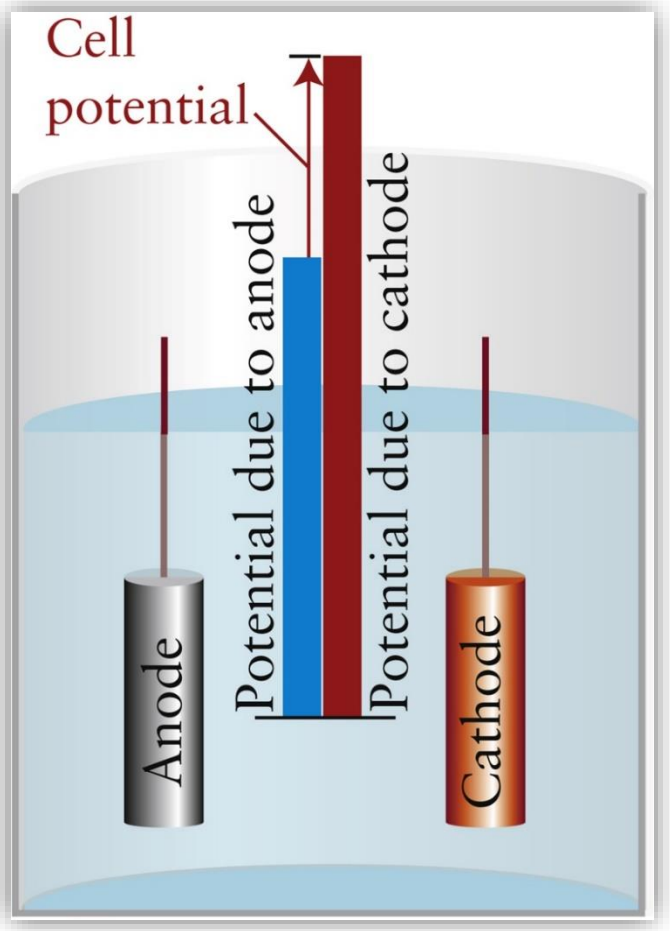
Topic 6M. Standard Potentials

6M.1 The Definition of Standard Potential

6M.2 The Electrochemical Series

The Definition of Standard Potential

- Standard potential
  - Each half-cell's characteristic contribution to the cell potential under standard conditions (all solutes present at 1 mol•L^{-1}; all gases at 1 bar)
  - A measure of the electron-pulling power of the reaction occurring at the electrode.
- In a galvanic cell, the reactions at each electrode pull in opposite directions.



The Definition of Standard Potential

- The cell's standard potential, E_{cell}°, is the difference between the standard potentials of the two electrodes.

$$E_{cell}^{\circ} = E^{\circ}(\text{electrode on right of cell diagram}) - E^{\circ}(\text{electrode on left})$$
$$= E_R^{\circ} - E_L^{\circ}$$

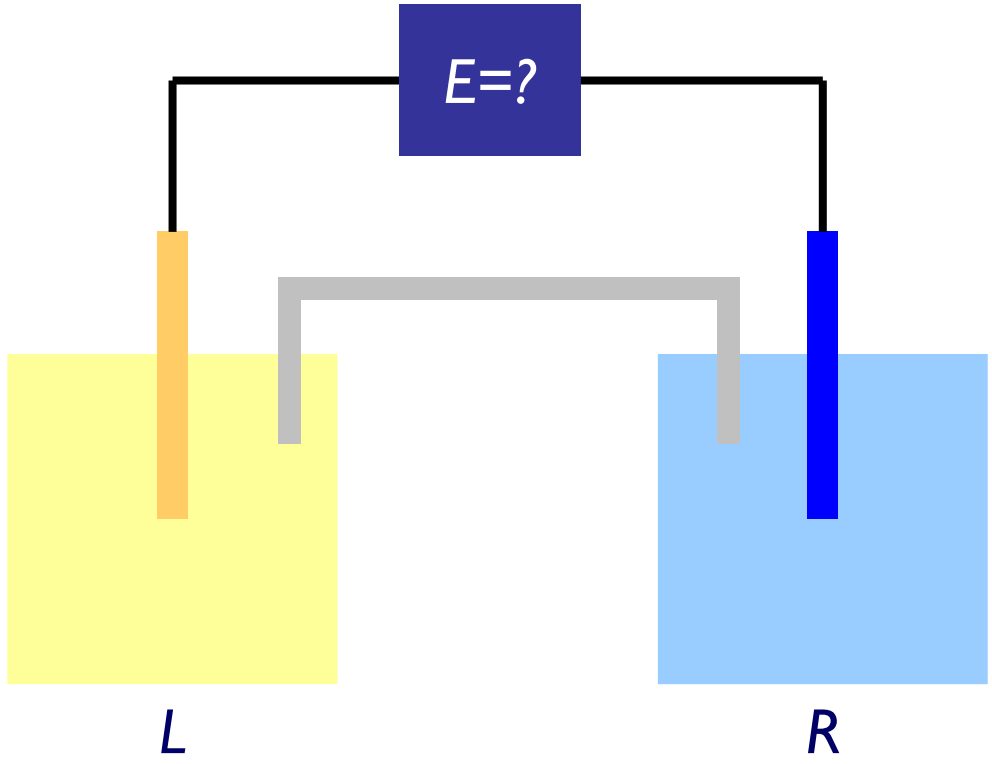
- $Fe(s)|Fe^{2+}(aq)||Ag^{+}(aq)|Ag(s)$

$$2\,Ag^{+}\,(aq) + Fe\,(s) \rightarrow 2\,Ag\,(s) + Fe^{2+}\,(aq)$$

$$E_{cell}^{\circ} = E^{\circ}(Ag^{+}/Ag) - E^{\circ}(Fe^{2+}/Fe) = 1.24\,V$$

The Definition of Standard Potential

- For a combination of an anode and a cathode, how much voltage difference (E) is generated? ($E = E_R^\circ - E_L^\circ$)
- Then, how can we determine E_R° and E_L° separately?
- Need a reference electrode!



