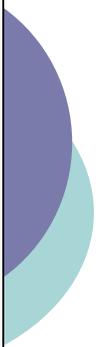## Review:
Balancing Redox Reactions

- Determine which species is oxidized and which species is reduced
  - Oxidation corresponds to an increase in the oxidation number of an element
  - Reduction corresponds to a decrease in the oxidation number of an element
- Write half reactions for oxidation and reduction processes
  - Oxidation reaction will have e⁻'s on the right side of equation
  - Reduction reaction will have e⁻'s on the left side of the equation

Review:
Balancing Redox Reactions
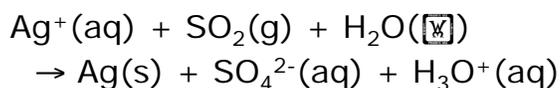
- Balance half reactions including charge balance
- Multiply each half reaction by a factor so that the total number of e⁻'s transferred in each reaction are equal
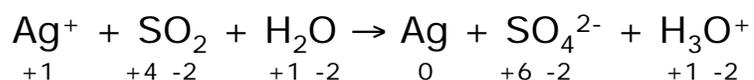- Add the resulting half reactions together to get the overall balanced redox equation

Review:
Balancing Redox Reactions

<u>Example:</u>
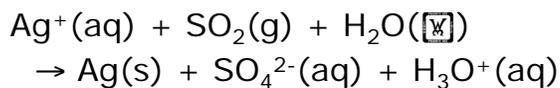
$Ag^+(aq) + SO_2(g) + H_2O(\ell)$
$\rightarrow Ag(s) + SO_4^{2-}(aq) + H_3O^+(aq)$

o Determine oxidation state of each element in reaction:

$$Ag^+ + SO_2 + H_2O \rightarrow Ag + SO_4^{2-} + H_3O^+$$

$+1 \qquad +4\ -2 \qquad +1\ -2 \qquad 0 \qquad +6\ -2 \qquad +1\ -2$

Review:
Balancing Redox Reactions

<u>Example:</u>

$Ag^+(aq) + SO_2(g) + H_2O(\ell)$
$\rightarrow Ag(s) + SO_4^{2-}(aq) + H_3O^+(aq)$

o Ag is reduced ($+1 \rightarrow 0$)
o S is oxidized ($+4 \rightarrow +6$)
o Oxidation half reaction:

$SO_2(g) + H_2O(\ell)$
$\rightarrow SO_4^{2-}(aq) + H_3O^+(aq) + 2\ e^-$
$SO_2(g) + 6\ H_2O(\ell)$
$\rightarrow SO_4^{2-}(aq) + 4\ H_3O^+(aq) + 2\ e^-$

Review:
Balancing Redox Reactions

Example:

Ag$^+$(aq) + SO$_2$(g) + H$_2$O(🖂)

$\rightarrow$ Ag(s) + SO$_4^{2-}$(aq) + H$_3$O$^+$(aq)
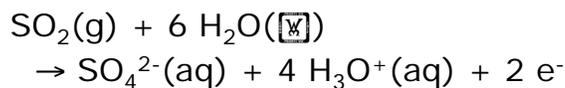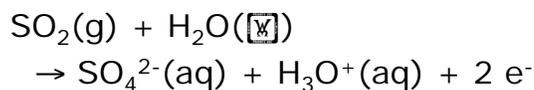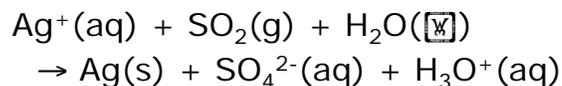
o Reduction half reaction:

Ag$^+$(aq) + e$^-$ $\rightarrow$ Ag(s)
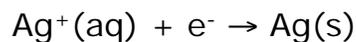
o Multiply reduction reaction by 2 to balance e$^-$'s transferred

2 Ag$^+$(aq) + 2 e$^-$ $\rightarrow$ 2 Ag(s)

Review:
Balancing Redox Reactions

Example:

Ag$^+$(aq) + SO$_2$(g) + H$_2$O(🖂)

$\rightarrow$ Ag(s) + SO$_4^{2-}$(aq) + H$_3$O$^+$(aq)
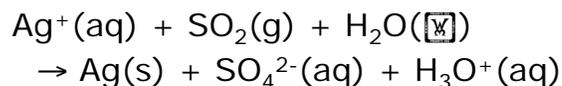
o Add balanced half reaction to get net reaction

