Short Course of Electrochemistry
L1: Thermodynamics and Faraday’s Law

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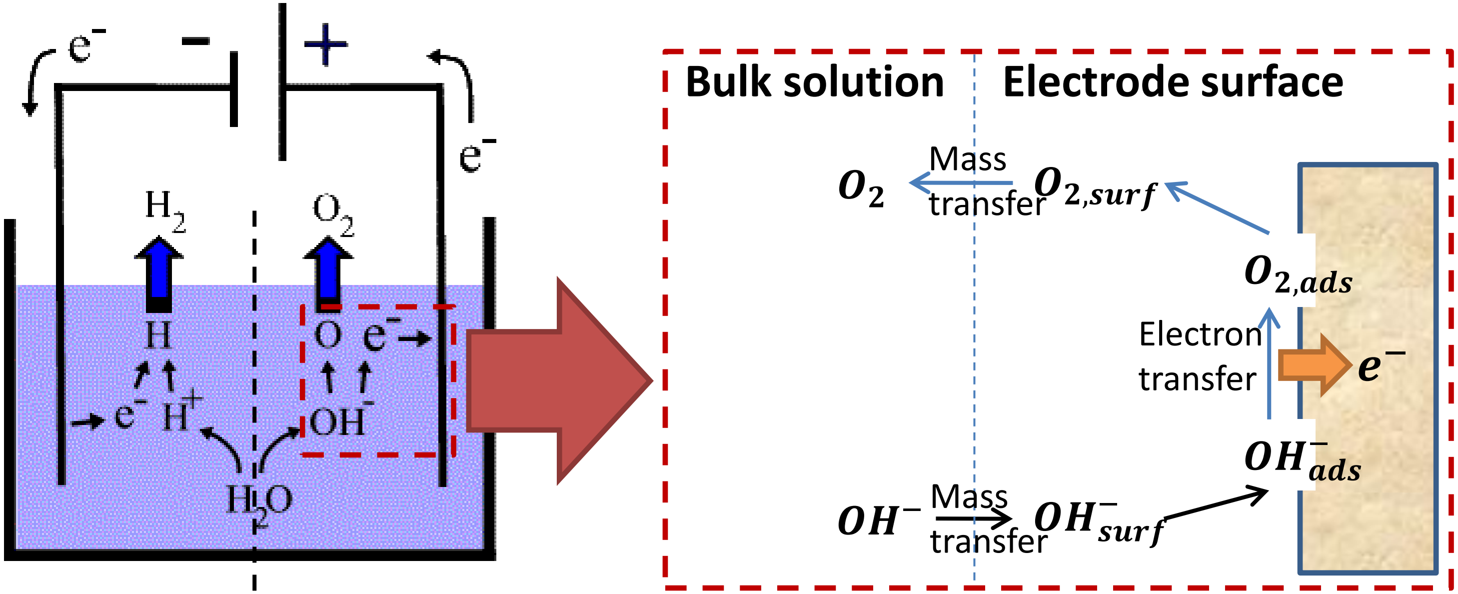
Thermodynamics of Electrochemistry

Electrochemistry

- Electrochemistry concerns with the interrelation of electrical and chemical effects.

