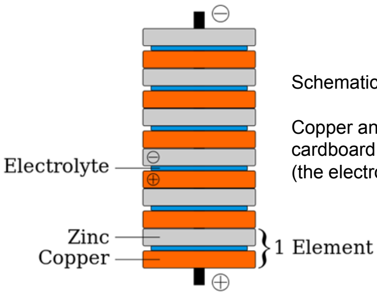
The Voltaic Cell

The **voltaic pile** was the first electrical battery that could continuously provide an electrical current to a circuit.

It was invented in 1800 by Alessandro Volta.

copper–zinc voltaic pile



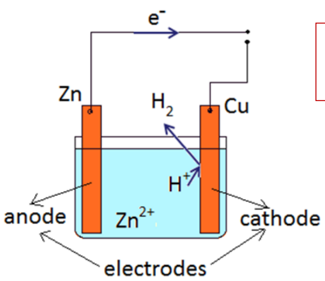
Schematics of a copper–zinc voltaic pile.

Copper and zinc discs are separated by cardboard or felt spacers soaked in salt water (the electrolyte).

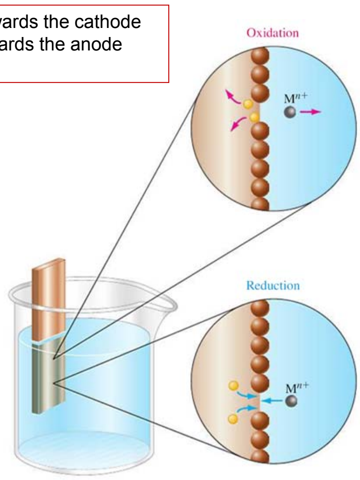
When connected:
- Zn was being consumed
- H_2 was produced on the cooper surface
- current flows but copper remain unaltered

afterwards, one can extract $ZnCl_2$ from the soaked cardboard

Schematics of the Volta pile



cations always move towards the cathode
anions always move towards the anode
(hence their names)

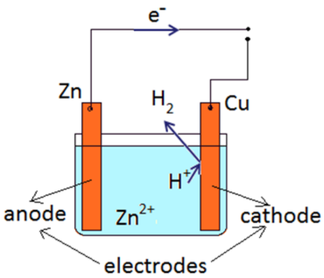


$Zn (s) \rightarrow Zn^{2+} + 2 e^-$ oxidation

$2 H^+ + 2 e^- \rightarrow H_2$ reduction

$Zn (s) + 2 H^+ \rightarrow Zn^{2+} + H_2$ redox reaction

Notation

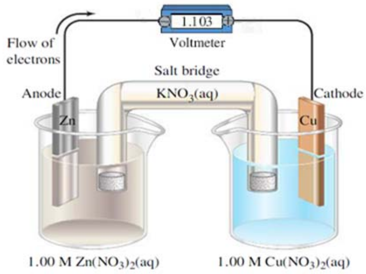


Zn(s) is the *reductant* and then is *oxidized*
H^+ is the *oxidant* ant then is *reduced*

Zn is the *reductant form* of the pair Zn^{2+}/Zn
Zn^{2+} is the *oxidant form* of the pair Zn2+/Zn

H^+ is the *oxidant form* of the pair H^+/H_2
H_2 is the *reductant form* of the pair H^+/H_2

Another possible pile



$Zn\ (s) \rightarrow Zn^{2+} + 2\,e^-$ oxidation

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

$Zn\ (s) + Cu^{2+} \rightarrow Zn^{2+} + Cu$ redox reaction

Why the reaction runs and the current flow is produced?

Experimental facts

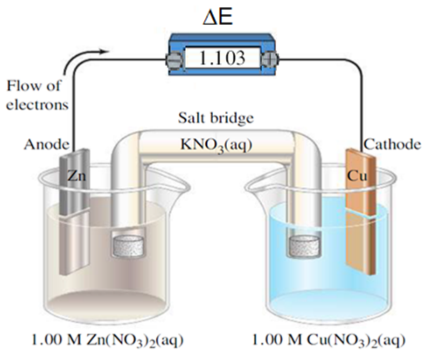
When fixing conc. in the Cu electrode:
ΔE proportional to Log $[Zn^{+2}]$

When fixing conc. in the Zn electrode:
ΔE proportional to Log $[Cu^{+2}]$

→ ΔE proportional Log $[Cu^{+2}]/[Zn^{+2}]$

Notation: ΔE^o when $[Cu^{+2}]=[Zn^{+2}]=1$ M

→ $\Delta E = \Delta E^o + k \text{ Log } [Cu^{+2}]/[Zn^{+2}]$



More experimental facts
ΔE and ΔE° depends on T
ΔE depends on the number n of electrons exchanged

At 25ºC $\Delta E = \Delta E^o + \frac{0.059}{n} \text{ Log } [Cu^{+2}]/[Zn^{+2}]$

Electrode potential

$\Delta E = E_{Cu} - E_{zn}$ and $\Delta E = \Delta E^o + \frac{0.059}{2}$ Log $[Cu^{+2}]/[Zn^{+2}]$