SO$_2$(g) + 6 H$_2$O(🖂) $\rightarrow$ SO$_4^{2-}$(aq) + 4 H$_3$O$^+$(aq) + 2 e$^-$

2 Ag$^+$(aq) + 2 e$^-$ $\rightarrow$ 2 Ag(s)

SO$_2$(g) + 2 Ag$^+$(aq) + 6 H$_2$O(🖂) $\rightarrow$

SO$_4^{2-}$(aq) + 2 Ag(s) + 4 H$_3$O$^+$(aq)
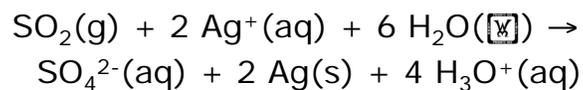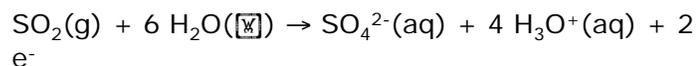
Electrochemical Cells

- When two half reactions are connected, we get an electrochemical cell that can generate a voltage potential and electrical current

Electrochemical Cells

Oxidation occurs at the **anode**
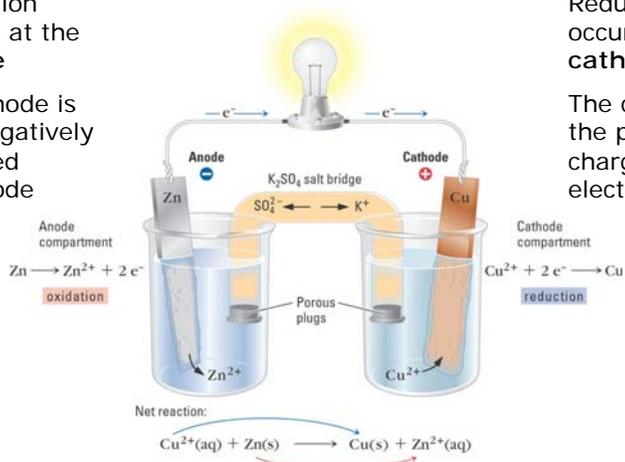
The anode is the negatively charged electrode

Reduction occurs at the **cathode**

The cathode is the positively charged electrode

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Electrochemical Cells

- Each half reaction has an electrical potential, E
- Electrical potential is a measure of how easily a species is reduced
  - e^-'s added to the species to reduce its oxidation state
- The emf (electromotive force) of a cell is a measure of how much work that cell can do

Electrochemical Cells

- Work for a cell is defined as:
  - Work = $q \cdot E_{cell}$
  - Work = $n \cdot F \cdot E_{cell}$
- The potential difference (E_{cell}) is measured in volts
- Charge is measured in coulombs
  - 1 e^- has a charge of 1.602×10^{-19} C
- F = 96,470 C/mol (Faraday's Constant)
- 1 volt = 1 Joule/1 coulomb

11/20/08

Electrochemical Cells

- The emf of a cell is determined by taking the difference between the potentials of the cathode and the anode:

  $E_{cell} = E_{cathode} - E_{anode} = E_+ - E_-$

- If E_{cell} is positive the electrochemical reaction will proceed as written
- If E_{cell} is negative, the reverse reaction will occur

Electrochemical Cells

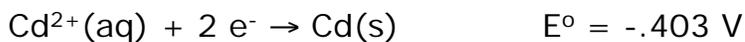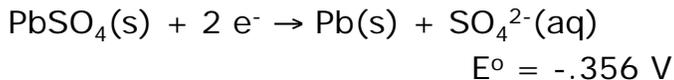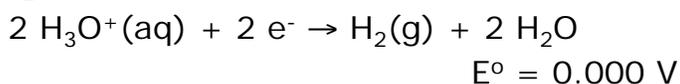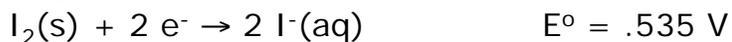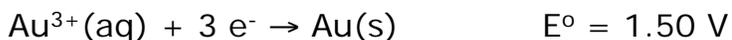- Values for the potential of various half reactions can be found in tables
- Values are listed under standard conditions
  - Gas phase species have a pressure of 1 atm
  - Aqueous species have activity of 1
- Tables give standard reduction potentials, E^o (Appendix H)

