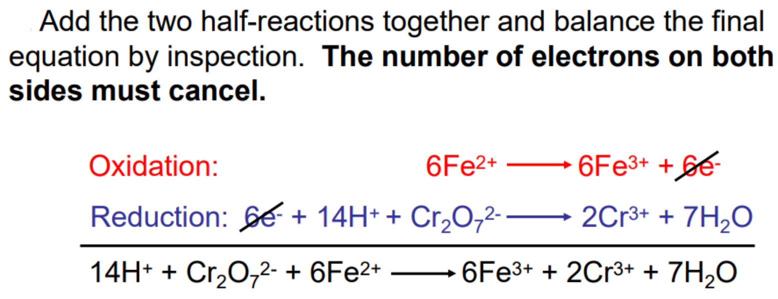
8.氧化还原化学Oxidation-Reduction Chemistry

- 分配氧化值Assigning Oxidation Numbers
    - 1. Elements = 0
    - 2. 单原子分子Monatomic ion = charge
    - 3. F: –1
    - 4. O: –2 (unless 过氧化物peroxide = –1)
    - 5. H: +1 (unless a 金属氢化物metal hydride = –1)
    - 6. 氧化值的和等于总电荷The sum of the oxidation numbers equals the overall charge (0 in a compound).
- 氧化值Oxidation Numbers
    - 为了记录什么得到了电子，什么失去了电子，我们给氧化值赋值To keep track of what loses electrons and what gains them, we assign oxidation numbers.
    - 如果一种元素的氧化数增加，则该元素被氧化If the oxidation number increases for an element, that element is oxidized.
    - 如果一种元素的氧化值降低，则该元素被还原If the oxidation number decreases for an element, that element is reduced.
- Half-Reactions
    - 氧化和还原分别书写和平衡The oxidation and reduction are written and balanced separately.
    - 我们将用它们来平衡氧化还原反应We will use them to balance a redox reaction.
    - For example, when Sn2+ and Fe3+ react

        $$\begin{aligned} \textit{Oxidation:} \quad & \mathrm{Sn^{2+}}(aq) \longrightarrow \mathrm{Sn^{4+}}(aq) + 2\mathrm{e^-} \\ \textit{Reduction:} \quad & 2\,\mathrm{Fe^{3+}}(aq) + 2\mathrm{e^-} \longrightarrow 2\,\mathrm{Fe^{2+}}(aq) \end{aligned}$$

    - 对于两个半反应，两侧的电子数应该是一样的

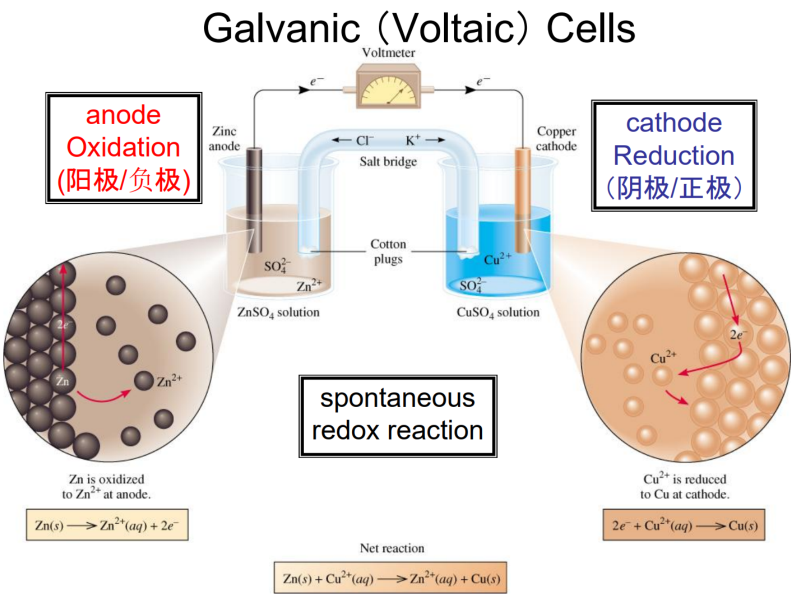
        

        Add the two half-reactions together and balance the final equation by inspection. **The number of electrons on both sides must cancel.**

        Oxidation: $6Fe^{2+} \longrightarrow 6Fe^{3+} + \cancel{6e^-}$

        Reduction: $\cancel{6e^-} + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$

        $14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$
- 原电池Voltaic Cells
    -



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

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

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

- 电动势Electromotive Force (emf)
    - 电池阳极和阴极之间的电位差称为电动势The potential difference between the anode and cathode in a cell is called the electromotive force (emf).
    - It is also called the cell potential and is designated E cell.
    - 它的单位是伏特(V), 一伏特等于一焦耳每库仑(1v = 1J /C)It is measured in volts (V). One volt is one joule per coulomb (1 V = 1 J/C).
- 标准还原电势Standard Reduction Potentials
    - 许多电极的还原电位已被测量并制成表格Reduction potentials for many electrodes have been measured and tabulated.
    - 将这些值与作为标准的氢的还原量进行比较The values are compared to the reduction of hydrogen as a standard.
    -

