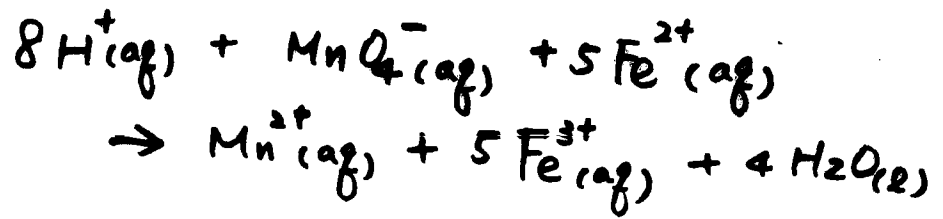


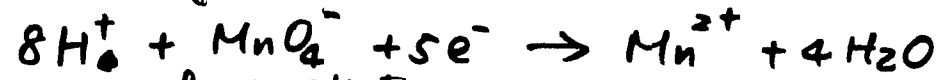
- 17.1 Galvanic cells
- 17.2 Standard Reduction Potentials
- 17.3 Cell Potential
- 17.4 Dependence of Cell Potential on Concentration
- 17.5 Batteries
- 17.6 Corrosion
- 17.7 Electrolysis
- 17.8 Commercial Electrolytic Processes

17.1 Galvanic Cells

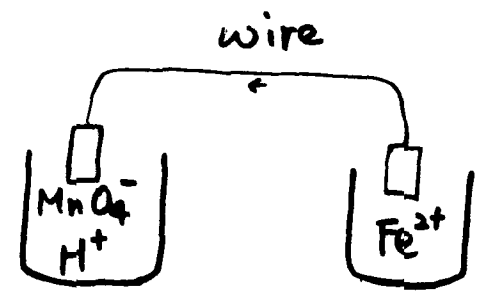
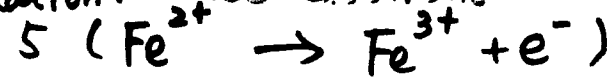
Oxidation-reduction (redox) reaction



Reduction: gain electrons



Oxidation: lose electrons

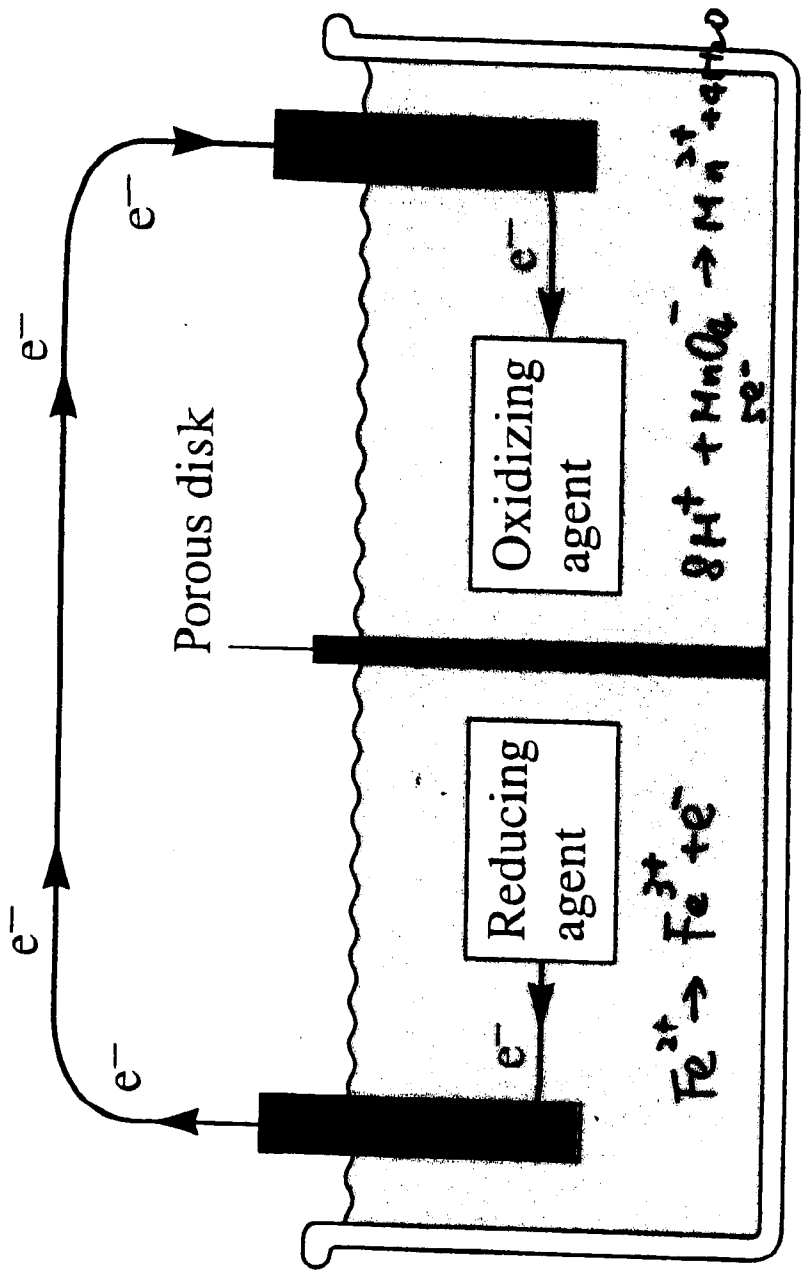


current flows for an instant and then ceases (非通路)

↓ or salt bridge or porous disk

See Fig. 17.2

Galvanic cell: a device in which chemical energy is changed to electrical energy.
 anode: Oxidation occurs
 cathode:



(a) Anode

(oxidation occurs)
陽極

(b) Cathode

(reduction occurs)
陰極

Figure 17.3

A schematic of a galvanic cell

Steven S. Zumdahl, Chemistry, © Houghton Mifflin Company. All Rights Reserved.

cell potential

a galvanic cell consists of:
an oxidizing agent in one compartment
to pull e^- from a reducing agent
in the other compartment

The "pull" or driving force on the electrons
is called the cell potential (E_{cell})

單位 volt (1 joule of work per
coulomb of charge transferred)

可用 voltmeter 測量 電位差

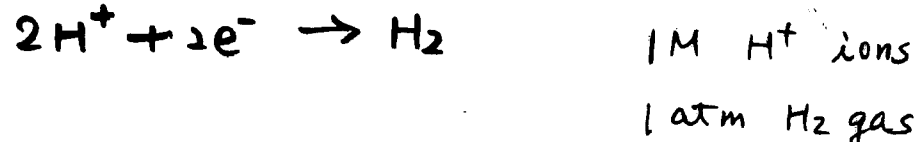
§ 17.2 Standard Reduction Potentials



The anode reaction: (oxidation occurs)



The cathode reaction: (reduction occurs)

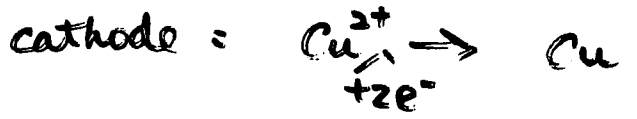
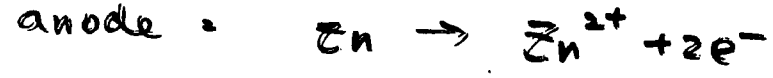
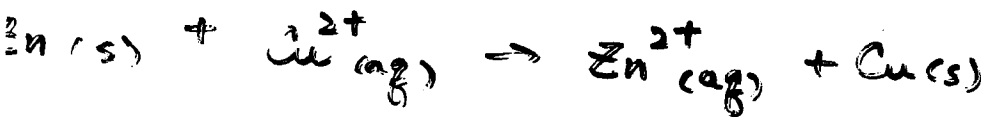


($[H^+] = 1M$ & $P_{H_2} = 1 atm$)