Water Electrolyzer



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

$$(2H_2O + 2e^- \rightarrow H_2 + 2OH^-)$$

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

http://www.nmsea.org/Curriculum/7_12/electrolysis/electrolysis.htm

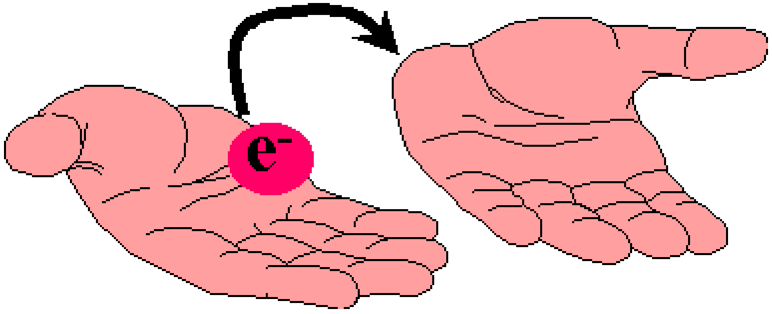
Electrochemical Principal

Oxidation and Reduction!
= Redox reaction

Oxidation (anode) - an increase in oxidation number

Reduction (cathode) - a decrease in oxidation number

Where there is oxidation,
there is reduction



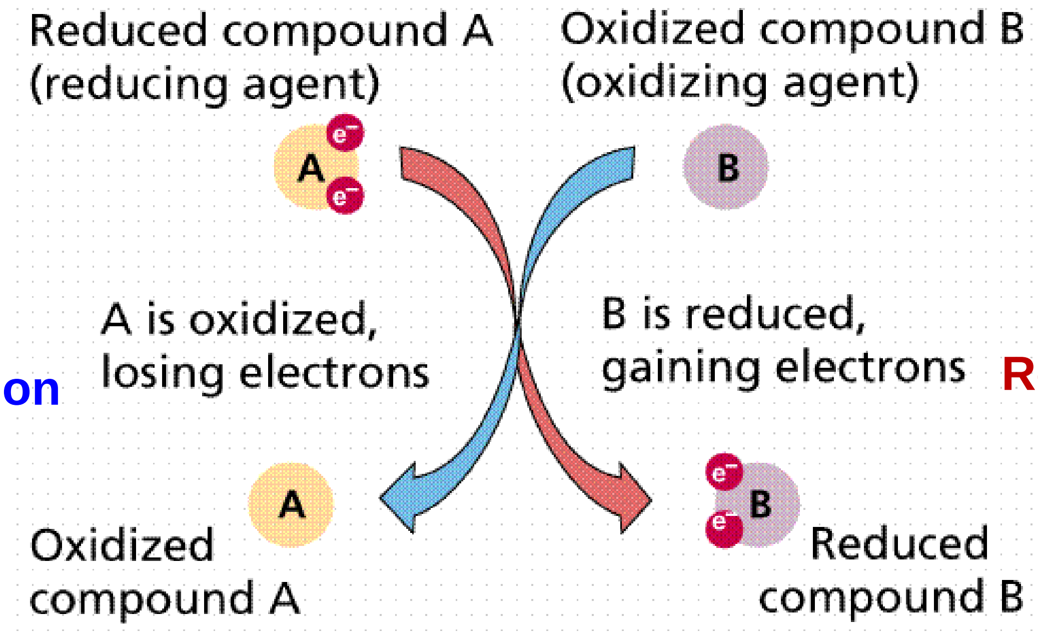
http://bouman.chem.georgetown.edu/S02/lect25/lect25.htm

Oxidation and Reduction

= Redox reaction

還原劑
Reductant

氧化劑
Oxidant



氧化反應
Oxidation reaction

還原反應
Reduction reaction

Electrochemical Applications

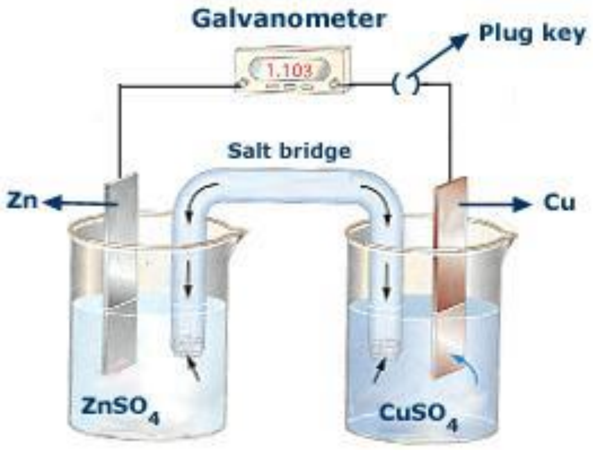
- **Energy conversion and storage**
  - Primary battery, secondary battery, fuel cell, supercapacitor
- **Analytical electrochemistry**
  - Linear sweep voltammetry, cyclic voltammetry, stripping voltammetry, impedance analysis
- **Metal electro-deposition and metal dissolution**
- **Corrosion**
  - Electrochemical machining, anodizing
- **Bio-electrochemistry**
- **Organic electrochemistry**
- **Photo-electrochemistry**
- **Dispersion/interface science**

Important Factors in Electrochemistry

- **Thermodynamics: 熱力學**
  - Cell potential 電位
  - At equilibrium condition
  - The limits of nature
- **Kinetics: 動力學**
  - Polarization 極化
  - Reaction rate
  - Reaction mechanism
- **Transport phenomena: 輸送現象**
  - Transport of momentum, heat, material, and charge
  - Uniformity
  - Mass and heat balance

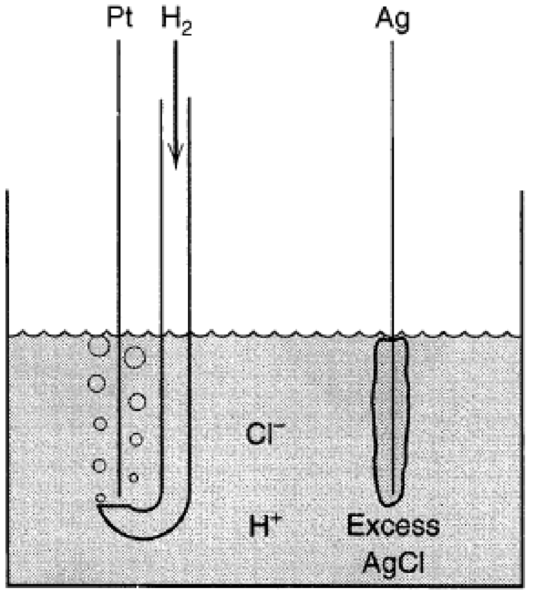
Electrode Process

- **An understanding of thermodynamic properties associated with electrode processes is fundamental in order to answer questions such as:**
  - Why is it that half-reactions in electrochemical cells proceed spontaneously in one direction and furnish current?
  - What is the effect of the salt bridge?
  - What is the effect of ion migration?