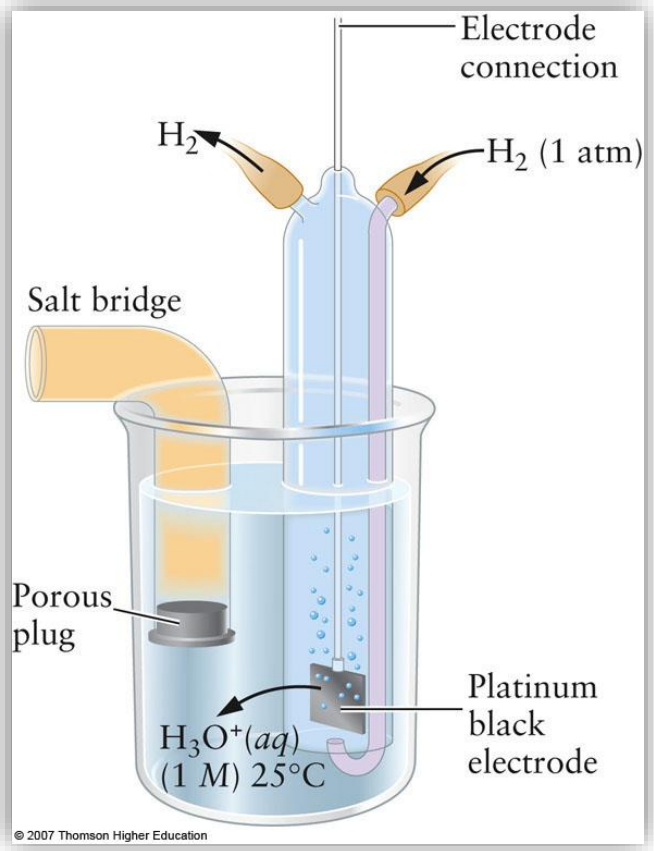
The Definition of Standard Potential

- Standard hydrogen electrode

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

  $E°(H^+/H_2) = 0$ at all temperatures, where

  $[H^+] = 1\ mol \cdot L^{-1}$ and $pH_2 = 1\ atm$



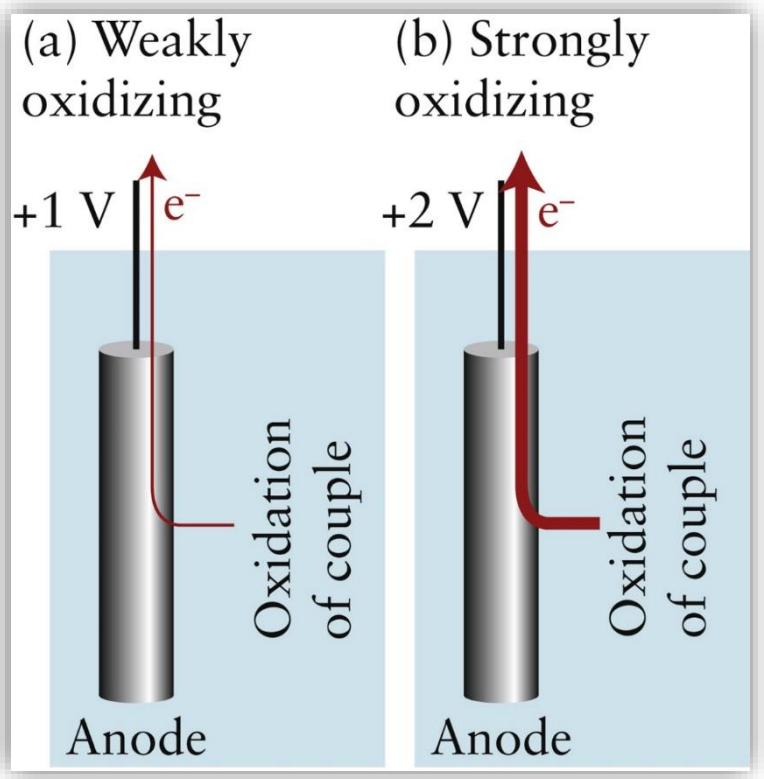
The Definition of Standard Potential

- $Pt(s)|H_2(g)|H^+(aq)||Cu^{2+}(aq)|Cu(s)$

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

  $E°(Cu^{2+}/Cu) = +\,0.34\,V$

- The more positive the standard potential, the more strongly oxidizing is the oxidizing member of the redox couple and the more likely that member will be to undergo reduction itself.