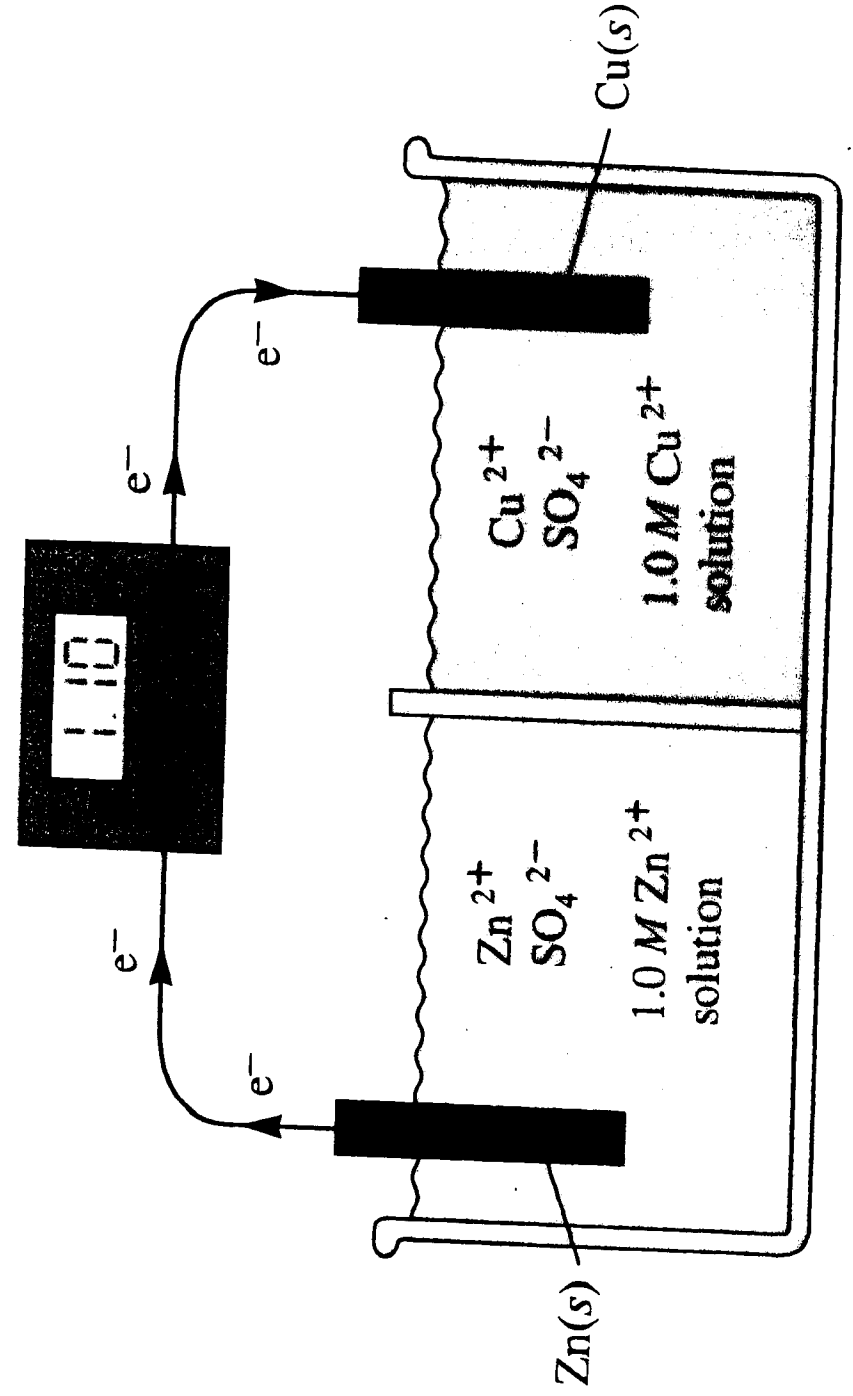
$\sum_{H^+ \rightarrow H_2}^{\circ} = 0$

$\sum_{cell}^{\circ} = \sum_{H^+ \rightarrow H_2}^{\circ} + \sum_{Zn \rightarrow Zn^{2+}}^{\circ}$

↑ 可測得 0.76V ↑ set 0V ↑ ∴ = 0.76V



$E_{cell}^{\circ} = E_{Zn \rightarrow Zn^{2+}}^{\circ} + E_{Cu^{2+} \rightarrow Cu}^{\circ}$
 ↑ 測得 = 1.10V ↑ 由另一電池 = 0.76V ↑ ∴ = 0.34V



Anode $Zn \rightarrow Zn^{2+} + 2e^-$ Cathode $Cu^{2+} + 2e^- \rightarrow Cu$

Figure 17.6
A Zn/Cu galvanic cell

Standard reduction potentials: 17-7

The E° values corresponding to reduction half-reactions with all solutes at 1 M and all gases at 1 atm

(see Table 17.1 & appendix 5.5) page 843

Ex 17.1 - galvanic cell by redox rx: (see page 844)

1. One of the reduction half-reactions must be reversed which means the sign of the potential for the reversed half rx must be reversed

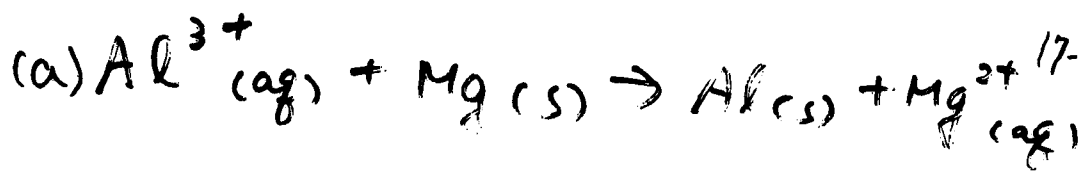
2. The value of E° is not changed when a half-reaction is multiplied by an integer.

(E° 是 "强度" intensive property)

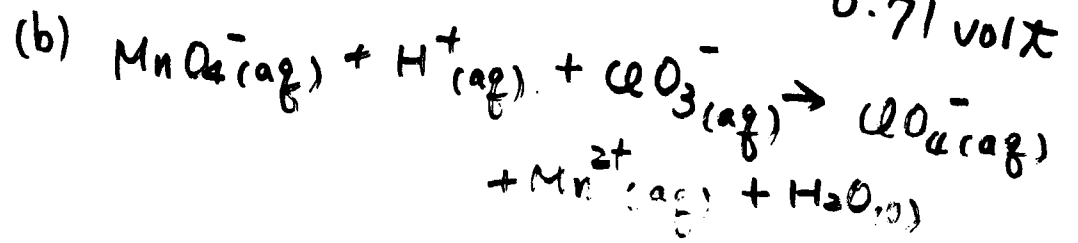
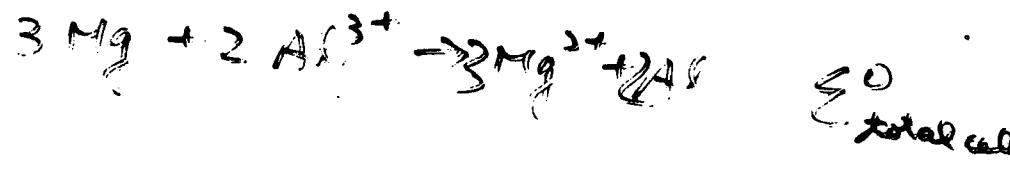
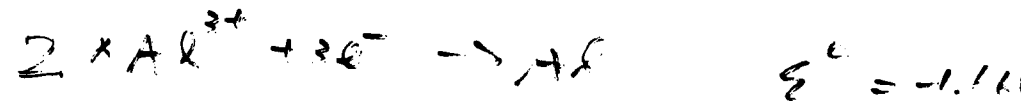
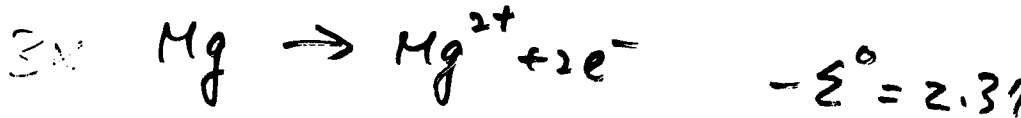
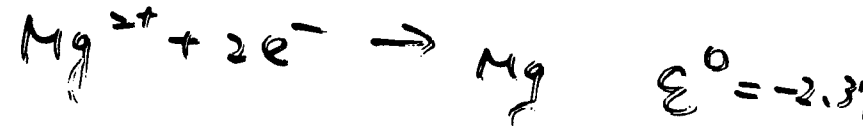
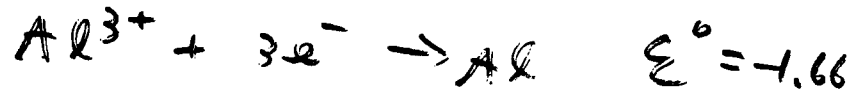
see Ex. 17.1 Galvanic cells (page 844)

