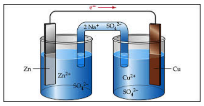
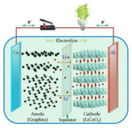
Chemistry 163B W2020
Lectures 24-25- Electrochemistry Quickie



Lectures 24-25 Winter 2020

Chemistry 163B

Electrochemistry



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activity coefficients for ions (HW8 #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 $\gamma_{Ba^{2+}} = \gamma_{Cl^-} = \gamma_\pm \quad (\gamma_+ = \gamma_- \equiv \gamma_\pm)$

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

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

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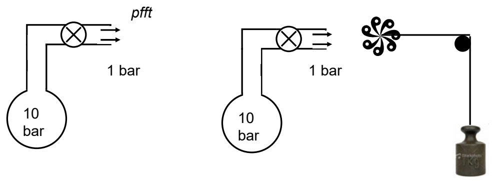
work of expansion

H_2 (10 bar) → H_2(1 bar)



only P-V
useless?

real w_{other}
useful?

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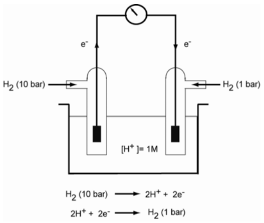
hydrogen pressure ['concentration'] cell (reaction I of III)



H_2 (10 bar) → $2H^+ + 2e^-$

$2H^+ + 2e^-$ → H_2 (1 bar)

H_2 (10 bar) → H_2(1bar)

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

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

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

---

dμ and work-other (previously done for dG)

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

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

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

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

REVERSIBILITY

w_{other} *(p. 292_{4th})* p. 292_{4th} $\tilde{\mu}$ vs μ 'perhaps' more rigorous *If you like* ➡

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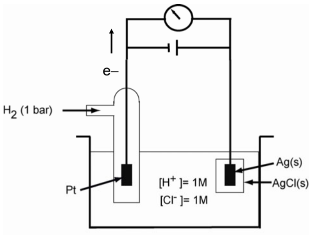
responsible for 3 redox reactions; here's II (HW8, prob #60)



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)

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

$\Delta\mu^\circ_f \approx \Delta G^\circ_f$ (kJ) 0 -109.79 0 -131.23 0 kJ/mol

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

$\boxed{\Delta\mu^\circ = \text{for 2 moles } e^{-} \text{ transferred}}$

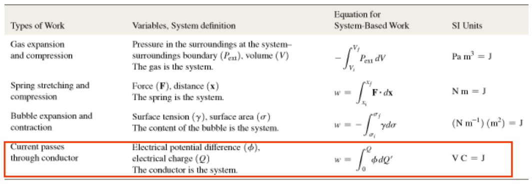
$e^{-} + \tfrac{1}{2} H_2\,(g, 1bar) + AgCl(s) \rightarrow H^{+}\,[1M] + Cl^{-}\,[1M] + Ag(s) + e^{-}$

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

$\boxed{\Delta\mu^\circ \text{ for 1 mole } e^{-} \text{ transferred}}$

and FINALLY w_{other}!!! (p. 32_{4th})

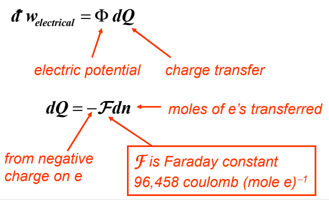
Table 2.1 Types of Work



Types of Work	Variables, System definition	Equation for System-Based Work	SI Units
Gas expansion and compression	Pressure in the surroundings at the system–surroundings boundary (P_{ext}), volume (V) The gas is the system.	$-\int_{V_i}^{V_f} P_{ext}\,dV$	$Pa\ m^3 = J$
Spring stretching and compression	Force ($\mathbf{F}$), distance ($\mathbf{x}$) The spring is the system.	$w = \int_{x_i}^{x_f} \mathbf{F}\cdot d\mathbf{x}$	$N\ m = J$
Bubble expansion and contraction	Surface tension (γ), surface area (σ) The content of the bubble is the system.	$w = -\int_{\sigma_i}^{\sigma_f} \gamma\,d\sigma$	$(N\ m^{-1})\ (m^2) = J$
Current passes through conductor	Electrical potential difference (ϕ), electrical charge (Q) The conductor is the system.	$w = \int_0^{Q} \phi\,dQ'$	$V\ C = J$

w_{other} (p. 292_{4th})

