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
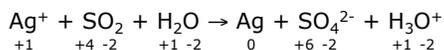
Review: Balancing Redox Reactions

- ○ 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
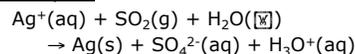
Review: Balancing Redox Reactions

Example:

$Ag^+(aq) + SO_2(g) + H_2O(l)$
$\rightarrow Ag(s) + SO_4^{2-}(aq) + H_3O^+(aq)$
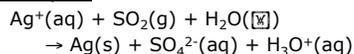
- ○ Determine oxidation state of each element in reaction:

$Ag^+ + SO_2 + H_2O \rightarrow Ag + SO_4^{2-} + H_3O^+$
+1   +4 -2   +1 -2   0   +6 -2   +1 -2

Review: Balancing Redox Reactions

Example:

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

- ○ Ag is reduced (+1 → 0)
- ○ S is oxidized (+4 → +6)
- ○ Oxidation half reaction:

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

Review: Balancing Redox Reactions

Example:

$Ag^+(aq) + SO_2(g) + H_2O(l)$
$\rightarrow Ag(s) + SO_4^{2-}(aq) + H_3O^+(aq)$
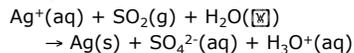
- ○ Reduction half reaction:

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

- ○ Multiply reduction reaction by 2 to balance e⁻'s transferred

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

Review: Balancing Redox Reactions

Example:

$Ag^+(aq) + SO_2(g) + H_2O(l)$
$\rightarrow Ag(s) + SO_4^{2-}(aq) + H_3O^+(aq)$
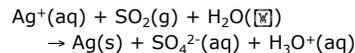
- ○ Add balanced half reaction to get net reaction

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

$SO_2(g) + 2 Ag^+(aq) + 6 H_2O(l) \rightarrow$
$SO_4^{2-}(aq) + 2 Ag(s) + 4 H_3O^+(aq)$

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

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

Electrochemical Cells

- The emf of a cell is determined by taking the difference between the potentials of the cathode and the anode:
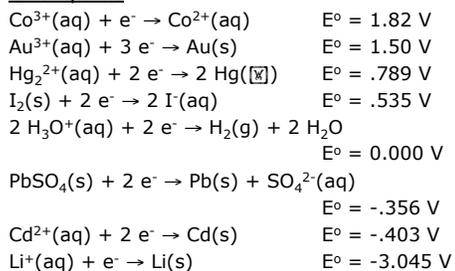
  $E_{cell} = E_{cathode} - E_{anode} = E_+ - E_-$

- 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)

2

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

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

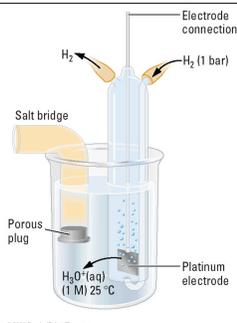## Electrochemical Cells

o Electrical potential cannot be measured on an absolute scale

o The standard hydrogen electrode (SHE) is defined as a reference electrode with a potential of $E^o = 0.00000000000$ V

o Potentials of all other half reaction are measured relative to the SHE
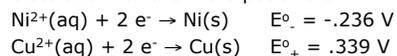
Electrochemical Cells

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
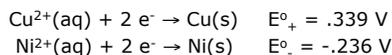
Step 1: write balanced half reactions for each electrode—the cathode is always the electrode with the more positive E^o
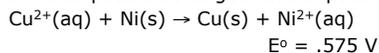
$Ni^{2+}(aq) + 2\ e^- \rightarrow Ni(s)$ $E^o_- = -.236$ V

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

   $Cu^{2+}(aq) + Ni(s) \rightarrow Cu(s) + Ni^{2+}(aq)$
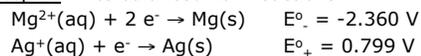
                  $E^o = .575$ V

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
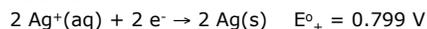
Step 1: write balanced half reactions

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

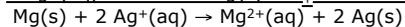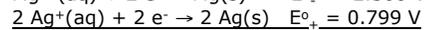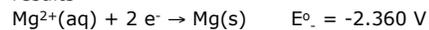$2 Ag^+(aq) + 2 e^- \rightarrow 2 Ag(s) \quad E^o_+ = 0.799 V$

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

$Mg^{2+}(aq) + 2 e^- \rightarrow Mg(s) \quad E^o_- = -2.360 V$
$2 Ag^+(aq) + 2 e^- \rightarrow 2 Ag(s) \quad E^o_+ = 0.799 V$
$Mg(s) + 2 Ag^+(aq) \rightarrow Mg^{2+}(aq) + 2 Ag(s)$
$E^o_{cell} = E^o_+ - E^o_- = 3.159 V$

