# CHEG 3128

# Battery – 2
# Current-Voltage Relationships

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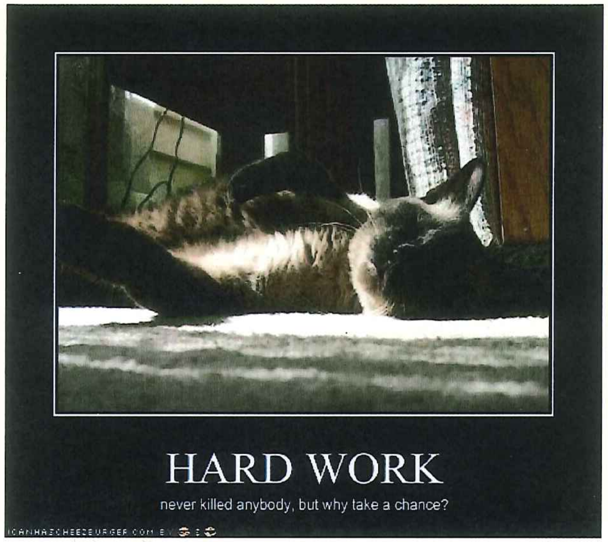
# How much work?

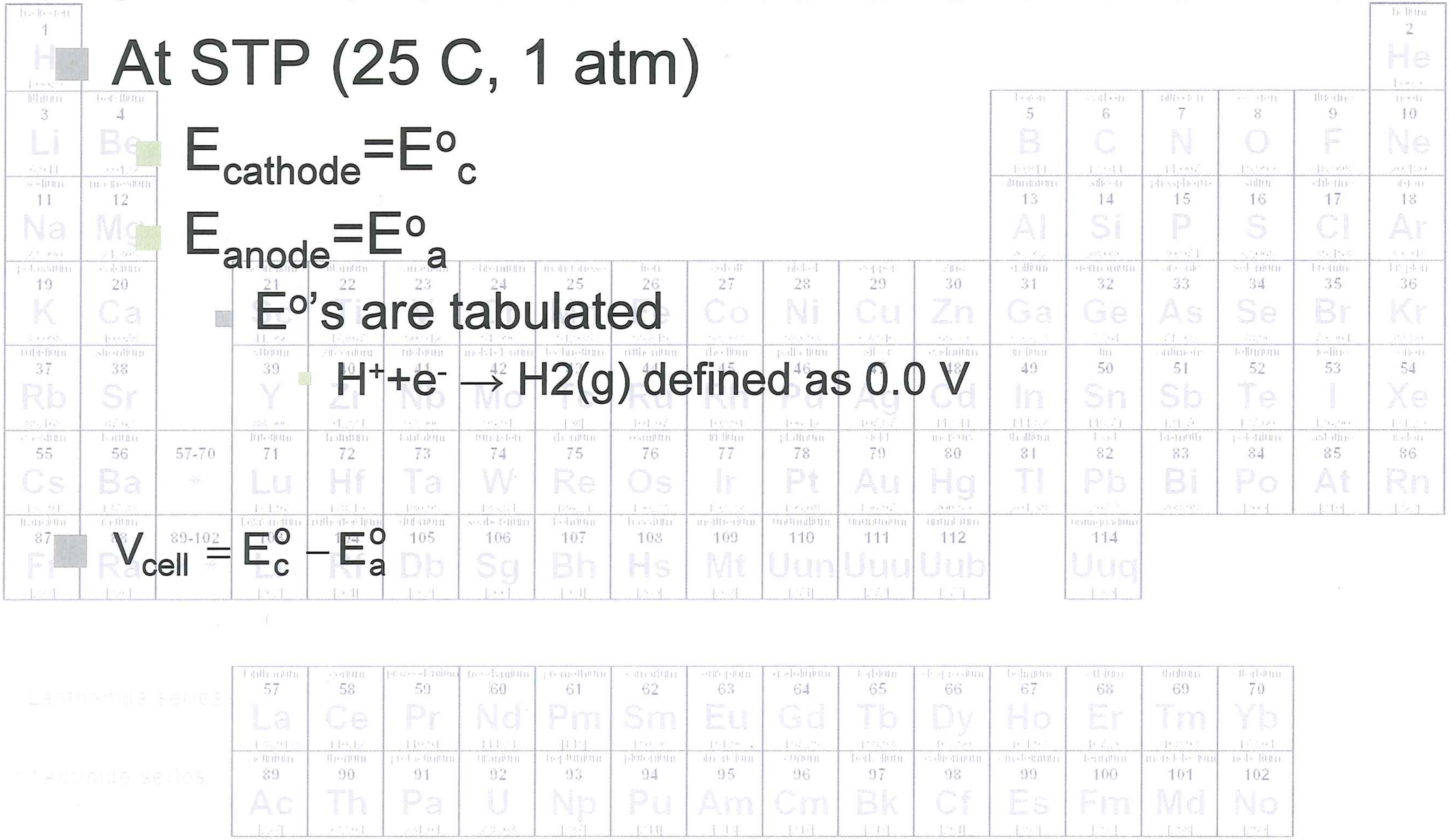
- Generalized Energy Balance
- Entropy Balance

$$W_{elec} = -\Delta G_{rxn}$$

$$\Delta G_{rxn} = -nFV_{cell} \longrightarrow V_{cell} = E_{cathode} - E_{anode}$$



# What is $V_{Cell}$ theoretically?

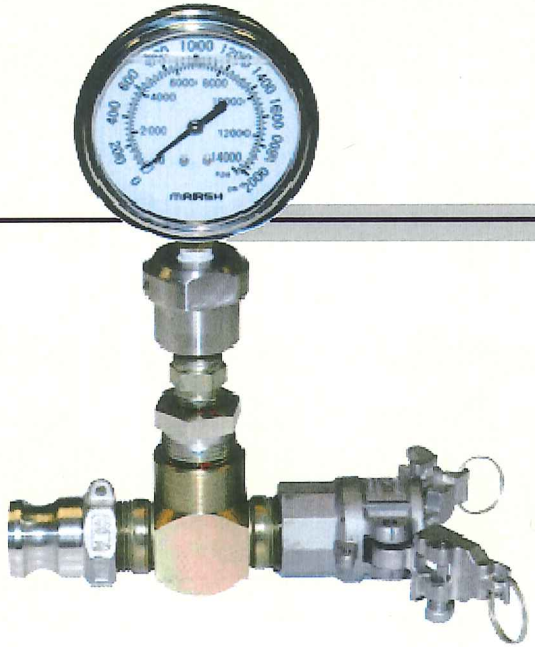


- At STP (25 C, 1 atm)
  - $E_{cathode} = E^o_c$
  - $E_{anode} = E^o_a$
    - $E^o$'s are tabulated
      - $H^+ + e^- \rightarrow H2(g)$ defined as 0.0 V
- $V_{cell} = E^o_c - E^o_a$

