CHEM 1A03: Intro. Chemistry I

Energy & Electrochemistry

Ch.20: Electrochemistry

McMaster University

Chemistry

http://en.wikipedia.org/wiki/File:Thermite_skillet.jpg
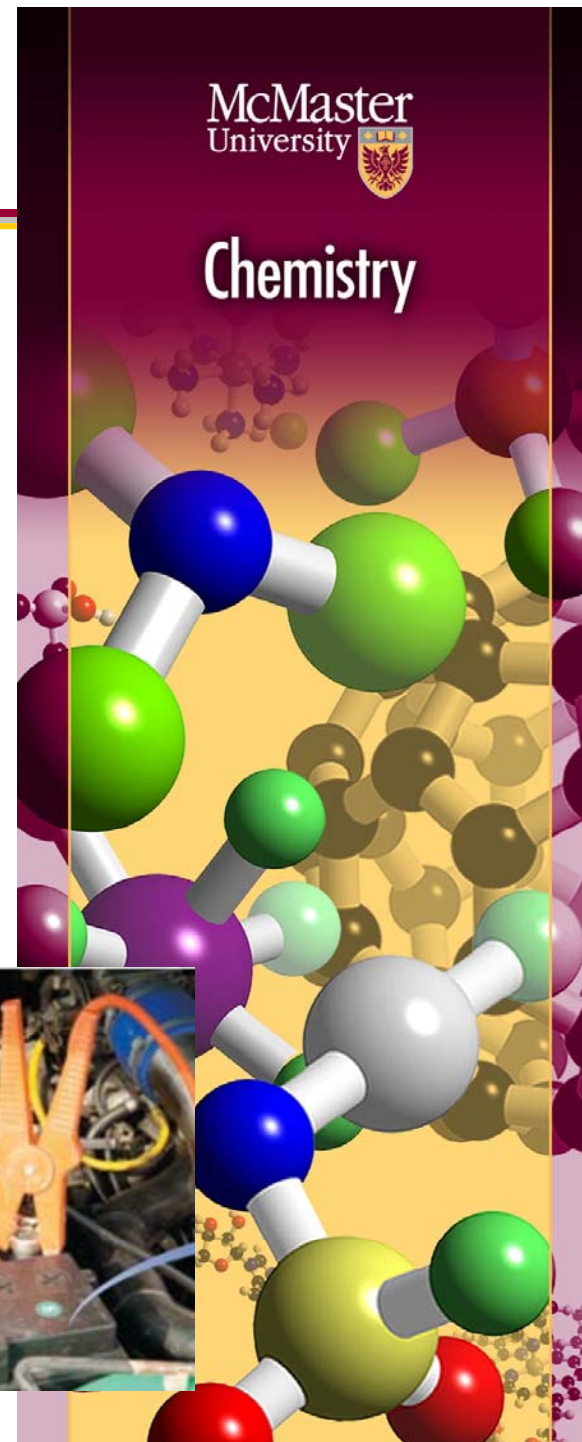
Redox Reactions: Examples

(a) Spontaneous:
$Cu + 2\,Ag^+ \rightarrow Cu^{2+} + 2\,Ag$
(recall Ch 5 demo, the Cu wire covered with Ag needles)

(b) Non-spontaneous:
$Cu + Zn^{2+} \rightarrow$ no reaction

(recall step in Lab 2:
$Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu$
<u>was</u> spontaneous)
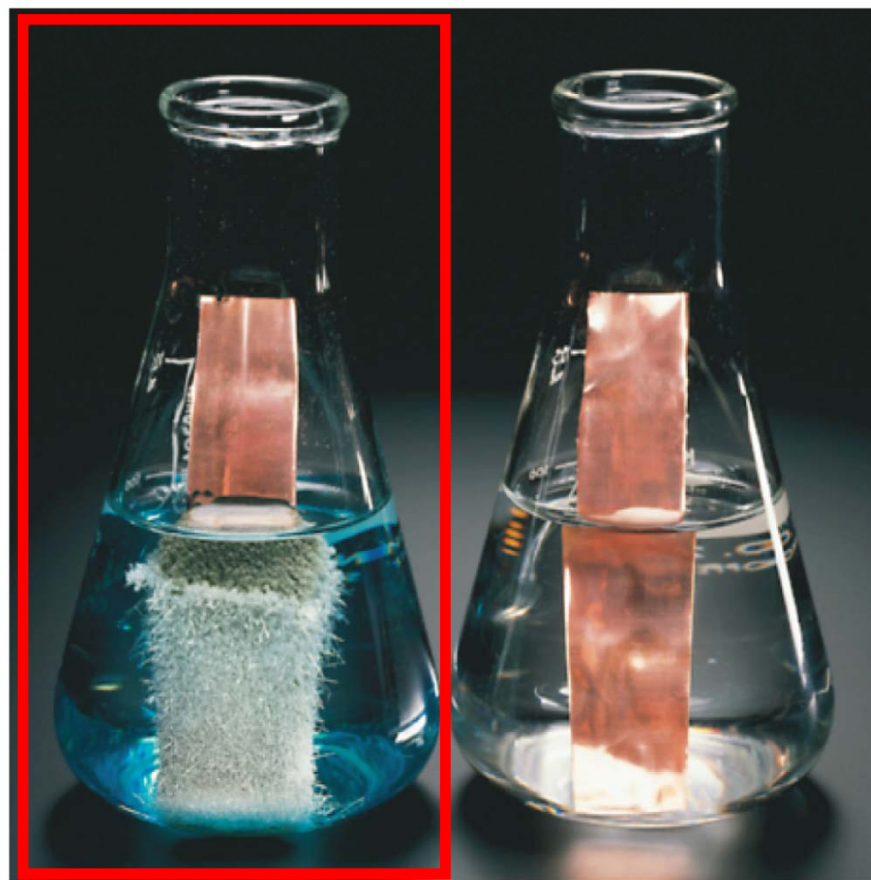
(a)   (b)

How can we harness the energy transfer in process (a)?

p. 864 (823, 9th ed.)

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Electrochemical Cells: Cu/Ag$^+$

- Two connected half-cells.

- The 2 half-reactions are separated, yet connected electrically (salt bridge, external wire).

- Solid metals = electrodes (anode, cathode).

- Movement of e$^-$ from anode to cathode generates voltage.

- Movement of cations and anions through salt bridge maintains electroneutrality in solution.