Shorthand Notation of EC Cells

- **Anode / Solution A // Solution B / Cathode**
  - “ / ” represents a phase boundary
  - “ // “ or represents a phase boundary which potential drop across the boundary can be negligible.
  - “ , “ separates two components in the same phase



Ag / AgCl / Cl^- // H^+ / H_2 / Pt

Anode: $2Ag + 2HCl \rightarrow 2AgCl + 2H^+ + 2e^-$
Cathode: $2H^+ + 2e^- \rightarrow H_2$

Example 1

Oxidation reaction : $Zn \Rightarrow Zn^{+2} + 2e^{-}$

Reduction reaction : $Cu^{+2} + 2e^{-} \Rightarrow Cu$

Overall reaction : $Zn + Cu^{+2} \Rightarrow Zn^{+2} + Cu$

$Zn / Zn^{2+}(aq) // Cu^{2+}(aq) / Cu$

Example 2

$Hg / Hg_2Cl_2 / Cl^-(aq) // Zn^{2+}(aq) / Zn$

The half reactions are:

Anode: $2Hg + 2Cl^- \rightarrow Hg_2Cl_2 + 2e^-$

Cathode: $Zn^{2+} + 2e^- \rightarrow Zn$

Energy and Potential

- The relationship between "energy" and "potential" is:

$$\Delta G = -nFE$$

ΔG: Gibbs free energy

n: Electron-transfer number

E: Potential

- Spontaneous and non-spontaneous
- $\Delta E > 0, \Delta G < 0$… Spontaneous
- $\Delta E < 0, \Delta G > 0$… Non-spontaneous

Standard Reduction Potential, E^0

$$\boldsymbol{Fe^{3+} + e^- \rightarrow Fe^{2+} \quad E^0 = 0.77\ V\ vs.SHE}$$

What are Fe^{3+} and Fe^{2+} concentrations? 1 M?

No! They are at **unit activity, a = 1**!

a = γ×C

a: Activity

γ: Activity coefficient

C: Molar concentration

However, γ is considered of 1 for most cases.

→ **Thinking of Formal Potential, $E^{0'}$, see p.52 (Bard)**

Table of Standard Reduction Potential

- **The standard potentials listed in the table are:**
  - Reduction potential
  - vs. SHE.
  - 25 °C
  - Gas=1 atm
  - Ionic activity=1

Hint: The **standard hydrogen electrode** (abbreviated **SHE**), also called **normal hydrogen electrode** (**NHE**). That implies that the pressure of hydrogen gas is 1 atm and the activity of hydrogen ions in the solution is 1 molar.

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

Thinking of RHE (Reversible hydrogen electrode)!

