

# Chap. 11 Electrochemical cells (8) - 1

## ~~Gen~~ General remarks

electrochem. cells: metal electrode ~~to~~ in a solution containing cations of the metal

Actually 2 such half-cells are needed to close the electrical circuit

when cations leave the electrode to go into the solution  $\rightarrow e^-$  left at electrode

$\rightarrow$  negative charge formed at the electrode

2 half-cells can be coupled to a full cell either by a wire & and a salt-bridge

$\rightarrow$  electrochemical cell.  $\nabla$  b.w.

equilibrium condition: electrochemical cell potential (not that of chemicals alone) of a species is the same in all parts of the cell

can be used to provide power = battery

external electrical potential can reverse the cell-reaction = force it to go into opposite direction of the spontaneous one

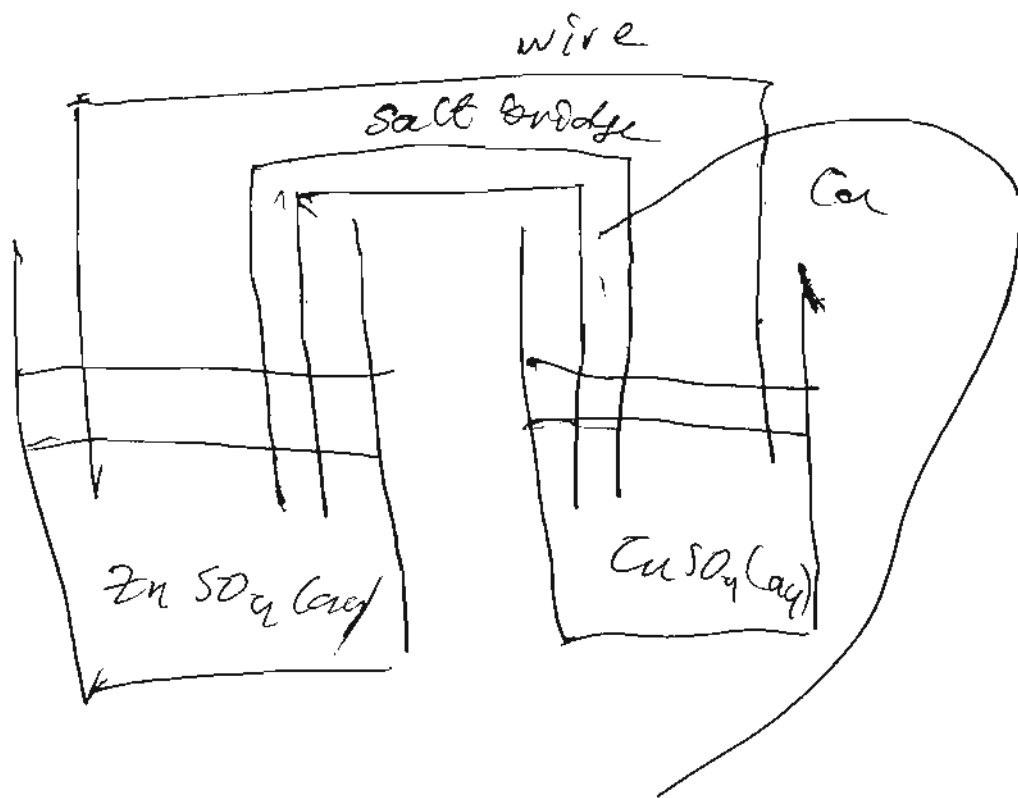
Effect of an electrical potential on chemical potential

Zn(s) immersed partially in a ZnSO<sub>4</sub>(aq) solution

$\rightarrow$  Zn<sup>2+</sup> goes into the solution

leaving e<sup>-</sup> behind

Ex. Daniell cell



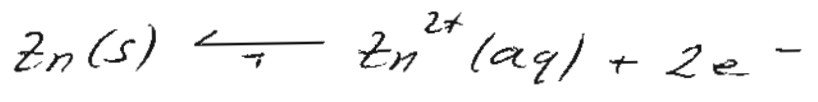
contains gel soaked in  
saturated or lower conc.  
 $KCl$  - solution

→ prevents solutions from  
direct mixing but  
transports charges ( $K^+$ ,  $Cl^-$ )

⇒ ⊖ charge on Zn(s)

⊕ charge in the solution

⇒ electrical potential difference  $\phi$   
= half-cell potential



equilibrium far on the left side

show in transp.

in equilibrium  $< 10^{-14}$  mol Zn dissolves in 1L solution  
out gives  $\phi \approx 1\text{V}$

the value of  $K$  and of  $\phi$  depends on the  
kind of metal  $\rightarrow = f(\Delta G_f^\circ(\text{Zn}^{2+}(\text{aq})))$

a half-cell potential cannot be measured directly,  
but relative to a reference half-cell  $\nabla$  b.w.

if a small potential  $\phi$  is applied, the chemical  
potentials of neutral atoms or molecules is not  
changed

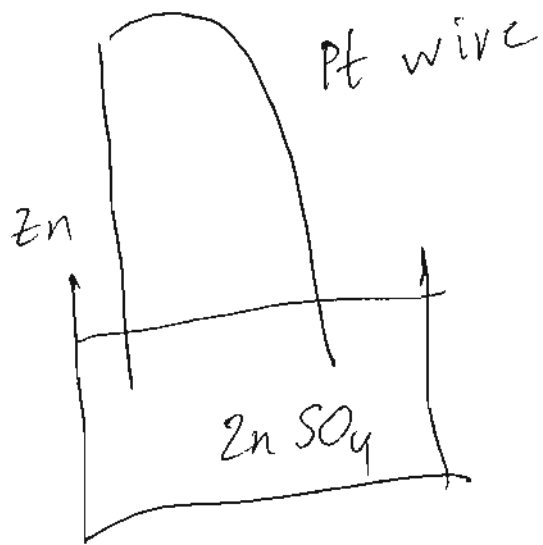
this not true for charged ions in solution

then: work  $dW_{\text{rev}}$  is required to transport  $dn$   
moles of charge reversibly from a uniform  
phase with  $\phi_1$  to another one, identical, but with  $\phi_2$

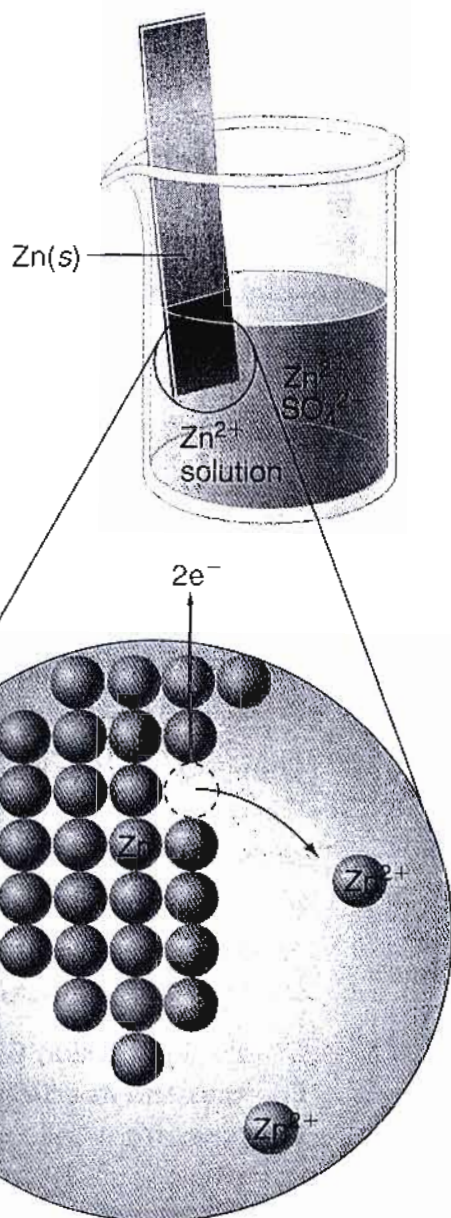
$$dW_{\text{rev}} = (\phi_2 - \phi_1) dQ \quad \text{only then } \Delta\phi \text{ can be measured}$$

$$dQ = -2F dn$$

$$F = 96485 \frac{\text{As}}{\text{mol}} (= \frac{\text{C}}{\text{mol}})$$



→  $\phi$  between the half-cell  $Zn | ZnSO_4(aq)$  and the half-cell  $Pt | ZnSO_4(aq)$   
not  $\phi_{Zn | ZnSO_4(aq)}$



**FIGURE 11.1**

When a Zn electrode is immersed in an aqueous solution containing  $\text{Zn}^{2+}(\text{aq})$  ions, a very small amount of the Zn goes into solution as  $\text{Zn}^{2+}(\text{aq})$ , leaving two electrons behind on the Zn electrode per ion formed.

The equilibrium position in this reaction lies far fewer than  $10^{-14}$  mol of the  $\text{Zn}(\text{s})$  dissolves in 1 liter. However, this minuscule amount of charge transfer between the Zn electrode and the electrolyte solution is sufficient to create a difference of approximately  $10^{-5}$  V between the Zn electrode and the electrolyte solution. Equilibrium is established for other metal electrodes. Because the equilibrium constant depends on  $\Delta G_f^\circ$  of the solvated metal ion, the equilibrium constant for the dissociation reaction and  $\phi$  depends on the identity of the metal.

Can  $\phi$  be measured directly? Let us assume that we are using two chemically inert Pt wires as probes. One Pt wire is placed in the Zn electrode and the second Pt wire is placed in the  $\text{ZnSO}_4$  solution. The difference in electrical potential between a Pt wire in contact with the Zn electrode and a Pt electrode in a  $\text{ZnSO}_4$  solution is the half-cell potential. This difference in electrical potential can only be measured between two electrodes of identical composition. For example, the difference in electrical potential across a resistor is measured by contacting the metal wire at each end with metal probes of identical composition connected to a voltmeter. Although we can not measure the half-cell potential  $\phi$  directly, it can be determined relative to a reference half-cell as will be discussed in Section 11.4.

How are chemical species affected by the electrical potential? In the approximation, the chemical potential of a **neutral** atom or molecule in a small electrical potential is applied to the environment of the atom or molecule. This is not the case for a **charged** species such as an  $\text{Na}^+$  ion. The work required to transfer  $dn$  moles of charge reversibly from one phase at an electrical potential  $\phi_1$  to a second, otherwise identical phase at potential  $\phi_2$  is equal to the product of the charge and potential between the two locations:

$$d'w_{rev} = (\phi_2 - \phi_1) dQ$$

In this equation,  $dQ = -zF dn$  is the charge transferred, where  $z$  is the charge in units of the electron charge (+1, -1, +2, -2, ...), and  $F$  is the absolute magnitude of the charge associated with the species. The Faraday constant has the numerical value  $96485 \text{ C mol}^{-1}$ .

Because the work being carried out in this reversible process is  $d'w_{rev} = dG$ , which is the difference in the electrical potential of a charged particle in the two phases:

$$dG = \tilde{\mu}_2 dn - \tilde{\mu}_1 dn$$

The electrochemical potential is a generalization of the chemical potential  $\mu$  to include the effect of an electrical potential on a charged particle. It is the sum of the chemical potential  $\mu$  and a term that results from the electrical potential:

non-expansion work only,  $dW_{rev} = dG$  (8)-3

$dG = \tilde{\mu}_2 dn - \tilde{\mu}_1 dn$   
there is a  
(difference in electrochemical potential  $\tilde{\mu}$   
of charged ions ~~between~~ <sup>in</sup> the 2 phases

$$\tilde{\mu} = \mu + z\phi F$$

so that  $\tilde{\mu} \rightarrow \mu$ , if  $\phi \rightarrow 0$

$$\tilde{\mu}_2 - \tilde{\mu}_1 = z(\phi_2 - \phi_1)F \quad \underline{\text{or}}$$

$$\tilde{\mu}_2 = \tilde{\mu}_1 + z(\phi_2 - \phi_1)F$$

only the electrical potential difference between 2 points can be measured

$\rightarrow$  one can set  $\phi_1 = 0$

$$\rightarrow \tilde{\mu}_2 = \tilde{\mu}_1 + z\phi F$$

particles flow into the direction in which their electrochemical potential decreases

$\rightarrow$   $\ominus$  ions flow to more positive  $\phi$

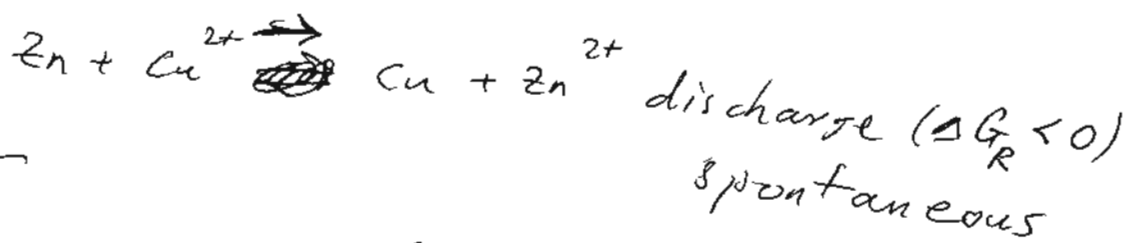
equilibrium condition not  $\Delta G_R = \sum_i \nu_i \mu_i = 0$

but  $\Delta G_R = \sum_i \nu_i \tilde{\mu}_i = 0$   $\nu_i$  coeff. in reaction equ.

to change  $\Delta G_R$  by  $P, T,$  or concentration is not easy

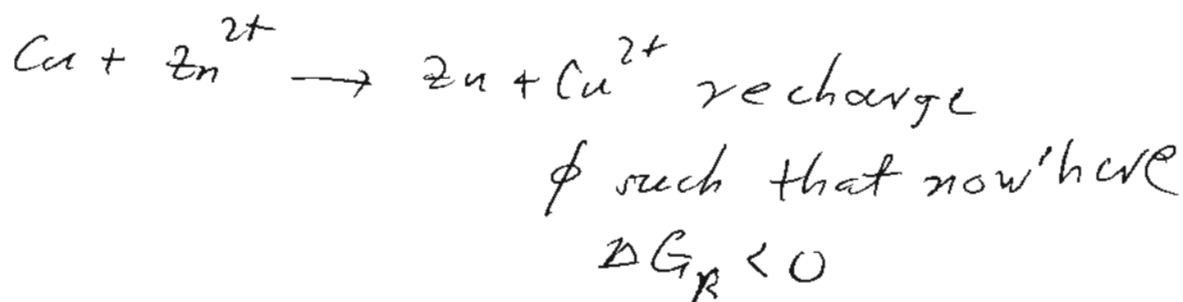
However, application of an electrical potential can easily change  $\tilde{\mu}$

Even a change in sign of  $\Delta G_R$  can easily ~~be~~ done by  $\phi$  (reversal of reactions) (8)-4  
simple example: recharging of a battery by application of  $\phi$



large enough  $\phi$ , in opposite direction of the cell potential

→ recharging



→  $\ominus$  charge on Zn electrode

$\text{Zn}^{2+}$  go in solution leaving  $2e^-$  on electrode

$\oplus$  charge on Cu electrode

Cu is deposited by ~~giving~~ the Cu electrode giving  $2e^-$  to  $\text{Cu}^{2+}$  ions

b.w.

~~Ca~~ poly atomic ions

$\text{PO}_4^{3-}$  phosphate

$\text{SO}_4^{2-}$  sulfate

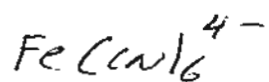
$\text{NO}_3^-$  nitrate

$\text{ClO}_3^-$  chlorate

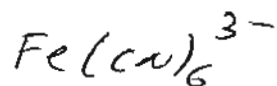
$\text{ClO}_4^-$  perchlorate

complexes

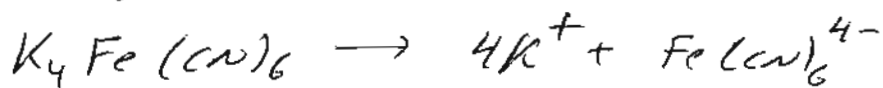
hexacyano ferrate (+II)



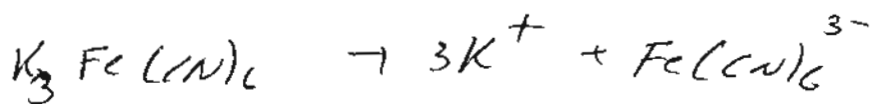
hexacyano ferrate (+III)



e.g.



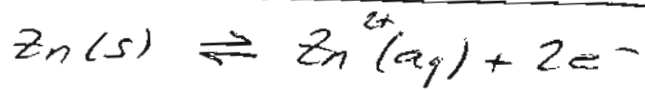
or





# Conventions and Standard States (9) - 1

## Measurement of reversible cell potentials



$\text{Zn}(s)$  is in standard state (no ions)

$$\Rightarrow \tilde{\mu}[\text{Zn}(s)] = \mu[\text{Zn}(s)] = \Delta G_f^\circ[\text{Zn}(s)] = 0$$

all happens in a single phase

$\Rightarrow \phi$  is the same for all solvated ions

Equilibrium conditions

Equil.

↓

$$\Delta G_R = \sum_i \nu_i \tilde{\mu}_i = \sum_i \nu_i \mu_i + F\phi \sum_i \nu_i z_i = \sum_i \nu_i \mu_i = 0$$

since:  $\sum_i \nu_i z_i = (\text{total charge, right side})$

$- (\text{total charge, left side})$

$$= 0$$

total charge right = total charge left

$\Rightarrow$  in a single phase  $\phi$  has <sup>no</sup> influence on equilibrium  
and we can set  $\phi = 0$

$\Rightarrow \tilde{\mu}_i = \mu_i$  for all ions in solution if it is a  
single phase!

$\mu_i$  from concentrations when they are low  
enough to get  $\gamma_{\pm}$  from DHLL  
or when the  $\gamma_{\pm}$  are known

$e^-$  in metal electrode:

$\phi \neq 0$  ~~the~~ potential difference between solution and electrode

standard state:  $\mu(e^- \text{ in electrode}) = 0$

$$\rightarrow \tilde{\mu}_{e^-} = -\phi F \text{ (for } e^- \text{ in electrode)}$$

to measure a half-cell potential only possible relative to another half-cell not absolute

example: ~~Daniell~~ Daniell cell (transp.)

Zn(s) in ZnSO<sub>4</sub>(aq), ZnSO<sub>4</sub> 100% dissociated

Cu(s) in CuSO<sub>4</sub>(aq), CuSO<sub>4</sub> 100% dissociated

half-cell connected by wire and salt bridge

salt bridge: KCl suspended in gel

allows current to flow through, but prevents

the direct mixing of the half-cell solutions.

wire connects Zn(left) to Cu(right)

$\Rightarrow$  the phases between which the potential is measured are not the same!

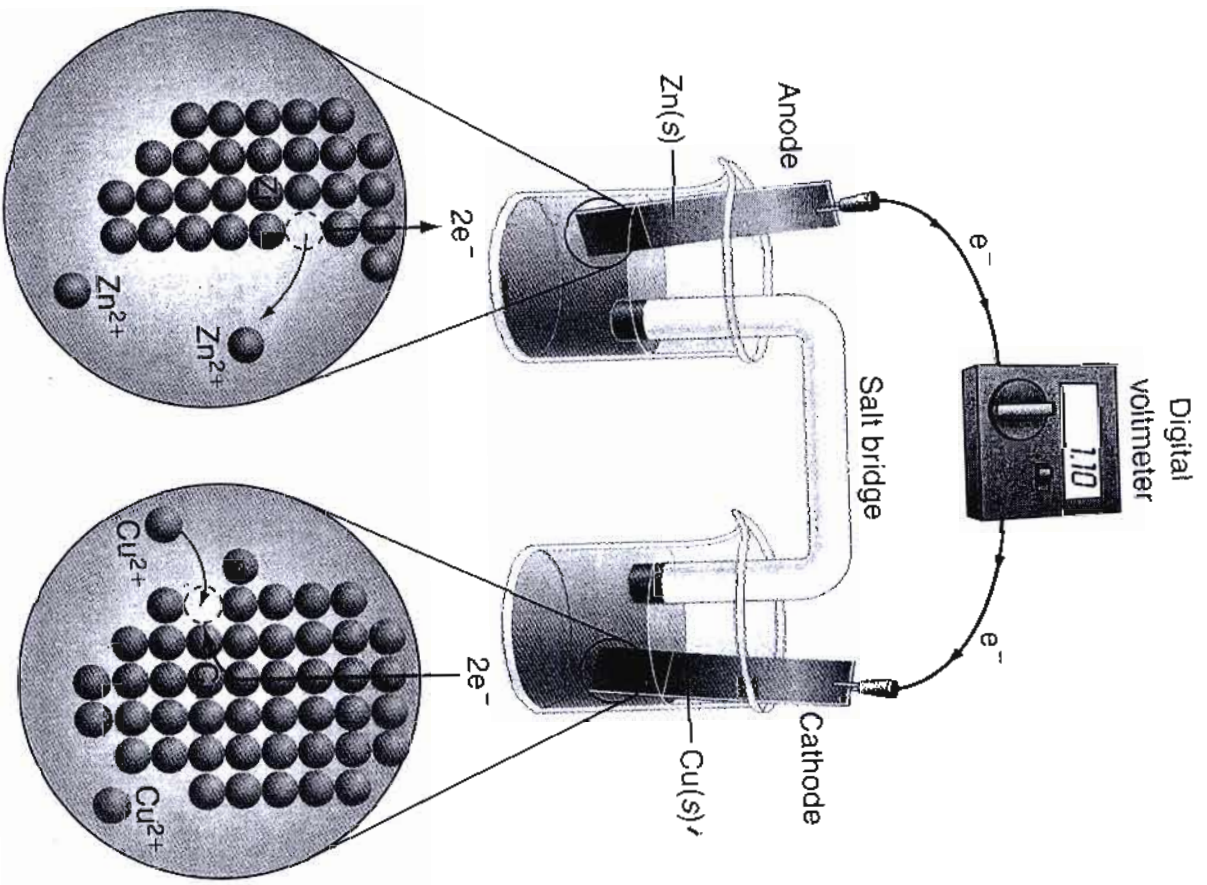
potential difference between half-cells

can be measured, but not the absolute  $\phi$  of a half-cell alone

to obtain half-cell potentials, one special half-cell is ~~the~~ defined as reference and

$\phi = 0$  is assigned to it (relative  $\phi$  to reference)

**FIGURE 11.2** Schematic diagram of the Daniell cell.  $Zn^{2+}/Zn$  and  $Cu^{2+}/Cu$  half-cells are connected through a salt bridge in the internal circuit. A voltmeter is shown in the external circuit. The inset shows the atomic level processes that occur at each electrode.