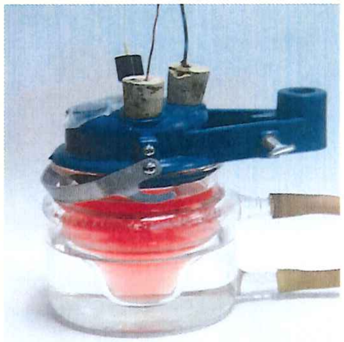
# Tabulated E°'s

| Half-reaction | E° (V) |
|---|---|
| $\frac{3}{2}$N $N_2(g) + H^+ + e^- \rightleftarrows HN_3(aq)$ | -3.09 −3.09 |
| Li+ + e− ⇄ Li(s) | -3.0401 −3.0401 |
| N2(g) + 4H2O + 2e− ⇄ 2NH2OH(aq) + 2OH− | -3.04 −3.04 |
| Cs+ + e− ⇄ Cs(s) | -3.026 −3.026 |
| Rb+ + e− ⇄ Rb(s) | -2.98 −2.98 |
| K+ + e− ⇄ K(s) | -2.931 −2.931 |
| Ba2+ + 2e− ⇄ Ba(s) | -2.912 −2.912 |
| La(OH)3(s) + 3e− ⇄ La(s) + 3OH− | -2.90 −2.90 |
| Sr2+ + 2e− ⇄ Sr(s) | -2.899 −2.899 |
| Ca2+ + 2e− ⇄ Ca(s) | -2.868 −2.868 |
| Eu2+ + 2e− ⇄ Eu(s) | -2.812 −2.812 |
| Ra2+ + 2e− ⇄ Ra(s) | -2.8 −2.8 |
| Na+ + e− ⇄ Na(s) | -2.71 −2.71 |
| La3+ + 3e− ⇄ La(s) | -2.379 −2.379 |
| Y3+ + 3e− ⇄ Y(s) | -2.372 −2.372 |
| Mg2+ + 2e− ⇄ Mg(s) | -2.372 −2.372 |
| $ZrO(OH)_2(s) + H_2O + 4e^- \rightleftarrows Zr(s) + 4OH^-$ | -2.36 −2.36 |
| $Al(OH)_4^- + 3e^- \rightleftarrows Al(s) + 4OH^-$ | -2.33 −2.33 |
| $Al(OH)_3(s) + 3e^- \rightleftarrows Al(s) + 3OH^-$ | -2.31 −2.31 |
| H2(g) + 2e− ⇄ 2H− | -2.25 −2.25 |
| Ac3+ + 3e− ⇄ Ac(s) | -2.20 −2.20 |
| Be2+ + 2e− ⇄ Be(s) | -1.85 −1.85 |
| U3+ + 3e− ⇄ U(s) | -1.66 −1.66 |
| Al3+ + 3e− ⇄ Al(s) | -1.66 −1.66 |
| Ti2+ + 2e− ⇄ Ti(s) | -1.63 −1.63 |
| ZrO2(s) + 4H+ + 4e− ⇄ Zr(s) + 2H2O | -1.553 −1.553 |
| Zr4+ + 4e− ⇄ Zr(s) | -1.45 −1.45 |
| TiO(s) + 2H+ + 2e− ⇄ Ti(s) + H2O | -1.31 −1.31 |
| Ti2O3(s) + 2H+ + 2e− ⇄ 2TiO(s) + H2O | -1.23 −1.23 |
| $Ti^{3+} + 3e^- \rightleftarrows Ti(s)$ | -1.21 −1.21 |
| Mn2+ + 2e− ⇄ Mn(s) | -1.185 −1.185 |
| Te(s) + 2e− ⇄ Te2− | -1.143 −1.143 |
| V2+ + 2e− ⇄ V(s) | -1.13 −1.13 |
| Nb3+ + 3e− ⇄ Nb(s) | -1.099 −1.099 |
| Sn(s) + 4H+ + 4e− ⇄ SnH4(g) | -1.07 −1.07 |
| SiO2(s) + 4H+ + 4e− ⇄ Si(s) + 2H2O | -0.91 −0.91 |
| B(OH)3(aq) + 3H+ + 3e− ⇄ B(s) + 3H2O | -0.89 −0.89 |
| $TiO^{2+} + 2H^+ + 4e^- \rightleftarrows Ti(s) + H_2O$ | -0.86 −0.86 |
| $Bi(s) + 3H^+ + 3e^- \rightleftarrows BiH_3$ | -0.8 −0.8 |
| H2H2O + 2e− ⇄ H2(g) + 2OH− | -0.8277 −0.8277 |
| Zn2+ + 2e− ⇄ Zn(Hg) | -0.7628 −0.7628 |
| Zn2+ + 2e− ⇄ Zn(s) | -0.7618 −0.7618 |
| $Ta_2O_5(s) + 10H^+ + 10e^- \rightleftarrows 2Ta(s) + 5H_2O$ | -0.75 −0.75 |
| Cr3+ + 3e− ⇄ Cr(s) | -0.74 −0.74 |
| Au[Au(CN)2]− + e− ⇄ Au(s) + 2CN− | -0.60 −0.60 |
| $Ta^{3+} + 3e^- \rightleftarrows Ta(s)$ | -0.6 −0.6 |
| $PbO(s) + H_2O + 2e^- \rightleftarrows Pb(s) + 2OH^-$ | -0.58 −0.58 |
| Ti2$TiO_2(s) + 2H^+ + 2e^- \rightleftarrows Ti_2O_3(s) + H_2O$ | -0.56 −0.56 |
| Ga3+ + 3e− ⇄ Ga(s) | -0.53 −0.53 |
| $U^{4+} + e^- \rightleftarrows U^{3+}$ | -0.52 −0.52 |
| P $H_3PO_2(aq) + H^+ + e^- \rightleftarrows P(white^{[8]}) + 2H_2O$ | -0.508 −0.508 |
| P $H_3PO_3(aq) + 2H^+ + 2e^- \rightleftarrows H_3PO_2(aq) + H_2O$ | -0.499 −0.499 |
| P $H_3PO_3(aq) + 3H^+ + 3e^- \rightleftarrows P(red)^{[8]} + 3H_2O$ | -0.454 −0.454 |
| Fe2+ + 2e− ⇄ Fe(s) | -0.44 −0.44 |
| C2$CO_2(g) + 2H^+ + 2e^- \rightleftarrows HOOCCOOH(aq)$ | -0.43 −0.43 |
| $Cr^{3+} + e^- \rightleftarrows Cr^{2+}$ | -0.42 −0.42 |
| Cd2+ + 2e− ⇄ Cd(s) | -0.40 −0.40 |
| GeO2(s) + 2H+ + 2e− ⇄ GeO(s) + H2O | -0.37 −0.37 |
| Cu2O(s) + H2O + 2e− ⇄ 2Cu(s) + 2OH− | -0.360 −0.360 |
| $PbSO_4(s) + 2e^- \rightleftarrows Pb(s) + SO_4^{2-}$ | -0.3588 −0.3588 |
| $PbSO_4(s) + 2e^- \rightleftarrows Pb(Hg) + SO_4^{2-}$ | -0.3505 −0.3505 |
| Eu3+ + e− ⇄ Eu2+ | -0.35 −0.35 |
| In3+ + 3e− ⇄ In(s) | -0.34 −0.34 |
| Tl+ + e− ⇄ Tl(s) | -0.34 −0.34 |
| Ge(s) + 4H+ + 4e− ⇄ GeH4(g) | -0.29 −0.29 |
| Co2+ + 2e− ⇄ Co(s) | -0.28 −0.28 |
| P H3PO4(aq) + 2H+ + 2e− ⇄ H3PO3(aq) + H2O | -0.276 −0.276 |
| $V^{3+} + e^- \rightleftarrows V^{2+}$ | -0.26 −0.26 |
| Ni2+ + 2e− ⇄ Ni(s) | -0.25 −0.25 |
| $As(s) + 3H^+ + 3e^- \rightleftarrows AsH_3(g)$ | -0.23 −0.23 |
| MoO2(s) + 4H+ + 4e− ⇄ Mo(s) + 2H2O | -0.15 −0.15 |
| Si(s) + 4H+ + 4e− ⇄ SiH4(g) | -0.14 −0.14 |
| $Sn^{2+} + 2e^- \rightleftarrows Sn(s)$ | -0.13 −0.13 |
| O2(g) + H+ + e− ⇄ HO2•(aq) | -0.13 −0.13 |
| Pb2+ + 2e− ⇄ Pb(s) | -0.13 −0.13 |
| $WO_2(s) + 4H^+ + 4e^- \rightleftarrows W(s) + 2H_2O$ | -0.12 −0.12 |
| $P(red) + 3H^+ + 3e^- \rightleftarrows PH_3(g)$ | -0.111 −0.111 |
| C $CO_2(g) + 2H^+ + 2e^- \rightleftarrows HCOOH(aq)$ | -0.11 −0.11 |
| Se(s) + 2H+ + 2e− ⇄ H2Se(g) | -0.11 −0.11 |
| C $CO_2(g) + 2H^+ + 2e^- \rightleftarrows CO(g) + H_2O$ | -0.11 −0.11 |
| SnO(s) + 2H+ + 2e− ⇄ Sn(s) + H2O | -0.10 −0.10 |
| SnO2(s) + 2H+ + 2e− ⇄ SnO(s) + H2O | -0.09 −0.09 |
| WO3(aq) + 6H+ + 6e− ⇄ W(s) + 3H2O | -0.09 −0.09 |
| $P(white) + 3H^+ + 3e^- \rightleftarrows PH_3(g)$ | -0.063 −0.063 |
| C HCOOH(aq) + 2H+ + 2e− ⇄ HCHO(aq) + H2O | -0.03 −0.03 |
| H $2H^+ + 2e^- \rightleftarrows H_2(g)$ | 0.0000 |
| $S_4O_6^{2-} + 2e^- \rightleftarrows 2S_2O_3^{2-}$ | +0.08 |
| Fe3O4(s) + 8H+ + 8e− ⇄ 3Fe(s) + 4H2O | +0.085 |
| $N_2(g) + 2H_2O + 6H^+ + 6e^- \rightleftarrows 2NH_4OH(aq)$ | +0.092 |
| HgO(s) + H2O + 2e− ⇄ Hg(l) + 2OH− | +0.0977 |
| $Cu(NH_3)_4^{2+} + e^- \rightleftarrows Cu(NH_3)_2^+ + 2NH_3$ | +0.10 |
| Ru(NH3)63+ + e− ⇄ Ru(NH3)62+ | +0.10 |