計算 E° of the cell

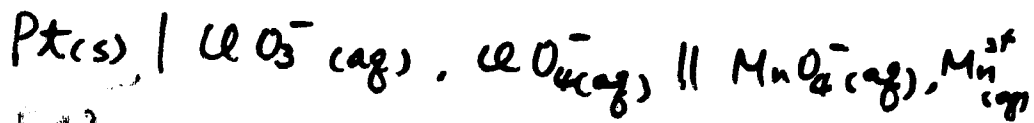
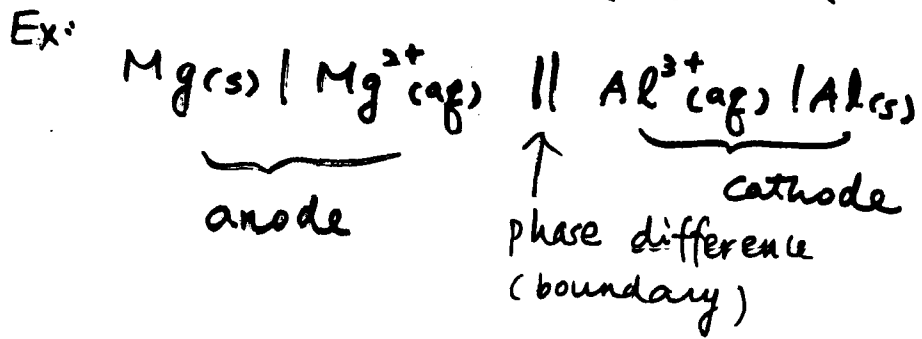
Give the balanced cell reaction



half rx



line notation (简便的表示表示 cell)



Ex 17.2

page 847

↑
电势

a cell will always run spontaneously in the direction that produces a positive cell potential.

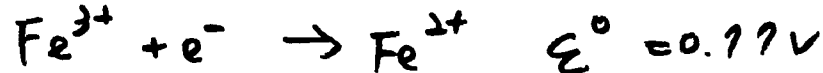
A complete description of a galvanic cell includes:

- The cell potential and the balanced cell rx.
- The direction of electron flow (由半反应还原电位推导出)
表示 anode and cathode

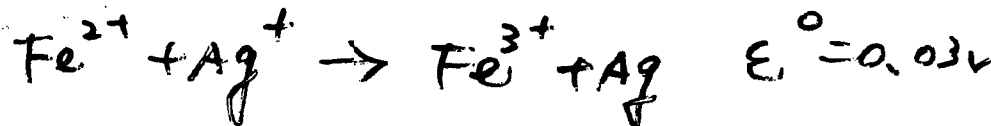
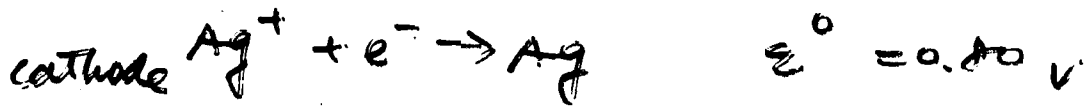
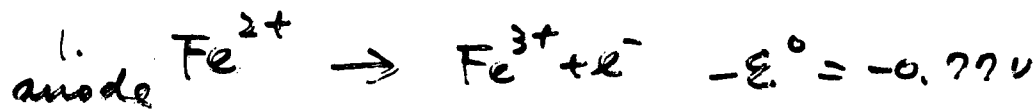
17-10

4. 加电极 (use chemically inert conductor). 如果 none of the subst participating in the half-rx is a conducting solid.

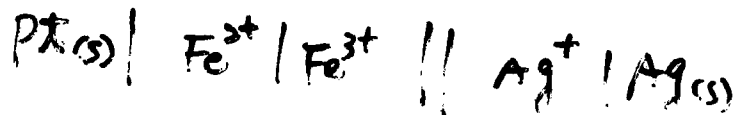
Ex 17.2 Describe the galvanic cell



sol'n:



2.



and Free Energy

The driving force that "push" electrons transferred through a wire:

$$emf = \text{potential difference (V)}$$

$$= \frac{\text{work (J)}}{\text{charge (C)}}$$

$$\mathcal{E} = \frac{-W \rightarrow \text{work done}}{q \rightarrow \text{charge}}$$

$$-W = q \mathcal{E}$$

But e^- 流动 will cause frictional heating 而损失能量

$$\therefore -W_{max} = q \mathcal{E}_{max}$$

Ex: a galvanic cell, $\mathcal{E}_{max} = 2.50V$
average potential $\mathcal{E} = 2.10V$.

請計算 推过 1.33 moles electrons 所做的功. 及 电池的 efficiency

Sol: 1 moles of $e^- = 1 \text{ Faraday}$
~~100~~ 96,485 Coulomb

$$W_{max} = -q \mathcal{E}_{max}$$

$$= -(1.33 \text{ moles} \times 96,485 \frac{\text{Coul}}{\text{mol}}) \times 2.50V$$

$$= -3.21 \times 10^5 \text{ J}$$

$$W_{(average)} = -q \mathcal{E}_{ave}$$

$$= -(1.33 \text{ moles} \times 96,485 \frac{\text{Coul}}{\text{mol}}) \times 2.10V$$

$$= -2.69 \times 10^5 \text{ J}$$

$$\text{Efficiency} = \frac{-2.69 \times 10^5}{-3.21 \times 10^5} \times 100\% = 83.8\%$$

$$W_{max} = \Delta G$$

$$-q \mathcal{E}_{max} \quad \left(q = \overset{\substack{\# \text{ of moles of electrons} \\ \uparrow \\ n}}{n} \overset{\substack{\text{faraday} \\ \uparrow \\ F}}{F} \right)$$

$$\therefore \Delta G = -n F \mathcal{E}_{max}$$

$$\Delta G^\circ = -n F E^\circ \quad \text{at standard conditions}$$

the maximum cell potential is directly related to the free energy difference between the reactants and the products in the cell.

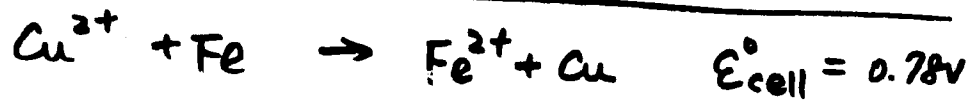
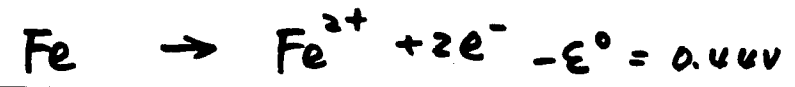
Ex. 17.3

using the data in Table 17.1, calculate ΔG° for the reaction



Is the rx spontaneous?

Sol:



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

$$= (-2 \text{ moles of electrons}) \cdot 96485 \frac{\text{coulomb}}{\text{mole}}$$

$$\times 0.78 \frac{\text{J}}{\text{coulomb}}$$

$$= -1.5 \times 10^5 \text{ J}$$

Spontaneous!

