

Chemistry 163B W2014

Lectures 24-25- Electrochemistry Quickie

Chemistry 163B

Electrochemistry

1

activity coefficients for ions (HW9 #58)

$$\text{BaCl}_2(s) \rightleftharpoons \text{Ba}^{2+}(aq) + 2\text{Cl}^-(aq)$$

$$K_{sp} = \frac{(a_{\text{Ba}^{2+}(aq)})(a_{\text{Cl}^-(aq)})^2}{(a_{\text{BaCl}_2(s)})}$$

$$a_{\text{BaCl}_2(s)} = 1$$

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

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

cannot determine $\gamma_{\text{Ba}^{2+}}$ and γ_{Cl^-} independently
but only $\gamma_{\text{Ba}^{2+}} = \gamma_{\text{Cl}^-} = \gamma_{\pm}$ ($\gamma_{\pm} = \gamma_{\pm} = \gamma_{\pm}$)

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

$$K_{sp} = (\gamma_{\pm})^3 [\text{Ba}^{2+}][\text{Cl}^-]^2$$

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work of expansion

$\text{H}_2(10 \text{ bar}) \rightarrow \text{H}_2(1 \text{ bar})$

3

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

$\text{H}_2(10 \text{ bar}) \rightarrow 2\text{H}^+ + 2\text{e}^-$
 $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(1 \text{ bar})$

$\text{H}_2(10 \text{ bar}) \rightarrow \text{H}_2(1 \text{ bar})$

$\Delta\mu = \Delta\mu^\circ + RT \ln Q_{\text{reaction}}$

$\Delta\mu^\circ = 0$ $\Delta\mu^\circ$ is for reaction $\text{H}_2(P=1 \text{ bar}) \rightarrow \text{H}_2(P=1 \text{ bar})$

$\Delta\mu = \Delta\mu^\circ + RT \ln \frac{P(1 \text{ bar})}{P(10 \text{ bar})} = -5.706 \text{ kJ per mole H}_2$ 4

$d\mu$ and work-other (did before for dG)

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

$$d\mu = \bar{d}q - Td\bar{S} - \bar{S}dT + VdP + \bar{d}w_{\text{other}} \quad (\text{very general})$$

≤ 0 by 2nd law

$$d\mu_{T,P} \leq \bar{d}w_{\text{other}}$$

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 $\text{H}_2(1 \text{ bar}) \rightarrow 2\text{H}^+[1M] + 2\text{e}^-$
reduction cathode $2\text{AgCl}(s) + 2\text{e}^- \rightarrow 2\text{Ag}(s) + 2\text{Cl}^-[1M]$

$2\text{e}^- + \text{H}_2(\text{g}, 1 \text{ bar}) + 2\text{AgCl}(s) \rightarrow 2\text{H}^+[1M] + 2\text{Cl}^-[1M] + 2\text{Ag}(s) + 2\text{e}^-$ 6

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

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

$\Delta\mu_f \approx \Delta G_f$ (kJ)	0	-109.79	0	-131.23	0
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$$\Delta\mu \approx \Delta G = -(0) - 2(-109.79) + 2(0) + 2(-131.23) + 2(0) = -42.88 \text{ kJ}$$

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

$$e^- + \frac{1}{2} H_2(g, 1atm) + AgCl(s) \rightarrow H^+[1M] + Cl^-[1M] + Ag(s) + e^-$$

$\Delta\mu \approx \Delta G = -21.44 \text{ kJ per } \frac{1}{2} \text{ mole } H_2$

$\Delta\mu$ 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)	$w = - \int_{V_i}^{V_f} P_{external} dV$	$\text{Pa m}^3 = \text{J}$
Stretching	Force (F), length (l)	$w = \int_{l_i}^{l_f} F \cdot dl$	$\text{N m} = \text{J}$
Surface expansion	Surface tension (γ), area (σ)	$w = \int_{\sigma_i}^{\sigma_f} \gamma \cdot d\sigma$	$(\text{N m}^{-1})(\text{m}^2) = \text{J}$
Electrical	Electrical potential (ϕ), electrical charge (Q)	$w = \int_{Q_i}^{Q_f} \phi dQ$	$\text{V C} = \text{J}$