0.460

Voltmeter

e$^-$ e$^-$

Salt bridge [KNO$_3$(aq)]

NO$_3^-$ K$^+$

Cu

Ag

Cu^{2+}
Cu^{2+}

Ag$^+$
NO$_3^-$

1.00 M Cu(NO$_3$)$_2$(aq)

1.00 M AgNO$_3$(aq)

Cu = anode
(oxidation)

Ag = cathode
(reduction)

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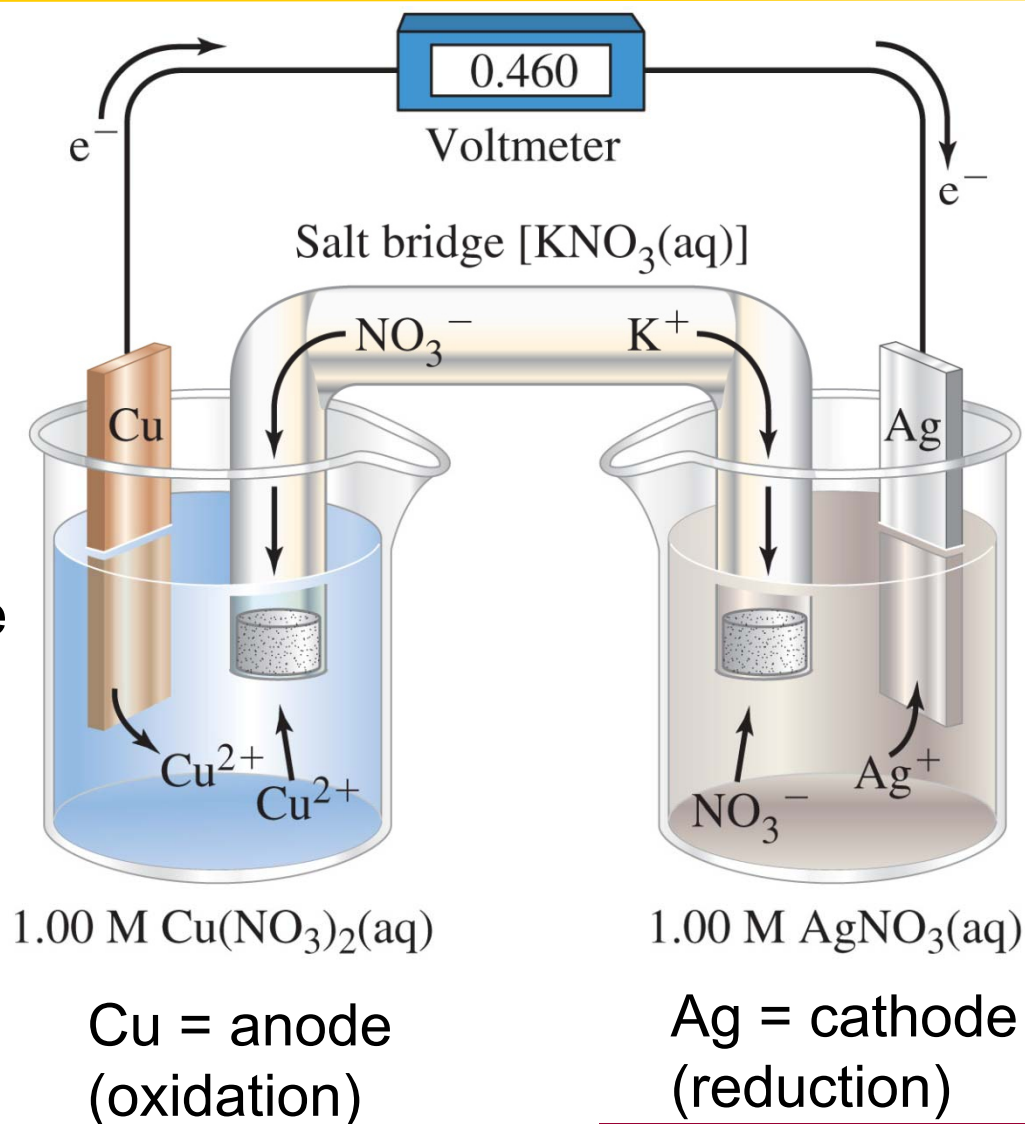
Electrochemical Cells

- Oxidation (anode): surface of electrode erodes as M^{n+} are produced; n e$^-$ then travel to cathode

  $M \rightarrow M^{n+} + n\ e^-$

- Reduction (cathode): cathode gains mass as M^{n+} ions gain n e$^-$ and form M(s)

  $M^{n+} + n\ e^- \rightarrow M$

p. 865 (822, 9th ed.)

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Chemistry
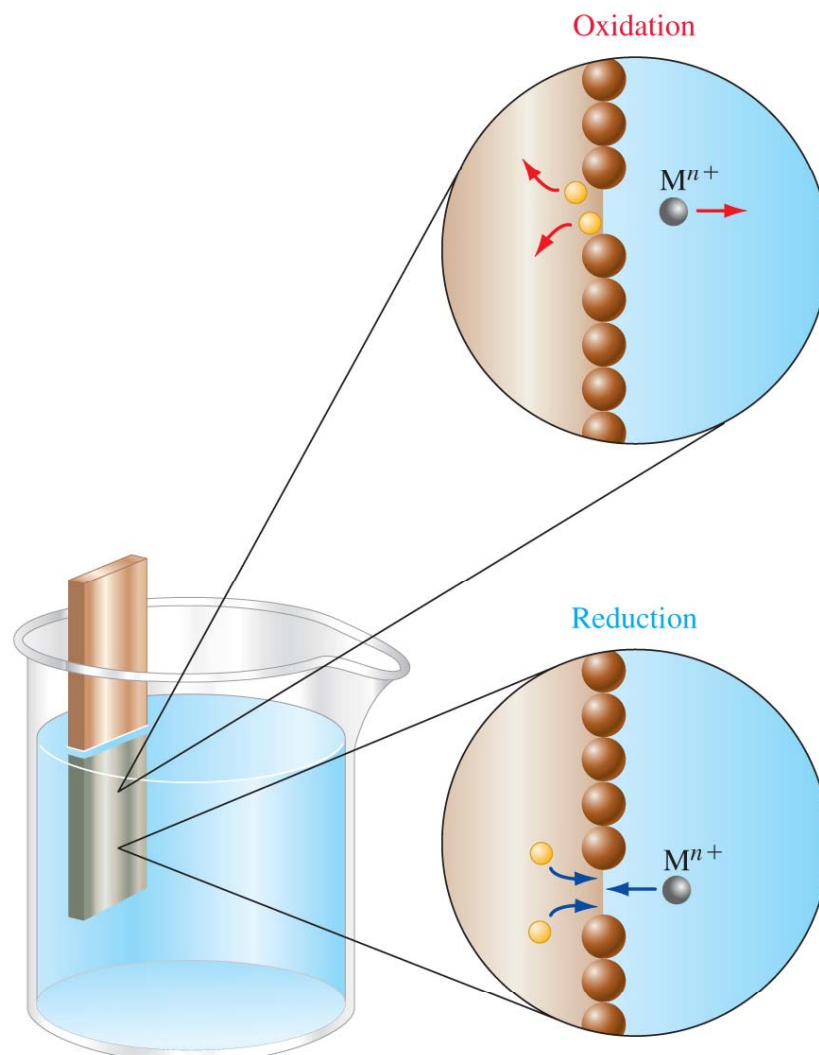
Electrochemical Cells

