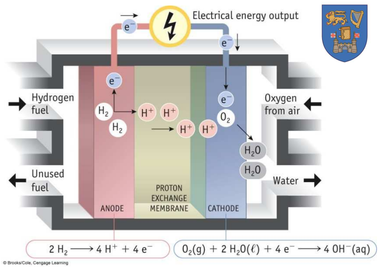

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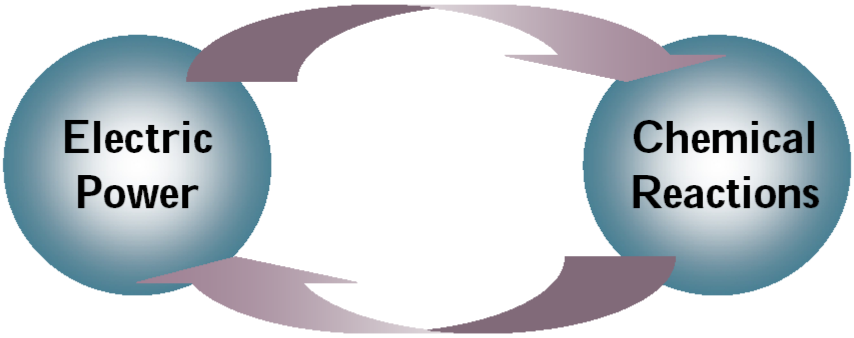
Lecture 13

Thermodynamics of Galvanic (Voltaic) Cells.

Electric power conversion in electrochemistry

Electrolysis / Power consumption

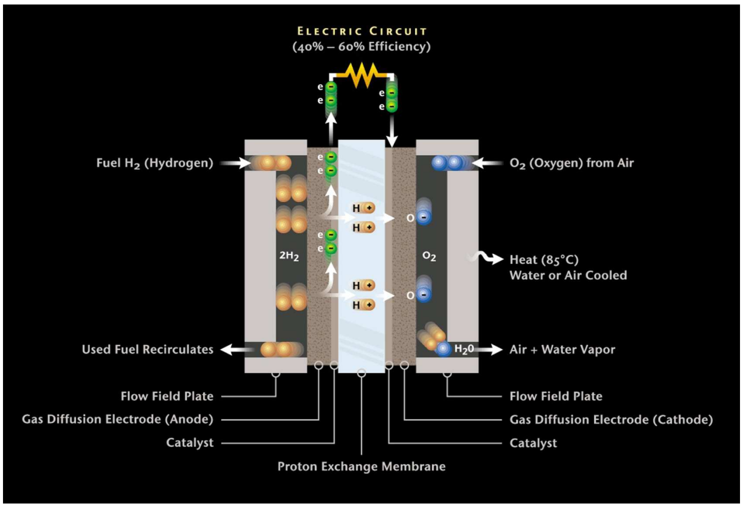


Electric Power

Chemical Reactions

Electrochemical battery / Power generation

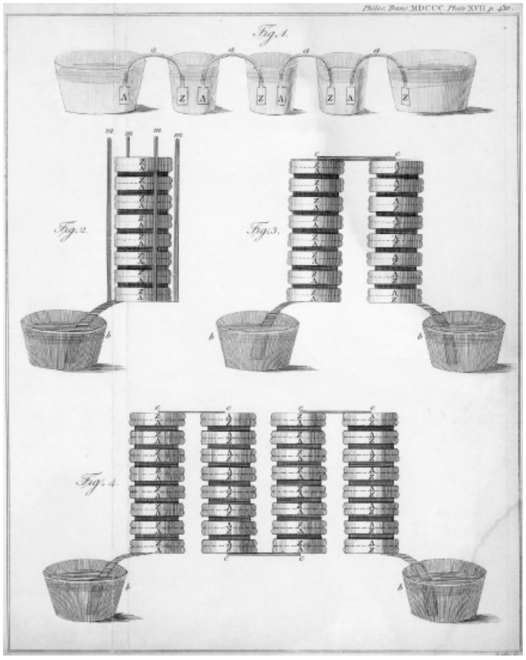
Ballard PEM Fuel Cell.



Electrochemistry

Alessandro Volta, 1745-1827, Italian scientist and inventor.

Luigi Galvani, 1737-1798, Italian scientist and inventor.



The Voltaic Pile

Drawing done by Volta to show the arrangement of silver and zinc disks to generate an electric current.

What voltage does a cell generate?

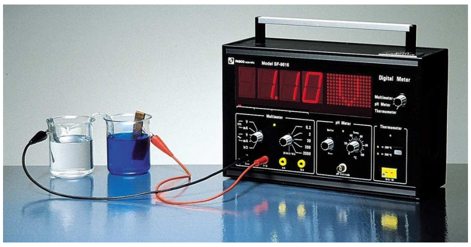
Operation of a Galvanic cell.

- In a Galvanic cell a spontaneous cell reaction produces electricity.
- Galvanic cells form the basis of energy storage and energy conversion devices (battery systems and fuel cells).
- Electrons leave a Galvanic cell at the anode (negative electrode), travel through the external circuit, and re-enter the cell at the cathode (positive electrode). The circuit is completed inside the cell by the electro-migration of ions through the salt bridge.
- We need to answer the following questions regarding Galvanic cells.
  - Can we devise a quantitative measure for the tendency of a specific redox couple to undergo oxidation or reduction?
  - Is the net cell reaction energetically feasible?
  - Can we compute useful thermodynamic quantities such as the change in Gibbs energy ΔG or the equilibrium constant for the cell reaction ?
  - The answer is yes to all of these questions.
  - We now discuss the thermodynamics of Galvanic cells.

