Chapter 18

Introduction to Electrochemistry

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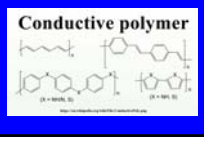
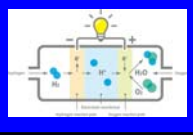
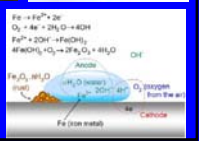
Electrochemistry

The study of chemical reactions that involve electron or charge transfer (e.g., ions).



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Redox Processes - electron transfer

- oxidation -
  - loss of electrons
  - oxidation number increases

$$Ag \rightarrow Ag^{+} + e^{-}$$

- reduction -
  - gain in electrons
  - decrease in oxidation number

$$Fe^{2+} + 2e^{-} \rightarrow Fe$$

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Redox Reactions

Both oxidation and reduction MUST occur in the reaction and the number of electrons exchanged MUST be balanced

Consider silver plating a copper penny

$$Cu + 2\,Ag^{+} \rightarrow Cu^{2+} + 2\,Ag$$

What is being oxidized? $Cu \rightarrow Cu^{2+} + 2e^{-}$

What is being reduced? $Ag^{+} + e^{-} \rightarrow Ag$ x 2

MUST balance number of electrons exchanged

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Balancing Redox Equations

half-reaction technique

$$Sn^{2+} + Fe^{3+} \Leftrightarrow Sn^{4+} + Fe^{2+}$$

$$Fe^{2+} + MnO_4^{-} \Leftrightarrow Fe^{3+} + Mn^{2+}$$

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$$Sn^{2+} + Fe^{3+} \Leftrightarrow Sn^{4+} + Fe^{2+}$$

$$Sn^{2+} \Leftrightarrow Sn^{4+} + 2\,e^{-}$$
$$e^{-} + Fe^{3+} \Leftrightarrow Fe^{2+}$$
$$2(e^{-} + Fe^{3+} \Leftrightarrow Fe^{2+})$$

$$Sn^{2+} + 2\,Fe^{3+} \Leftrightarrow Sn^{4+} + 2\,Fe^{2+}$$

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$Fe^{2+} + MnO_4^- \Leftrightarrow Fe^{3+} + Mn^{2+}$

$MnO_4^- + ? e^- \Leftrightarrow Mn^{2+}$

$-1 = 1(x)_{Mn} + 4(-2)_O$ $\quad +2$

$x = +8 - 1 = +7$

$MnO_4^- + ? e^- \Leftrightarrow Mn^{2+}$

$+7 \quad +2$

$MnO_4^- + 5 e^- \Leftrightarrow Mn^{2+}$

$MnO_4^- + 5 e^- \Leftrightarrow Mn^{+2} + 4H_2O$

$MnO_4^- + 8 H^+ + 5 e^- \Leftrightarrow Mn^{2+} + 4H_2O$

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$Fe^{2+} + MnO_4^- \Leftrightarrow Fe^{3+} + Mn^{2+}$

$MnO_4^- + 8 H^+ + 5 e^- \Leftrightarrow Mn^{2+} + 4H_2O$

$Fe^{2+} \Leftrightarrow Fe^{3+} + e^-$

$5(Fe^{2+} \Leftrightarrow Fe^{3+} + e^-)$

$5Fe^{2+} + MnO_4^- + 8H^+ \Leftrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

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Energy Conversions with Cells

galvanic cell

Chemical potential energy ⇄ Electrical potential energy

electrolytic cell

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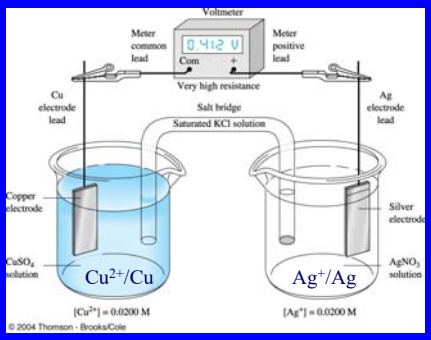
Galvanic Cell (I)



$$2Ag^+ + Cu \rightleftharpoons 2Ag + Cu^{2+}$$

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Galvanic Cell (II)

$$Cu^{2+} + Zn \rightleftharpoons Cu + Zn^{2+}$$

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Electrochemical Cells

- A complete cell contains:
  - Conducting electrodes (metal, carbon)
  - completed circuit (for electrons to flow)
  - a salt bridge (usually!)
  - an electrolyte solution
  - chemical species that undergo reaction
  - interfaces or junctions