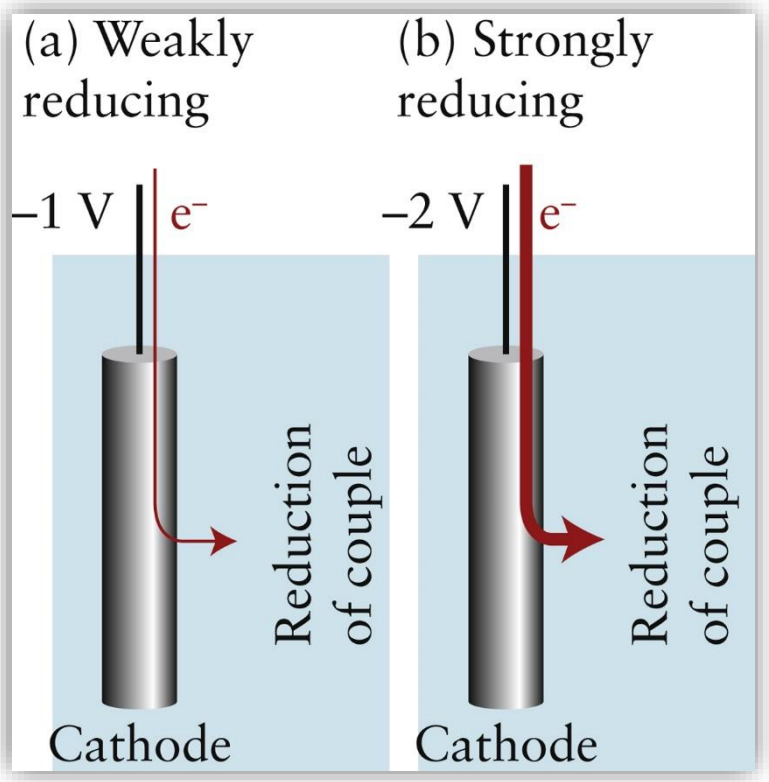
The Definition of Standard Potential

- $Pt(s)|H_2(g)|H^+(aq)||Zn^{2+}(aq)|Zn(s)$

  $Zn^{2+}\ (aq) + H_2\ (g) \rightarrow Zn\ (s) + 2\ H_2\ (aq)$

  $E°(Zn^{2+}/Zn) = -0.76\,V$

- The more negative the potential, the more strongly reducing is the redox couple.