Electrochemical Cells

The difference in electrical potential between the anode and cathode is called:

- **cell voltage**
- **electromotive force (emf)**
- **cell potential**



Cell Diagram

$\mathrm{Zn}\ (s) + \mathrm{Cu}^{2+}\ (aq) \longrightarrow \mathrm{Cu}\ (s) + \mathrm{Zn}^{2+}\ (aq)$

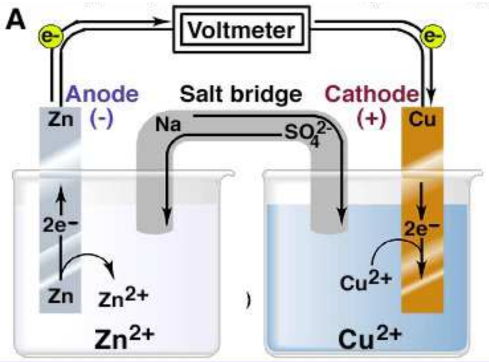
$[\mathrm{Cu}^{2+}] = 1\ M$ & $[\mathrm{Zn}^{2+}] = 1\ M$

$\mathrm{Zn}\ (s) \mid \mathrm{Zn}^{2+}\ (1\ M) \parallel \mathrm{Cu}^{2+}\ (1\ M) \mid \mathrm{Cu}\ (s)$

anode cathode

19.2

Galvanic cell movie.



Oxidation half-reaction
$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

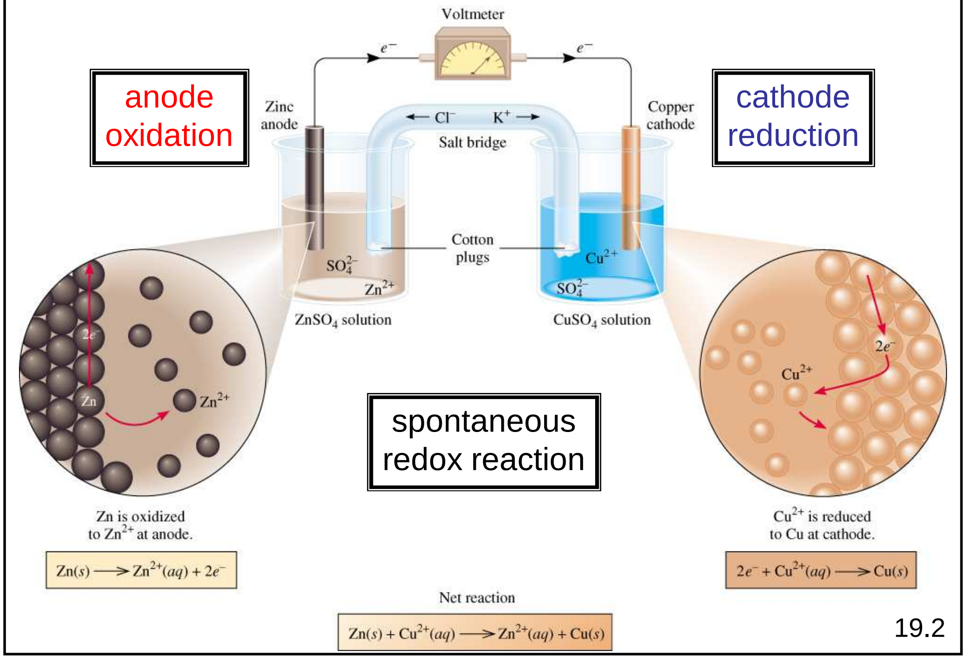
Reduction half-reaction
$2e^- + Cu^{2+}(aq) \longrightarrow Cu(s)$

Overall (cell) reaction
$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

© McGraw-Hill Higher Education/Stephen Frisch, photographer

A Voltaic Cell Based on the Zinc-Copper Reaction

Electrochemical Cells



anode
oxidation

cathode
reduction

spontaneous
redox reaction

Zn is oxidized to Zn^{2+} at anode.

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

Cu^{2+} is reduced to Cu at cathode.

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

Net reaction

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

Electron flow in a Galvanic Cell.

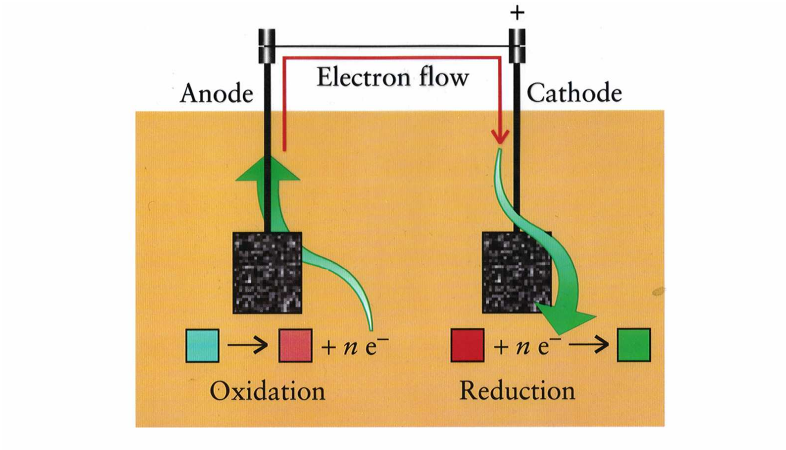


Figure 18.9
Loretta Jones and Peter Atkins, CHEMISTRY: MOLECULES, MATTER, AND CHANGE, Fourth Edition

T173

Notation for a Voltaic Cell

components of anode compartment

(oxidation half-cell)

components of cathode compartment

(reduction half-cell)

phase of lower oxidation state | phase of higher oxidation state || phase of higher oxidation state | phase of lower oxidation state

phase boundary between half-cells

Examples: Zn(*s*) | Zn^{2+}(*aq*) || Cu^{2+}(*aq*) | Cu (*s*)