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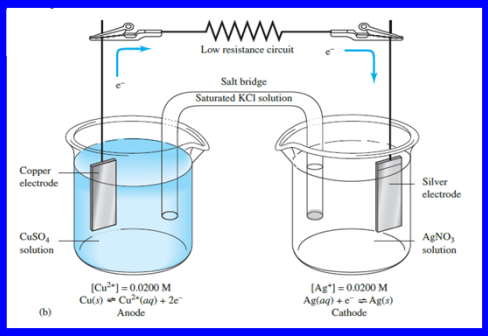
A galvanic cell doing work



$Cu + 2Ag^+ \Leftrightarrow Cu^{2+} + 2Ag$

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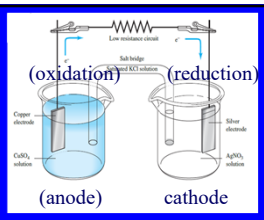
Convention

Reduction at Cathode (Ag)

Oxidation at Anode (Cu)



Liquid Junction

the interface between electrochemical solution and the salt bridge (liquid-liquid interface) → could develop a small junction potential

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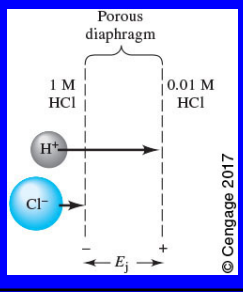
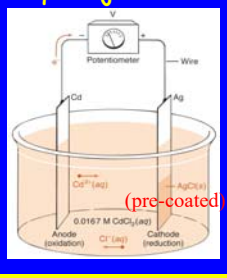
Galvanic Cell (III), w/o liquid junction

- Origin of Liquid Junction Potentials: Difference in ion mobility

HCl (1.0 M)|HCl (0.01 M)





Anode (Negtive electrode):

$Cd \rightarrow Cd^{2+} + 2e^-$

Cathode (Positive electrode):

$AgCl + e^- \rightarrow Ag + Cl^-$

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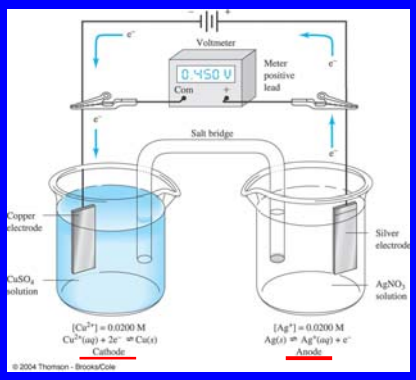
Electrolytic Cell



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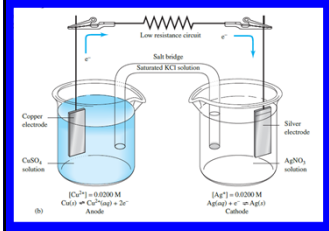
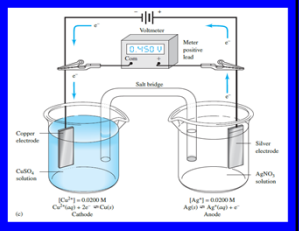
Anode vs Cathode

Anode: electrode with oxidation process
Cathode: electrode with reduction process





- Depends on the type of electrochemical cell
- Determined by the redox process

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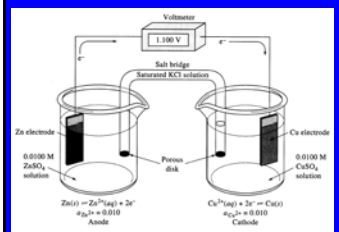
Shorthand Cell Notation ("Plus right rule", "ABC order")



Convention

- Anode—on the left
- Cathode-right
- |--interface
- ||--salt bridge (two liquid-liquid interfaces
- Activity/concentration/ pressure included

(-) $Zn|ZnSO_4(a_{Zn^{2+}} = 0.0100\ M)||CuSO_4(a_{Cu^{2+}}\ 0.0100M)|Cu$ (+)

(Anode, negative) (salt bridge) (cathode, positive)

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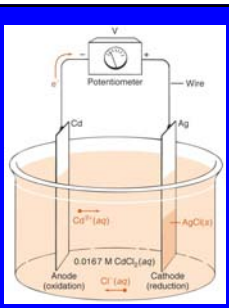

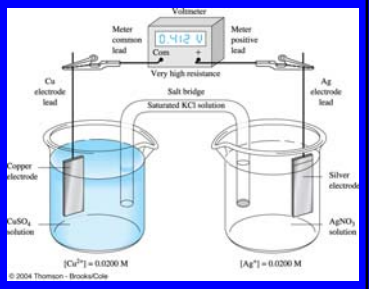

(Anode, -) $Cd|CdCl_2(0.0167M)|AgCl|Ag$ (Cathode, +)