Table 17.1 Standard reduction potentials at 25°C (298K) for many common half-reactions

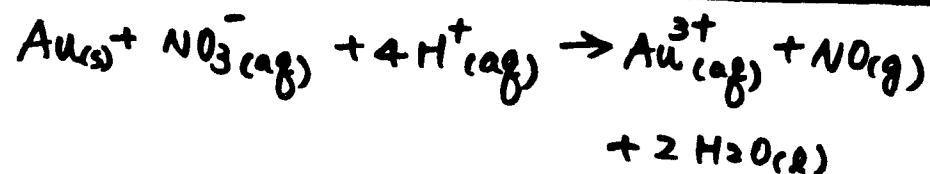
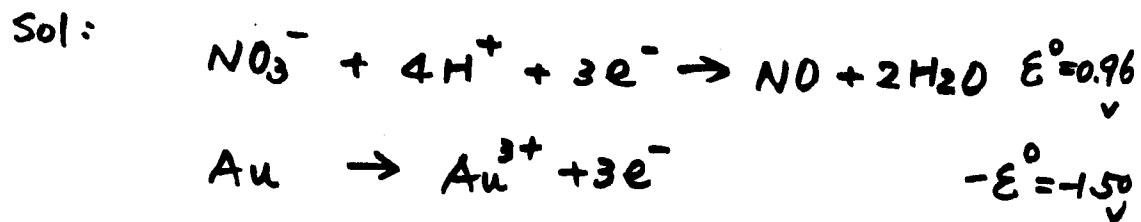
Half-reaction	ϵ° (V)	Half-reaction	ϵ° (V)
$\text{F}_2 + 2e^- \rightarrow 2\text{F}^-$	2.87	$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$	0.40
$\text{Ag}^+ + e^- \rightarrow \text{Ag}$	1.99	$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	0.34
$\text{Co}^{3+} + e^- \rightarrow \text{Co}^{2+}$	1.82	$\text{H}_2\text{Cl}_2 + 2e^- \rightarrow 2\text{HCl} + 2\text{Cl}^-$	0.26
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.78	$\text{AgCl} + e^- \rightarrow \text{Ag} + \text{Cl}^-$	0.22
$\text{MnO}_4^- + 4\text{H}^+ + 3e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	1.70	$\text{SO}_4^{2-} + 4\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$	0.20
$\text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.69	$\text{Cu}^2+ + e^- \rightarrow \text{Cu}^+$	0.16
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{MnO} + 2\text{H}_2\text{O}$	1.68	$\text{H}^+ + 2e^- \rightarrow \text{H}_2$	0.00
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	1.60	$\text{Fe}^{3+} + 3e^- \rightarrow \text{Fe}$	-0.036
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	1.51	$\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$	-0.13
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	1.51	$\text{Sn}^{2+} + 2e^- \rightarrow \text{Sn}$	-0.14
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	1.50	$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$	-0.25
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	1.46	$\text{PbSO}_4 + 2e^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.35
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	1.36	$\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd}$	-0.40
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	1.33	$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$	-0.44
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	1.23	$\text{Cr}^{3+} + e^- \rightarrow \text{Cr}^{2+}$	-0.50
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	1.21	$\text{Cr}^{3+} + 3e^- \rightarrow \text{Cr}$	-0.73
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	1.20	$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$	-0.76
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	1.09	$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.83
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	1.00	$\text{Mn}^{2+} + 2e^- \rightarrow \text{Mn}$	-1.18
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	0.99	$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$	-1.66
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	0.96	$\text{H}_2 + 2e^- \rightarrow 2\text{H}^-$	-2.23
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	0.954	$\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$	-2.37
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	0.91	$\text{La}^{3+} + 3e^- \rightarrow \text{La}$	-2.37
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	0.80	$\text{Na}^+ + e^- \rightarrow \text{Na}$	-2.71
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	0.80	$\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}$	-2.76
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	0.77	$\text{Ba}^{2+} + 2e^- \rightarrow \text{Ba}$	-2.90
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	0.68	$\text{K}^+ + e^- \rightarrow \text{K}$	-2.92
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	0.56	$\text{Li}^+ + e^- \rightarrow \text{Li}$	-3.05
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	0.54		
$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	0.52		

Steven S. Zumdahl, Chemistry, © Houghton Mifflin Company. All Rights Reserved.

$$\Delta G^\circ < 0 \Rightarrow \text{spontaneous}$$

Ex. 17.4

1M HNO₃ + Au metal



$$E^\circ_{\text{cell}} = 0.96\text{V} - 1.50\text{V} = -0.54\text{V}$$

$E^\circ_{\text{cell}} < 0 \Rightarrow$ will not occur spontaneously at standard conditions

17.4 Dependence of cell potential on concentration

Le Chatelier's principle

Ex. 17.5. (page 805)

Concentration Cells: cells which both ⁽⁷⁻¹⁾ compartments have the same component but at different concentrations is called "concentration cells"

The Nernst Equation

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (1)$$

Q: reaction quotient

$$\therefore \Delta G = -nFE$$

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

in equation (1)

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

$$\boxed{E = E^\circ - \frac{RT}{nF} \ln(Q)} \quad (2)$$

cell potential

Concentrations of the cell compartment components

at 25°C, equation (2) =

$$\boxed{E = E^\circ - \frac{0.0592}{n} \log(Q)}$$

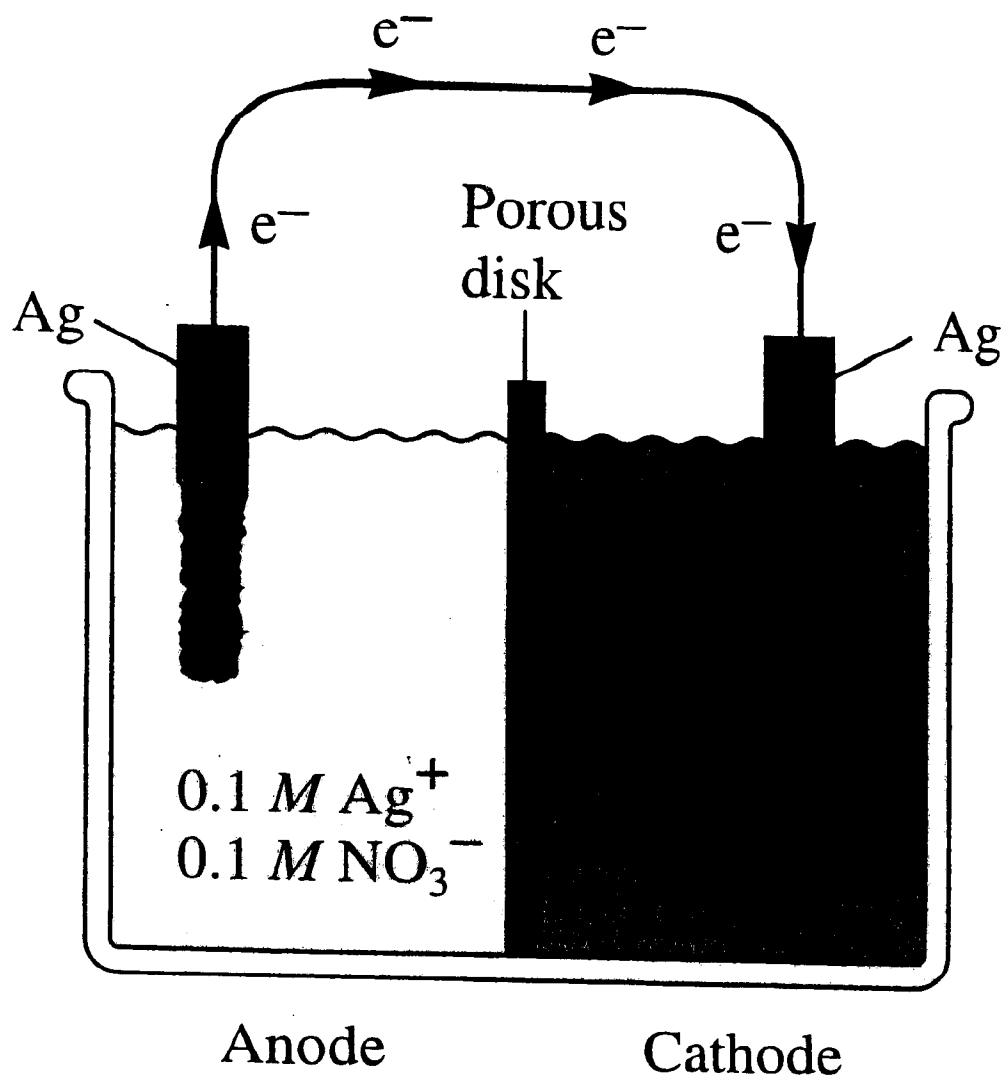
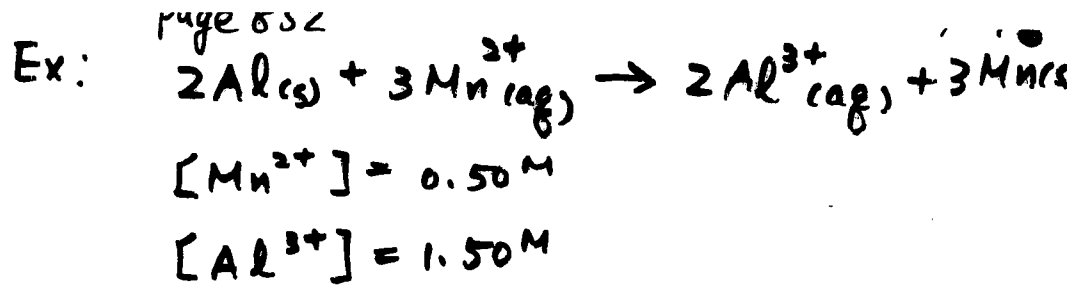


