Chapter 19

Electrochemistry

Part II

Nonstandard States

- The spontaneity of a chemical reaction at a condition other than the standard states (a *nonstandard state* means that concentrations are *NOT* 1 *M*) can be predicted using ***Nernst Equation***.

Since $\Delta G^{o} = -nFE^{o}$ and $\Delta G = -nFE$

then:

$$\Delta G = \Delta G^{o} + RT\ln Q \quad \leftarrow \text{(from Chapter 18)}$$

$$-nFE = -nFE^{o} + RT\ln Q$$

dividing the whole equation by $-nF$; and setting T = 298 K :

$$E = E^{o} - \frac{0.0257\,\text{V}}{n}\ln Q \quad \text{or} \quad E = E^{o} - \frac{0.0592\,\text{V}}{n}\log Q$$

19.5

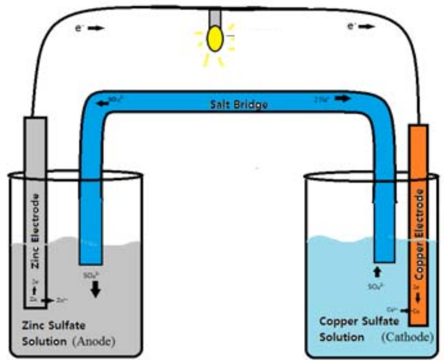
Nonstandard States

$$E = E^{\circ} - \frac{0.0592\,\text{V}}{n}\log Q$$

- Electrons flow spontaneously form the anode to cathode. Product concentration increases and the reactant concentration decreases.

  So as time proceeds *Q* increases and *E* decreases.

  When equilibrium is reached (*Q* = *K*), there is no net flow of electrons (*E* = 0) and we get:



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

$$E^{\circ} = \frac{0.0592\ \text{V}}{n}\log K$$ ← *Section 19.4*

Dr. Al-Saadi 3

19.5

Conditions other than Standard State

- <u>Example:</u>

  Predict whether the following reaction occurs spontaneously at 298 K:

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

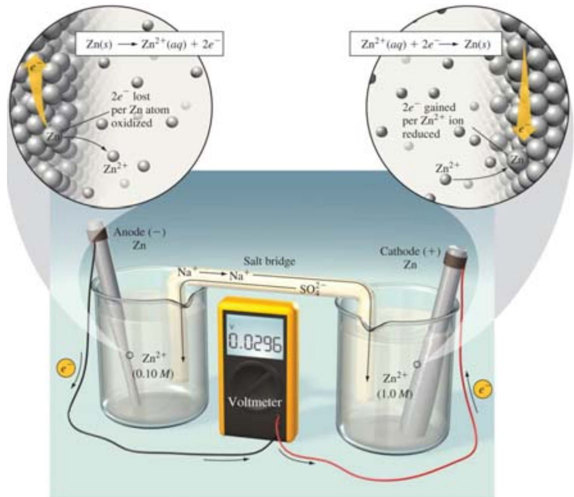
  when $[Fe^{2+}]$ = 0.60 *M* and $[Cd^{2+}]$ = 0.010 *M*.

Dr. Al-Saadi 4

19.5

Concentration Cells

- ***Concentration cells*** are galvanic cells with two half-cells composed of the same material but are different in ion concentrations.
- Concentration cells produces some potential due to the difference in concentrations.



Dr. Al-Saadi

5

19.5

Concentration Cells

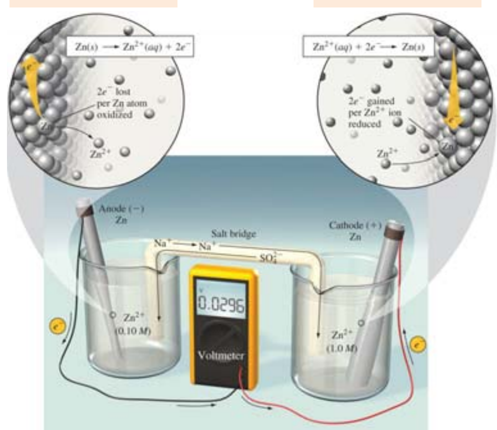
Low concentration

High concentration

- Where does the reduction take place?

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

  According to *Le Châtelier's principle*, the half-cell with a higher concentration of Zn^{2+} ions will undergo reduction. Thus, oxidation takes place in the lower concentration compartment.