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

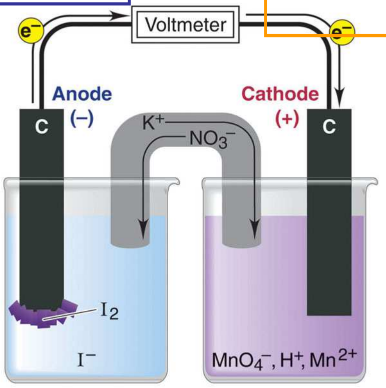
graphite | I^-(*aq*) | I_2(*s*) || H^+(*aq*), MnO_4^-(*aq*) | Mn^{2+}(*aq*) | *graphite*

↑
inert electrode

Figure 21.6 **A voltaic cell using inactive electrodes**

Oxidation half-reaction
$2I^-(aq) \longrightarrow I_2(s) + 2e^-$

Reduction half-reaction
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$



Overall (cell) reaction
$2MnO_4^-(aq) + 16H^+(aq) + 10I^-(aq) \longrightarrow 2Mn^{2+}(aq) + 5I_2(s) + 8H_2O(l)$

Sample Problem 21.2: **Diagramming Voltaic Cells**

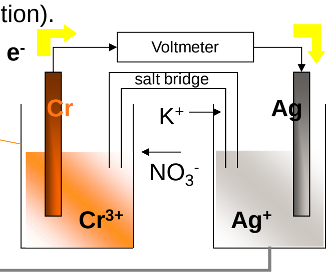
PROBLEM: Diagram, show balanced equations, and write the notation for a voltaic cell that consists of one half-cell with a Cr bar in a $Cr(NO_3)_3$ solution, another half-cell with an Ag bar in an $AgNO_3$ solution, and a KNO_3 salt bridge. Measurement indicates that the Cr electrode is negative relative to the Ag electrode.

PLAN: Identify the oxidation and reduction reactions and write each half-reaction. Associate the (-)(Cr) pole with the anode (oxidation) and the (+) pole with the cathode (reduction).

SOLUTION:

Oxidation half-reaction
$Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^-$

Reduction half-reaction
$Ag^+(aq) + e^- \longrightarrow Ag(s)$



Overall (cell) reaction
$Cr(s) + Ag^+(aq) \longrightarrow Cr^{3+}(aq) + Ag(s)$

$Cr(s)\ |\ Cr^{3+}(aq)\ ||\ Ag^+(aq)\ |\ Ag(s)$

Why Does a Voltaic Cell Work?

The spontaneous reaction occurs as a result of the different abilities of materials (such as metals) to give up their electrons and the ability of the electrons to flow through the circuit.

$E_{cell} > 0$ for a spontaneous reaction

1 Volt (V) = 1 Joule (J)/ Coulomb (C)

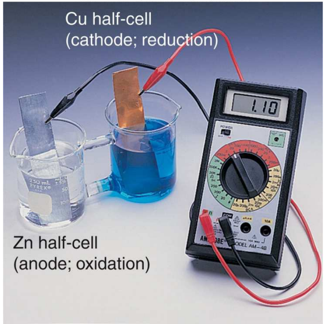


Table 21.1 Voltages of Some Voltaic Cells

Voltaic Cell	Voltage (V)
Common alkaline battery	1.5
Lead-acid car battery (6 cells = 12V)	2.0
Calculator battery (mercury)	1.3
Electric eel (~5000 cells in 6-ft eel = 750V)	0.15
Nerve of giant squid (across cell membrane)	0.070

Standard redox potentials.

- Given a specific redox couple we would like to establish a way by which the reducibility or the oxidizibility of the couple can be determined.
- This can be accomplished by devising a number scale, expressed in units of volts of standard electrode potentials E^0.
- Redox couples exhibiting highly negative E^0 values are readily oxidised.
- Redox couples exhibiting highly positive E^0 values are readily reduced.
- Hence the more positive the E^0 value of a redox couple, the greater the tendency for it to be reduced.
- The electrode potential of a single redox couple A/B is defined with respect to a standard zero of potential. This reference is called the standard hydrogen reference electrode (SHE).
- $E^0(A,B)$ is called the standard reduction potential for the reduction process $A + ne^- \rightarrow B$, and it is defined as the measured cell potential obtained for the Galvanic cell formed by coupling the A/B electrode system with a hydrogen reference electrode.
- The cell configuration is

$$Pt, H_2 \,|\, H^+(aq) \,\|\, A(aq), B(aq) \,|\, M$$

$$E^0{}_{Cell} = E^0_{Cathode} - E^0_{anode}$$

Standard Reduction Potential E^0

- E^0 (measured in volts V) is for the reaction as written.
- The more positive E^0 the greater the tendency for the substance to be reduced.
- The half-cell reactions are reversible.
- The sign of E^0 changes when the reaction is reversed.
- Changing the stoichiometric coefficients of a half-cell reaction ***does not*** change the value of E^0.

Table 21.2 Selected Standard Electrode Potentials (298K)

Half-Reaction	E^0(V)
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$MnO_2(g) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(g) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$N_2(g) + 5H^+(aq) + 4e^- \rightleftharpoons N_2H_5^+(aq)$	-0.23
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.44
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	-0.83
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	-3.05