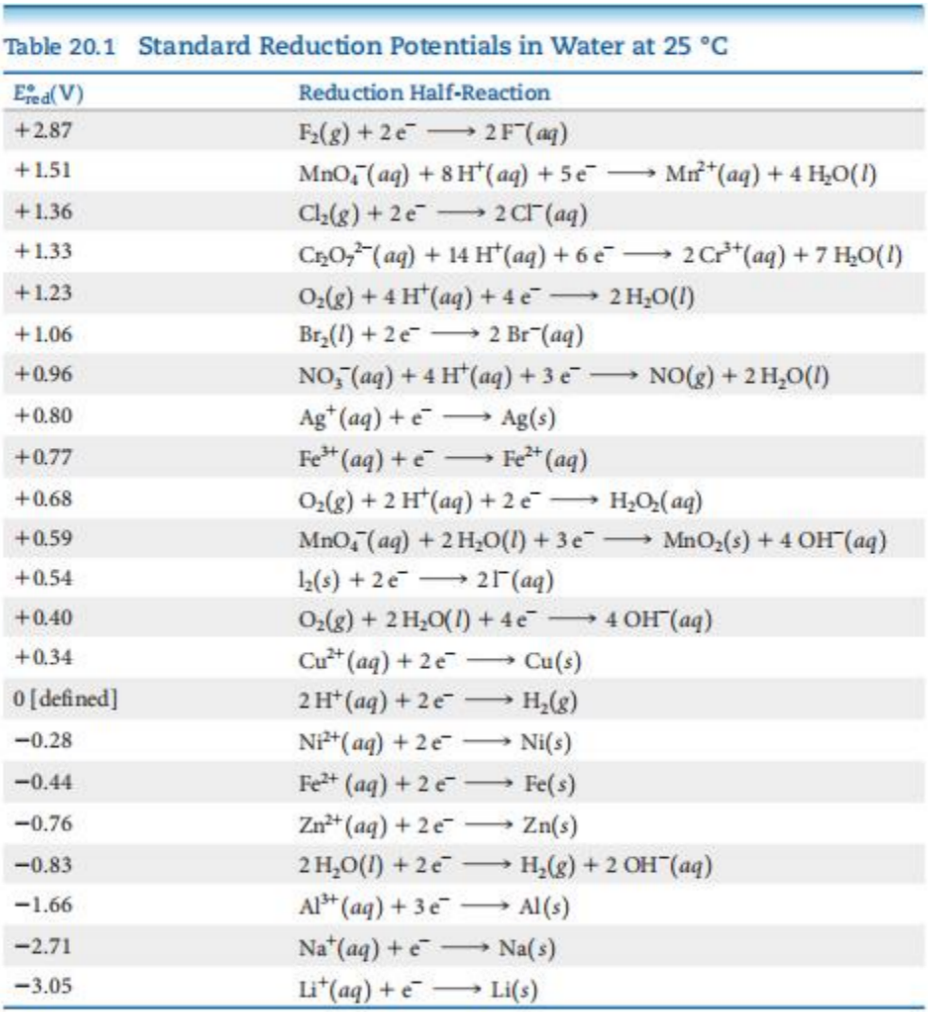
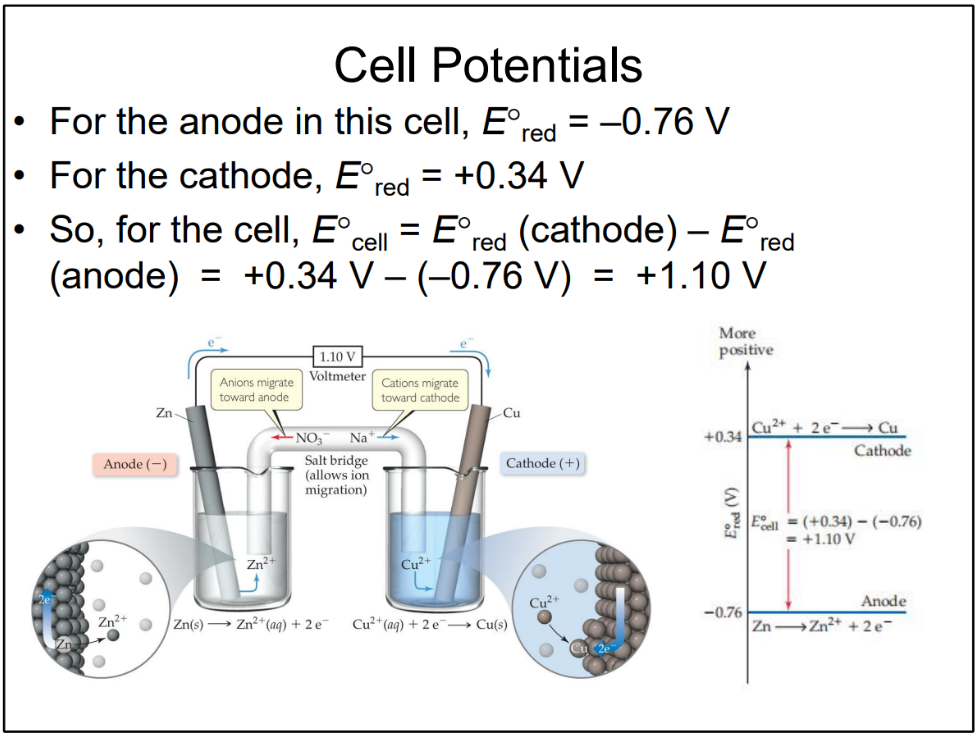


