Overview of Chapter 20

Electrochemistry

- Oxidation/Reduction (Redox) Reactions
- Electrochemical Cells
- E° and E
- E° and K
- E° and ΔG

Today's Topics:

- Voltage at non standard conditions
- Voltage and ΔG
- Voltage and K_{eq}

Table 20.1 Standard Reduction Potentials in Aqueous Solution at 25 °C*

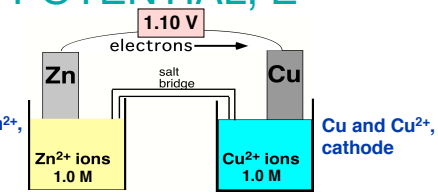
Reduction Half-Reaction		$E°$ (V)
$F_2(g) + 2e^-$	$\longrightarrow 2F^-(aq)$	+2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	+1.77
$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$	$\longrightarrow PbSO_4(s) + 2H_2O(l)$	+1.685
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Au^3^+(aq) + 3e^-$	$\longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	+1.229
$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	+1.08
$NO_3^-(aq) + 4H^+(aq) + 3e^-$	$\longrightarrow NO(g) + 2H_2O(l)$	+0.96
$OCl^-(aq) + H_2O(l) + 2e^-$	$\longrightarrow Cl^-(aq) + 2OH^-(aq)$	+0.89
$Hg^{2+}(aq) + 2e^-$	$\longrightarrow Hg(l)$	+0.855
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	+0.799
$Hg_2^{2+}(aq) + 2e^-$	$\longrightarrow 2Hg(l)$	+0.789
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	+0.771
$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	+0.535
$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	+0.337
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	+0.15
$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0.00
$Sn^{2+}(aq) + 2e^-$	$\longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.25
$V^{3+}(aq) + e^-$	$\longrightarrow V^{2+}(aq)$	−0.255
$PbSO_4(s) + 2e^-$	$\longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.356
$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.44
$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.763
$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.8277
$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.714
$K^+(aq) + e^-$	$\longrightarrow K(s)$	−2.925
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.045

Increasing strength of oxidizing agents

Increasing strength of reducing agents

* In volts (V) versus the standard hydrogen electrode.

CELL POTENTIAL, E

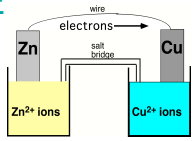


Cu^{2+} (1 M) + 2e- ⇆ Cu (s)
Zn (s) + 2e- ⇆ Zn^{2+} (1 M)

Cu^{2+} + Zn ⇆ Cu (s) + Zn^{2+}

$E°_{cell} = E°_{cathode} - E°_{anode}$
$E°_{cathode} = 0.34V$
$E°_{anode} = -0.76V$
$E°_{cell} = 0.34V - (-0.76V) = 1.10V$

CELL POTENTIAL, E



- E is the cell potential, measured in Volts (V)
- Under standard conditions (25°C, 1M conc, 1atm P) we have the STANDARD CELL POTENTIAL, E°
- At non standard concentrations, we can calculate the voltage from the Nernst equation

E = E° - (0.0257/n) ln Q at 25°C

Q = reaction quotient for reaction
n = number of moles of electrons transferred

Table of Standard Reduction Potentials

oxidizing ability of ion

	E° (V)
Cu^{2+} + 2e- → Cu	+0.34
2 H^+ + 2e- → H	0.00
Zn^{2+} + 2e- → Zn	-0.76

reducing ability of element

Standard Redox Potentials, E^o

Any substance on the right will reduce any substance higher than it on the left.

- Zn can reduce H^+ and Cu^{2+}.
- H_2 can reduce Cu^{2+} but not Zn^{2+}
- Cu cannot reduce H^+ or Zn^{2+}.

oxidizing ability of ion

	E^o (V)
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$2H^+ + 2e^- \rightarrow H_2$	0.00
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76

reducing ability of element

Using Standard Potentials, E^o

- Which is the best oxidizing agent:

  O_2, H_2O_2, or Cl_2?

  _____

- Which is the best reducing agent:

  Hg, Al, or Sn?

  _____

E° and Thermodynamics

E° is related to ΔG°:

$$\Delta G^o = -nFE^o$$

n is the number of moles of electrons transferred

F = Faraday constant

$F = 9.6485 \times 10^4$ coulombs/mol

$= 9.6485 \times 10^4$ J/V•mol of e^-

Units of electricity:

1 coulomb (C) is the charge on a mole of electrons

1 Joule = 1 Coulomb x 1 Volt

1 Ampere (A) = 1 Coulomb/sec

E^o and ΔG^o

$\Delta G^o = -nFE^o$

For a product-favored reaction

Reactants ----> Products

$\Delta G^o < 0$ and so $E^o > 0$

E^o is positive

For a reactant-favored reaction

Reactants <---- Products

$\Delta G^o > 0$ and so $E^o < 0$

E^o is negative