CHEG 3128

Battery – 1
Electrochemical Fundamentals

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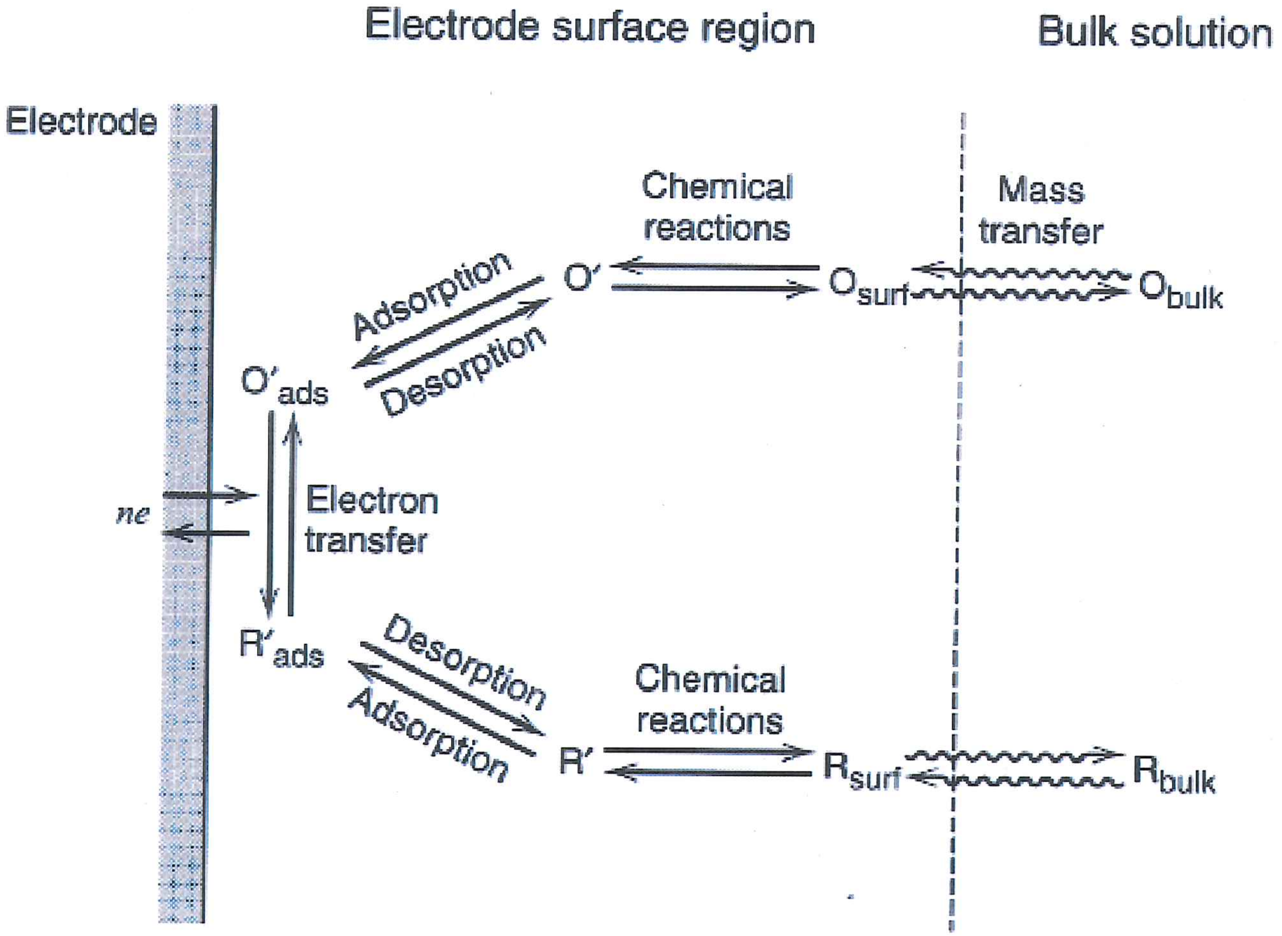
Redox Processes

- Reduction
  - Electron Accepting
    - $O + ne^- \rightarrow R$
- Oxidation
  - Electron Donating
    - $R \rightarrow O + ne^-$
- Equilibrium

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

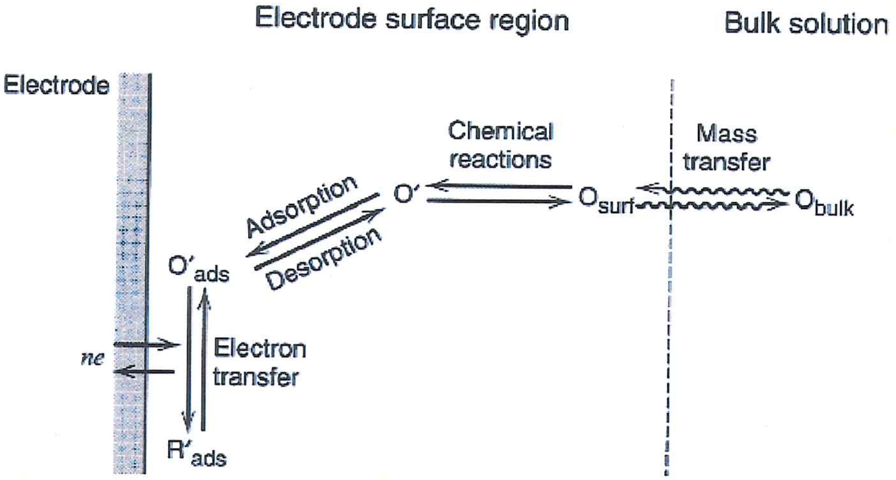
    - Always written in the reduction form

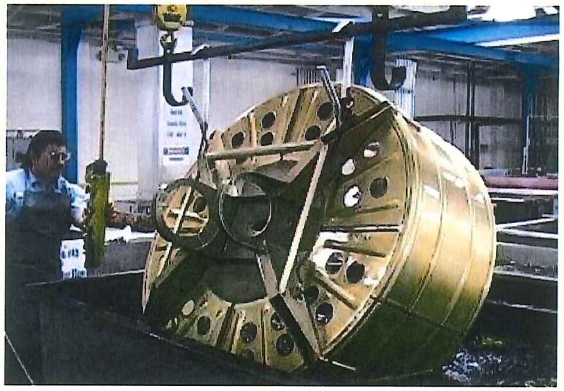
All Electrochemical Processes Occur on a surface



Types of Reactions

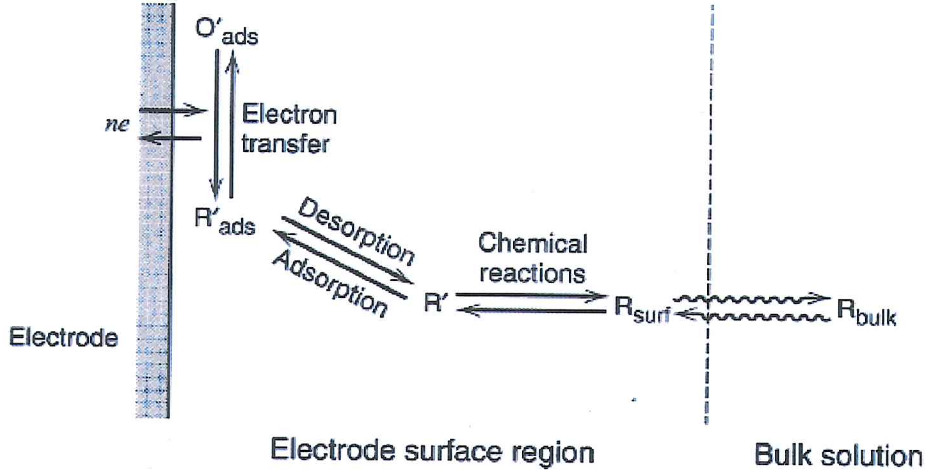
- 1. Electrodeposition (reduction)
  - $Cr^{+2} + 2e^{-} \rightarrow Cr(s)$
  - $Al^{+3} + 3e^{-} \rightarrow Al(s)$
  - $Ag^{+} + e^{-} \rightarrow Ag(s)$





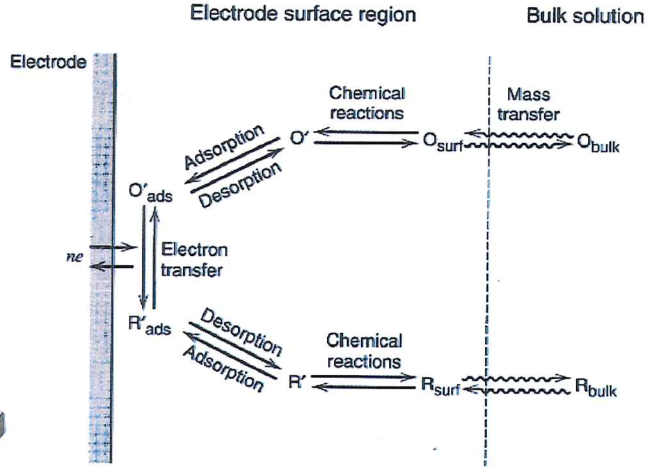
Types of Reactions

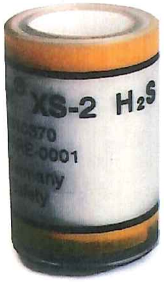
- 2. Corrosion (oxidation)
  - $Fe(s) \rightarrow Fe^{+3} + 3e^{-}$
  - $Li(s) \rightarrow Li^{+} + e^{-}$
  - $Cu(s) \rightarrow Cu^{+2} + 2e^{-}$



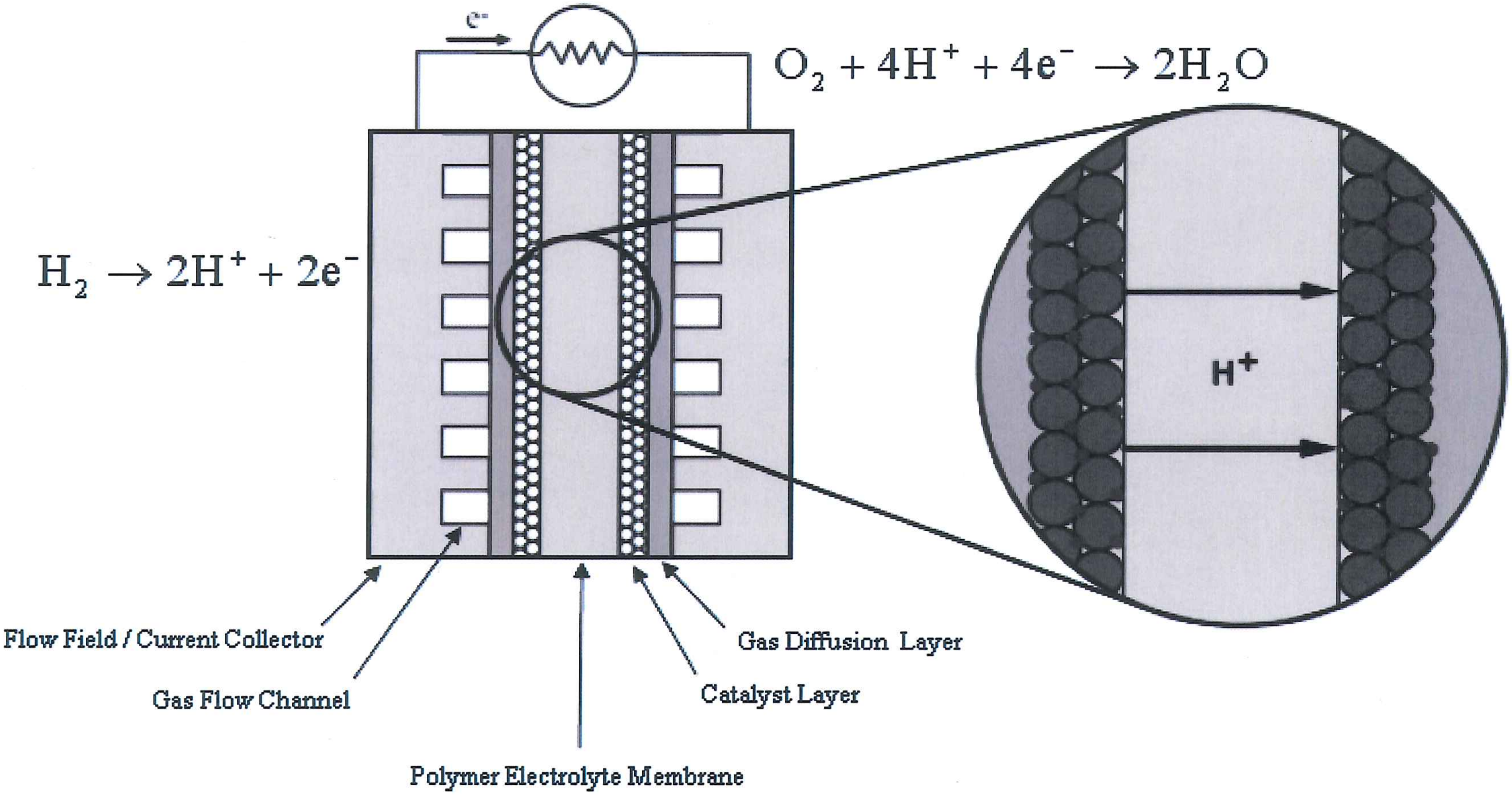
Types of Reactions

- 3. Electrocatalysis
  - i) Pure Redox
    - $Cu^{+2} + e^{-} \rightarrow Cu^{+1}$
    - $Fe(CN)_6^{-3} + e^{-} \rightarrow Fe(CN)_6^{-4}$
  - ii) Traditional Catalysis
    - $2Cl^{-}(aq) \rightarrow Cl_2(g) + 2e^{-}$
    - $O_2(g) + 4H^{+} + 4e^{-} \rightarrow 2H_2O$