Figure 17.9
A silver concentration cell

Steven S. Zumdahl, Chemistry, © Houghton Mifflin Company. All Rights Reserved.



sol:
$$E_{cell} = E_{cell}^{\circ} - \frac{0.0592}{n} \log(Q)$$

$E_{cell}^{\circ} = 0.48 V$

$$Q = \frac{[Al^{3+}]^2}{[Mn^{2+}]^3} = \frac{(1.50 M)^2}{(0.50 M)^3} = 18$$

6 electrons in reaction $n = 6$

$$\therefore E_{cell} = 0.48 - \frac{0.0592}{6} \log 18$$

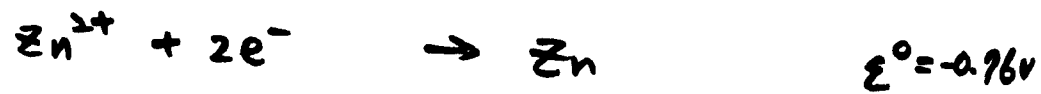
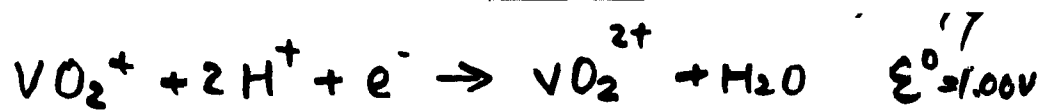
$$= 0.47 V$$

At equilibrium, $Q = K$ (equilibrium constant)

$E_{cell} = 0$

Dead battery

at equilibrium, the components in the two compartments have the same free energy



where $T = 25^{\circ}\text{C}$

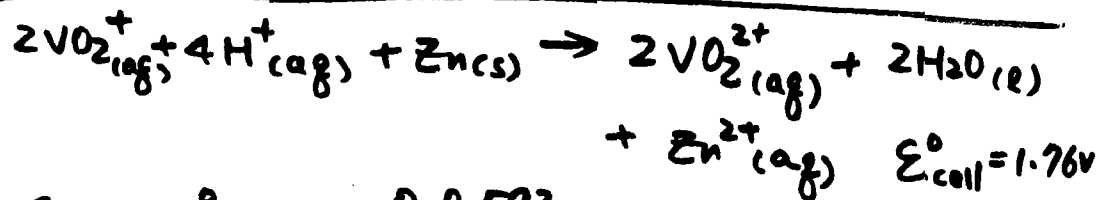
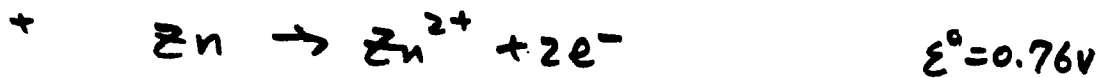
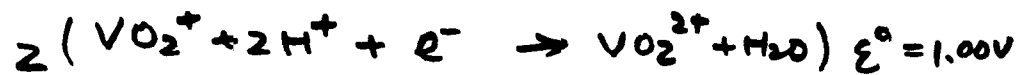
$$[\text{VO}_2^+] = 2.0\text{M}$$

$$[\text{H}^+] = 0.50\text{M}$$

$$[\text{VO}_2^{2+}] = 1.0 \times 10^{-2}\text{M}$$

$$[\text{Zn}^{2+}] = 1.0 \times 10^{-1}\text{M}$$

Sol:



$$\epsilon = \epsilon^{\circ}_{\text{cell}} - \frac{0.0592}{n} \log(Q)$$

$$= 1.76 - \frac{0.0592}{2} \log \frac{(1.0 \times 10^{-1})(1.0 \times 10^{-2})^2}{(2.0)^2(0.50)^4}$$

$$= 1.76 + 0.13 = 1.89\text{V}$$

#

Ion - Selective Electrodes 電極 17-20

∴ Cell potential is sensitive to the conc of the reactants and products

∴ measure potentials

→ can determine the concentration of an ion

Ex. pH meter:

- (1) a standard electrode of known potential
- (2) a special "glass" electrode that changes potential depending on the conc. of H^+ ions in the solution
- (3) a potentiometer that measures the potential between the two electrodes.

glass electrode: contains a reference solution of dilute hydrochloric acid in contact w/ a thin glass membrane (page 856)

Ion-selective electrodes

17-201

$\epsilon^\circ, \Delta G^\circ \Rightarrow$ we can calculate the equilibrium constants for redox rx.

At equilibrium,

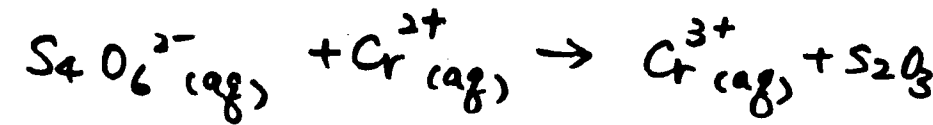
$$\epsilon_{\text{cell}} = 0 \quad \text{and} \quad Q = K$$

$$\epsilon = \epsilon^\circ - \frac{0.0592}{n} \log(Q) \quad \text{at } 25^\circ$$

$$0 = \epsilon^\circ - \frac{0.0592}{n} \log\left(\frac{Q}{K}\right)$$

$$\therefore \log K = \frac{n \epsilon^\circ}{0.0592} \quad \text{at } 25^\circ\text{C}$$

Ex 17.8 (page 856)



calculate ϵ° and K (at 25°C)

