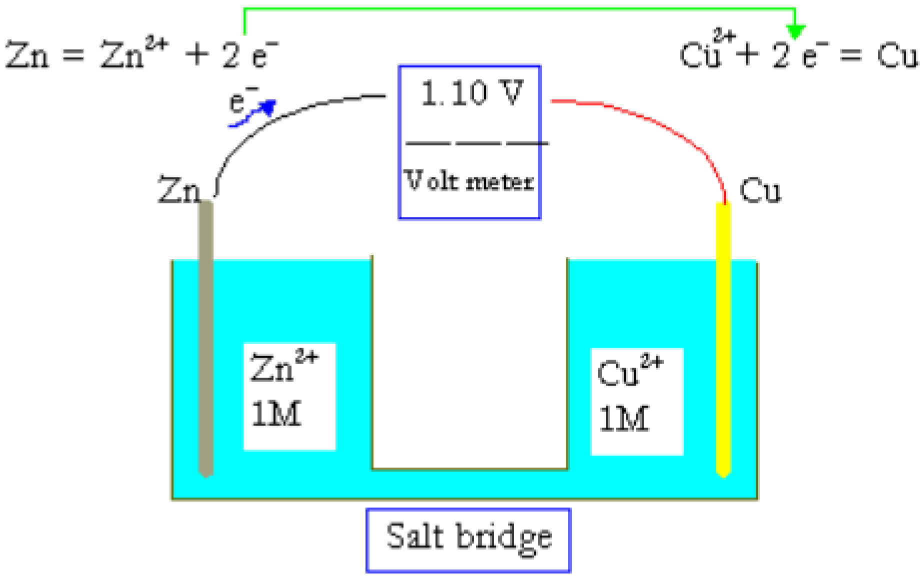
Electromotive Force (EMF)

The electromotive force (EMF) is the maximum potential difference between two electrodes of a galvanic or voltaic cell. This quantity is related to the tendency for an element, a compound or an ion to acquire (i.e. gain) or release (lose) electrons. For example, the maximum potential between Zn and Cu of a well known cell

$$\mathbf{Zn_{(s)}|Zn^{2+}(1M)||Cu^{2+}(1M)|Cu_{(s)}}$$

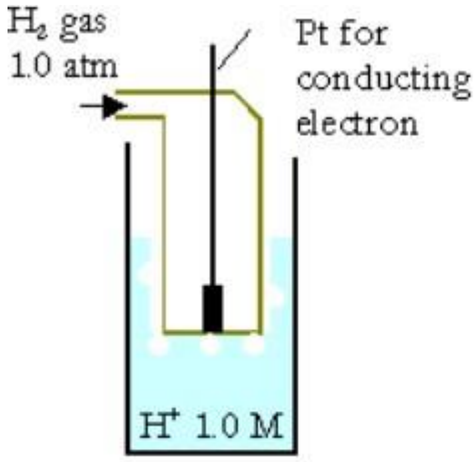
has been measured to be 1.100 V. A concentration of 1 M in an ideal solution is defined as the standard condition, and 1.100 V is thus the standard electromotive force, ΔE^o, or standard cell potential for the Zn−Cu galvanic cell.



The standard cell potential, ΔE^o, of a galvanic cell can be evaluated from the standard reduction potentials of the two half cells E^o. The reduction potentials are measured against the standard hydrogen electrode (SHE):

$$\mathbf{Pt(s)|H_2(g,1.0atm)|H^+(1.0M)}$$

Its reduction potential or oxidation potential is defined to be exactly zero.



Standard Hydrogen Electrode (SHE)

The reduction potentials of all other half-cells measured in volts against the SHE are the difference in electrical potential energy per coulomb of charge.

Note that the unit for energy J = Coulomb volt, and the Gibbs free energy *G* is the product of charge *q* and potential difference *E*:

G in J = *q E* in C V

for electric energy calculations.

Evaluating Standard Cell Potential ΔE° of Galvanic Cells

A galvanic cell consists of two half-cells. The convention in writing such a cell is to put the (reduction) cathode on the right-hand side, and the (oxidation) anode on the left-hand side. For example, the cell

$$Pt|H_2|H^+||Zn^{2+}|Zn$$

consists of the oxidation and reduction reactions:

- **$H_2 \rightarrow 2e^- + 2H^+$ anode (oxidation) reaction**
- **$Zn^{2+} + 2e^- \rightarrow Zn$ cathode (reduction) reaction**

If the concentrations of H^+ and Zn^{2+} ions are 1.0 M and the pressure of H_2 is 1.0 atm, the voltage difference between the two electrodes would be -0.763 V (the Zn electrode being the negative electrode). The conditions specified above are called the standard conditions and the EMF so obtained is the standard reduction potential.

Note that the above cell is in reverse order compared to that given in many textbooks, but this arrangement gives the standard reduction potentials directly, because the Zn half cell is a reduction half-cell. The negative voltage indicates that the reverse chemical reaction is spontaneous. This corresponds to the fact that Zn metal reacts with an acid to produce H_2 gas.

As another example, the cell

$$Pt|H_2|H^+||Cu^+|Cu$$

consists of an oxidation and a reduction reaction:

- $H_2 \rightarrow 2e^- + 2H^+$ anode reaction
- $Cu^{2+} + 2e^- \rightarrow Cu$ cathode reaction

and the standard cell potential is 0.337 V. The positive potential indicates a spontaneous reaction,

$$Cu^{2+} + H_2 \rightarrow Cu + 2H+$$

but the potential is so small that the reaction is too slow to be observed.