Example Cell : Proton Exchange Membrane Fuel Cell



$H_2 \rightarrow 2H^+ + 2e^-$

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Anode and Cathode

- Faradaic and non-faradaic processes
  - Faradaic – electrochemcial reactions
    - Note: Electrochemical reactions have both chemical and electrochemical steps! What are the implications?
  - Non-faradaic – adsorption/desorption, double layer charging/discharging (we'll discuss this in detail next time)
- Must be electrically conducting
- Minimize distance between them
  - Ionic movement through electroltye is akin to a pure Ohmic resistance

Electrolyte

- Liquids: Dissolved salts in a solvent
    - Mostly discuss aqueous in this class
- Solids: Ion conducting groups
- Provides a media for ion transport
- Since the electrolyte solvates the ions (which complete the electrochemical circuit), the reactant must also be solvated in the electrolyte to react

    - This leads to the so-called electrochemical “Three Phase Boundary”

Three Phase boundary

- For an electrochemical reaction to occur, we MUST have three things present
  - Reactant
  - Catalyst/Electrode
  - Electrolyte
- Designing this interface is critical for device performance
  - Void Space
    - Reactant mass transport
  - Maximize interface between catalyst and electrolyte

Table of Standard Potentials – 25oC, 1 bar, 1M

Half-reaction	E° (V)
$\frac{3}{2}N_2(g) + H^+ + e^- \rightleftarrows HN_3(aq)$	-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
$Ti2TiO_2(s) + 2H^+ + 2e^- \rightleftarrows Ti_2O_3(s) + H_2O$	-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
$P\ H_3PO_3(aq) + 3H^+ + 3e^- \rightleftarrows P(red)^{[9]} + 3H_2O$	-0.454 −0.454
Fe2+ + 2e− ⇄ Fe(s)	-0.44 −0.44
$C2CO_2(g) + 2H^+ + 2e^- \rightleftarrows HOOCCOOH(aq)$	-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
$PbO\ \alpha\text{-}PbO_2(s) + 4H^+ + 2e^- \rightleftarrows Pb^{2+} + 2H_2O$	+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

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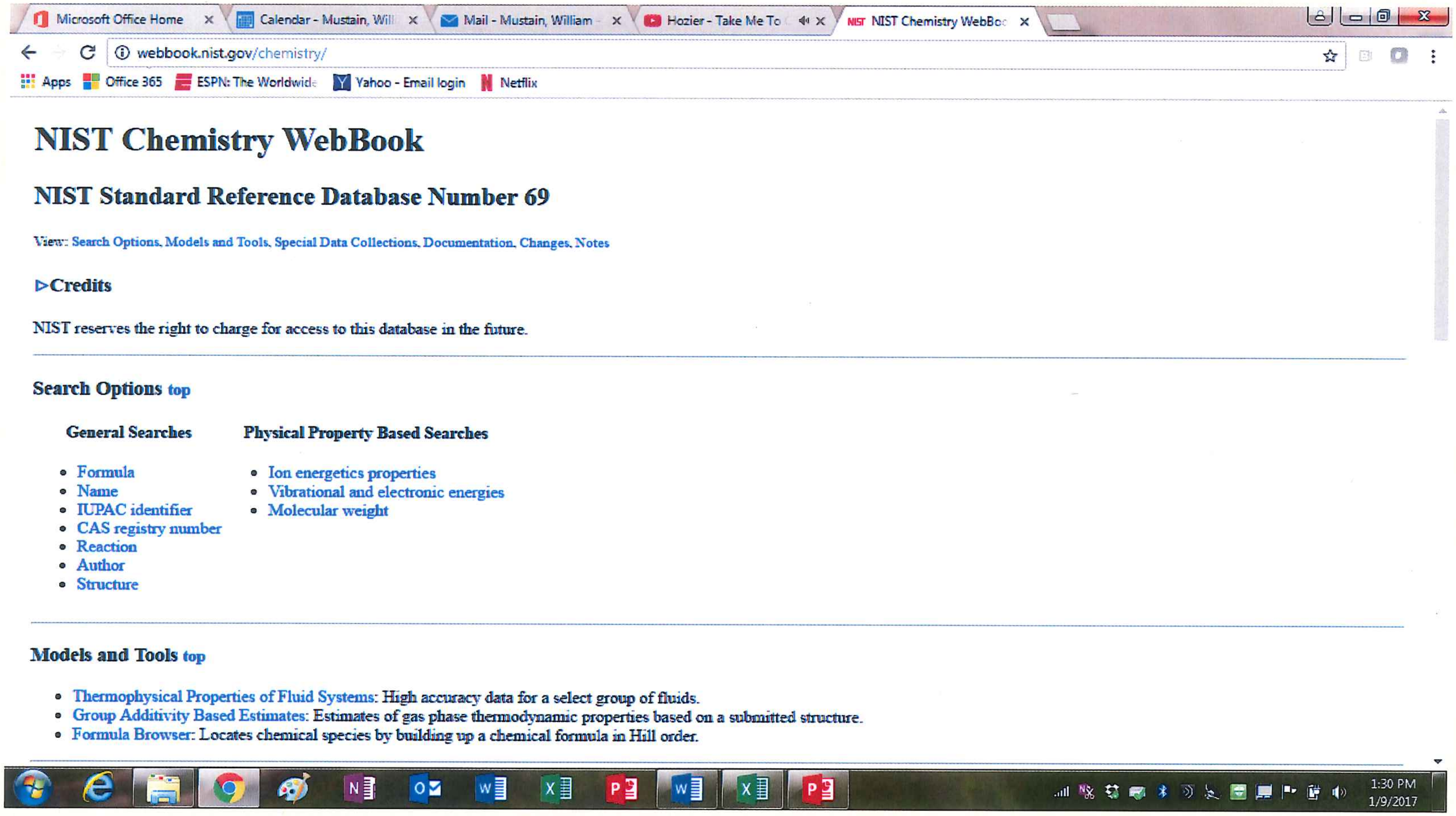

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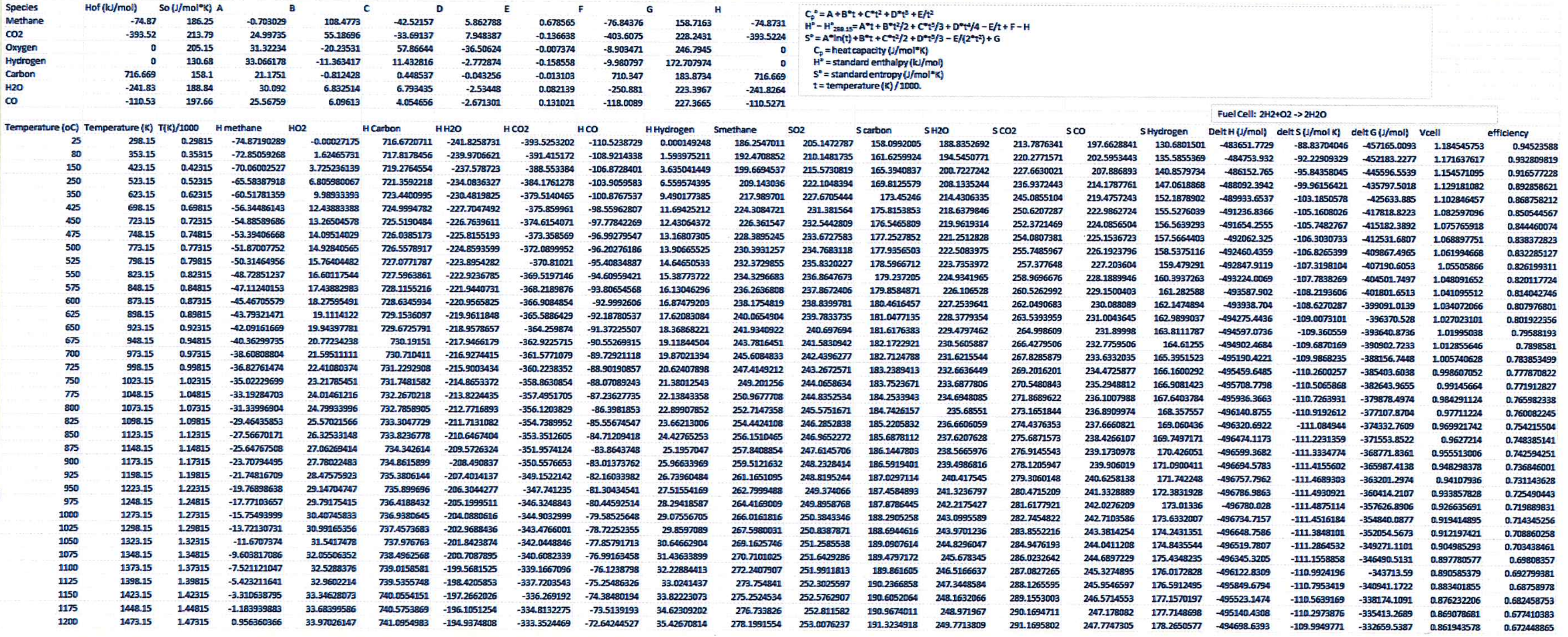
Formula Name IUPAC identifier CAS registry number Reaction Author Structure	Ion energetics properties Vibrational and electronic energies Molecular weight

Models and Tools top

- Thermophysical Properties of Fluid Systems: High accuracy data for a select group of fluids.
- Group Additivity Based Estimates: Estimates of gas phase thermodynamic properties based on a submitted structure.
- Formula Browser: Locates chemical species by building up a chemical formula in Hill order.