6

Electrochemical Cells

Examples:

$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$ $E^o = 1.82$ V

$Au^{3+}(aq) + 3 e^- \rightarrow Au(s)$ $E^o = 1.50$ V

$Hg_2^{2+}(aq) + 2 e^- \rightarrow 2 Hg(☒)$ $E^o = .789$ V

$I_2(s) + 2 e^- \rightarrow 2 I^-(aq)$ $E^o = .535$ V

$2 H_3O^+(aq) + 2 e^- \rightarrow H_2(g) + 2 H_2O$

                       $E^o = 0.000$ V

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

                       $E^o = -.356$ V

$Cd^{2+}(aq) + 2 e^- \rightarrow Cd(s)$ $E^o = -.403$ V

$Li^+(aq) + e^- \rightarrow Li(s)$ $E^o = -3.045$ V
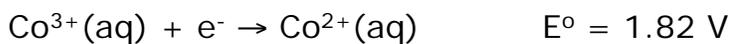
Electrochemical Cells

- Electrical potential cannot be measured on an absolute scale
- The standard hydrogen electrode (SHE) is defined as a reference electrode with a potential of $E^o = 0.00000000000$ V
- Potentials of all other half reaction are measured relative to the SHE

Electrochemical Cells

Electrode
connection

H_2

H_2 (1 bar)

Salt bridge

Porous
plug

$H_3O^+(aq)$
(1 M) 25 °C

Platinum
electrode
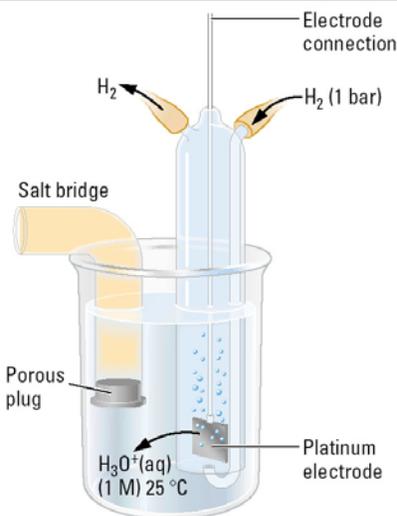
Figure 19.7

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Electrochemical Cells

Example:

Determine the potential when a copper electrode in a solution of copper nitrate is connected to a nickel electrode in a solution of nickel nitrate

Step 1: write balanced half reactions for each electrode—the cathode is always the electrode with the more positive E^o

$Ni^{2+}(aq) + 2 e^- \rightarrow Ni(s)$ $E^o_- = -.236$ V

$Cu^{2+}(aq) + 2 e^- \rightarrow Cu(s)$ $E^o_+ = .339$ V

Electrochemical Cells

Example:

Step 2: if necessary, multiply half reaction by factor to balance e⁻'s transferred
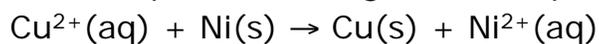
$Cu^{2+}(aq) + 2 e^- \rightarrow Cu(s)$ $E^o_+ = .339$ V

$Ni^{2+}(aq) + 2 e^- \rightarrow Ni(s)$ $E^o_- = -.236$ V

Step 3: add half reactions to get net reaction, and add potentials to get net cell potential

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

$E^o = .575$ V

Because E^o for the cell is positive, the reaction proceeds as written

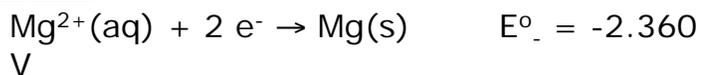# Electrochemical Cells

Example:

Determine E^o for a Mg^{2+} solution with Pt electrode connected to a Ag^+ solution with a Ag electrode

Step 1: write balanced half reactions

$Mg^{2+}(aq) + 2 e^- \rightarrow Mg(s)$ $E^o_- = -2.360$ V

$Ag^+(aq) + e^- \rightarrow Ag(s)$ $E^o_+ = 0.799$ V

Electrochemical Cells

Example:

Step 2: multiply anode reaction by 2 to balance e$^-$'s

$2\ Ag^+(aq) + 2\ e^- \rightarrow 2\ Ag(s)$ $E^o_+ = 0.799\ V$

E^o is a function only of the species being reduced or oxidized, not by how many there are
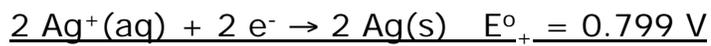
We do not multiply the value of E^o by the same factor used to balance the e$^-$'s transferred

Electrochemical Cells

Example:

Step 3: add half reaction and E^o's to get results

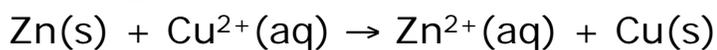$Mg^{2+}(aq) + 2\ e^- \rightarrow Mg(s)$ $E^o_- = -2.360\ V$

$\underline{2\ Ag^+(aq) + 2\ e^- \rightarrow 2\ Ag(s)\ \ \ \ E^o_+ = 0.799\ V}$

$Mg(s) + 2\ Ag^+(aq) \rightarrow Mg^{2+}(aq) + 2\ Ag(s)$
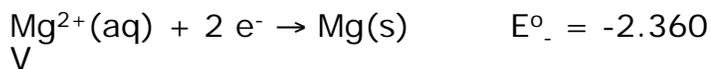
$E^o_{cell} = E^o_+ - E^o_- = 3.159\ V$

Electrochemical Cells

○ Shorthand notation for electrochemical cells
  - Phase changes are represented by a single vertical line
  - Salt bridges are represented by double vertical lines
  - Begin with anode reaction (oxidation)

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

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

Electrochemical Cells

○ <u>Example:</u>

Write the shorthand notation for the cell:

$H_2(g) + AgCl(s) \rightarrow H^+(aq) + Cl^-(aq) + Ag(s)$

   0   +1 -1   +1   -1   0
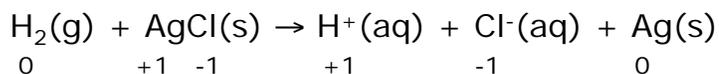
○ H is oxidized; Ag is reduced

○ Notation for anode:

$H_2(g),Pt|H^+(aq)$

○ Notation for cathode:

$Cl^-(aq),AgCl(s)|Ag(s)$

○ Overall:

$H_2(g),Pt|H^+(aq)||Cl^-(aq),AgCl(s)|Ag(s)$

E^o and ΔG^o

- The electrochemical potential, E^o, and Gibb's free energy, ΔG^o, are related:

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

   n = # electrons transferred

   F = Faraday's Constant

   = 96,470 C/mol

E^o and ΔG^o

- Reminder:
  - an electrochemical rxn occurs spontaneously if E is positive
  - Any rxn is spontaneous if ΔG is negative
- If E^o is positive, then ΔG^o must be negative

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

E^o and ΔG^o
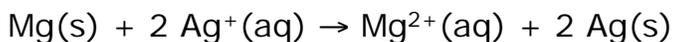
Example:
Find ΔG^o for the reaction
$$Mg(s) + 2\ Ag^+(aq) \rightarrow Mg^{2+}(aq) + 2\ Ag(s)$$
$$E^o = 3.16\ V$$
2 e^-'s are transferred in the process

$$\Delta G^o = -(2)(96500\ C/mol)(3.16\ J/C)$$
$$= -609.9\ kJ/mol$$

E^o, ΔG^o, and K

○ Since we know relation between ΔG^o and E^o and between ΔG^o and K, we can determine equilibrium constant for electrochemical reaction

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

$$\Delta G^o = -RT\ lnK$$

$$-nFE^o = -RT\ lnK$$

$$E^o = \frac{RT}{nF}\ lnK = \frac{.0257\ V}{n}\ lnK$$

at T = 298 K

13

E^o, ΔG^o, and K

- If we convert from natural log to common log (base 10), we get

$$E^o = \frac{.0592\ V}{n}\ logK \quad \text{at T = 298 K}$$

  or

$$K = 10^{\left(\frac{nE^o}{.0592\ V}\right)}$$

Concentration and E^o

- E at non-standard concentrations can be determined from our knowledge of ΔG under non-standard conditions:

  $\Delta G = \Delta G^o + RT\ lnQ$

- Q is called the *Reaction Quotient*—same mathematical form as K_{eq}

  $aA + bB \rightarrow cC + dD$
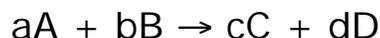
$$Q = \frac{A_C^c A_D^d}{A_A^a A_B^b} \quad \text{A_X is activity of species X}$$

Concentration and E^o

$\Delta G = \Delta G^o + RT \ln Q$

Substituting $\Delta G = -nFE$ gives:

$-nFE_{cell} = -nFE^o_{cell} + RT \ln Q$

Divide by $-nF$:

$E_{cell} = E^o_{cell} - RT/nF \ln Q$

$$E_{cell} = E^o_{cell} - \frac{.0592}{n} \log Q$$

Nernst Equation

Concentration and E^o

Example:

Find potential of the following cell:

$Cu(s) | Cu^{2+}(.0037M) || Ag^+(.016M) | Ag(s)$
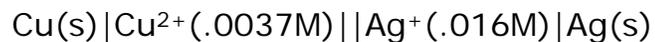
Step 1: write half reactions w/ E^o's

oxidation: $Cu(s) \rightarrow Cu^{2+} + 2\ e^-$ $E^o = -.337\ V$

reduction: $Ag^+ + e^- \rightarrow Ag(s)$ $E^o = .799\ V$
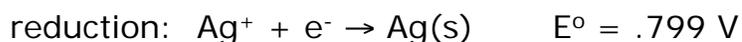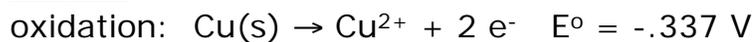
Step 2: write balanced net reaction

$Cu(s) + 2\ Ag^+ \rightarrow Cu^{2+} + 2\ Ag(s)$ $E^o = .462\ V$

Concentration and E^o

Example:

$Cu(s) + 2\ Ag^+ \rightarrow Cu^{2+} + 2\ Ag(s)$ $E^o = .462\ V$
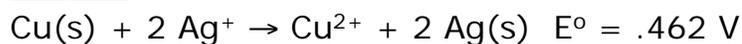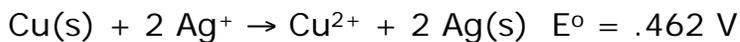
Step 3: write expression for Q:

$$Q = \frac{[Cu^{2+}]}{[Ag^+]^2}$$

Step 4: solve for E

$$E = E^o - \frac{.0592\ V}{n} \log Q$$

$$= .462\ V - \frac{.0592\ V}{2} \log\left(\frac{.0037}{.016^2}\right)$$

$$= .427\ V$$

Reference Electrodes

○ Although E^o's are measured relative to the standard hydrogen electrode, it is impractical to use the SHE in normal applications

○ A number of reference electrodes have been developed that provide ease of use and stable E^o's
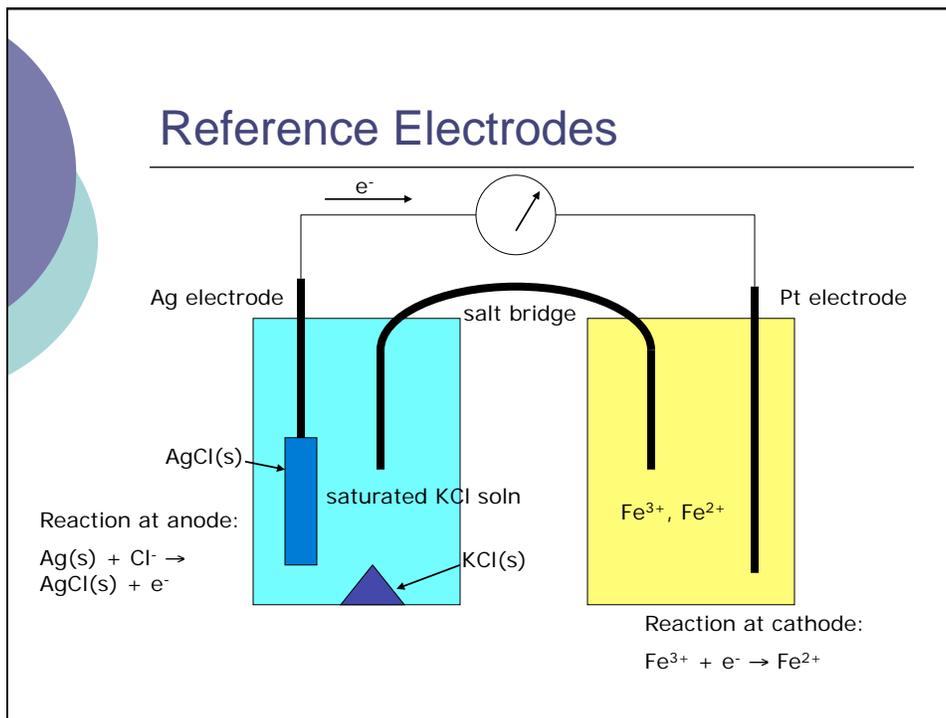
Reference Electrodes