(-) $Cu|Cu^{2+}$ $(0.0200\ M)||Ag^+(0.0200\ M)|Ag$ (+)

or (-) $Cu|CuSO_4(0.0200\ M)||AgNO_3(0.0200\ M)|Ag$ (+)

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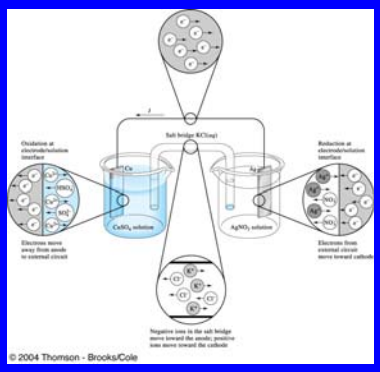
Movement of Charge in Galvanic Cell



Functions of salt bridge:

- To complete the circuit of an electrochemical cell
- To balance the charge of the two half cells

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Electrode Potentials—Nernst Equation

Ox + ne = Red ("half cell" reaction)

$$E = E^0 + \frac{RT}{nF}\ln\frac{a_{OX}}{a_{Red}} \qquad \{\ln b = \log_e^b = \frac{\log_{10}^b}{\log_{10}^e}\}$$

$$= E^0 + \frac{8.316 \bullet 298.15}{n \bullet 96485.31 \bullet \log 2.718}\log\frac{a_{OX}}{a_{Red}} = E^0 + \frac{0.05918}{n}\log\frac{a_{OX}}{a_{Red}}$$

where E^0 is the standard potential (i.e, when $a_{OX} = a_{Red} = 1$)

R is the gas constant (8.316 J $mol^{-1}K^{-1}$), T is the temperature (K),

n is the number of electrons transferred, F Faraday constant 96485.31 C mol^{-1}

$a_X = \gamma_X[X]$

γ_X is the activity coefficient of solute X.

γ_X varies with the presence of other ions (ionic strength)

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Formal/Conditional Potentials

$$E = E^0 + \frac{RT}{nF}\ln\frac{a_{OX}}{a_{Red}} = E^0 + \frac{RT}{nF}\ln\frac{\gamma_{OX}[OX]}{\gamma_{Red}[Red]}$$

$$= \{E^0 + \frac{RT}{nF}\ln\frac{\gamma_{OX}}{\gamma_{Red}}\} + \frac{RT}{nF}\ln\frac{[OX]}{[Red]}$$

$$= E^{0'} + \frac{RT}{nF}\ln\frac{[OX]}{[Red]} = E^{0'} - \frac{RT}{nF}\ln\frac{[Red]}{[OX]}$$

($E^{0'}$ – formal/conditional potential)

e.g., Hydrogen

$2H^+ + 2e = H_2$ (g) $E^0 = 0$,

$E^{0'} = -0.005$ V in 1 M HCl, $HClO_4$

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Example 18-2

Write Nernst expressions for the following half-cell reactions:

(1) $Zn^{2+} + 2e = Zn$ (s)

(2) $Fe^{3+} + e = Fe^{2+}$(s)

(3) $2H^+ + 2e = H_2$(g)

(4) $MnO_4^- + 5e + 8H^+ = Mn^{2+} + 4H_2O$

(5) $AgCl(s) + e = Ag(s) + Cl^-$

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$$(1) E = E^0 + \frac{RT}{2F}Ln\frac{[Zn^{2+}]}{[Zn]} = E^0 + \frac{0.0592}{2}\log\frac{[Zn^{2+}]}{1}$$

$$(2) E = E^0 + \frac{0.0592}{1}\log\frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$(3) E = E^0 + \frac{0.0592}{2}\log\frac{[H^+]^2}{p_{H_2}}$$

$$(4) E = E^0 + \frac{0.0592}{5}\log\frac{[MnO_4^-][H^+]^8}{[Mn^{2+}][H_2O]^4} = E^0 + \frac{0.0592}{5}\log\frac{[MnO_4^-][H^+]^8}{[Mn^{2+}]}$$

$$(5) E = E^0 + \frac{0.0592}{1}\log\frac{[AgCl(s)]}{[Ag(s)][Cl^-]} = E^0 + \frac{0.0592}{1}\log\frac{1}{[Cl^-]}$$