$\Delta G\ (T)$ for $2H_2 + O_2 \rightarrow 2H_2O$



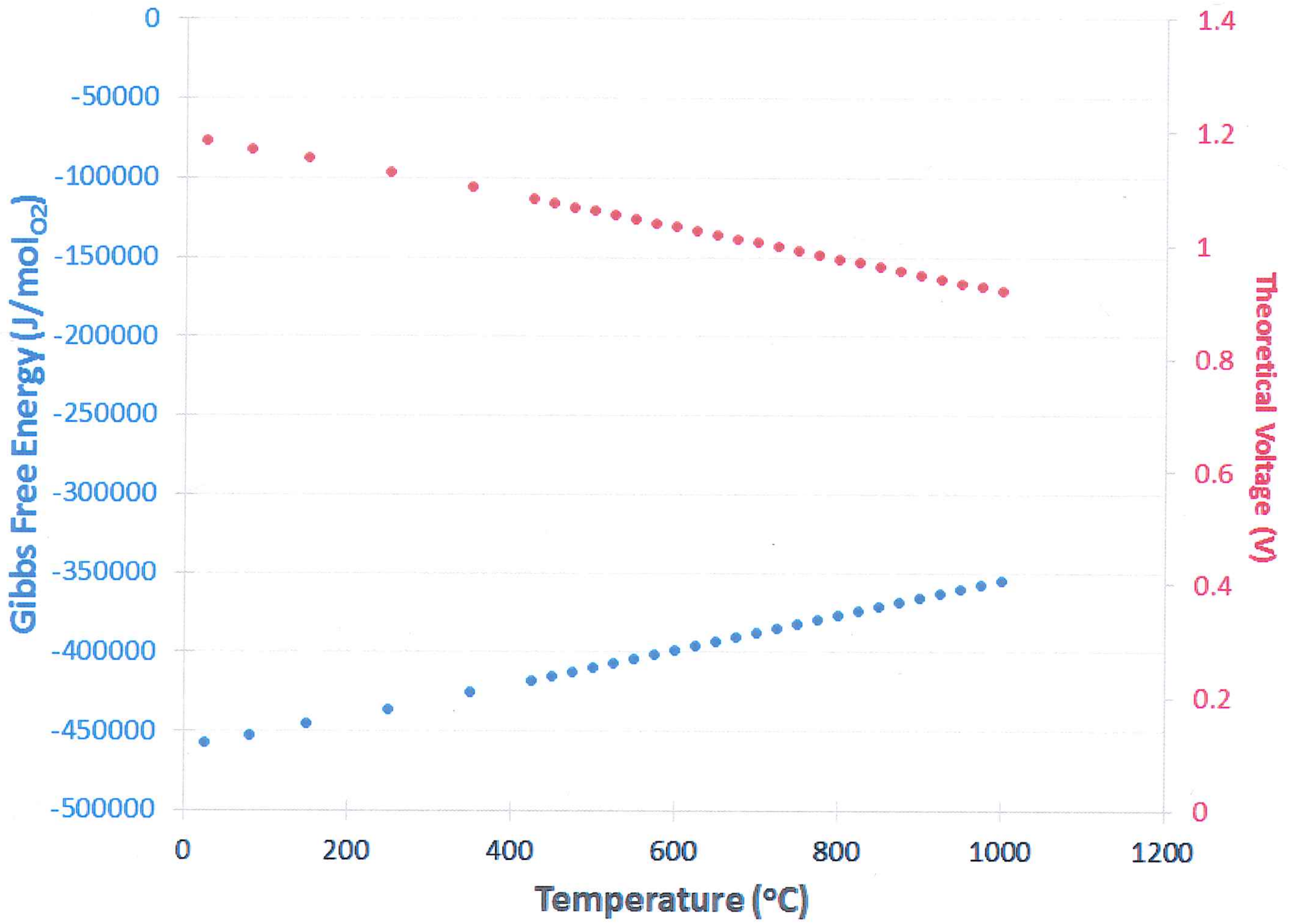
Species	Hof (kJ/mol)	So (J/mol*K)	A	B	C	D	E	F	G	H
Methane	-74.87	186.25	-0.703029	108.4773	-42.52157	5.862788	0.678565	-76.84376	158.7163	-74.8731
CO2	-393.52	213.79	24.99735	55.18696	-33.69137	7.948387	-0.136638	-403.6075	228.2431	-393.5224
Oxygen	0	205.15	31.32234	-20.23531	57.86644	-36.50624	-0.007374	-8.903471	246.7945	0
Hydrogen	0	130.68	33.066178	-11.363417	11.432816	-2.772874	-0.158558	-9.980797	172.707974	0
Carbon	716.669	158.1	21.1751	-0.812428	0.448537	-0.043256	-0.013103	710.347	183.8734	716.669
H2O	-241.83	188.84	30.092	6.832514	6.793435	-2.53448	0.082139	-250.881	223.3967	-241.8264
CO	-110.53	197.66	25.56759	6.09613	4.054656	-2.671301	0.131021	-118.0089	227.3665	-110.5271

$C_p^\circ = A + B*t + C*t^2 + D*t^3 + E/t^2$
$H^\circ - H^\circ_{298.15} = A*t + B*t^2/2 + C*t^3/3 + D*t^4/4 - E/t + F - H$
$S^\circ = A*\ln(t) + B*t + C*t^2/2 + D*t^3/3 - E/(2*t^2) + G$
C_p = heat capacity (J/mol*K)
H° = standard enthalpy (kJ/mol)
S° = standard entropy (J/mol*K)
t = temperature (K) / 1000.