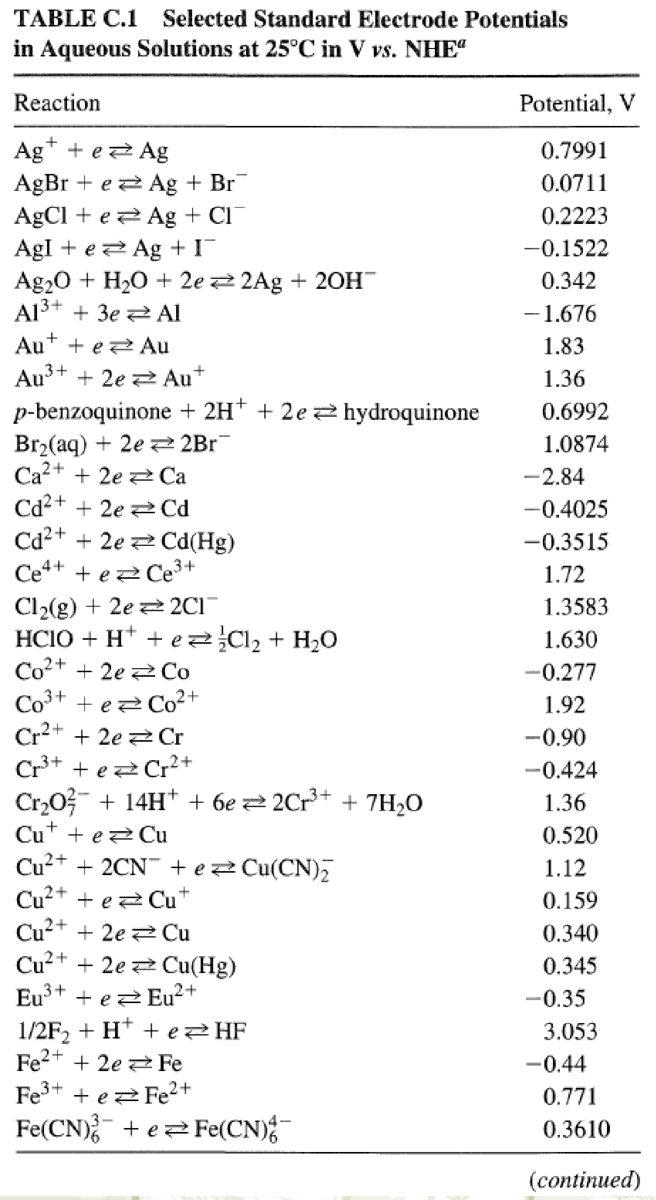


TABLE C.1 Selected Standard Electrode Potentials in Aqueous Solutions at 25°C in V *vs.* NHE[a]

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)

Free Energy and Cell Potential

★ $$\Delta G_{cell} = -nFE_{cell}$$

Given that, by convention, the half-reaction on the left is considered to be an oxidation and that on the right a reduction we have

$$E_{cell} = \underbrace{E_{right}}_{\text{Cathode}} - \underbrace{E_{left}}_{\text{Anode}}$$

Hint:
E_{right} and E_{left} are "reduction potentials"

where E_{right} and E_{left} are the potentials of each half-cell, obtained from the Nernst equation.

$E_{cell} < 0$ → Non-spontaneous.

$E_{cell} > 0$ → Spontaneous!

Example

$$\Delta G^0_{cell} = -nFE^0_{cell} \Rightarrow E^0_{cell} = -\frac{\Delta G^0_{cell}}{nF}$$

Half-cell reaction:

$$Cu^{2+} + 2e^- \rightarrow Cu \quad E^0 = 0.340\,V$$

$$Zn^{2+} + 2e^- \rightarrow Zn \quad E^0 = -0.760\,V$$

Zn-Cu battery:

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

$$E^0_{cell} = 0.340 - (-0.760) = 1.10\,V$$

$$\Delta G^0_{cell} = -2 \times 96485 \times 1.10 = -212\,\frac{kJ}{mol}$$

Example

Hg / Hg$_2$Cl$_2$ / Cl$^-$(aq) // Zn^{2+}(aq) / Zn

⇩

$$2Hg + 2Cl^- + Zn^{2+} \rightarrow Hg_2Cl_2 + Zn$$

⇩

$$Zn^{2+} + 2e^- \rightarrow Zn \quad E^0 = -0.76\ V$$

$$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^- \quad E^0 = 0.27\ V$$

⇩

$$E^0_{cell} = -0.76 - 0.27 = -1.03\ V$$

$$\Delta G^0_{cell} = -2 \times 96485 \times -1.03 = 199\frac{kJ}{mol}$$

Example

$$Ag + e^{-} \rightarrow Ag \quad E^{0} = 0.80\ V$$
$$Cu^{2+} + 2e^{-} \rightarrow Cu \quad E^{0} = 0.34\ V$$

$$2Ag^{+} + Cu \rightarrow 2Ag + Cu^{2+} \quad E^{0}_{cell} = ?$$

Wrong Answer:

$$E_{cell} = 0.80 \times 2 - 0.34 = 1.26\ V$$

Correct Answer:

$$E_{cell} = 0.80 - 0.34 = 0.46\ V$$

Why?

Calculation from ΔG change

$$Ag + e^{-} \rightarrow Ag \quad E_1^0 = 0.80\,V$$
$$Cu^{2+} + 2e^{-} \rightarrow Cu \quad E_2^0 = 0.34\,V$$

$$2Ag^{+} + Cu \rightarrow 2Ag + Cu^{2+} \quad E_{cell}^0 = ?$$

$$\boxed{\begin{array}{c} 2\Delta G_1^0 - 1\Delta G_2{}^0 = \Delta G_3^0 \\ 2 \times 1FE_1^0 - 1 \times 2FE_2^0 = 2FE_{cell}^0 \\ 2F \times 0.80 - 2F \times 0.34 = 2FE_{cell}^0 \\ E_{cell}^0 = 0.46\,V \end{array}}$$

The addition of half-cell reactions to form an overall-cell reaction can be carried out through direct addition of potentials.

Example

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad E_1^0 = 0.70\ V$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad E_2^0 = 1.76\ V$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E_3^0 = ?$$

Rules for combination of half cell potentials:

Don’t combine each half-cell potential!