Oxidation: occurs at anode (Cu) $Cu(s) \rightarrow Cu^{2+}(aq) + 2\ e^-$

Reduction: occurs at cathode (Ag) $2\ Ag^+(aq) + 2\ e^- \rightarrow 2\ Ag(s)$

"An ox and a red cat", or vowels (O, A) / consonants (C, R)

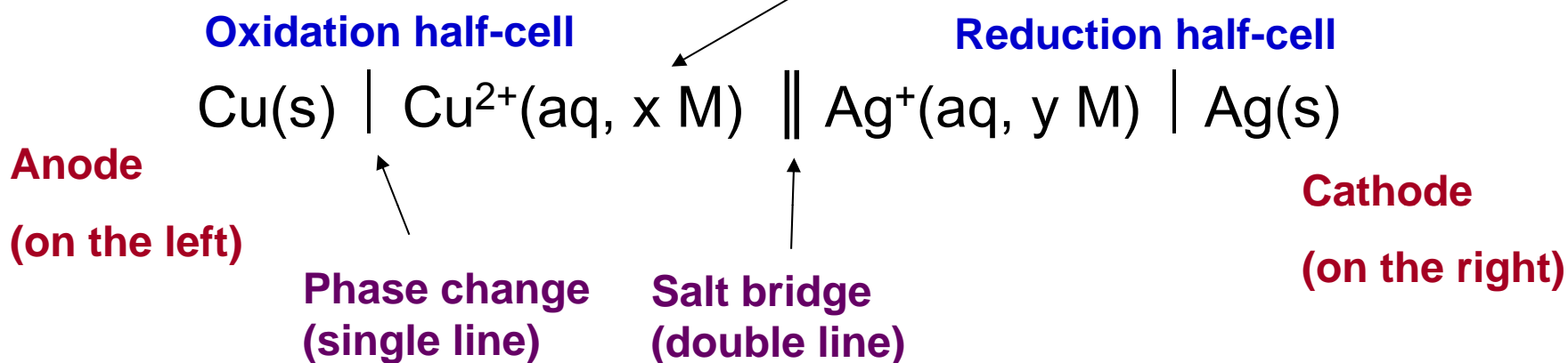Overall cell reaction: $Cu(s) + 2\ Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2\ Ag(s)$

- Galvanic (voltaic) cell: results from spontaneous chemical reactions (our example above)

- Electrolytic cell: uses electricity to accomplish non-spontaneous chemical change

Cell Diagrams

- Symbolic notation of cell:

Concentration is specified (1M = standard)

Oxidation half-cell   **Reduction half-cell**

$$Cu(s) \mid Cu^{2+}(aq,\ x\ M) \parallel Ag^{+}(aq,\ y\ M) \mid Ag(s)$$

Anode

(on the left)

Cathode

(on the right)

Phase change (single line)   **Salt bridge (double line)**

- Sometimes an electrode is inert (does not chemically participate, but is needed for electron transfer to occur).

- For example:

Pressure is specified (1bar = standard) ~ 1 atm

Pt = inert electrode (cathode)

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

iClicker Question #1

What is the correct cell diagram for the following reaction at standard conditions?

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

(A) $Mg(s) \parallel Mg^{2+}(aq) \parallel Sn^{2+}(aq) \parallel Sn(s)$

(B) $Sn(s) \mid Sn^{2+}(aq, 1M) \parallel Mg^{2+}(aq, 1M) \mid Mg(s)$

(C) $Mg^{2+}(aq, 1M) \mid Mg(s) \parallel Sn(s) \mid Sn^{2+}(aq, 1M)$

(D) $Sn^{2+}(aq, 1M) \mid Sn(s) \parallel Mg(s) \mid Mg^{2+}(aq, 1M)$

(E) $Mg(s) \mid Mg^{2+}(aq, 1M) \parallel Sn^{2+}(aq, 1M) \mid Sn(s)$

Standard Electrode Potentials

- Absolute half-cell potentials cannot be measured
- All potentials are measured relative to the standard hydrogen electrode (SHE); assigned a potential of 0 V.

$$2\ H^+(a = 1)\ +\ 2\ e^- \overset{\text{On Pt}}{\rightleftarrows}\ H_2(g,\ 1\ \text{bar}) \qquad E\degree = \text{exactly 0 volt (V)}$$

Simplify: a = 1 becomes $[H^+]$ = 1 M; 1 bar = 1 atm

Half-cell diagram:

$$Pt(s)\ |\ H_2(g,\ 1\ \text{atm})\ |\ H^+(aq,\ 1\ M)$$

- Standard electrode potentials ($E\degree$) report tendency for <u>reduction</u> to occur ($E\degree_{red}$)
- Standard conditions: conc. = 1 M, pressures = 1 atm.