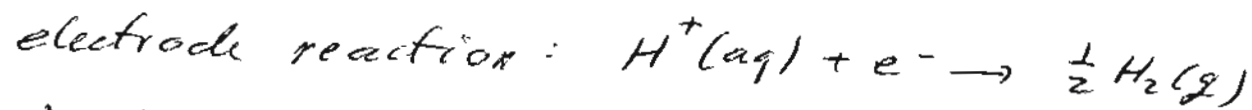


is immersed in a solution of  $CuSO_4$ , which is completely dissociated to form  $Cu^{2+}$  (aq)

Then  $\phi$  of each half-cell can be obtained by combining it with the reference half-cell

reference half-cell with  $\phi = 0$  (assigned):

standard hydrogen electrode



half-cell reactions are always written as reductions and also tabulated  $E^\circ$  values are always for reductions

equilibrium condition in std.  $H_2$  half-cell:

$$\mu_{H^+(aq)} + \tilde{\mu}_e = \frac{1}{2} \mu_{H_2(g)}$$

in real half-cells the reduction can be reversed

$\mu_{H_2(g)}$  ( $\mu_{H^+(aq)}$ ) are separated into a standard state part and an activity dependant part:

$$\mu_{H^+}^\circ + RT \ln a_{H^+} - F\phi_{H^+/H_2} = \frac{1}{2} \mu_{H_2}^\circ + \frac{1}{2} RT \ln f_{H_2}$$

$f_{H_2}$ : fugacity of  $H_2(g)$

transp.: standard hydrogen electrode

acid such as  $HCl(aq)$

$$a_{H_2} = a_{H^+} = 1$$

$H_2(g)$  bubbles over Pt electrode

Pt: catalyst for fast equilibrium

Thomas Engel and Philip Reid, "Physical Chemistry, 3rd Ed", Pearson Benjamin Education, Inc., 2013.

**DESCRIPTION:**

Electrolyte Solutions (Ch 10), electrochemical cells (Ch 11), Transport Phenomena (Ch 34), Elementary Chemical Kinetics (Ch 35) and Complex Reaction

the electrochemical potential of the electron. The

$$\phi_{H^+/H_2} = \frac{1}{2} \mu_{H_2}^\circ + \frac{1}{2} RT \ln f_{H_2} \quad (11.12)$$

in gas. Solving Equation (11.12) for  $\phi_{H^+/H_2}$

$$-\frac{1}{2} \mu_{H_2}^\circ - \frac{RT}{F} \ln \frac{f_{H_2}^{1/2}}{a_{H^+}} \quad (11.13)$$

cell has its standard state potential, designated 0,

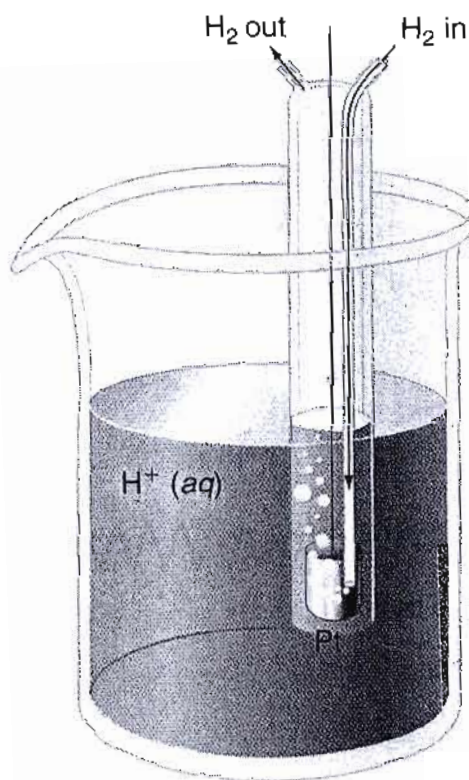
$$\phi_{H^+/H_2} = \frac{\mu_{H^+}^\circ}{F} \quad (11.14)$$

$\Delta G_f^\circ(H^+, aq) = \mu_{H^+}^\circ = 0$  was introduced.

$$\phi_{H^+/H_2} = 0 \quad (11.15)$$

A hydrogen electrode is a convenient **reference electrode** whose potentials of all other half-cells can be measured. As shown in Figure 11.3. To achieve equilibrium on a half-cell  $e^- \rightleftharpoons 1/2 H_2(g)$  is carried out over a Pt catalyst to establish a standard state for the activity of  $H^+(aq)$ . The standard state based on molarity. Therefore,  $a_i \rightarrow c_i$  is a (hypothetical) aqueous solution of  $H^+(aq)$  with a concentration of  $c^\circ = 1 \text{ mol L}^{-1}$ .

The value 0 is that values for the electrical potential can be measured by measuring their potential relative to the  $H^+/H_2$  half-cell. The electrochemical cell in Figure 11.4 is assigned to  $I_2(g)$  activities both have the value 1. Although the absolute potential for half-cell potentials can be determined. In



**FIGURE 11.3**

The standard hydrogen electrode consists of a solution of an acid such as HCl,  $H_2$  gas, and a Pt catalyst electrode that allows the equilibrium in the half-cell reaction to be established rapidly. The activities of  $H_2$  and  $H^+$  are equal to one.

$$\phi_{H^+/H_2} = \frac{1}{F} (\mu_{H^+}^\circ - \frac{1}{2} \mu_{H_2}^\circ) - \frac{RT}{F} \ln \frac{\sqrt{p_{H_2}}}{a_{H^+}} \quad (9) - 4$$

standard state potential  $\phi_{H^+/H_2}^\circ$  if all  $a_i = 1$

$$\mu_{H_2}^\circ = \Delta G_f^\circ (H_2(g)) = 0$$

$$f = \frac{P_{\text{real gas}}}{P_{\text{ideal gas}}} = 1$$

$$\Rightarrow \phi_{H^+/H_2}^\circ = \frac{\mu_{H^+}^\circ}{F}$$

hypothetical standard state in which  $P_{\text{real gas}} = P_{\text{ideal gas}}$  at 1 bar

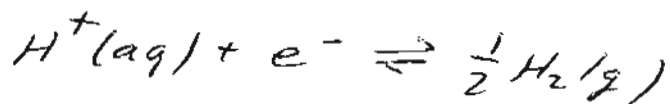
convention was (10.1)  $\Delta G_f^\circ (H^+, aq) = \mu_{H^+}^\circ = 0$

$$\Rightarrow \phi_{H^+/H_2}^\circ = 0$$

$\Rightarrow$  standard hydrogen electrode has 0 potential

so it is the reference relative to which all other half-cell potentials can be obtained

to ensure that the equilibrium



is established fast, a Pt electrode (catalyst) is used

standard state for  $a_{H^+}$ : Henry's law standard state based on molarity

$$\Rightarrow a_i \rightarrow c_i \text{ when } c_i \rightarrow 0$$

this standard state: hypothetical

$H^+(aq)$  solution which is an ideal solution at  $c_0 = 1M$

that shows ideal solution behavior at a concentration of  $c^\circ = 1 \text{ mol L}^{-1}$ .

The usefulness of the result  $\phi_{\text{H}^+/\text{H}_2}^\circ = 0$  is that values for the electrical potential can be assigned to individual half-cells by measuring their potential relative to the  $\text{H}^+/\text{H}_2$  half-cell. For example, the cell potential of the electrochemical cell in Figure 11.4 is assigned to the  $\text{Zn}/\text{Zn}^{2+}$  half-cell if the  $\text{H}^+(aq)$  and  $\text{H}_2(g)$  activities both have the value 1. Although not directly measurable, absolute values for half-cell potentials can be determined. In Supplemental Section 11.16 it is shown that the absolute potential of the standard hydrogen electrode is  $-4.44 \pm 0.02 \text{ V}$ . Because only changes in energy rather than absolute energies can be measured, chemists generally use half-cell potentials relative to the standard hydrogen electrode assuming that  $\phi_{\text{H}^+/\text{H}_2}^\circ = 0$ .

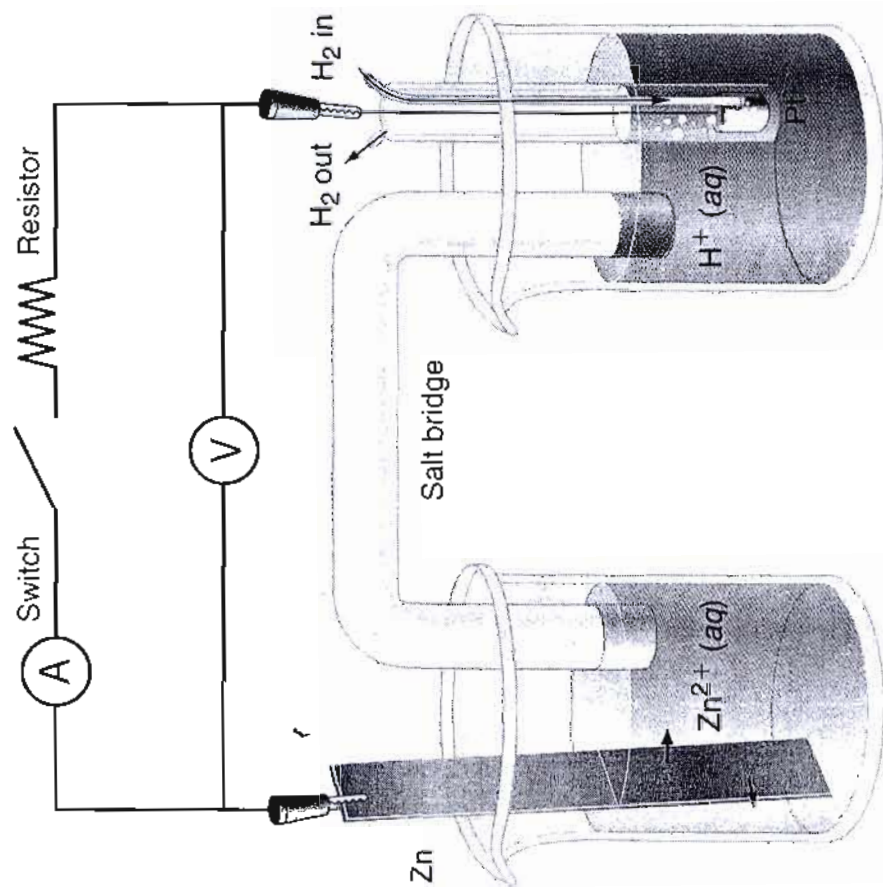


FIGURE 11.4

In a cell consisting of a half-cell and the standard hydrogen electrode, the entire cell voltage is assigned to the half-cell.

$\phi_{H^+/H_2} = 0 \Rightarrow$  values of the electrical  $\phi$ -S potential can be assigned to any half-cell, by measuring its potential relative to a  $H^+/H_2$  half-cell

transp. entire cell voltage =  $Zn^{2+}/Zn$  half-cell potential if activities for  $H^+$  and  $H_2$  are 1 (activity of  $H_2$ : fugacity  $f_{H_2} = P_{H_2}$ )

half-cell potentials alone cannot be measured, but absolute values can be determined in a tricky way (11.16)

$\Rightarrow$  absolute half-cell potential of the standard hydrogen electrode:  $-4.44 \pm 0.02V$

only, changes in energy can be measured  
no absolute ones ( $\Delta U$  yes,  $U$  not)

usually half-cell potentials relative to the standard hydrogen electrode are used

reversible cell potential: emf  $E$

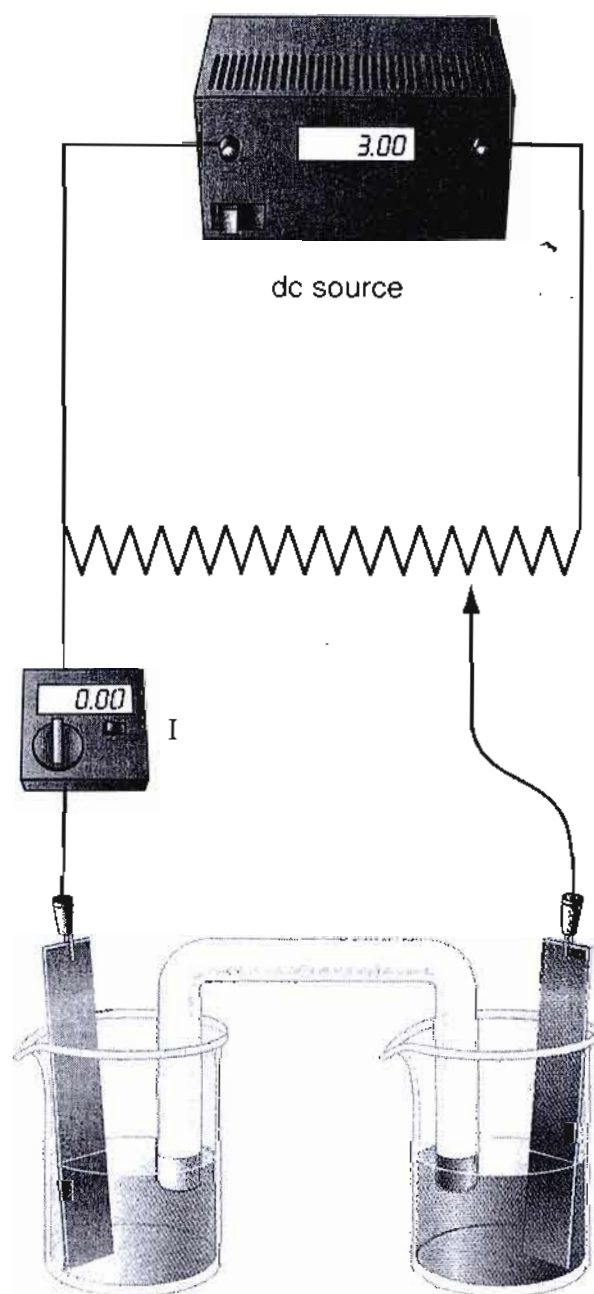
electromotive force directly related to

$$\Delta G, \Delta H, \Delta S: \Delta G = -nFE$$

transp. measurement of emf

dc source with sliding contact connected to a voltmeter, sliding contact to positive cell terminal





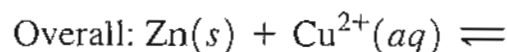
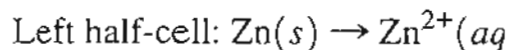
**FIGURE 11.5**  
Schematic diagram showing how the reversible cell potential is measured.

## 11.3 Measurement of the Cell Potential

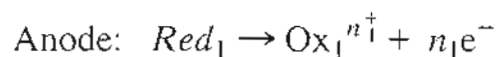
The cell potential measured under reversible conditions is a function of  $G$ ,  $H$ , and  $S$ . The reversible cell potential (**emf**), is determined in an experiment depicted in Figure 11.5. The voltage is applied to a potentiometer circuit with a sliding contact connected to the positive cell terminal as shown, and the galvanometer sensing device labeled  $I$  shows a null current. At this voltage applied through the potentiometer exactly balances the emf measured in this way is the reversible cell potential. If the contact is moved to a position slightly to the left of this position, the current flows in the external circuit in one direction. However, if the contact is moved slightly to the right of this position, the current flows in the external circuit in the opposite direction, showing that the emf has been reversed. Because a small variation in the direction of spontaneous change, the criterion for equilibrium is also demonstrated. This also demonstrates that the direction of spontaneous change is reversed by changing the electrochemical potentials of the electrodes relative to that in the other electrode using a

## 11.4 Chemical Reactions in Cells and the Nernst Equation

What reactions occur in the Daniell cell shown in Figure 11.5 when connected through the external circuit, Zn atoms leave the solution, and  $\text{Cu}^{2+}$  ions are deposited as Cu atoms on the electrode. In the external circuit, it is observed that electrons flow through the wire from the Zn electrode to the Cu electrode. The following electrochemical reactions:



In the left half-cell, Zn is being oxidized to  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  is being reduced to Cu. By convention, the electrode at which oxidation occurs is the **anode**, and the electrode at which reduction occurs is the **cathode**. The electrode at which oxidation occurs in an electrochemical cell must contain a species in an oxidized form and a reduced form. For a general redox reaction, the half-cell reactions and the overall reaction can be written as follows:



⑨ - 6

The applied voltage opposes the cell potential

When amperemeter shows  $I=0$   
(reversible) then voltage measured  
 $= emf$

slider moved little left of this point

→ current will flow

to the right: current in opposite direction

⇒ reversed cell reaction

small change in applied voltage

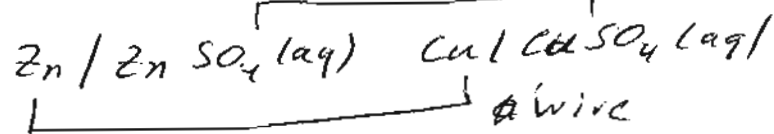
→ reversal of direction of spontaneous change

⇒ reversible:

direction of spontaneous change can be reversed by changing the electrochemical potential of the electrons in one of the electrodes relative to the other with an external voltage

# chemical reactions in cells & Nernst Equation (10) - 1

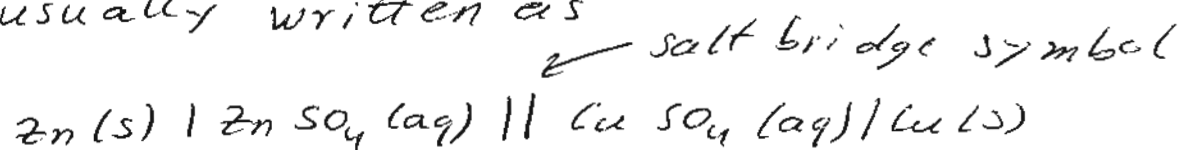
Daniell cell:



Zn leaves Zn(s) as  $\text{Zn}^{2+}(\text{aq})$ ,  $\text{Cu}^{2+}(\text{aq})$  is deposited as Cu atoms on Cu(s)

$\Rightarrow e^-$  flow through the wire from Zn(s) to Cu(s) electrode

usually written as

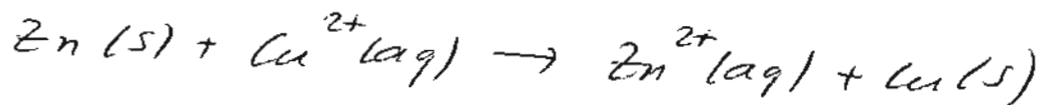


↑  
from solid to solution

left half-cell:  $\text{Zn}(s) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2e^-$  Oxidation

right half-cell:  $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}(s)$  Reduction

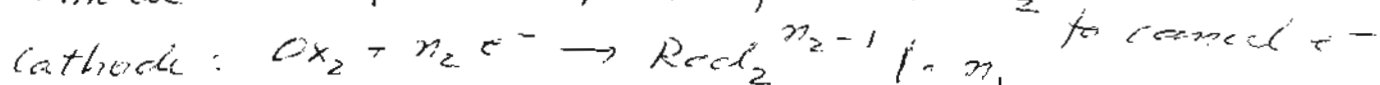
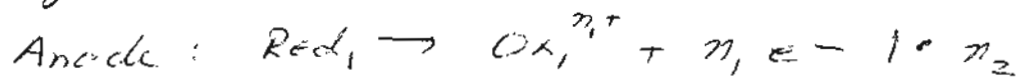
overall: (always cancel the electrons, here 2)



left: Zn oxidized to  $\text{Zn}^{2+}$  = anode (electrode where oxidation happens)