Table 20.1 Standard Reduction Potentials in Water at 25 °C

E°_{red}(V)	Reduction Half-Reaction
+2.87	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$
+1.51	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$
+1.36	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$
+1.33	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
+1.23	$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$
+1.06	$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$
+0.96	$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$
+0.54	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$
+0.40	$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
0 [defined]	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$
−0.28	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$
−0.44	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$
−0.76	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$
−0.83	$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
−1.66	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$
−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

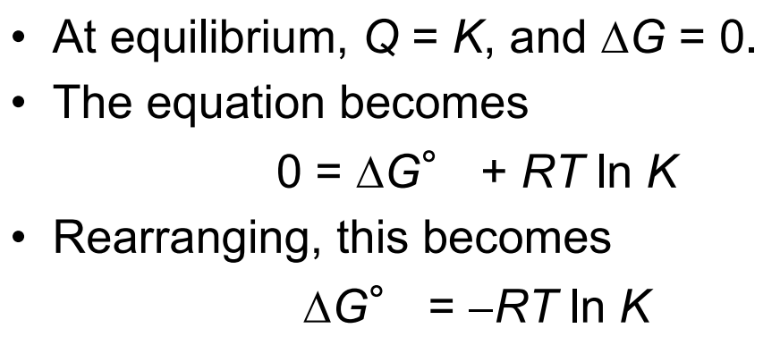
- Standard Hydrogen Electrode
  - By definition as the standard, the reduction potential for hydrogen is 0 V
  - 2 H+(aq, 1M) + 2e-→H2(g, 1 atm)
- 标准电池电势Standard Cell Potentials
  - 电池电势=负极电势-正极电势 E°cell = E°red(cathode) – E°red(anode)
  -



Cell Potentials

- For the anode in this cell, E°_{red} = –0.76 V
- For the cathode, E°_{red} = +0.34 V
- So, for the cell, $E^\circ_{cell} = E^\circ_{red}$ (cathode) – E°_{red} (anode) = +0.34 V – (–0.76 V) = +1.10 V

- 氧化剂和还原剂Oxidizing and Reducing Agents
  - 在标准条件下，E°red值越正，还原趋势越大The more positive the value of E°red, the greater the tendency for reduction under standard conditions.
  - 最强的氧化剂具有最大的正还原电位The strongest oxidizers have the most positive reduction potentials.
  - 最强的还原剂具有最大的负还原电位The strongest reducers have the most negative reduction potentials.
- 自由能和氧化还原Free Energy and Redox
  - 自发氧化还原反应产生正的电池电位或电动势Spontaneous redox reactions produce a positive cell potential, or emf.
  - E° = E°red(reduction) – E°red(oxidation)
  - 注意，这不仅适用于原电池，而且适用于所有氧化还原反应Note that this is true for ALL redox reactions, not only for voltaic cells
  - 由于吉布斯自由能是自发性的度量，正电动势对应于负ΔG Since Gibbs free energy is the measure of spontaneity, positive emf corresponds to negative ΔG
  - ΔG = –nFE (F is the 法拉第常数Faraday constant, 96485 C/mol.)
- 自由能和平衡常数Free Energy and the Equilibrium Constant
  - 在任何标准或非标准条件下，自由能的变化都可以用这种方法求得Under any conditions, standard or nonstandard, the free energy change can be found this way
  - 范特霍夫等温公式
    - ΔG = ΔG° + RT ln Q
      - ΔG°是同一温度、标准压强下的吉布斯自由能
      - R是气体常数

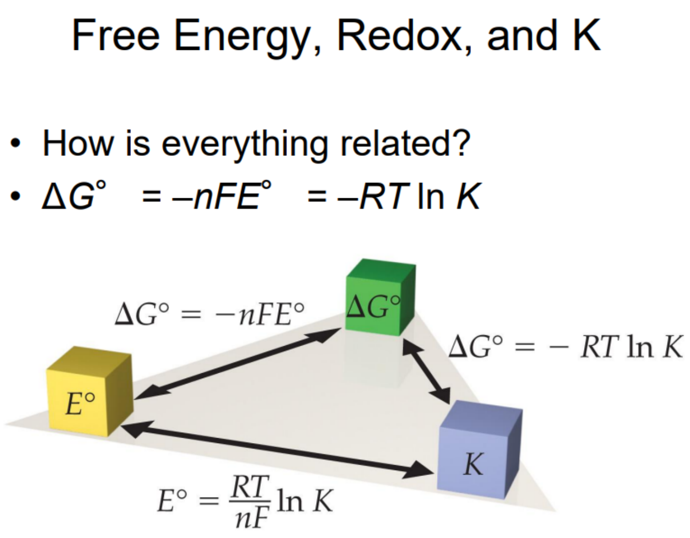
      - T是温度
    - 吉布斯自由能随温度和压强变化很大，次公式可求出非标准状况下的吉布斯自由能
    - 温度的变化在ΔG0的使用上表现出来，不同的温度使用不同的ΔG0
    - 非标准状况的ΔG0需要通过定义式(即吉布斯等温公式$\Delta G=\Delta H - T\Delta S$)计算
    - 压强或浓度的变化在Q的表达上表现出来
  - 在标准条件下，浓度为1M，所以$Q = 1$, $\ln Q = 0$最后一项去掉Under standard conditions, concentrations are 1 M ,so $Q = 1$ and $\ln Q = 0$; the last term drops out
- 自由能与平衡Free Energy and Equilibrium
  - 