You MUST combine each Gibbs free energy!

$$\Delta G_1^0 + \Delta G_2^0 = \Delta G_3^0$$

$$2FE_1^0 + 2FE_2^0 = 4FE_3^0$$

$$2F \times 0.70 + 2F \times 1.76 = 4FE_3^0$$

$$E_3^0 = 1.23\ V$$

Nernst Equation

- **the Nernst equation is an equation that relates the cell or the half-cell potential at any point in time to the standard electrode potential, temperature, activity, and reaction quotient of the underlying reactions and species used.**
- Case I, half-cell reaction

$$aA + ne^- \rightarrow cC \quad E^0$$

$$E = E^0 + \frac{RT}{nF} ln \frac{a_A^a}{a_C^c}$$

- Case II, cell reaction

$$aA + bB \rightarrow cC + dD \quad E_{cell}^0$$

$$E_{cell} = E_{cell}^0 + \frac{RT}{nF} ln \frac{a_A^a a_B^b}{a_C^c a_D^d}$$

Example: Zn-Cu Battery

$$Cu^{2+} + 2e^- \rightarrow Cu \quad E^0 = 0.337\,V$$
$$Zn^{2+} + 2e^- \rightarrow Zn \quad E^0 = -0.7628\,V$$

If $[Cu^{2+}] = 0.1$ M and $[Zn^{2+}] = 1.0$ M at 25 °C, what are half-cell potentials and overall-cell potential of Zn-Cu battery? All activity coefficients are equal to unity.

$$E_{Zn^{2+}/Zn} = -0.76 + \frac{RT}{2F}\ln[Zn^{2+}] = -0.76 + \frac{0.05916}{2}\log 1 = -0.76$$

$$\boxed{\frac{RT}{nF}\ln C = \frac{0.05916}{n}\log C}$$

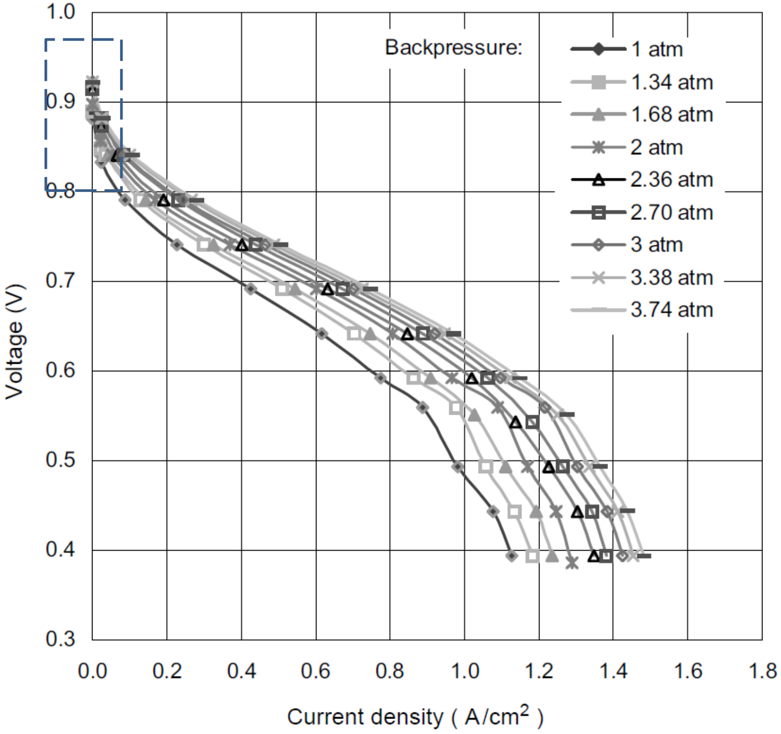
$$E_{Cu^{2+}/Cu} = 0.34 + \frac{RT}{2F}\ln[Cu^{2+}] = 0.34 + \frac{0.05916}{2}\log 10^{-1} = 0.31042$$

$$E_{cell} = E_{Cu^{2+}/Cu} - E_{Zn^{2+}/Zn} = [0.34 - (-0.76)] + \frac{RT}{2F}(\ln\frac{[Cu^{2+}]}{[Zn^{2+}]}) = 1.10 + \frac{0.05916}{2}\log\frac{10^{-1}}{1} = 1.07042$$

Concentration Effect on Fuel Cell

Anode: $H_2 \rightarrow 2H^+ + 2e^- \quad E^0 = 0\ V$
Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E^0 = 1.23\ V$
Overall: $2H_2 + O_2 \rightarrow 2H_2O \quad E^0_{cell} = 1.23\ V$

$$E_{cell} = E^0_{cell} + \frac{RT}{nF} ln \boxed{\frac{P^2_{H_2} P_{O_2}}{a^2_{H_2O}}}$$



High pressure of H2/air shows a high performance, but what is the drawback?

