Chemistry 163B W2014
Lectures 24-25- Electrochemistry Quickie

Chemistry 163B

Electrochemistry

1

activity coefficients for ions (HW9 #58)

$$BaCl_2(s) \rightleftarrows Ba^{2+}(aq) + 2\,Cl^-(aq)$$

$$K_{sp} = \frac{\left(a_{Ba^{2+}(aq)}\right)\left(a_{Cl^-(aq)}\right)^2}{\left(a_{BaCl_2(s)}\right)}$$

$$a_{BaCl_2(s)} = 1$$

$$a_{Ba^{2+}(aq)} = \gamma_{Ba^{2+}}\left[Ba^{2+}\right]$$

$$a_{Cl^-(aq)} = \gamma_{Cl^-}\left[Cl^-\right]$$

cannot determine $\gamma_{Ba^{2+}}$ *and* γ_{Cl^-} *independently*

but only $\gamma_{Ba^{2+}} = \gamma_{Cl^-} = \gamma_\pm \quad (\gamma_+ = \gamma_- \equiv \gamma_\pm)$

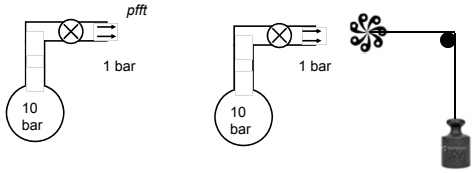
$$K_{sp} = \frac{(\gamma\pm)^3}{1}\,\frac{\left(\left[Ba^{2+}\right]/1M\right)\left(\left[Cl^-\right]/1M\right)^2}{(1)}$$

$$K_{sp} = (\gamma\pm)^3\left[Ba^{2+}\right]\left[Cl^-\right]^2$$

2

work of expansion

H_2 (10 bar) ⟶ H_2(1 bar)



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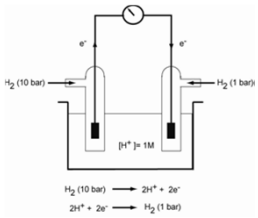
hydrogen pressure ['concentration'] cell (reaction I of III)



H_2 (10 bar) ⟶ H_2(1bar)

$$\Delta\mu = \Delta\mu^* + \underline{R}T\ln Q_{reaction}$$

$\Delta\mu^* = 0$ $\quad \Delta\mu^*$ is for reaction $H_2(P = 1\text{ bar}) \rightarrow H_2(P = 1\text{ bar})$

$$\Delta\mu = \Delta\mu^* + \underline{R}T\ln\frac{P(1\text{ bar})}{P(10\text{ bar})} = -5.706\ \textbf{kJ per mole } H_2$$

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dμ and work-other (did before for dG)

$$d\mu = d\bar{H} - Td\bar{S} - \bar{S}dT$$

$$d\mu = \underbrace{dq - Td\bar{S}}_{\leq 0 \text{ by 2nd law}} - \bar{S}dT + VdP + dw_{other} \quad \text{(very general)}$$

$$d\mu_{T,P} \leq dw_{other}$$

for a spontaneous process at constant T,P
the MAXIMUM work done ON SURROUNDINGS
is $|\Delta\mu|$ and this occurs when the process approaches

REVERSIBILITY

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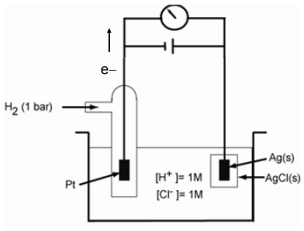
responsible for 3 redox reactions; here's II (HW9, prob #60)



oxidation *anode* H_2 (1 bar) ⟶ $2H^+$ [1M] + $2e^-$

reduction *cathode* $2AgCl(s) + 2e^-$ ⟶ $2Ag(s) + 2Cl^-$ [1M]

$2e^- + H_2$ (g, 1 bar) + 2AgCl(s) ⟶ $2H^+$ [1M] + $2Cl^-$ [1M] + 2Ag(s) + $2e^-$

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Δμ for the reaction

(see Appendix A, Table 4.1 for data; additional decimal places from other tables)

$2e^- + H_2$ (g, 1atm) + 2AgCl(s) ⟶ $2H^+$ [1M] + $2Cl^-$ [1M] + 2Ag(s) + $2e^-$

$\Delta\mu_f \approx \Delta G_f$ (kJ)	0	-109.79	0	-131.23	0

$\Delta\mu \approx \Delta G$ = - (0) -2 (-109.79) + 2(0) + 2(-131.23) + 2 (0) = -42.88 kJ