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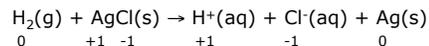
- Shorthand notation for electrochemical cells
  - Phase changes are represented by a single vertical line
  - Salt bridges are represented by double vertical lines
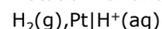 - Begin with anode reaction (oxidation)

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

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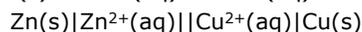
Electrochemical Cells

- Example:

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
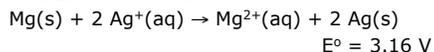 - Any rxn is spontaneous if ΔG is negative
- If E^o is positive, then ΔG^o must be negative

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

4

E^o and ΔG^o

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

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

E^o, ΔG^o, and K

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

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

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

$-nFE^o = -RT\ lnK$

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

$\qquad\qquad\qquad\qquad$ at T = 298 K

E^o, ΔG^o, and K

o If we convert from natural log to common log (base 10), we get
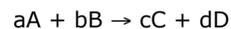
$E^o = \dfrac{.0592\ V}{n}\ logK \qquad$ at T = 298 K

or

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

Concentration and E^o

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

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

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

$\qquad aA + bB \rightarrow cC + dD$

$Q = \dfrac{A_C^c A_D^d}{A_A^a A_B^b} \qquad$ A_X is activity of species X

Concentration and E^o

$\Delta G = \Delta G^o + RT\ lnQ$
Substituting $\Delta G = -nFE$ gives:
$-nFE_{cell} = -nFE^o_{cell} + RT\ lnQ$
Divide by $-nF$:
$E_{cell} = E^o_{cell} - RT/nF\ lnQ$

$E_{cell} = E^o_{cell} - \dfrac{.0592}{n}\ logQ \qquad$ Nernst Equation

Concentration and E^o

Example:
Find potential of the following cell:
$\qquad Cu(s)|Cu^{2+}(.0037M)||Ag^+(.016M)|Ag(s)$
Step 1: write half reactions w/ E^o's
oxidation: $Cu(s) \rightarrow Cu^{2+} + 2\ e^-$ $\quad E^o = -.337\ V$
reduction: $Ag^+ + e^- \rightarrow Ag(s)$ $\qquad E^o = .799\ V$
Step 2: write balanced net reaction
$Cu(s) + 2\ Ag^+ \rightarrow Cu^{2+} + 2\ Ag(s)$ $\ E^o = .462\ V$
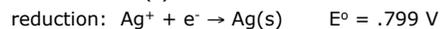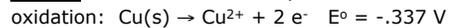
Concentration and E^o

Example:

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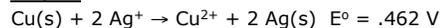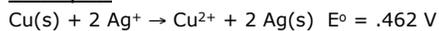
Step 3: write expression for Q:

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

Step 4: solve for E

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

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

$$= .427 \text{ V}$$

Reference Electrodes

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

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

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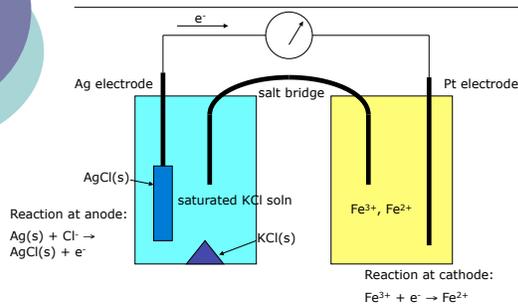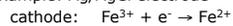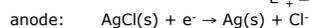## Reference Electrodes

e$^-$

Ag electrode   salt bridge   Pt electrode

AgCl(s)

Reaction at anode: saturated KCl soln   Fe^{3+}, Fe^{2+}

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

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

Reference Electrodes

Example: Ag/AgCl electrode

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

$E^o_+ = 0.771$ V

anode: $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$
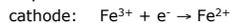
$E^o_- = 0.222$ V

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

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

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

When the solution is saturated with KCl(aq), the value of E$_-$ is 0.197 V

Reference Electrodes

Example:

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

$E^o_+ = 0.771$ V

anode: $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$(sat'd KCl)
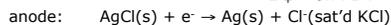
$E_- = 0.197$ V

The potential for the cell is:

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

$$= .771 - .0592 \log\left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\right) - 0.197$$

However, because the anode is saturated with KCl, [Cl$^-$] is constant, so the cell potential depends only on the concentrations of [Fe^{3+}] and [Fe^{2+}]

Reference Electrodes

Calomel Electrode

o ½$Hg_2Cl_2(s) + e^- \rightarrow Hg(ᵡ) + Cl^-(aq)$

$E^o = 0.268$ V
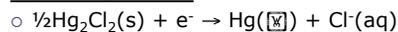
o If the solution surrounding the electrode is saturated with KCl so the [Cl$^-$] remains constant, then this electrode maintains a constant potential of E = 0.241 V

$Hg_2Cl_2(s)|Hg(ᵡ)|Cl^-(aq)$[sat'd]