$Zn(s) \mid Zn^{2+}(0.10\ M) \parallel Zn^{2+}(1.0\ M) \mid Zn(s)$

Dr. Al-Saadi

6

19.5

Concentration Cells

Oxidation: $Zn(s) \rightarrow Zn^{2+}(aq)\ (0.10\ M) + 2e^-$

Reduction: $Zn^{2+}(aq)\ (1.0\ M) + 2e^- \rightarrow Zn(s)$

Overall: $Zn^{2+}(aq)\ (1.0\ M) \rightarrow Zn^{2+}(aq)\ (0.10\ M)$

- The cell potential is:

$$E = E^\circ - \frac{0.0592\ \text{V}}{n}\log\frac{[Zn^{2+}]_{dilute}}{[Zn^{2+}]_{conc.}}$$

equal to zero

  - E of the concentration cell above is 0.030 V. In general, concentration cells have small potentials.
  - As the process continues, E gradually decreases. When $[Zn^{2+}]_{dilute}$ becomes equal to $[Zn^{2+}]_{conc.}$ then E becomes zero.

Dr. Al-Saadi 7

19.6

Batteries

- A ***battery*** is a galvanic cell, or a series of cells connected, that can convert stored chemical energy into electrical energy and deliver a self-contained source of direct electric current.

Dry cells

Alkaline batteries

Dr. Al-Saadi 8

19.6

Dry Cells and Alkaline Batteries

- They are used in many tools such as flashlight, toys, and other electronic devices.
- No liquids or solutions are contained (*dry*).
- Zn container in contact with MnO_2 and an electrolyte.
- They are called "primary batteries'; which means they are *non*-rechargeable. In other words, the electrochemical process can not be reversed.

Dr. Al-Saadi 9

19.6

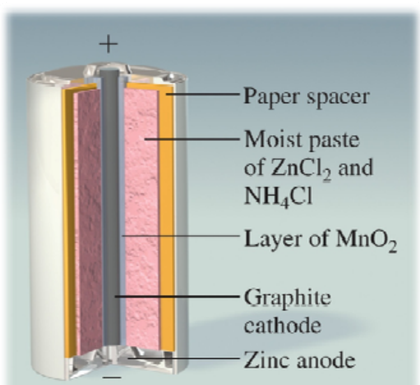
Dry Cells

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

Cathode: $2NH_4^+(aq) + 2MnO_2(s) + 2e^- \longrightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$

Overall: $Zn(s) + 2NH_4^+(aq) + 2MnO_2(s) \longrightarrow Zn^{2+}(aq) + Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$

- Zinc is being oxidized and manganese is being reduced.
- The voltage produced is about 1.5 V.



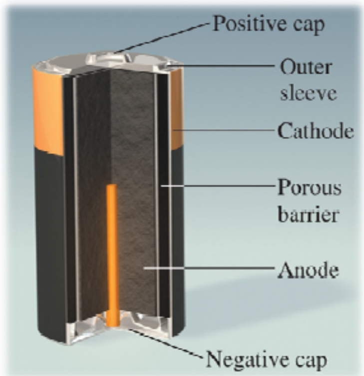
Dr. Al-Saadi 10

19.6

Alkaline Batteries

$$\text{Cathode: } 2MnO_2(s) + 2H_2O(l) + 2e^- \longrightarrow 2MnO(OH)(s) + 2OH^-(aq)$$
$$\text{Anode: } Zn(s) + 2OH^-(aq) \longrightarrow Zn(OH)_2(s) + 2e^-$$
$$\text{Overall: } Zn(s) + 2MnO_2(s) + 2H_2O(l) \longrightarrow Zn(OH)_2(s) + 2MnO(OH)(s) + 2OH^-(aq)$$

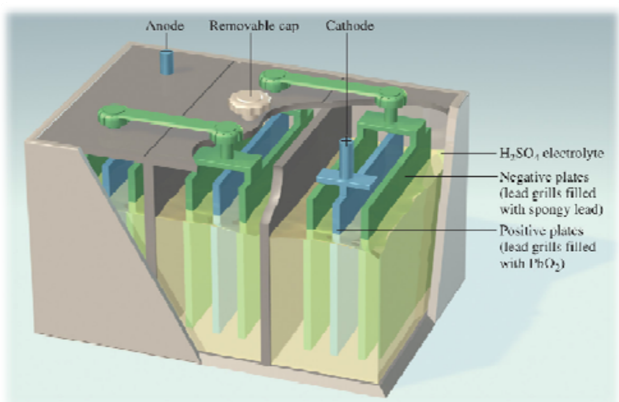
- The reaction takes place in a *basic medium* (*alkaline*).
- Zinc is being oxidized, and manganese is being reduced.
- More superior and more efficient.