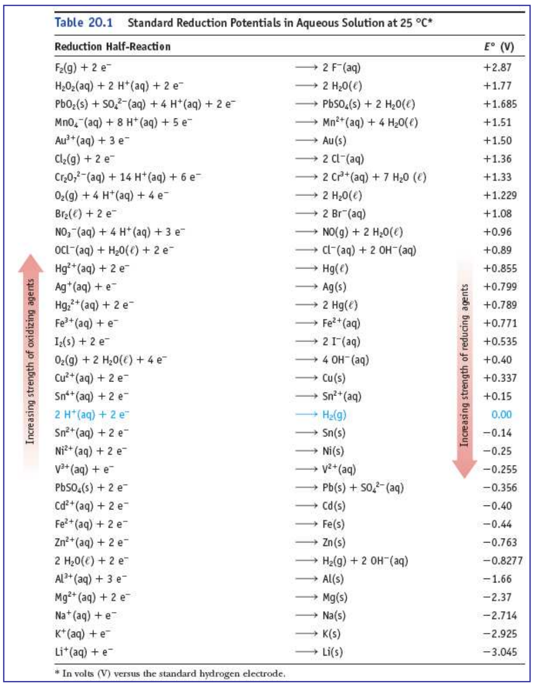


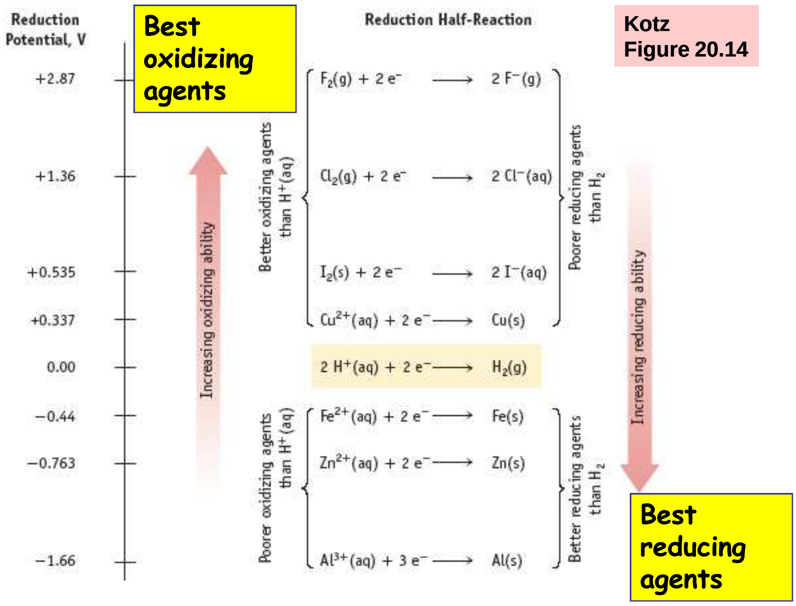
Table 20.1 Standard Reduction Potentials in Aqueous Solution at 25 °C*

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

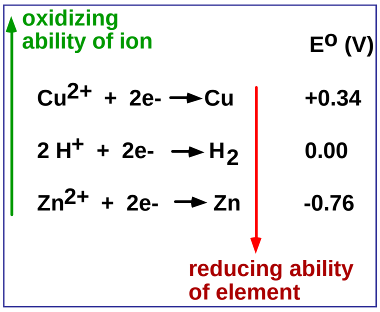
* In volts (V) versus the standard hydrogen electrode.



Kotz Figure 20.14

Potential Ladder for Reduction Half-Reactions

Standard Redox Potentials, E^o



oxidizing ability of ion

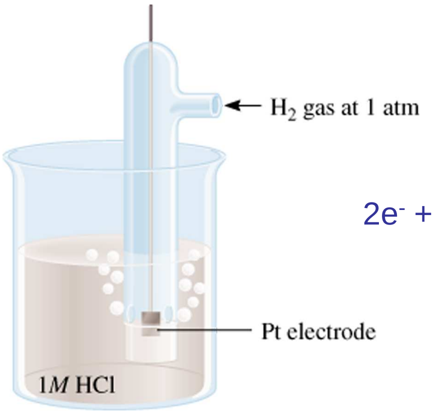
	E^o (V)
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$2H^+ + 2e^- \rightarrow H_2$	0.00
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76

reducing ability of element

- 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+}.

Standard Electrode Potentials

Standard reduction potential (E^0) is the voltage associated with a **reduction reaction** at an electrode when all solutes are 1 *M* and all gases are at 1 atm.



Reduction Reaction

$$2e^- + 2H^+ (1\ M) \longrightarrow 2H_2\ (1\ atm)$$

$$E^0 = 0\ V$$

Standard hydrogen electrode (SHE)

Standard Redox Potentials, E°

Ox. agent $Cu^{2+} + 2e^- \longrightarrow Cu$ +0.34

$2\,H^+ + 2e^- \longrightarrow H_2$ 0.00

$Zn^{2+} + 2e^- \longrightarrow Zn$ -0.76 Red. agent

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

Northwest-southeast rule: product-favored reactions occur between
- reducing agent at southeast corner
- oxidizing agent at northwest corner

Standard Redox Potentials, E°

CATHODE $Cu^{2+} + 2e^- \longrightarrow Cu$ +0.34

$2\,H^+ + 2e^- \longrightarrow H_2$ 0.00

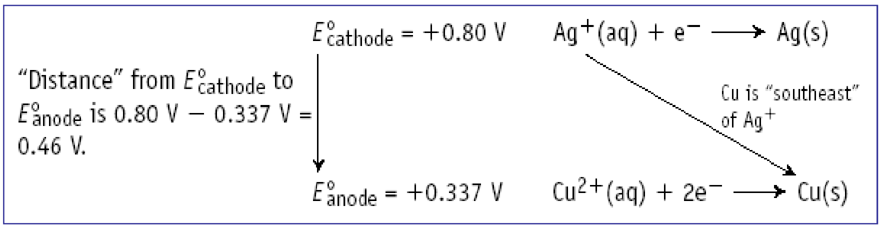
$Zn^{2+} + 2e^- \longrightarrow Zn$ -0.76 ANODE

Northwest-southeast rule:
- reducing agent at southeast corner
  = ANODE
- oxidizing agent at northwest corner
  = CATHODE

Standard Redox Potentials, E°

$E°_{net}$ = “distance” from “top” half-reaction (cathode) to “bottom” half-reaction (anode)

$$E°_{net} = E°_{cathode} - E°_{anode}$$



“Distance” from $E°_{cathode}$ to $E°_{anode}$ is 0.80 V − 0.337 V = 0.46 V.