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

$$d w_{electrical} = \Phi dQ$$

electric potential charge transfer

$$dQ = -\mathcal{F}dn$$

from negative charge on e \mathcal{F} is Faraday constant
96,458 coulomb (mole e^-)⁻¹

$$d w_{electrical} = -\Phi \mathcal{F}dn$$

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

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

E & R p260 $z \equiv -n$

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

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sign of Φ and spontaneity

$$\Delta\mu_{r,p} \leq w_{other}$$

$$\Delta\mu_{r,p} < -n\mathcal{F}\Phi_{cell}^{irrev} \quad \Phi_{cell}^{irrev} \text{ for irreversible}$$

$$\Delta\mu_{r,p} = -n\mathcal{F}\Phi_{cell} \quad \Phi_{cell} = \mathcal{E}mf \text{ for reversible}$$

$\Delta\mu_{r,p} < 0 \text{ spontaneous} \Rightarrow \Phi > 0 \text{ spontaneous}$

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Δμ vs Φ

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

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

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

$T = 298\text{K}$

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

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

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

oxidation anode: $H_2(1 \text{ bar}) \rightarrow 2H^+[1M] + 2e^-$

reduction cathode: $2AgCl(s) + 2e^- \rightarrow 2Ag(s) + 2Cl^-[1M]$

Φ_0
0.22233 V

$$2e^- + H_2(g, 1bar) + 2AgCl(s) \rightarrow 2H^+[1M] + 2Cl^-[1M] + 2Ag(s) + 2e^- \quad 0.22233 \text{ V}$$

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example incorporating activities

$$2e^- + H_2(g, 1\text{ bar}) + 2AgCl(s) \rightarrow 2H^+[1M] + 2Cl^-[1M] + 2Ag(s) + 2e^-$$

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

$a_{AgCl} = a_{Ag} = 1$
 $a_{H^+} = \gamma_{H^+} [H^+]$ $a_{Cl^-} = \gamma_{Cl^-} [Cl^-]$
 can't independently measure γ_{H^+} and γ_{Cl^-}
 $\gamma_{H^+} = \gamma_{Cl^-} = \gamma_{\pm}$

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

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example incorporating activities

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

0.22233 V 2 e⁻s

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

unless: have dropped standard state concs and pressure from denominators

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example incorporating activities

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

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

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

$\Delta\mu = -n\mathcal{F}\Phi$
 $\Delta\mu = -2\text{ mol} (96,485\text{ C mol}^{-1}) (0.22233\text{ V})$
 $\Delta\mu = -4.290 \times 10^4\text{ CV} = -42.90\text{ kJ}$

$\Delta\mu^\circ = -42.88\text{ kJ for 2 moles } e^- \text{ transferred [from } \Delta\mu_{1e^-} \text{ earlier]}$

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intensive ϕ vs extensive $\Delta\mu$ $\phi = -(\Delta\mu/n\mathcal{F})$

$H_2(g, 1\text{ bar}) \rightarrow 2H^+[1M] + 2e^-$	$\Phi^\circ = 0\text{ V}$
$2e^- + 2AgCl(s) \rightarrow 2Cl^-[1M] + 2Ag(s)$	$\Phi^\circ = 0.22233\text{ V}$

$2e^- + H_2(g, 1\text{ bar}) + 2AgCl(s) \rightarrow 2H^+[1M] + 2Cl^-[1M] + 2Ag(s) + 2e^-$
 $\Phi_{\text{cell}}^\circ = 0.22233\text{ V}$

$\Delta\mu = -42.88\text{ kJ for 2 moles } e^- \text{ transferred}$

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

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intensive ϕ vs extensive $\Delta\mu$ $\phi = -(\Delta\mu/n\mathcal{F})$

$\frac{1}{2}H_2(g, 1\text{ bar}) \rightarrow H^+[1M] + e^-$	$\Phi^\circ = 0\text{ V}$
$e^- + AgCl(s) \rightarrow Cl^-[1M] + Ag(s)$	$\Phi^\circ = 0.22233\text{ V}$

$e^- + \frac{1}{2}H_2(g, 1\text{ bar}) + AgCl(s) \rightarrow H^+[1M] + Cl^-[1M] + Ag(s) + e^-$
 $\Phi_{\text{cell } 1e^-}^\circ = 0.22233\text{ V}$