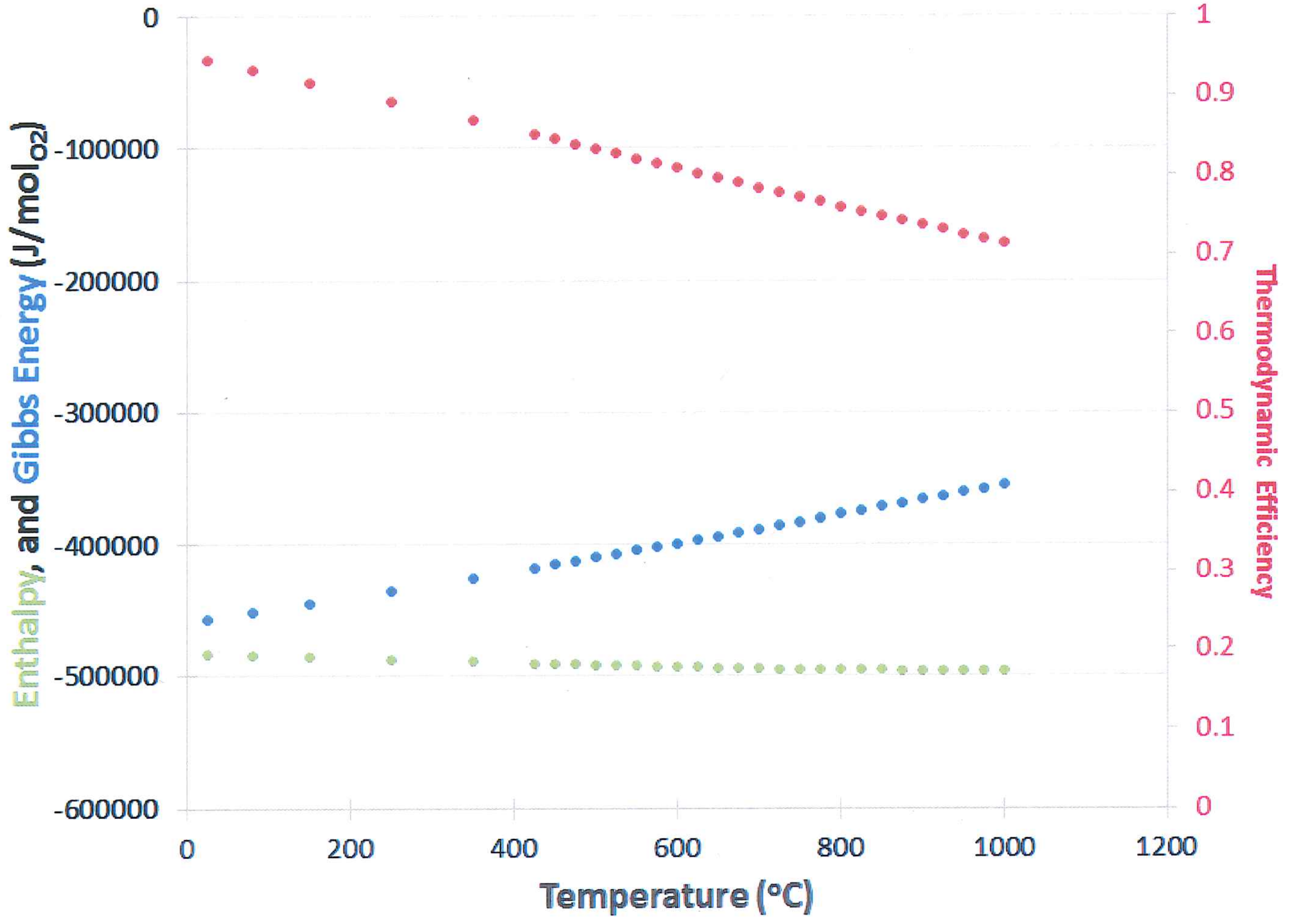
Fuel Cell: 2H2+O2 -> 2H2O

Temperature (oC)	Temperature (K)	T(K)/1000	H methane	HO2	H Carbon	H H2O	H CO2	H CO	H Hydrogen	Smethane	SO2	S carbon	S H2O	S CO2	S CO	S Hydrogen	Delt H (J/mol)	delt S (J/mol K)	delt G (J/mol)	Vcell	efficiency
25	298.15	0.29815	-74.87190289	-0.00027175	716.6720711	-241.8258731	-393.5253202	-110.5238729	0.000149248	186.2547011	205.1472787	158.0992005	188.8352692	213.7876341	197.6628841	130.6801501	-483651.7729	-88.83704046	-457165.0093	1.184545753	0.94523588
80	353.15	0.35315	-72.85059268	1.62465731	717.8178456	-239.9706621	-391.415172	-108.9214338	1.593975211	192.4708852	210.1481735	161.6259924	194.5450771	220.2771571	202.5953443	135.5855369	-484753.932	-92.22909329	-452183.2277	1.171637617	0.932809819
150	423.15	0.42315	-70.06002527	3.725236139	719.2764554	-237.578723	-388.553384	-106.8728401	3.635041449	199.6694537	215.5730819	165.3940837	200.7227242	227.6630021	207.886893	140.8579734	-486152.765	-95.84358045	-445596.5539	1.154571095	0.916577228
250	523.15	0.52315	-65.58387918	6.805980067	721.3592218	-234.0836327	-384.1761278	-103.9059583	6.559574395	209.143036	222.1048394	169.8125579	208.1335244	236.9372443	214.1787761	147.0618868	-488092.3942	-99.96156421	-435797.5018	1.129181082	0.892858621
350	623.15	0.62315	-60.51781359	9.98933393	723.4400995	-230.4819825	-379.5140465	-100.8767537	9.490177385	217.989701	227.6705444	173.45246	214.4306335	245.0855104	219.4757243	152.1878902	-489933.6537	-103.1850578	-425633.885	1.102846457	0.868758212
425	698.15	0.69815	-56.34486143	12.43883388	724.9994782	-227.7047492	-375.859961	-98.55962807	11.69425212	224.3084721	231.381564	175.8153853	218.6379846	250.6207287	222.9862724	155.5276039	-491236.8366	-105.1608026	-417818.8223	1.082597096	0.850544567
450	723.15	0.72315	-54.88589686	13.26504578	725.5190484	-226.7639611	-374.6154071	-97.77842269	12.43064372	226.361547	232.5442809	176.5465809	219.9619314	252.3721469	224.0856504	156.5639293	-491654.2555	-105.7482767	-415182.3892	1.075765918	0.844460074
475	748.15	0.74815	-53.39406668	14.09514029	726.0385173	-225.8155193	-373.358569	-96.99279547	13.16807305	228.3895245	233.6727583	177.2527852	221.2512828	254.0807381	225.1536723	157.5664403	-492062.325	-106.3030733	-412531.6807	1.068897751	0.838372823
500	773.15	0.77315	-51.87007752	14.92840565	726.5578917	-224.8593599	-372.0899952	-96.20276186	13.90665525	230.3931257	234.7683118	177.9356503	222.5083975	255.7485967	226.1923796	158.5375116	-492460.4359	-106.8265399	-409867.4965	1.061994668	0.832285127
525	798.15	0.79815	-50.31464956	15.76404482	727.0771787	-223.8954282	-370.81021	-95.40834887	14.64650533	232.3729855	235.8320227	178.5966712	223.7353972	257.377648	227.203604	159.479291	-492847.9119	-107.3198104	-407190.6053	1.05505866	0.826199311
550	823.15	0.82315	-48.72851237	16.60117544	727.5963861	-222.9236785	-369.5197146	-94.60959421	15.38773722	234.3296683	236.8647673	179.237205	224.9341965	258.9696676	228.1889946	160.3937263	-493224.0069	-107.7838269	-404501.7497	1.048091652	0.820117724
575	848.15	0.84815	-47.11240153	17.43882983	728.1155216	-221.9440731	-368.2189876	-93.80654568	16.13046296	236.2636808	237.8672406	179.8584871	226.106528	260.5262992	229.1500403	161.282588	-493587.902	-108.2193606	-401801.6513	1.041095512	0.814042746
600	873.15	0.87315	-45.46705579	18.27595491	728.6345934	-220.9565825	-366.9084854	-92.9992606	16.87479203	238.1754819	238.8399781	180.4616457	227.2539641	262.0490683	230.088089	162.1474894	-493938.704	-108.6270287	-399091.0139	1.034072066	0.807976801
625	898.15	0.89815	-43.79321471	19.1114122	729.1536097	-219.9611848	-365.5886429	-92.18780537	17.62083084	240.0654904	239.7833735	181.0477135	228.3779354	263.5393959	231.0043645	162.9899037	-494275.4436	-109.0073101	-396370.528	1.027023101	0.801922356
650	923.15	0.92315	-42.09161669	19.94397781	729.6725791	-218.9578657	-364.259874	-91.37225507	18.36868221	241.9340922	240.697694	181.6176383	229.4797462	264.998609	231.89998	163.8111787	-494597.0736	-109.360559	-393640.8736	1.01995038	0.79588193
675	948.15	0.94815	-40.36299735	20.77234238	730.19151	-217.9466179	-362.9225715	-90.55269315	19.11844504	243.7816451	241.5830942	182.1722921	230.5605887	266.4279506	232.7759506	164.61255	-494902.4684	-109.6870169	-390902.7233	1.012855646	0.7898581
700	973.15	0.97315	-38.60808804	21.59511111	730.710411	-216.9274415	-361.5771079	-89.72921118	19.87021394	245.6084833	242.4396277	182.7124788	231.6215544	267.8285879	233.6332035	165.3951523	-495190.4221	-109.9868235	-388156.7448	1.005740628	0.783853499
725	998.15	0.99815	-36.82761474	22.41080374	731.2292908	-215.9003434	-360.2238352	-88.90190857	20.62407898	247.4149212	243.2672571	183.2389413	232.6636449	269.2016201	234.4725877	166.1600292	-495459.6485	-110.2600257	-385403.6038	0.998607052	0.777870822
750	1023.15	1.02315	-35.02229699	23.21785451	731.7481582	-214.8653372	-358.8630854	-88.07089243	21.38012543	249.201256	244.0658634	183.7523671	233.6877806	270.5480843	235.2948812	166.9081423	-495708.7798	-110.5065868	-382643.9655	0.99145664	0.771912827
775	1048.15	1.04815	-33.19284703	24.01461216	732.2670218	-213.8224435	-357.4951705	-87.23627735	22.13843358	250.9677708	244.8352534	184.2533943	234.6948085	271.8689622	236.1007988	167.6403784	-495936.3663	-110.7263931	-379878.4974	0.984291124	0.765982338
800	1073.15	1.07315	-31.33996904	24.79933996	732.7858905	-212.7716893	-356.1203829	-86.3981853	22.89907852	252.7147358	245.5751671	184.7426157	235.68551	273.1651844	236.8909974	168.357557	-496140.8755	-110.9192612	-377107.8704	0.97711224	0.760082245
825	1098.15	1.09815	-29.46435853	25.57021566	733.3047729	-211.7131082	-354.7389952	-85.55674547	23.66213006	254.4424108	246.2852838	185.2205832	236.6606059	274.4376353	237.6660821	169.060436	-496320.6922	-111.084944	-374332.7609	0.969921742	0.754215504
850	1123.15	1.12315	-27.56670171	26.32533148	733.8236778	-210.6467404	-353.3512605	-84.71209418	24.42765253	256.1510465	246.9652272	185.6878112	237.6207628	275.6871573	238.4266107	169.7497171	-496474.1173	-111.2231359	-371553.8522	0.9627214	0.748385141
875	1148.15	1.14815	-25.64767508	27.06268414	734.342614	-209.5726324	-351.9574124	-83.8643748	25.1957047	257.8408854	247.6145706	186.1447803	238.5665976	276.9145543	239.1730978	170.426051	-496599.3682	-111.3334774	-368771.8361	0.955513006	0.742594251
900	1173.15	1.17315	-23.70794495	27.78022483	734.8615899	-208.490837	-350.5576653	-83.01373762	25.96633969	259.5121632	248.2328414	186.5919401	239.4986816	278.1205947	239.906019	171.0900411	-496694.5783	-111.4155602	-365987.4138	0.948298378	0.736846001
925	1198.15	1.19815	-21.74816709	28.47575923	735.3806144	-207.4014137	-349.1522142	-82.16033982	26.73960484	261.1651095	248.8195244	187.0297114	240.417545	279.3060148	240.6258138	171.742248	-496757.7962	-111.4689303	-363201.2974	0.94107936	0.731143628
950	1223.15	1.22315	-19.76898638	29.14704747	735.899696	-206.3044277	-347.741235	-81.30434541	27.51554169	262.7999488	249.374066	187.4584893	241.3236797	280.4715209	241.3328889	172.3831928	-496786.9863	-111.4930921	-360414.2107	0.933857828	0.725490443
975	1248.15	1.24815	-17.77103657	29.79175415	736.4188432	-205.1999511	-346.3248843	-80.44592514	28.29418587	264.4169009	249.8958768	187.8786445	242.2175427	281.6177921	242.0276209	173.01336	-496780.028	-111.4875114	-357626.8906	0.926635691	0.719889831
1000	1273.15	1.27315	-15.75493999	30.40745833	736.9380645	-204.0880616	-344.9032999	-79.58525648	29.07556705	266.0161816	250.3843346	188.2905258	243.0995589	282.7454822	242.7103586	173.6332007	-496734.7157	-111.4516184	-354840.0877	0.919414895	0.714345256
1025	1298.15	1.29815	-13.72130731	30.99165356	737.4573683	-202.9688436	-343.4766001	-78.72252355	29.8597089	267.5980031	250.8387871	188.6944616	243.9701236	283.8552216	243.3814254	174.2431351	-496648.7586	-111.3848101	-352054.5673	0.912197421	0.708860258
1050	1323.15	1.32315	-11.6707374	31.5417478	737.976763	-201.8423874	-342.0448846	-77.85791713	30.64662904	269.1625746	251.2585538	189.0907614	244.8296047	284.9476193	244.0411208	174.8435544	-496519.7807	-111.2864532	-349271.1101	0.904985293	0.703438461
1075	1348.15	1.34815	-9.603817086	32.05506352	738.4962568	-200.7087895	-340.6082339	-76.99163458	31.43633899	270.7101025	251.6429286	189.4797172	245.678345	286.0232642	244.6897229	175.4348235	-496345.3205	-111.1558858	-346490.5131	0.897780577	0.69808357
1100	1373.15	1.37315	-7.521121047	32.5288376	739.0158581	-199.5681525	-339.1667096	-76.1238798	32.22884413	272.2407907	251.9911813	189.861605	246.5166637	287.0827265	245.3274895	176.0172828	-496122.8309	-110.9924196	-343713.59	0.890585379	0.692799381
1125	1398.15	1.39815	-5.423211641	32.9602214	739.5355748	-198.4205853	-337.7203543	-75.25486326	33.0241437	273.754841	252.3025597	190.2366858	247.3448584	288.1265595	245.9546597	176.5912495	-495849.6794	-110.7953419	-340941.1722	0.883401855	0.68758978
1150	1423.15	1.42315	-3.310638795	33.34628073	740.0554151	-197.2662026	-336.269192	-74.38480194	33.82223073	275.2524534	252.5762907	190.6052064	248.1632066	289.1553003	246.5714553	177.1570197	-495523.1474	-110.5639169	-338174.1091	0.876232206	0.682458753
1175	1448.15	1.44815	-1.183939883	33.68399586	740.5753869	-196.1051254	-334.8132275	-73.5139193	34.62309202	276.733826	252.811582	190.9674011	248.971967	290.1694711	247.178082	177.7148698	-495140.4308	-110.2973876	-335413.2689	0.869078681	0.677410383
1200	1473.15	1.47315	0.956360366	33.97026147	741.0954983	-194.9374808	-333.3524469	-72.64244527	35.42670814	278.1991554	253.0076237	191.3234918	249.7713809	291.1695802	247.7747305	178.2650577	-494698.6393	-109.9949771	-332659.5387	0.861943578	0.672448865

ΔG (T) for $2H_2 + O_2 \rightarrow 2H_2O$



ΔH (T) and ΔG (T) for $2H_2 + O_2 \rightarrow 2H_2O$



Extra Resources

- "Electrochemical Methods: Fundamentals and Applications", 2nd Edition. Allen J. Bard and Larry R. Faulkner.

CHEG 3128 - Battery 1

All reactions are electron transfer processes
- what I mean is that every reacting system is a combination of complementary redox reactions.

For instance, take the combustion of H_2

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$$

→ Is this spontaneous? Exo/Endo thermic?

→ How do we capture energy?

→ As heat → $\Delta H(T)$

→ In this reaction, what is oxidized?

" , what is reduced?

What if I write it like this:

$$(H_2 \rightarrow 2H^+ + 2e^-) \times 2$$

$$2H_2 \rightarrow 4H^+ + 4e^-$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

Total $2H_2 + O_2 \rightarrow 2H_2O$

Reductions are e^- accepting reactions

Oxidations are e^- donatin reactions

∴ H is oxidized from H(0) → H(1+)

O is reduced from O(0) → O(2-)

In a chemical system, we recover the energy from this RXN as heat. H_2 combustion is used in combined cycle power plants. The combustion heat creates stam, which tuns a turbine, spinning a shaft between 2 magnets & looped Cu wire → the rotation of the shaft in the magnetic field (Physics 2!) produces a current.

What if we didn't need to do that? what if we could directly use the electrons from the 1/2 reactions? → this is electrochemical engineering. One such system is a proton exchange membrane fuel cell.

↳ Diagram on next page

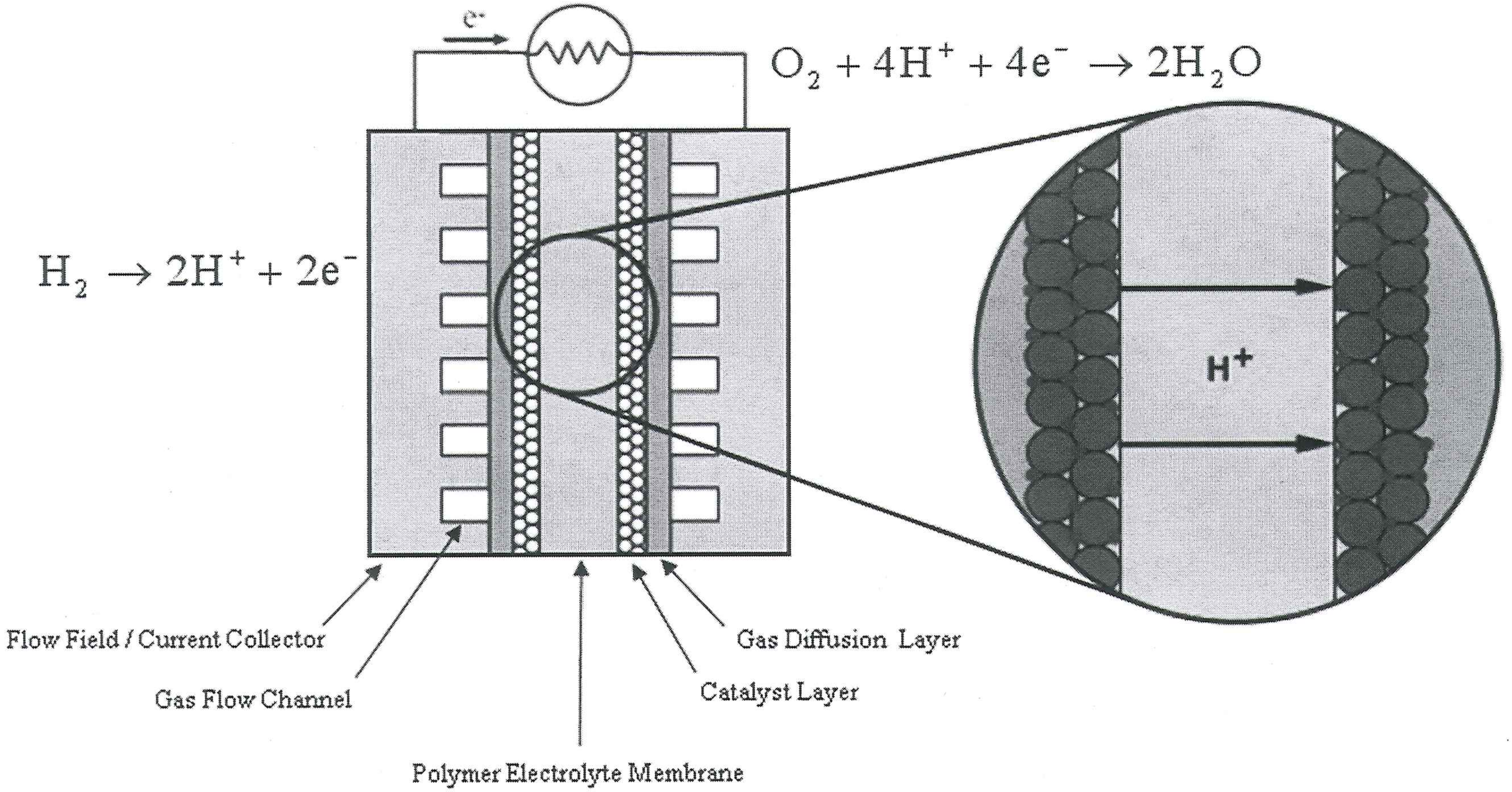
→ oxidations happen @ the anode

- (−) "negative" electrode

→ reduction happen @ the cathode

- (+) "positive" electrode

How much energy can we get from electrochemical processes?