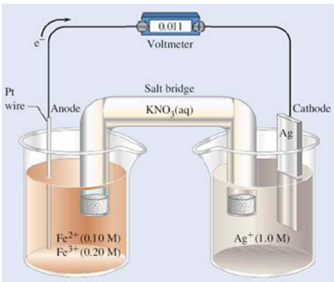
$\Delta E^o = E^o_{Cu} - E^o_{Zn}$

Suggest:

$$\begin{cases} E_{Cu} = E^o_{Cu} + \frac{0.059}{2} \text{ Log } [Cu^{+2}] \\ E_{Zn} = E^o_{Zn} + \frac{0.059}{2} \text{ Log } [Zn^{+2}] \end{cases}$$

Convention: $E^o\ (H^+/H_2) = 0$

pure solid, activity =1



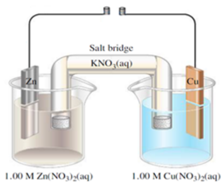
Analogous, we may experimentally check $[Ag^+]$=1M:

$$\Delta E = \Delta E^o + \frac{0.059}{1} \text{ Log } [Fe^{+3}]/[Fe^{+2}]$$

Nernst law:

$$E = E^o + \frac{0.059}{n} \text{ Log [ox]/[red]}$$

How can we identify the sense of a redox reaction from the knowledge of potentials



Which is the sense of the electronic flux?

Negative electrons produce negative potential at the battery terminal !

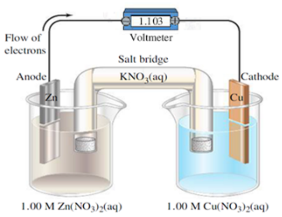
From electrode potential tables:

E^0 (Zn^{+2} / Zn^0)= -0,76 v.; E^0 (Cu^{+2} / Cu^0)=0.337 v.

→ Zn is then the negative battery terminal (and Cu the positive one)

At Zn electrons are produced: $Zn^0 \rightarrow Zn^{+2} + 2\,e^-$

At Cu the electrons are collected: $Cu^{+2} + 2\,e^- \rightarrow Cu^0$



Adjusting redox reactions

- The oxidation index (OI) of elements in natural state is zero
- The hydrogen OI is +1 (except in metallic hidryde that is -1
- The oxigen OI is -2 (except in peroxides like H_2O_2 that is -1)
- The OI of the first and second column elements in the is +1 and +2 respectively
- The halogen (F, Cl, Br, I) OI in binary compounds is -1
- The sum of OIs in a (neutral) molecule is zero
- The sum of OIs in an ion equals its charge

Examples:

$$CaCO_3 \quad Ca(+2) \quad O(-2) \quad C(+4) \quad +2+4+3\cdot(-2)=0$$

$$NaMnO_4 \quad Na(+1) \quad O(-2) \quad Mn(+7) \quad +1+4\cdot(-2)+7=0$$

$$K_2Cr_2O_7 \quad K(+1) \quad O(-2) \quad Cr(+6) \quad 2\cdot(+1)+7\cdot(-2)+2\cdot(+6)=0$$

$$NO_3^- \quad O(-2) \quad N(+5) \quad 3\cdot(-2)+5=-1$$

Adjusting redox reactions (cont.)

$$KMnO_4 + H_2SO_4 + NaCl \rightarrow Na_2SO_4 + K_2SO_4 + MnSO_4 + Cl_2 + H_2O$$

$$MnO_4^- \rightarrow Mn^{2+} \qquad reduction: +7 \rightarrow +2$$

$$Cl^- \rightarrow Cl_2 \qquad oxidation: -1 \rightarrow 0$$

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

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

$$2\cdot(\ MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O\ )$$

$$5\cdot(\ 2Cl^- \rightarrow Cl_2 + 2e^-\ )$$

$$2MnO_4^- + 16H^+ + 10Cl^- \rightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$$

$$\boxed{2KMnO_4 + 8H_2SO_4 + 10NaCl \rightarrow 2MnSO_4 + 5Cl_2 + 8H_2O + K_2SO_4 + 5Na_2SO_4}$$

38. Balance these equations for redox reactions occurring in acidic solution.

(a) $P_4(s) + NO_3^- \longrightarrow H_2PO_4^- + NO(g)$

(b) $S_2O_3^{2-} + MnO_4^- \longrightarrow SO_4^{2-} + Mn^{2+}$

(c) $HS^- + HSO_3^- \longrightarrow S_2O_3^{2-}$

(d) $Fe^{3+} + NH_3OH^+ \longrightarrow Fe^{2+} + N_2O(g)$

39. Balance these equations for redox reactions in basic solution.

(a) $MnO_2(s) + ClO_3^- \longrightarrow MnO_4^- + Cl^-$

(b) $Fe(OH)_3(s) + OCl^- \longrightarrow FeO_4^{2-} + Cl^-$

(c) $ClO_2 \longrightarrow ClO_3^- + Cl^-$

(d) $Ag(s) + CrO_4^{2-} \rightarrow Ag^+ + Cr(OH)_3(s)$

Applications: pile types and corrossion

See Petrucci sections:

20-5 Batteries: Producing Electricity Through Chemical Reactions

20-6 Corrosion: Unwanted Voltaic Cells