$\Delta\mu$ =for 2 moles e^- transferred

$e^- + ½\ H_2$ (g, 1atm) + AgCl(s) ⟶ H^+ [1M] + Cl^- [1M] + Ag(s) + e^-

$\Delta\mu \approx \Delta G$=-21.44 kJ per ½ mole H_2

$\Delta\mu$ for 1 mole e^- transferred

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and FINALLY w_{other} !!! (p. 20)

TABLE 2.1 Types of Work

Types of Work	Variables	Equation for Work	Conventional Units
Volume expansion	Pressure (P), volume (V)	$w = -\int_{V_i}^{V_f} P_{external}\, dV$	Pa m^3 = J
Stretching	Force (F), length (l)	$w = \int_{l_i}^{l_f} \mathbf{F} \cdot d\mathbf{l}$	N m = J
Surface expansion	Surface tension (γ), area (σ)	$w = \int_{\sigma_i}^{\sigma_f} \boldsymbol{\gamma} \cdot d\boldsymbol{\sigma}$	$(N\ m^{-1})(m^2)$ = J
Electrical	Electrical potential (ϕ), electrical charge (Q)	$w = \int_0^Q \phi\, dQ'$	V C = J

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w_{other} (p. 260) *p. 260 μ vs μ is overcomplicated* BUT

$$dw_{electrical} = \Phi\, dQ$$

electric potential *charge transfer*

$dQ = -\mathcal{F} dn$ ← *moles of e's transferred*

from negative charge on e

$\mathcal{F}$ *is Faraday constant 96,458 coulomb (mole e)$^{-1}$*

$$dw_{electrical} = -\Phi \mathcal{F} dn$$

$$w_{electrical} = -n\mathcal{F}\Phi \quad \text{(n electrons transferred)}$$

$$(w = -n\mathcal{F}\mathcal{E}) \quad \mathcal{E} = electromotive\ force = \Phi_{rev}$$

E & R p260 z ≡ -n

UNITS: [w] = [Q] [Φ]
joule= coulomb × volt

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sign of Φ and spontaneity

$$\Delta\mu_{T,P} \le w_{other}$$

$\Delta\mu_{T,P} < -n\mathcal{F}\ \Phi_{cell}^{irrev}$ $\quad \Phi_{cell}^{irrev}$ for irreversible

$\Delta\mu_{T,P} = -n\mathcal{F}\ \Phi_{cell}$ $\quad \Phi_{cell} = \mathcal{E}mf$ for reversible

$\Delta\mu_{T,P}$ < 0 spontaneous ⇒ Φ > 0 spontaneous

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Δμ vs Φ

$$\Delta\mu = \Delta\mu^\circ + RT \ln Q_{reaction} = -n\mathcal{F}\Phi$$

$$\Phi = -\underbrace{\frac{\Delta\mu^\circ}{n\mathcal{F}}}_{\Phi^\circ} - \frac{RT}{n\mathcal{F}} \ln Q_{reaction}$$

$$\Phi = \Phi^\circ - \frac{RT}{n\mathcal{F}} \ln Q_{reaction}$$

$$T = 298K$$

$$\Phi = \Phi^\circ - \frac{0.02569\ \text{V}}{\bar{n}} \ln Q_{reaction}$$

n = moles electrons transferred
[n] = mol
$\bar{n}$ = n × mol^{-1}
[$\bar{n}$] = *unitless*

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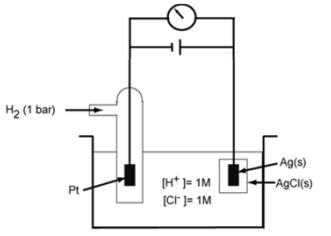
responsible for 3 redox reactions; here's II (HW9, prob #60)



		Φ_0
oxidation *anode*	H_2 (1 bar) ⟶ $2H^+$ [1M] + $2e^-$	0
reduction *cathode*	2AgCl(s) + $2e^-$ ⟶ 2Ag(s) +$2Cl^-$ [1M]	0.22233 V

$2e^- + H_2$ (g, 1bar) + 2AgCl(s) ⟶ $2H^+$ [1M] +$2Cl^-$ [1M] +2Ag(s) + $2e^-$ 0.22233 V

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example incorporating activities