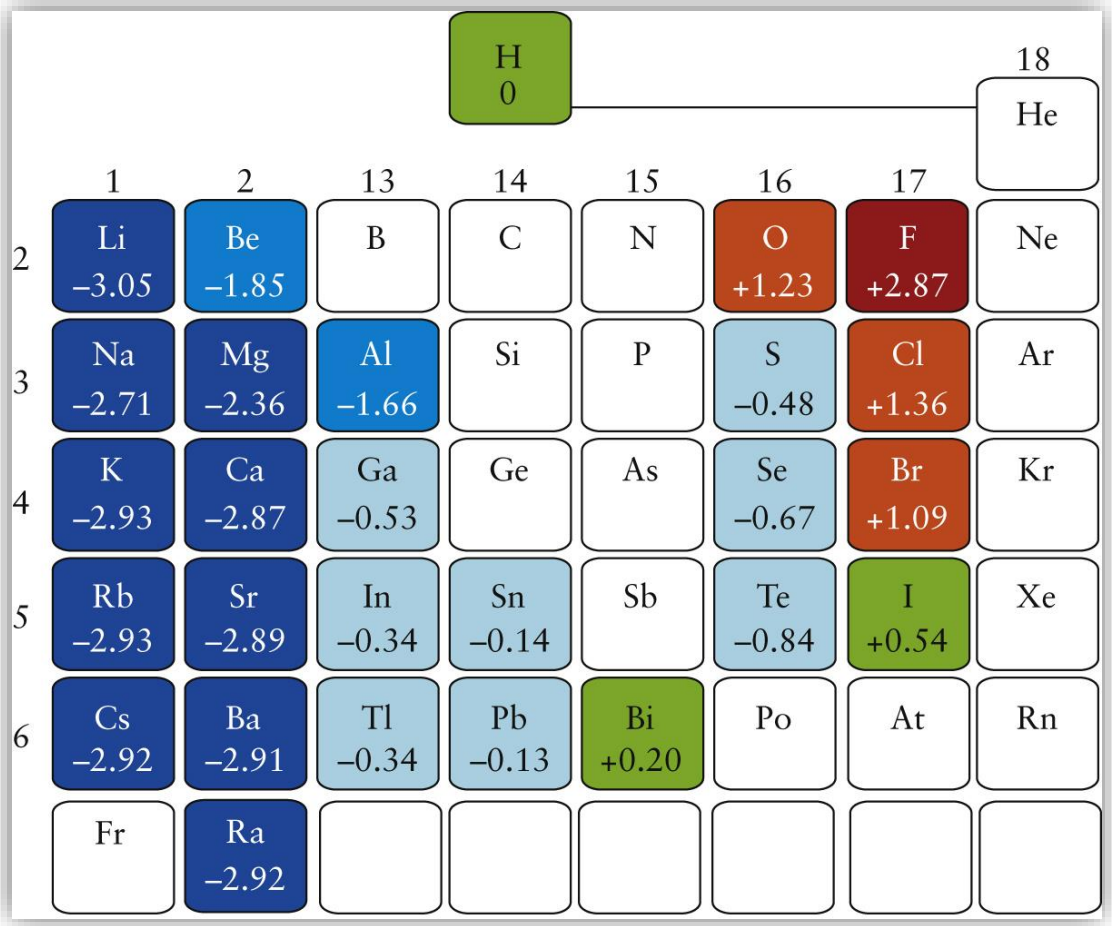
The Definition of Standard Potential

TABLE 6M.1 Standard Potentials at 25 °C*

Species	Reduction half-reaction	$E°$/V
Oxidized form is strongly oxidizing		
F_2/F^-	$F_2(g) + 2\,e^- \longrightarrow 2\,F^-(aq)$	+2.87
Au^+/Au	$Au^+(aq) + e^- \longrightarrow Au(s)$	+1.69
Ce^{4+}/Ce^{3+}	$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-,H^+/Mn^{2+},H_2O$	$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O\,(l)$	+1.51
Cl_2/Cl^-	$Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(aq)$	+1.36
$Cr_2O_7^{2-},H^+/Cr^{3+},H_2O$	$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$	+1.33
$O_2,H^+/H_2O$	$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$	+1.23; +0.82 at pH = 7
Br_2/Br^-	$Br_2(l) + 2\,e^- \longrightarrow 2\,Br^-(aq)$	+1.09
$NO_3^-,H^+/NO,H_2O$	$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^- \longrightarrow NO(g) + 2\,H_2O(l)$	+0.96
Ag^+/Ag	$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
Fe^{3+}/Fe^{2+}	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
I_2/I^-	$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq)$	+0.54
$O_2,H_2O/OH^-$	$O_2(g) + 2\,H_2O(l) + 4\,e^- \longrightarrow 4\,OH^-(aq)$	+0.40; +0.82 at pH = 7
Cu^{2+}/Cu	$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$	+0.34
$AgCl/Ag,Cl^-$	$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
H^+/H_2	$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$	0, by definition
Fe^{3+}/Fe	$Fe^{3+}(aq) + 3\,e^- \longrightarrow Fe(s)$	−0.04
$O_2,H_2O/HO_2^-,OH^-$	$O_2(g) + H_2O(l) + 2\,e^- \longrightarrow HO_2^-(aq) + OH^-(aq)$	−0.08
Pb^{2+}/Pb	$Pb^{2+}(aq) + 2\,e^- \longrightarrow Pb(s)$	−0.13
Sn^{2+}/Sn	$Sn^{2+}(aq) + 2\,e^- \longrightarrow Sn(s)$	−0.14
Fe^{2+}/Fe	$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$	−0.44
Zn^{2+}/Zn	$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$	−0.76
$H_2O/H_2,OH^-$	$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq)$	−0.83; −0.42 at pH = 7
Al^{3+}/Al	$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$	−1.66
Mg^{2+}/Mg	$Mg^{2+}(aq) + 2\,e^- \longrightarrow Mg(s)$	−2.36
Na^+/Na	$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
K^+/K	$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
Li^+/Li	$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05
Reduced form is strongly reducing		

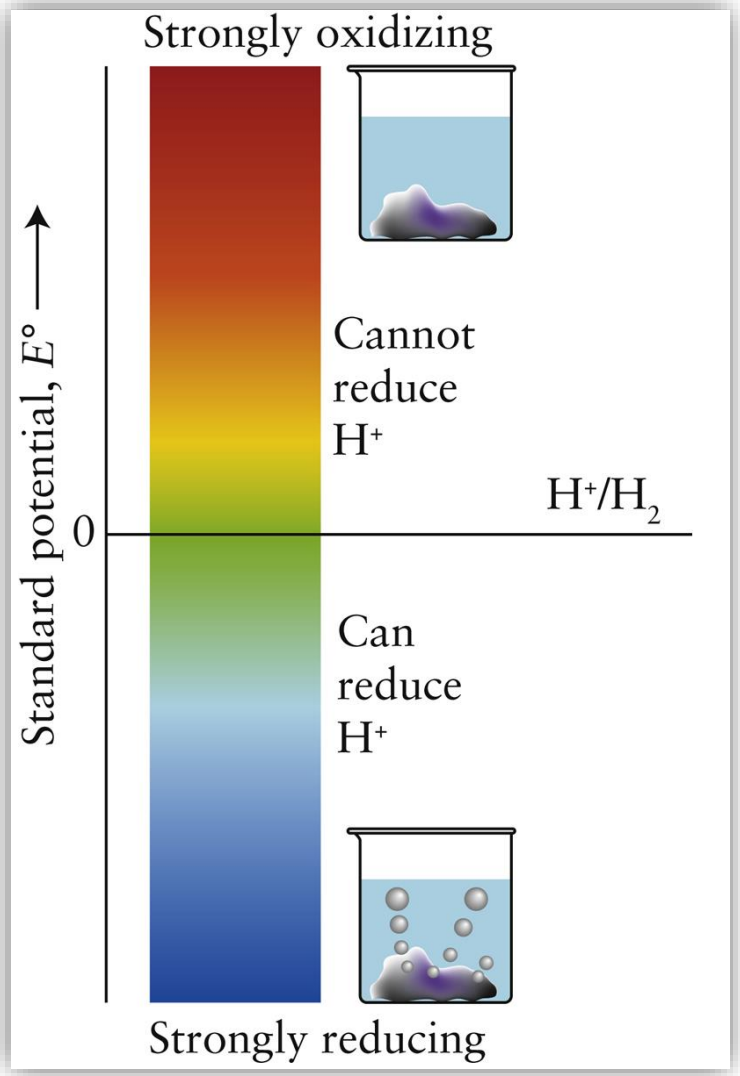
*For a more extensive table, see Appendix 2B.

The Definition of Standard Potential



The Electrochemical Series

- $E°(X^+/X) > 0$: favors reduction : $X^+ + e^- \rightarrow X$
- $E°(X^+/X) < 0$: favors oxidation : $X^+ + e^- \leftarrow X$



The Electrochemical Series

- For a given Galvanic cell, $X|X^+||Y^+|Y$
  Cell voltage = $E°(Y^+/Y) - E°(X^+/X)$