e-
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
$H_2 \rightarrow 2H^+ + 2e^-$
H^+
Flow Field / Current Collector
Gas Flow Channel
Polymer Electrolyte Membrane
Catalyst Layer
Gas Diffusion Layer

Let's do an energy / Entropy Balance on one electrode:

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

Generalized Energy Balance

$$U_E = U_B + \sum H^{mass}_{in} - \sum H^{mass}_{out} + Q + W$$

- Break up work term:

$$W = -(P\Delta V + W_{elec})$$

Entropy Balance

$$S_E = S_B + \sum S^{mass}_{in} - \sum S^{mass}_{out} + \frac{\Sigma Q}{T} + S_T$$

$$U_E = U_B + \sum H^{mass}_{in} - \sum H^{mass}_{out} + Q - P\Delta V - W_{elec}$$

Assumptions: 1) Closed System

2) All electrochemical RXNs are reversible

$$U_E = U_B + Q - P\Delta V - W_{ELEC}$$

$$S_E = S_B + \frac{Q}{T}$$

$$Q = T\Delta S$$

$$U_E - U_B + P\Delta V = Q - W_{ELEC}$$

$$\Delta U + P\Delta V = T\Delta S - W_{Elec}$$

$$\Delta H - T\Delta S = -W_{elec}$$

$$\Delta G = -W_{elec}$$

$$\boxed{W_{elec} = -\Delta G}$$

Units: $W = J/mol = \overbrace{\text{charge} \cdot \text{potential}}^{ECE}$

$= Q \cdot E$

$Q = \text{charge/mole reactant} = n \cdot F$

$\text{mole } e^-/\text{mol reactant} \cdot C/\text{mole } e^-$

$$W = -\Delta G = nFE$$

$$\boxed{\Delta G = -nFE}$$

[redacted]

@ STP, 25°C, 1 bar (or 1M)

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

where E° is called the "Standard Potential"

How to find the standard potential for an individual reaction?

First, know that we it impossible to know how much energy we have in a system, which is why we ALWAYS report them as ΔG, ΔH, etc.

Therefore, we need an internal standard

ΔG for $2H^+ + 2e^- \rightleftharpoons H_2(g)$ @ 25°C, 1 bar $= 0$

$$E^\circ_{H^+/H_2} = 0.0V$$

Oxygen Reduction in acid media

$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O_{(l)} \quad ①$$

$$2H_2 \rightleftharpoons 4H^+ + 4e^- \quad ② \rightarrow 2x \text{ reference!}$$

$$O_2 + 2H_2 \rightleftharpoons 2H_2O$$

$$\Delta g^\circ_{f,H_2O} = -237{,}200 \text{ J/mol}$$

$$\Delta g^\circ_{f,O_2} = 0. \text{ J/mol}$$

$$\Delta g^\circ_{f,H_2} = 0 \text{ J/mol}$$

$$\Delta G^\circ = 2(-237{,}200 \text{ J/mol}) - [0 \text{ J/mol} + 2(0 \text{ J/mol})]$$

$$\Delta G^\circ = -474{,}400 \text{ J/mol}$$

$$\Delta G^\circ_{RXN} = -nFV_{Th}$$

$$V_{Th} = \frac{-\Delta G^\circ_{RXN}}{nF} = \frac{-(-474{,}400 \text{ J/mol})}{4 \text{ mol e}^-\text{/mol} \cdot 96485.3 \text{ C/mol e}^-} = 1.229 \text{ V}$$

↓

Positive cell voltages mean spontaneous!

↓

galvanic cell

you could also use this to determine specific potentials where reactions occur

$$V_{Th} = E^\circ_{Cathode} - E^\circ_{Anode}$$

$$1.229 = E^\circ_{Cathode} - 0.0 \text{V}$$

$$\boxed{E^\circ_{O_2} = 1.229 \text{ V}}$$

Do we need to do that work every time?

<u>No</u> → most electrochemical redox couples are tabulated

→ Some can be found in Appendix C
- Page 808 in B&F, Ed 2
→ Also attached to next page

How does our ORR calculated E° compare with the Table? They are EXACTLY THE SAME!

Now, let's answer our question about the Daniell cell....

What if we attached the Cu foil to the ⊕ terminal
- Cathode
$$Cu^{+2} + 2e^{-} \rightarrow Cu(s)$$
- Zn foil to the ⊖ terminal
- Anode
$$Zn \rightarrow Zn^{+2} + 2e^{-}$$

$$E^\circ_{Cu|Cu^{+2}} = 0.34\ V$$

$$E^\circ_{Zn|Zn^{+2}} = -0.76\ V$$

$$V_{Th} = E^\circ_C - E^\circ_A = 0.34V - (-0.76V) = 1.1V$$

↓

galvanic! will occur spontaneously

What if we connected this the other way?

Cathode : $Zn^{+2} + 2e^- \rightarrow Zn_{(s)}$

Anode : $Cu_{(s)} \rightarrow Cu^{+2} + 2e^-$

$$V_{Th} = E^\circ_C - E^\circ_A = -0.76 - 0.34 = -1.1V$$

↓

nonspontaneous!

↳ Electrolytic cell

How would we "recharge" this cell?

Make $\Delta G < 0$, so, we have to apply a voltage > 1.1V on the cell to make it go!

→ That's why you plug your phone in!

"Electrochemical Methods", 2nd Edition

APPENDIX

C

REFERENCE TABLES

TABLE C.1 Selected Standard Electrode Potentials in Aqueous Solutions at 25°C in V *vs.* NHE[a]

Reaction	Potential, V
$Ag^+ + e \rightleftarrows Ag$	0.7991
$AgBr + e \rightleftarrows Ag + Br^-$	0.0711
$AgCl + e \rightleftarrows Ag + Cl^-$	0.2223
$AgI + e \rightleftarrows Ag + I^-$	−0.1522
$Ag_2O + H_2O + 2e \rightleftarrows 2Ag + 2OH^-$	0.342
$Al^{3+} + 3e \rightleftarrows Al$	−1.676
$Au^+ + e \rightleftarrows Au$	1.83
$Au^{3+} + 2e \rightleftarrows Au^+$	1.36
p-benzoquinone + $2H^+ + 2e \rightleftarrows$ hydroquinone	0.6992
$Br_2(aq) + 2e \rightleftarrows 2Br^-$	1.0874
$Ca^{2+} + 2e \rightleftarrows Ca$	−2.84
$Cd^{2+} + 2e \rightleftarrows Cd$	−0.4025
$Cd^{2+} + 2e \rightleftarrows Cd(Hg)$	−0.3515
$Ce^{4+} + e \rightleftarrows Ce^{3+}$	1.72
$Cl_2(g) + 2e \rightleftarrows 2Cl^-$	1.3583
$HClO + H^+ + e \rightleftarrows \frac{1}{2}Cl_2 + H_2O$	1.630
$Co^{2+} + 2e \rightleftarrows Co$	−0.277
$Co^{3+} + e \rightleftarrows Co^{2+}$	1.92
$Cr^{2+} + 2e \rightleftarrows Cr$	−0.90
$Cr^{3+} + e \rightleftarrows Cr^{2+}$	−0.424
$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftarrows 2Cr^{3+} + 7H_2O$	1.36
$Cu^+ + e \rightleftarrows Cu$	0.520
$Cu^{2+} + 2CN^- + e \rightleftarrows Cu(CN)_2^-$	1.12
$Cu^{2+} + e \rightleftarrows Cu^+$	0.159
$Cu^{2+} + 2e \rightleftarrows Cu$	0.340
$Cu^{2+} + 2e \rightleftarrows Cu(Hg)$	0.345
$Eu^{3+} + e \rightleftarrows Eu^{2+}$	−0.35
$1/2F_2 + H^+ + e \rightleftarrows HF$	3.053
$Fe^{2+} + 2e \rightleftarrows Fe$	−0.44
$Fe^{3+} + e \rightleftarrows Fe^{2+}$	0.771
$Fe(CN)_6^{3-} + e \rightleftarrows Fe(CN)_6^{4-}$	0.3610

(continued)

TABLE C.1 *(continued)*

Reaction	Potential, V
$2H^+ + 2e \rightleftarrows H_2$	0.0000
$2H_2O + 2e \rightleftarrows H_2 + 2OH^-$	−0.828
$H_2O_2 + 2H^+ + 2e \rightleftarrows 2H_2O$	1.763
$2Hg^{2+} + 2e \rightleftarrows Hg_2^{2+}$	0.9110
$Hg_2^{2+} + 2e \rightleftarrows 2Hg$	0.7960
$Hg_2Cl_2 + 2e \rightleftarrows 2Hg + 2Cl^-$	0.26816
$Hg_2Cl_2 + 2e \rightleftarrows 2Hg + 2Cl^-$ (sat'd. KCl)	0.2415
$HgO + H_2O + 2e \rightleftarrows Hg + 2OH^-$	0.0977
$Hg_2SO_4 + 2e \rightleftarrows 2Hg + SO_4^{2-}$	0.613
$I_2 + 2e \rightleftarrows 2I^-$	0.5355
$I_3^- + 2e \rightleftarrows 3I^-$	0.536
$K^+ + e \rightleftarrows K$	−2.925
$Li^+ + e \rightleftarrows Li$	−3.045
$Mg^{2+} + 2e \rightleftarrows Mg$	−2.356
$Mn^{2+} + 2e \rightleftarrows Mn$	−1.18
$Mn^{3+} + e \rightleftarrows Mn^{2+}$	1.5
$MnO_2 + 4H^+ + 2e \rightleftarrows Mn^{2+} + 2H_2O$	1.23
$MnO_4^- + 8H^+ + 5e \rightleftarrows Mn^{2+} + 4H_2O$	1.51
$Na^+ + e \rightleftarrows Na$	−2.714
$Ni^{2+} + 2e \rightleftarrows Ni$	−0.257
$Ni(OH)_2 + 2e \rightleftarrows Ni + 2OH^-$	−0.72
$O_2 + 2H^+ + 2e \rightleftarrows H_2O_2$	0.695
$O_2 + 4H^+ + 4e \rightleftarrows 2H_2O$	1.229
$O_2 + 2H_2O + 4e \rightleftarrows 4OH^-$	0.401
$O_3 + 2H^+ + 2e \rightleftarrows O_2 + H_2O$	2.075
$Pb^{2+} + 2e \rightleftarrows Pb$	−0.1251
$Pb^{2+} + 2e \rightleftarrows Pb(Hg)$	−0.1205
$PbO_2 + 4H^+ + 2e \rightleftarrows Pb^{2+} + 2H_2O$	1.468
$PbO_2 + SO_4^{2-} + 4H^+ + 2e \rightleftarrows PbSO_4 + 2H_2O$	1.698
$PbSO_4 + 2e \rightleftarrows Pb + SO_4^{2-}$	−0.3505
$Pd^{2+} + 2e \rightleftarrows Pd$	0.915
$Pt^{2+} + 2e \rightleftarrows Pt$	1.188
$PtCl_4^{2-} + 2e \rightleftarrows Pt + 4Cl^-$	0.758
$PtCl_6^{2-} + 2e \rightleftarrows PtCl_4^{2-} + 2Cl^-$	0.726
$Ru(NH_3)_6^{3+} + e \rightleftarrows Ru(NH_3)_6^{2+}$	0.10
$S + 2e \rightleftarrows S^{2-}$	−0.447
$Sn^{2+} + 2e \rightleftarrows Sn$	−0.1375
$Sn^{4+} + 2e \rightleftarrows Sn^{2+}$	0.15
$Tl^+ + e \rightleftarrows Tl$	−0.3363
$Tl^+ + e \rightleftarrows Tl(Hg)$	−0.3338
$Tl^{3+} + 2e \rightleftarrows Tl^+$	1.25
$U^{3+} + 3e \rightleftarrows U$	−1.66
$U^{4+} + e \rightleftarrows U^{3+}$	−0.52
$UO_2^+ + 4H^+ + e \rightleftarrows U^{4+} + 2H_2O$	0.273
$UO_2^{2+} + e \rightleftarrows UO_2^+$	0.163

(continued)

TABLE C.1 *(continued)*

Reaction	Potential, V
$V^{2+} + 2e \rightleftarrows V$	−1.13
$V^{3+} + e \rightleftarrows V^{2+}$	−0.255
$VO^{2+} + 2H^+ + e \rightleftarrows V^{3+} + H_2O$	0.337
$VO_2^+ + 2H^+ + e \rightleftarrows VO^{2+} + H_2O$	1.00
$Zn^{2+} + 2e \rightleftarrows Zn$	−0.7626
$ZnO_2^{2-} + 2H_2O + 2e \rightleftarrows Zn + 4OH^-$	−1.285

[a] The data in this table are mainly taken from A. J. Bard, J. Jordan, and R. Parsons, Eds., "Standard Potentials in Aqueous Solutions," Marcel Dekker, New York, 1985 (prepared under the auspices of the Electrochemistry and Electroanalytical Chemistry Commissions of IUPAC). Other sources of standard potentials and thermodynamic data include: (1) A. J. Bard and H. Lund, Eds., "The Encyclopedia of the Electrochemistry of the Elements," Marcel Dekker, New York, 1973–1986. (2) G. Milazzo and S. Caroli, "Tables of Standard Electrode Potentials," Wiley-Interscience, New York, 1977. The data here are referred to the NHE based on a 1-atm standard state for H_2. See the footnote in Section 2.1.5 concerning the recent change in standard state.