| N2H4(aq) + 4H2O + 2e− ⇄ 2NH4+ + 4OH− | +0.11 |
| Mo H2MoO4(aq) + 6H+ + 6e− ⇄ Mo(s) + 4H2O | +0.11 |
| $Ge^{4+} + 4e^- \rightleftarrows Ge(s)$ | +0.12 |
| $C(s) + 4H^+ + 4e^- \rightleftarrows CH_4(g)$ | +0.13 |
| C $HCHO(aq) + 2H^+ + 2e^- \rightleftarrows CH_3OH(aq)$ | +0.13 |
| S(s) + 2H+ + 2e− ⇄ H2S(g) | +0.14 |
| $Sn^{4+} + 2e^- \rightleftarrows Sn^{2+}$ | +0.15 |
| Cu2+ + e− ⇄ Cu+ | +0.159 |
| S $HSO_4^- + 3H^+ + 2e^- \rightleftarrows SO_2(aq) + 2H_2O$ | +0.16 |
| UO22+ + e− ⇄ UO2+ | +0.163 |
| S $SO_4^{2-} + 4H^+ + 2e^- \rightleftarrows SO_2(aq) + 2H_2O$ | +0.17 |
| $TiO^{2+} + 2H^+ + e^- \rightleftarrows Ti^{3+} + H_2O$ | +0.19 |
| $Bi^{3+} + 2e^- \rightleftarrows Bi^+$ | +0.2 |
| $SbO^+ + 2H^+ + 3e^- \rightleftarrows Sb(s) + H_2O$ | +0.20 |
| As $H_3AsO_3(aq) + 3H^+ + 3e^- \rightleftarrows As(s) + 3H_2O$ | +0.24 |
| $GeO(s) + 2H^+ + 2e^- \rightleftarrows Ge(s) + H_2O$ | +0.26 |
| $UO_2^+ + 4H^+ + e^- \rightleftarrows U^{4+} + 2H_2O$ | +0.273 |
| $Re^{3+} + 3e^- \rightleftarrows Re(s)$ | +0.300 |
| $Bi^{3+} + 3e^- \rightleftarrows Bi(s)$ | +0.32 |
| $VO^{2+} + 2H^+ + e^- \rightleftarrows V^{3+} + H_2O$ | +0.34 |
| $Cu^{2+} + 2e^- \rightleftarrows Cu(s)$ | +0.340 |
| Fe $[Fe(CN)_6]^{3-} + e^- \rightleftarrows [Fe(CN)_6]^{4-}$ | +0.36 |
| $O_2(g) + 2H_2O + 4e^- \rightleftarrows 4OH^-(aq)$ | +0.40 |
| Mo $H_2MoO_4 + 6H^+ + 3e^- \rightleftarrows Mo^{3+} + 2H_2O$ | +0.43 |
| $Bi^+ + e^- \rightleftarrows Bi(s)$ | +0.50 |
| C $CH_3OH(aq) + 2H^+ + 2e^- \rightleftarrows CH_4(g) + H_2O$ | +0.50 |
| S $SO_2(aq) + 4H^+ + 4e^- \rightleftarrows S(s) + 2H_2O$ | +0.50 |
| $Cu^+ + e^- \rightleftarrows Cu(s)$ | +0.520 |
| C CO(g) + 2H+ + 2e− ⇄ C(s) + H2O | +0.52 |
| I2(s) + 2e− ⇄ 2I− | +0.54 |
| $I_3^- + 2e^- \rightleftarrows 3I^-$ | +0.53 |
| Au $[AuI_4]^- + 3e^- \rightleftarrows Au(s) + 4I^-$ | +0.56 |
| As $H_3AsO_4(aq) + 2H^+ + 2e^- \rightleftarrows H_3AsO_3(aq) +$ | +0.56 |
| Au $[AuI_2]^- + e^- \rightleftarrows Au(s) + 2I^-$ | +0.58 |
| $MnO_4^- + 2H_2O + 3e^- \rightleftarrows MnO_2(s) + 4OH^-$ | +0.59 |
| $S_2O_3^{2-} + 6H^+ + 4e^- \rightleftarrows 2S(s) + 3H_2O$ | +0.60 |
| Mo $H_2MoO_4(aq) + 2H^+ + 2e^- \rightleftarrows MoO_2(s) +$ | +0.65 |
| $O_2(g) + 2H^+ + 2e^- \rightleftarrows H_2O_2(aq)$ | +0.70 |
| $Tl^{3+} + 3e^- \rightleftarrows Tl(s)$ | +0.72 |
| $PtCl_6^{2-} + 2e^- \rightleftarrows PtCl_4^{2-} + 2Cl^-$ | +0.726 |
| Se $H_2SeO_3(aq) + 4H^+ + 4e^- \rightleftarrows Se(s) + 3H_2O$ | +0.74 |
| $PtCl_4^{2-} + 2e^- \rightleftarrows Pt(s) + 4Cl^-$ | +0.758 |
| $Fe^{3+} + e^- \rightleftarrows Fe^{2+}$ | +0.77 |
| Ag+ + e− ⇄ Ag(s) | +0.7996 |
| Hg22+ + 2e− ⇄ 2Hg(l) | +0.80 |
| $MnO_4^- + H^+ + e^- \rightleftarrows HMnO_4^-$ | +0.90 |
| Hg $2Hg^{2+} + 2e^- \rightleftarrows Hg_2^{2+}$ | +0.91 |
| Pd2+ + 2e− ⇄ Pd(s) | +0.915 |
| Au $[AuCl_4]^- + 3e^- \rightleftarrows Au(s) + 4Cl^-$ | +0.93 |
| $MnO_2(s) + 4H^+ + e^- \rightleftarrows Mn^{3+} + 2H_2O$ | +0.95 |
| Au $[AuBr_2]^- + e^- \rightleftarrows Au(s) + 2Br^-$ | +0.96 |
| $Br_2(l) + 2e^- \rightleftarrows 2Br^-$ | +1.066 |
| $Br_2(aq) + 2e^- \rightleftarrows 2Br^-$ | +1.0873 |
| Au $[AuCl_2]^- + e^- \rightleftarrows Au(s) + 2Cl^-$ | +1.15 |
| $Ag_2O(s) + 2H^+ + 2e^- \rightleftarrows 2Ag(s) + H_2O$ | +1.17 |
| $ClO_3^- + 2H^+ + e^- \rightleftarrows ClO_2(g) + H_2O$ | +1.18 |
| Pt2+ + 2e− ⇄ Pt(s) | +1.188 |
| $ClO_2(g) + H^+ + e^- \rightleftarrows HClO_2(aq)$ | +1.19 |
| I $2IO_3^- + 12H^+ + 10e^- \rightleftarrows I_2(s) + 6H_2O$ | +1.20 |
| $ClO_4^- + 2H^+ + 2e^- \rightleftarrows ClO_3^- + H_2O$ | +1.20 |
| $O_2(g) + 4H^+ + 4e^- \rightleftarrows 2H_2O$ | +1.23 |
| $MnO_2(s) + 4H^+ + 2e^- \rightleftarrows Mn^{2+} + 2H_2O$ | +1.23 |
| $Tl^{3+} + 2e^- \rightleftarrows Tl^+$ | +1.25 |
| $Cl_2(g) + 2e^- \rightleftarrows 2Cl^-$ | +1.36 |
| $Cr_2O_7^{--} + 14H^+ + 6e^- \rightleftarrows 2Cr^{3+} + 7H_2O$ | +1.33 |
| $CoO_2(s) + 4H^+ + e^- \rightleftarrows Co^{3+} + 2H_2O$ | +1.42 |
| N $2NH_3OH^+ + H^+ + 2e^- \rightleftarrows N_2H_5^+ + 2H_2O$ | +1.42 |
| I $2HIO(aq) + 2H^+ + 2e^- \rightleftarrows I_2(s) + 2H_2O$ | +1.44 |
| $Ce^{4+} + e^- \rightleftarrows Ce^{3+}$ | +1.44 |
| $BrO_3^- + 5H^+ + 4e^- \rightleftarrows HBrO(aq) + 2H_2O$ | +1.45 |
| PbO $\alpha$-$PbO_2(s) + 4H^+ + 2e^- \rightleftarrows Pb^{2+} + 2H_2O$ | +1.468 |
| Br $2BrO_3^- + 12H^+ + 10e^- \rightleftarrows Br_2(l) + 6H_2O$ | +1.48 |
| Cl $2ClO_3^- + 12H^+ + 10e^- \rightleftarrows Cl_2(g) + 6H_2O$ | +1.49 |
| $MnO_4^- + 8H^+ + 5e^- \rightleftarrows Mn^{2+} + 4H_2O$ | +1.51 |
| O $HO_2^\bullet + H^+ + e^- \rightleftarrows H_2O_2(aq)$ | +1.51 |
| $Au^{3+} + 3e^- \rightleftarrows Au(s)$ | +1.52 |
| $NiO_2(s) + 4H^+ + 2e^- \rightleftarrows Ni^{2+} + 2OH^-$ | +1.59 |
| $Ag_2O_3(s) + 6H^+ + 4e^- \rightleftarrows 2Ag^+ + 3H_2O$ | +1.67 |
| Cl $HClO_2(aq) + 2H^+ + 2e^- \rightleftarrows HClO(aq) + H_2O$ | +1.67 |
| $Pb^{4+} + 2e^- \rightleftarrows Pb^{2+}$ | +1.69 |
| $MnO_4^- + 4H^+ + 3e^- \rightleftarrows MnO_2(s) + 2H_2O$ | +1.70 |