L. Wang, A. Husar, T. Zhou, H. Liu, A parametric study of PEM fuel cell performances. Int.J. Hydrogen Energy, 28 (2003) 1263-1272

http://sa.ylib.com/read/readshow.asp?FDocNo=655&CL=18

Temperature Variation of Nernst Eq’n

$$E_{cell} = E^0_{cell} + \frac{RT}{nF} ln \boxed{\frac{P^2_{H_2} P_{O_2}}{a^2_{H_2O}}}$$

Anode: $H_2 \rightarrow 2H^+ + 2e^- \quad E^0 = 0\ V$

Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E^0 = 1.23\ V$

Overall: $2H_2 + O_2 \rightarrow 2H_2O \quad E^0_{cell} = 1.23\ V$

- **For example, the fuel cell is operated by 1 atm H_2/Air with temperature 25°C. If the cell temperature is increased to specific temperatures, maybe “someone” think that the potential is:**
- **25°C,** $E_{cell} = 1.23 + \frac{8.314 \times 298}{4F} ln\left(1^2 \times 0.2\right) = 1.220\ V$
- **80°C,** $E_{cell} = 1.23 + \frac{8.314 \times 353}{4F} ln\left(1^2 \times 0.2\right) = 1.218\ V$
- **600°C,** $E_{cell} = 1.23 + \frac{8.314 \times 1073}{4F} ln\left(1^2 \times 0.2\right) = 1.200\ V$

Are these calculation correct? Not exactly.

Temperature Variation and Gibbs Free Energy

$$aA + bB \rightarrow cC + dD \quad E^0_{cell}$$

$$E_{cell} = E^0_{cell} + \frac{RT}{nF} ln \frac{a^a_A a^b_B}{a^c_C a^d_D}$$

$$E^0_{cell} \Rightarrow E^0_{cell}(T)$$

The standard cell potential should be changed to the specific temperature from 25°C.

At constant pressure:

$$\because \Delta G^0 = -nFE^0$$

$$\therefore \frac{\partial E^0}{\partial T} = -\frac{1}{nF}\frac{\partial \Delta G^0}{\partial T} = \frac{1}{nF}\Delta S^0$$