$\Delta\mu = -21.44\text{ kJ for 1 moles } e^- \text{ transferred}$

$$\Phi_{\text{cell } 1e^-} = \Phi_{\text{cell}}^\circ - \frac{0.02569\text{ V}}{1} \ln \left[\frac{a_{H^+} a_{Cl^-} a_{Ag(s)}^1}{a_{H_2}^{\frac{1}{2}} a_{AgCl(s)}^1} \right]$$

Φ° intensive same as for 2 mole e⁻s
 Φ is oomph per electron

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intensive ϕ vs extensive $\Delta\mu$ $\phi = -(\Delta\mu/n\mathcal{F})$

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

$\Delta\mu = -42.88\text{ kJ for 2 moles } e^- \text{ transferred}$

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

$\Delta\mu = -21.44\text{ kJ for 1 moles } e^- \text{ transferred}$

$\Phi_{\text{cell } 2e^-} = \Phi_{\text{cell } 1e^-}$
 same

$\Delta\mu$ extensive: depends on stoichiometry

→

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

←

Φ intensive: independent of 'how reaction is written' oomph 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

	$\Phi^{\circ'}_{\text{red}}(\text{V})$ pH7
standard REDUCTION potentials	
$2e^- + 2\text{CytC}(\text{Fe}^{3+}) \rightarrow 2\text{CytC}(\text{Fe}^{2+})$	0.25
$2e^- + \frac{1}{2}\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$	0.816
reaction: the oxidation of CytC(Fe²⁺)	$\Phi^{\circ'}(\text{V})$
<i>oxidation</i> $2\text{CytC}(\text{Fe}^{2+}) \rightarrow 2\text{CytC}(\text{Fe}^{3+}) + 2e^-$	-0.25
<i>reduction</i> $2e^- + \frac{1}{2}\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$	0.816
$\frac{1}{2}\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{CytC}(\text{Fe}^{2+}) \rightarrow 2\text{CytC}(\text{Fe}^{3+}) + \text{H}_2\text{O}(\text{l})$	$? = \Phi^{\circ'}_{\text{cell}}$
↑ standard state [H ⁺]=10 ⁻⁷	19


biological example (redox equation III)

$\frac{1}{2}\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{CytC}(\text{Fe}^{2+}) \rightarrow 2\text{CytC}(\text{Fe}^{3+}) + \text{H}_2\text{O}(\text{l})$

$$\Phi_{\text{cell}} = \Phi_{\text{cell}}^{\circ'} - \frac{RT}{n\mathcal{F}} \ln [Q] = \Phi_{\text{cell}}^{\circ'} - \frac{RT}{n\mathcal{F}} \ln \left[\frac{\dots\dots}{\dots\dots \left(\frac{\gamma_{\pm} [\text{H}^+]}{10^{-7} \text{ M}} \right)^2 \left(\frac{\gamma_{\text{O}_2} P_{\text{O}_2}}{1 \text{ bar}} \right)^{1/2} \dots} \right]$$

standard state'

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



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

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

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

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

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

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

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ΔC_p from Φ

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

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

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

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

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

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relationships on final

Electrochemistry:

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

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

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

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batteries and fuel cells

battery -

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

fuel cell-

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

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

compare:
 $w_{\text{electrical}}$ (on sum) from lead storage battery
 $\Delta G = -377 \text{ kJ mol}^{-1}$, $\Delta H = -228 \text{ kJ mol}^{-1}$
 with
 w_{P-V} (on sum) of heat engine using $q_{\text{upper}} = -\Delta H_{\text{storage battery}}$

heat engine: $T_1 = 600\text{K}$, $T_2 = 300\text{K}$
 $\epsilon = (600-300)/600 = 0.5$
 $w_{P-V} = (0.5) * 228 \text{ kJ mol}^{-1} = 114 \text{ kJ mol}^{-1}$

battery: $\Delta G = -377 \text{ kJ mol}^{-1}$, $T = 300\text{K}$
 $w_{\text{electrical}} = -\Delta G = 377 \text{ kJ mol}^{-1}$

the winner:

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

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types of batteries

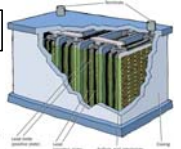
Lead storage
 $\text{Pb(s)} \text{ oxidized to } \text{Pb}^{2+}$ $\text{PbO}_2 \text{ reduced to } \text{Pb}^{2+}$

$$\text{PbSO}_4(\text{s}) + 4 \text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2\text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2 \text{H}_2\text{O}(\text{l}) \quad (11.54)$$

$$\text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^- \quad E^\circ = -0.356 \text{ V} \quad (11.55)$$

respectively, and the overall reaction is

$$\text{PbO}_2(\text{s}) + \text{Pb}(\text{s}) + 2 \text{H}_2\text{SO}_4(\text{aq}) \rightleftharpoons 2 \text{PbSO}_4(\text{s}) + 2 \text{H}_2\text{O}(\text{l}) \quad E^\circ = 2.04 \text{ V} \quad (11.56)$$

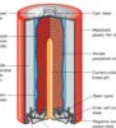


Alkaline storage (no liquids)
 $\text{Zn(s)} \text{ oxidized to } \text{Zn}^{2+}$ $\text{MnO}_2 \text{ reduced to } \text{Mn}_2\text{O}_3$

$$\text{Zn}(\text{s}) + 2\text{OH}(\text{aq}) \rightarrow \text{ZnO}(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \quad +1.26\text{V}$$

$$2\text{MnO}_2(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3(\text{s}) + 2\text{OH}^-(\text{aq}) \quad 0.275$$

$$\text{Zn}(\text{s}) + 2\text{MnO}_2(\text{s}) \rightarrow \text{ZnO}(\text{s}) + \text{Mn}_2\text{O}_3(\text{s}) \quad +1.5 \text{ V}$$



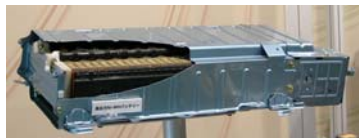
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types of batteries

NiMH- Nickel Metal Hydride
 $M = \text{'intermetallic compound'}$, e.g. $M = \text{AB}_5$,
 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

$$\text{H}_2\text{O} + \text{M} + \text{e}^- \rightarrow \text{OH}^- + \text{MH}$$

$$\text{Ni}(\text{OH})_2 + \text{OH}^- \rightarrow \text{NiO}(\text{OH}) + \text{H}_2\text{O} + \text{e}^-$$


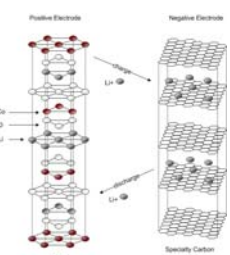
High power Ni-MH battery of Toyota NHW20 Prius

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Li-ion batteries

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.

$$\text{LiCoO}_2 \rightleftharpoons \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^-$$

$$x\text{Li}^+ + xe^- + 6\text{C} \rightleftharpoons \text{Li}_x\text{C}_6$$


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

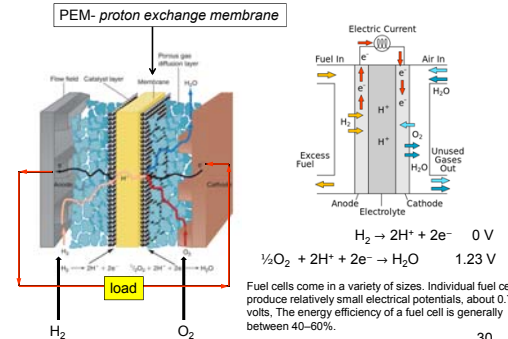
Zinc	1.5V	Non-rechargeable —first the forerunner and later an inexpensive alternative to Alkaline batteries. However, reductions in the price of Alkalines have made both Zinc-Carbon and Zinc-Chloride batteries all but obsolete.
Alkaline	1.5V	Rechargeable —Alkaline rechargeable batteries are lower capacity (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



$$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \quad 0 \text{ V}$$

$$\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O} \quad 1.23 \text{ V}$$

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

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

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

VS

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

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

$$\tilde{\mu}_i^{(j)} = \mu_i^{(j)} + (\tilde{d}w_i^{(j)})_{elec}$$

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



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