# Deviations from STP



- $v_o O + ne^- \leftrightarrow v_R R$
- $\Delta G = \Delta G^o + RT\ln\left[\frac{a_R^{\nu_R}}{a_o^{\nu_o}}\right]$



## Nernst Equation

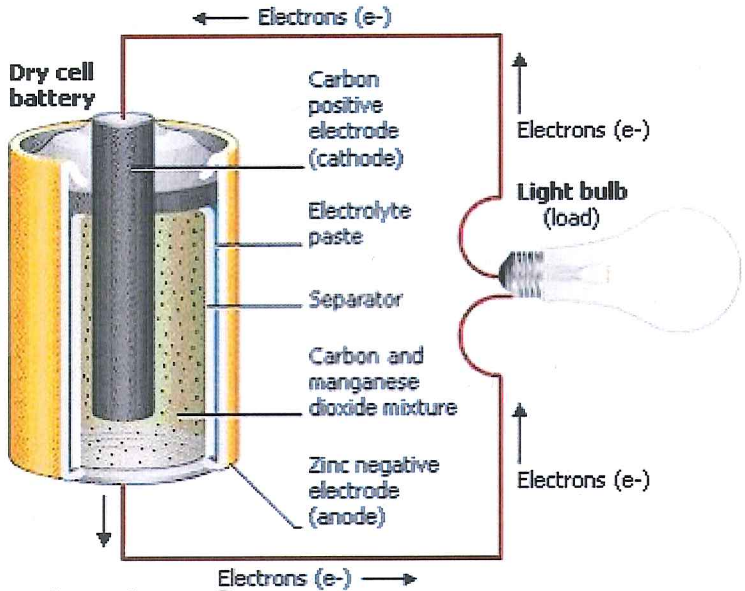
- $E_{eq} = E^{o'} + \frac{RT}{nF}\ln\left[\frac{C_o^{\nu_o}}{C_R^{\nu_R}}\right]$

  or

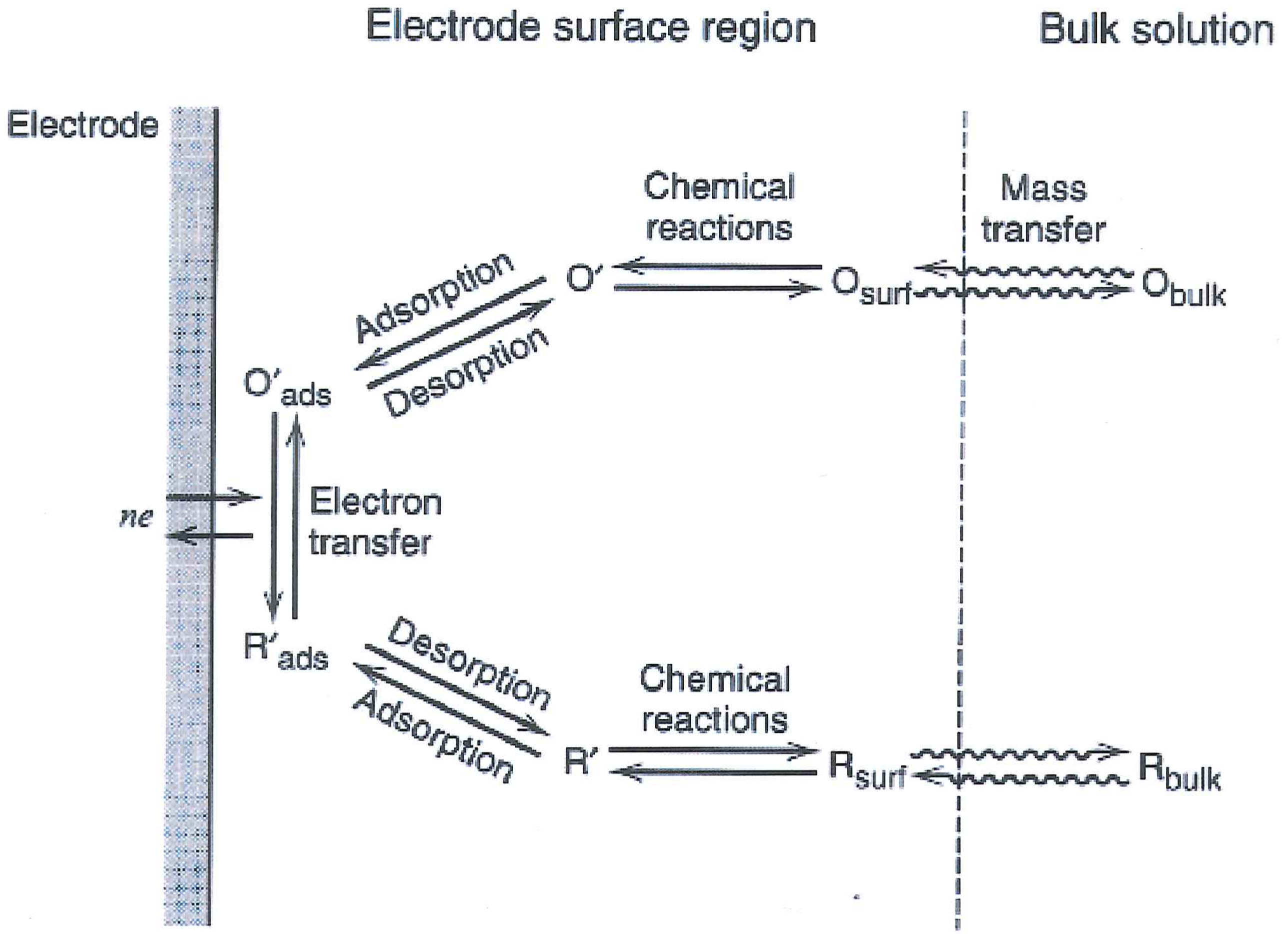
- $E_{eq} = E^{o'} + \frac{RT}{nF}\ln\left[\frac{P_o^{\nu_o}}{P_R^{\nu_R}}\right]$

# The E Word?

- Equilibrium
  - $v_o O + ne^- \leftrightarrow v_R R$
  - Implies no net reaction
    - How much current is that?
      - Is that useful?
    - What if we want to power a device?
      - Provide Electrochemical driving force
        - Electrode potentials deviate from Nernst potential, $E_{eq}$
    - There will be a i-V relationship characteristic to cell design



# What fundamental processes influence the i-V relationship in an electrochemical cell?



- Kinetics
- Mass Transfer

# Kinetics

- Chemical Kinetics
    - Rate expression
    - Free energy change vs. reaction coordinate
- Electrochemical Kinetics
    - Analogy with chemical kinetics
    - Effect of surface potential
    - Current-Overpotential Equation
        - Butler-Volmer Kinetics

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

Assume: Elementary RXN kinetics

$$r_f = k_f^* C_A$$

$$r_b = k_b^* C_B$$

where $k_i^* = k_i \exp\left[-\frac{E_{A,i}}{RT}\right]$

: meaning of $k^*$: $\frac{\#\text{ of collisions}}{\text{time}} \cdot$ probability RXN occurs

units: $s^{-1}$

$$r_T = k_f \exp\left[\frac{-E_{A,f}}{RT}\right] C_A - k_b \exp\left[\frac{-E_{A,b}}{RT}\right] C_B$$

Units: $\frac{1}{s} \cdot \frac{mol}{cm^3} = \frac{mol}{cm^3 \cdot s}$

↓

Homogeneous RXNs scale w/volume

@ Equilibrium: $r_T = 0$

$$\therefore\ k_f \exp\left[\frac{-E_{A,f}}{RT}\right] C_A = k_b \exp\left[\frac{-E_{A,b}}{RT}\right] C_B = \nu_0$$

↓

$\nu_0 \equiv$ exchange velocity

↓

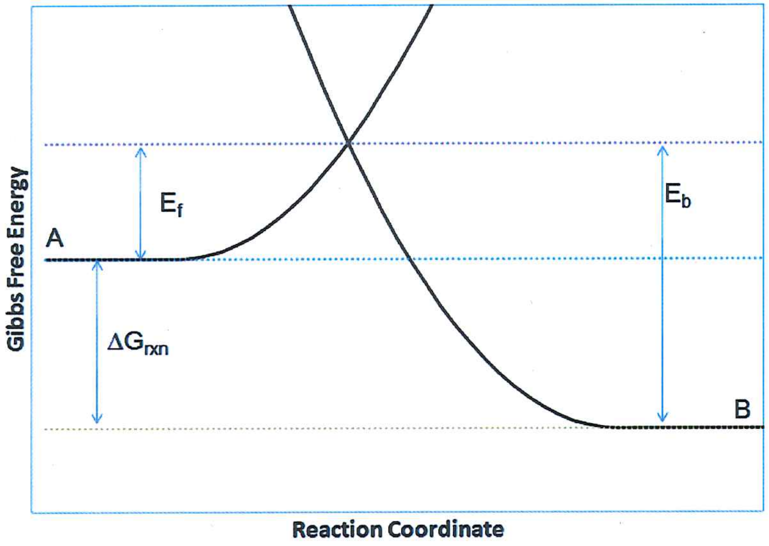
rate the RXNs occur @ equilibrium

↓

magnitude of $\nu_0$ indicates if kinetics are "fast" or "slow"

