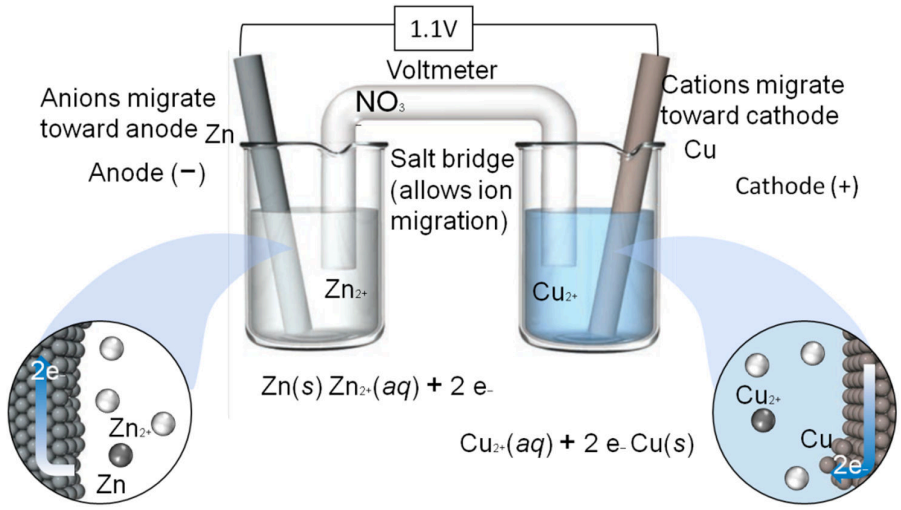
Electrochemistry

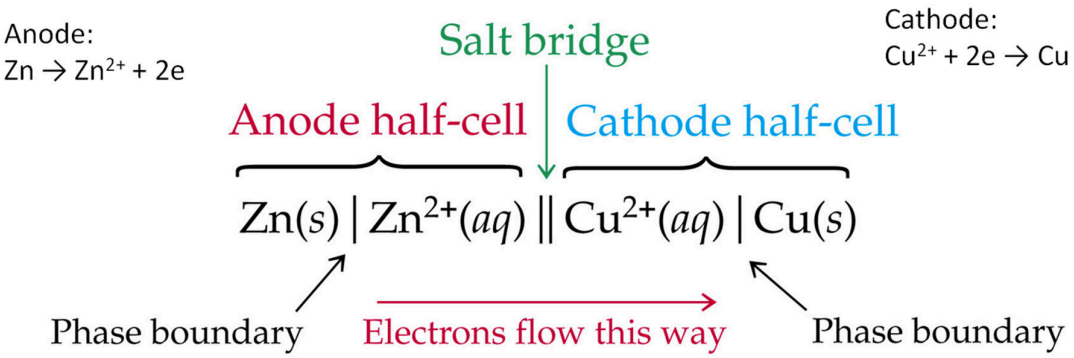
Electrochemistry is the study of chemical processes that cause electrons to move

Voltaic cell



Cell notation

- Anode on left, cathode on right
- Electrons flow from left to right
- Oxidation on left, reduction on right
- Single vertical = electrode/electrolyte boundary
- Double vertical = salt bridge

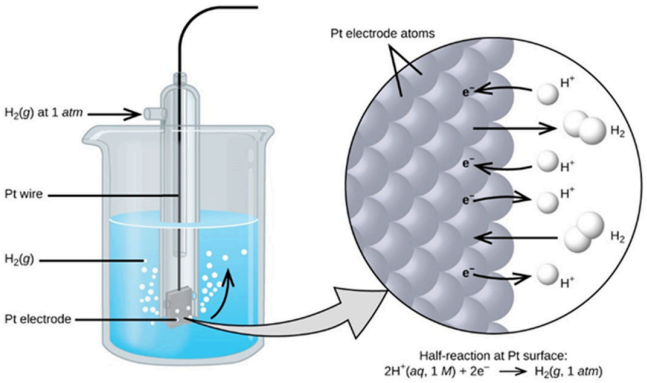


Cell Potential

- The cell potential, E_{cell}, is the measure of the **potential difference between two half cells** in an electrochemical cell. The potential difference is caused by the ability of electrons to flow from one half cell to the other.
- This difference in potential energy is also called an electomotive force (emf) and is measured in terms of volts
- While it is impossible to determine the electrical potential of a single electrode, we can assign an electrode the value of zero and then use it as a reference

Standard Hydrogen Electrode (SHE)

$2H^+(aq,1M)+2e^- \rightleftharpoons H_2\,(g,1atm) \quad E°=0V$



$Pt(s) \mid H_2(g,1atm) \mid H^+(aq,1M) \parallel Cu^{2+}(aq,1M) \mid Cu(s)$

Anode (oxidation):