Dr. Al-Saadi 11

19.6

Lead Storage Batteries



- This type of batteries is widely used in automobiles. They are used to power the engine ignition circuit, to operate electric devices in the car, and to start the engine.

Dr. Al-Saadi 12

19.6

Lead Storage Batteries

Anode: $Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$

Cathode: $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$

Overall: $Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$

- Consist of six identical cells connected in series.
- Composed of lead (Pb) anode and lead dioxide (PbO_2) cathode, immersed in H_2SO_4 electrolyte solution (38% by mass).
- Each cell delivers ≈ 2 V × 6 cell ≈ 12 V (total).
- It is rechargeable by reversing the electrochemical reactions by applying an external voltage (jump start). Known as *electrolysis*.

19.6

Lithium-Ion Batteries

- They are used in electronic and mobile devices like cell phones, digital cameras, mp3 players, laptops, etc.
- The main component is lithium (Li) which is the lightest metal (making the battery too light) and has the strongest negative reduction potential among metals (making it a powerful reducing agent).

Anode: $Li(s) \longrightarrow Li^+ + e^-$

Cathode: $Li^+ + CoO_2 + e^- \longrightarrow LiCoO_2(s)$

Overall: $Li(s) + CoO_2 \longrightarrow LiCoO_2(s)$

Lithium-ion batteries have an overall potential of 3.4 V (larger than normal batteries).
They can be recharged hundreds of time without losing much of its efficiency.

19.6

Fuel Cells

- Combustion reactions are redox reactions.

  $CH_4\ (g) + O_2\ (g) \rightarrow CO_2\ (g) + H_2O\ (g)$ + energy

  However, they don't efficiently provide electric energy.
- The above redox reaction can be accomplished by using efficient, clean so-called ***fuel cells***.

$$\begin{array}{ll} \textit{Anode:} & 2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^- \\ \textit{Cathode:} & O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq) \\ \hline \textit{Overall:} & 2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \end{array}$$

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{cathode} - E^\circ_{anode} \\ &= 0.40\ V - (-0.83\ V) \\ &= 1.23\ V \end{aligned}$$

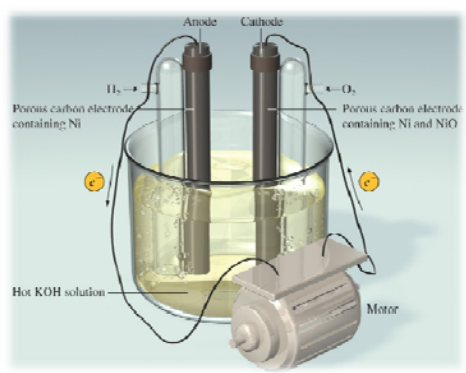
The reaction in a fuel cell is spontaneous under standard conditions.

Dr. Al-Saadi 15

19.6

Fuel Cells

- A **fuel cell** is an electrochemical cell that converts a source fuel into an electric current. It generates electricity inside a cell through reactions between a fuel and an oxidant
- Fuel cell don't store chemical energy like other batteries. Reactants must be constantly supplied to produce energy continuously.
- Fuel cells are clean, noise free, and environmentally friendly compared to other cells.

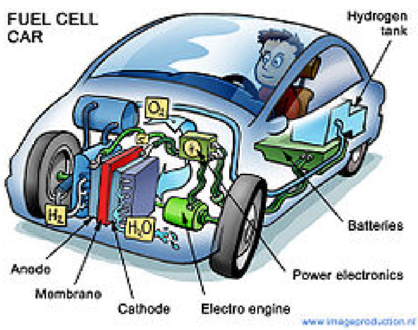


$$\begin{array}{ll} \textit{Anode:} & 2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^- \\ \textit{Cathode:} & O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq) \\ \hline \textit{Overall:} & 2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \end{array}$$

Dr. Al-Saadi 16

19.6

Fuel Cells



Dr. Al-Saadi 17

19.7

Electrolysis

- ***Electrolysis*** is the process that uses electric energy to force a nonspontaneous chemical reaction to take place.

  One main application of electrolysis is to recharge some batteries by reversing the ordinary chemical process.
- An ***electrolytic cell*** is the cell used to carry out electrolysis.