# Simple, 1st Order Reaction

- $A \underset{k_b}{\overset{k_f}{\longleftrightarrow}} B$
- $r_T = r_f - r_b = k_f C_A - k_b C_b$
  - $k_f = exp\left[\frac{-E_f}{RT}\right]$
  - $k_b = exp\left[\frac{-E_b}{RT}\right]$



- $r_T = k_f \exp\left[\frac{-E_f}{RT}\right] C_A - k_b \exp\left[\frac{-E_b}{RT}\right] C_b$
- At Equilibrium, $r_T$=0
  - $k_f C_A = k_b C_b = \upsilon_o$
    - $\upsilon_o$ is the exchange velocity

# Application to electrochemical systems:

$$O + ne^- \rightleftharpoons R$$

→ remember, we are @ one electrode, NOT the full cell

$$r_T = \frac{i}{nFA} = k_f \exp\left[\frac{-E_{A,f}}{RT}\right] \underbrace{C_O\Big|_{x=0}}_{\downarrow} - k_b \exp\left[\frac{-E_{A,b}}{RT}\right] C_R\Big|_{x=0}$$

@ electrode surface

So, what does k mean here?

$$k \sim \frac{\text{\# of molecules near surface}}{\text{size of surface}} \cdot \frac{\text{\# of collisions}}{\text{time}} \cdot \text{probability}$$

$$\frac{cm^3}{cm^2} \cdot s^{-1}$$

$$k \text{ units: } \frac{cm^3}{cm^2} \cdot \frac{1}{s} = \frac{cm}{s}$$

$$\text{overall: } \underset{\uparrow \atop k}{\frac{cm}{s}} \cdot \underset{\uparrow \atop C_i}{\frac{mol}{cm^3}} = \frac{mol}{cm^2 \cdot s}$$

$$\text{units check: } \frac{i}{nFA} = \frac{\frac{C}{s}}{\frac{mole^-}{mol} \cdot \frac{C}{mole^-} \cdot cm^2} = \frac{mol}{cm^2 \cdot s}$$

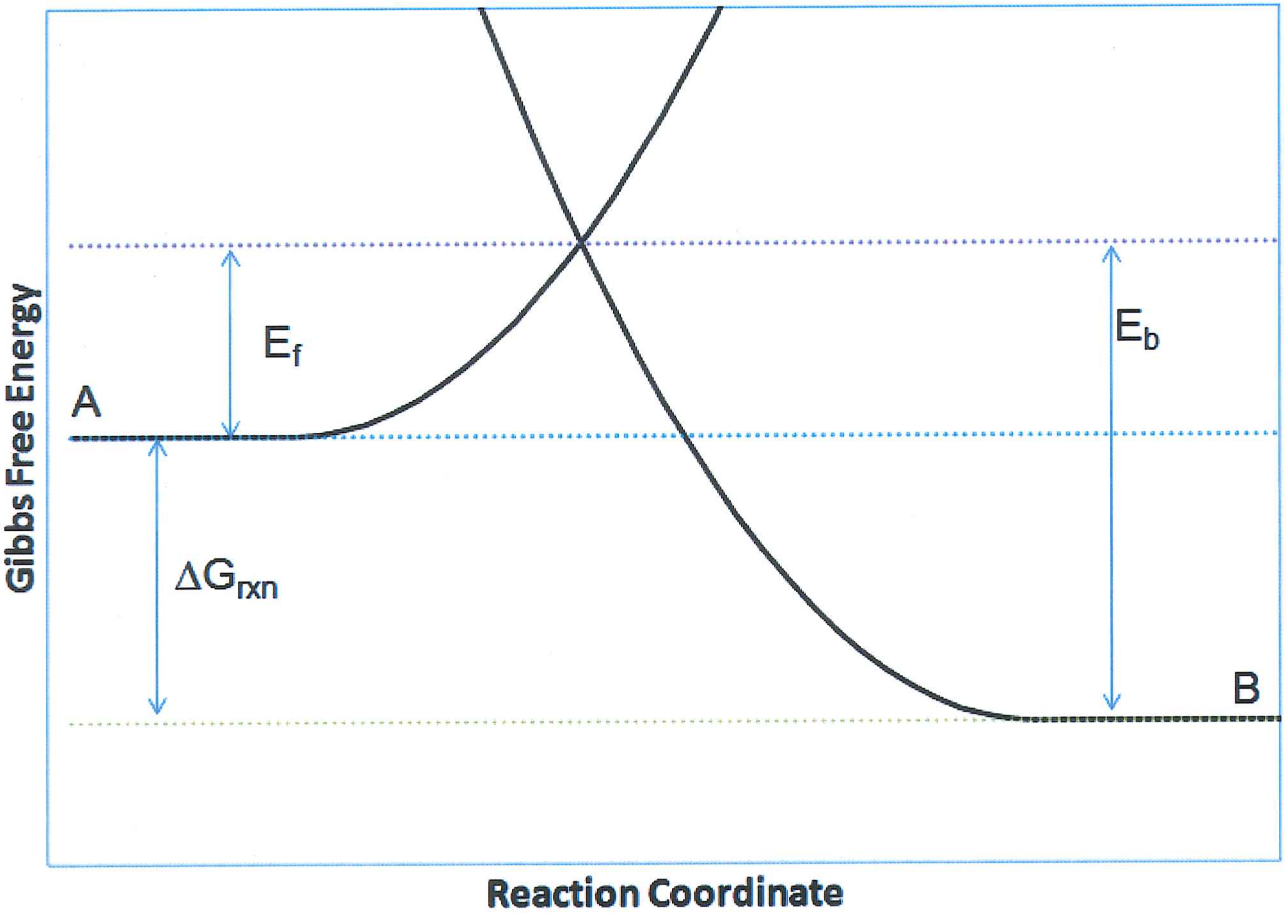
# Electrochemical Kinetics

- $O + ne^- \leftrightarrow R$
  - $r_T = \frac{i}{nFA} = k_f \exp\left[\frac{-E_f}{RT}\right] C_O(x=0) - k_b \exp\left[\frac{-E_b}{RT}\right] C_R(x=0)$
- Three cases:
  - $E = E_{eq}$, $i = 0$
  - $E > E_{eq}$ , $i = ?$
  - $E < E_{eq}$ , $i = ?$
- How does the electrode potential affect the surface free energy?