Table C.2 Selected Formal Potentials in Aqueous Solution at 25°C in V *vs.* NHE[a]

Reaction	Conditions	Potential, V
$Cu(II) + e \rightleftarrows Cu$	$1\,M\,NH_3 + 1\,M\,NH_4^+$	0.01
	$1\,M$ KBr	0.52
$Ce(IV) + e \rightleftarrows Ce(III)$	$1\,M\,HNO_3$	1.61
	$1\,M$ HCl	1.28
	$1\,M\,HClO_4$	1.70
	$1\,M\,H_2SO_4$	1.44
$Fe(III) + e \rightleftarrows Fe(II)$	$1\,M$ HCl	0.70
	$10\,M$ HCl	0.53
	$1\,M\,HClO_4$	0.735
	$1\,M\,H_2SO_4$	0.68
	$2\,M\,H_3PO_4$	0.46
$Fe(CN)_6^{3-} + e \rightleftarrows Fe(CN)_6^{4-}$	$0.1\,M$ HCl	0.56
	$1\,M$ HCl	0.71
	$1\,M\,HClO_4$	0.72
$Sn(IV) + 2e \rightleftarrows Sn(II)$	$1\,M$ HCl	0.14

[a] The data in this table are taken mainly from G. Charlot, "Oxidation-Reduction Potentials," Pergamon, London, 1958. Additional values are found in J. J. Lingane, "Electroanalytical Chemistry," Interscience, New York, 1958, and L. Meites, Ed., "Handbook of Analytical Chemistry," McGraw-Hill, New York, 1963.

In class: Cu/Zn demo →

Al/"Cu" demo

↳ what is the rxn that is really happening?

↳ how do we know?

↓

"Scale-up" to "practical" solution → Aluminum can
↓
Cu or other rod

→ what happens when we don't have ∞ resistance + current is allowed to flow?

↳ Is this enough energy/power to run anything?

→ Discuss assignment 1 for Battery lab

→ what if our device is not @STP?

→ $\Delta G = \Delta G(T,P,N)$ ....

Remember: $\Delta G = \Delta G(T, \underset{\substack{\downarrow \\ \text{or } [C]}}{P}, N)$

How does impact cell voltage?

$2H_2 + O_2 \rightarrow 2H_2O$

2 ways to find $\Delta G(T)$
↓
1. Method in SVN (attached) → ΔC_p method

2. Use webbook.nist.gov/chemistry
→ NIST chemistry Webbook

to find $g_f(T)$ → Then do ΔG = Products - Reactants
↓
This is my preferred method, but either will work
↓
Excel spreadsheet attached
↓
ΔG vs T + V vs. T

→ Also what is efficiency?

→TD = $\frac{\Delta G}{\Delta H}$

→ Voltage eff = $\frac{V}{V_{in}}$ → total $\eta = \left(\frac{\Delta G}{\Delta H}\right)\left(\frac{V}{V_{in}}\right)$

↳ importance? → Later!

SVN ΔH(T)

4.6 TEMPERATURE DEPENDENCE OF ΔH°

In the foregoing sections, standard heats of reaction are discussed for a reference temperature of 298.15 K. In this section we treat the calculation of standard heats of reaction at other temperatures from knowledge of the value at the reference temperature.

The general chemical reaction may be written:

$$|\nu_1|A_1 + |\nu_2|A_2 + \cdots \to |\nu_3|A_3 + |\nu_4|A_4 + \cdots$$

where $|\nu_i|$ is a stoichiometric coefficient and A_i stands for a chemical formula. The species on the left are reactants; those on the right, products. The sign convention for ν_i is as follows:

positive (+) *for products* and *negative* (−) *for reactants*

The ν_i with their accompanying signs are called stoichiometric *numbers*. For example, when the ammonia synthesis reaction is written:

$$N_2 + 3H_2 \to 2NH_3$$

then $$\nu_{N_2} = -1 \qquad \nu_{H_2} = -3 \qquad \nu_{NH_3} = 2$$

This sign convention allows the definition of a standard heat of reaction to be expressed mathematically by the equation:

$$\Delta H^\circ \equiv \sum_i \nu_i H_i^\circ \tag{4.14}$$

where H_i° is the enthalpy of species i in its standard state and the summation is over all products and reactants. The standard-state enthalpy of a chemical compound is equal to its heat of formation plus the standard-state enthalpies of its constituent elements. If the standard-state enthalpies of all elements are arbitrarily set equal to zero as the basis of calculation, then the standard-state enthalpy of each compound is its heat of formation. In this event, $H_i^\circ = \Delta H_{f_i}^\circ$ and Eq. (4.14) becomes:

$$\Delta H^\circ = \sum_i \nu_i \, \Delta H_{f_i}^\circ \tag{4.15}$$

where the summation is over all products and reactants. This formalizes the procedure described in the preceding section for calculation of standard heats of other reactions from standard heats of formation. Applied to the reaction,

$$4HCl(g) + O_2(g) \to 2H_2O(g) + 2Cl_2(g)$$

Eq. (4.15) is written:

$$\Delta H^\circ = 2\Delta H_{f_{H_2O}}^\circ - 4\Delta H_{f_{HCl}}^\circ$$

With data from Table C.4 for 298.15 K, this becomes:

$$\Delta H_{298}^\circ = (2)(-241{,}818) - (4)(-92{,}307) = -114{,}408 \text{ J}$$

in agreement with the result of Ex. 4.5.

SVN ΔH(T)

For standard reactions, products and reactants are always at the standard-state pressure of 1 bar. Standard-state enthalpies are therefore functions of temperature only, and by Eq. (2.21),

$$dH_i^\circ = C_{P_i}^\circ \, dT$$

where subscript i identifies a particular product or reactant. Multiplying by ν_i and summing over all products and reactants gives:

$$\sum_i \nu_i \, dH_i^\circ = \sum_i \nu_i C_{P_i}^\circ \, dT$$

Since ν_i is a constant, it may be placed inside the differential:

$$\sum_i d(\nu_i H_i^\circ) = d \sum_i \nu_i H_i^\circ = \sum_i \nu_i C_{P_i}^\circ \, dT$$

The term $\sum_i \nu_i H_i^\circ$ is the standard heat of reaction, defined by Eq. (4.14) as ΔH°. The standard heat-capacity change of reaction is defined similarly:

$$\Delta C_P^\circ \equiv \sum_i \nu_i C_{P_i}^\circ \tag{4.16}$$

As a result of these definitions, the preceding equation becomes:

$$\boxed{d\,\Delta H^\circ = \Delta C_P^\circ \, dT} \tag{4.17}$$

This is the fundamental equation relating heats of reaction to temperature. Integration gives:

$$\Delta H^\circ = \Delta H_0^\circ + R \int_{T_0}^{T} \frac{\Delta C_P^\circ}{R} dT \tag{4.18}$$

where ΔH° and ΔH_0° are heats of reaction at temperature T and at reference temperature T_0 respectively. If the temperature dependence of the heat capacity of each product and reactant is given by Eq. (4.4), then the integral is given by the analog of Eq. (4.7) ($\tau \equiv T/T_0$):

$$\int_{T_0}^{T} \frac{\Delta C_P^\circ}{R} dT = (\Delta A) T_0(\tau - 1) + \frac{\Delta B}{2} T_0^2(\tau^2 - 1) + \frac{\Delta C}{3} T_0^3(\tau^3 - 1) + \frac{\Delta D}{T_0}\left(\frac{\tau - 1}{\tau}\right) \tag{4.19}$$

where by definition, $\Delta A \equiv \sum_i \nu_i A_i$

with analogous definitions for ΔB, ΔC, and ΔD.

An alternative formulation results when a mean heat capacity change of reaction is defined in analogy to Eq. (4.8):

$$\frac{\langle \Delta C_P^\circ \rangle_H}{R} = \Delta A + \frac{\Delta B}{2} T_0(\tau + 1) + \frac{\Delta C}{3} T_0^2(\tau^2 + \tau + 1) + \frac{\Delta D}{\tau T_0^2} \tag{4.20}$$

Equation (4.18) then becomes:

$$\Delta H^\circ = \Delta H_0^\circ + \langle \Delta C_P^\circ \rangle_H (T - T_0) \tag{4.21}$$

SVN ΔC_p method to find $\Delta H(T) + \Delta G(T)$

13.4 EFFECT OF TEMPERATURE ON THE EQUILIBRIUM CONSTANT

Since the standard-state temperature is that of the equilibrium mixture, the standard property changes of reaction, such as ΔG° and ΔH°, vary with the equilibrium temperature. The dependence of ΔG° on T is given by Eq. (13.13), which may be rewritten:

$$\frac{d(\Delta G^\circ/RT)}{dT} = \frac{-\Delta H^\circ}{RT^2}$$

In view of Eq. (13.11b), this becomes:

$$\boxed{\frac{d\ln K}{dT} = \frac{\Delta H^\circ}{RT^2}} \tag{13.14}$$

Equation (13.14) gives the effect of temperature on the equilibrium constant, and hence on the equilibrium conversion. If ΔH° is negative, i.e., if the reaction is exothermic, the equilibrium constant decreases as the temperature increases. Conversely, K increases with T for an endothermic reaction.

If ΔH°, the standard enthalpy change (heat) of reaction, is assumed independent of T, integration of Eq. (13.14) from a particular temperature T' to an arbitrary temperature T leads to the simple result:

$$\ln\frac{K}{K'} = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T} - \frac{1}{T'}\right) \tag{13.15}$$

This approximate equation implies that a plot of $\ln K$ vs. the reciprocal of absolute temperature is a straight line. Figure 13.2, a plot of $\ln K$ vs. $1/T$ for a number of common reactions, illustrates this near linearity. Thus, Eq. (13.15) provides a reasonably accurate relation for the interpolation and extrapolation of equilibrium-constant data.

The *rigorous* development of the effect of temperature on the equilibrium constant is based on the definition of the Gibbs energy, written for a chemical species in its standard state:

$$G_i^\circ = H_i^\circ - TS_i^\circ$$

Multiplication by ν_i and summation over all species gives:

$$\sum_i \nu_i G_i^\circ = \sum_i \nu_i H_i^\circ - T\sum_i \nu_i S_i^\circ$$

As a result of the definition of a standard property change of reaction, this reduces to:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{13.16}$$

The standard heat of reaction is related to temperature:

$$\Delta H^\circ = \Delta H_0^\circ + R\int_{T_0}^{T} \frac{\Delta C_P^\circ}{R}dT \tag{4.18}$$

SVN ΔG(T)

The temperature dependence of the standard entropy change of reaction is developed similarly. Equation (6.21) is written for the standard-state entropy of species i at the constant standard-state pressure $P°$:

$$dS_i^\circ = C_{P_i}^\circ \frac{dT}{T}$$

Multiplying by ν_i, summing over all species, and invoking the definition of a standard property change of reaction yields:

$$d\Delta S^\circ = \Delta C_P^\circ \frac{dT}{T}$$

Integration gives:

$$\Delta S^\circ = \Delta S_0^\circ + R\int_{T_0}^{T} \frac{\Delta C_P^\circ}{R}\frac{dT}{T} \tag{13.17}$$

where ΔS° and ΔS_0° are standard entropy changes of reaction at temperature T and at reference temperature T_0 respectively. Equations (13.16), (4.18), and (13.17) are combined to yield:

$$\Delta G^\circ = \Delta H_0^\circ + R\int_{T_0}^{T} \frac{\Delta C_P^\circ}{R}dT - T\Delta S_0^\circ - RT\int_{T_0}^{T} \frac{\Delta C_P^\circ}{R}\frac{dT}{T}$$

However,
$$\Delta S_0^\circ = \frac{\Delta H_0^\circ - \Delta G_0^\circ}{T_0}$$

Whence,

$$\Delta G^\circ = \Delta H_0^\circ - \frac{T}{T_0}(\Delta H_0^\circ - \Delta G_0^\circ) + R\int_{T_0}^{T} \frac{\Delta C_P^\circ}{R}dT - RT\int_{T_0}^{T} \frac{\Delta C_P^\circ}{R}\frac{dT}{T}$$

Finally, division by RT yields:

$$\frac{\Delta G^\circ}{RT} = \frac{\Delta G_0^\circ - \Delta H_0^\circ}{RT_0} + \frac{\Delta H_0^\circ}{RT} + \frac{1}{T}\int_{T_0}^{T} \frac{\Delta C_P^\circ}{R}dT - \int_{T_0}^{T} \frac{\Delta C_P^\circ}{R}\frac{dT}{T} \tag{13.18}$$

Recall that by Eq. (13.11b), $\ln K = -\Delta G^\circ/RT$.