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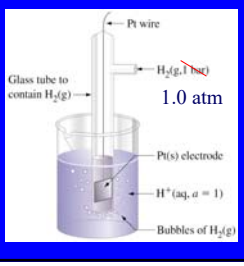
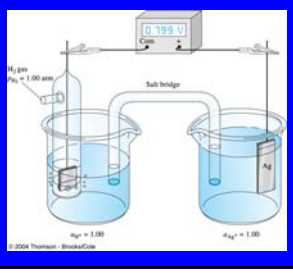
Standard (Normal) Hydrogen Electrode (SHE, NHE)

One cannot measure potential on each electrode independently – only differences





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$$2H^+ + 2e \rightleftarrows H_2(g)$$

$$Pt|H_2\ (p = 1.00\ atm)|H^+\ (a_{H^+} = 1.00\ M)||\ldots$$

(an half–cell)

Features of the standard hydrogen electrode (S.H.E):

- Potential is assigned to be 0.000 V
- The half-cell can be acted as an anode or a cathode
- Pt is an electron carrier and does not take part in reaction
- Pt coated with fine particles ('Pt black') to provide large surface area
- It is cumbersome to operate

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Oxidizing Power Increases ↑

TABLE 18-1

Standard Electrode Potentials*

Reaction	E^0 at 25°C, V
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$	+1.359
$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-$	+1.087
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-$	+1.065
$Ag^+ + e^- \rightleftharpoons Ag(s)$	+ 0.799
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+ 0.771
$I_3^- + 2e^- \rightleftharpoons 3I^-$	+ 0.536
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	+ 0.337
$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O$	+ 0.334
$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$	+ 0.268
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$	+ 0.222
$Ag(S_2O_3)_2^{3-} + e^- \rightleftharpoons Ag(s) + 2S_2O_3^{2-}$	+ 0.017
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	**0.000**
$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-$	− 0.151
$PbSO_4 + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}$	− 0.350
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$	− 0.403
$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	− 0.763

*See Appendix 5 for a more extensive list.

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Reducing Power Increases ↓

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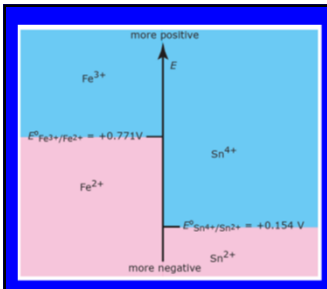
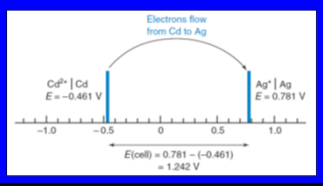


Redox ladder diagram for Fe^{3+}/Fe^{2+} and for Sn^{4+}/Sn^{2+}. The areas shaded in **blue** show the potential range where the oxidized forms are the predominate species; the reduced forms are the predominate species in the areas shaded in **pink**. Note that a more positive potential favors the oxidized form.



An intuitive view of cell potentials

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Standard Potentials

- Measured versus the S.H.E (0.00 V)
- The activity of one for the species of interest = 1 at a known temperature in a cell with the S.H.E.
- Arises from simple equilibria.
- Depends on the electrode materials used.

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Electrochemical Cell Potentials —Nernst Equation

- The Nernst equation can be derived from the equation linking free energy changes to the reaction quotient:

$\Delta G = \Delta G^0 + RT \ln Q$ where Q is the reaction quotient

$\because \Delta G = -nF\Delta E$ ΔE is the electrochemical cell potential

$\Delta G^0 = -nF\Delta E^0$ ΔE^0 is the standard electrochemical cell potential

$$\therefore \Delta E = \Delta E^0 - \frac{RT}{nF} \ln Q$$

$$= \Delta E^0 - \frac{0.0592}{n} \log Q \text{ at 298 K (25 °C)}$$

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$$\Delta E(or\ E_{cell}) = E_{cathode(+)} - E_{anode(-)}$$

$$For\ aA + bB + ... \rightleftharpoons pP + sS + ...$$

(n electrons involved)

$$Q = \frac{a_P^p \cdot a_S^s ...}{a_A^a \cdot a_B^b ...}$$

Example: Calculate the cell potential of following:

1. $Cu|CuSO_4$ (0.05 M)$||Ag^+$ (0.005M)$|Ag$ at 25 °C
2. $Zn + 2HCl$ (0.10 M) = $ZnCl_2$ (0.05 M) + H_2 (g, 0.20 atm)
3. $5Fe^{2+}$ (0.10 M)+ MnO_4^- (0.05 M) + $8H^+$ (1.0 M) = $5Fe^{3+}$ (0.05 M) + Mn^{2+} (0.001 M) + $4H_2O$

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Solutions:

1.
$$\Delta E_{cell} = E(+) - E(-) = E_{Ag^+/Ag} - E_{Cu^{2+}/Cu}$$
$$= (E^0_{Ag^+/Ag} + \frac{0.0592}{2}\log\frac{[Ag^+]^2}{1}) - (E^0_{Cu^{2+}/Cu} + \frac{0.0592}{2}\log\frac{[Cu^{2+}]}{1})$$
$$= (0.799 + \frac{0.0592}{2}\log\frac{0.005^2}{1}) - (0.344 + \frac{0.0592}{2}\log\frac{0.05}{1})$$
$$= 0.663 - 0.305 = 0.358\ V$$

2.
$$\Delta E_{cell} = \Delta E^0_{cell} - \frac{0.0592}{2}\log\frac{[ZnCl_2]\times p_{H2}}{[Zn][HCl]^2}$$
$$= (E^0_{H^+/H_2} - E^0_{Zn^{2+}/Zn}) - \frac{0.0592}{2}\log\frac{0.05\times 0.20}{1\times 0.10^2}$$
$$= (0 - (-.763)) - 0 = 0.763\ V$$

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Redox Reaction
Equilibrium Constant Calculation

When the reaction reaches equalibrium

$$\because \Delta G = 0\ (\Delta E = 0),\ Q = K_{eq}$$

$$\therefore \Delta G^0 = -RT\ln K_{eq}$$

$$\text{or } -nF\Delta E^0 = -RT\ln K_{eq}$$

$$\ln K_{eq} = \frac{nF\Delta E^0}{RT}$$

$$\text{or } \log K_{eq} = \frac{n\Delta E^0}{0.0592}\ (\text{at } 298K)$$

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IF, USING "Plus Right Rule" Convention

i, ?

$Cu|CuSO_4\ (0.05\ M)||Ag^+\ (0.005\ M)|Ag$

$$2Ag^+ + Cu \underset{\Delta E<0}{\overset{\Delta E>0}{\rightleftharpoons}} 2Ag^+ + Cu^{2+}$$

- $E_{cell} > 0$, the reaction will proceed to the right → when the cell is first connected
- $E_{cell} < 0$, the reaction will proceed to the left ← when the cell is first connected
- $E_{cell} = 0$ what do you think?

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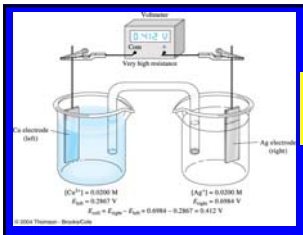
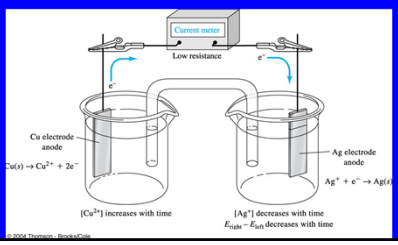


$E_{cell} > 0, \Delta G < 0$

$Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag$



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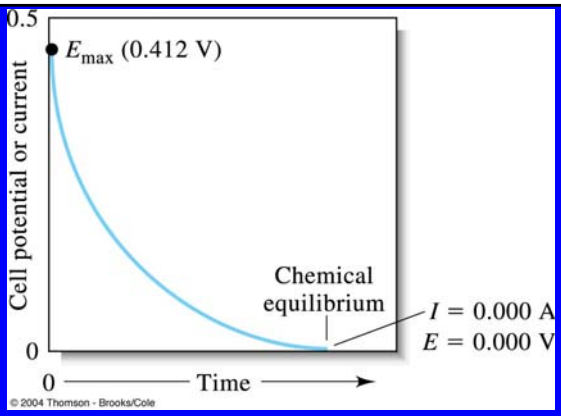

Discharging a Galvanic Cell

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Chapter 18 Summary

- Oxidation/reduction reactions, oxidant/reductant
- Balancing redox reactions
- Types of electrochemical cells: galvanic and electrolytic cells
- Electrode potentials
- Standard electrode and cell potentials
- Standard hydrogen electrode (SHE)
- Standard electrode potential
- Nernst equation
- Plus right rule ("ABC" rule), shorthand notation, and schematic representation of cells

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Important Equations

Free energy

$$\Delta G^0 = -nF\Delta E^0_{cell} = -RT \ln K_{eq}$$

$$\log K_{eq} = \frac{n\Delta E^0}{0.0592} \text{ (at 298K)}$$

Cell potential

$$E_{cell} = E_{right} - E_{left}$$

Nerst equation

For $aA + bB + ...+ ne \rightleftharpoons cC + dD + ...$

$$E = E^0 - \frac{RT}{nF} \ln \frac{[C]^c[D]^d...}{[A]^a[B]^b...}$$

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