Standard Reduction Potentials ($E°_{red}$)

Table 20.1: Selected Standard Electrode (Reduction) Potentials at 25°C

	$E°_{red}$, V
$F_2(g) + 2\,e^- \rightarrow 2\,F^-$	+2.866
$Cu^{2+}(aq) + 2\,e- \rightarrow Cu(s)$	+0.340
$2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$	0
$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$	–0.763
$Li^+(aq) + e^- \rightarrow Li(s)$	–3.040

Species most easily reduced (on left side, at <u>most</u> positive potential)

Species most easily oxidized (on right side, at <u>least</u> positive potential)

iClicker Question #2

From the following list of standard potentials, identify the best reducing agent.

$$E^{\circ}_{red}, V$$

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$		+0.771
$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$		+0.340
$Sn^{2+}(aq) + 2\,e^- \rightarrow Sn(s)$		–0.137

A) Fe^{3+}

B) $Sn(s)$

C) Sn^{2+}

D) $Cu(s)$

E) Cu^{2+}

Standard Cell Potentials ($E°_{cell}$)

- $E°_{cell}$ = voltage of a cell formed from 2 standard electrodes

  Can be expressed as: $E°$(cathode(right)) – $E°$(anode(left))

  - ALTERNATIVELY -

- For a given half-cell we can say $E°_{ox} = -E°_{red}$
  (reverse the sign on the potential for the oxidation half-cell)

  e.g., Zn^{2+}/Zn $E°_{red}$ = –0.763, therefore $E°_{ox}$ = +0.763

- Then $\boxed{E°_{cell} = E°_{red} + E°_{ox}}$

p. 870-871 (828-829, 9th ed.)

Standard Cell Potentials ($E°_{cell}$)

- Note: a standard potential is an *intensive* property – it does not depend on the amount of substance reacting

- We <u>do not</u> multiply $E°_{red}$ or $E°_{ox}$ by a factor even if we multiply a half-reaction by a factor when balancing.

> $E°_{cell} > 0$ = spontaneous

- Magnitude of cell potential indicates driving force for cell

  e.g., under standard conditions:

  oxidation of metallic Zn by Cu^{2+} ($E°_{cell}$ = 1.100V) has a greater tendency to go to completion than does oxidation of metallic Cu by Ag^+ ions ($E°_{cell}$ = 0.4600V)

iClicker Question #3

Write the cell reaction for the "most spontaneous" cell.

$E^{\circ}{}_{red}$

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ +0.771 V

$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$ +0.340 V

$Sn^{2+}(aq) + 2\ e^- \rightarrow Sn(s)$ −0.137 V

What is the cell potential (V) for this cell?

(A) 0.908
(B) 0.455
(C) 1.679
(D) 1.012
(E) 0.634

$2\ Fe^{3+}(aq) + Sn(s) \rightarrow 2\ Fe^{2+}(aq) + Sn^{2+}(aq)$

$E^{\circ}{}_{cell} = E^{\circ}{}_{red} + E^{\circ}{}_{ox} = +0.771 + (+0.137)\ V = 0.908\ V$

Note: $E^{\circ}{}_{red}$ is <u>not</u> multiplied by 2!

Spontaneity: E^{o}_{cell} and ΔG°

- Electromotive force or cell potential (E_{cell})

  joule = volt x coulomb (or volt = energy/unit charge)

  $w_{elec} = zFE_{cell}$,   where work = $-\Delta G$ (see box p. 795)

  z = # e$^-$ transferred; F = 96485 C/mol e$^-$ (Faraday constant)

$$\Delta G = -zFE_{cell}$$ Eq. 20.15   Non-standard conditions

$$\Delta G^{o} = -zFE^{o}_{cell}$$ Eq. 20.16   Standard conditions: Reactants, products in standard states

Positive E_{cell} or E°_{cell} = spontaneous

Negative ΔG or ΔG° = spontaneous

Spontaneity: E°_{cell} and K

$$\Delta G^{o} = -zFE^{o}_{cell}$$ Eq. 20.15   and

$$\Delta G^{o} = -RT \ln K$$ Eq. 19.13; combine:

Eq. 20.16

K > 1 means products are favoured

K > 1 means ln K > 0 , therefore $E^{\circ}_{cell} > 0$
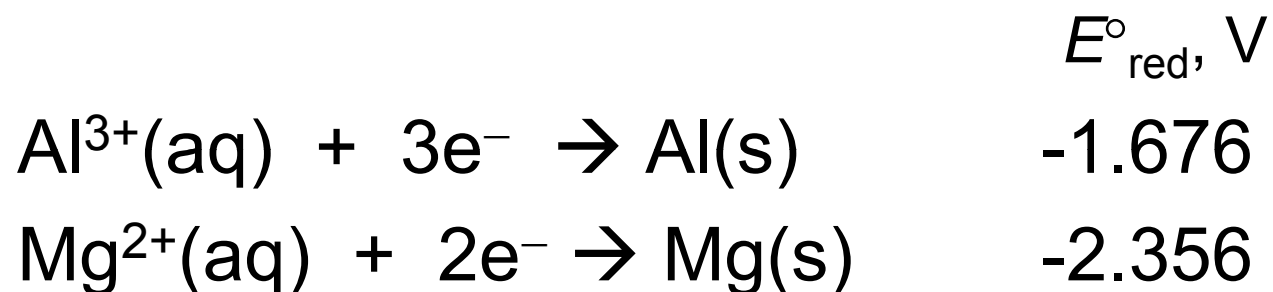
Linking Relationships: E, G, K

K

Equilibrium composition measurements

Ch 7

$$\Delta G° = -RT\ln K$$

$$E°_{cell} = \frac{RT}{zF}\ln K$$

Calorimetry: $\Delta H_f°$

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

ΔG°

E°cell

Electrical measurements: $E°$ and $E°_{cell}$

Calorimetry and theoretical calculations: $S°$ and $\Delta S°$

$$\Delta G° = -nFE°_{cell}$$

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Spontaneous process:

ΔG° < 0

E°cell > 0

K > 1
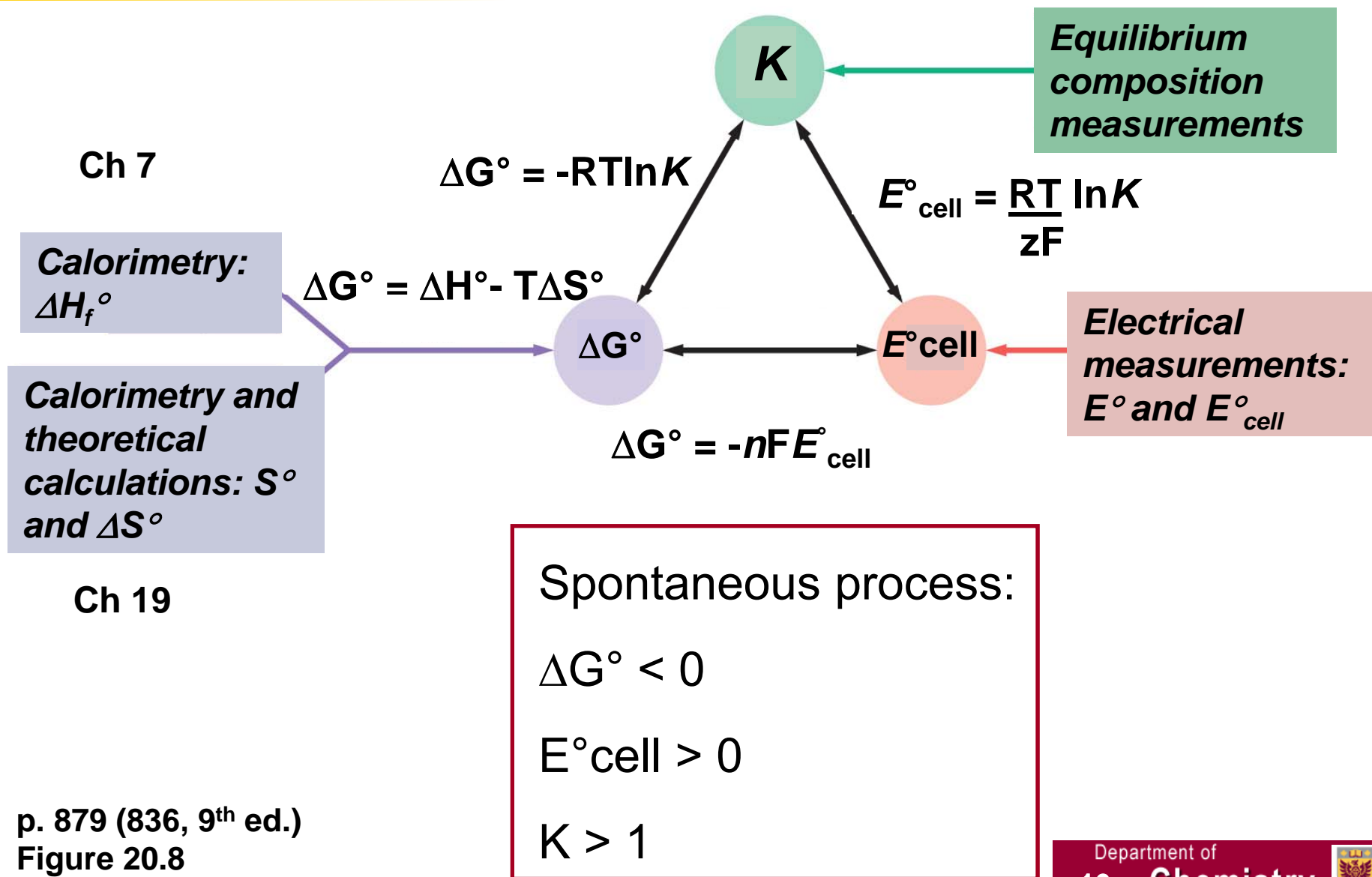
p. 879 (836, 9th ed.)
Figure 20.8

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Take-home Questions:

1. Calculate $\Delta G°$ for the spontaneous cell produced from the following:

$$E°_{red}, \text{V}$$

$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$ -1.676

$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$ -2.356

2. Calculate K for the above cell, at 25°C.

Solutions

1.

Reduction: $2\,Al^{3+}(aq) + 6\,e^- \rightarrow 2\,Al(s)$ $E^o_{red} = -1.676$ V

Oxidation: $3\,Mg(s) \rightarrow 3\,Mg^{2+}(aq) + 6\,e^-$ $E^o_{ox} = +2.356$ V

Overall: $2\,Al^{3+}(aq) + 3\,Mg(s) \rightarrow 2\,Al(s) + 3\,Mg^{2+}(aq)$

$E^o_{cell} = 0.680$ V

and z = 6

$$\Delta G^o = -zFE^o_{cell}$$
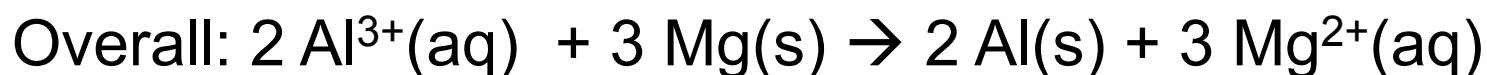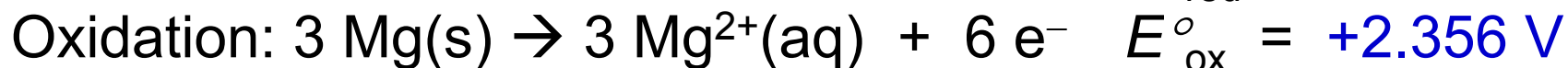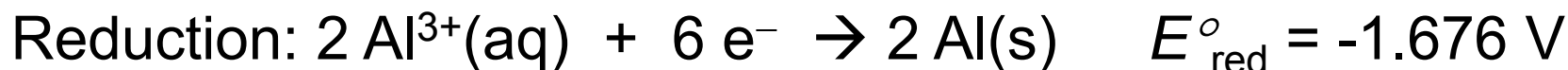
$$\Delta G^o = -(6\ mol\ e^-)(96485\ C/mol\ e^-)(0.680\ V) = -393,659\ VC$$
$$\text{or } -393.7\ kJ$$

2. $\Delta G° = -RT\ln K$ or $\ln K = -\Delta G°/RT$

$\ln K = 393.7\ kJ\ /\ (8.314 \times 10^{-3})\ J/K\ mol)(298\ K)$

$\ln K = 158.9$ and $K = e^{272.0} = 1.03 \times 10^{69}$

Non-standard Cell Potentials (E_{cell})

- Concentrations ≠ 1 M and/or pressures ≠ 1 atm

- Nernst equation:

$$E_{cell} = E^o{}_{cell} - \frac{RT}{zF}\ln Q$$

R = gas constant (J/K mol)

T = temperature (K)

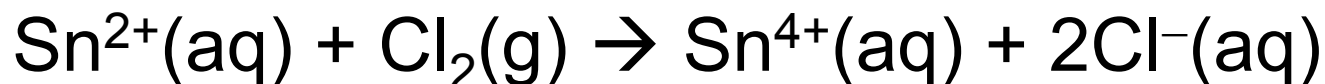z = # of e⁻ transferred

F = Faraday constant (96485 C/mol)

Q = reaction quotient

Often written as: Eq. 20.18
at 25°C

$$E_{cell} = E^o{}_{cell} - \frac{0.0592}{z}\log Q$$

Writing Q or K for thermodynamics

$$Sn^{2+}(aq) + Cl_2(g) \rightarrow Sn^{4+}(aq) + 2Cl^-(aq)$$

$$K = \frac{a_{Sn4+}a_{Cl-}}{a_{Sn2+}a_{Cl2}} = \frac{[Sn^{4+}][Cl^-]^2}{[Sn^{2+}]P_{Cl2}}$$

All concentrations and pressures are taken with respect to reference concentrations (1 M) or pressures (1 bar, $\approx$ 1 atm)

We can write a K expression with concentrations and pressures together because of activity (a).

iClicker #4: Using the Nernst Equation

For the reaction

$2 Fe^{3+}(aq, 0.50 M) + Cu(s) \rightarrow 2 Fe^{2+}(aq, 0.50M) + Cu^{2+}(aq, 0.50 M)$

Write the *Q* expression.