$E°_{cathode}$ = +0.80 V $Ag^+(aq) + e^- \longrightarrow Ag(s)$

Cu is “southeast” of Ag^+

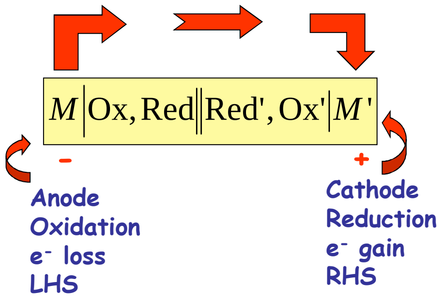
$E°_{anode}$ = +0.337 V $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

$E°_{net}$ for Cu/Ag^+ reaction = +0.46 V

Standard cell potentials.

- The standard potential E^0_{cell} developed by a Galvanic cell reflects the values of the standard potentials associated with the two component half reactions.
- This can be computed using the following simple procedure.
- The two half reactions are written as reduction processes.
- For any combination of two redox couples to form a Galvanic cell, the half reaction exhibiting the more positive E^0 value occurs as a reduction process and is written on the RHS of the cell diagram, as the positive pole of the cell.
- In contrast, the half reaction which has the more negative E^0 value is written on the LHS of the cell diagram as the negative pole of the cell, and will occur as an oxidation process.
- The overall cell reaction is given as the sum of the two component redox processes and the net cell potential is given by the expression presented across.

$$E^0_{cell} = E^0_{RHS} - E^0_{LHS} = E^0_{cathode} - E^0_{anode}$$



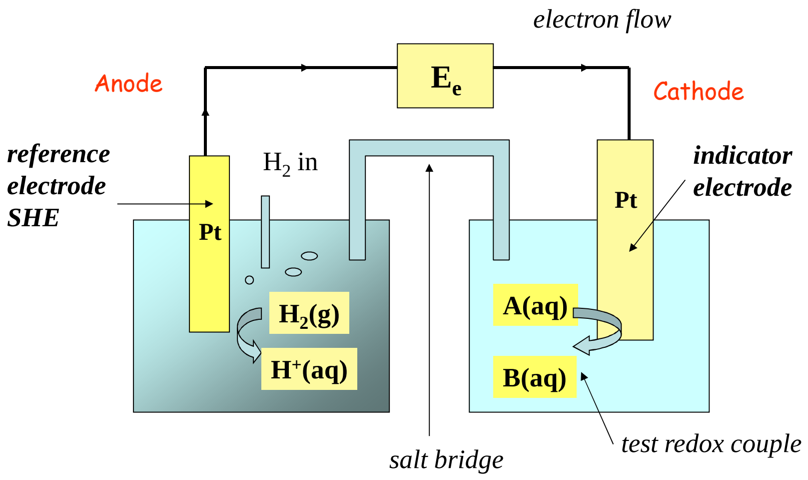
$$M \,|\, \mathrm{Ox}, \mathrm{Red} \,\|\, \mathrm{Red}', \mathrm{Ox}' \,|\, M'$$

−

Anode
Oxidation
e^- loss
LHS

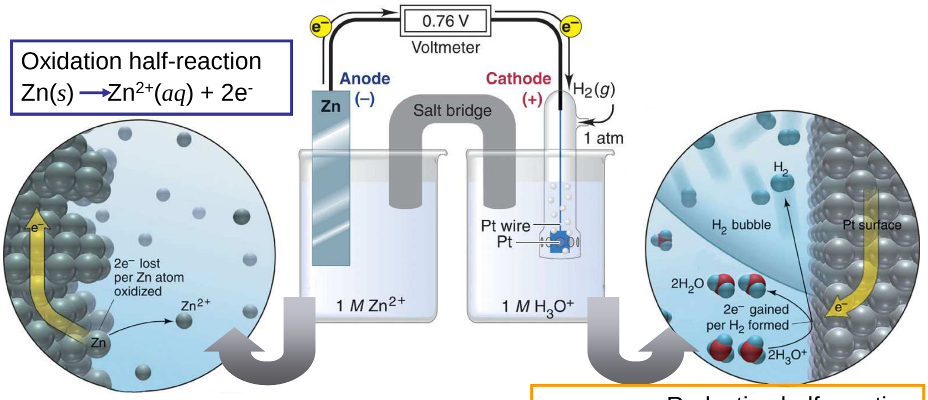
+

Cathode
Reduction
e^- gain
RHS



$$Pt, H_2\left|H^+(aq)\right\|A(aq), B(aq)\left|M\right.$$

Figure 21.7 **Determining an unknown $E^0_{\text{half-cell}}$ with the standard reference (hydrogen) electrode**



Oxidation half-reaction
$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Reduction half-reaction
$2H_3O^+(aq) + 2e^- \longrightarrow H_2(g) + 2H_2O(l)$

Overall (cell) reaction
$Zn(s) + 2H_3O^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g) + 2H_2O(l)$

Sample Problem 21.3: Calculating an Unknown $E^0_{half\text{-}cell}$ from E^0_{cell}

PROBLEM: A voltaic cell houses the reaction between aqueous bromine and zinc metal:

$$Br_2(aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + 2Br^-(aq) \qquad E^0_{cell} = 1.83V$$

Calculate $E^0_{bromine}$ given $E^0_{zinc} = -0.76V$

PLAN: The reaction is spontaneous as written since the E^0_{cell} is (+). Zinc is being oxidized and is the anode. Therefore the $E^0_{bromine}$ can be found using $E^0_{cell} = E^0_{cathode} - E^0_{anode}$.