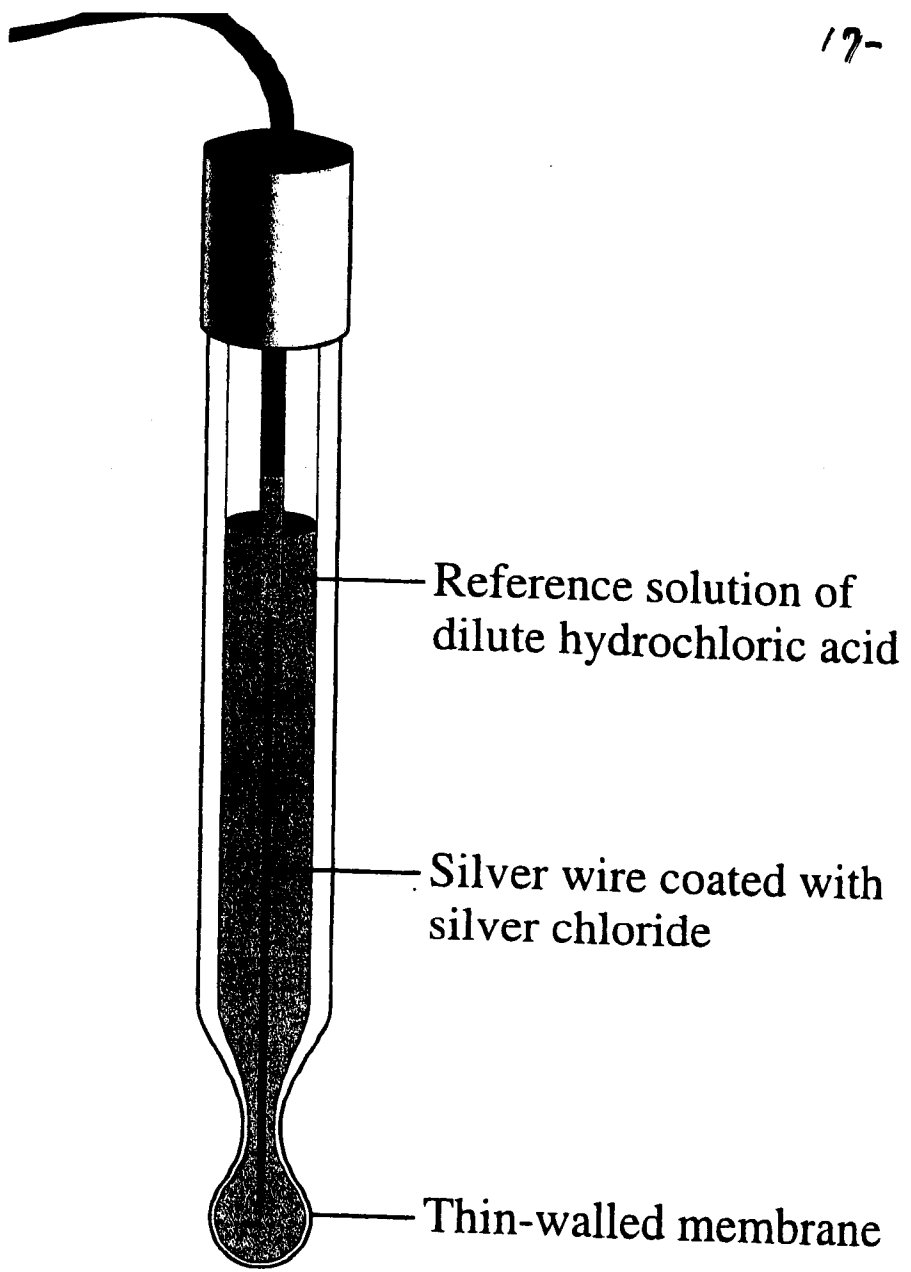
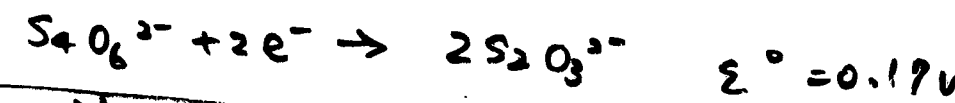
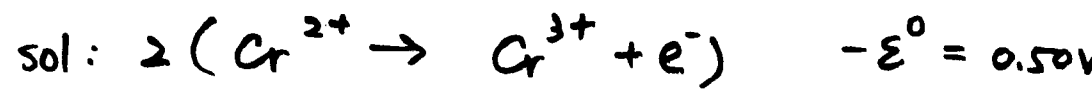


Figure 17.12
A glass electrode for measuring pH

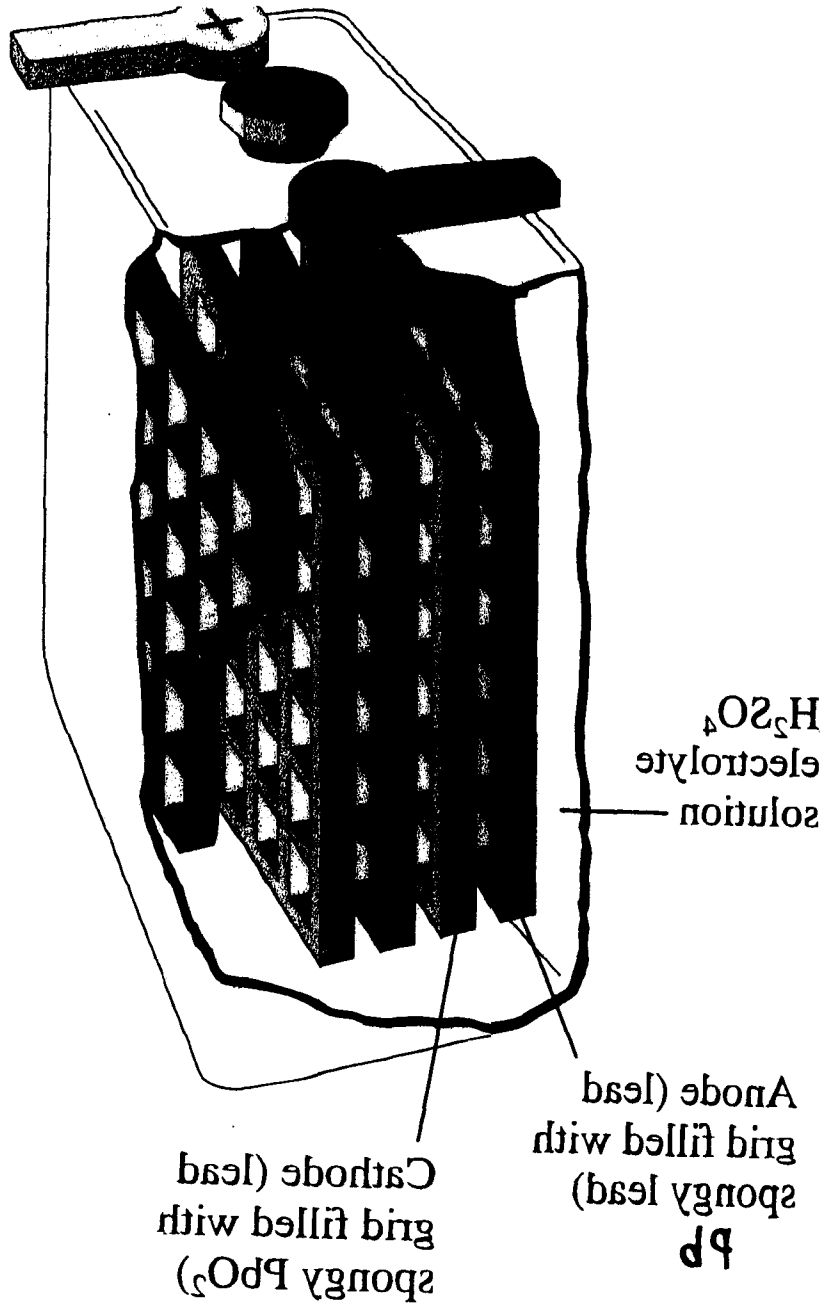


Figure 17.13
Schematic of a lead storage battery

Steven S. Zumdahl, Chemistry, © Houghton Mifflin Company. All Rights Reserved.

$$\log K = \frac{11 \cdot 2}{0.0592} = \frac{2(0.01)}{0.0592} = 22.6 \quad 17-2$$

$$K = 10^{22.6} = 4 \times 10^{22}$$

§ 17.5 Batteries

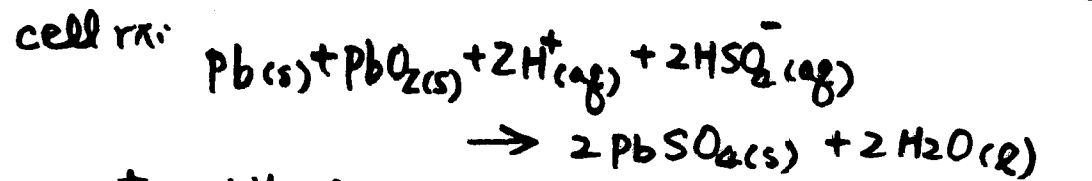
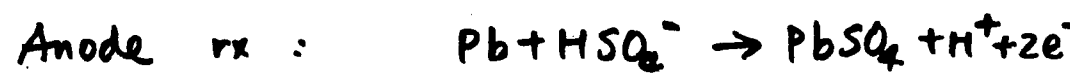
a battery: a galvanic cell or, more commonly, a group of galvanic cells connected in series.