Question: Will an increase in $[Fe^{3+}]$ cause E_{cell} to increase or decrease?

(A) increase

(B) decrease

$$E_{cell} = E^o{}_{cell} - \frac{RT}{zF} \ln Q$$

$$Q = \frac{[Fe^{2+}]^2 [Cu^{2+}]}{[Fe^{3+}]^2}$$

Increase in $[Fe^{3+}]$ causes *Q* to decrease

$\ln Q$ therefore decreases

E_{cell} therefore increases

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Concentration Cells

- Identical electrodes with different ion concentrations
- Anode and cathode are the same $\therefore E^\circ_{cell} = 0$
- Voltage still possible because of ion concentrations

Cathode:
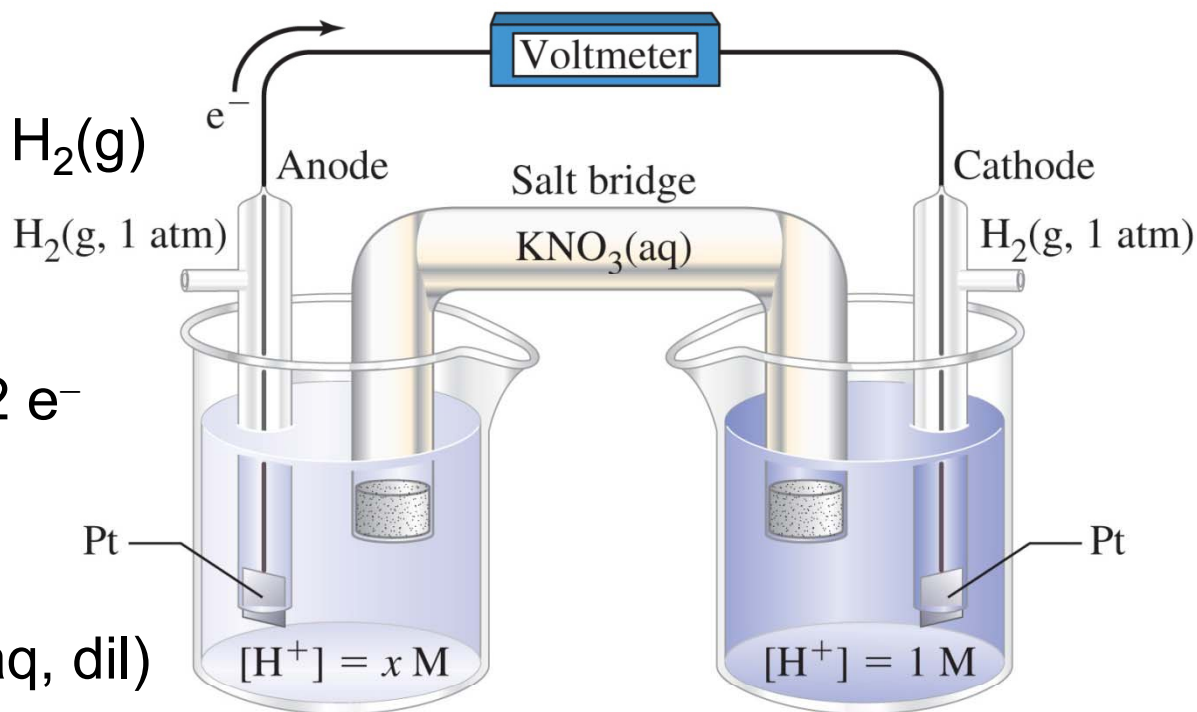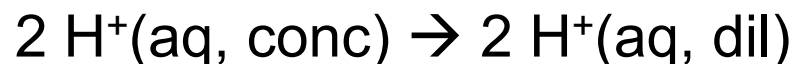
$2 \text{ H}^+(\text{aq, conc}) + 2 \text{ e}^- \rightarrow \text{H}_2(\text{g})$

Anode:

$\text{H}_2(\text{g}) \rightarrow 2 \text{ H}^+(\text{aq, dil}) + 2 \text{ e}^-$

Overall:

$2 \text{ H}^+(\text{aq, conc}) \rightarrow 2 \text{ H}^+(\text{aq, dil})$

p. 883-885
(839-840,
9th ed.)

This applies to (aq) metal ions, too: Lab 4
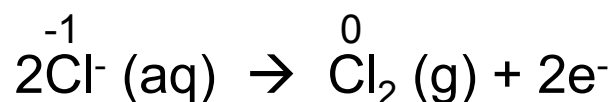Think about how to write Q

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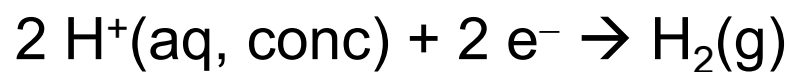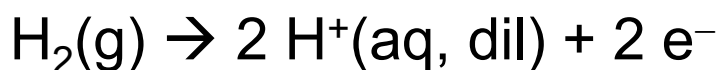
The Chloralkali Process: Electrolytic Cell

- Industrial synthesis of Cl_2, H_2 & NaOH derived from the electrolysis of salt solution (brine) → Water sanitation & alternative fuel

- Electrolysis is a non-spontaneous redox reaction that requires external energy (voltage) to drive the chemical transformation