Cell Type	Chemical reaction	Electric energy
Galvanic	Spontaneous	Produced
Electrolytic	Nonspontaneous	consumed

Dr. Al-Saadi 18

19.7

Electrolysis

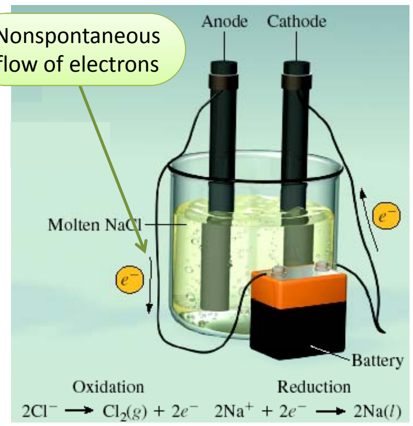
- *Electrolysis of molten NaCl.*

  This process can be used to produce sodium metal and chlorine gas from NaCl (m.p. = 800°C).

  Molten NaCl is used as medium that allows the flow of electrons.

  However, the E°_{cell} for this process is – 4 V. The battery serves to push the electrons in the direction they would not flow spontaneously.

Nonspontaneous flow of electrons



Anode (oxidation):	$2Cl^-(l) \longrightarrow Cl_2(g) + 2e^-$	E° = +1.36 V
Cathode (reduction):	$2Na^+(l) + 2e^- \longrightarrow 2Na(l)$	E° = - 2.71
Overall:	$2Na^+(l) + 2Cl^-(l) \longrightarrow 2Na(l) + Cl_2(g)$	E°_{cell} = - 4.07 V

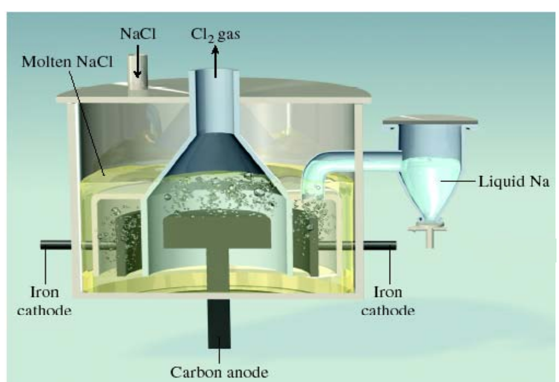
Dr. Al-Saadi 19

19.7

Electrolysis

- *Downs cell.*

  It is used for large-scale electrolysis of NaCl.



Anode (oxidation):	$2Cl^-(l) \longrightarrow Cl_2(g) + 2e^-$
Cathode (reduction):	$2Na^+(l) + 2e^- \longrightarrow 2Na(l)$
Overall:	$2Na^+(l) + 2Cl^-(l) \longrightarrow 2Na(l) + Cl_2(g)$

Dr. Al-Saadi 20

19.7

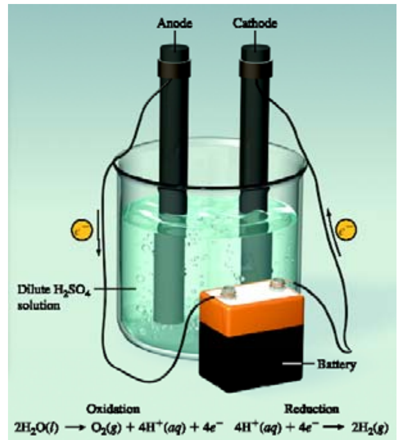
Electrolysis

- *Electrolysis of water.*

  At normal conditions, water will not spontaneously decompose into hydrogen and oxygen gases.

$H_2O(l) \rightarrow H_2(g) + O_2(g)$ $\Delta G° = 474.4$ kJ/mol

Very highly nonspontaneous



Anode: $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$

Cathode: $4H^+(aq) + 4e^- \longrightarrow 2H_2(g)$

Overall: $2H_2O(l) \longrightarrow O_2(g) + 2H_2(g)$

Dr. Al-Saadi 21

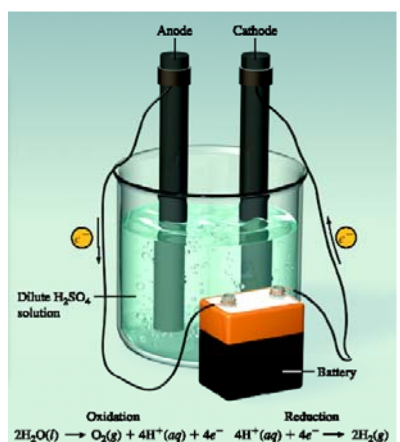
19.7

Electrolysis

- *Electrolysis of water.*

  Pure water does not have sufficient ions, so 0.1 *M* H_2SO_4 solution is used to conduct electric current and establish the circuit.

  There is no net consumption of H_2SO_4 in the over all reaction.