    - At equilibrium, $Q = K$, and $\Delta G = 0$.
    - The equation becomes

    $$0 = \Delta G^\circ + RT \ln K$$

    - Rearranging, this becomes

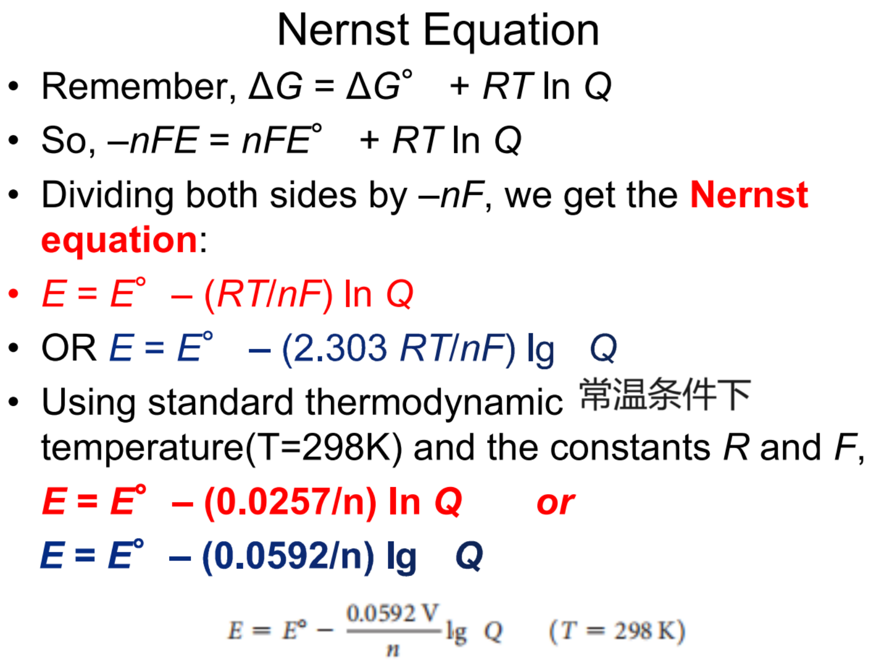
    $$\Delta G^\circ = -RT \ln K$$

- 

  Free Energy, Redox, and K

  - How is everything related?
  - $\Delta G^\circ = -nFE^\circ = -RT \ln K$

- 能斯特方程Nernst Equation
  - n是转移电子的数量



Nernst Equation

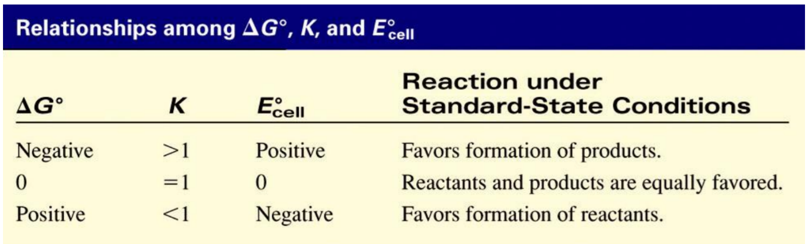
- Remember, $\Delta G = \Delta G^\circ + RT \ln Q$
- So, $-nFE = nFE^\circ + RT \ln Q$
- Dividing both sides by $-nF$, we get the **Nernst equation**:
- $E = E^\circ - (RT/nF) \ln Q$
- OR $E = E^\circ - (2.303\ RT/nF) \lg Q$
- Using standard thermodynamic 常温条件下 temperature(T=298K) and the constants R and F,

  $E = E^\circ - (0.0257/n) \ln Q$ ***or***

  $E = E^\circ - (0.0592/n) \lg Q$

$$E = E^\circ - \frac{0.0592\text{ V}}{n} \lg Q \qquad (T = 298\text{ K})$$

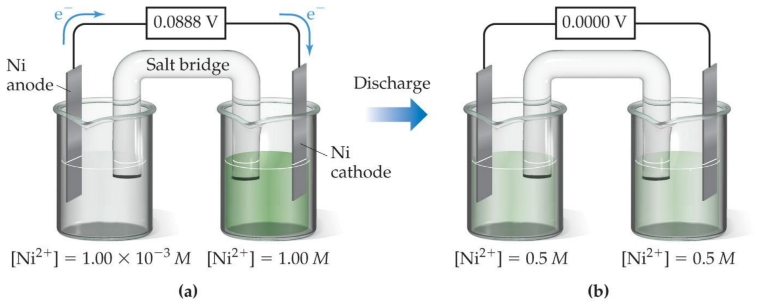
- 氧化还原反应的自发性Spontaneity of Redox Reactions
  -



Relationships among ΔG°, K, and E°_{cell}

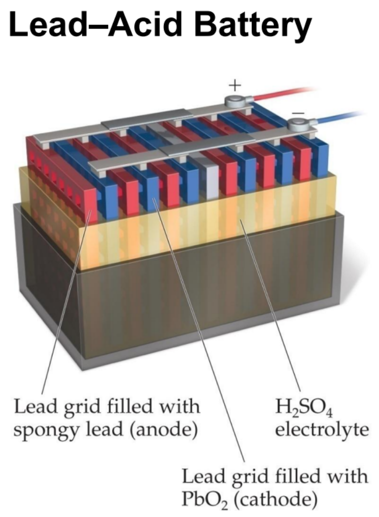
ΔG°	K	E°_{cell}	Reaction under Standard-State Conditions
Negative	>1	Positive	Favors formation of products.
0	=1	0	Reactants and products are equally favored.
Positive	<1	Negative	Favors formation of reactants.