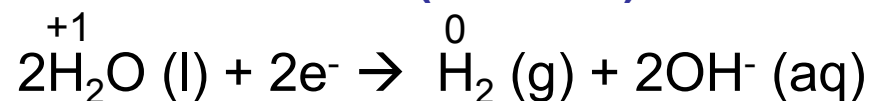$$2Cl^- (aq) + 2H_2O (l) \rightarrow Cl_2 (g) + H_2 (g) + 2OH^- (aq)$$
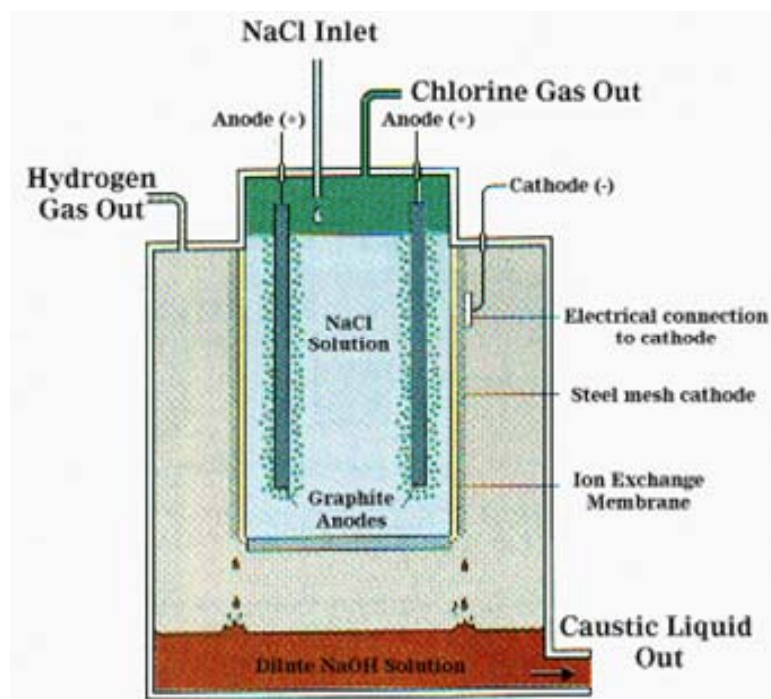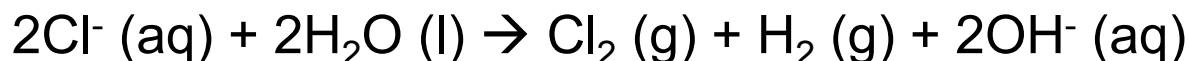
Half-cell Reactions

Oxidation (Anode)

$$\overset{-1}{2Cl^-} (aq) \rightarrow \overset{0}{Cl_2} (g) + 2e^-$$

Reduction (Cathode)

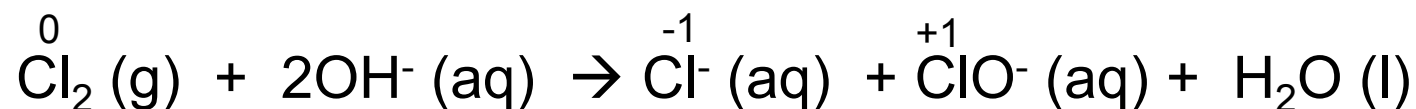$$\overset{+1}{2H_2O} (l) + 2e^- \rightarrow \overset{0}{H_2} (g) + 2OH^- (aq)$$

Chloralkali Process: 3 Products from 1!

▪ Semi-permeable membrane helps maintain electroneutrality, but prevents mixing of products generated → Cl$_2$ disproportionation
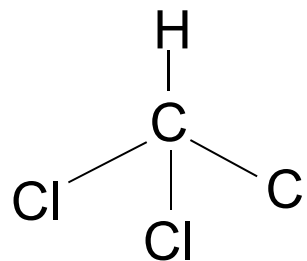
$$\overset{0}{Cl_2} \text{ (g)} + 2OH^- \text{ (aq)} \rightarrow \overset{-1}{Cl^-} \text{ (aq)} + \overset{+1}{ClO^-} \text{ (aq)} + H_2O \text{ (l)}$$

▪ Cl$_2$ (g) → Valuable commodity as it is widely used as a disinfectant during water treatment or transformed into "bleach" → NaClO

$$2NaOH \text{ (aq)} + Cl_2 \text{ (g)} \longrightarrow NaCl \text{ (aq)} + NaClO \text{ (aq)} + H_2O \text{ (l)}$$

▪ Concern regarding chlorination of drinking water include residual odour/taste & generation of toxic by-products trihalomethanes
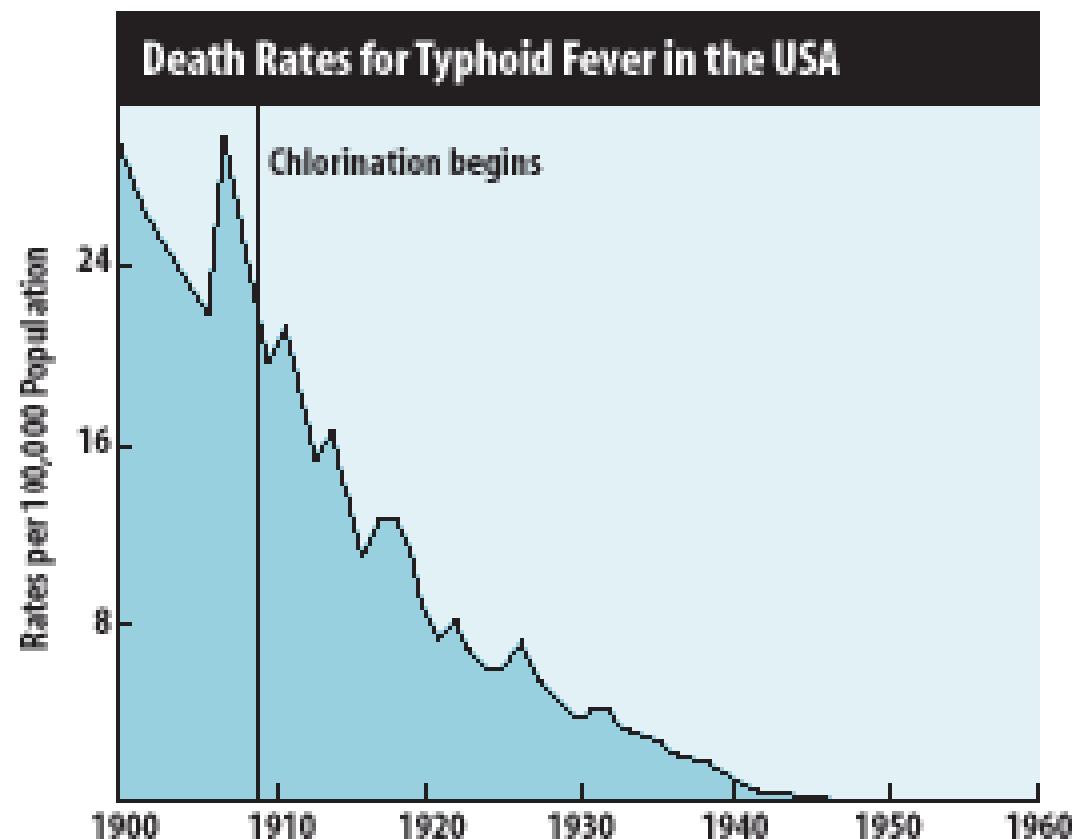
Chloroform: Suspected Carcinogen