↳ Activation Energy
→ I'll show you how

# $E = E_{eq}$

$$O + ne^- \leftrightarrow R$$
$$\Delta G = -nFE$$

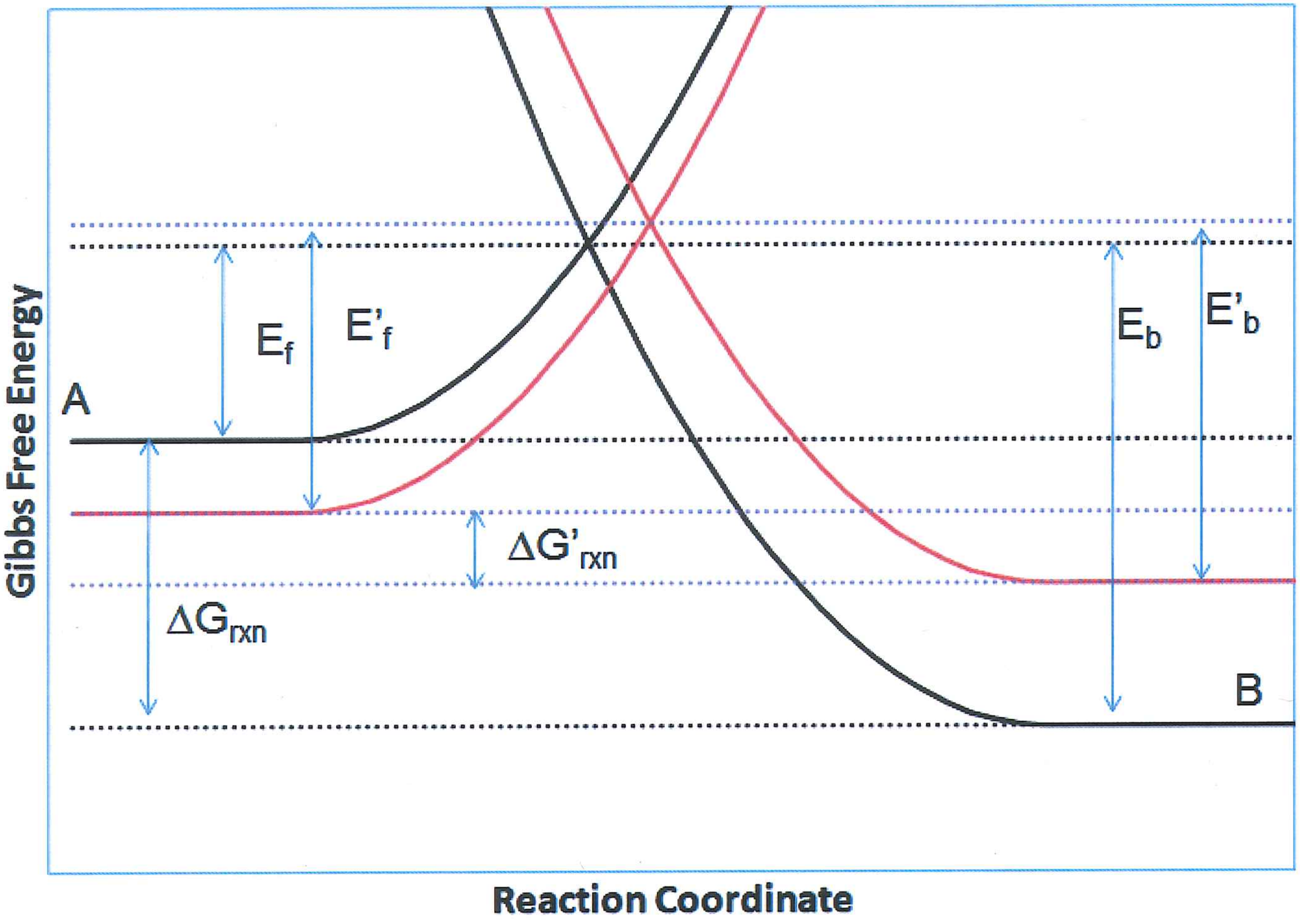


- $$\frac{i}{nFA} = k_f \exp\left[\frac{-E_f}{RT}\right] C_A(x=0) - k_b \exp\left[\frac{-E_b}{RT}\right] C_b(x=0) = 0$$

# $E > E_{eq}$

→ changing Surface E, impacts surface free energy

$O + ne^- \leftrightarrow R$
$\Delta G = -nFE$



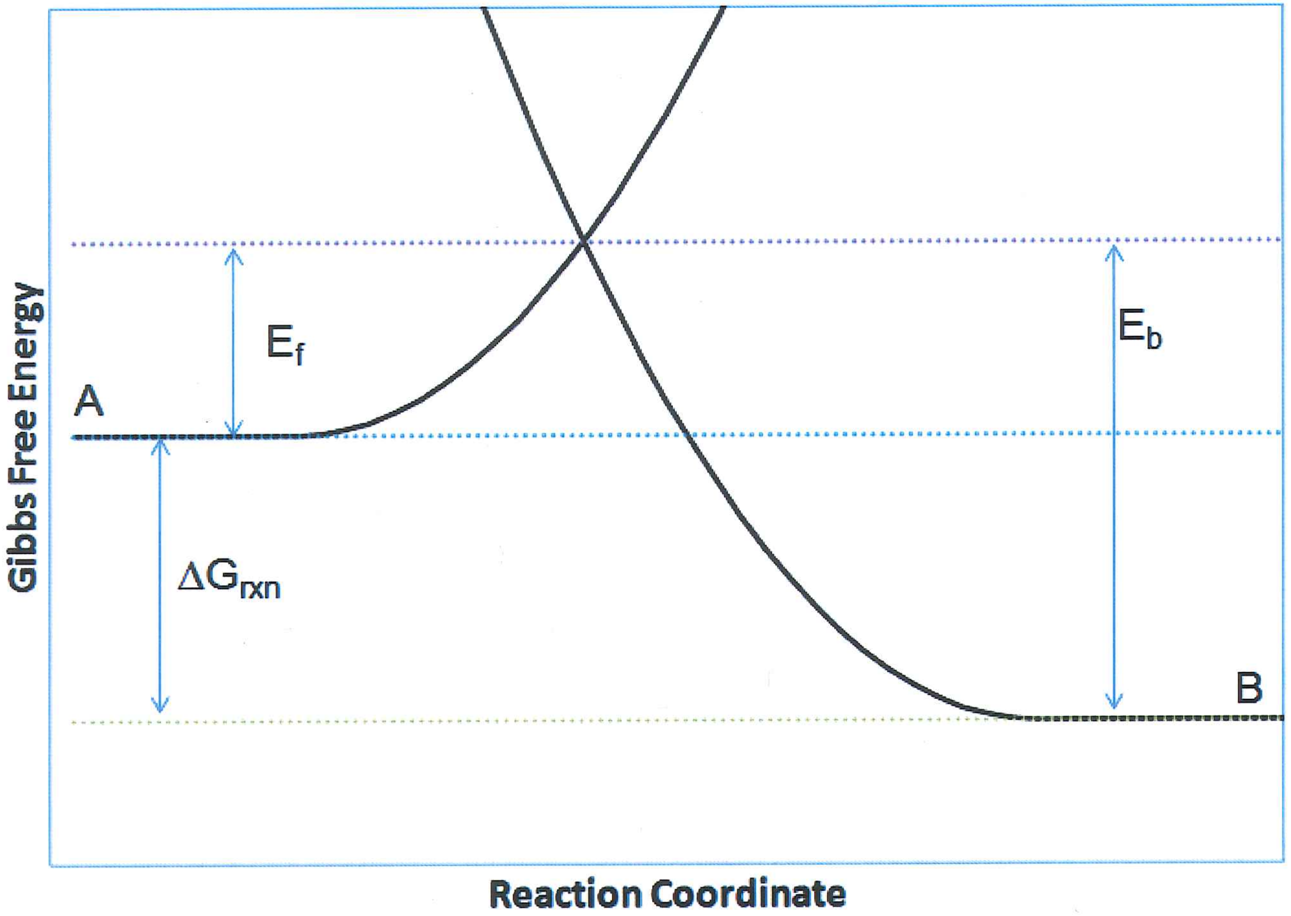
relative to the surface
↑

# Results: $E > E_{eq}$

- $E'_f > E_f$
- $E'_b < E_b$
- $$\frac{i}{nFA} = k_f \exp\left[\frac{-E_f'}{RT}\right] C_A(x=0) - k_b \exp\left[\frac{-E_b'}{RT}\right] C_b(x=0)$$
- Oxidation (anode)