If $E°(Y^+/Y) > E°(X^+/X)$,

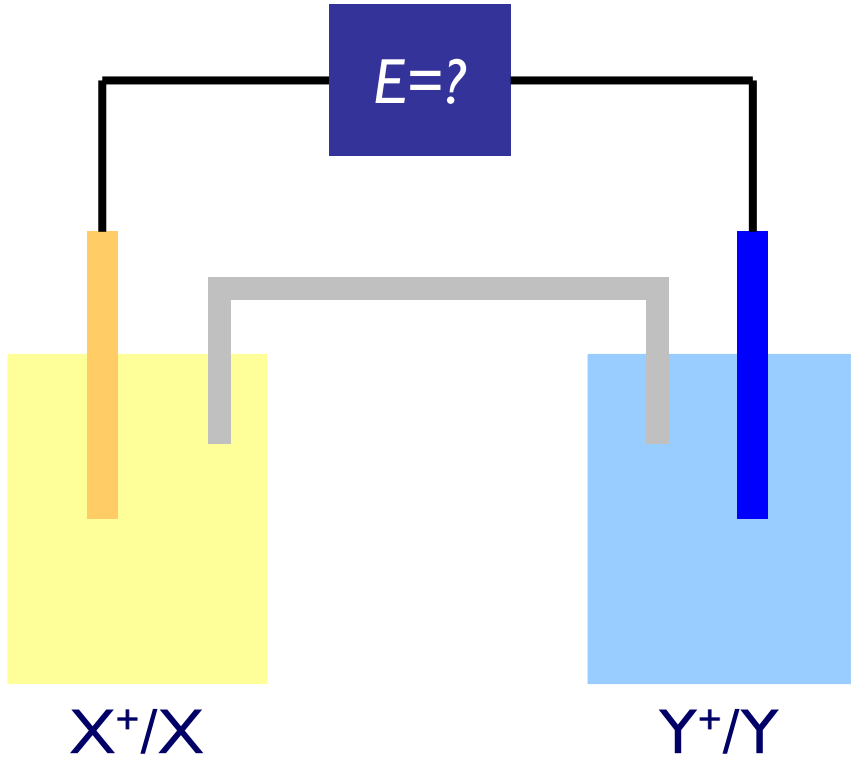
Y^+ will be reduced

$X + Y^+ \rightarrow X^+ + Y$

If $E°(Y^+/Y) < E°(X^+/X)$,

X^+ will be reduced

$Y + X^+ \rightarrow Y^+ + X$



The Electrochemical Series

- $Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$

$E°(Zn^{2+}/Zn) = -0.76\,V$

$E°(Cu^{2+}/Cu) = 0.34\,V$

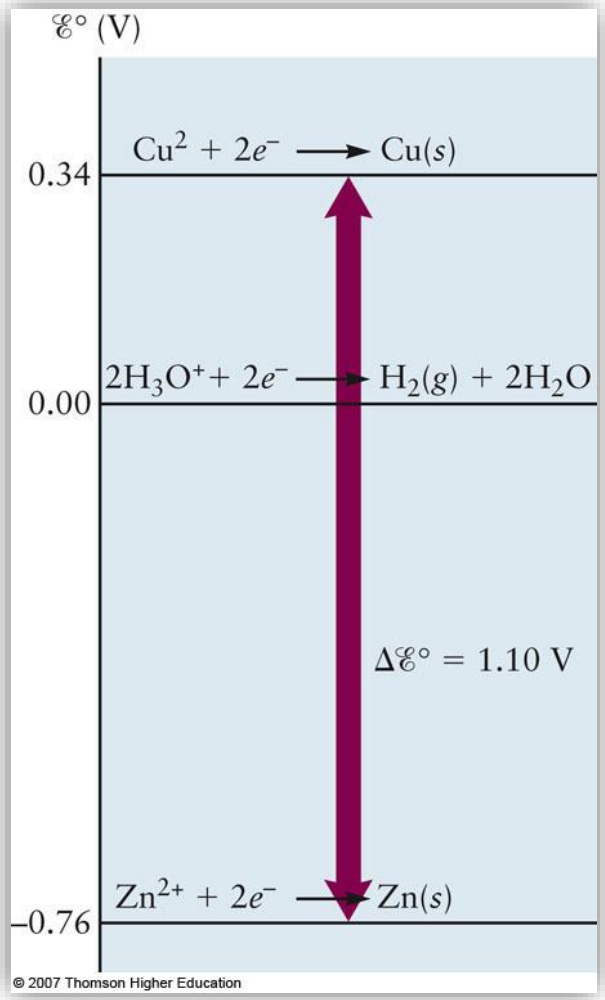
$E°_{cell} = E°(Cu^{2+}/Cu) - E°(Zn^{2+}/Zn)$

$= 0.34 - (-0.76) = 1.11$ volts

Cu^{2+} will be reduced and oxidize Zn

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

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



The Electrochemical Series

- Can $E°(Ce^{4+}/Ce)$ be calculated from $E°(Ce^{3+}/Ce)$ and $E°(Ce^{4+}/Ce^{3+})$?
  - Find $E°$ values for the related half-reactions.
  - Convert $E°$ values to $\Delta G°$.
  - Combine the half-reactions and determine $\Delta G°$ for the desired reaction.
  - Convert $\Delta G°$ into $E_{cell}°$ for the desired reaction.