CHCl$_3$

Chlorination & Human Health

Death Rates for Typhoid Fever in the USA

Chlorination begins

Rates per 100,000 Population

24

16
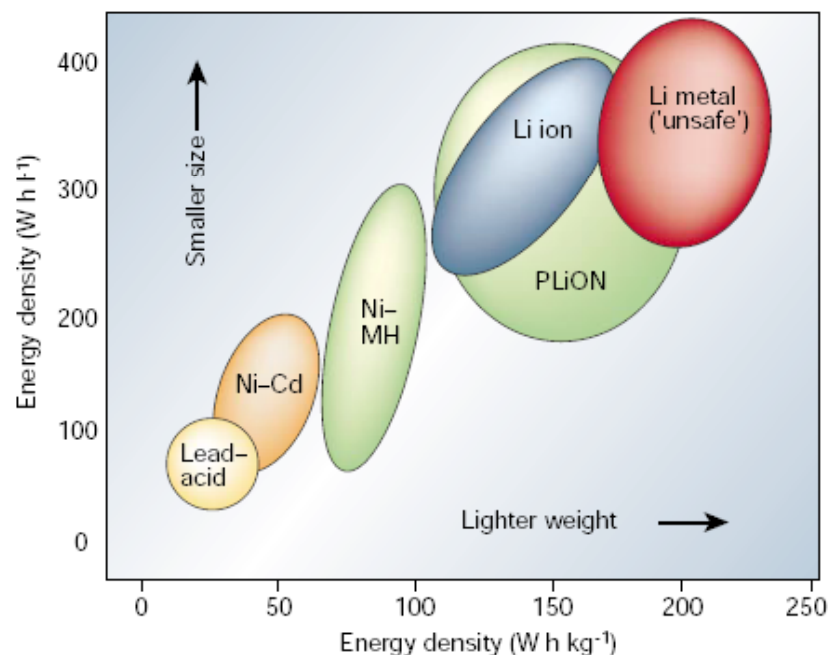
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1900 1910 1920 1930 1940 1950 1960

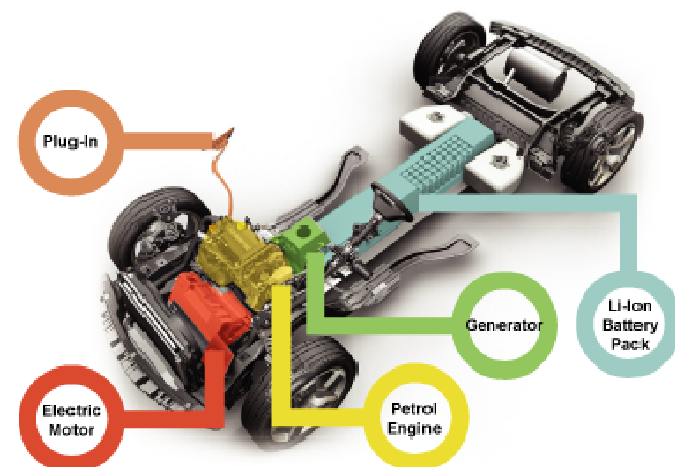**Source: US Centers for Disease Control and Prevention, Summary of Notifiable Diseases, 1997.**
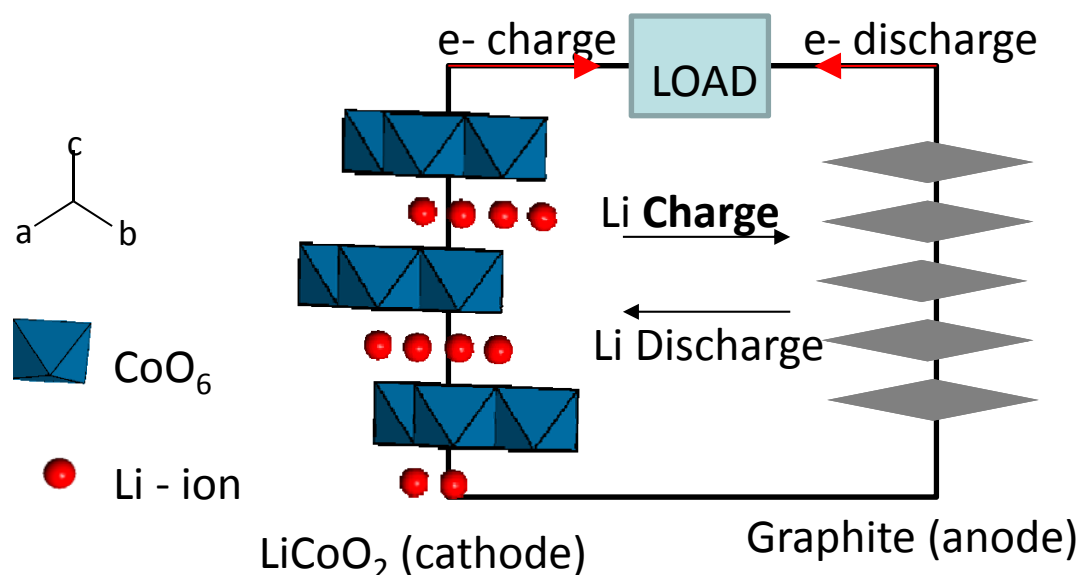
Li-ion Batteries

- Account for 63% of portable batteries worldwide since being commercialized by Sony in 1990

Tarascon, J.-M., Armand, M., *Nature*, **414**, 2001, 359

e- charge   LOAD   e- discharge

Li **Charge**

Li Discharge

CoO$_6$

Li - ion

LiCoO$_2$ (cathode)

Graphite (anode)

http://movementbureau.blogs.com/photos/uncategorized/gm_volt_analysis2.png