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

SCE

Voltmeter

Indicator electrode

Reference electrode

Silver wire coated with AgCl

Platinum wire

Saturated solution of KCl and Hg_2Cl_2

Solid calomel $(Hg_2Cl_2(s))$

HCl(aq)(1 M)

Mercury

Porous plug

Thin glass membrane

Sample solution

© 2005 Brooks/Cole - Thomson

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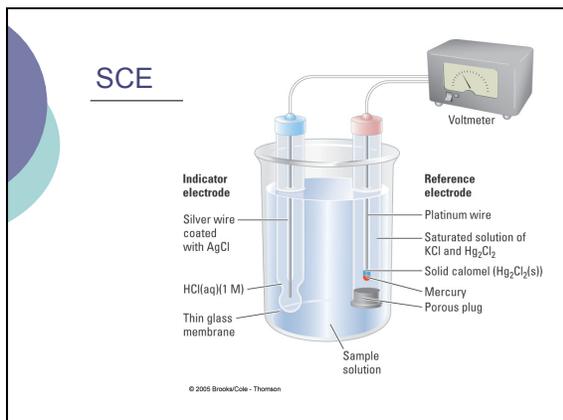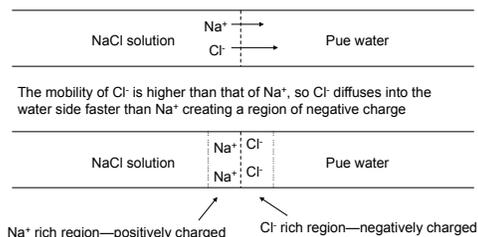
o Anytime electrolyte solutions with different concentrations are in contact, a junction potential is formed
o The gradient in concentrations induces movement from the higher concentration side of the contact region to the lower concentration side
o Differing mobilities of ions create regions in the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

Junction Potentials

NaCl solution | Na^+ → | Pue water
| Cl^- → |

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^- | Pue water
| Na^+ : Cl^- |

Na^+ rich region—positively charged

Cl^- rich region—negatively charged

Junction Potentials

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

Indicating Electrodes

o The indicating electrode is designed to detect the analyte species
o 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

o There are two types of indicating electrodes we will discuss—metal electrodes and ion specific electrodes
o Metal electrodes use the metal of interest as the electrode material and detect metal ion in solution

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

$Cu^+ + e^- \rightarrow Cu(s)$ $\qquad E^o = 0.518$ 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
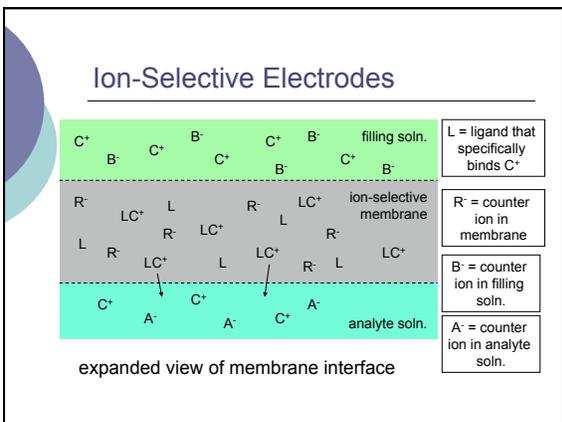
○ The total potential of a cell containing an indicator electrode and a reference electrode is:

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

Ion-Selective Electrodes

internal ref. electrode

ion-selective electrode

filling soln.

ion-selective membrane

external ref. electrode

analyte soln.

Ion-Selective Electrodes

expanded view of membrane interface

C⁺ B⁻ C⁺ B⁻ filling soln. B⁻ C⁺ C⁺ C⁺ B⁻	L = ligand that specifically binds C⁺
R⁻ L R⁻ LC⁺ ion-selective membrane LC⁺ LC⁺ membrane R⁻ L R⁻ LC⁺ L R⁻ LC⁺ LC⁺ L LC⁺ R⁻ L LC⁺	R⁻ = counter ion in membrane
	B⁻ = counter ion in filling soln.
C⁺ C⁺ A⁻ A⁻ A⁻ C⁺ analyte 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

C⁺ B⁻ C⁺ B⁻ filling soln. B⁻ C⁺ C⁺ C⁺ B⁻	L = ligand that specifically binds C⁺
R⁻ L R⁻ LC⁺ ion-selective membrane LC⁺ L membrane R⁻ LC⁺ R⁻ L R⁻ LC⁺ LC⁺ LC⁺ L LC⁺ R⁻ L	R⁻ = counter ion in membrane
	B⁻ = counter ion in filling soln.
C⁺ C⁺ A⁻ A⁻ A⁻ C⁺ analyte soln.	A⁻ = counter ion in analyte soln.

Indicating Electrodes

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

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:

$\Delta G = -nFE_O$ 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 °C