Topic 6N. Applications of Standard Potentials

6N.1 Standard Potentials and Equilibrium Constants

6N.2 The Nernst Equation

6N.3 Ion-Selective Electrodes

6N.4 Corrosion

Standard Potentials and Equilibrium Constants

- Standard potentials and equilibrium constants

$$\Delta G_r^\circ = -RT\ln K$$

$$\Delta G_r^\circ = -n_r F E_{cell}^\circ$$

$$n_r F E_{cell}^\circ = RT\ln K$$

$$\rightarrow \ln K = n_r F E_{cell}^\circ / RT$$

  - A large positive E_{cell}° has $K >> 1$
  - A large negative E_{cell}° has $K << 1$

The Nernst Equation

- Nernst equation

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

$$-n_r F E_{cell} = -n_r F E_{cell}^\circ + RT\ln Q$$

$$E_{cell} = E_{cell}^\circ - \frac{RT}{n_r F}\ln Q$$

$$E_{cell} = E_{cell}^\circ - \frac{0.025\,693\ \text{V}}{n_r}\ln Q$$

$$E_{cell} = E_{cell}^\circ - \frac{RT\ln 10}{n_r F}\log Q = E_{cell}^\circ - \frac{0.059\,160\ \text{V}}{n_r}\log Q$$

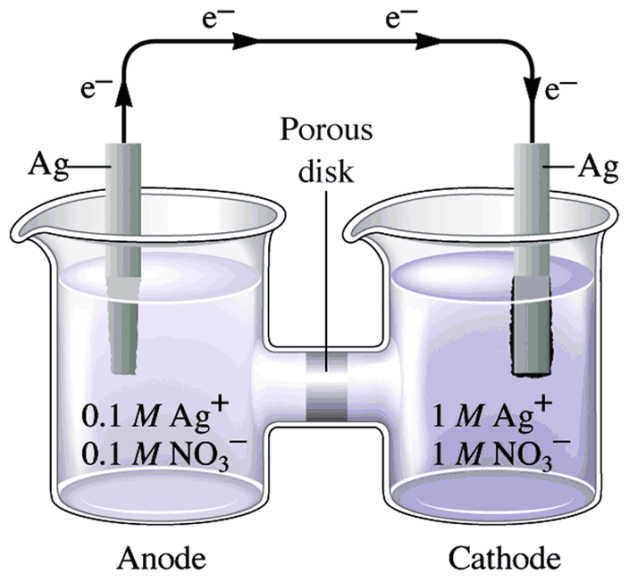
The Nernst Equation

- Concentration cell: a cell in which both compartments have the same components but at different concentrations.
  - $Ag(s)|Ag^+(aq,L)||Ag^+(aq,R)|Ag(s)$ $\quad Ag^+(aq,R) \rightarrow Ag^+(aq,l)$

$$E_{cell} = E_{cell}^\circ - (0.025\,693\,V/n_R) \times \ln Q = -(0.025\,693\,V/n_R) \times \ln Q$$

$$Q = [Ag^+]_L/[Ag^+]_R = [Ag^+]_L \text{ with } [Ag^+]_R = 1\ mol \cdot L^{-1}$$

$$E_{cell} = -(0.025\,693\,V/n_R) \times \ln[Ag^+]_L$$



Ion-Selective Electrodes

- Ion-selective electrode: an electrode sensitive to the concentration of a particular ion
- pH meter: one electrode is sensitive to the H_3O^+ concentration and another electrode with a fixed potential serves as a reference.

Ion-Selective Electrodes

- In case the calomel electrode is used as a reference for pH meter

$$Hg_2Cl_2\,(s) + 2\,e^- \rightarrow 2\,Hg\,(l) + 2\,Cl^-\,(aq) \qquad E° = 0.27\,V$$

$$Hg_2Cl_2(s) + H_2(g) \longrightarrow 2\,H^+(aq) + 2\,Hg(l) + 2\,Cl^-(aq) \qquad Q = \frac{[H^+]^2[Cl^-]^2}{P_{H_2}}$$

$$E_{cell} = E_{cell}° - \frac{RT}{2F}\ln([H^+]^2[Cl^-]^2)$$

$$E_{cell} = \overbrace{E_{cell}° - \frac{RT}{F}\ln[Cl^-]}^{E_{cell}'} - \frac{RT}{F}\ln[H^+]$$

$$E_{cell} = E_{cell}' - \frac{RT}{F}\ln 10 \times \overbrace{\log[H^+]}^{-pH}$$

$$= E_{cell}' + (0.0592\,V) \times pH$$

Corrosion

- Corrosion: unwanted oxidation of a metal

  $2\ H_2O\ (l) + 2\ e^- \rightarrow H_2\ (g) + 2\ OH^-\ (aq)$

  $E° = -0.83\,V$ at pH = 14 → $-0.42\,V$ at pH = 7

  - Any metal with a standard potential more negative than $-0.42\,V$ can reduce water at pH = 7 while itself is oxidized.

Corrosion

- Corrosion of iron

$$O_2\,(g) + 4\,H^+\,(aq) + 4\,e^- \rightarrow 2\,H_2O\,(l)$$

$E°$ = + 1.23 V at pH = 0 → + 0.81 V at pH = 7

$$2\,Fe(s) \longrightarrow 2\,Fe^{2+}(aq) + 4\,e^-$$

$$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$$

$$\text{Overall: } 2\,Fe(s) + O_2(g) + 4\,H^+(aq) \longrightarrow 2\,Fe^{2+}(aq) + 2\,H_2O(l)$$