Ag electrode

Pt electrode

salt bridge

e^-

AgCl(s)

saturated KCl soln

Fe^{3+}, Fe^{2+}

Reaction at anode:

$Ag(s) + Cl^- \rightarrow$
$AgCl(s) + e^-$

KCl(s)

Reaction at cathode:

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

Reference Electrodes

Example:

cathode: $Fe^{3+} + e^- \rightarrow Fe^{2+}$

$$E^o_+ = 0.771 \text{ V}$$

anode: $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(\text{sat'd KCl})$

$$E^o_- = 0.222 \text{ V}$$

We can now write expressions for the potentials of each electrode:

$$E_+ = E^o_+ - \frac{.0592}{1}\log\left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\right)$$

$$E_- = E^o_- - \frac{.0592}{1}\log[Cl^-]$$

Reference Electrodes

Example:

cathode: $Fe^{3+} + e^- \rightarrow Fe^{2+}$

$$E^o_+ = 0.771 \text{ V}$$

anode: $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(\text{sat'd KCl})$
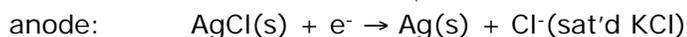
$$E^o_- = 0.222 \text{ V}$$

The potential for the cell is:

$$E_{cell} = E_+ - E_-$$

$$= .771 - .0592\log\left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\right) - \left\{.222 - .0592\log[Cl^-]\right\}$$

However, because the anode is saturated with KCl, [Cl⁻] is constant, so the cell potential depends only on the concentrations of [Fe³⁺] and [Fe²⁺]

Reference Electrodes

Ag|AgCl Electrode
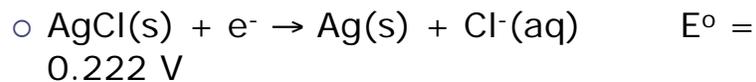
○ $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$ $E^o = 0.222 \text{ V}$

○ If the solution surrounding the electrode is saturated with KCl so the [Cl⁻] remains constant, then this electrode maintains a constant potential of E = 0.197 V

Ag(s)|AgCl(s)|Cl⁻(aq)[sat'd]

Reference Electrodes

Calomel Electrode

- $\frac{1}{2}Hg_2Cl_2(s) + e^- \rightarrow Hg(\square) + Cl^-(aq) \quad E^o = 0.268$ V
- If the solution surrounding the electrode is saturated with KCl so the [Cl$^-$] remains constant, then this electrode maintains a constant potential of E = 0.241 V

  $Hg_2Cl_2(s)|Hg(\square)|Cl^-(aq)[sat'd]$

- This is referred to as the SCE—saturated calomel electrode

SCE

Voltmeter

Indicator electrode

Silver wire coated with AgCl

HCl(aq)(1 M)

Thin glass membrane

Reference electrode

Platinum wire

Saturated solution of KCl and Hg_2Cl_2

Solid calomel ($Hg_2Cl_2(s)$)

Mercury

Porous plug

Sample solution

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Junction Potentials

- Anytime electrolyte solution with different concentrations are in contact, a junction potential is formed
- The gradient in concentrations induces movement from higher concentration side of contact region to lower concentration side
- Differing mobilities of ions create regions in the solution where charge builds up

Junction Potentials

NaCl solution	$Na^+ \longrightarrow$ $Cl^- \longrightarrow$	Pue water

The mobility of Cl^- is higher than that of Na^+, so Cl^- diffuses into the water side faster than Na^+ creating a region of negative charge