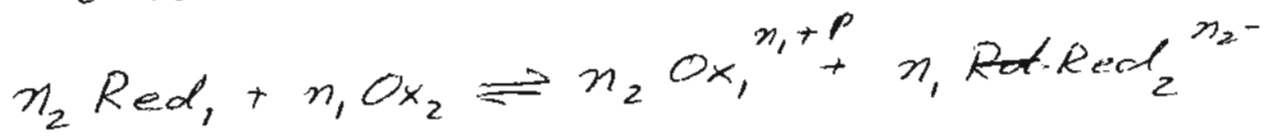
right:  $\text{Cu}^{2+}$  reduced to Cu = cathode (electrode where reduction happens)

each half-cell must contain a chemical (species) which can exist in oxidized and reduced form  
general Redox reactions:



overall:  $n_1$  Anode +  $n_2$  cathode (10)-2

cancel  $n_1 \cdot n_2 e^-$



NO electrons in an overall reaction (must be)

$e^-$  produced in Anode are consumed in

Cathode

$$\Delta G_R = \tilde{\mu}_{\text{Zn}^{2+}} + \tilde{\mu}_{\text{Cu}} - \tilde{\mu}_{\text{Cu}^{2+}} - \tilde{\mu}_{\text{Zn}}$$

$$\Rightarrow \Delta G_R = \mu_{\text{Zn}^{2+}}^0 - \mu_{\text{Cu}^{2+}}^0 + RT \ln Q$$

in  $Q$ : like equilibrium constant but  
not with equil. concentrations

only in  $Q$  if they are dissolved in  
a solvent

pure  $l$  and  $s$  are not in  $Q$

gases are as partial pressures

reversible reaction  $\Rightarrow$  electrical work is done

= charge  $\times$  potential difference through which

the charge is moved

$$\Delta G_R = -nF \Delta \phi$$

$n e^-$  transferred in redox reaction

$$Q = \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \quad \frac{\text{no solids}}{\text{no liquids}} \quad \frac{\text{products}}{\text{reactants}}$$

reaction ratio

$$\Rightarrow \Delta G_R = \Delta G_R^0 + RT \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}} \quad (10) - 3$$

$\Delta\phi$  is the measured potential difference due to the spontaneous cell reaction  
 $a_{Zn^{2+}}$ ,  $a_{Cu^{2+}}$  are the values given for the cell

$n=2$  in this example

in the general case:  $n = n_1 \cdot n_2$

$$\Delta\phi \sim \Delta G_R$$

if reversible cell:  $\Delta\phi = E$

the electro motive force, emf

$\Rightarrow \Delta G_R = -2FE$  in this example

$$-2FE = \Delta G_R^0 + RT \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$$

standard state:  $a_{Zn^{2+}} = a_{Cu^{2+}} = 1$

$$\Rightarrow \Delta G_R^0 = -2FE^0$$

$$-2FE = -2FE^0 + RT \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}} \quad \left| \cdot \left(-\frac{1}{2F}\right)\right.$$

$$E = E^0 - \frac{RT}{2F} \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$$

general case with transfer of  $n$  electrons in the cell reaction:

$$E = E^0 - \frac{RT}{nF} \ln Q \quad \underline{\text{Nernst equation}}$$

$Q$ : reaction ratio

cell given  
then on left side write oxidation (10) - 4  
on right side write reduction

$$\text{then } E_{\text{cell}}^{\circ} = E_{\text{right}}^{\circ} - E_{\text{left}}^{\circ}$$

add half reactions together, such that  $e^{-}$  are cancelled

no. of cancelled  $e^{-} = n$  in Nernst equation

then with given concentrations form

$$Q = \frac{\text{product ion concentrations}}{\text{reactant ion concentrations}}$$

in  $Q$  include liquids only when they are dissolved in the solvent, gases as partial pressures, do not put pure liquids or solids into  $Q$

small concentrations: molarity ok

larger " : molality is better

large " : activities based on molality best

Then calculate

$$E = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln Q$$

if  $E = 0 \Rightarrow$  equilibrium is achieved

if  $E > 0 \Rightarrow \Delta G_{\text{R}}^{\circ} < 0 \Rightarrow$  reaction proceeds as you have written (left oxidation, right reduction)

if  $E < 0 \Rightarrow \Delta G_{\text{R}}^{\circ} > 0 \Rightarrow$  reaction proceeds in the reversal of what you have written

at 298.15 K  $\frac{RT}{F} = 25.7 \text{ mV}$

$\Rightarrow$  at 298.15 K:  $E = E^0 - \frac{25.7 \text{ mV}}{n} \ln Q$

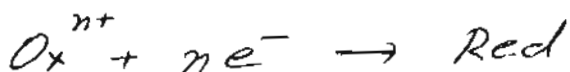
or with  $\ln x = 2.303 \log_{10} x$ :

$E = E^0 - \frac{59.16 \text{ mV}}{n} \log_{10} Q$

transp.    graphs     $\frac{E - E^0}{RT/F}$  VS  $\log_{10} Q$

straight lines, slope  $\frac{1}{n}$

Nernst equation can also be used for half-cell reactions, usually written as reductions:



equilibrium:  $\mu_{Ox^{n+}} + n\tilde{\mu}_{e^-} = \mu_{Red}$

electron in metal electrode:

$\tilde{\mu}_{e^-} = -\phi F$

$\Rightarrow \mu_{Ox^{n+}}^0 + RT \ln a_{Ox^{n+}} - nF\phi_{Ox/Red}$

$= \mu_{Red}^0 + RT \ln a_{Red}$

$a = \frac{c}{c_0}$     activity coefficient    dimensionless

gases:  $f = \gamma \frac{P}{P^0}$     fugacity, dimensionless b.w.     $\frac{P}{P^0}$   
fugacity coefficient    instead of  $\frac{P}{P^0}$

$\phi_{Ox/Red} = -\frac{\mu_{Red}^0 - \mu_{Ox^{n+}}^0}{nF} = \frac{RT}{nF} \ln \frac{a_{Red}}{a_{Ox^{n+}}}$      $f_{10}$  must be used

$f$ : effective pressure of a real gas,  $f^0$ : fugacity of the gas if it would be ideal at 1 bar =  $1 \text{ bar} = 1 \text{ f}^0 = P$  hypothetical

fugacity coefficient.

$$f = \gamma(P, T) P$$

$$\gamma(P, T) = \exp \left[ \int_0^P \frac{z-1}{P'} dP' \right]$$

$z$ : compression factor

$$z = \frac{V_m^{\text{real}}}{V_m^{\text{ideal}}} \text{ from equation of state}$$

$$\Rightarrow \frac{f}{f_0} = \gamma(P, T) \frac{P}{P_0}$$



$$\Delta_R^\circ + RT \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}} \quad (11.24)$$

Since  $a_{Cu^{2+}} = 1$ , and Equation (11.24) takes the form  
allows Equation (11.24) to be rewritten as

$$- \frac{RT}{2F} \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}} \quad (11.25)$$

involving the transfer of  $n$  moles of electrons,

$$\Delta_R^\circ - \frac{RT}{nF} \ln Q \quad (11.26)$$

Equation (11.26) is known as the Nernst equation. The preceding equation is known as the Nernst equation. The preceding equation can be written in the form

$$\Delta_R^\circ - \frac{0.05916 \text{ V}}{n} \log_{10} Q \quad (11.27)$$

The Nernst equation allows the emf for an electrochemical cell to be calculated if  $E^\circ$  is known for each species and if  $E^\circ$  is known. The Nernst equation can be derived from the overall cell reaction. For a redox reaction, the equilibrium condition for



$$n \tilde{\mu}_{e^-} = \mu_{\text{Red}} \quad (11.29)$$

The chemical potential of an electron in a metal (Equation 11.29) can be written in the form

$$\begin{aligned} \mu_{\text{Ox/Red}} &= \mu_{\text{Red}}^\circ + RT \ln a_{\text{Red}} \\ - \frac{RT}{nF} \ln \frac{a_{\text{Red}}}{a_{\text{Ox}^{n+}}} & \\ \frac{a_{\text{Red}}}{a_{\text{Ox}^{n+}}} & \end{aligned} \quad (11.30)$$

is in the same form as the Nernst equation, but the reaction quotient  $Q$  appears in the denominator. An example of the application of the Nernst equation is shown in Example Problem 11.1.

Example Problem 11.1: Calculate the cell potential  $E$  for a Zn-Cu cell when  $a_{H^+} = 0.770$  and  $f_{H_2} = 1.13$ .

$$E = \frac{0.05916 \text{ V}}{2} \log_{10} \frac{0.770}{\sqrt{1.13}} = 0.0083 \text{ V}$$

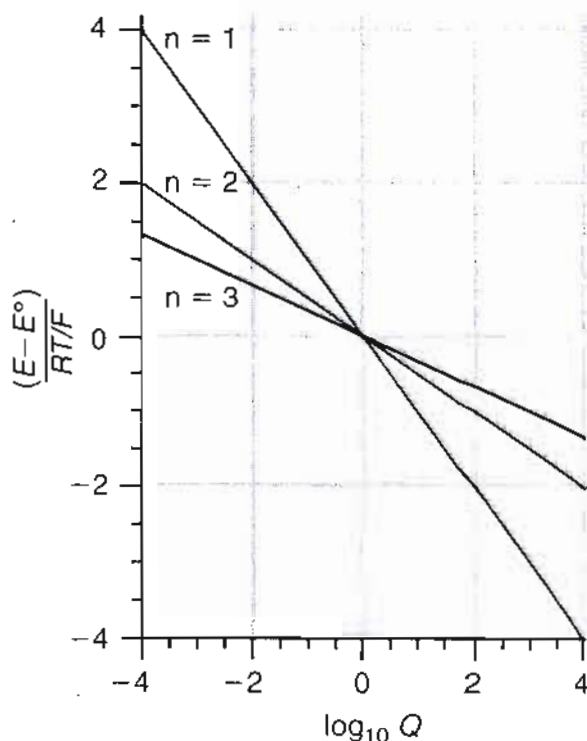


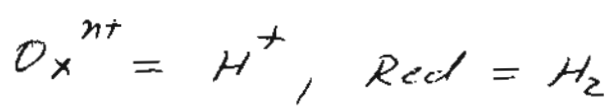
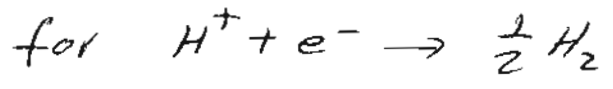
FIGURE 11.6

The cell potential  $E$  varies linearly with  $\log Q$ . The slope of a plot of  $(E - E^\circ)/(RT/F)$  is inversely proportional to the number of electrons transferred in the redox reaction.

$$\Rightarrow E_{Ox/Red} = E_{Ox/Red}^{\circ} - \frac{RT}{nF} \ln \frac{a_{Red}}{a_{Ox}^{nt}}$$

↑  
reduction potential

Calculate  $E$  for the  $H^+/H_2$  half-cell, when  $a_{H^+} = 0.770$ ,  $f_{H_2} = 1.13$



$$E = E^{\circ} - \frac{0.05916 \text{ V}}{n} \log_{10} \frac{\sqrt{f_{H_2}}}{a_{H^+}}$$

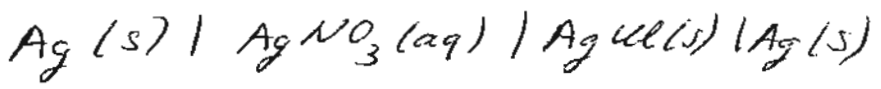
$$= E^{\circ} - \frac{0.05916 \text{ V}}{1} \log_{10} \frac{\sqrt{1.13}}{0.770}$$

$E^{\circ} = 0$  for standard hydrogen electrode

$$E = - \frac{0.05916 \text{ V}}{1} \log_{10} \frac{\sqrt{1.13}}{0.770} = -8.29 \cdot 10^{-3} \text{ V}$$

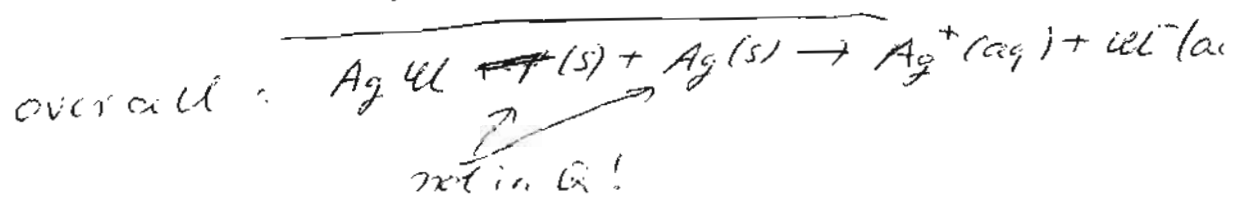
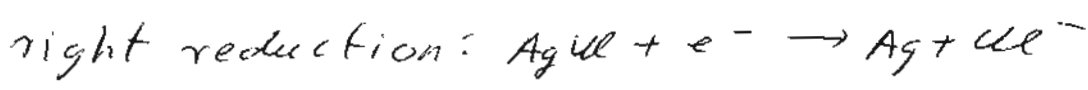
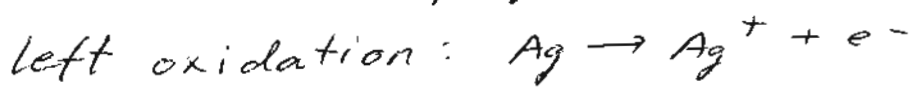
error in book (+0.0083 V) with  $\frac{0.770}{\sqrt{1.13}}$   
solubility products

Use the cell



and  $E_{Ag^+/Ag}^{\circ} = 0.7996 \text{ V}$  and  $E_{AgCl/Ag}^{\circ} = 0.22233 \text{ V}$

to determine  $K_{sp}(AgCl)$ .



$$E = E^{\circ} - \frac{RT}{F} \ln a_{\text{Ag}^+} \cdot a_{\text{Cl}^-}$$

(10) - 7

$$= E^{\circ} - \frac{RT}{F} \ln K_{\text{sp}}$$

$$E^{\circ} = E^{\circ}_{\text{right}} - E^{\circ}_{\text{left}} = E^{\circ}_{\text{AgCl}/\text{Ag}} - E^{\circ}_{\text{Ag}^+/\text{Ag}}$$

$$= (0.22233 - 0.7996) \text{ V}$$

$$= -0.5773 \text{ V}$$

$$E = \cancel{E^{\circ}} - 0.5773 \text{ V} - 25.7 \text{ mV} \ln K_{\text{sp}}$$

$K_{\text{sp}}$  has no unit

in equilibrium ( $K_{\text{sp}}$  or  $K$  valid) /  $E=0$

~~for  $K_{\text{sp}}$~~

$$\rightarrow 0 = E^{\circ} - 25.7 \text{ mV} \ln K_{\text{sp}}$$

$$\ln K_{\text{sp}} = \frac{E^{\circ}}{25.7 \text{ mV}} = \frac{-0.5773 \text{ V}}{25.7 \cdot 10^{-3} \text{ V}} = -22.4630$$

$$K_{\text{sp}} = \exp(-22.4630) = 1.76 \cdot 10^{-10}$$

if there would be  $0.01 \text{ M AgNO}_3$  solution,

then do not calculate  $E$  with Nernst equation

still in equilibrium ( $Q = K_{\text{sp}}$  unchanged)

and  $E = 0$

only  $a_{\text{AgCl}} = \frac{K_{\text{sp}}}{a_{\text{Ag}^+}}$  will be smaller, when  $c_{\text{Ag}^+} = 0.01 \text{ M}$  gets larger

= less  $\text{AgCl}$  will be dissolved

but  $K_{\text{sp}}$  will be the same!

$E^\circ$  from standard electrode potentials  $(11)^{-1}$

$\Delta G_R^\circ$  and  $\Delta S_R^\circ$  from cell potentials (emf)

In App. B, Data Tables 11.1 & 11.2 half-cell potentials are listed, always as reduction potentials!

A cell is made from 2 half cells. Spontaneous reaction direction given by relative emfs of the half cells.

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

$$\Delta G_R^\circ(\text{reduction}) = -\Delta G_R^\circ(\text{oxidation})$$

~~half-cell~~:  $E^\circ(\text{reduction}) = E^\circ(\text{oxidation})$

half-cell:  $E^\circ = -\frac{\Delta G_R^\circ}{nF}$  is intensive

although  $\Delta G_R^\circ$  and  $n$  are both extensive, ( $n$ )  
their ratio  $E^\circ$  is intensive

$\Rightarrow E^\circ$  unchanged, when all stoichiometric coefficients in the reaction are multiplied by the same integer  $n'$ , since

$$\Delta G_R^\circ(n') = n' \Delta G_R^\circ \quad \text{then} \quad E^\circ(n') = -\frac{n' \Delta G_R^\circ}{nn'F} = -\frac{\Delta G_R^\circ}{nF} = E^\circ(n)$$

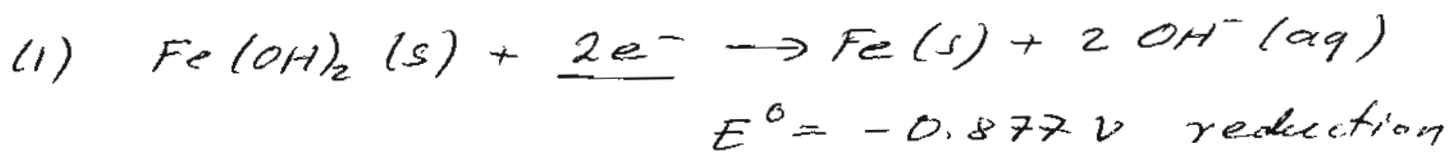
$$E_{\text{cell}}^\circ = E_{\text{right}}^\circ(\text{reduction}) - \underbrace{E_{\text{left}}^\circ(\text{oxidation})}_{\substack{\text{reduction} \\ = E_{\text{left}}^\circ(\text{oxidation})}} \quad \text{put}$$

$\ominus$  because all  $E^\circ$  are for reductions, put  
we put oxidation to the left

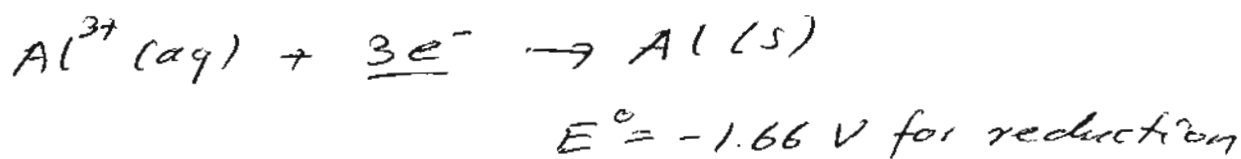
$$E_{\text{cell}}^{\circ} = E_{\text{right}}^{\circ} - E_{\text{left}}^{\circ} \quad (11) - 2$$

also if overall reaction is multiplied by any number  $n'$

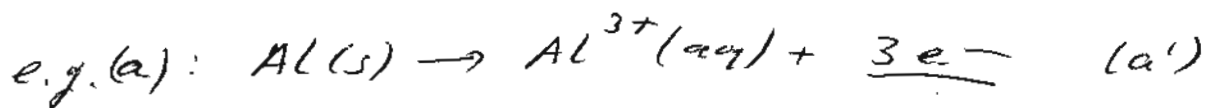
Assume a cell made with a half-cell, where the reduction is



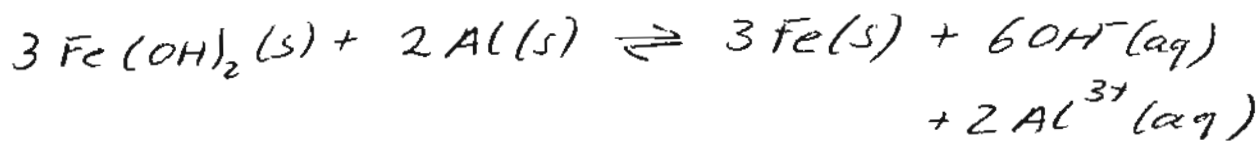
To make a cell it is combined e.g. with



But one of the reactions must be an oxidation:



then  $(1) \cdot 3 + (\text{a}') \cdot 2$  cancels the  $e^-$ :



(a) reversed because 1 equation must be oxidation and the other one reduction!

the overall reaction is spontaneous if  $\Delta G_R^{\circ} < 0$

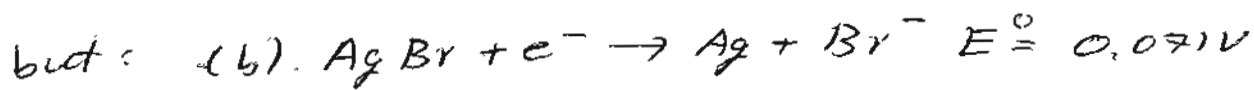
$$\Rightarrow E^{\circ} > 0$$

$E^{\circ}$  does not change when  $n$  is multiplied in

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{reduction}}^{\circ} (1) + E_{\text{oxidation}}^{\circ} (\text{a}') \\ &= E^{\circ} \text{ reduction (1)} - E^{\circ} \text{ reduction (a)} \\ &= -0.877 \text{ V} - (-1.66 \text{ V}) = 0.783 \text{ V} > 0 \end{aligned}$$

$$E_{\text{oxidation}}^{\circ}(a') = -E_{\text{reduction}}^{\circ}(a) \quad (11) - 3$$

$E^{\circ} = 0.783 \text{ V} > 0 \Rightarrow$  overall reaction is spontaneous  $\Rightarrow$   $\text{Fe}(\text{OH})_2$  reduction and Al oxidation will happen in the cell now:

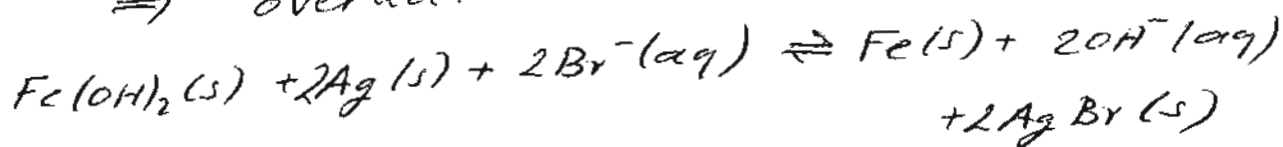


(b) must be reversed to oxidation

(1) - (b)  $\cdot 2$  cancels the electrons

(b) must be reversed because one of the reactions must be oxidation, the other one reduction

$\Rightarrow$  overall:

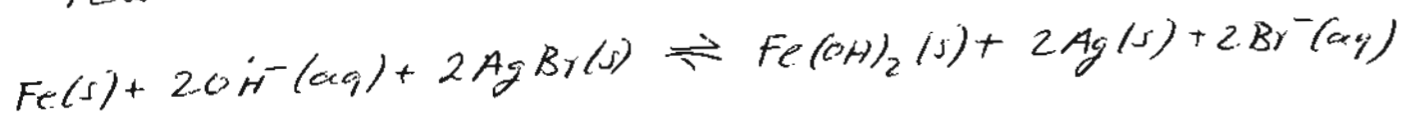


$$E_{\text{cell}}^{\circ} = E_{\text{reduction}}^{\circ}(1) + E_{\text{oxidation}}^{\circ}(b \text{ reversed})$$

$$= E_{\text{reduction}}^{\circ}(1) - E_{\text{reduction}}^{\circ}(b \text{ reversed})$$

$$= -0.877 \text{ V} - 0.077 \text{ V} = -0.95 \text{ V} < 0$$

$E^{\circ} < 0 \Rightarrow$  in the standard state the reverse reaction of the above is spontaneous:



is spontaneous:  $E^{\circ} = 0.95 \text{ V}$  for the reverse

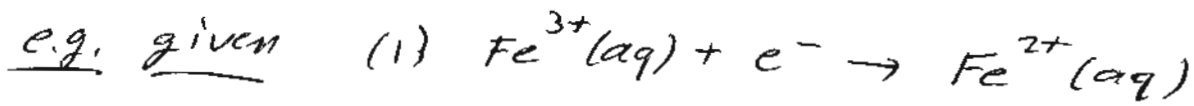
reaction  $E^{\circ} > 0 \Rightarrow \Delta G_{\text{R}}^{\circ} < 0$

$$E_{\text{cell}}^{\circ}(\text{reversed reaction}) = -E_{\text{cell}}^{\circ}(\text{reaction})$$

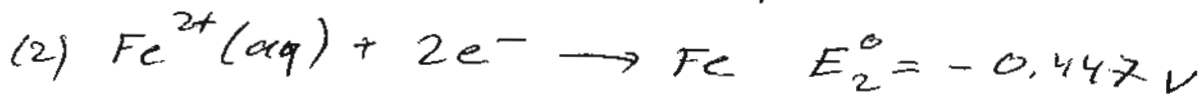
$\Delta G$  is a state-function

⑩-4

$\Rightarrow$  half-cell potential of an electrode can be calculated from two other half-cell potentials, provided they have a reduced or oxidized species (chemical) in common (= Hess's law)



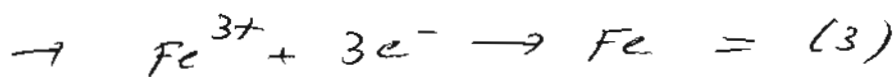
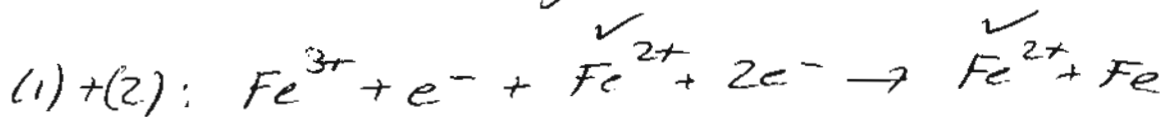
$$E_1^{\circ} = 0.771 \text{ V}$$



Question: What is  $E_3^{\circ}$  for  $\text{Fe}^{3+} + 3e^- \rightarrow \text{Fe}$

step 1 combine equation (1) and (2) such that equation (3) results

try 1: (1) + (2): yields  $\text{Fe}^{3+}$  on the left, cancels  $\text{Fe}^{2+}$ , and gives Fe on the right as in (3)



step 2: combine  $\Delta G_R^{\circ}(1)$  and  $\Delta G_R^{\circ}(2)$  in the same way as you combined equations (1) and (2) which yields  $\Delta G_R^{\circ}(3)$  (Hess's law)

The  $E_1^\circ$  and  $E_2^\circ$  values cannot be directly (11)-5 combined to get  $E_3^\circ$  because  $E^\circ$  values are intensive and for combinations like that extensive quantities as  $\Delta G$  are needed:

$$\Delta G_R^\circ(1) = -n_1 F E_1^\circ = -96485 \frac{\text{C}}{\text{mol}} \cdot 0.771 \text{V} = -74.39 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta G_R^\circ(2) = -n_2 F E_2^\circ = -96485 \frac{\text{C}}{\text{mol}} (-0.447 \text{V}) = 86.26 \frac{\text{kJ}}{\text{mol}}$$

$$\begin{aligned} \Delta G_R^\circ(3) &= \Delta G_R^\circ(1) + \Delta G_R^\circ(2) = (-74.39 + 86.26) \frac{\text{kJ}}{\text{mol}} \\ &= 11.87 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

$$E_3^\circ = E_{\text{Fe}^{3+}/\text{Fe}}^\circ = -\frac{\Delta G_R^\circ}{nF} = \frac{-11.87 \cdot 10^3 \frac{\text{J}}{\text{mol}}}{3 \cdot 96485 \frac{\text{As}}{\text{mol}}}$$

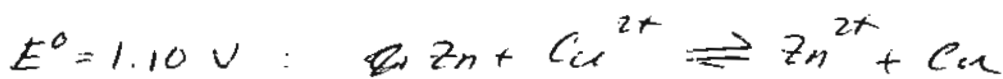
$$= -0.041 \text{V} = -41 \text{mV}$$

$$1 \text{C} = 1 \text{As}, \quad 1 \text{J} = 1 \text{VAs}$$

$$\Delta G_R = -nF\Delta\phi$$

$$\Rightarrow \Delta G_R^\circ = -nFE^\circ, \quad \Delta G_R = -nFE$$

Daniell cell, measured under standard conditions:



$$\rightarrow \Delta G_R^\circ = -nFE^\circ = -2 \cdot 96485 \frac{\text{C}}{\text{mol}} \cdot 1.10 \text{V} = -212 \frac{\text{kJ}}{\text{mol}}$$

$$\text{Thermodynamics: } \Delta S_R = -\left(\frac{\partial \Delta G_R}{\partial T}\right)_P = nF\left(\frac{\partial E}{\partial T}\right)_P$$

measure  $E(T)$  or  $E^\circ(T) \rightarrow \Delta S_R$  or  $\Delta S_R^\circ$



cell:

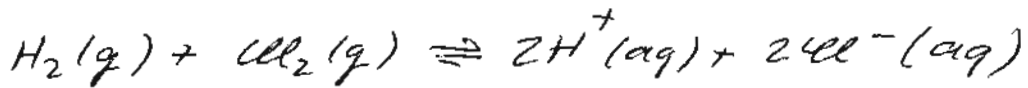
(11) - 6

$\text{Cl}_2(\text{g}) / \text{Cl}^-(\text{aq})$  + standard hydrogen electrode

$\rightarrow E_{\text{cell}}^{\circ} = E_{\text{Cl}_2/\text{Cl}^-}^{\circ} = +1.36 \text{ V}$  and the slope

of  $E^{\circ}$  vs  $T$  is  $\left(\frac{\partial E^{\circ}}{\partial T}\right)_p = -1.20 \cdot 10^{-3} \text{ V/K}$

What is  $\Delta S_R^{\circ}$  for



$E_{\text{Cl}_2/\text{Cl}^-}^{\circ} > 0 \Rightarrow \text{Cl}_2$  is reduced,  $\text{H}_2$  oxidized

$$\Delta S_R^{\circ} = nF \left(\frac{\partial E^{\circ}}{\partial T}\right)_p, \quad n=2$$

$$= 2 \cdot 96485 \frac{\text{C}}{\text{mol}} \left(-1.20 \cdot 10^{-3} \frac{\text{V}}{\text{K}}\right)$$

$$= -2.3 \cdot 10^2 \frac{\text{J}}{\text{K mol}}$$

App. B, Data Table 10.1  $\rightarrow S_m^{\circ}$  values:

$$\Delta S_R^{\circ} = 2 \cdot S_m^{\circ}(\text{H}^+, \text{aq}) + 2 \cdot S_m^{\circ}(\text{Cl}^-, \text{aq})$$

products

$$- S_m^{\circ}(\text{H}_2, \text{g}) - S_m^{\circ}(\text{Cl}_2, \text{g})$$

- reactants

$$= (2 \cdot 0 + 2 \cdot 56.5 - 130.7 - 223.1) \frac{\text{J}}{\text{K mol}}$$

$$= -2.408 \cdot 10^2 \frac{\text{J}}{\text{K mol}}$$

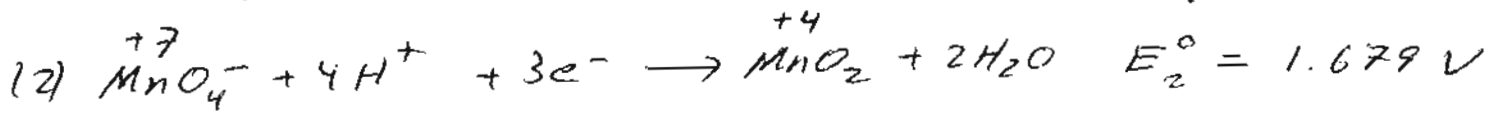
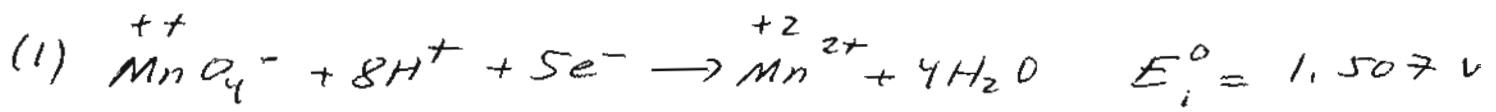
$\Rightarrow$  4.5% error in  $\Delta S_R^{\circ}$  calculated from

$$\left(\frac{\partial E^{\circ}}{\partial T}\right)_p$$

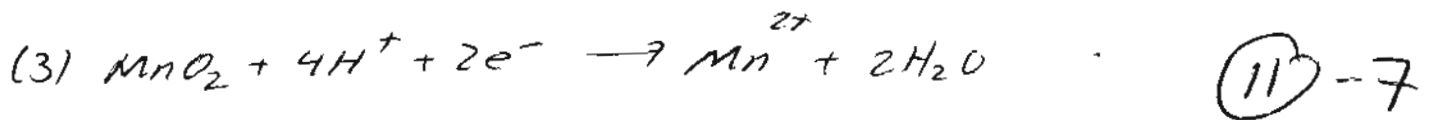
reason:  $E^{\circ}(T)$  measurements have a

limited precision  $\Rightarrow \Delta S_R^{\circ}$  also!

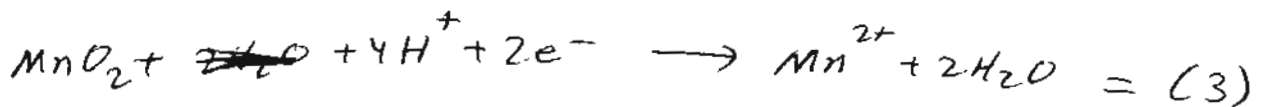
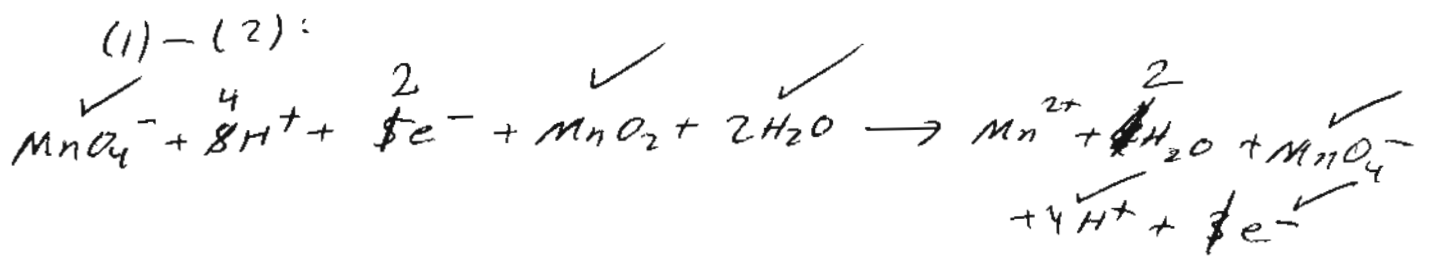
Other example for  $E_3^{\circ}$  from  $E_1^{\circ}$  &  $E_2^{\circ}$



$E_3^{\circ}$  for



try: (1) - (2):  $\text{MnO}_4^-$  cancels  
 $\text{Mn}^{2+}$  on ~~right~~ <sup>left</sup> side  
 $\text{Mn}^{2+}$  on right side



$$\overset{\circ}{E}_3 \Delta G_R^{\circ}(3) = \Delta G_R^{\circ}(1) - \Delta G_R^{\circ}(2)$$

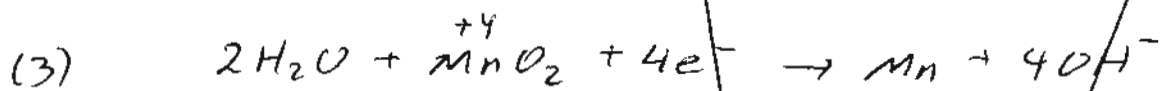
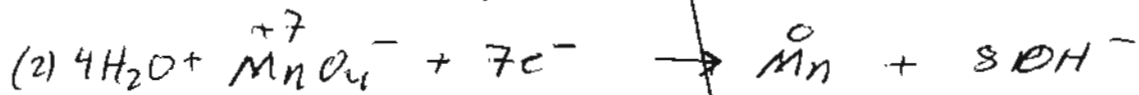
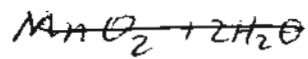
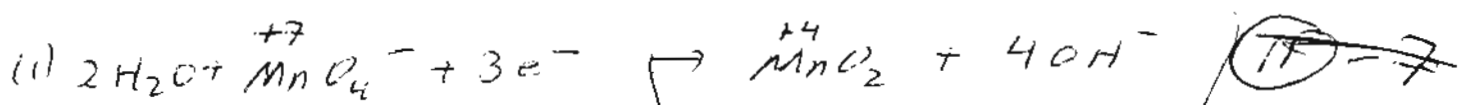
$$-n_3 FE_3^{\circ} = -n_1 FE_1^{\circ} + n_2 FE_2^{\circ}$$

$$E_3^{\circ} = \frac{n_1}{n_3} E_1^{\circ} - \frac{n_2}{n_3} E_2^{\circ}$$

$$= \frac{1}{n_3} (n_1 E_1^{\circ} - n_2 E_2^{\circ})$$

$$= \frac{1}{2} (5 \cdot 1.507 - 3 \cdot 1.679) \text{ V}$$

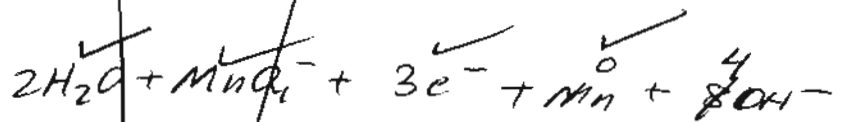
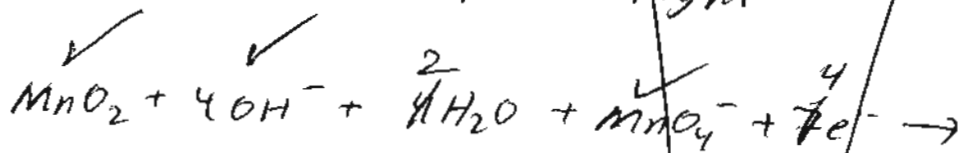
$$= 1.249 \text{ V}$$



-(1) + (2):  $\text{MnO}_4^-$  cancels

$\text{MnO}_2$  left

$\overset{0}{\text{Mn}}$  right



(2) - (1):



$$\Rightarrow -\Delta G_R^\circ(1) + \Delta G_R^\circ(2) = \Delta G_R^\circ(3)$$

$$-n_1 F E_1^\circ + n_2 F E_2^\circ = n_3 F E_3^\circ$$

$$n_3 E_3^\circ = n_2 E_2^\circ - n_1 E_1^\circ$$

$$E_3^\circ = \frac{n_2}{n_3} E_2^\circ - \frac{n_1}{n_3} E_1^\circ$$

$$= \frac{7}{4} E_2^\circ - \frac{3}{4} E_1^\circ$$

$$= \frac{1}{4} (7E_2^\circ - 3E_1^\circ)$$

Relation  $E_{\text{cell}}$  with  $K$ ,  $E^\circ$ , activity coefficients

cell reaction = Redox reaction

in equilibrium  $\Rightarrow E = 0$

since when  $E = 0 \Rightarrow \Delta G_R = 0 \rightarrow$  reaction ratio  $Q = K$

Nernst. equ.  $E = E^\circ - \frac{RT}{nF} \ln Q$

equilibrium:  $E = 0 = E^\circ - \frac{RT}{nF} \ln K$

$\rightarrow E^\circ = \frac{RT}{nF} \ln K \Rightarrow \Delta G_R^\circ = -nFE^\circ = -RT \ln K$

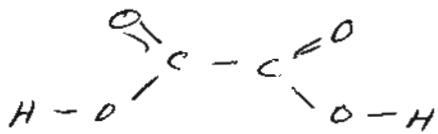
standard cell potential:  $a_i = 1$  is standard state

$\rightarrow K$  is correct, but it is impractical to adjust all  $a_i$  to 1

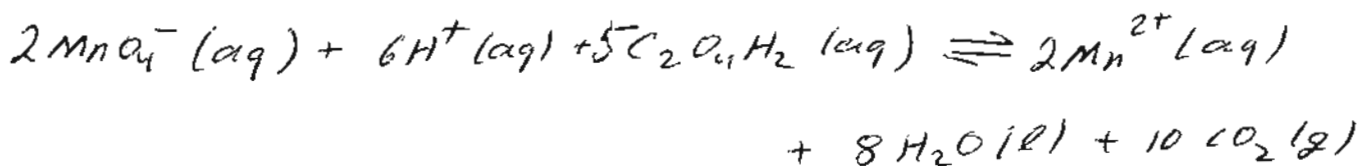
however, good that we can obtain  $K$  from tabulated  $E^\circ$  values

from overall cell reaction, half-reaction can be obtained to get the value of  $n$

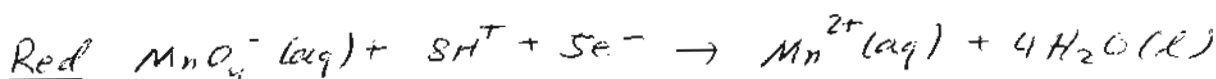
example oxidation of oxalic acid  $C_2O_4H_2$



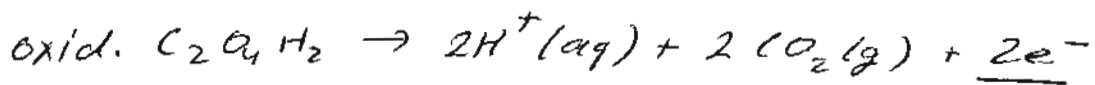
with  $\text{MnO}_4^-$  at 298.15 K:



$\overset{+7}{\text{MnO}_4^-}$  reduced to  $\overset{+2}{\text{Mn}^{2+}}$ .  $5e^-$  involved:



$$E^\circ = 1.51 \text{ V}$$



(12)-2

2  $\ominus$  needed to have charge 0 on both sides

$$E^{\circ} = -0.49 V$$

Red. 2 + Oxid. 5

$\Rightarrow 10e^-$  are cancelled  $\Rightarrow n = 10$

no changes in  $E^{\circ}$  by multiplications

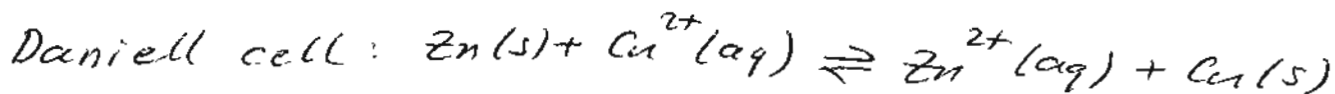
$$E^{\circ} = E^{\circ}_{red}(MnO_4^-) - E^{\circ}_{red}(\text{oxalic acid})$$

$$\begin{aligned} \Delta G^{\circ} &= -nFE^{\circ} = -10 \cdot 96485 \frac{C}{mol} (1.51 + 0.49) V \\ &= -1.93 \cdot 10^2 \frac{kJ}{mol} \end{aligned}$$

$$1 C \cdot V = 1 VAs = 1 J$$

$$\ln K = -\frac{\Delta G^{\circ}}{RT} = \frac{1.93 \cdot 10^5 \frac{J}{mol}}{8.314 \frac{J}{Kmol} \cdot 298.15 K} = 778$$