SOLUTION: anode: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ $\quad E = +0.76$

E^0_{Zn} as $Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$ is -0.76V

$$E^0_{cell} = E^0_{cathode} - E^0_{anode} = 1.83 = E^0_{bromine} - (-0.76)$$

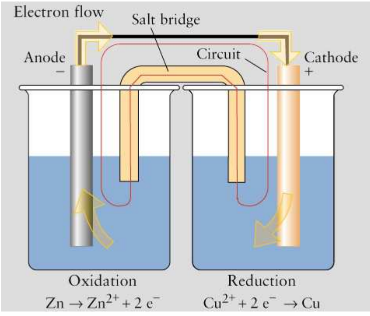
$$E^0_{bromine} = 1.86 - 0.76 = 1.07V$$

- By convention, electrode potentials are written as reductions.
- When pairing two half-cells, you must reverse one reduction half-cell to produce an oxidation half-cell. Reverse the sign of the potential.
- The reduction half-cell potential and the oxidation half-cell potential are added to obtain the E^0_{cell}.
- When writing a spontaneous redox reaction, the left side (reactants) must contain the stronger oxidizing and reducing agents.

Example: $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

Zn(s)	Cu²⁺(aq)	Zn²⁺(aq)	Cu(s)
stronger reducing agent	*stronger oxidizing agent*	*weaker oxidizing agent*	*weaker reducing agent*

Relationship between the change in Gibbs energy for the cell reaction and the cell potential.



- When a spontaneous reaction takes place in a Galvanic cell, electrons are deposited in one electrode (the site of oxidation or anode) and collected from another (the site of reduction or cathode), and so there is a net flow of current which can be used to perform electrical work W_e.
- From thermodynamics we note that the maximum electrical work W_e done at constant temperature and pressure is equal to the change in Gibbs energy ΔG for the net cell reaction.
- We apply basic physics to evaluate the electrical work W_e done in moving n mole electrons through a potential difference given by E_{cell}.

Transferring 1 electron :

$$\boxed{W_e = qE_{cell} = -eE_{cell}}$$

Transferring 1 mole electrons :

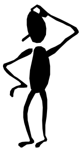
$$\boxed{W_e = -N_A eE_{cell}}$$

Transferring n mole electrons :

$$\boxed{W_e = -nN_A eE_{cell}}$$

Relationship between thermodynamics of cell reaction and observed cell potential.

$$\boxed{\begin{aligned}\Delta G = W_e &= -neN_A E_{cell}\\ &= -nFE_{cell}\end{aligned}}$$



What is the standard emf of an electrochemical cell made of a Cd electrode in a 1.0 *M* $Cd(NO_3)_2$ solution and a Cr electrode in a 1.0 *M* $Cr(NO_3)_3$ solution?

$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$ $E^0 = -0.40$ V Cd is the stronger oxidizer

$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$ $E^0 = -0.74$ V Cd will oxidize Cr

Anode (oxidation): $Cr(s) \longrightarrow Cr^{3+}(1\ M) + \bigcirc\!\!\!\!\!\!3e^-$ x 2

Cathode (reduction): $2e^- + Cd^{2+}(1\ M) \longrightarrow Cd(s)$ x 3

$$2Cr(s) + 3Cd^{2+}(1\ M) \longrightarrow 3Cd(s) + 2Cr^{3+}(1\ M)$$

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$E^0_{cell} = -0.40 - (-0.74)$$

$$E^0_{cell} = 0.34\ \text{V}$$

Thermodynamics of cell reactions.

- The change in Gibbs energy for the overall cell reaction is related to the observed net cell potential generated.
- When the standard cell potential E^0_{cell} is positive, the Gibbs energy ΔG^0 is negative and vice versa.
- Once ΔG^0 for a cell reaction is known, then the equilibrium constant K for the cell reaction can be readily evaluated.
- These expressions are valid for standard conditions : T = 298 K, p = 1 atm (or 1 bar); c = 1 mol L^{-1}.

Faraday constant : 96,500 C mol^{-1}

$$\Delta G^0 = -nFE^0_{cell}$$

electrons transferred in cell reaction

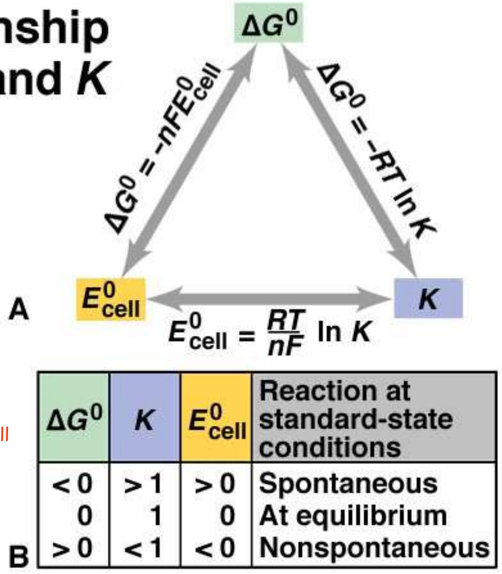
$$\Delta G^0 = -RT \ln K$$

$$K = \exp\left[-\frac{\Delta G^0}{RT}\right] = \exp\left[\frac{nFE^0_{cell}}{RT}\right]$$

Gas Constant : 8.314 J mol^{-1} K^{-1}

Temperature (K)

Interrelationship of ΔG^0, E^0, and K



ΔG^0	K	E^0_{cell}	Reaction at standard-state conditions
< 0	> 1	> 0	Spontaneous
0	1	0	At equilibrium
> 0	< 1	< 0	Nonspontaneous

A. Any one of these thermodynamic parameters can be used to find the other two.

B. The signs of ΔG° and E°_{cell} determine the reaction direction at standard-state conditions.

Sample Problem 21.5: Calculating K and ΔG^0 from E^0_{cell}

PROBLEM: Lead can displace silver from solution:

$$Pb(s) + 2Ag^+(aq) \longrightarrow Pb^{2+}(aq) + 2Ag(s)$$

As a consequence, silver is a valuable by-product in the industrial extraction of lead from its ore. Calculate K and ΔG^0 at 25^0C for this reaction.

PLAN: Break the reaction into half-reactions, find the E^0 for each half-reaction and then the E^0_{cell}.