$2e^- + H_2$ (g, 1bar) + 2AgCl(s) ⟶ $2H^+$ [1M] + $2Cl^-$ [1M] + 2Ag(s) $+2e^-$

$$\Phi = \Phi^\circ - \frac{0.02569\ \text{V}}{\overline{n}} \ln\left[\frac{a_{H^+}^2\, a_{Cl^-}^2\, a^2_{(\ldots)}}{a_{H_2}\, a^2_{AgCl(s)}}\right]$$

$a_{AgCl} = a_{Ag} = 1$

$a_{H^+} = \gamma_{H^+}[H^+]$ $\quad a_{Cl^-} = \gamma_{Cl^-}[Cl^-]$

can't independently measure γ_{H^+} and γ_{Cl^-}

$\gamma_{H^+} = \gamma_{Cl^-} = \gamma_\pm$

$$\Phi = \Phi^\circ - \frac{0.02569\ \text{V}}{\overline{n}} \ln\left[\frac{\gamma_\pm^4 [H^+]^2 [Cl^-]^2}{\gamma_{H_2} P_{H_2}}\right]$$

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example incorporating activities

$$\Phi = \Phi^\circ - \frac{0.02569\ \text{V}}{\overline{n}} \ln\left[\frac{\gamma_\pm^4 [H^+]^2 [Cl^-]^2}{\gamma_{H_2} P_{H_2}}\right]$$

0.22233 V $\quad$ $\overline{n}$ = 2 e's

$$\Phi = 0.22233\ \text{V} - \frac{0.02569\ \text{V}}{2} \ln\left[\frac{\gamma_\pm^4 [1M]^2 [1M]^2}{\gamma_{H_2}(1\ \text{bar})}\right]$$

unitless, have dropped standard state conc's and pressure from denominators

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example incorporating activities

$$\Phi = 0.22233 - \frac{0.02569\ \text{V}}{2} \ln\left[\frac{\gamma_\pm^4 [1M]^2 [1M]^2}{\gamma_{H_2}(1\ \text{bar})}\right]$$

- Calculate γ's from observed Φ (HW9, prob 60)
- If γ's =1

$$\Phi = 0.22233\ \text{V} - \frac{0.02569\ \text{V}}{2} \ln[1] = 0.22233\ \text{V} = \Phi^\circ$$

$$\Delta\mu = -n\mathcal{F}\Phi$$

$$\Delta\mu = -2\ mol\ (96{,}485\ C mol^{-1})\ (0.22233\ V)$$

$$\Delta\mu = -4.290 \times 10^4\ CV = -42.90\ kJ$$

$\Delta\mu^\circ$ = -42.88 kJ for 2 moles e^- transferred [from $\Delta\mu_f^\circ$ earlier]

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intensive Φ vs extensive Δμ $\quad \Phi = -(\Delta\mu/n\mathcal{F})$

H_2 (g, 1 bar) ⟶ $2H^+$ [1M] $+2e^-$ $\quad \Phi^\circ$= 0 V

$2e^- + 2AgCl(s)$ ⟶ $2Cl^-$ [1M] + 2Ag(s) $\quad \Phi^\circ$= 0.22233 V

$2e^- + H_2$ (g, 1 bar) + 2AgCl(s) ⟶ $2H^+$ [1M] + $2Cl^-$ [1M] + 2Ag(s) $+2e^-$

Φ_{cell}°= 0.22233 V

Δμ = -42.88 kJ for 2 moles e^- transferred

$$\Phi_{cell\ 2e's} = \Phi_{cell} - \frac{0.02569\ \text{V}}{2} \ln\left[\frac{a_{H^+}^2\, a_{Cl^-}^2\, a^2_{(\ldots)}}{a_{H_2}\, a^2_{AgCl(s)}}\right]$$

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intensive Φ vs extensive Δμ $\quad \Phi = -(\Delta\mu/n\mathcal{F})$

½H_2 (g, 1 bar) ⟶ H^+ [1M] $+e^-$ $\quad \Phi^\circ$= 0 V

e^- + AgCl(s) ⟶ Cl^- [1M] + Ag(s) $\quad \Phi^\circ$= 0.22233 V

$e^- + ½H_2$ (g, 1 bar) + AgCl(s) ⟶ H^+ [1M] + Cl^- [1M] + Ag(s) $+e^-$

Φ_{cell}°= 0.22233 V

Δμ = -21.44 kJ for 1 moles e^- transferred

Φ° intensive same as for 2 mole e's

Φ is oomph per electron

$$\Phi_{cell\ 1e} = \Phi_{cell} - \frac{0.02569\ \text{V}}{1} \ln\left[\frac{a_{H^+}^1\, a_{Cl^-}^1\, a^1_{(\ldots)}}{a^{1/}_{(\ldots)}\, a^1_{AgCl(s)}}\right]$$