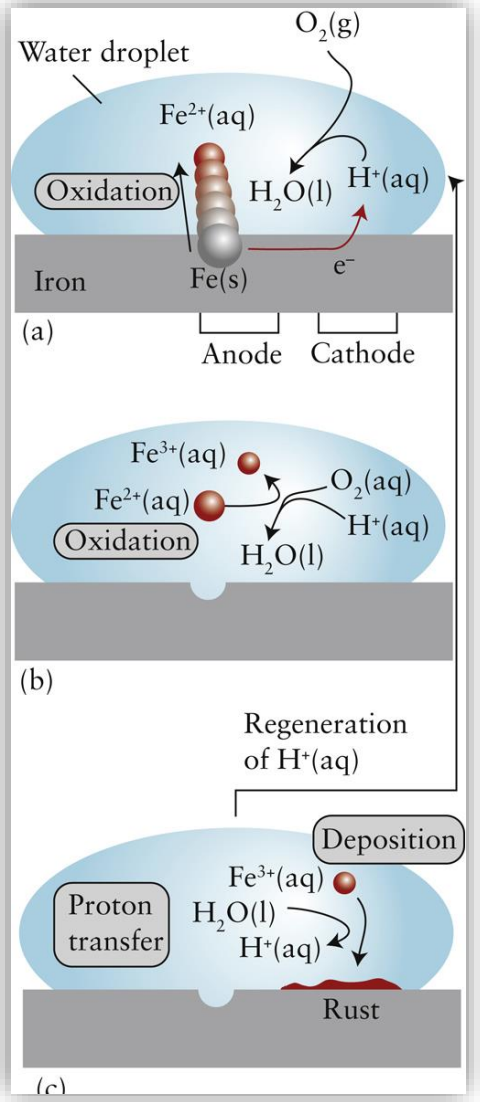
$$2\,Fe^{2+}(aq) \longrightarrow 2\,Fe^{3+}(aq) + 2\,e^-$$

$$\tfrac{1}{2}\,O_2(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow 2\,H_2O(l)$$

$$\text{Overall: } 2\,Fe^{2+}(aq) + \tfrac{1}{2}\,O_2(g) + 2\,H^+(aq) \longrightarrow 2\,Fe^{3+}(aq) + H_2O(l)$$

$$4\,H_2O(l) + 2\,Fe^{3+}(aq) \longrightarrow 6\,H^+(aq) + Fe_2O_3{\cdot}H_2O(s)$$

$$2\,Fe(s) + \tfrac{3}{2}\,O_2(g) + H_2O(l) \longrightarrow Fe_2O_3{\cdot}H_2O(s)$$



Corrosion

- Preventing corrosion
  - Galvanization of metal with Zn

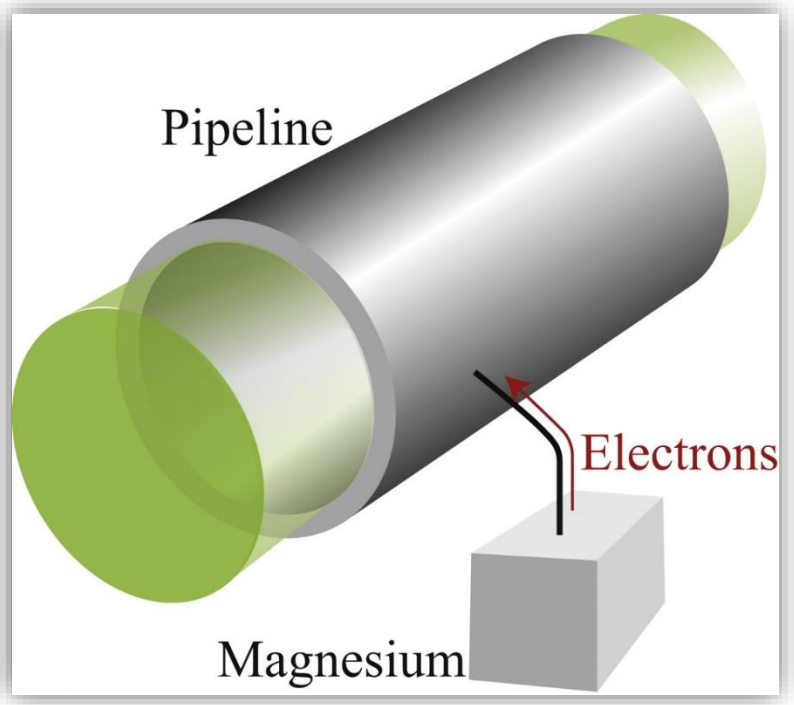
$Zn^{2+} + 2\ e^- \rightarrow Zn : E° = -0.76\,V$

$Fe^{2+} + 2\ e^- \rightarrow Fe : E° = -0.44\,V$

Zinc corrodes sacrificially: Zinc oxidizes before iron can be oxidized, and hence protects the Iron.

Corrosion

- Preventing corrosion
  - Cathodic protection: the electrochemical protection of a metal object by connecting it to a more strongly reducing metal



Topic 6O. Electrolysis

6O.1 Electrolytic Cells

6O.2 The Products of Electrolysis

6O.3 Applications of Electrolysis

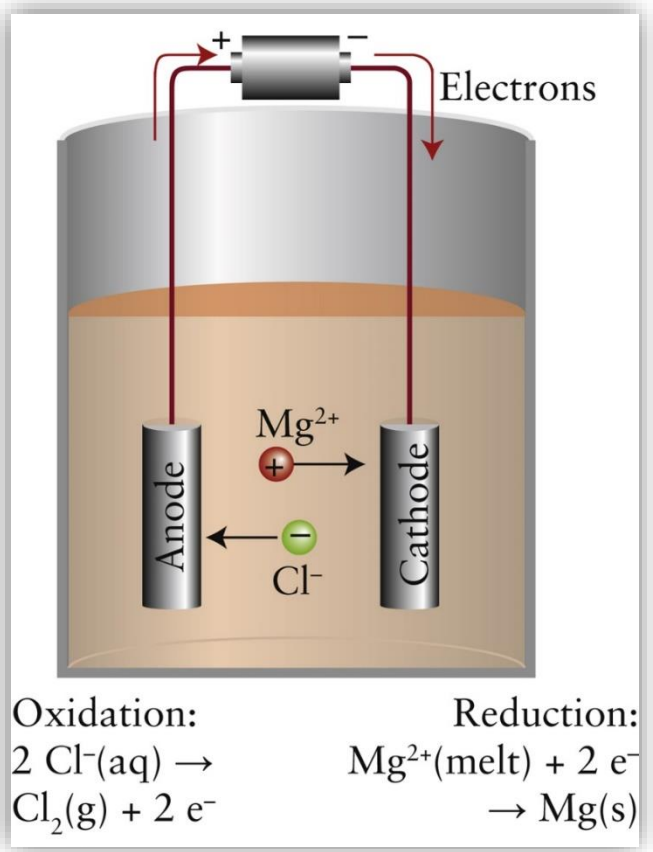
Electrolytic Cells

- Electrolytic cell: an electrochemical cell in which electrolysis takes place
  - Unlike a galvanic cell, in an electrolytic cell a current must be supplied by an external electrical power source for reaction to occur.
  - Mg production by the Dow process