Lead storage Battery

1915 自动式大汽车

-30°F to 120°F
rough roads.

} Lead storage battery
仍可使用



automobile lead storage battery

$E_{cell} \approx 2$



17-25

Other batteries

17-24

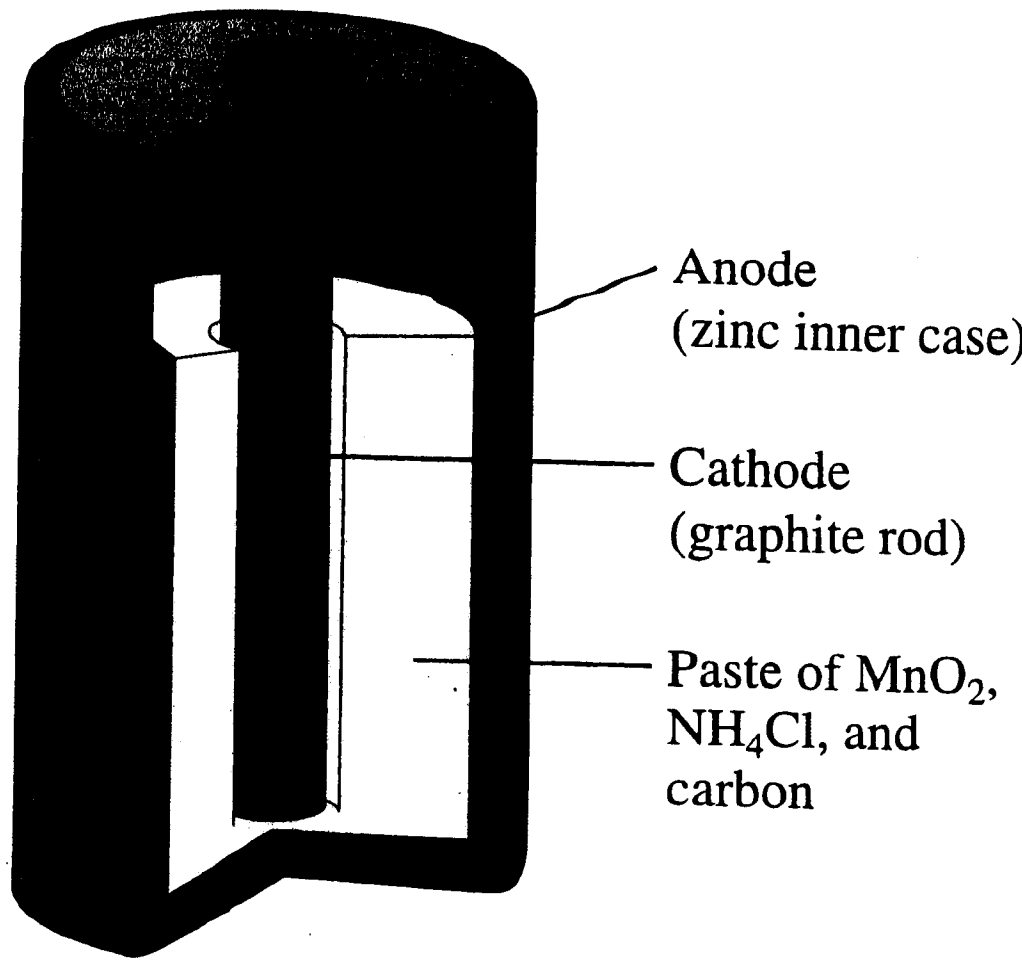


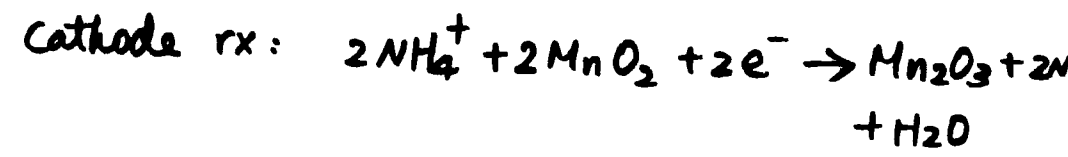
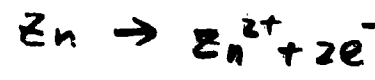
Figure 17.14
Schematic of a dry cell battery

Steven S. Zumdahl, Chemistry, © Houghton Mifflin Company. All Rights Reserved.

dry cell battery

Acid version:

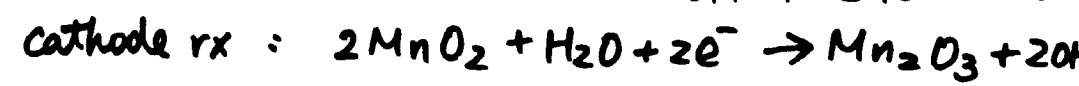
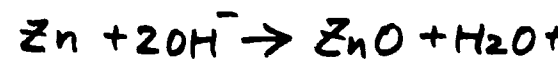
Anode rx:



$$E_{\text{cell}} = 1.5\text{V}$$

alkaline version:

Anode rx:

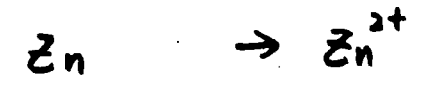


alkaline dry cell battery 壽命較長

∴ Zn 氧化 較為 快速 (in acidic conditions)

silver cell

Anode



mercury cell

Zn

Cathode



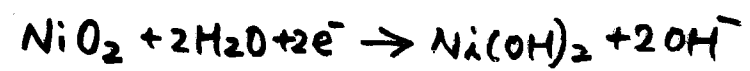
HgO

nickel-cadmium battery

Anode



Cathode



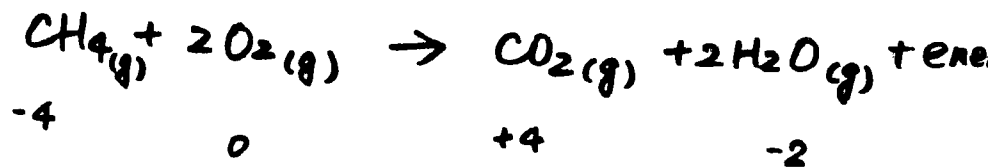
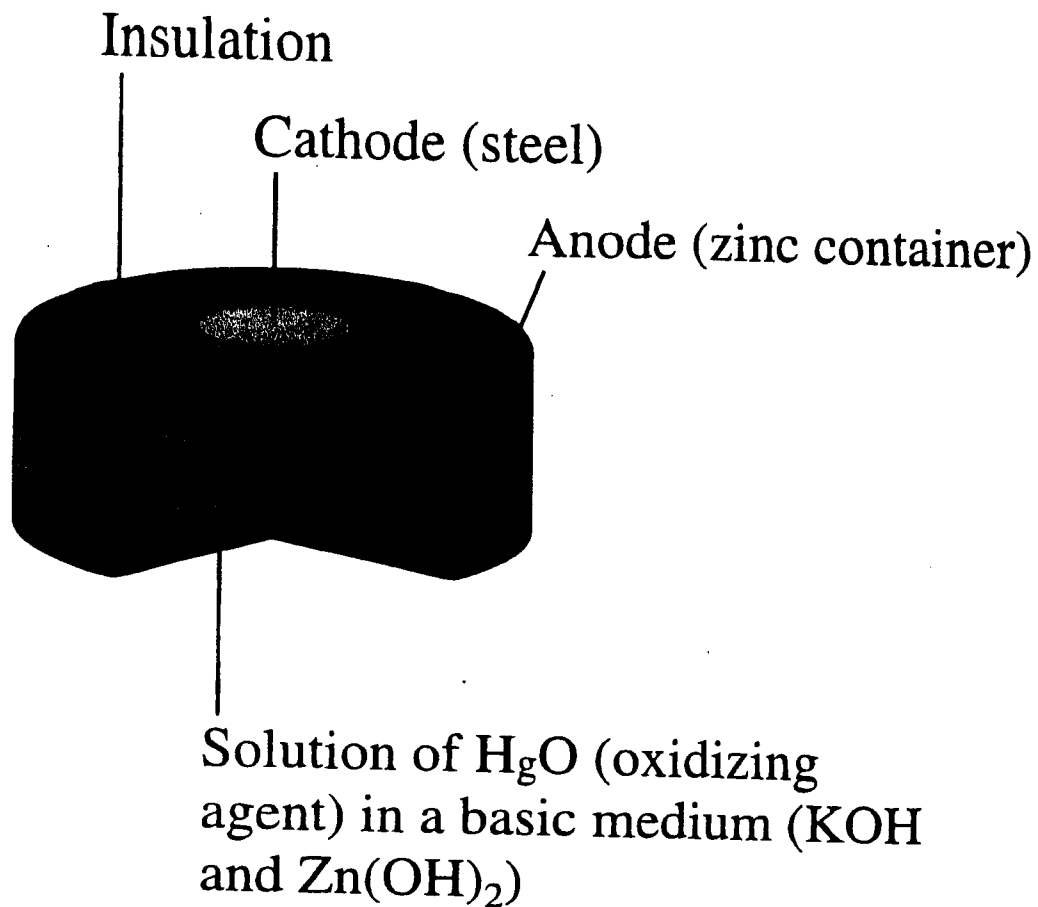
∴ products 都 黏 在 電 極 上 ∴ 可 以 recharge