SOLUTION: $Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$ $E^0 = -0.13V$

$Ag^+(aq) + e^- \longrightarrow Ag(s)$ $E^0 = 0.80V$

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

$2X \left(Ag^+(aq) + e^- \longrightarrow Ag(s) \right)$

$E^0 = 0.13V$

$E^0 = 0.80V$

$E^0_{cell} = 0.93V$

$$E^0_{cell} = \frac{0.592V}{n} \log K$$

$$\log K = \frac{n \times E^0_{cell}}{0.592V} = \frac{(2)(0.93V)}{0.592V}$$

$K = 2.6 \times 10^{31}$

$$\Delta G^0 = -nFE^0_{cell} = -(2)(96.5kJ/mol^*V)(0.93V)$$

$\Delta G^0 = -1.8 \times 10^2 kJ$

The Nernst equation.

The potential developed by a Galvanic cell depends on the composition of the cell.
From thermodynamics the Gibbs energy change for a chemical reaction ΔG varies with composition of the reaction mixture in a well defined manner.
We use the relationship between ΔG and E to obtain the Nernst equation.

Nernst eqn.holds for single redox couples and net cell reactions.

$$\Delta G = \Delta G^0 + RT \ln Q$$

$$\Delta G - -nFE \quad \Delta G^0 = -nFE^0$$

$$-nFE = -nFE^0 + RT \ln Q$$

$$E = E^0 - \frac{RT}{nF} \ln Q$$

T = 298K

$$E = E^0 - \frac{0.0592}{n} \log Q$$

Reaction quotient

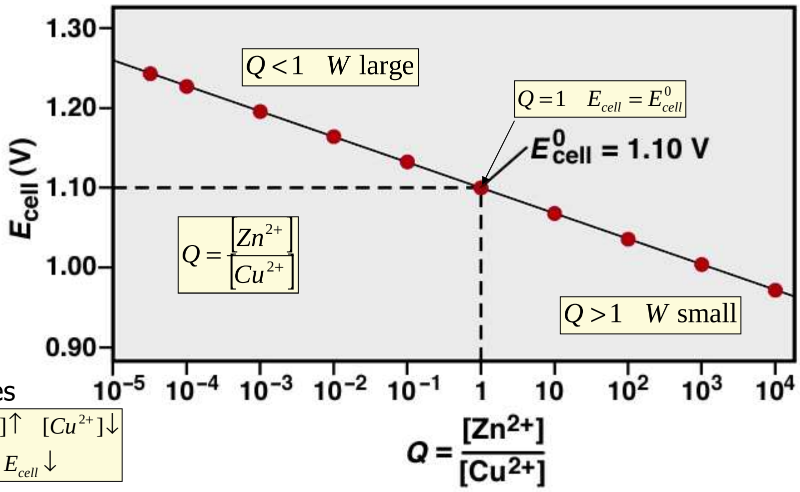
$$Q \cong \frac{[\text{products}]}{[\text{reactants}]}$$

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

$$E_{cell} = E^0_{cell} - \frac{0.059}{2}\log\left\{\frac{[Zn^{2+}]}{[Cu^{2+}]}\right\}$$

Equilibrium $\Delta G = 0$
$E_{cell} = 0 \quad Q = K$
$W = 0$

Dead cell



As cell operates

$[Zn^{2+}]\uparrow \quad [Cu^{2+}]\downarrow$
$Q\uparrow \quad E_{cell}\downarrow$

Sample Problem 21.6: Using the Nernst Equation to Calculate E_{cell}

PROBLEM: In a test of a new reference electrode, a chemist constructs a voltaic cell consisting of a Zn/Zn^{2+} half-cell and an H_2/H^+ half-cell under the following conditions:

$[Zn^{2+}] = 0.010M \qquad [H^+] = 2.5M \qquad P_{H_2} = 0.30atm$

Calculate E_{cell} at 25^0C.

PLAN: Find E^0_{cell} and Q in order to use the Nernst equation.

SOLUTION: Determining E^0_{cell} :

$2H^+(aq) + 2e^- \longrightarrow H_2(g) \qquad E^0 = 0.00V$

$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s) \qquad E^0 = -0.76V$

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \qquad E^0 = +0.76V$

$$Q = \frac{P_{H_2} \times [Zn^{2+}]}{[H^+]^2}$$

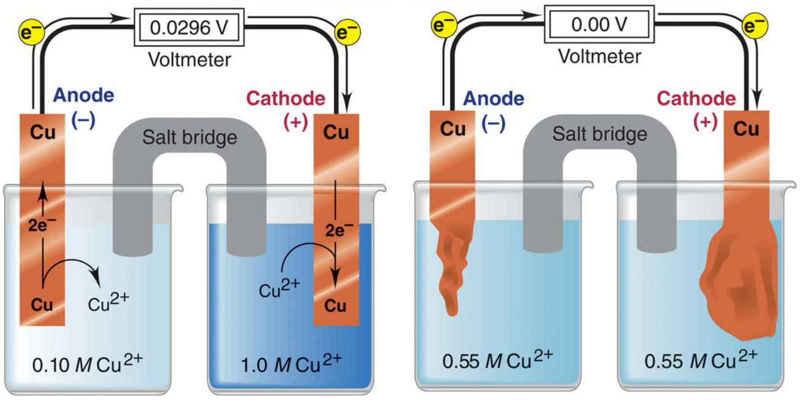
$$Q = \frac{(0.30)(0.010)}{(2.5)^2}$$

$Q = 4.8\times10^{-4}$

$$E_{cell} = E^0_{cell} - \frac{0.0592V}{n}\log Q$$

$E_{cell} = 0.76 - (0.0592/2)\log(4.8\times10^{-4}) = \boxed{0.86V}$

Figure 21.11 **A concentration cell based on the Cu/Cu^{2+} half-reaction**



Oxidation half-reaction
$Cu(s) \rightarrow Cu^{2+}(aq, 0.1M) + 2e^-$

Reduction half-reaction
$Cu^{2+}(aq, 1.0M) + 2e^- \rightarrow Cu(s)$

Overall (cell) reaction
$Cu^{2+}(aq,1.0M) \rightarrow Cu^{2+}(aq, 0.1M)$

Sample Problem 21.7: **Calculating the Potential of a Concentration Cell**

PROBLEM: A concentration cell consists of two Ag/Ag^+ half-cells. In half-cell A, electrode A dips into 0.0100M $AgNO_3$; in half-cell B, electrode B dips into 4.0×10^{-4}M $AgNO_3$. What is the cell potential at 298K? Which electrode has a positive charge?