NaCl solution	Na^+ : Cl^- Na^+ : Cl^-	Pue water

Na^+ rich region—positively charged Cl^- rich region—negatively charged

Junction Potentials

- The negatively charged, Cl^- rich region inhibits further movement of Cl^- and enhances movement of Na^+ to the right
- The resulting separation of charge creates an electrical potential that contributes to the potential measured for a galvanic cell
- Junction potentials are on the order of mV, but depending on E_{cell}, may introduce significant error in the analysis of an analyte
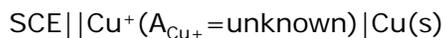
Indicating Electrodes

- The indicating electrode is designed to detect the analyte species
- There are several varieties of indicating electrodes:

  Metal electrodes: used to detect metal ions
    electrode is made of metal being analyzed

  Ion-selective electrodes: designed to detect a specific analyte ion—no redox chemistry involved

Indicating Electrodes

○ There are two types of indicating electrodes we will discuss—metal electrodes and ion specific electrodes

○ Metal electrodes use the metal of interest as the electrode material and detect metal ion in solution

$SCE||Cu^+(A_{Cu+}=unknown)|Cu(s)$

$Cu^+ + e^- \rightarrow Cu(s)$ $E^o = 0.518$ V

$E_+ = .518V - .0592 \log\{1/(A_{Cu+})\}$
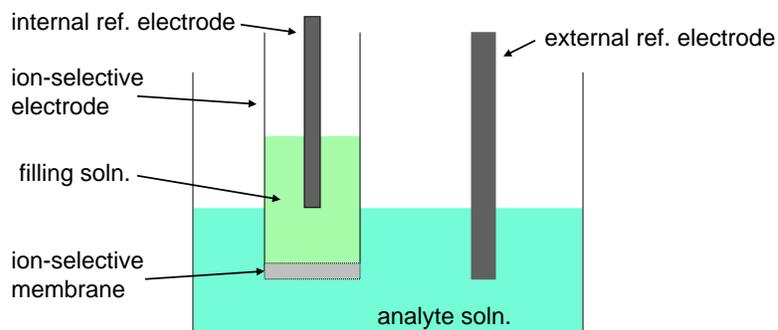
$E_{cell} = E_+ - E_{ref} = .518V - .0592 \log\{1/(A_{Cu+})\} - .241V$

$pCu = -\log(A_{Cu+}) = (.277 - E_{cell})/.0592$

Cell Potential

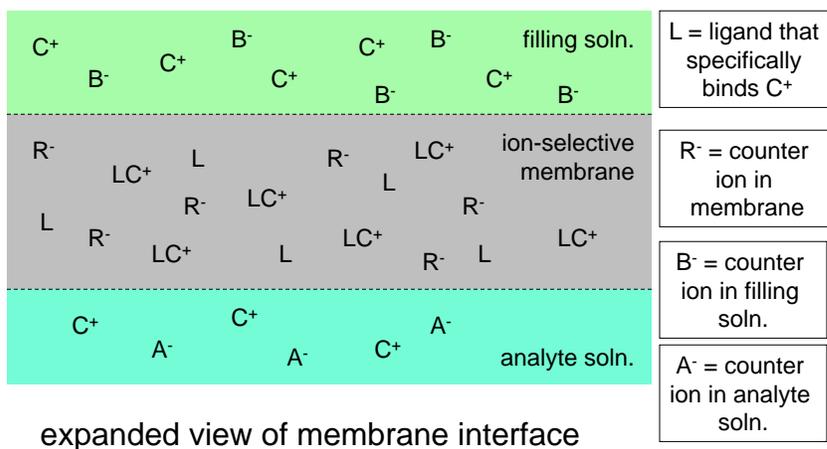○ The total potential of a cell containing an indicator electrode and a reference electrode is:

$E_{cell} = E_{ind} - E_{ref}$

Ion-Selective Electrodes

internal ref. electrode →
ion-selective electrode →
filling soln. →
ion-selective membrane →
external ref. electrode ←
analyte soln.