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intensive Φ vs extensive Δμ $\quad \Phi = -(\Delta\mu/n\mathcal{F})$

Δμ = -42.88 kJ for 2 moles e^- transferred

$$\Phi_{cell\ 2e's} = \Phi_{cell} - \frac{0.02569\ \text{V}}{2} \ln\left[\frac{a_{H^+}^2\, a_{Cl^-}^2\, a^2_{(\ldots)}}{a_{H_2}\, a^2_{AgCl(s)}}\right]$$

$\Delta\mu_{2e} = 2\Delta\mu_{1e}$ two times greater

$\Phi_{cell\ 2e} = \Phi_{cell\ 1e}$ same

Δμ = -21.44 kJ for 1 moles e^- transferred

$$\Phi_{cell\ 1e} = \Phi_{cell} - \frac{0.02569\ \text{V}}{1} \ln\left[\frac{a_{H^+}^1\, a_{Cl^-}^1\, a^1_{(\ldots)}}{a^{1/}_{(\ldots)}\, a^1_{AgCl(s)}}\right]$$

Δμ extensive: depends on stoichiometry ⟶ $\Delta\mu = -n\mathcal{F}\Phi$ ⟵ ***Φ intensive: independent of 'how reaction is written' ooomph PER electron***

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biological example: cytochrome C iron containing enzyme (reaction III)

CytC=cytochrome C
standard state pH=7, [H+]=10^{-7}

standard REDUCTION potentials	$\Phi^{\circ\prime}_{red}$(V) pH7
$2e^- +$ $2CytC(Fe^{3+}) \longrightarrow 2CytC(Fe^{2+})$	0.25
$2e^- + \frac{1}{2}O_2(g) + 2H^+(aq) \longrightarrow H_2O(\ell)$	0.816

reaction: the oxidation of CytC(Fe^{2+})	$\Phi^{\circ\prime}$(V)
oxidation $2CytC(Fe^{2+}) \longrightarrow 2CytC(Fe^{3+}) + 2e^-$	- 0.25
reduction $2e^- + \frac{1}{2}O_2(g) + 2H^+(aq) \longrightarrow H_2O(\ell)$	0.816
$\frac{1}{2}O_2(g) + 2H^+(aq) + 2CytC(Fe^{2+}) \longrightarrow 2CytC(Fe^{3+}) + H_2O(\ell)$	?= $\Phi^{\circ\prime}_{cell}$

standard state $[H^+]=10^{-7}$

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biological example (redox equation III)

$\frac{1}{2}O_2(g) + 2H^+(aq) + 2CytC(Fe^{2+}) \longrightarrow 2CytC(Fe^{3+}) + H_2O(\ell)$

$$\Phi_{cell} = \Phi^{\circ\prime}_{cell} - \frac{RT}{n\mathcal{F}}\ln[Q] = \Phi^{\circ\prime}_{cell} - \frac{RT}{n\mathcal{F}}\ln\left[\frac{\cdots\cdots}{\cdots\cdots\left(\frac{\gamma_{\pm}[H^+]}{10^{-7}M}\right)^2\left(\frac{\gamma_{O_2}P_{O_2}}{1bar}\right)^{\frac{1}{2}}\cdots}\right]$$

standard state '

what's $\Phi^{o\prime}$?
what's Q ?
what's n ?

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Φ and thermodynamic derivatives, etc. (HW9, prob #59)

$$\boxed{\Delta\mu = -n\mathcal{F}\Phi \qquad \Phi = -\frac{\Delta\mu}{n\mathcal{F}}}$$

$$\Delta\mu^\circ = -RT\ln K_{eq} \quad \Rightarrow \quad \Phi^\circ = \frac{RT}{n\mathcal{F}}\ln K_{eq}$$

$$\left(\frac{\partial\Delta\mu}{\partial T}\right)_p = -\Delta\bar{S} \quad \Rightarrow \quad \left(\frac{\partial\Phi}{\partial T}\right)_p = \frac{\Delta\bar{S}}{n\mathcal{F}}$$

$$\left(\frac{\partial\frac{\Delta\mu}{T}}{\partial T}\right)_p = -\frac{\Delta\bar{H}}{T^2} \quad \Rightarrow \quad \left(\frac{\partial\frac{\Phi}{T}}{\partial T}\right)_p = \frac{\Delta\bar{H}}{n\mathcal{F}T^2}$$