- 浓差电池Concentration Cells
  -

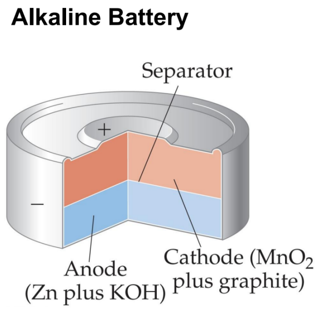


  - 注意，能斯特方程表明，一个电池可以在两个电极上有相同的物质，称为浓度电池Notice that the Nernst equation implies that a cell could be created that has the same substance at both electrodes, called a concentration cell.
  - 对于这样的电池，E°cell为0，但Q不为0 For such a cell, E°cell would be 0, but Q would not
  - 因此，只要浓度不同，E就不会为0 Therefore, as long as the concentrations are different, E will not be 0
- 电化学的一些应用Some Applications of Electrochemistry
  - 电池Batteries
  - 防腐蚀Prevention of corrosion

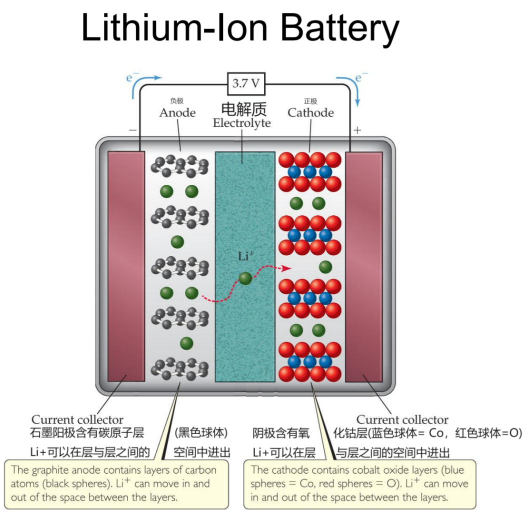
  - 电解Electrolysis
- 电池的一些例子Some Examples of Batteries
  - 铅酸蓄电池:反应物和生成物均为固体，故Q为1，电势与浓度无关;然而，用铅和硫酸制成(有害)Lead–acid battery: reactants and products are solids, so Q is 1 and the potential is independent of concentrations; however, made with lead and sulfuric acid (hazards).



  - 碱性电池:最常见的原电池Alkaline battery: most common primary battery.



  - 镍镉电池和镍氢电池:重量轻，可充电;镉是有毒且重的，所以氢化物正在取代它Ni–Cd and Ni–metal hydride batteries: light weight, rechargeable; Cd is toxic and heavy, so hydrides are replacing it.
  - 锂离子电池:可充电、轻便;产生比镍基电池更高的电压Lithium-ion batteries: rechargeable, light; produce more voltage than Ni-based batteries.

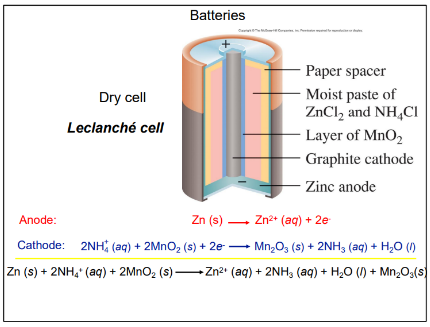


石墨阳极含有碳原子层(黑色球体) Li+可以在层与层之间的空间中进出

The graphite anode contains layers of carbon atoms (black spheres). Li^+ can move in and out of the space between the layers.

阴极含有氧化钴层(蓝色球体= Co，红色球体=O) Li+可以在层与层之间的空间中进出

The cathode contains cobalt oxide layers (blue spheres = Co, red spheres = O). Li^+ can move in and out of the space between the layers.