# $E = E_{eq}$

$$O + ne^- \leftrightarrow R$$
$$\Delta G = -nFE$$

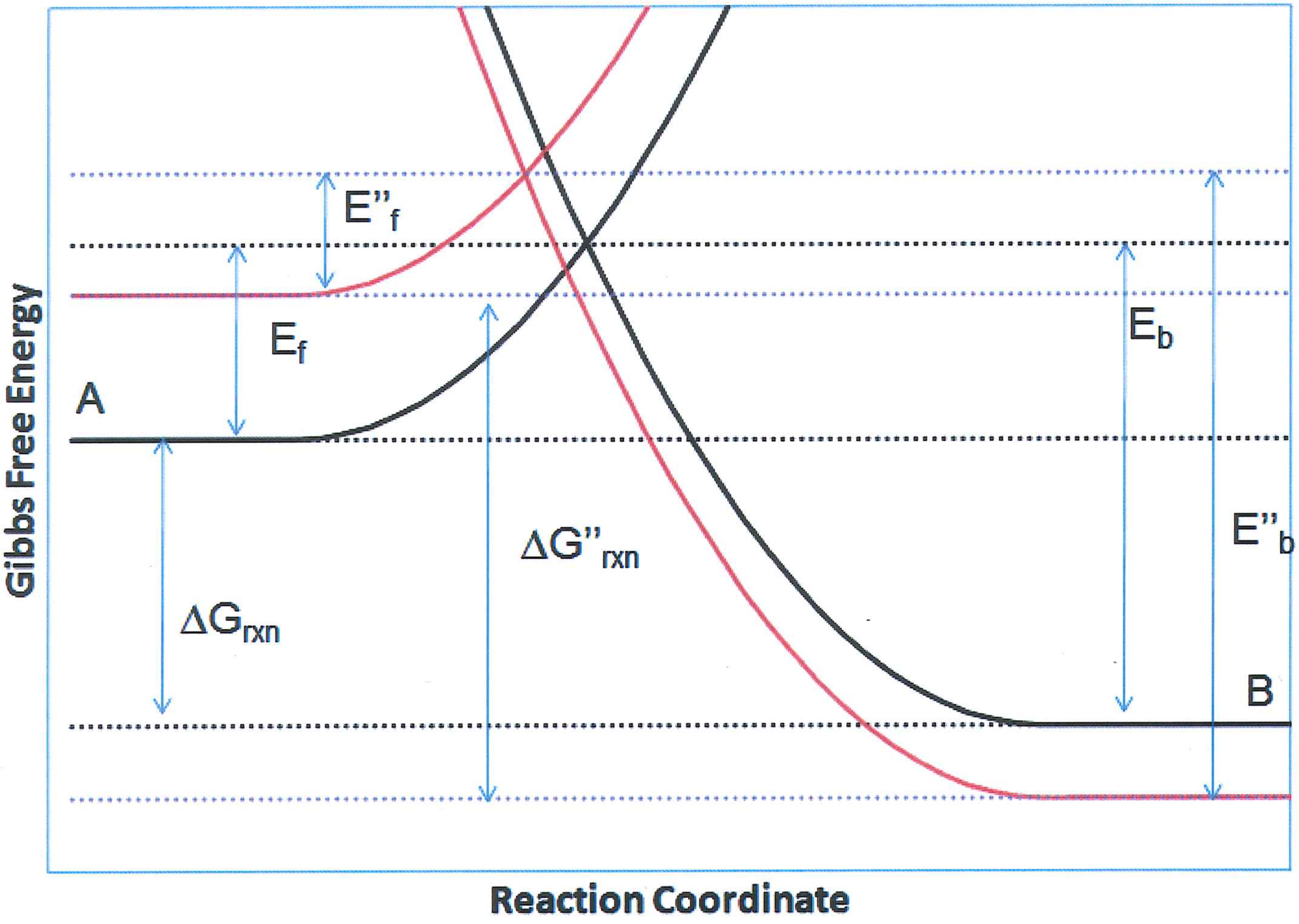


- $$\frac{i}{nFA} = k_f \exp\left[\frac{-E_f}{RT}\right] C_A(x=0) - k_b \exp\left[\frac{-E_b}{RT}\right] C_b(x=0) = 0$$

# $E < E_{eq}$

$O + ne^- \leftrightarrow R$
$\Delta G = -nFE$

Again, relative to surface



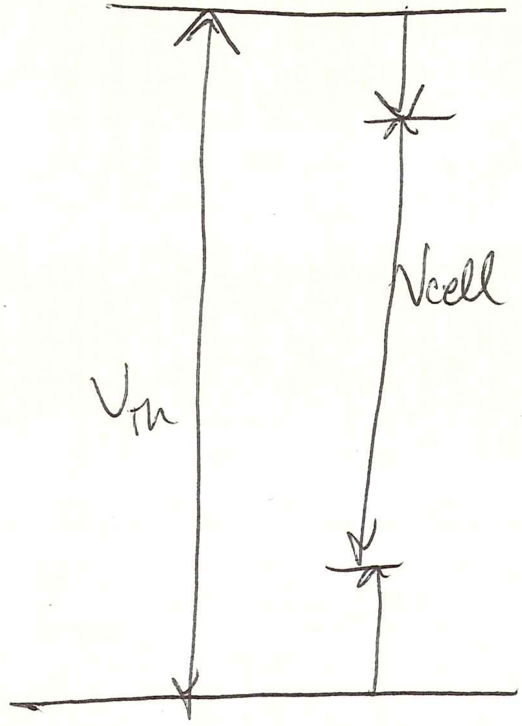
# Results: $E < E_{eq}$

- $E''_f < E_f$
- $E''_b > E_b$
- $$\frac{i}{nFA} = k_f \exp\left[\frac{-E_f''}{RT}\right] C_A(x=0) - k_b \exp\left[\frac{-E_b''}{RT}\right] C_b(x=0)$$
- Reduction (cathode)

# What does this mean for a real device?

- We have our thermodynamic limitation, which give the maximum attainable cell voltage
  - $V_{Thermo} = E^{eq}_{c} - E^{eq}_{a}$
  - At cathode: $E < E_{eq}$
  - At anode: $E > E_{eq}$

- $V_{cell} < V_{thermo}$
  - For a “galvanic device



# How are $E_f$ and $E_f''$ Related?

- How large is the overall energy shift?
  - $\Delta G_{surface} = F(E-E_{eq})$
- How is that shared relative to reduction and oxidation?
  - $E_f'' = E_f + \alpha F(E - E_{eq})$
  - $E_b'' = E_b - (1-\alpha)F(E - E_{eq})$
    - $\alpha \equiv$ transfer coefficient (RXN & system) specific
      - $0 < \alpha < 1$
        - Perfectly reversible: $\alpha = 0.5$
        - Typical values: $0.3 < \alpha < 0.7$

# How does this impact expressions for the forward and reverse reactions?

- $r_f = k_f \exp\left[\frac{-E_f''}{RT}\right]\exp\left[\frac{-\alpha F}{RT}\left(E - E_{eq}\right)\right]C_o(x=0)$

  $r_b = k_b \exp\left[\frac{-E_b''}{RT}\right]\exp\left[\frac{(1-\alpha)F}{RT}\left(E - E_{eq}\right)\right]C_R(x=0)$

$$r_T = \frac{i}{nFA} = k_f \exp\left[\frac{-E_f''}{RT}\right]\exp\left[\frac{-\alpha F}{RT}\left(E - E_{eq}\right)\right]C_o(x=0) - k_b \exp\left[\frac{-E_b''}{RT}\right]\exp\left[\frac{(1-\alpha)F}{RT}\left(E - E_{eq}\right)\right]C_R(x=0)$$

- Remember $k_f$ & $k_b$ are linked by $\Delta G$
  - We can combine those into a single $k^*$…..

# Current-Potential Equation

- …. and find a common exchange velocity, $i_o$, called the “exchange current”
  - $i_o \equiv nFAk^* C_O^{1-\alpha} C_R^{\alpha}$
- Final Rate Equation:

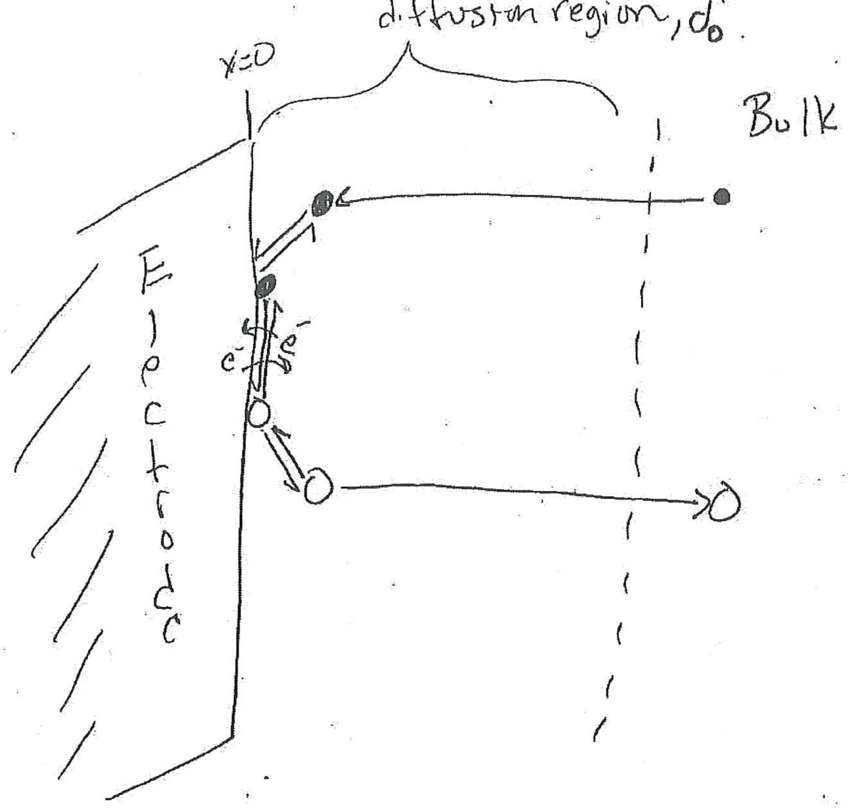
$$i = i_o\left( \exp\left[\frac{-\alpha F}{RT}\left(E - E_{eq}\right)\right]\frac{C_o(x=0)}{C_o^*} - \exp\left[\frac{(1-\alpha)F}{RT}\left(E - E_{eq}\right)\right]\frac{C_R(x=0)}{C_R^*} \right)$$

- With no Mass Transfer Effects ($C = C^*$):

$$i = i_o\left( \exp\left[\frac{-\alpha F}{RT}\left(E - E_{eq}\right)\right] - \exp\left[\frac{(1-\alpha)F}{RT}\left(E - E_{eq}\right)\right] \right)$$

# Intro to Mass Transfer –

A couple weeks ago: $O + ne^- \rightleftharpoons R$



We've spent the last few lectures discussing the reaction

But How do the reactants come to the surface?