Note: 這個運算是簡化的結果，並沒有考慮溫度改變對於熱容量變化的影響。

Temperature Effect on Fuel Cell

- **When the product is liquid water:**

$$\frac{\partial E^0}{\partial T} = \frac{1}{nF}\Delta S^0$$

$$= \frac{1}{4F}[2 \times 69.96 - (2 \times 130.66 + 205.17)]$$

$$= -0.85\frac{mV}{K}$$

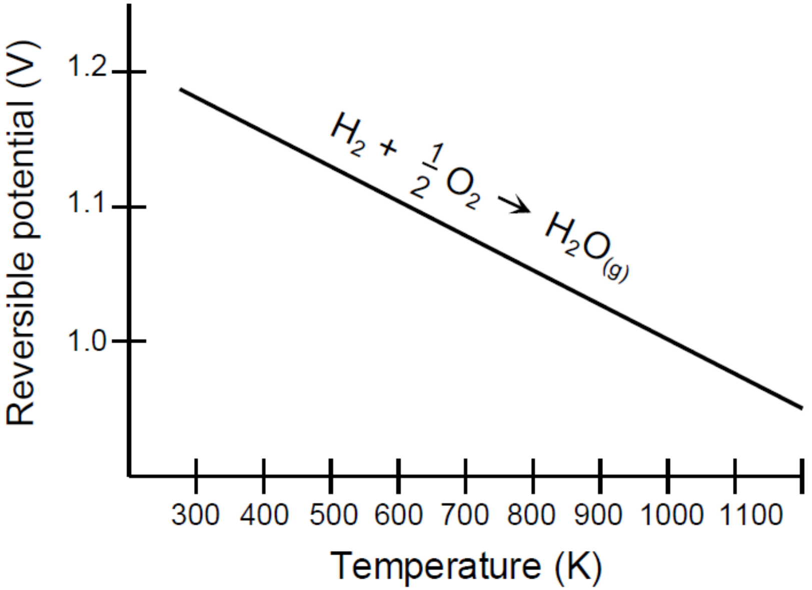
- **When the product is vapor water:**

$$\frac{\partial E^0}{\partial T} = \frac{1}{nF}\Delta S^0$$

$$= \frac{1}{4F}[2 \times 188.8 - (2 \times 130.74 + 205.25)]$$

$$= -0.23\frac{mV}{K}$$

		S^0 @ 298 K (J/mol×K)
H_2	g	130.66
O_2	g	205.17
H_2O	g	188.84
H_2O	l	69.96



Energy Change and Potential

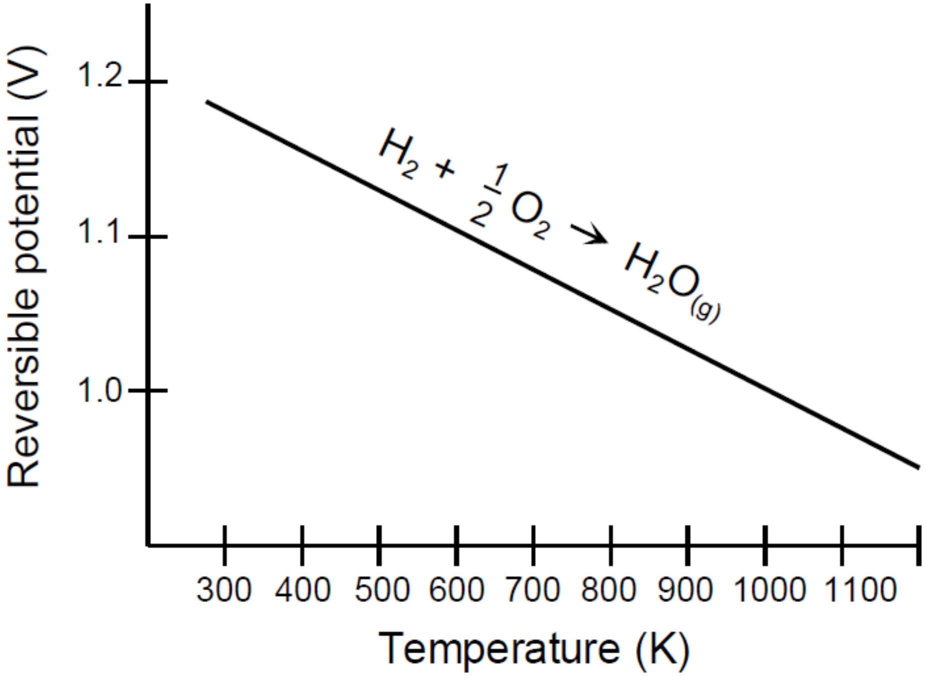
@298.15 K	$\Delta H\ (\frac{kJ}{mol})$	$\Delta S\ (\frac{kJ}{mol\ K})$	$\Delta G\ (\frac{kJ}{mol})$
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O_{(l)}$	-286.02	-0.1633	-237.34
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O_{(g)}$	-241.98	-0.0444	-228.74

$C_P = a + bT + CT^2$	a	b	c
H_2	28.91404	-0.00084	2.01×10^{-6}
O_2	25.84512	0.012987	-3.90×10^{-6}
$H_2O_{(g)}$	30.62644	0.009621	1.18×10^{-6}

- $\Delta H_T = \Delta H_{298.15} + \Delta a(T - 298.15) + \frac{\Delta b(T^2 - 298.15^2)}{2} + \frac{\Delta c(T^3 - 298.15^3)}{3}$
- $\Delta S_T = \Delta S_{298.15} + \Delta a \ln\left(\frac{T}{298.15}\right) + \Delta b(T - 298.15) + \frac{\Delta c(T^2 - 298.15^2)}{2}$
- $\Delta G_T = \Delta H_T - T\Delta S_T = -nFE \Rightarrow \boxed{E = -\frac{\Delta G_T}{nF}}$

OCP of Fuel Cell

OCP = Open-circuit-potential = Reversible potential



Temperature	25℃ (298K)	80℃ (353K)	100℃ (373K)	205℃ (478K)	650℃ (923K)	800℃ (1073K)	1100℃ (1373K)
Cell Type		PEFC	AFC	PAFC	MAFC	ITSOFC	TSOFC
Ideal Voltage	1.18	1.17	1.16	1.14	1.03	0.99	0.91

Water Dissociation, E^0_{water}

Acid solution

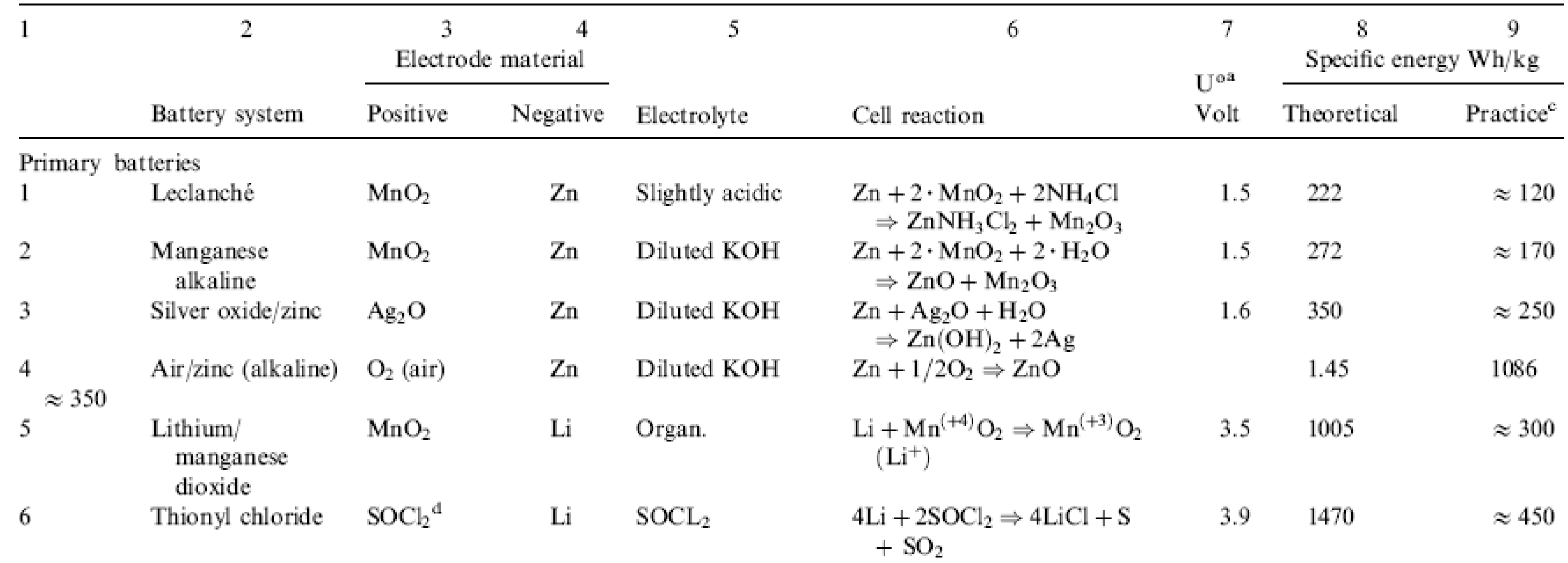
$2H^+ + 2e^- \rightarrow H_2$	0 (by definition)
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	$+1.23$