Batteries

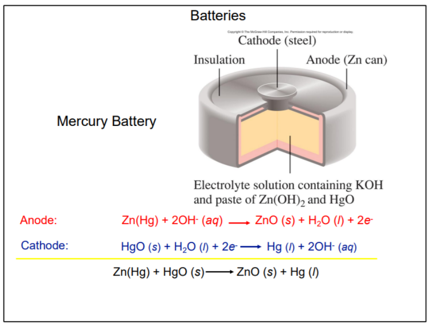
Dry cell

Leclanché cell

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

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

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

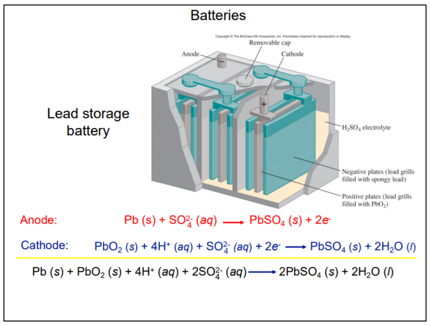

Batteries

Mercury Battery

Anode: $Zn(Hg) + 2OH^-\ (aq) \longrightarrow ZnO\ (s) + H_2O\ (l) + 2e^-$

Cathode: $HgO\ (s) + H_2O\ (l) + 2e^- \longrightarrow Hg\ (l) + 2OH^-\ (aq)$

$Zn(Hg) + HgO\ (s) \longrightarrow ZnO\ (s) + Hg\ (l)$

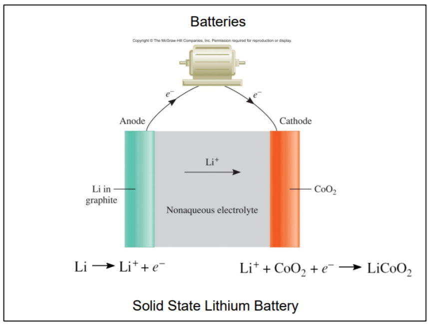

Batteries

Lead storage battery

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

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

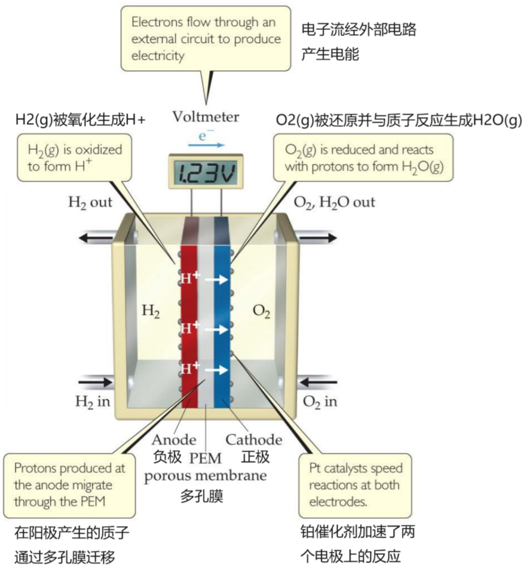
$Pb\ (s) + PbO_2\ (s) + 4H^+\ (aq) + 2SO_4^{2-}\ (aq) \longrightarrow 2PbSO_4\ (s) + 2H_2O\ (l)$


Batteries

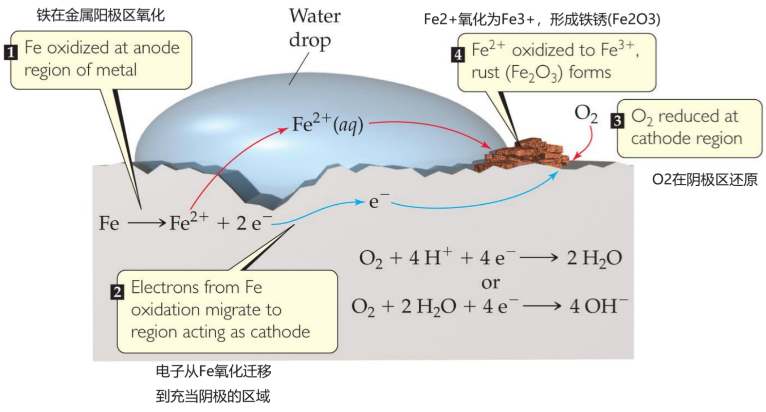
$Li \longrightarrow Li^+ + e^-$ $Li^+ + CoO_2 + e^- \longrightarrow LiCoO_2$

Solid State Lithium Battery

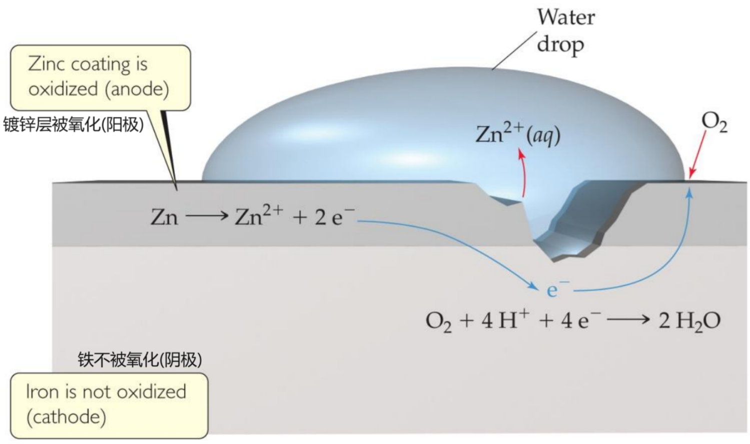
- 燃料电池Fuel Cells
  - 当燃料燃烧时，产生的能量可以转化为电能When a fuel is burned, the energy created can be converted to electrical energy.
  - 通常，这种转换的效率只有40%，其余的都以热量的形式散失了Usually, this conversion is only 40% efficient, with the remainder lost as heat.
  - 将化学能直接转化为电能的效率有望提高，这是燃料电池的基础The direct conversion of chemical to electrical energy is expected to be more efficient and is the basis for fuel cells.
  - 燃料电池不是电池;能源必须持续不断地供应Fuel cells are NOT batteries; the source of energy must be continuously provided.
  - 氢燃料电池Hydrogen Fuel Cells
    - 在这个电池里，氢和氧形成水In this cell, hydrogen and oxygen form water.
    - 这种电池的效率是燃烧电池的两倍The cells are twice as efficient as combustion.
    - 电池使用氢气和空气中的氧气作为燃料The cells use hydrogen gas as the fuel and oxygen from the air.
    -