$K = e^{778} \Rightarrow K$  so large that there is complete conversion reactants into products in equilibrium



$$E^{\circ} = 1.10 V \text{ at } 298.15 K$$

$$n = 2$$

What is  $K$  at 298.15 K?

$$\ln K = -\frac{\Delta G^{\circ}}{RT} = \frac{nFE^{\circ}}{RT} = \frac{2 \cdot 96485 \frac{As}{mol} \cdot 1.10 V}{8.314 \frac{J}{Kmol} \cdot 298.15 K} = 85.63$$

$$K = e^{85.63} = 1.55 \cdot 10^{37}$$

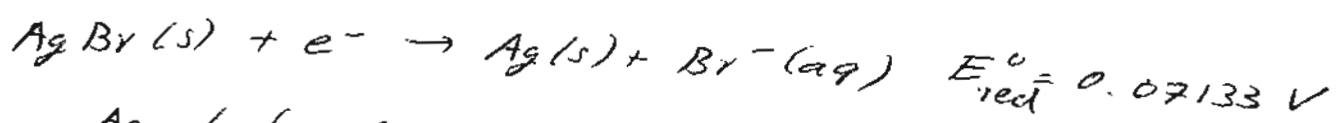
not possible by measuring  $a_{Zn^{2+}}$ ,  $a_{Cu^{2+}}$  <sup>(12)</sup> -3  
spectroscopically!

methods would have to be correct over >30  
orders of magnitude

but for electrochemical determination only  
voltmeter needed (1.10V)

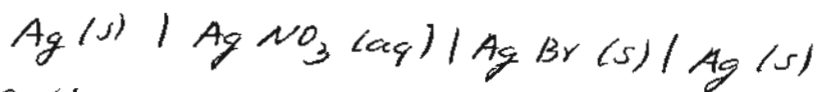
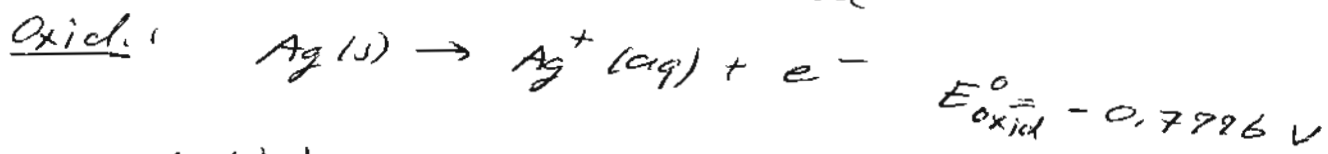
solubility products for only weakly soluble  
electrolytes

e.g.  $K_{sp}(AgBr)$  at 298.15K:



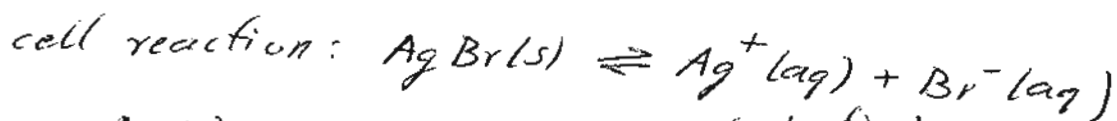
Ag electrode plated with AgBr by electrolysis

Ag(s) | AgBr(s) electrode



left oxid.

right reduction



Ag(s) cancels  $E^{\circ} = E_{right}^{\circ}(\text{reduction}) + E_{left}^{\circ}(\text{oxidation})$

$$= [0.07133 + (-0.7996)] V$$

$$= -0.7283 V$$

$$\ln K_{sp} (E=0) = \ln(a_{Ag^+} a_{Br^-}) = \frac{nFE^{\circ}}{RT} \left( -\frac{\Delta G^{\circ}}{RT} \right), n=1$$

$$= \frac{1 \cdot 96485 \frac{As}{mol} \cdot (-0.7283 V)}{8.314 \frac{J}{K \cdot mol} \cdot 298.15 K} = -28.35$$

$$K_{sp} = e^{-28.35} = 4.88 \cdot 10^{-13}$$

2 half-cells

Wrong in book

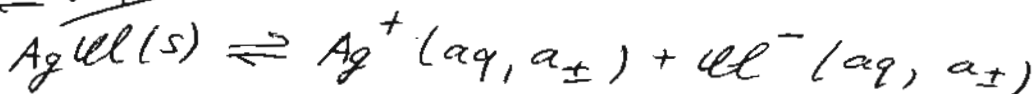
(12) - 4

~~left~~ right  $\text{AgNO}_3$  at  $a_{\pm} = 1$  p. 269

~~right~~ left  $\text{AgNO}_3$  at  $a_{\pm} = 1 + \text{NaCl(aq)}$  enough for all  $\text{Ag}^+$  as  $\text{AgCl} \downarrow$

$E = 0.29 \text{ V}$ , what is  $K_{sp}(\text{AgCl})$ ?

~~right~~ left:



$$K_{sp} = a_{\text{Ag}^+} a_{\text{Cl}^-} = a_{\pm}^2 \quad T = 298.15 \text{ K}, n = 1$$

half-cell reactions are the same:

$\text{Ag}^+ | \text{Ag}$  reduction and oxidation

$$\Rightarrow E^{\circ} = 0 = E^{\circ}_{\text{Ag}^+ | \text{Ag}} - E^{\circ}_{\text{Ag}^+ | \text{Ag}} \quad \text{overall: } \text{Ag}^+(a_{\pm} = 1) \rightleftharpoons \text{Ag}(s)$$

$$E = E^{\circ} - \frac{RT}{nF} \ln K_{sp} \frac{a_{\text{Ag}^+}}{a_{\text{Ag}} = 1} \quad \text{b.w.}$$
$$= -59.16 \text{ mV} \log_{10} \frac{a_{\pm}}{1} = -59.16 \text{ mV} \log_{10} \sqrt{K_{sp}}$$

$\rightarrow a_{\pm} = 1$  (left/right)  
 ~~$\text{Ag}(s)$  not in  $Q$~~

$$= -\frac{1}{2} \cdot 59.16 \text{ mV} \cdot \log_{10} K_{sp}$$

$$\log_{10} K_{sp} = -\frac{2E}{59.16 \cdot 10^{-3} \text{ V}} = -\frac{2 \cdot 0.29 \text{ V}}{59.16 \cdot 10^{-3} \text{ V}} = -9.804$$

$$K_{sp} = 10^{-9.804} = 1.57 \cdot 10^{-10}$$

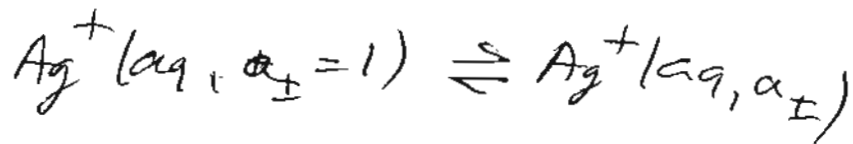
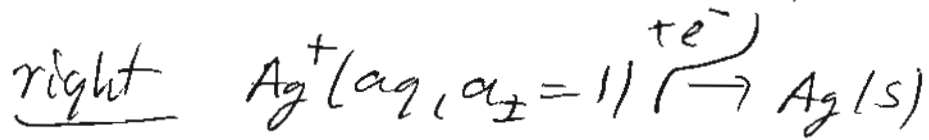
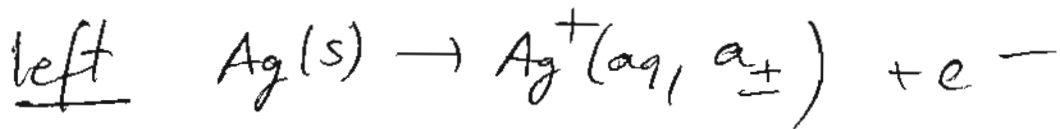
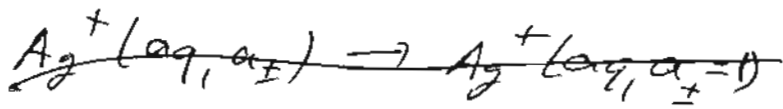
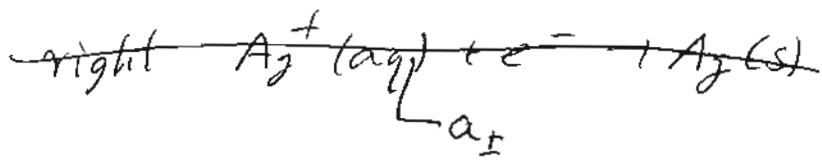
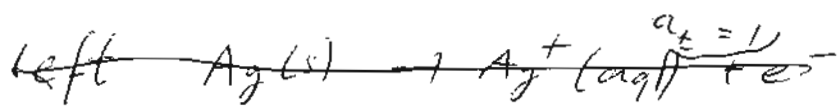
Problem for  $E^{\circ}$  determination:

$\gamma_{\pm}$  for a concentration

best way measure  $E_{\text{cell}}$  at small concentrations

where  $\gamma_{\pm} \rightarrow 1$

not near  $a_{\pm} = 1$  where  $\gamma_{\pm} \neq 1$  significantly



$$E = E^0 - \frac{RT}{F} \ln \frac{a_{\pm}}{a_{\pm}=1}$$

$$= E^0 - \frac{RT}{F} \ln a_{\pm}$$



cell:  $\text{Ag}^+|\text{Ag}$  electrode (right) (12) - 5

+ standard hydrogen electrode (left)  
at 298 K:



$$Q = \frac{1}{a_{\text{Ag}^+}}$$

$\text{H}_2(\text{g})$ ,  $\text{H}^+(\text{aq})$  at  $a_{\text{H}^+} = 1$  and  $a_{\text{H}_2} = 1$

in the standard hydrogen electrode

$\Rightarrow \text{H}^+, \text{H}_2$  not in  $Q$

$\text{Ag}^+$  from dissociation of  $\text{AgNO}_3(\text{aq})$

in the  $\text{Ag}^+|\text{Ag}$  electrode

$$a_{\pm}^{\nu} = a_+^{\nu_+} a_-^{\nu_-} \quad \begin{array}{l} \nu_+ = \nu_- = 1 \\ \nu = \nu_+ + \nu_- = 2 \end{array}$$

$$\rightarrow a_{\pm}^2 = a_{\text{Ag}^+} a_{\text{NO}_3^-} \Rightarrow a_{\pm} = a_{\text{Ag}^+} = a_{\text{NO}_3^-}$$

also:  $\gamma_{\pm} = \gamma_{\text{Ag}^+} = \gamma_{\text{NO}_3^-}$ ,  $m_{\text{Ag}^+} = m_{\text{NO}_3^-} = m_{\pm} = m$

$$E = E_{\text{Ag}^+|\text{Ag}}^0 + \frac{RT}{F} \ln a_{\text{Ag}^+}$$

$$(Q = \frac{1}{a_{\text{Ag}^+}} \Rightarrow \ln Q = -\ln a_{\text{Ag}^+})$$

$$E = E_{\text{Ag}^+|\text{Ag}}^0 + \frac{RT}{F} \ln \frac{m}{m_0} + \frac{RT}{F} \ln \gamma_{\pm}$$

low concentrations  $\Rightarrow$  DHLL is ok

$$\Rightarrow \ln \gamma_{\pm} = -1.173 \sqrt{\frac{m}{m_0}} \quad \text{at } 298 \text{ K}$$

$$E = 59.15 \text{ mV} \cdot \log_{10} \frac{m}{m_0}$$

(12)-6

$$= E_{\text{Ag}^+/\text{Ag}}^0 - 25.17 \text{ mV} \cdot 1.173 \sqrt{\frac{m}{m_0}}$$

$\frac{RT}{F}$  for  $\ln$ 
DHLL

$$E = 59.15 \text{ mV} \cdot \log_{10} \frac{m}{m_0} = E_{\text{Ag}^+/\text{Ag}}^0 - 30.13 \text{ mV} \sqrt{\frac{m}{m_0}}$$

mixing of  $\gamma$  factors in book, p. 270:

DHLL is

$$\log_{10} \gamma_{\pm} = -0.5092 \sqrt{I/M}$$

$$\text{and } \ln \gamma_{\pm} = -1.173 \sqrt{I/M}$$

$$\frac{RT}{F} = 25.17 \text{ mV}$$

$$\Rightarrow \frac{RT}{F} \ln x = 59.15 \text{ mV} \log_{10} x$$

measure  $E = 59.15 \text{ mV} \log_{10} \frac{m}{m_0}$  at different

values of  $m$

$\propto$  plot of  $E = 59.15 \text{ mV} \log_{10} \frac{m}{m_0}$  vs  $\sqrt{\frac{m}{m_0}}$

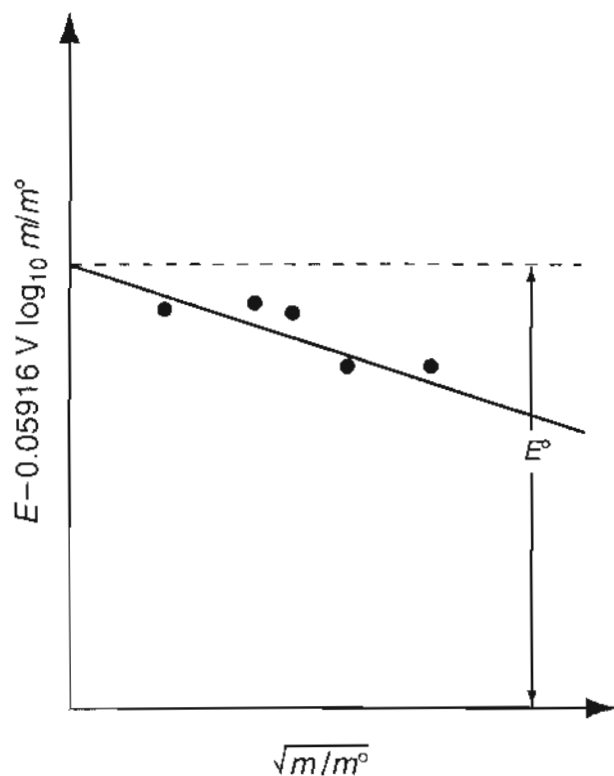
$\rightarrow$  straight line (transparency)

intercept at  $m=0$ :  $E_{\text{Ag}^+/\text{Ag}}^0$

With measured  $E_{\text{Ag}^+/\text{Ag}}^0$  and  $E$ , with

$$E = E_{\text{Ag}^+/\text{Ag}}^0 + \frac{RT}{F} \ln \frac{m}{m_0} + \frac{RT}{F} \ln \gamma_{\pm}$$

$\ln \gamma_{\pm}$  and  $\gamma_{\pm}$  can be calculated



**FIGURE 11.7**  
The value of  $E^\circ$  and the activity coefficient can be measured by plotting the left-hand side of Equation (11.42) against the square root of the molality.

## Determination of $E^\circ$

# 11.8 Coefficients Using an Electrochemical Cell

The main problem in determining standard potential: activity coefficient  $\gamma_{\pm}$  for a given solute concentration measurements of the cell potential at low concentration unit activity, where  $\gamma_{\pm}$  differs appreciably from 1. Consider the  $\text{Ag}^+/\text{Ag}$  and standard hydrogen electrode half-cell reaction  $\text{Ag}^+(aq) + 1/2 \text{H}_2(g) \rightleftharpoons \text{Ag}(s) + \text{H}^+(aq)$  and activities of  $\text{H}_2(g)$  and  $\text{H}^+(aq)$  are 1, they do not appear from the dissociation of  $\text{AgNO}_3$ . Recall that the activity is measured directly. It must be calculated from the molality  $a_{\pm}^{\nu} = a_{+}^{\nu+} a_{-}^{\nu-}$ . In this case,  $a_{\pm}^2 = a_{\text{Ag}^+} a_{\text{NO}_3^-}$  and  $\gamma_{\pm} = \gamma_{\text{Ag}^+} = \gamma_{\text{NO}_3^-}$  and  $m_{\text{Ag}^+} = m_{\text{NO}_3^-} = m_{\pm} = m$ .

$$E = E_{\text{Ag}^+/\text{Ag}}^\circ + \frac{RT}{F} \ln a_{\text{Ag}^+} = E_{\text{Ag}^+/\text{Ag}}^\circ + \frac{R}{F} \ln a_{\text{Ag}^+}$$

At low enough concentrations, the Debye–Hückel limiting law  $\log \gamma_{\pm} = -0.5092 \sqrt{m_{\pm}/m^\circ}$  at 298 K as discussed in Section 11.4, Equation (11.41) can be rewritten in the form

$$\begin{aligned} E - 0.05916 \log_{10}(m/m^\circ) &= E_{\text{Ag}^+/\text{Ag}}^\circ - 0.05916 \log_{10} \gamma_{\pm} \\ &= E_{\text{Ag}^+/\text{Ag}}^\circ - 0.05916 \log_{10} \gamma_{\pm} \end{aligned}$$

The left-hand side of this equation can be calculated as a function of  $\sqrt{(m/m^\circ)}$ . The results will resemble the Debye–Hückel limiting law. The extrapolation of the line that best fits the data to  $m = 0$  (vertical axis). Once  $E^\circ$  has been determined, Equation (11.42) can be used to calculate activity coefficients.

Electrochemical cells provide a powerful method for measuring activity coefficients because cell potentials can be measured more accurately than colligative properties such as freezing point depression. Although the Debye–Hückel limiting law was unnecessary to use the limiting law to calculate activity coefficients.

## 11.9 Cell Nomenclature and Standard Cell Potentials of Electrochemical Cells

It is useful to use an abbreviated notation to describe a cell. The abbreviated notation for a cell is written as follows:

Electrochemistry is a very good method for  $\gamma_{\pm}$  determination (12)-7  
it is far more easy than colligative properties like

freezing point depression of solutions  
boiling point elevation of solutions  
vapor pressure lowering over solutions  
osmotic pressure of solutions

DHL was only used to get  $E^{\circ}$  around  $m \approx 0$ ,  
but then  $\gamma_{\pm}$  is obtained without use of  
DHL (only good when  $m \rightarrow 0$ )

- Types of cells

(13) - 1

- Electrochemical Series

Cell symbol

Abbreviated notation to describe cells

Includes all species of the cell reaction and as vertical lines also phase boundaries and the metal electrodes at the left and right ends of the symbol

left Anode = half-cell in which Oxidation happens

right Cathode = half-cell in which Reduction happens

Large and small ions diffuse with different speeds in an electric field

fast diffusing ions (like  $H^+$ ) can travel further in the same time than slow ones (like  $Cl^-$ ) through liquid-liquid junctions

Steady state: a dipole layer is formed across the junction and vector of ion transfers across the layer become equal

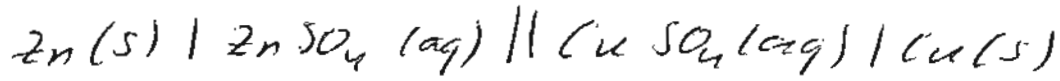
$\Rightarrow$  small junction potentials between liquids of different composition or concentration develops is mostly eliminated by a salt bridge

salt bridge: ||

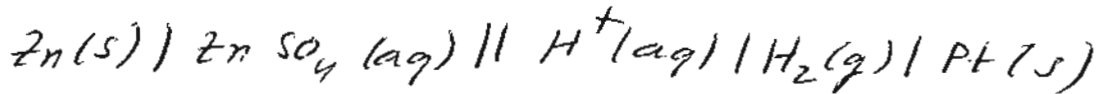
(13)-2

different phases in contact with  $e^-$  transfer: |

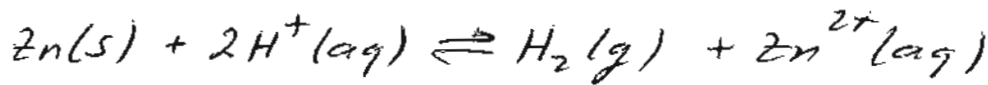
Daniell cell with salt bridge:



$\text{Zn} | \text{Zn}^{2+}$  + standard hydrogen electrode:



cell reaction:



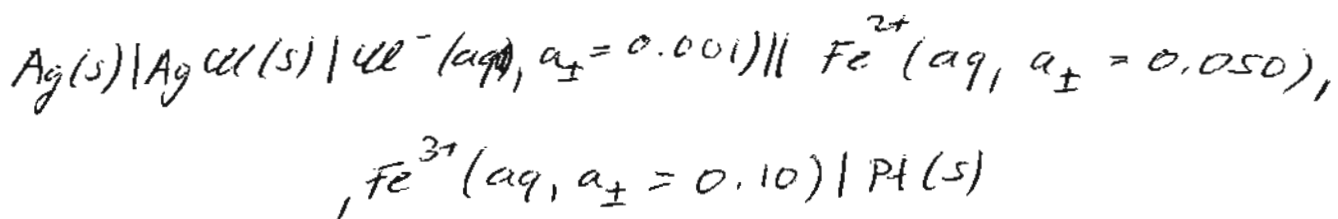
Sometimes solutions are ~~is~~ separated by porous membranes to prevent direct mixing

→ the junction potential is not eliminated

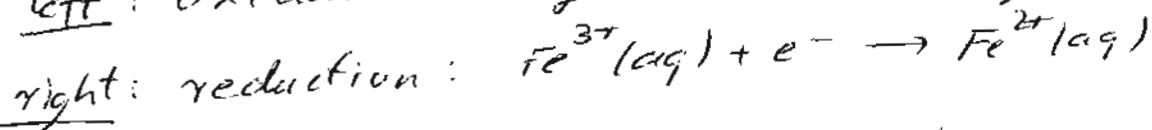
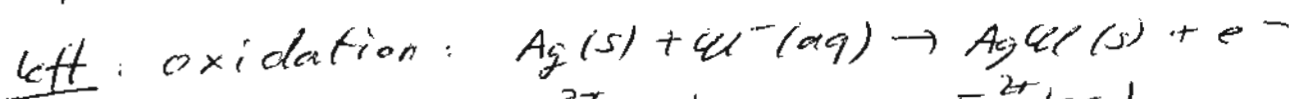
~~$e^-$  move from left~~ → slightly wrong EMF

$e^-$  move from left to right (anode to cathode, oxidation to reduction) through a wire

# of  $e^-$  such that the Redox equation is ok



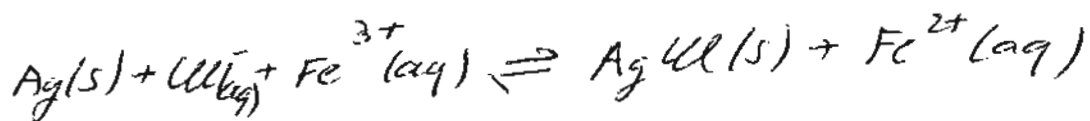
half-cell reactions, overall reaction?