    Anode reaction: $2\ Cl^-\ (melt) \rightarrow Cl_2\ (g) + 2\ e^-$

    Cathode reaction: $Mg^{2+}\ (melt) + 2\ e^- \rightarrow Mg(l)$
  - A rechargeable battery

    Functions as a galvanic cell when it is doing work (discharge) and as an electrolytic cell when it is being charged.



Electrolytic Cells

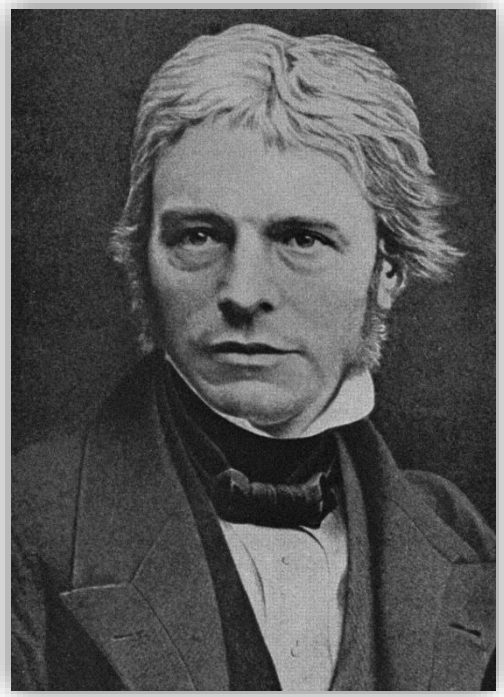
- Water electrolysis

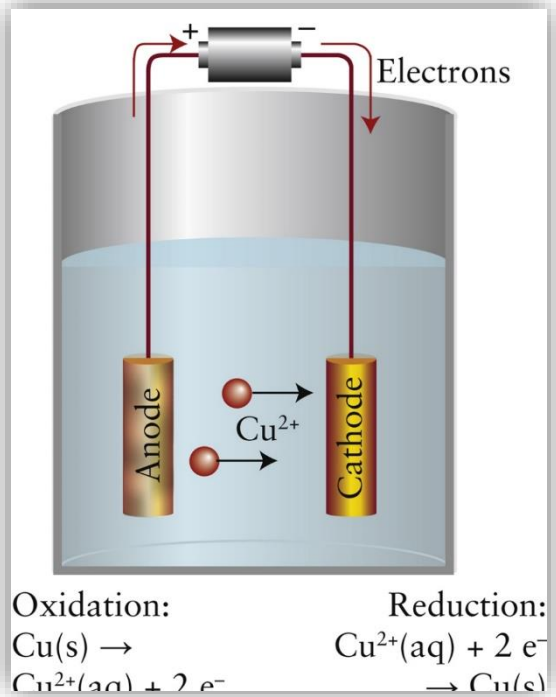
  $2\ H_2O\ (l) \rightarrow 2\ H_2\ (g) + O_2\ (g)$ $\quad E^\circ = -1.23\,V$ at pH = 7

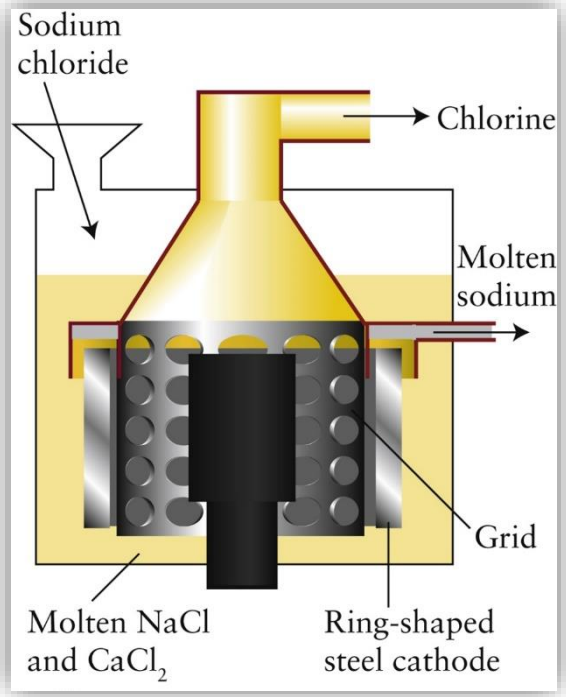
- In practice, the applied potential difference must usually be substantially greater than the cell potential to achieve a significant rate of product formation.
- Overpotential: the additional potential difference

The Products of Electrolysis

- Faraday's law of electrolysis: the amount of product formed or reactant consumed by an electric current is stoichiometrically equivalent to the amount of electrons supplied.





Applications of Electrolysis

- Electrolysis is used industrially to extract metals from their salts; to prepare chlorine, fluorine, and sodium hydroxide; to refine copper; and in electroplating.