Base/Neutral solution

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.83
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	$+0.40$

Side Reaction due to Water Dissociation

- **Water dissociation potential,**
  - E^0_{water} = -1.23 V
- **Any applied potential larger than |1.23| V is supposed to automatically decompose water.**



1	2	3	4	5	6	7	8	9
		Electrode material					Specific energy Wh/kg	
	Battery system	Positive	Negative	Electrolyte	Cell reaction	U^{oa} Volt	Theoretical	Practice[c]
Primary batteries								
1	Leclanché	MnO_2	Zn	Slightly acidic	$Zn + 2 \cdot MnO_2 + 2NH_4Cl \Rightarrow ZnNH_3Cl_2 + Mn_2O_3$	1.5	222	≈ 120
2	Manganese alkaline	MnO_2	Zn	Diluted KOH	$Zn + 2 \cdot MnO_2 + 2 \cdot H_2O \Rightarrow ZnO + Mn_2O_3$	1.5	272	≈ 170
3	Silver oxide/zinc	Ag_2O	Zn	Diluted KOH	$Zn + Ag_2O + H_2O \Rightarrow Zn(OH)_2 + 2Ag$	1.6	350	≈ 250
4 ≈ 350	Air/zinc (alkaline)	O_2 (air)	Zn	Diluted KOH	$Zn + 1/2O_2 \Rightarrow ZnO$		1.45	1086
5	Lithium/ manganese dioxide	MnO_2	Li	Organ.	$Li + Mn^{(+4)}O_2 \Rightarrow Mn^{(+3)}O_2 (Li^+)$	3.5	1005	≈ 300
6	Thionyl chloride	$SOCl_2$[d]	Li	$SOCL_2$	$4Li + 2SOCl_2 \Rightarrow 4LiCl + S + SO_2$	3.9	1470	≈ 450

Faraday’s Law of Electrochemistry

Thinking of Cell Potential

- **Cell potential calculated by Nernst equation (or $E_{cell} = E_{right} - E_{left}$) is based on "thermodynamic equilibrium situation", indicating as follows:**
  - No current flows in this experiment ($i = 0$).
  - No net faradaic reaction occurs.
  - Many of the variables (electrode area, mass transfer, electrode geometry) do not affect the potential directly.

Height ~ Gate ~ Water Flow

Potential Connection Current

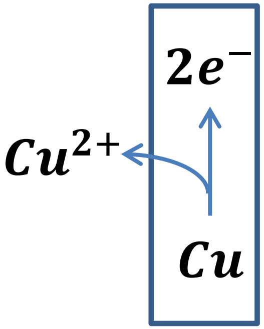
Shimen reservoir
石門水庫

Ref: http://www.tia.org.tw/report/PS0931206.htm

Faraday's law

- **The amount of chemical reaction caused by the flow of current is proportional to the amount of electricity passed.**

$$\frac{dN}{dt} = \frac{1}{nF}\frac{dQ}{dt} = \frac{i}{nF}$$



Question

- During the 4.0 h electrodeposition of copper from a copper sulfate (Cu_SO_4) solution, 140.0 g of Cu was deposited. What was the current flowing through the cell?
- Answer:

$$\frac{dN}{dt} = \frac{i}{nF}$$

$$140\ g\ Cu \Rightarrow 2.20\ mol\ Cu$$

$$\frac{2.20}{4 \times 60 \times 60} = \frac{i}{2 \times 96500}$$

$$i = 29.47\ A$$