Pt as catalyst is not involved

no of  $e^-$  is the same in both ⇒

simple adding yields cell reaction



spontaneous direction is unknown without  $E_{\text{cell}}$

if  $E_{\text{cell}}$  is known, then:

$E_{\text{cell}} > 0$  reaction proceeds as written with oxidation left, reduction right

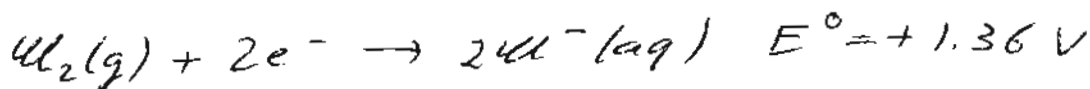
$E_{\text{cell}} = 0$  equilibrium

$E_{\text{cell}} < 0$  reaction proceeds reversed

some half-cell types:

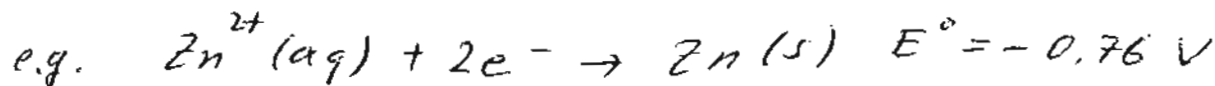
standard hydrogen of type ions(aq) | gas

same type:  $\text{Cl}_2 | \text{Cl}^-$  half-cell:



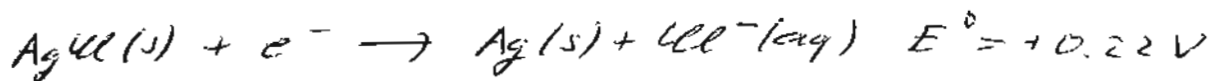
type metal + metal ions(aq): both electrodes

in the Daniell cell are of this type:

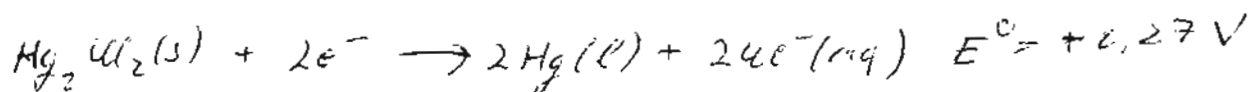


Many reference electrodes are a metal coated with an insoluble salt of the metal immersed in a solution that contains the anion of the insoluble salt

e.g.  $\text{Ag} | \text{AgCl}$  electrode:

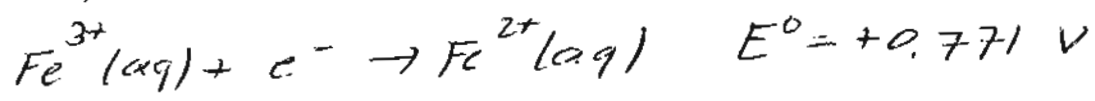


or calomel (= mercurous chloride  $\text{Hg}_2\text{Cl}_2$  which contains  $\text{Hg}_2^{2+}$  ions) electrode:



common type.

both ions (oxidized and reduced) are in the same aq solution, electrochemically inert catalyst like Pt for electrical ~~contact~~ connection to the solution:



In App. B in Table 11.1 & 11.2: standard reduction potentials of many half-cell reactions given. When a cell consists of 2 of these half-cells with  $E_1^{\circ}$  and  $E_2^{\circ}$  (both for reduction):

$$E_{cell}^{\circ} = E_1^{\circ} - E_2^{\circ}$$

the minus sign is for that half-cell <sup>reaction</sup> which is an oxidation in the cell reaction

$E_{cell}^{\circ} > 0$  (thus  $\Delta G^{\circ} < 0$ ) if the reduction potential  $E_1^{\circ}$  is more positive than  $E_2^{\circ}$

"more positive" means "smaller absolute values" for negative numbers

⇒ strength as oxidizing agent follows the order of reduction potential values

### Electrochemical Series:

oxidation of neutral metals → to the most common oxidation state of the metal in order of decreasing  $E^{\circ}$



**TABLE 11.3**  
The Electrochemical Series**Most Strongly Reducing**  
(The metal is least easily oxidized.)

Gold  
(most positive reduction potential)

Platinum

Palladium

Silver

Rhodium

Copper

Mercury  
(Hydrogen; zero reduction potential  
by convention)

Lead

Tin

Nickel

Iron

Zinc

Chromium

Vanadium

Manganese

Magnesium

Sodium

Calcium

Potassium

Rubidium

Cesium

Lithium  
(most negative reduction potential)

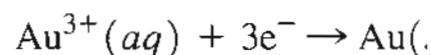
**Least Strongly Reducing**  
(The metal is most easily oxidized.)

## 11.10 The Electroche

Tables 11.1 and 11.2 (see Appendix B, Data commonly encountered half-cells. The emf of a cells with standard reduction potentials  $E_1^\circ$  and

$$E_{cell}^\circ = E_1^\circ - E_2^\circ$$

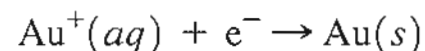
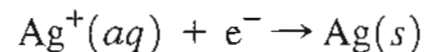
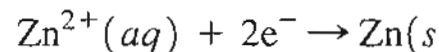
The potential  $E_{cell}^\circ$  will be positive and, potential for reaction 1 is more positive than the positive strength of a species as an oxidizing agent value of its reduction potential in Table 11.2. Table 11.3 is obtained if the oxidation of neutral state is considered. For example, the emf of the reduction reaction



In a redox couple formed from two entries in the list, the species lying higher in the list will be reduced and the species lying lower will be oxidized in the spontaneous reaction. For example, in the copper-zinc cell, the spontaneous reaction is the copper-zinc reaction:  $\text{Zn}^{2+}(aq) + \text{Cu}(s)$  and not the reverse reaction.

### EXAMPLE PROBLEM 11.8

For the reduction of the permanganate ion  $\text{MnO}_4^-$  ( $E^\circ = +1.51 \text{ V}$ ). The reduction reactions and standard reduction potentials for  $\text{Zn}^{2+}$  and  $\text{Au}^+$  are given here:



Which of these metals will be oxidized by the permanganate ion?

### Solution

The cell potentials assuming the reduction of the permanganate ion and the oxidation of the metal are

$$\text{Zn: } 1.51 \text{ V} + 0.761 \text{ V}$$

What is higher in the series oxidizes  
any lower one, is reduced by any lower  
one

higher one is reduced by lower one which  
is oxidized in a spontaneous cell reaction

the higher in the list: is less easy oxidized  
→ becomes reduced to the  
metal (more noble)

the lower in the list: is more easy oxidized

entry for gold: is for the reduction

most common oxidation state:  $\text{Au}^{3+}$

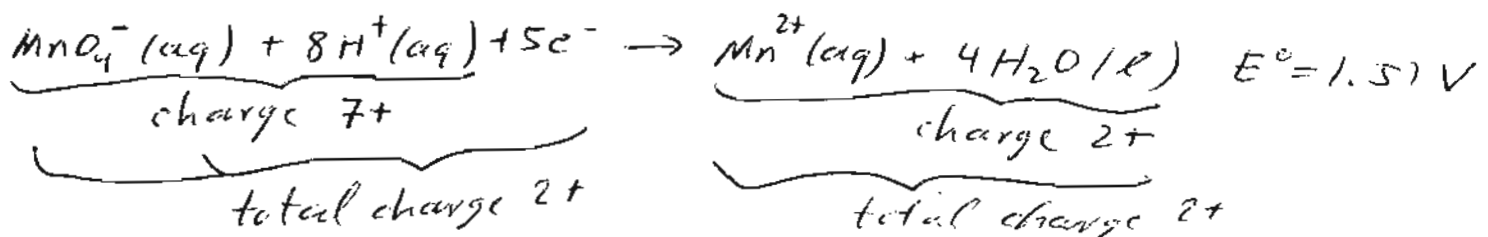


Au most stable metal = Au "likes" most to be reduced

~~reduction of  $\text{MnO}_4^-$~~  the metal

reduction of  $\text{MnO}_4^-$  to  $\text{Mn}^{2+}$  in acidic solution

(in basic solution the reduction only goes to  $\text{MnO}_2(\text{s})$ ):



⇒  $5\text{e}^-$  needed on the left to make it a  
total charge of  $2+$  on both sides

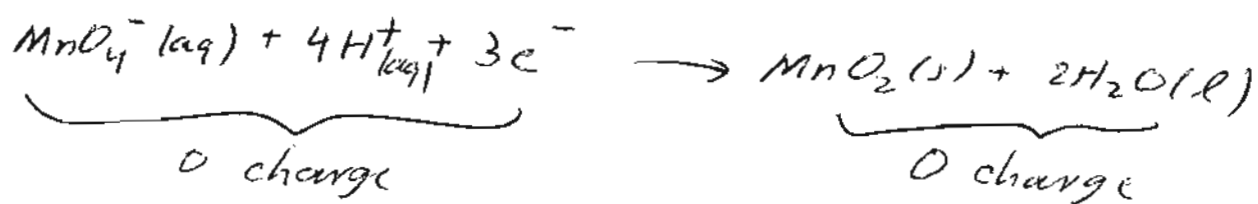
the total charges must be the same (13) - 6  
of 1 on both sides

→ fixes the no. of  $e^-$  and their side

$8H^+$  are needed to form  $4H_2O$  from the  
4 O atoms in  $MnO_4^-$

in basic ~~acid~~ solution:

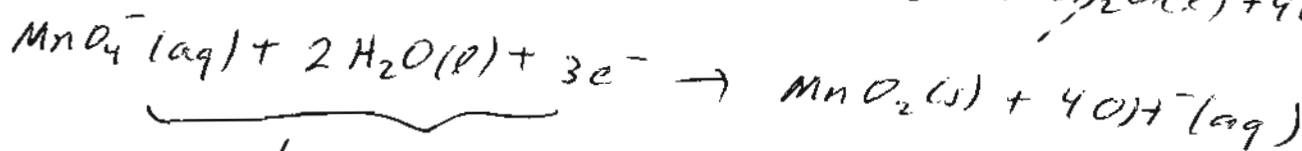
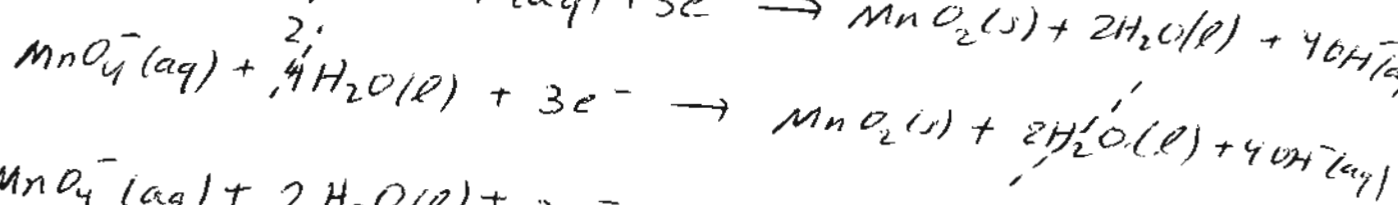
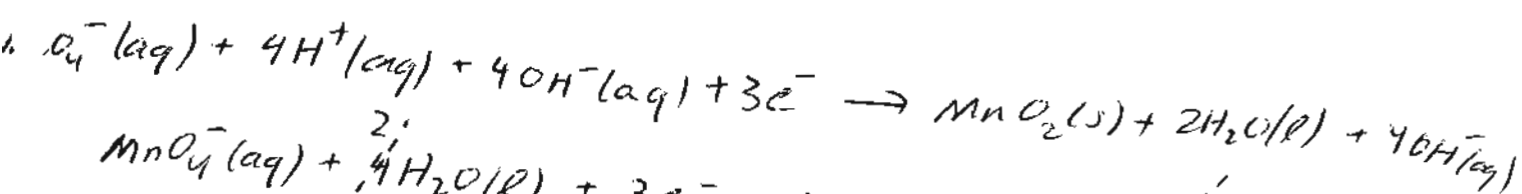
1. step: do as if it is acidic:



2. step: add on both sides the same  
number of  $OH^-$  ions so that each  $H^+$   
can form  $H_2O$  with one  $OH^-$

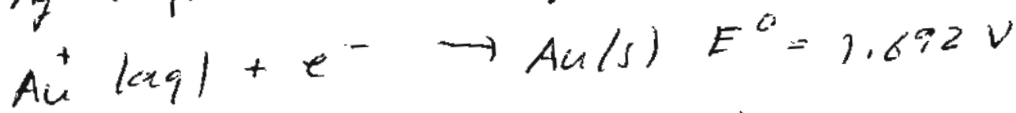
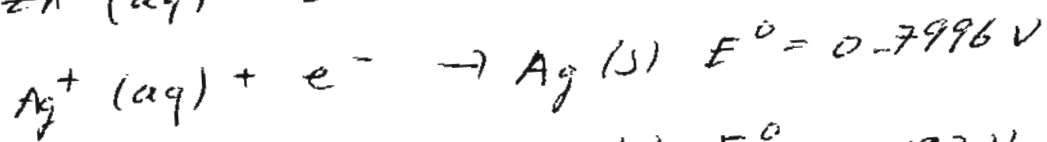
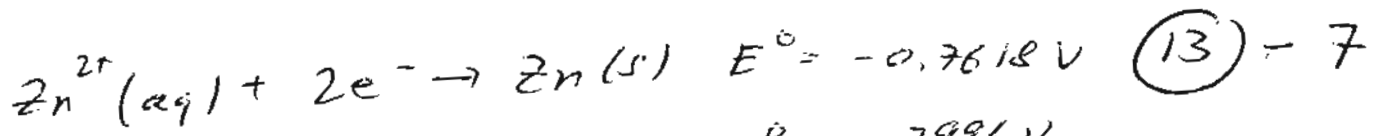
after cancel what is possible

above:  $4H^+ \rightarrow 4OH^-$  needed on both  
sides



charge 4-

charge 4-



Which ones are oxidized by  $\text{MnO}_4^-$  ions in acidic solution?  $\rightarrow \text{MnO}_4^-$  is reduced in the standard state

$$\Rightarrow E_{\text{cell}}^\circ = E_{\text{MnO}_4^-/\text{Mn}^{2+}}^\circ - E_{\text{X}}^\circ$$

reduction                      oxidation  
+ sign                                      - sign

$$\begin{aligned} \underline{\text{Zn}} \quad E_{\text{cell}}^\circ &= E_{\text{MnO}_4^-/\text{Mn}^{2+}}^\circ - E_{\text{Zn}^{2+}/\text{Zn}}^\circ = (1.51 + 0.7618) \text{ V} \\ &= 2.27 \text{ V} > 0 \\ &\text{spontaneous} \end{aligned}$$

$\Rightarrow$  Zn is spontaneously oxidized by  $\text{MnO}_4^-$

$$\begin{aligned} \underline{\text{Ag}} \quad E_{\text{cell}}^\circ &= E_{\text{MnO}_4^-/\text{Mn}^{2+}}^\circ - E_{\text{Ag}^+/\text{Ag}}^\circ = (1.51 - 0.7996) \text{ V} \\ &= 0.710 \text{ V} > 0 \end{aligned}$$

Ag is also spontaneously oxidized by  $\text{MnO}_4^-$

$$\begin{aligned} \underline{\text{Au}} \quad E_{\text{cell}}^\circ &= E_{\text{MnO}_4^-/\text{Mn}^{2+}}^\circ - E_{\text{Au}^+/\text{Au}}^\circ = (1.51 - 1.692) \text{ V} \\ &= -0.18 \text{ V} < 0 \end{aligned}$$

Au<sup>+</sup> is spontaneously reduced by  $\text{MnO}_4^-$

Au is not oxidized by  $\text{MnO}_4^-$

nothing happens because  $\text{MnO}_4^-$  has no higher oxidation state to be oxidized

$E_{\text{cell}}^\circ > 0 \Rightarrow \Delta G < 0$  for  $\text{MnO}_4^-$  reduction and X oxidation

Zn and Ag are oxidized, with Au<sup>+</sup> nothing happens

# -Thermodynamics of Batteries and (19) -1

## Fuel cells

Batteries, Fuel Cells: Electrochemical cells to

maximize output power/weight (volume) ratio.

batteries contain the reactants for the cell reaction

primary batteries: recharging not possible

secondary batteries: recharging possible

fuel cells: continuous flow of reactants from outside

maximum electrical work produced by a cell:

$$W_{el} = -\Delta G_R$$

$$\Delta G = \Delta H - T\Delta S \Rightarrow W_{el} = -\Delta H_R \left[ 1 - \frac{T\Delta S_R}{\Delta H_R} \right]$$

operation usually at about 300K

maximum work from a reversible heat engine  
working between  $T_h$  (hot) and  $T_c$  (cold)

$$W_{th} = q_{hot} \cdot \varepsilon$$

$q_{hot}$  = heat absorbed from hot reservoir

$\varepsilon$ : efficiency of a reversible heat engine

$$q_{hot} = -\Delta H_R, \quad \varepsilon = \frac{T_h - T_c}{T_h}$$

$$W_{th} = -\Delta H_R \left[ \frac{T_h - T_c}{T_h} \right] \text{ examples } T_h = 600\text{K}, T_c = 300\text{K}$$

reaction in the lead-acid car battery:

$$\Delta G_R^\circ = -376.97 \frac{\text{kJ}}{\text{mol}} \quad \Delta H_R^\circ = -227.58 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta S_R^\circ = 501.1 \frac{\text{J}}{\text{K mol}}$$

$$W_{el} = 227.58 \frac{\text{kJ}}{\text{mol}} \left[ 1 - \frac{501.1 \cdot 10^{-3} \frac{\text{kJ}}{\text{K mol}} \cdot 300\text{K}}{-227.58 \frac{\text{kJ}}{\text{mol}}} \right] = 377.91 \frac{\text{kJ}}{\text{mol}}$$

$$W_{th} = 227.58 \frac{\text{kJ}}{\text{mol}} \frac{600 - 300}{600} = 113.79 \frac{\text{kJ}}{\text{mol}}$$

$$\frac{w_{el}}{w_{th}} = \frac{377.91}{113.79} = 3.32$$

(17) - 2

⇒ a battery produces much more work than a heat engine

invention of lead-acid battery: 1859

but it is still in use

power to start a car engine:  $\approx 1 \text{ kW}$

⇒ capacity of a battery has to be  $\approx 100 \text{ A}$

+ 500 - 100 recharging cycles must be possible

product of cell reaction: solid, which in recharging must be converted back to solid reactants.

products, reactants have different structures & densities

⇒ mechanical stress in anode & cathode

→ partial destruction of them

→ no. of recharging cycles is limited!