17-25-1

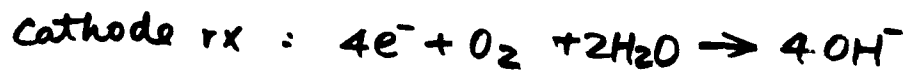
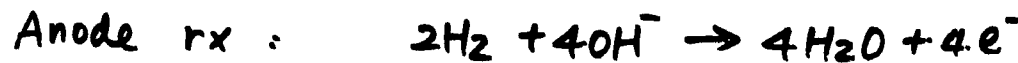
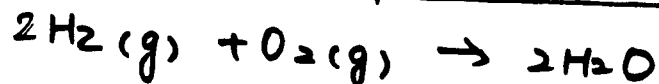
fuel cells

17-26

a fuel cell is a galvanic cell for which the reactants are continuously supplied



fuel cell used by The Apollo missions:



see Fig. 17.16

500 pounds for space vehicles

not practical for general use

§ 17.6 Corrosion 腐蝕

Corrosion : The process of returning metals to their natural state (自然腐蝕)
corrosion 就是氧化 of the metal

Figure 17.15
A mercury battery

Al

-1.7 V

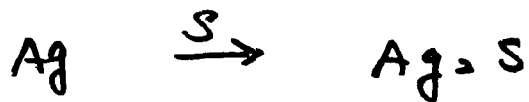
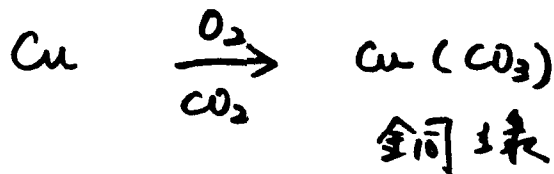
→ easy to oxidized by O₂

but Al₂O₃

-0.6 V

→ behave much like a noble metal

用漆做 coating, 防止 corrosion



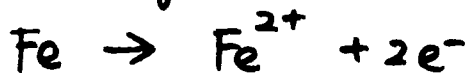
Au → no oxidation

Reduction potential = 1.50 V

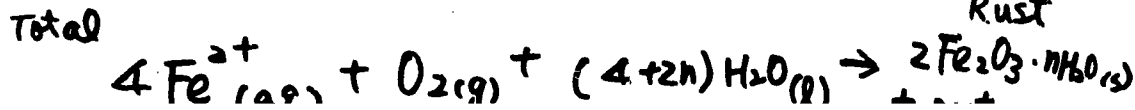
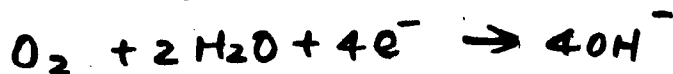
O₂ reduction potential = 1.23

Corrosion of Iron

anodic region:



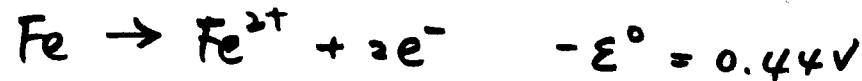
cathodic region:



PREVENTION of Corrosion

17.

Zn used to coat steel (called galvanic)



∴ Zn 較 Fe 易氧化 ∴ 先氧化 Zn, Fe remains in a reducing state.

Alloy 亦可防 corrosion

如 不銹鋼 steel Fe + Cr + Ni

§ 17.7 Electrolysis 電解

electrolytic cell: use electrical energy to produce chemical change.

Electrolysis: forcing a ~~own~~ current through a cell to produce change for which the cell potential is negative

(~~galvanic~~ galvanic cell 自發電池)

⊕ chemical energy → electrical energy

how much chemical change occurs with the flow of a given current for a specified time.

see page 866

step 1 to step 4

1. current & time
(I)

$$\frac{\text{Coul}}{\text{sec}} \times \text{sec} = \text{Coulomb}$$

(电量 \times 时间 used)

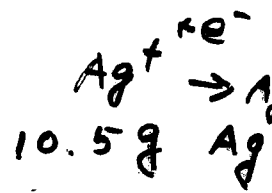
2. 电量 \rightarrow e^-

$$\frac{\text{Coulomb}}{\text{Faraday}} = \text{mole of } e^-$$

3. mole of $e^- \rightarrow$ mole product

Ex. 17.9.

5.00 A for how long \rightarrow produce



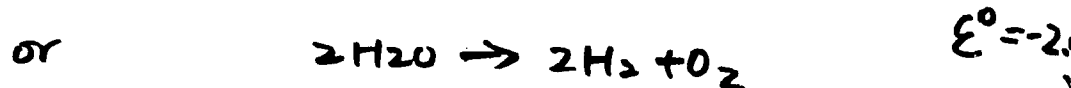
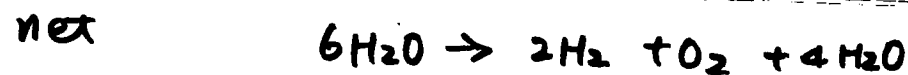
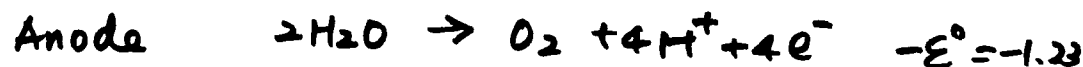
$$\text{sol: } \frac{10.5 \text{ g Ag}}{107.868 \text{ g/mol}} = \text{mole Ag}$$

$$= \text{mole } e^-$$

$$= \text{Coulomb } e^-$$

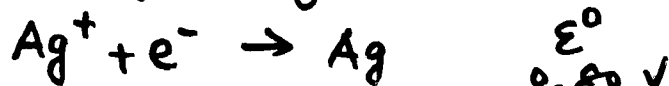
$$= \text{Current} \times \text{time}$$

Electrolysis of water



see page 869 Fig 17.20.

Electrolysis of mixtures of ions

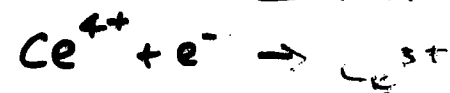


which one is easily reduced,

Ex. 17.10

Table 17.1

17-3


 E°
1.70


§17.8 Commercial Electrolytic Process

Production of Aluminum