PLAN: E^0_{cell} will be zero since the half-cell potentials are equal. E_{cell} is calculated from the Nernst equation with half-cell A (higher $[Ag^+]$) having Ag^+ being reduced and plating out, and in half-cell B Ag(s) will be oxidized to Ag^+.

SOLUTION: Ag^+(aq, 0.010M) half-cell A $\longrightarrow$ Ag^+(aq, 4.0×10^{-4}M) half-cell B

$$E_{cell} = E^0_{cell} - \frac{0.0592V}{1} \log \frac{[Ag^+]_{dilute}}{[Ag^+]_{concentrated}}$$

$$E_{cell} = 0\ V - 0.0592 \log 4.0\times10^{-2} = 0.0828V$$

Half-cell A is the cathode and has the positive electrode.

Determination of thermodynamic parameters from E_{cell} vs temperature data.

Measurement of the zero current cell potential E as a function of temperature T enables thermodynamic quantities such as the reaction enthalpy ΔH and reaction entropy ΔS to be evaluated for a cell reaction.

$$E = a + b(T - T_0) + c(T - T_0)^2 + \cdots$$

a, b and c etc are constants, which can be positive or negative.
T_0 is a reference temperature (298K)

$$\left(\frac{\partial E}{\partial T}\right)_P \leftarrow$$

Temperature coefficient of zero current cell potential obtained from experimental E=E(T) data.
Typical values lie in range 10^{-4} - 10^{-5} VK^{-1}

Gibbs-Helmholtz eqn.

$$\Delta H = \Delta G - T\left(\frac{\partial \Delta G}{\partial T}\right)_P$$

$$\downarrow$$

$$\Delta G = -nFE$$

$$\Delta H = -nFE - T\left\{\frac{\partial}{\partial T}(-nFE)\right\}$$

$$= -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_P$$

$$\Delta H = -nF\left\{E - T\left(\frac{\partial E}{\partial T}\right)_P\right\}$$

- Once ΔH and ΔG are known then ΔS may be evaluated.

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

$$\Delta S = \frac{1}{T}\left\{-nFE + nFT\left(\frac{\partial E}{\partial T}\right)_P + nFE\right\}$$

$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P$$

- Electrochemical measurements of cell potential conducted under conditions of zero current flow as a function of temperature provide a sophisticated method of determining useful thermodynamic quantities.

Figure 21.18

The processes occurring during the discharge and recharge of a lead-acid battery

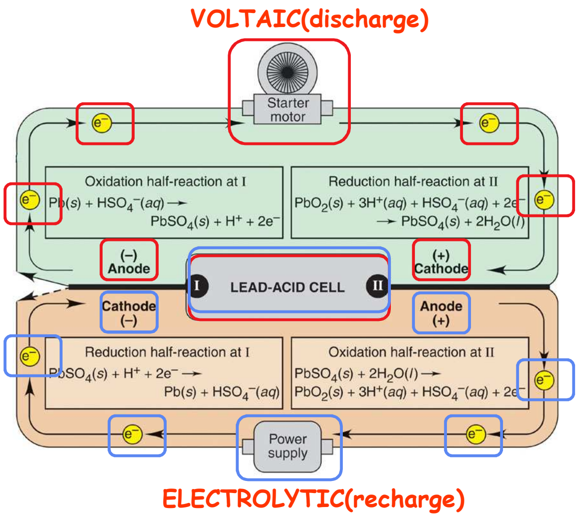
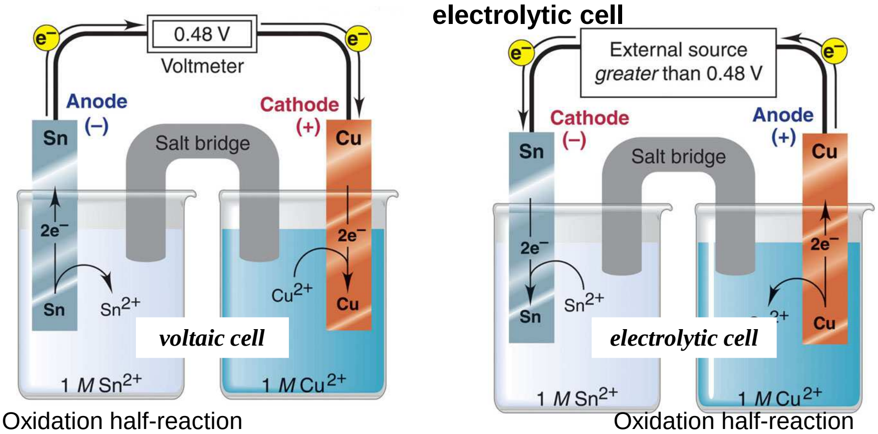


Figure 21.17

The tin-copper reaction as the basis of a voltaic and an electrolytic cell



Oxidation half-reaction

$Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$

Reduction half-reaction

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

Overall (cell) reaction

$Sn(s) + Cu^{2+}(aq) \rightarrow Sn^{2+}(aq) + Cu(s)$

Oxidation half-reaction

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

Reduction half-reaction

$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$

Overall (cell) reaction

$Sn(s) + Cu^{2+}(aq) \rightarrow Sn^{2+}(aq) + Cu(s)$