Anode: $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$

Cathode: $4H^+(aq) + 4e^- \longrightarrow 2H_2(g)$

Overall: $2H_2O(l) \longrightarrow O_2(g) + 2H_2(g)$

Dr. Al-Saadi 22

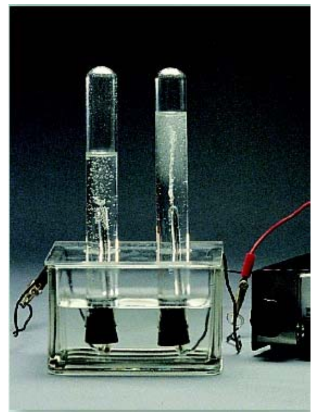
19.7

Electrolysis

- *Electrolysis of water.*

  Pure water does not have sufficient ions, so 0.1 *M* H_2SO_4 solution is used to conduct electric current and establish the circuit.

  There is no net consumption of H_2SO_4 in the over all reaction.



Anode: $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$

Cathode: $4H^+(aq) + 4e^- \longrightarrow 2H_2(g)$

Overall: $2H_2O(l) \longrightarrow O_2(g) + 2H_2(g)$

Dr. Al-Saadi 23

19.7

Quantitative Applications of Electrolysis

- The amount (mass) of products formed during an electrolysis process can be calculated by measuring the *current* (in amperes) that passes through an electrolytic cell in a given period of *time*.

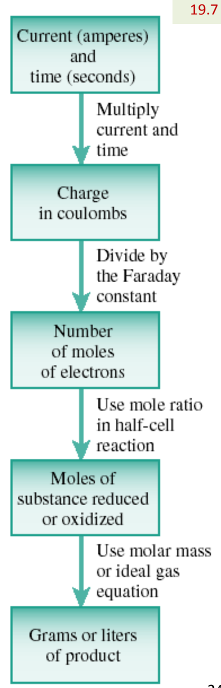
  Then:

  1 C = 1 Amp × 1 s

  and:

  96500 C = 1 mol e-

  Thus, from electrochemical equations, the number of moles (and hence the mass) of products can be calculated.



Dr. Al-Saadi 24

19.7

Quantitative Applications of Electrolysis

- Example:

  A constant current of 0.912 A is passed through an electrolytic cell containing molten $MgCl_2$ for 18 h. What mass of solid Mg is produced?

Cathode (reduction)	$Mg^{2+} + 2e^- \rightarrow Mg\ (s)$	$E^\circ = -2.37$ V
Anode (oxidation)	$2Cl^- \rightarrow 2e^- + Cl_2\ (g)$	$E^\circ = -1.36$ V
Overall	$Mg^{2+} + 2Cl^- \rightarrow Mg\ (s) + Cl_2\ (g)$	$E^\circ_{cell} = -3.73$ V

The quantities of magnesium metal and chlorine gas depends on the number of e^-'s that pass through the electrolytic cell.

19.7

Quantitative Applications of Electrolysis

- Example (*continue*):

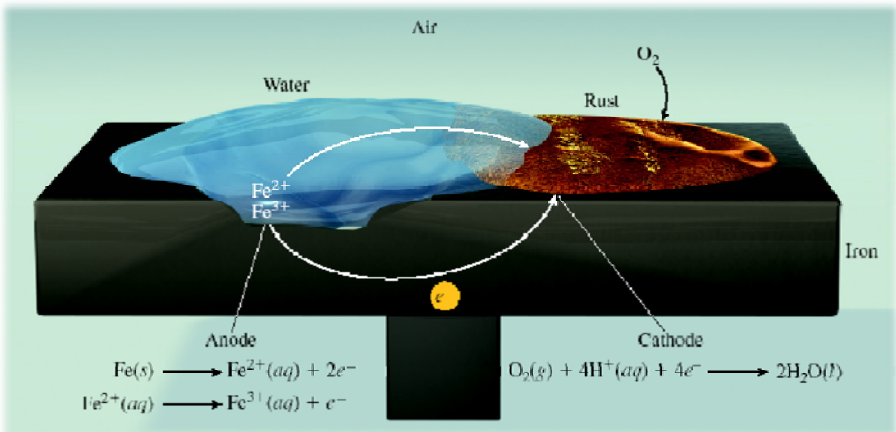
  A constant current of 0.912 A is passed through an electrolytic cell containing molten $MgCl_2$ for 18 h. What mass of Mg is produced?

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

19.8

Corrosion

- Corrosion is formation of rust (Fe_2O_3) , and it is an electrochemical process.



Dr. Al-Saadi

27