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ΔC_p from Φ

$$\left(\frac{\partial\Delta\mu}{\partial T}\right)_p = -\Delta\bar{S} \quad \Rightarrow \quad \left(\frac{\partial\Phi}{\partial T}\right)_p = \frac{\Delta\bar{S}}{n\mathcal{F}}$$

$$\Delta\mu = \Delta\bar{H} - T\Delta\bar{S}$$

$$\Delta\bar{H} = \Delta\mu + T\Delta\bar{S} = -n\mathcal{F}\Phi + Tn\mathcal{F}\left(\frac{\partial\Phi}{\partial T}\right)_p$$

$$\left(\frac{\partial\Delta\bar{H}}{\partial T}\right)_p = \Delta C_p = -n\mathcal{F}\left(\frac{\partial\Phi}{\partial T}\right)_p + n\mathcal{F}\left(\frac{\partial\Phi}{\partial T}\right)_p + n\mathcal{F}T\left(\frac{\partial^2\Phi}{\partial T^2}\right)_p$$

$$\Delta C_p = n\mathcal{F}T\left(\frac{\partial^2\Phi}{\partial T^2}\right)_p$$

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relationships on final

Electrochemistry:

- $\Delta\mu_{reaction} = -n\mathcal{F}\Phi_{cell}$

$$\Phi = \Phi^\circ - \frac{RT}{n\mathcal{F}}\ln Q$$

$$\Phi = \Phi^\circ - \frac{0.02569\ \mathrm{V}}{\bar{n}}\ln Q \quad at\ T = 298K$$

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batteries and fuel cells

battery -
- nicely package electrochemical cell
- closed system
- runs irreversibly ($\Phi < \mathcal{E}$)
- may be recharged (storage battery)

fuel cell-
- electrochemical cell
- open system (reactants continuously flow in)

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efficiency of $w_{electrical}$ vs $w_{P\text{-}V}$

compare:

$w_{electrical}$ (on surr) from lead storage battery
ΔG=-377 kJ mol^{-1}, ΔH =-228 kJ mol^{-1}

with

$w_{P\text{-}V}$ (on surr) of heat engine using q_{upper}= -$\Delta H_{storage\ battery}$

heat engine: T_u=600K, T_L=300K
ϵ=(600-300)/600= 0.5
$w_{P\text{-}V}$=(0.5)*228 kJ mol^{-1} = 114 kJ mol^{-1}

battery: ΔG=-377 kJ mol^{-1} . T=300K
$w_{electrical}$=- ΔG = 377 kJ mol^{-1}

the winner:

$$\frac{w_{electrical}}{w_{P-V}} = \frac{377}{114} = 3.31$$

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types of batteries

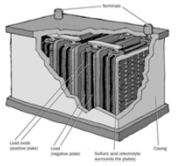
Lead storage
Pb(s) oxidized to Pb^{2+} PbO_2 reduced to Pb^{2+}

$PbO_2(s) + 4\,H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2\,H_2O(l)$
$E^\circ = 1.685$ V (11.54)

$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$ $E^\circ = -0.356$ V (11.55)

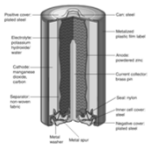
respectively, and the overall reaction is

$PbO_2(s) + Pb(s) + 2\,H_2SO_4(aq) \rightleftharpoons 2\,PbSO_4(s) + 2\,H_2O(l)$ $E^\circ = 2.04$ V (11.56)



Alkaline storage (no liquids)
Zn(s) oxidized to Zn^{2+} MnO_2 reduced to Mn_2O_3

Zn (s) + 2OH$^-$(aq) → ZnO (s) + H_2O (l) + 2e− +1.26V
2MnO_2 (s) + H_2O (l) + 2e− →Mn_2O_3 (s) + 2OH− (aq) 0.275
Zn (s) + 2MnO_2 (s) → ZnO (s) + **Mn_2O_3 (s)** **+1.5 V**



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types of batteries

NiMH- Nickel Metal Hydride
M='intermetallic compound', e.g. M=AB_5,
A is a rare earth mixture of lanthanum, cerium, neodymium, praseodymium
B is nickel, cobalt, manganese, and/or aluminum