- 腐蚀Corrosion
  - 腐蚀是氧化Corrosion is oxidation
  - 它的俗名是生锈Its common name is rusting.
  -



  - 防腐蚀Preventing Corrosion
    - 用一种更容易氧化的金属涂在铁上防止腐蚀Corrosion is prevented by coating iron with a metal that is more readily oxidized.
    - 当锌更容易被氧化时，阴极保护就会发生，因此牺牲金属来防止铁生锈Cathodic protection occurs when zinc is more easily oxidized, so that metal is sacrificed to keep the iron from rusting.
    -



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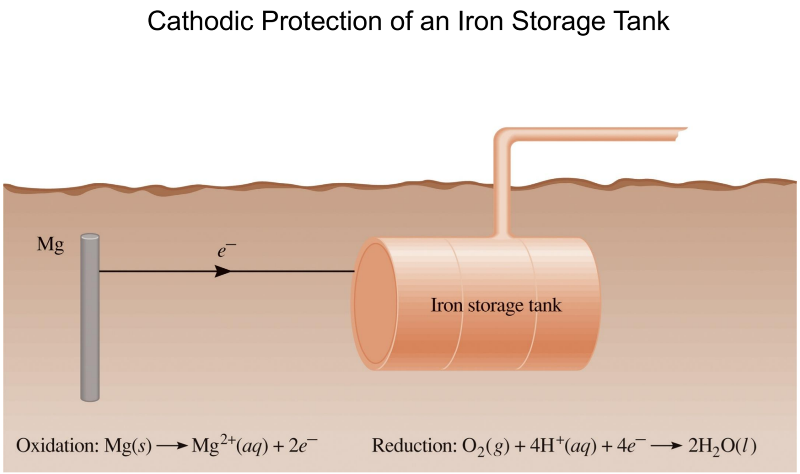
Cathodic Protection of an Iron Storage Tank

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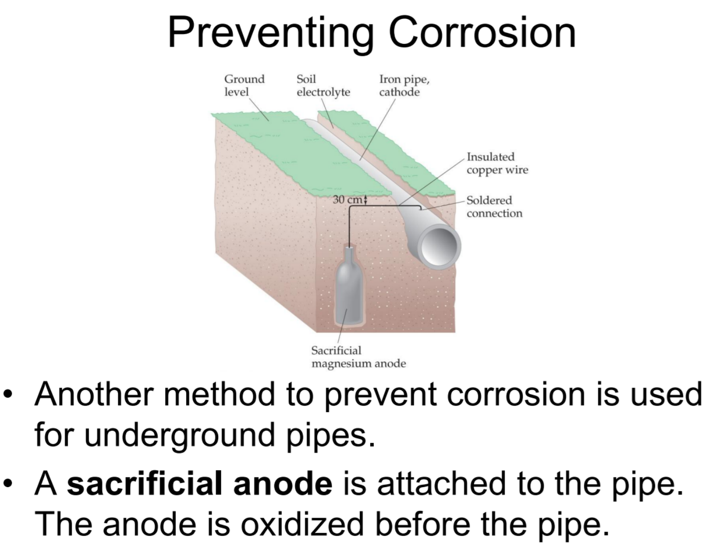
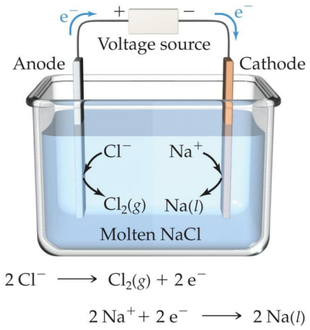
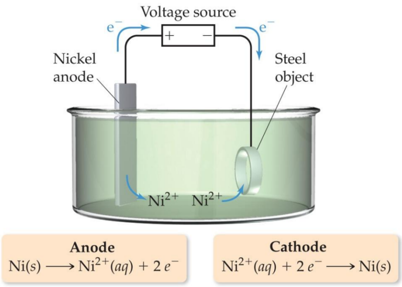
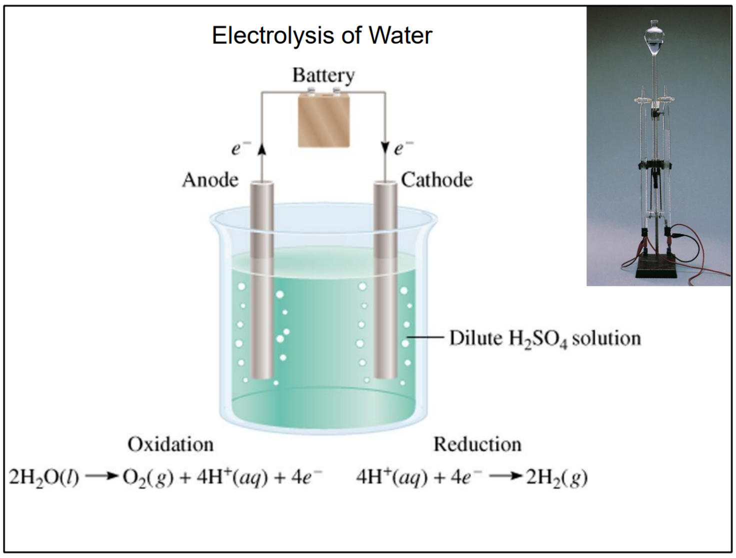