When the temperature dependence of the heat capacity of each species is given by Eq. (4.4), the first integral on the right side of Eq. (13.18) is given by Eq. (4.19), represented for computational purposes by:

$$\int_{T_0}^{T} \frac{\Delta C_P^\circ}{R}dT = \mathrm{IDCPH(T0,T;DA,DB,DC,DD)}$$

where "D" denotes "Δ". Similarly, the second integral is given by the analog of Eq. (5.15):

$$\int_{T_0}^{T} \frac{\Delta C_P^\circ}{R}\frac{dT}{T} = \Delta A \ln\tau + \left[\Delta B\, T_0 + \left(\Delta C\, T_0^2 + \frac{\Delta D}{\tau^2 T_0^2}\right)\left(\frac{\tau+1}{2}\right)\right](\tau - 1) \tag{13.19}$$

where
$$\tau \equiv \frac{T}{T_0}$$

Calculating ΔH_{rxn} + ΔG_{rxn} from Shomate Equation
↳ NIST Chemistry Webbook

Species	Hof (kJ/mol)	So (J/mol*K)	A	B	C	D	E
Methane	-74.87	186.25	-0.703029	108.4773	-42.52157	5.862788	0.678565
CO2	-393.52	213.79	24.99735	55.18696	-33.69137	7.948387	-0.136638
Oxygen	0	205.15	31.32234	-20.23531	57.86644	-36.50624	-0.007374
Hydrogen	0	130.68	33.066178	-11.363417	11.432816	-2.772874	-0.158558
Carbon	716.669	158.1	21.1751	-0.812428	0.448537	-0.043256	-0.013103
H2O	-241.83	188.84	30.092	6.832514	6.793435	-2.53448	0.082139
CO	-110.53	197.66	25.56759	6.09613	4.054656	-2.671301	0.131021

Temperature (oC)	Temperature (K)	T(K)/1000	H methane	HO2	H Carbon	H H2O	H CO2
25	298.15	0.29815	-74.87190289	-0.00027175	716.6720711	-241.8258731	-393.5253202
80	353.15	0.35315	-72.85059268	1.62465731	717.8178456	-239.9706621	-391.415172
150	423.15	0.42315	-70.06002527	3.725236139	719.2764554	-237.578723	-388.553384
250	523.15	0.52315	-65.58387918	6.805980067	721.3592218	-234.0836327	-384.1761278
350	623.15	0.62315	-60.51781359	9.98933393	723.4400995	-230.4819825	-379.5140465
425	698.15	0.69815	-56.34486143	12.43883388	724.9994782	-227.7047492	-375.859961
450	723.15	0.72315	-54.88589686	13.26504578	725.5190484	-226.7639611	-374.6154071
475	748.15	0.74815	-53.39406668	14.09514029	726.0385173	-225.8155193	-373.358569
500	773.15	0.77315	-51.87007752	14.92840565	726.5578917	-224.8593599	-372.0899952
525	798.15	0.79815	-50.31464956	15.76404482	727.0771787	-223.8954282	-370.81021
550	823.15	0.82315	-48.72851237	16.60117544	727.5963861	-222.9236785	-369.5197146
575	848.15	0.84815	-47.11240153	17.43882983	728.1155216	-221.9440731	-368.2189876
600	873.15	0.87315	-45.46705579	18.27595491	728.6345934	-220.9565825	-366.9084854
625	898.15	0.89815	-43.79321471	19.1114122	729.1536097	-219.9611848	-365.5886429
650	923.15	0.92315	-42.09161669	19.94397781	729.6725791	-218.9578657	-364.259874
675	948.15	0.94815	-40.36299735	20.77234238	730.19151	-217.9466179	-362.9225715
700	973.15	0.97315	-38.60808804	21.59511111	730.710411	-216.9274415	-361.5771079
725	998.15	0.99815	-36.82761474	22.41080374	731.2292908	-215.9003434	-360.2238352
750	1023.15	1.02315	-35.02229699	23.21785451	731.7481582	-214.8653372	-358.8630854
775	1048.15	1.04815	-33.19284703	24.01461216	732.2670218	-213.8224435	-357.4951705
800	1073.15	1.07315	-31.33996904	24.79933996	732.7858905	-212.7716893	-356.1203829
825	1098.15	1.09815	-29.46435853	25.57021566	733.3047729	-211.7131082	-354.7389952
850	1123.15	1.12315	-27.56670171	26.32533148	733.8236778	-210.6467404	-353.3512605
875	1148.15	1.14815	-25.64767508	27.06269414	734.342614	-209.5726324	-351.9574124
900	1173.15	1.17315	-23.70794495	27.78022483	734.8615899	-208.490837	-350.5576653
925	1198.15	1.19815	-21.74816709	28.47575923	735.3806144	-207.4014137	-349.1522142
950	1223.15	1.22315	-19.76898638	29.14704747	735.899696	-206.3044277	-347.741235
975	1248.15	1.24815	-17.77103657	29.79175415	736.4188432	-205.1999511	-346.3248843
1000	1273.15	1.27315	-15.75493999	30.40745833	736.9380645	-204.0880616	-344.9032999

F	G	H
-76.84376	158.7163	-74.8731
-403.6075	228.2431	-393.5224
-8.903471	246.7945	0
-9.980797	172.707974	0
710.347	183.8734	716.669
-250.881	223.3967	-241.8264
-118.0089	227.3665	-110.5271

$C_p° = A + B*t + C*t^2 + D*t^3 + E/t^2$

$H° − H°_{298.15} = A*t + B*t^2/2 + C*t^3/3 + D*t^4/4 − E/t + F − H$

$S° = A*\ln(t) + B*t + C*t^2/2 + D*t^3/3 − E/(2*t^2) + G$

C_p = heat capacity (J/mol*K)

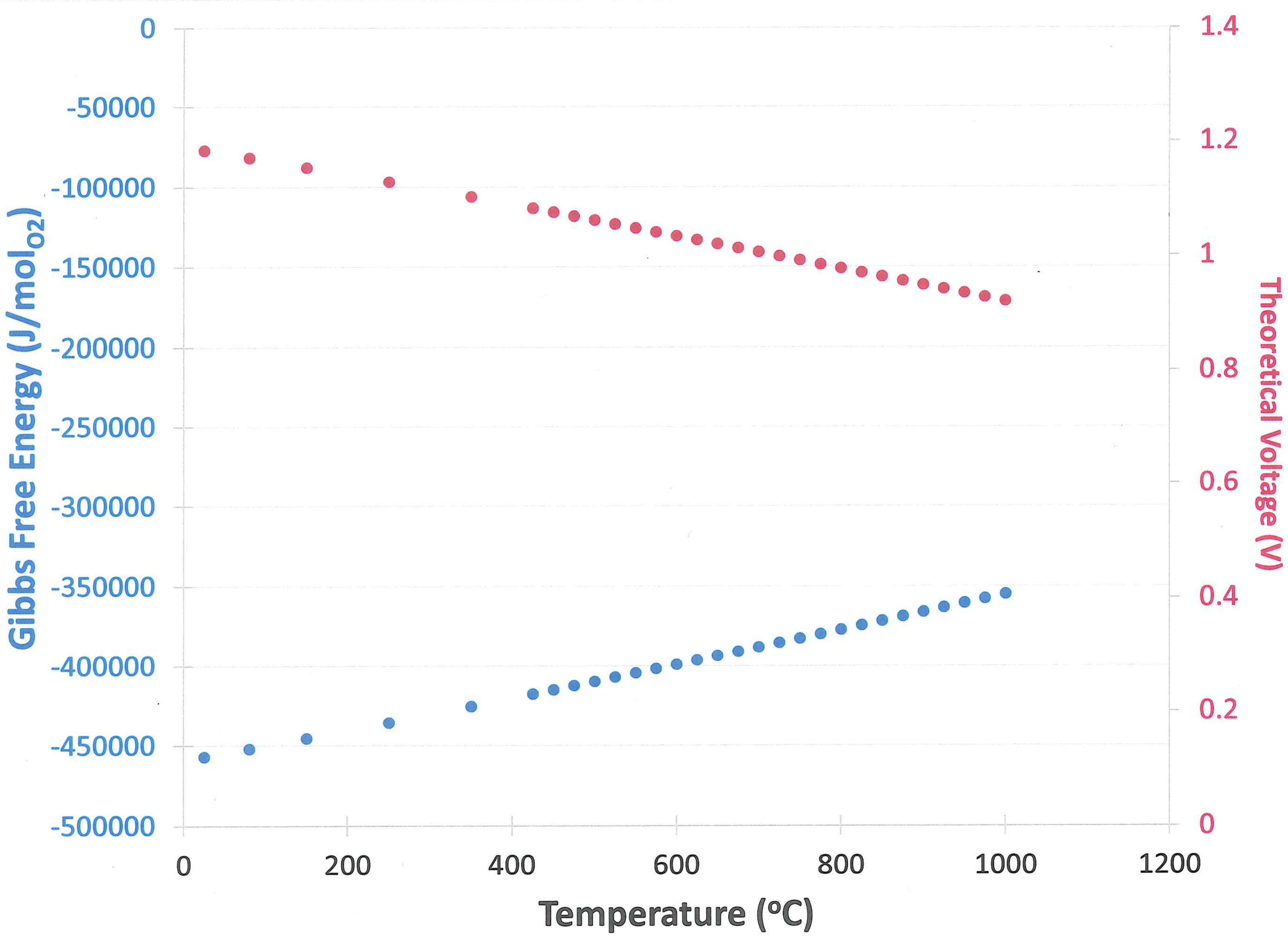
H° = standard enthalpy (kJ/mol)

S° = standard entropy (J/mol*K)

