

LiON, 2.5 V

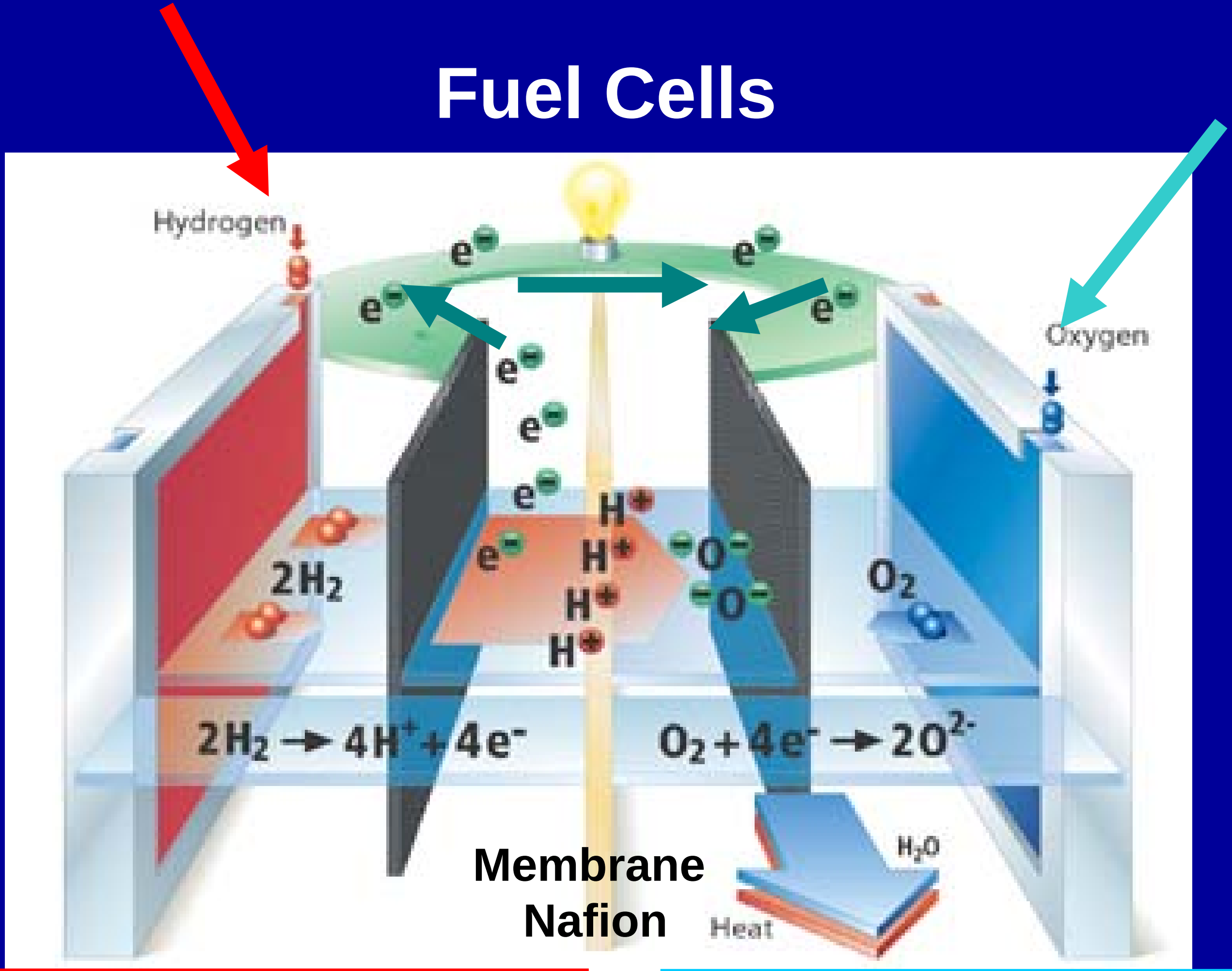
$\mathrm{Li} \rightarrow \mathrm{Li}^{+} + e^{-}$

$x\,\mathrm{Li}^{+} + \mathrm{TiS}_2 + x\,e^{-} \rightarrow \mathrm{Li}_x\mathrm{TiS}_2$ $(x = 0\text{-}1)$





Fuel Cells



Anode: $2\ H_2 \leftrightarrows + 4\ H^+ + 4\ e^-$

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

$$2\ H_2 + O_2 \leftrightarrows 2\ H_2O$$