### lead-acid battery

electrodes of Pb powder and  $\text{PbO}_2/\text{PbSO}_4$  mixture, supported in a Pb frame

the electrodes are immersed in a container with conc.  $\text{H}_2\text{SO}_4$

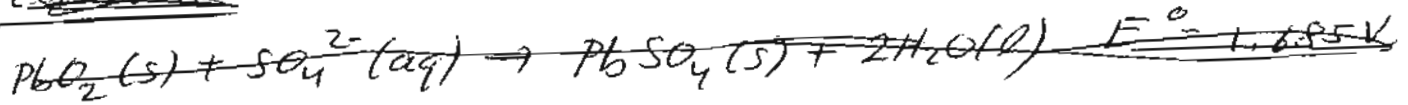
when the battery is discharged an external voltage must be applied to convert the products back to reactants

→ recharging possible

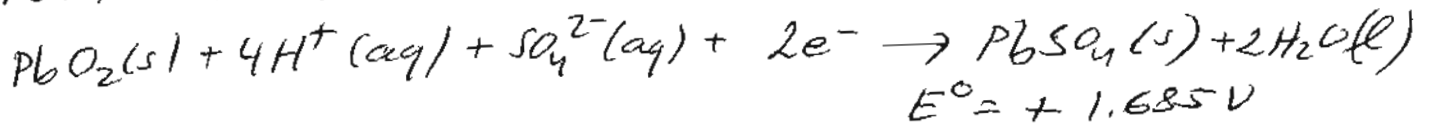
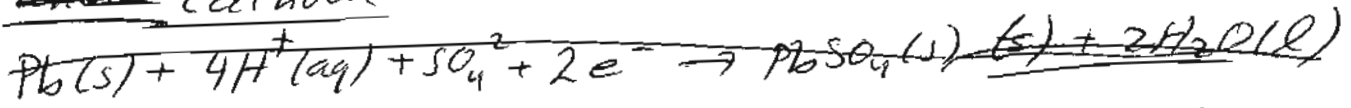
in recharging, role of cathode and anode must be reversed

overall and half-cell reactions for the (14)-3 discharge process:

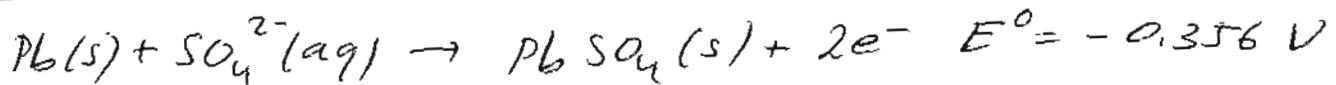
~~cathode~~



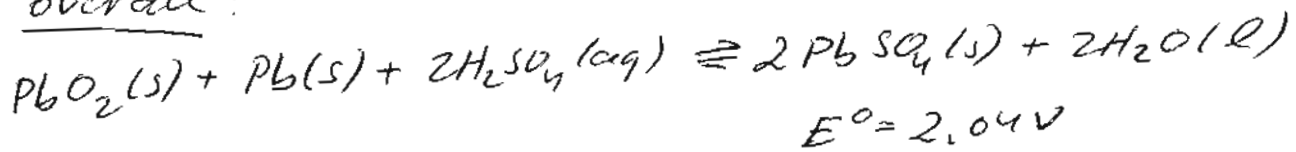
~~anode~~ cathode



anode



overall:



for recharging: reverse the arrows of half-reactions  
change signs of half-cell emf's

to yield 12 V: 6 such cells are needed

efficiency: 90% of charge used in recharging  
are obtained in discharging

side reactions like  $\text{H}_2\text{O}$  electrolysis are minimal  
in recharging, but only 50% of the lead reacts

⇒ decrease of power/mass (Pb is heavy!)

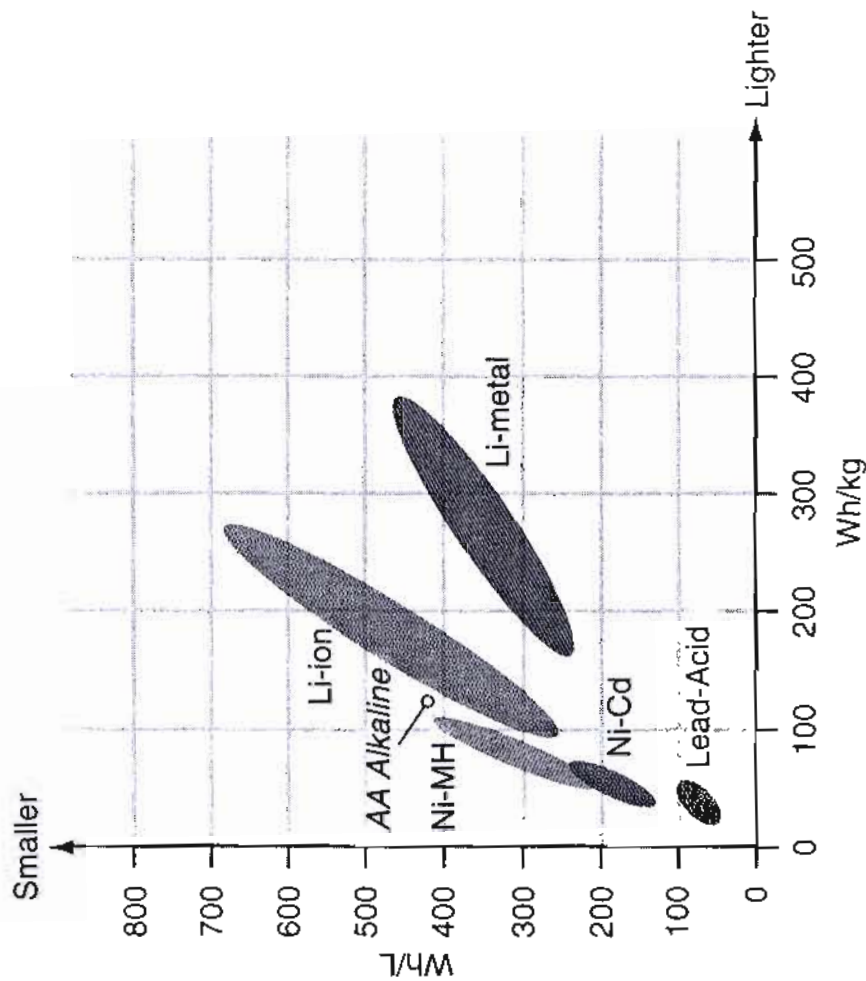
Also: in discharge side-reactions occur without  
a flow of current

→ the capacity of a lead-acid battery is  
reduced by 0.5% per day by self discharge  
without flow of current

transp. energy/L vs energy/kg    1 Wh = 1 AAs = 1 J  
lead-acid lowest in energy/L & energy/kg

## FIGURE 11.8

number of different batteries are classified with their specific energy density per unit volume and per unit mass.



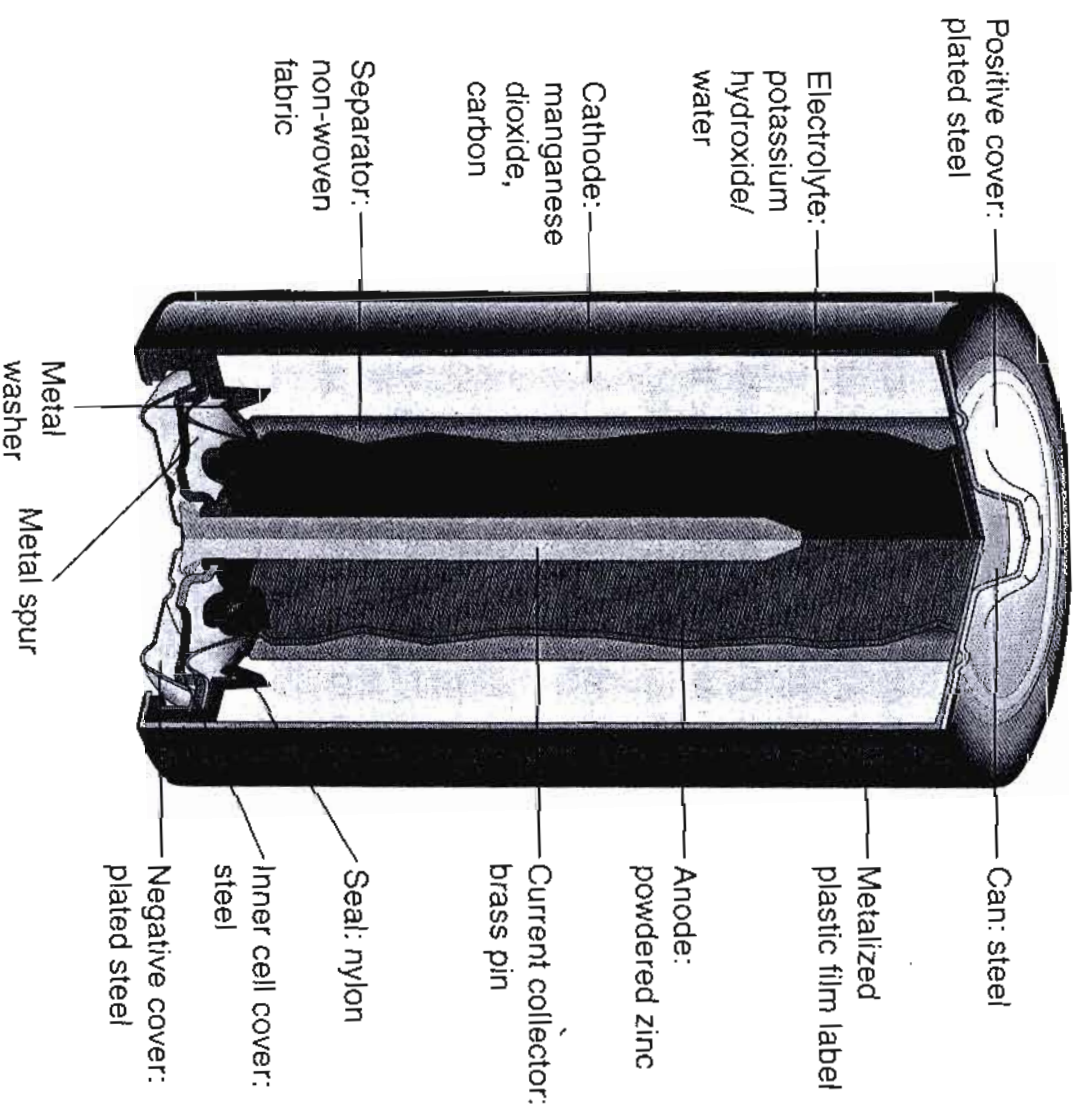
This means that side reactions such as the electrolysis of water play a minimal role in charging the battery. However, only about 50% of the lead in the battery is converted between  $\text{PbO}_2$  and  $\text{PbSO}_4$ . Because Pb has a large atomic mass, this limited convertibility decreases the power per unit mass figure of merit for the battery. Parasitic side reactions also lead to a self-discharge of the cell without current flowing in the external circuit. For the lead-acid battery, the capacity is diminished by approximately 0.5% per day through self-discharge.

As batteries have become more common in portable devices such as cell phones and laptop computers, energy density is a major criterion in choosing the most suitable



battery chemistry for a specific application. Figure 11.8 shows a comparison of different battery types. The lead-acid battery has the lowest specific energy either in terms of volume or mass. Next we discuss the chemistry of three commonly used rechargeable batteries: the alkaline, nickel metal hydride, and lithium ion batteries.

The individual elements of the alkaline cell are shown in Figure 11.9. The anode in this cell is powdered zinc, and the cathode is in the form of a  $MnO_2$  paste mixed with



RE 11.9

atic diagram of an alkaline cell.

## transp. alkaline cell

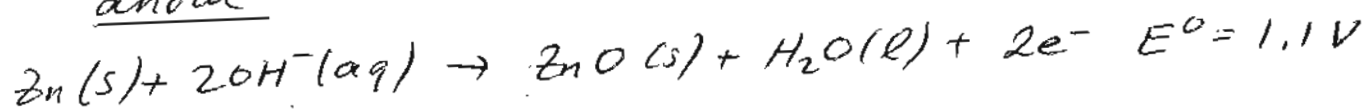
(14) -4

anode: powdered Zn

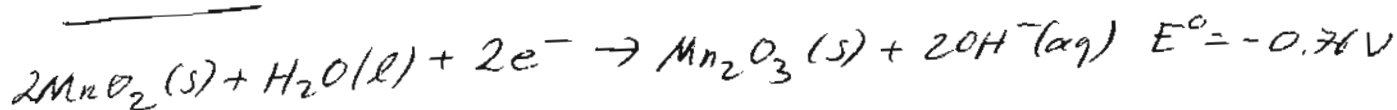
cathode:  $MnO_2$  paste mixed with powdered carbon to increase conductivity

electrolyte: KOH (alkaline)

anode



cathode



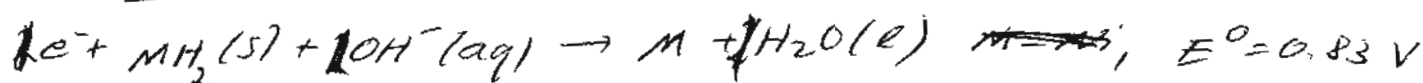
## Nickel metal hydride battery

used in hybrid cars (engine electric & fuel)  
gasoline engines for higher speeds

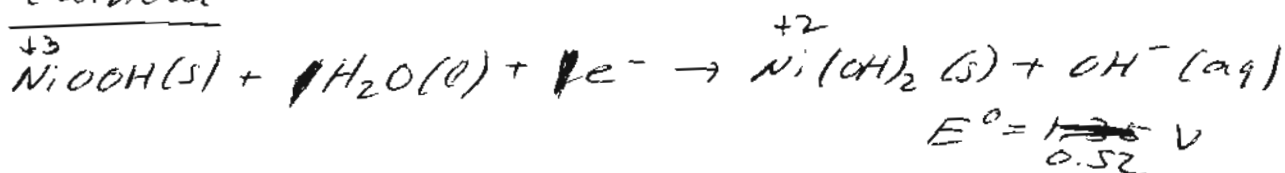
Toyota Prius: 28 modules of 6 cells each

→ total of 201.6 V, capacity  $\approx$  ~~1100~~ 1100 Wh

anode



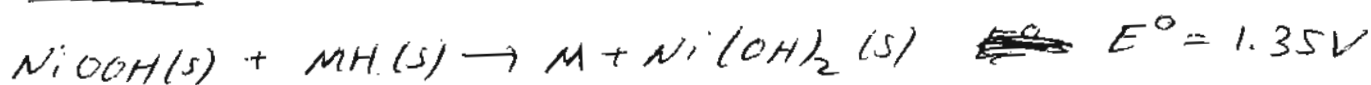
cathode



M is an alloy containing V, Ti, Zr, Ni, Cr, Co, Fe

electrolyte: KOH

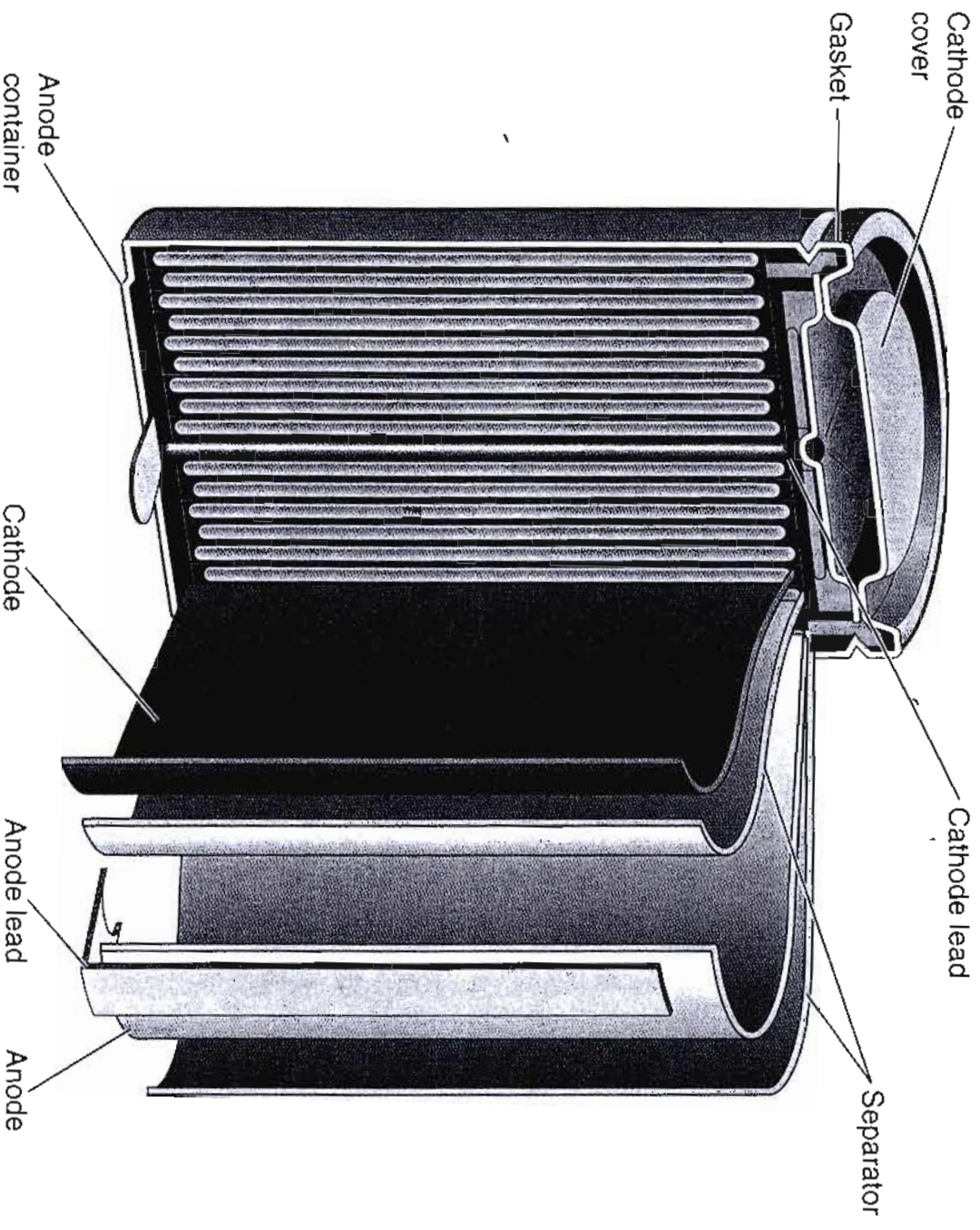
overall:



## Li-ion batteries

e.g. in cell phones (high energy density  
= small batteries, as needed)

DISSOLVED lithium carbonate. Aqueous electrolytes would limit the cell voltage because at larger potentials, water is reduced or oxidized. Figure 11.11 shows a number of materials that can be used as electrodes. Materials that fall outside of the band gap of the electrolyte are unsuitable because their use initiates reduction or oxidation of the solvent. It would appear that carbon is unsuitable, but the formation of a thin solid/ electrolyte interface layer stabilizes carbon with respect to solvent reactions, and it is the



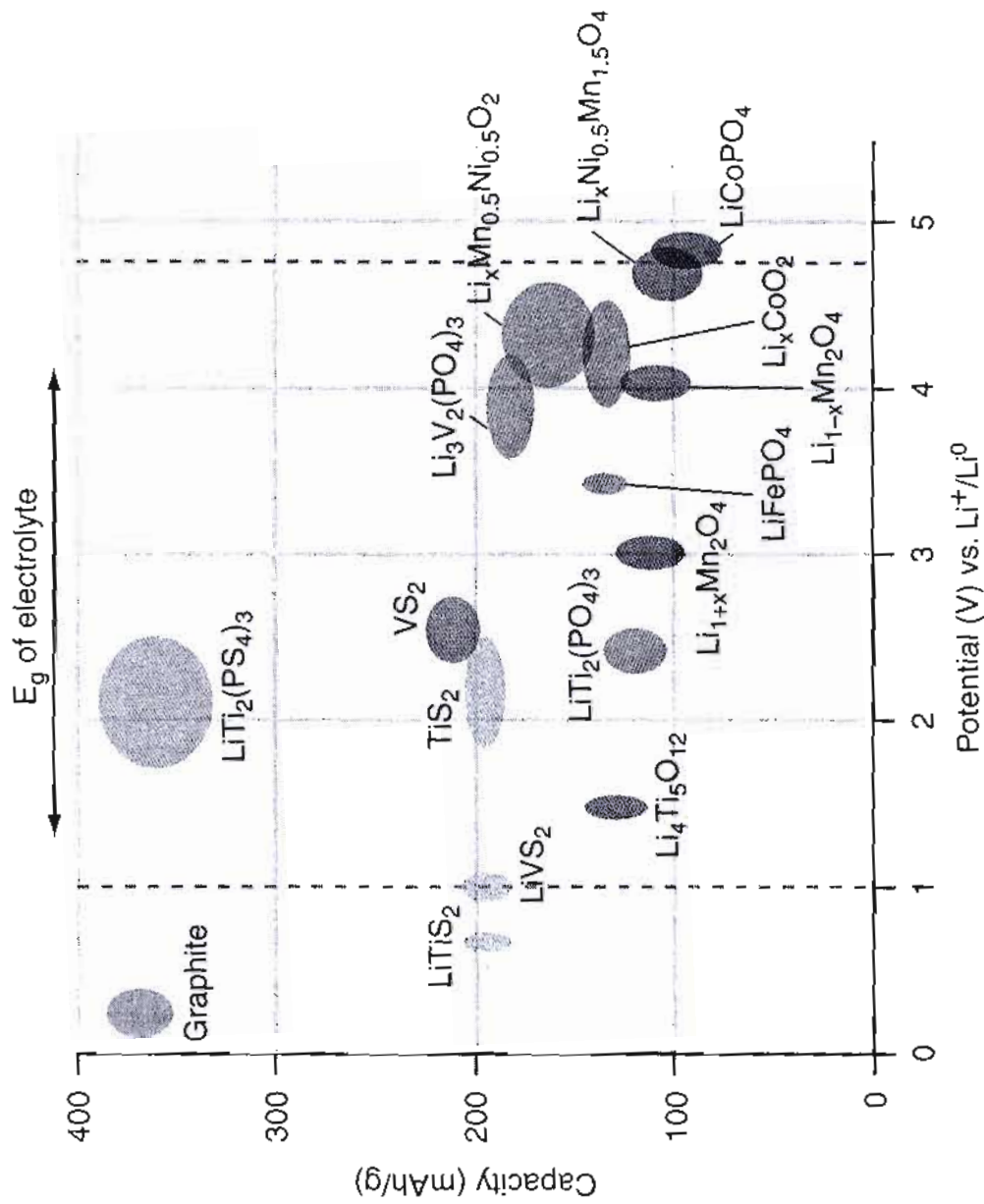
**FIGURE 11.10**

Schematic structure of a cylindrical lithium ion battery. The anode and cathode material are formed of thin sheets to optimize the transport kinetics of  $\text{Li}^+$  ions

FIGURE 11.11

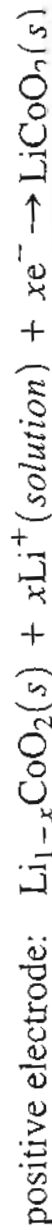
The cell potential of a lithium ion battery versus the energy density per unit mass or a number of electrode materials is shown. The dashed lines indicate the voltage range in which 1M LiPF<sub>6</sub> in a 1:1 mixture of ethylene carbonate and diethyl carbonate is stable with respect to reduction or oxidation.