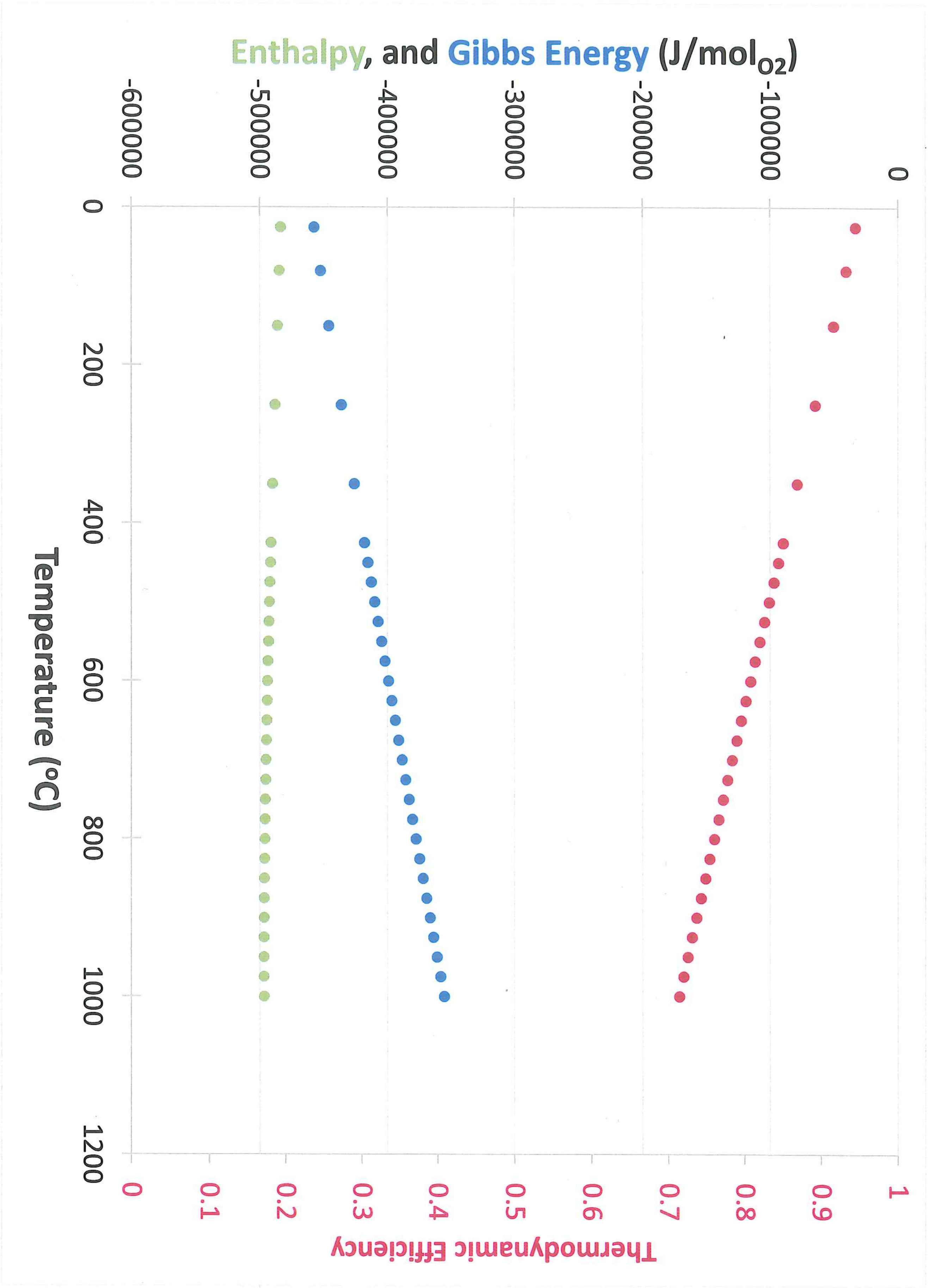
H CO	H Hydrogen	Smethane	SO2	S carbon	S H2O	S CO2	S CO
-110.5238729	0.000149248	186.2547011	205.1472787	158.0992005	188.8352692	213.7876341	197.6628841
-108.9214338	1.593975211	192.4708852	210.1481735	161.6259924	194.5450771	220.2771571	202.5953443
-106.8728401	3.635041449	199.6694537	215.5730819	165.3940837	200.7227242	227.6630021	207.886893
-103.9059583	6.559574395	209.143036	222.1048394	169.8125579	208.1335244	236.9372443	214.1787761
-100.8767537	9.490177385	217.989701	227.6705444	173.45246	214.4306335	245.0855104	219.4757243
-98.55962807	11.69425212	224.3084721	231.381564	175.8153853	218.6379846	250.6207287	222.9862724
-97.77842269	12.43064372	226.361547	232.5442809	176.5465809	219.9619314	252.3721469	224.0856504
-96.99279547	13.16807305	228.3895245	233.6727583	177.2527852	221.2512828	254.0807381	225.1536723
-96.20276186	13.90665525	230.3931257	234.7683118	177.9356503	222.5083975	255.7485967	226.1923796
-95.40834887	14.64650533	232.3729855	235.8320227	178.5966712	223.7353972	257.377648	227.203604
-94.60959421	15.38773722	234.3296683	236.8647673	179.237205	224.9341965	258.9696676	228.1889946
-93.80654568	16.13046296	236.2636808	237.8672406	179.8584871	226.106528	260.5262992	229.1500403
-92.9992606	16.87479203	238.1754819	238.8399781	180.4616457	227.2539641	262.0490683	230.088089
-92.18780537	17.62083084	240.0654904	239.7833735	181.0477135	228.3779354	263.5393959	231.0043645
-91.37225507	18.36868221	241.9340922	240.697694	181.6176383	229.4797462	264.998609	231.89998
-90.55269315	19.11844504	243.7816451	241.5830942	182.1722921	230.5605887	266.4279506	232.7759506
-89.72921118	19.87021394	245.6084833	242.4396277	182.7124788	231.6215544	267.8285879	233.6332035
-88.90190857	20.62407898	247.4149212	243.2672571	183.2389413	232.6636449	269.2016201	234.4725877
-88.07089243	21.38012543	249.201256	244.0658634	183.7523671	233.6877806	270.5480843	235.2948812
-87.23627735	22.13843358	250.9677708	244.8352534	184.2533943	234.6948085	271.8689622	236.1007988
-86.3981853	22.89907852	252.7147358	245.5751671	184.7426157	235.68551	273.1651844	236.8909974
-85.55674547	23.66213006	254.4424108	246.2852838	185.2205832	236.6606059	274.4376353	237.6660821
-84.71209418	24.42765253	256.1510465	246.9652272	185.6878112	237.6207628	275.6871573	238.4266107
-83.8643748	25.1957047	257.8408854	247.6145706	186.1447803	238.5665976	276.9145543	239.1730978
-83.01373762	25.96633969	259.5121632	248.2328414	186.5919401	239.4986816	278.1205947	239.906019
-82.16033982	26.73960484	261.1651095	248.8195244	187.0297114	240.417545	279.3060148	240.6258138
-81.30434541	27.51554169	262.7999488	249.374066	187.4584893	241.3236797	280.4715209	241.3328889
-80.44592514	28.29418587	264.4169009	249.8958768	187.8786445	242.2175427	281.6177921	242.0276209
-79.58525648	29.07556705	266.0161816	250.3843346	188.2905258	243.0995589	282.7454822	242.7103586

Fuel Cell: 2H2+O2 -> 2H2O

S Hydrogen	Delt H (J/mol)	delt S (J/mol K)	delt G (J/mol)	Vcell	efficiency
130.6801501	-483651.7729	-88.83704046	-457165.0093	1.184545753	0.94523588
135.5855369	-484753.932	-92.22909329	-452183.2277	1.171637617	0.932809819
140.8579734	-486152.765	-95.84358045	-445596.5539	1.154571095	0.916577228
147.0618868	-488092.3942	-99.96156421	-435797.5018	1.129181082	0.892858621
152.1878902	-489933.6537	-103.1850578	-425633.885	1.102846457	0.868758212
155.5276039	-491236.8366	-105.1608026	-417818.8223	1.082597096	0.850544567
156.5639293	-491654.2555	-105.7482767	-415182.3892	1.075765918	0.844460074
157.5664403	-492062.325	-106.3030733	-412531.6807	1.068897751	0.838372823
158.5375116	-492460.4359	-106.8265399	-409867.4965	1.061994668	0.832285127
159.479291	-492847.9119	-107.3198104	-407190.6053	1.05505866	0.826199311
160.3937263	-493224.0069	-107.7838269	-404501.7497	1.048091652	0.820117724
161.282588	-493587.902	-108.2193606	-401801.6513	1.041095512	0.814042746
162.1474894	-493938.704	-108.6270287	-399091.0139	1.034072066	0.807976801
162.9899037	-494275.4436	-109.0073101	-396370.528	1.027023101	0.801922356
163.8111787	-494597.0736	-109.360559	-393640.8736	1.01995038	0.79588193
164.61255	-494902.4684	-109.6870169	-390902.7233	1.012855646	0.7898581
165.3951523	-495190.4221	-109.9868235	-388156.7448	1.005740628	0.783853499
166.1600292	-495459.6485	-110.2600257	-385403.6038	0.998607052	0.777870822
166.9081423	-495708.7798	-110.5065868	-382643.9655	0.99145664	0.771912827
167.6403784	-495936.3663	-110.7263931	-379878.4974	0.984291124	0.765982338
168.357557	-496140.8755	-110.9192612	-377107.8704	0.97711224	0.760082245
169.060436	-496320.6922	-111.084944	-374332.7609	0.969921742	0.754215504
169.7497171	-496474.1173	-111.2231359	-371553.8522	0.9627214	0.748385141
170.426051	-496599.3682	-111.3334774	-368771.8361	0.955513006	0.742594251
171.0900411	-496694.5783	-111.4155602	-365987.4138	0.948298378	0.736846001
171.742248	-496757.7962	-111.4689303	-363201.2974	0.94107936	0.731143628
172.3831928	-496786.9863	-111.4930921	-360414.2107	0.933857828	0.725490443
173.01336	-496780.028	-111.4875114	-357626.8906	0.926635691	0.719889831
173.6332007	-496734.7157	-111.4516184	-354840.0877	0.919414895	0.714345256



Gibbs Free Energy (J/mol$_{O2}$)
0
-50000
-100000
-150000
-200000
-250000
-300000
-350000
-400000
-450000
-500000
0
200
400
600
800
1000
1200
Temperature (°C)
Theoretical Voltage (V)
1.4
1.2
1
0.8
0.6
0.4
0.2
0


Enthalpy, and Gibbs Energy (J/mol$_{O2}$)
0
-100000
-200000
-300000
-400000
-500000
-600000
0
200
400
600
800
1000
1200
Temperature (°C)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Thermodynamic Efficiency

What if our reaction is not @ STP?

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

$$\Delta G = \Delta G^\circ + RT \ln\left(\frac{a_R^{\nu_R}}{a_O^{\nu_O}}\right)$$

$$-nFE_{eq} = -nFE^\circ + RT \ln\left(\frac{a_R^{\nu_R}}{a_O^{\nu_O}}\right)$$

$$E_{eq} = E^\circ - \frac{RT}{nF} \ln\left(\frac{a_R^{\nu_R}}{a_O^{\nu_O}}\right)$$

$$\boxed{E_{eq} = E^\circ + \frac{RT}{nF} \ln\left(\frac{a_O^{\nu_O}}{a_R^{\nu_R}}\right)} \Longrightarrow \text{Nernst Equation}$$

for liquid: $a_i = \gamma_i C_i$

for vapor: $a_i = \gamma_i P_i$

for solid $a_i \cong \underline{1}$

For liquids:

$$E_{eq} = E^{o} + \frac{RT}{nF} \ln\left(\frac{\gamma_O^{\nu_O} C_O^{\nu_O}}{\gamma_R^{\nu_R} C_R^{\nu_R}}\right)$$

$$\underbrace{E_{eq} = E^{o} + \frac{RT}{nF} \ln\left(\frac{\gamma_O^{\nu_O}}{\gamma_R^{\nu_R}}\right)}_{E^{o\prime} \equiv \text{Formal Potential}} + \frac{RT}{nF} \ln\left(\frac{C_O^{\nu_O}}{C_R^{\nu_R}}\right)$$

$$E^{o\prime} = E^{o} + \frac{RT}{nF} \ln\left(\frac{\gamma_O^{\nu_O}}{\gamma_R^{\nu_R}}\right)$$

When $\gamma_O = \gamma_R = 1$:

$E^{o\prime} = E^{o}$ ⇒ Common Assumption!

$$\boxed{E_{eq} = E^{o\prime} + \frac{RT}{nF} \ln\left(\frac{C_O^{\nu_O}}{C_R^{\nu_R}}\right)}$$

⇒ Most common Form of the Nernst Eqn!

→ relate to Al/Air cell $[O_2] \sim 2\times10^{-4}$ M

$[Al(OH)_4^-] \sim$ <u>very</u> low (initially ~ 0!)

Example :

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

ν_{ene} $O \rightarrow Fe^{+3}$, $\nu_o = 1$

$R \rightarrow Fe^{+2}$, $\nu_R = 1$

$$E_{eq} = E^{o'} + \frac{RT}{nF} \ln \frac{[Fe^{+3}]}{[Fe^{+2}]}$$

if we assume : $\gamma_o = \gamma_R \approxeq 1$

$E^{o'} \doteq E^o$

$$E_{eq} = E^o + \frac{RT}{nF} \ln \frac{[Fe^{+3}]}{[Fe^{+2}]}$$

$$\boxed{E_{eq} = 0.77V + \frac{RT}{nF} \ln \frac{[Fe^{+3}]}{[Fe^{+2}]}}$$

Example 2 : $Fe^{+2} + 2e^- \rightleftharpoons Fe(s)$

Assume γ_i's $= 1$

$$E_{eq} = E^o + \frac{RT}{nF} \ln\left(\frac{a_{Fe^{+2}}}{a_{Fe}}\right)$$

$$E_{eq} = E^o + \frac{RT}{nF} \ln a_{Fe^{+2}} = E^o + \frac{RT}{nF} \ln(\gamma_{Fe^{+2}} C_{Fe^{+2}})$$!

$$E_{eq} = E^o + \frac{RT}{nF} \ln [Fe^{+2}]$$

$$\boxed{E_{eq} = -0.44 + \frac{RT}{nF} \ln [Fe^{+2}]}$$