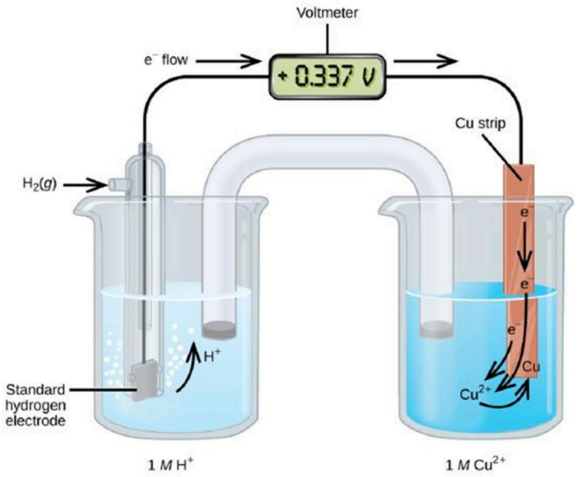
$$H_2(g) \longrightarrow 2H^+(aq)+2e^-$$

Cathode (reduction):

$$Cu^{2+}(aq)+2e^- \longrightarrow Cu(s)$$

Overall:

$Cu^{2+}(aq)+H_2(g) \longrightarrow 2H^+(aq)+Cu(s)$



$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

$$+0.34V = E^o_{Cu^{2+}/Cu} - E^o_{H^+/H_2}$$

$$= E^o_{Cu^{2+}/Cu} - 0$$

$$= E^o_{Cu^{2+}/Cu}$$

Table 16.1 The Standard emf Series

	Electrode Reaction	Standard Electrode Potential, V°(V)
↑ Increasingly inert (cathodic)	$Au^{3+} + 3e^- \rightarrow Au$	+1.420
	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.229
	$Pt^{2+} + 2e^- \rightarrow Pt$	~+1.2
	$Ag^+ + e^- \rightarrow Ag$	+0.800
	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.771
	$O_2 + 2H_2O + 4e^- \rightarrow 4(OH^-)$	+0.401
	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.340
	$2H^+ + 2e^- \rightarrow H_2$	0.000
	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.126
	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.136
	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.250
	$Co^{2+} + 2e^- \rightarrow Co$	−0.277
	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.403
	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.440
Increasingly active (anodic) ↓	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.744
	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.763
	$Al^{3+} + 3e^- \rightarrow Al$	−1.662
	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.363
	$Na^+ + e^- \rightarrow Na$	−2.714
	$K^+ + e^- \rightarrow K$	−2.924

Cell Potential – Free Energy

In galvanic cells, chemical energy is converted into electrical energy, which can do work. The electrical work is the product of the charge transferred multiplied by the potential difference (voltage):

$$\text{Electrical work} = \text{volts} \times (\text{charge in coulombs})$$

The charge on 1 mole of electrons is given by Faraday's constant (F)

$$F = 9.648 \times 10^4\ C\ mol^{-1}$$

Therefore,

$$\text{Total charge} = (\text{number of moles of } e^-) \times F = nF$$

$$E_{cell} = -w_{ele}/nF \text{ or } w_{ele} = -nFE_{cell}$$

$$\Delta G = w_{max} = w_{ele} = -nFE_{cell}$$

Nernst Equation

- The general Nernst equation correlates the Gibb's Free Energy ΔG and the EMF of a chemical system known as the galvanic cell.
- For the reaction

  a A + b B → c C + d D

  reaction quotient,

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

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

$$-nF\Delta E = -nF\Delta E^\circ + RT \ln Q$$

R - gas constant (8.314 J mol^{-1} K^{-1})

T - temperature (in K)

Q - reaction quotient

F - Faraday constant (96485 C mol^{-1})

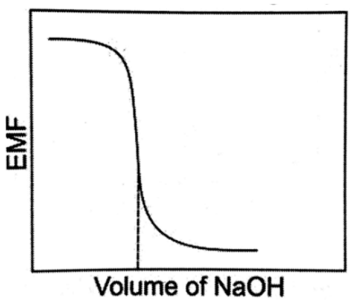
$$\Delta E = \Delta E^o - \frac{RT}{nF} \ln \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

This is known as the **Nernst equation**.

Neutralization reactions

Hydrogen, glass or antimony electrodes are used as indicator electrodes. Calomel –Reference electrode.

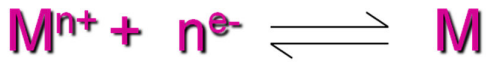
$E = E^o - 0.0591 \log [H^+]$



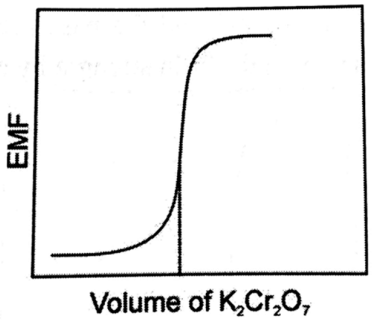
Mixture of acids having different strength like acetic acid and HCl can be titrated. In this case, the first break appears in the curve when the stronger of the two acids is neutralized and the second when neutralization is complete.

Oxidation –reduction reactions

The determining factor in redox reaction is the ratio of the conc. of oxidized and reduced forms of certain ion species.



$E = E^o - RT/nF \ln [O]/[R]$



During the oxidation of a reducing agent or the reduction of an oxidizing agent, the ratio and therefore the potential, changes more rapidly near the end point of the reaction.

Usually a bright Pt electrode is used as an indicator electrode.