Source: Goodenough J. B. and Kim Y. *Chemistry of Materials* 22 (2010), 587.



most widely used anode electrode. Using a carbon anode and LiCoO<sub>2</sub>(s) as the cathode allows a cell potential of 3.7 V to be achieved. As Figure 11.11 shows, higher potentials are possible, but batteries with long life cycles using materials other than LiCoO<sub>2</sub>(s) have not yet been developed.

Rechargeable lithium batteries have the following half-cell reactions while discharging the battery:



the electrodes contain  $Li^+$  ions

different binding strength of  $Li^+$  in 2 materials

→ cell voltage

transp. schematic  $Li^+$  ion battery

2 electrodes are separated by electrolyte

saturated (with electrolyte) polymer membrane

$Li^+$  ions move through those membranes

electrolyte:  $Li$  salt in organic solvent

e.g. 1M  $LiPF_6$  solution in an ethylene carbonate / diethyl carbonate mixture

aqueous solutions electrolyte would limit the cell voltage to 1.2 V

> 1.2V :  $H_2O$  would be oxidized or reduced

transp. materials used as electrolytes

bandgap inside dashed lines the electrolyte is stable

carbon is made useful by the formation

of a thin solid/electrolyte layer, which can stabilize carbon against reactions with the solvent

most common is a carbon anode and a

$LiCoO_2$  cathode: 3.7 V for the cell

higher voltage is possible

up to now only batteries with long life cycles

could only be made with  $LiCoO_2(s)$

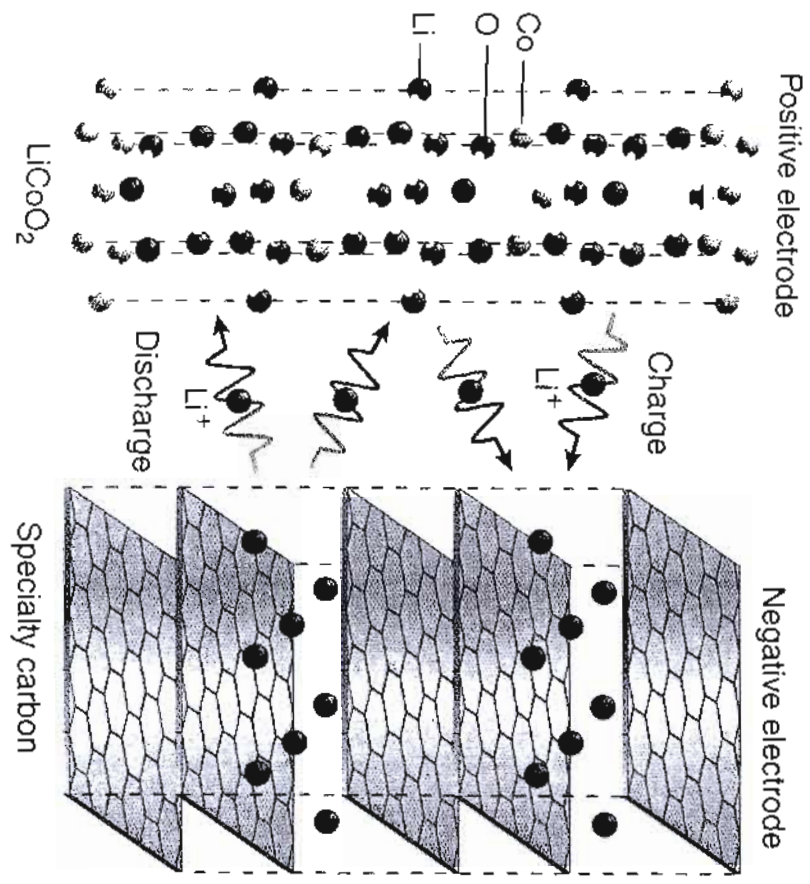
(11.62)

(11.63)

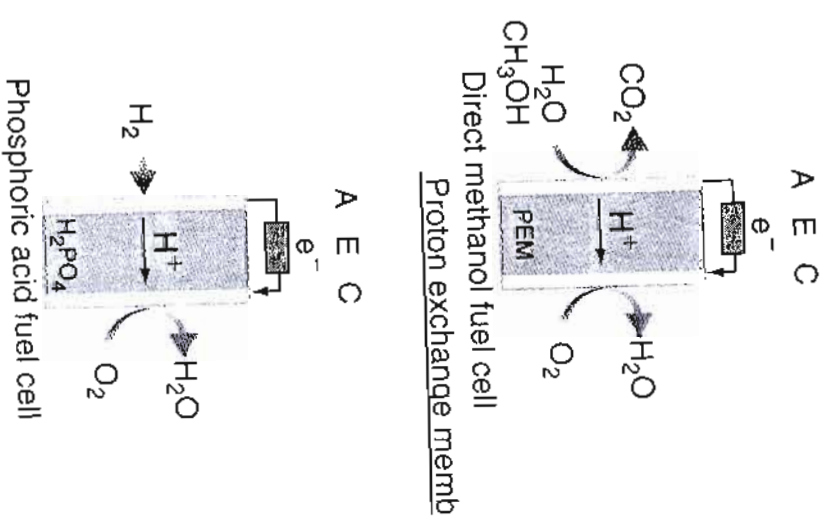
negative electrode:  $CLi_x \rightarrow C(s) + xLi^+(solution) + xe^-$   
 right arrows indicate the discharge directions. In these equations,  $x$  is a small positive number. The overall cell reaction is



The fully charged battery has a cell potential of  $\sim 3.7 \text{ V}$ . The structures of  $LiCoO_2(s)$  and  $CLi_x$  are shown schematically in Figure 11.12.  $CLi_x$  designates  $Li$  intercalated between sheets of graphite; it is not a stoichiometric compound. In a lithium-ion battery the lithium ions are transported to and from the cathode or anode with the transition metal, cobalt (Co), in  $Li_xCoO_2$  being oxidized from  $Co^{3+}$  to  $Co^{4+}$  during charging, and reduced from  $Co^{4+}$  to  $Co^{3+}$  during discharge.

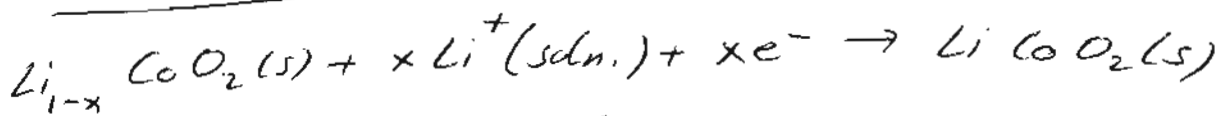


The heart of this fuel cell is solid electrolyte. This membrane moving in the internal circuit, allow rapid charge transport at low potentials. The membrane presents polymeric forms of perfluorinated fully hydrated. The membrane micelles  $\sim 4 \text{ nm}$  in diameter, corner of the cavities and character of the polymer provides rigid

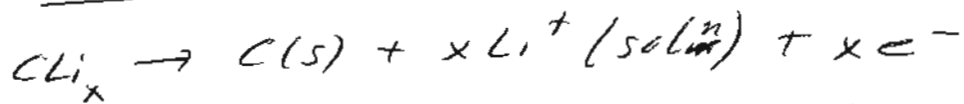


positive electrode:

(14)-6

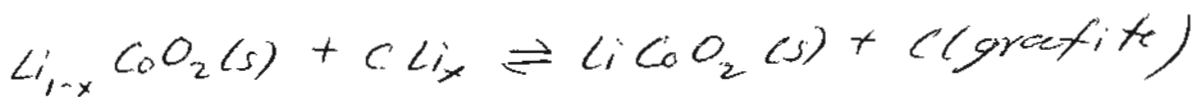


negative electrode



discharge reactions

$x$  small, but  $x > 0$  overall:  $E^\circ \approx 3.7 \text{ V}$



transp. structures of  $\text{LiCoO}_2$  and  $\text{C}\text{Li}_x$

$\text{C}\text{Li}_x$ : Li intercalated between graphite layers  
not stoichiometric

$\text{Li}^+$  ions are transported between cathode and anode

in this transport Co in  $\text{Li}_{1-x}\text{CoO}_2$  is oxidized from  $\text{Co}^{3+}$  to  $\text{Co}^{4+}$  in the charging process

and reduced from  $\text{Co}^{4+}$  to  $\text{Co}^{3+}$  in discharge

### Fuel Cells

Advantage over batteries: continuously refueled

no down-time for charging

Most of the different ways to construct

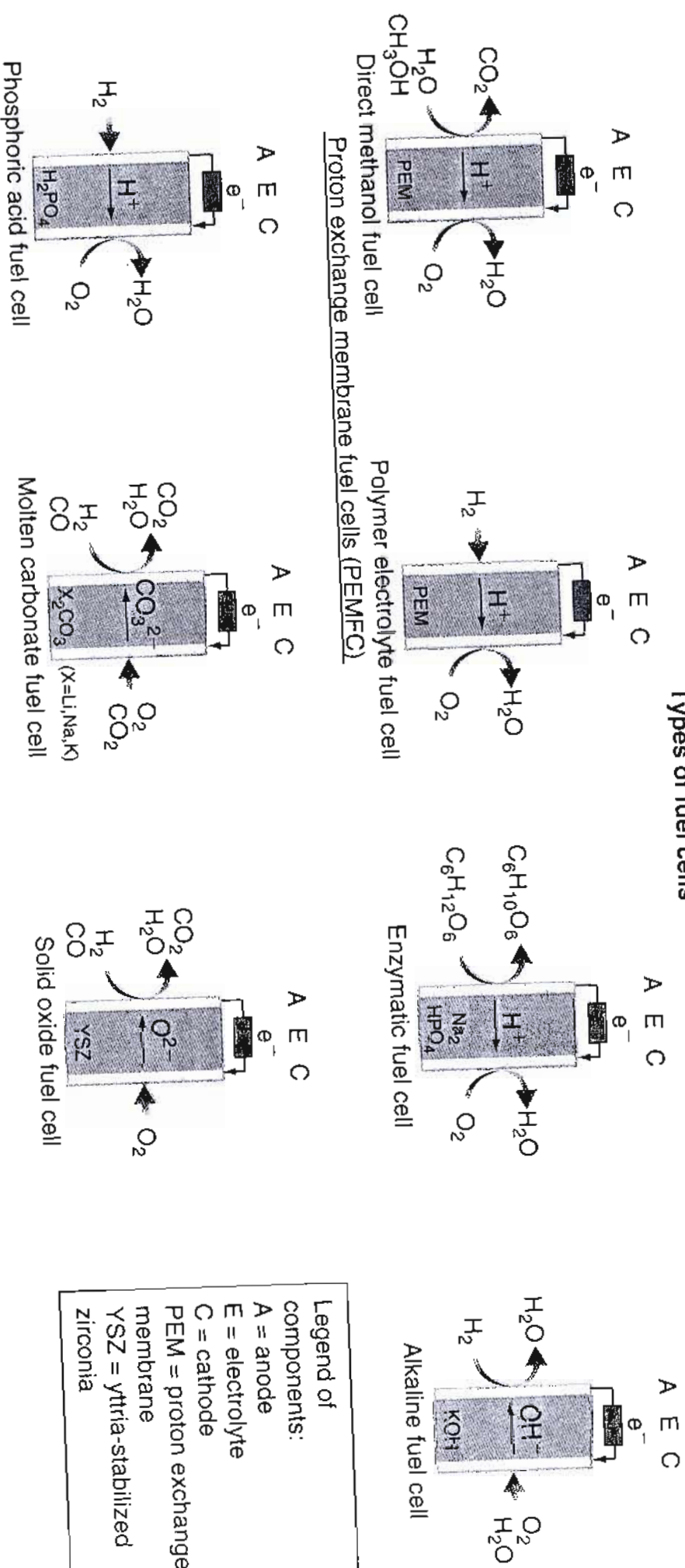
fuel cells are still under development

only phosphoric acid fuel cells are on the market

The heart of this fuel cell is the proton exchange membrane (PEM). This membrane facilitates the passage of  $H^+$  from the anode to the solid electrolyte. This membrane prevents the passage of electrons and negative ions from the cathode in the internal circuit, and it also prevents electrons and negative ions from moving in the opposite direction. The membrane must be thin ( $\sim 10\text{--}100\ \mu\text{m}$ ) to allow rapid charge transport at reasonably high current densities and must be unreactive under the potentials present in the cell. The most widely used membranes are polymeric forms of perfluorosulfonic acids. These membranes are quite conductive if fully hydrated. The membrane structure consists of spherical cavities, or inverted micelles  $\sim 4\ \text{nm}$  in diameter, connected by cylindrical channels  $\sim 1\ \text{nm}$  in diameter. The interior of the cavities and channels is lined with  $\text{SO}_3^-$  groups. The  $-\text{CF}_2-$  backbone of the polymer provides rigidity, makes the membrane unreactive, and increases the

PAFC, phosphoric acid fuel cell; MCFC, molten carbonate fuel cell; and SOFC, solid oxide fuel cell. (Legend of components: A, anode; E, electrolyte; PEM proton exchange membrane and C, cathode (YSZ) yttria-stabilized zirconia.)  
 Source: Sundmacher, K. Fuel Cell Engineering: Toward the Design of Efficient Electrochemical Power Plants. *Industrial Engineering Chemical Research* 49 (2010): 10159–10182, fig 4.

### Types of fuel cells



Legend of components:  
 A = anode  
 E = electrolyte  
 C = cathode  
 PEM = proton exchange membrane  
 YSZ = yttria-stabilized zirconia



all fuel cells use  $O_2$  from air and  $H_2$  as fuel,  $H_2$  can be produced in the cell: reforming of hydrocarbons, methanol, or glucose

(19)-7

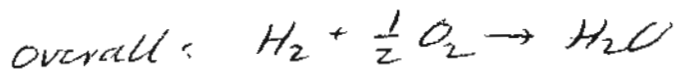
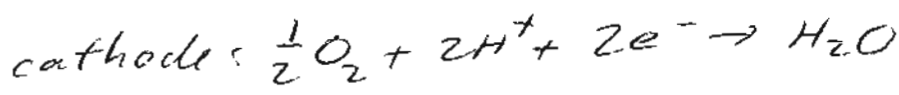
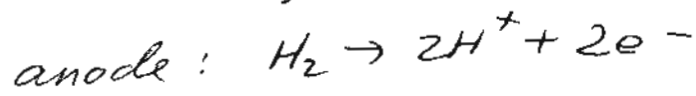
best known Proton Exchange Membrane  
Fuel Cell (PEMFC)

which use  $H_2$  as fuel

First used in NASA Gemini flights in 1960-s

transp. types of fuel cells

Diagram of PEMFC



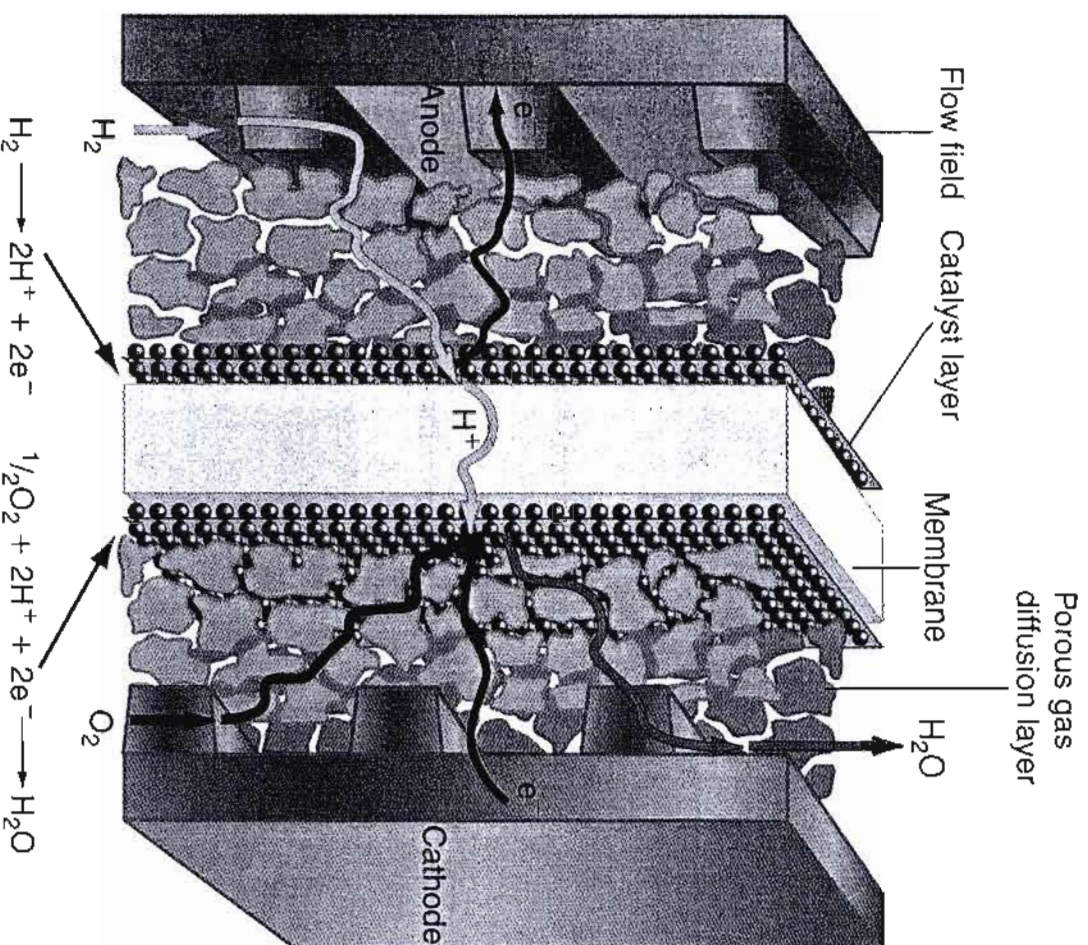
both electrodes have channels to transport  $H_2$  and  $O_2$  to catalyst & membrane

A diffusion layer (porous for gas diffusion) cares for uniform delivery of reactants and for the separation of the produced  $H_2O$  from the gases

A membrane is coated with the catalysts

Pt or Pt alloys

which catalyzes  $H^+$  formation and the reaction of  $O_2$  with  $H^+$

**FIGURE 11.15**

Schematic diagram of a proton exchange membrane fuel cell. The half-cell reactions are shown. The channels in the anode and cathode facilitate the supply of  $H_2$  to the cell and carry away the  $H_2O$  reaction product. The gas diffusion layer ensures that the reactants are uniformly distributed over the membrane surface.

less sensitive to poisoning by CO. However, operation at these temperatures requires proton exchange membranes that use ionic liquids other than water to maintain a high conductivity.

The goals of much current research on fuel cells are to develop inexpensive cata-

most important

(14) - 8

proton exchange membrane as a solid electrolyte allows  $H^+$  to pass from anode to cathode

membrane only 10-100  $\mu m$  thick

it must be unreactive at the cell potential  
mostly used: polymeric forms of

perfluoro sulfonic acids

membranes highly conductive

(high currents)