Preventing Corrosion

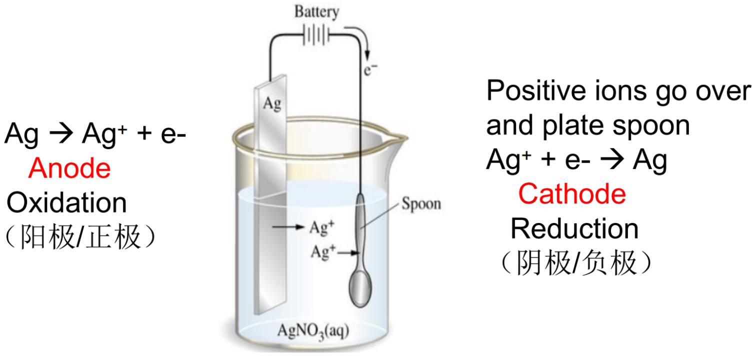
- Another method to prevent corrosion is used for underground pipes.
- A **sacrificial anode** is attached to the pipe. The anode is oxidized before the pipe.

- 电解Electrolysis
  - 在电化学中，如果外界的电驱动反应，就会发生非自发反应Nonspontaneous reactions can occur in electrochemistry IF outside electricity is used to drive the reaction.
  - 利用电能产生化学反应称为电解Use of electrical energy to create chemical reactions is called electrolysis.
  -





- 

- 电镀Electroplating
  - 把金属电镀在表面上，要镀上金属的材料是阴极，阳极是由用于电镀的金属制成的To electroplate metals onto a surface. The material to be plated with a metal is the cathode. The anode is made of the metal used for the plating
  - 

- 氧化还原滴定Oxidation-Reduction (Redox) Titrations
  - 基于分析物和滴定剂之间的氧化还原反应Based on an oxidation-reduction reaction between analyte and titrant
  - 对于氧化还原滴定，监测滴定反应的电位而不是一种物质的浓度是方便的For a redox titration it is convenient to monitor the titration reaction’s potential instead of the concentration of one species.
  - 能斯特方程将溶液的电位与参与氧化还原反应的反应物和生成物的浓度联系起来Nernst equation relates a solution’s potential to the concentrations of reactants and products that

participate in the redox reaction.

- 滴定平衡
  - 每次加入滴定剂后，被滴定剂和滴定剂之间的反应达到平衡状态After each addition of titrant the reaction between the titrand(被滴定剂) and the titrant(滴定剂) reaches a state of equilibrium.
  - $$E_{B_{ox}/B_{red}} = E_{A_{ox}/A_{red}} = E_{\text{system}}$$
  - 这是一个重要的观察结果，因为它允许我们使用半反应来监测滴定过程This is an important observation as it allows us to use either half-reaction to monitor the titration's progress.
- 滴定平衡前Before the equivalence point
  - 滴定混合物由已知数量的被滴定剂的氧化和还原形式组成The titration mixture consists of appreciable quantities of the titrand’s oxidized and reduced forms.
  - 然而，未反应滴定剂的浓度非常小The concentration of unreacted titrant, however, is very small.
  - 电位是根据被滴定剂的半反应来计算的The potential is calculated as the titrand’s half-reaction
  - $$E_{\text{system}} = E^{\circ}_{A_{ox}/A_{red}} - \frac{RT}{nF}\ln\frac{[A_{red}]}{[A_{ox}]}$$
- 滴定平衡后After the equivalence point
  - 用能斯特方程计算滴定剂半反应的势是比较容易的It is easier to calculate the potential using the Nernst equation for the titrant’s half-reaction
  - $$E_{\text{system}} = E^{\circ}_{B_{ox}/B_{red}} - \frac{RT}{nF}\ln\frac{[B_{red}]}{[B_{ox}]}$$
- 滴定平衡时At the equivalence point

Calculating the Titration Curve

Calculate the titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+} in a matrix of 1 M $HClO_4$.

At the equivalence point, the potential, E_{eq}, are identical.

$$E_{eq} = E^{o}_{Fe^{3+}/Fe^{2+}} - 0.0592 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$E_{eq} = E^{o}_{Ce^{4+}/Ce^{3+}} - 0.0592 \log \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

$$2E_{eq} = E^{o}_{Fe^{3+}/Fe^{2+}} + E^{o}_{Ce^{4+}/Ce^{3+}} - 0.0592 \log \frac{[Fe^{2+}][Ce^{3+}]}{[Fe^{3+}][Ce^{4+}]}$$

Because $[Fe^{2+}] = [Ce^{4+}]$ and $[Ce^{3+}] = [Fe^{3+}]$ at the equivalence point, the log term has a value of zero and the equivalence point's potential is:

$$E_{eq} = \frac{E^{o}_{Fe^{3+}/Fe^{2+}} + E^{o}_{Ce^{4+}/Ce^{3+}}}{2} = \frac{0.767\ \text{V} + 1.70\ \text{V}}{2} = 1.23\ \text{V}$$