- Diffusion → chemical potential (i.e. conc. gradient)
- Convection → natural (density gradients)
  forced (stirring)
- Migration → Movement of a charged body in an electric field

Major Takeaways so far:

1. Electrochemical cells scale w/surface area NOT volume

2. In "galvanic" cells the voltage decreases with increasing current
    - anode potential increases
    - cathode potential decreases

Let's demonstrate both of these

1. Surface area vs. volume → get power curves

A) System 1: Cu. Foil in $CuSO_4$ sln → C
Zn screw in $ZnSO_4$ sln → A
→ Ice cube tray

B) system 2: same foils, larger plastic container

C) System 3: Zn Powder/slurry electrode
Cu Powder Electrode (on Cu foil)

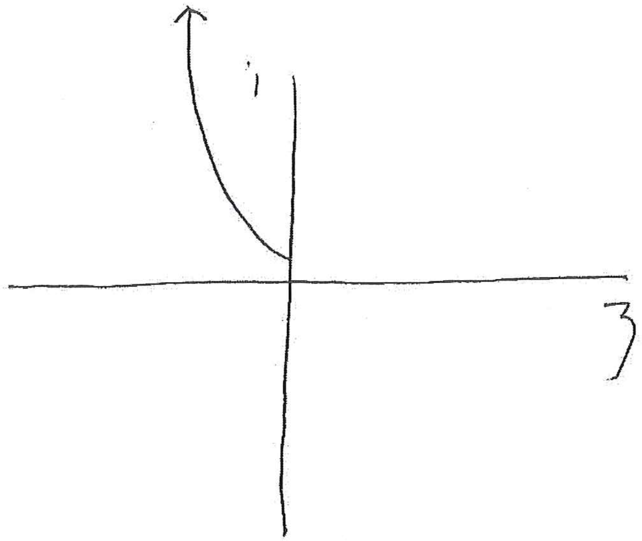
2. Measure 2 voltages in Expts A-C → one as total cell voltage
→ other vs. anode E

Mass transfr Limiting Current.

According to Kinetics w/o MT:

Bailance between kinetics + MT

$$i = i_0 \exp[-\alpha f \eta]$$



exponentially increasing function

if $i_0 = 10^{-3}$ A, $n = 1$

| $i$(A) | $\eta$(V) |
|---|---|
| 0.0025 | -0.05 |
| 0.007 | -0.1 |
| 0.049 | -0.2 |
| 0.91 | -0.35 |
| 16.8 | -0.5 |

(17)

Let's assume that the concentration gradient is linear:

$$v_{MT} = \frac{i}{nFA} = \frac{D_o[C_o^* - C_o(x=0)]}{\delta_o}$$

what is the maximum rate of mass transport?

-happens when $C_o(x=0) \simeq 0$

$$v_{MT} = \frac{i}{nFA} = \frac{D_o C_o^*}{\delta_o}$$

$$\frac{i}{nFA} = m_o C_o^*$$

$$i_{l,} = nFA\, m_o C_o^*$$

where $i_l$ is called the "limiting current"

Let's give some #'s

$n=1$, $F = 96485.3$, $A = 1\,cm^2$, $m_o = 1\,cm/s$, $C_o^* = 0.01\,M$

$0.1\,M =$

$= 10^{-5}\,mol/cm^3$

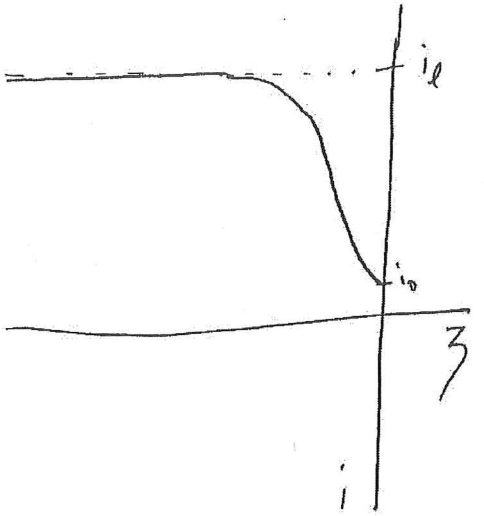
$$i_l = 0.96A$$

@ $\zeta = 0.5V$, how can

$i = 16.8A$, when $i_\ell = 0.96A$ ?

→ simply, it cannot

- So, what should it look like?



→ No matter what the overpotential is, $i$ cannot be greater than $i_\ell$

# Example 2: PEM Fuel Cell

Cathode : $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ , $E^\circ = 1.23\,V$

Anode : $H_2 \longrightarrow 2H^+ + 2e^-$ , $E^\circ = 0.0\,V$ → default

$\eta_{ORR}$ is typically 300 → 500 mV during operat.

$\eta_{H_2/H^+}$ is typically 30 → 60 mV during operat.

$$\underset{\substack{\Downarrow \\ \text{at least 3 ORDERS of MAG.}}}{i_{0\,H_2/H} \text{ is } \ggg} i_{0\,O_2/H_2O}$$

so $$V_{PEM} = \underbrace{(1.23 - 0.0)}_{V_{TH}} - |0.4| - |0.03| = 0.8\,V$$

↓

> 30% Loss in energy just to get it moving!

$\eta_c$ is not usually equal to $\eta_a$

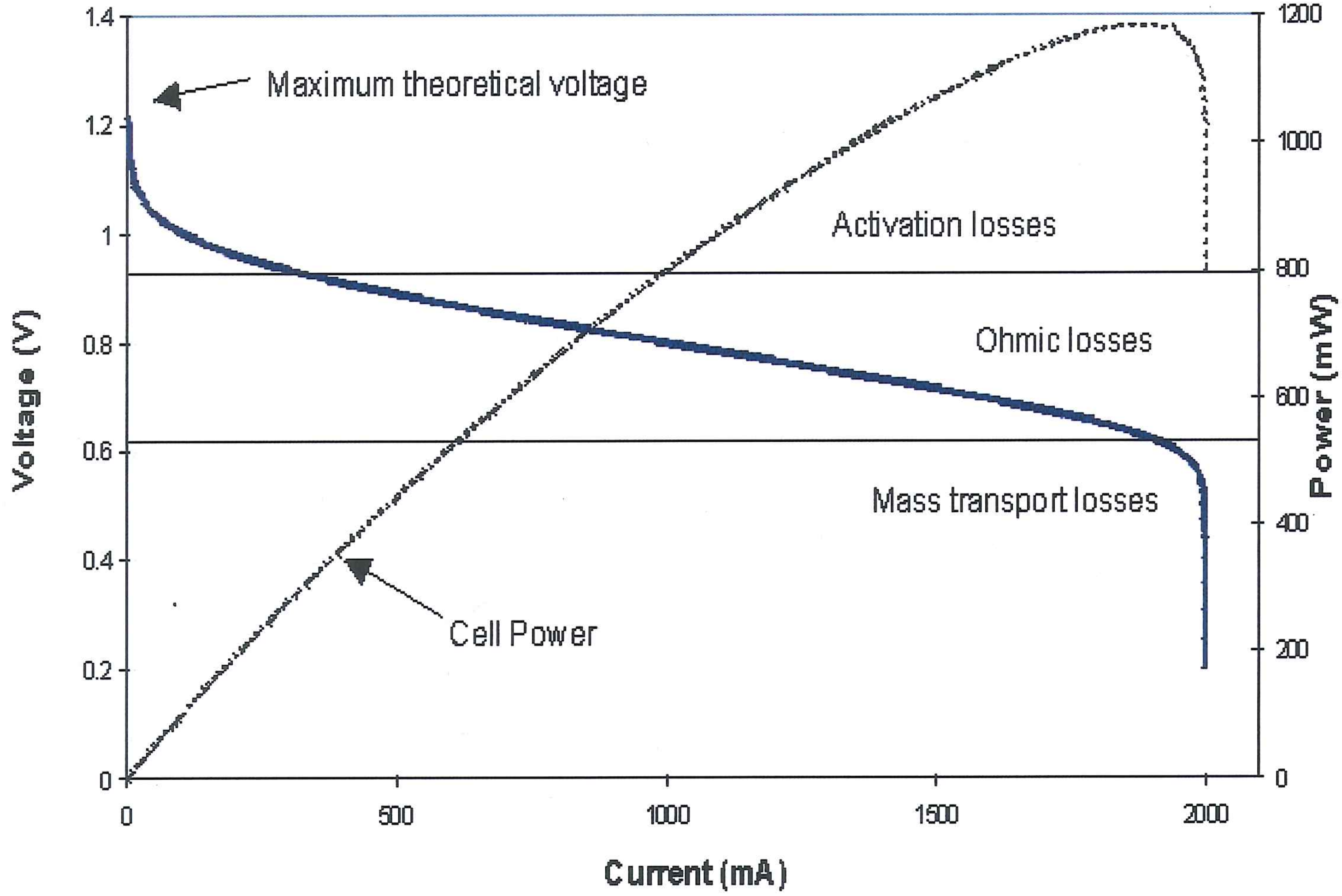
- $i_0$ will be different for the two processes!

What if we wanted to change the cell?

$$V = V_{TH} + |\eta_c| + |\eta_A|$$

In electrolytic mode, $V$ is ALWAYS $> V_{Th}$

# Example: PEM Polarization Curve



# Extra Resources

- “Electrochemical Methods: Fundamentals and Applications”, 2$^{nd}$ Edition. Allen J. Bard and Larry R. Faulkner.