Ion-Selective Electrodes

C+ B- C+ B- filling soln.
B- C+ C+ C+ B-
B- B-

R- LC+ ion-selective membrane
LC+ L R- LC+
R- LC+ L R-
L R- LC+ LC+
R- LC+ L LC+ R- L LC+

C+ C+ A-
A- A- C+
C+ analyte soln.

expanded view of membrane interface

L = ligand that specifically binds C+

R- = counter ion in membrane

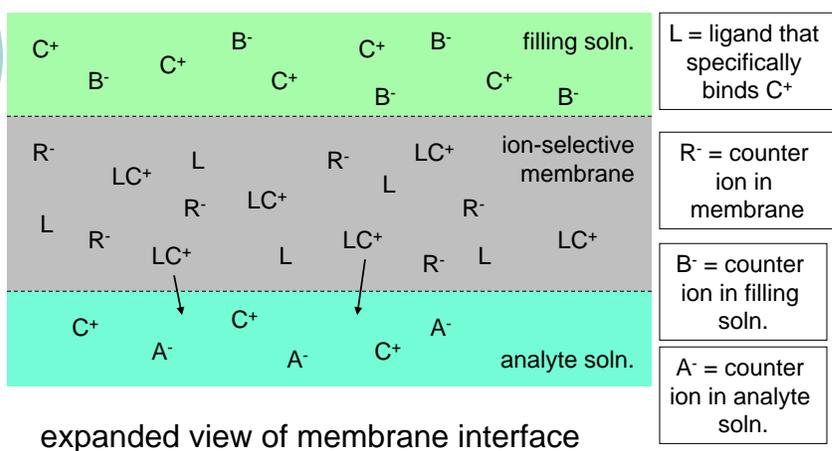B- = counter ion in filling soln.

A- = counter ion in analyte soln.

Indicating Electrodes

○ Membrane allows transport of C^+ across interface, but not A^-, R^-, or B^-

○ The $[C^+]$ is greater in the membrane than in analyte solution

○ As C^+ moves into analyte solution, an electrical potential forms across the interface

   The resulting charge imbalance in the membrane limits the amount of C^+ that can move across the membrane interface

Ion-Selective Electrodes

expanded view of membrane interface

L = ligand that specifically binds C^+

R^- = counter ion in membrane

B^- = counter ion in filling soln.

A^- = counter ion in analyte soln.

Indicating Electrodes

$\Delta G = \Delta G_{solv} + \Delta G_{change\ in\ activity\ of\ C+}$

ΔG_{solv} arises from difference in solvents between membrane and analyte solution

$\Delta G = \Delta G_{solv} - RT\ \ln(\mathcal{A}_{Mem}/\mathcal{A}_{Out})$

$\mathcal{A}_{Mem}$ = activity of C^+ in membrane

$\mathcal{A}_{Out}$ = activity of C^+ in outer (analyte) soln.

Indicating Electrodes

The potential difference across the membrane interface creates a free energy contribution:

$\Delta G = -nFE_O \qquad$ n = charge on C^+

At equilibrium, the total free energy of the system must be zero:

$\Delta G_{solv} - RT\ \ln(\mathcal{A}_{Mem}/\mathcal{A}_{Out}) - nFE_{Out} = 0$

Solving for E_{Out} (the potential across the outer interface) gives:

$E_O = \Delta G_{solv}/nF - (RT/nF)\ln(\mathcal{A}_{Mem}/\mathcal{A}_{Out})$

Indicating Electrodes

There is an analogous term, E_{In}, for the interface between the membrane and the filling solution, but because the concentration of C^+ in the filling solution is higher, this potential is essentially constant

Indicating Electrodes

The total potential for the cell is now:

$E_{cell} = E_{Out} - E_{in}$

$= \Delta G_{solv}/nF - (RT/nF)\ln(\mathcal{A}_{Mem}/\mathcal{A}_{Out}) - E_{In}$

$= \Delta G_{solv}/nF - (RT/nF)\ln(\mathcal{A}_{Mem}) + (RT/nF)\ln(\mathcal{A}_{Out}) - E_{In}$

    constant   constant

      constant

Finally:

$E_{cell} = $ constant $ + (RT/nF)\ln(\mathcal{A}_{Out})$

$= $ constant $ + (.05916/n)\log(\mathcal{A}_{Out})$ at 25 ^{o}C