Ni^{2+} oxidized to Ni^{3+} H^+ reduced to H^-, "M" oxidized

$H_2O + M + e^- \rightarrow OH^- + MH$
$Ni(OH)_2 + OH^- \rightarrow NiO(OH) + H_2O + e^-$

High power Ni-MH battery of Toyota NHW20 Prius

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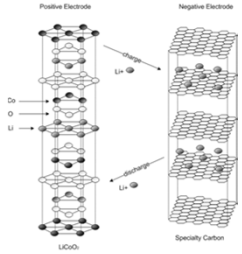
Li-ion batteries

$LiCoO_2 \rightleftarrows Li_{1-x}CoO_2 + xLi^+ + xe^-$

$xLi^+ + xe^- + 6C \rightleftarrows Li_xC_6$



Li-ion batteries can pack more energy into smaller and lighter weight units than other types of batteries. Those attributes have spurred enormous growth in their use for cell phones, laptop computers, and other portable electronic devices.

A downside of Li-ion cells, however, is that they contain a flammable electrolyte solution consisting of lithium salts in organic solvents such as ethylene carbonate and ethyl methyl carbonate. This is not the case for other commercial battery types.

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battery property comparison

Zinc	**1.5V**	**Non-rechargeable**–first the forerunner and later an inexpensive alternative to Alkaline batteries. However, reductions in the price of Alkalines have made both Zinc-Carbon and Zinc-Chloride batteries all but obsolete.
Alkaline	**1.5V**	**Rechargeable–** Alkaline rechargeable batteries are lower capacity (don't hold a charge as long) than the more popular NiMH rechargeables. The advantage of the rechargeable Alkaline over the NiMH or the NiCAD is that it loses its charge gradually.
Nickel-Metal Hydride (NiMH)	**1.25V**	**Rechargeable-** Lightweight and rechargeable, the NiMH has a higher capacity than the NiCAD plus you can throw it away since it doesn't contain toxic metals and it isn't classed as a hazardous waste item.
Lithium ion	**3.6V**	**Rechargeable–** For a given voltage, a lithium ion battery is smaller in size and lighter in weight than a nickel cadmium (NiCd) or nickel metal hydride (NiMH) battery. In addition, lithium ion has virtually no self-discharge. This allows a lithium ion battery to be stored for months without losing charge. The battery chemistries can be compared as follows:

http://batteryuniversity.com/learn/article/whats_the_best_battery

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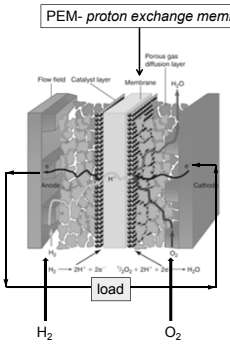
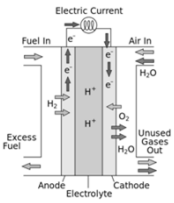
fuel cells

PEM- *proton exchange membrane*





$H_2 \rightarrow 2H^+ + 2e^-$ 0 V

$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$ 1.23 V

Fuel cells come in a variety of sizes. Individual fuel cells produce relatively small electrical potentials, about 0.7 volts, The energy efficiency of a fuel cell is generally between 40–60%.

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End of Lecture

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$\tilde{\mu}_i$ *the electrochemical potential*

$$dG - \bar{d}w_{elec} = -SdT + VdP + \sum_{i,\gamma} \mu_i^{(\gamma)} dn_i^{(\gamma)}$$

$$(\Delta G_{reaction})_{T,P} - w_{elec} = \sum_{i,\gamma} \nu_i^{(\gamma)} \mu_i^{(\gamma)} = (\Delta \mu_{reaction}) \leq 0$$

VS

$$dG = -SdT + VdP + \sum_{i,\gamma} \tilde{\mu}_i^{(\gamma)} dn_i^{(\gamma)}$$

$$(\Delta G_{reaction})_{T,P} = \sum_{i,\gamma} \nu_i^{(\gamma)} \tilde{\mu}_i^{(\gamma)} \leq 0$$

$$\tilde{\mu}_i^{(\gamma)} = \mu_i^{(\gamma)} + \left(\bar{d}w_i^{(\gamma)}\right)_{elec}$$

$\tilde{\mu}_i$ assigns electrical work to each species including electrons transferred

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