BUT



$đ w_{electrical} = \Phi\, dQ$

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)$^{-1}$

$$\boxed{\begin{array}{l} đ w_{electrical} = -\Phi \mathcal{F} dn \\ w_{electrical} = -n\mathcal{F}\,\Phi \quad \text{(n electrons transferred)} \\ (w = -n\mathcal{F}\mathcal{E}) \quad \mathcal{E} = \text{electromotive force} = \Phi_{rev} \\ \text{E\&R}_{4th}\ \text{p260 z} \equiv \text{-n} \end{array}}$$

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

sign of Φ and spontaneity

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

$$\Delta\mu_{T,P} < -n\mathcal{F}\ \Phi^{irrev}_{cell} \qquad \Phi^{irrev}_{cell} \text{ for irreversible}$$

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

$\Delta\mu_{T,P} < 0$ spontaneous $\Rightarrow \boxed{\Phi > 0 \text{ spontaneous}}$

$\Delta\mu_{T,P} < 0$ spontaneous $\Rightarrow \Phi > 0$ spontaneous
when an external 'reverse potential' is applied so no electrons flow, the value will be that for reversible
$-n\mathcal{F}\ \mathcal{E}_{mf_{cell}} = \Delta\mu$ even if the reactants and products are not at equilibrium conditions, in the absence of reverse potential,

Φ vs concentration

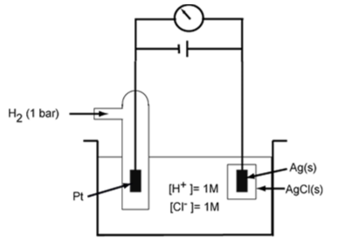
$$\Delta\mu = \Delta\mu^\circ + \boldsymbol{RT}\ln \boldsymbol{Q}_{reaction} = -n\mathcal{F}\Phi$$

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

$$\boxed{\begin{array}{l} \Phi = \Phi^\circ - \dfrac{RT}{n\mathcal{F}}\ln Q_{reaction} \\ T = 298K \\ \Phi = \Phi^\circ - \left[\dfrac{0.02569}{\overline{n}}\ln Q_{reaction}\right]\text{V} \end{array}}$$

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

responsible for 3 redox reactions; here's II (HW8, prob #60)



		Φ_0
oxidation *anode*	$H_2\,(1\ bar) \longrightarrow 2H^{+}\,[1M] + 2e^{-}$	0
reduction *cathode*	$2AgCl(s) + 2e^{-} \longrightarrow 2Ag(s) + 2Cl^{-}\,[1M]$	0.22233

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

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example incorporating activities

$2e^{-} + H_2\ (g, P_{H2}) + 2AgCl(s) \rightarrow 2H^{+}\ [H^{+}] + 2Cl^{-}\ [Cl^{-}] + 2Ag(s) + 2e^{-}$

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

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

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

$$\text{can't independently meansure } \gamma_{H^+} \text{and } \gamma_{Cl^-}$$

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

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

example incorporating activities

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

0.22233 V 2 e's

$$\Phi = 0.22233 - \frac{0.02569}{2} \ln \underbrace{\left[\frac{\gamma_{\pm}^4 [H^+]^2 [Cl^-]^2}{\gamma_{H_2} (P_{H_2(g)})}\right]}_{\text{unitless; have dropped standard state concs and pressure from denominators}}$$

- Calculate γ's from observed Φ (HW#8, prob 60)

calculate $\Delta\mu$ from Φ

$\Delta\mu^{\circ}$ from Φ° (γ's=1)

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

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

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

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

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

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

H_2 (g, 1 bar) → $2H^{+}$ [1M] +$2e^{-}$ Φ°= 0 V

$2e^{-}$ + 2AgCl(s) → $2Cl^{-}$ [1M] + 2Ag(s) Φ°= 0.22233 V

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

Φ_{cell}°= 0.22233 V

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

$2e^{-}$ +H_2 (g, P_{H2}) + 2AgCl(s) → $2H^{+}$ [H^{+}] + $2Cl^{-}$ [Cl^{-}] + 2Ag(s) +$2e^{-}$

$\Phi_{cell\ 2e's}$

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

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

½H_2 (g, 1 bar) → H^{+} [1M] +e^{-} Φ°= 0 V

e^{-} + AgCl(s) → Cl^{-} [1M] + Ag(s) Φ°= 0.22233 V

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

Φ_{cell}°= 0.22233 V

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

$$\Delta\mu^{\circ} = -n\mathcal{F}\Phi^{\circ}$$
$$= -(\mathbf{1mol\ e's})(96485\ \mathbf{C\ mol^{-1}})(0.22233\ \mathbf{V})$$
$$= 2.145 \times 10^4\ \mathbf{C\ V = 21.45\ kJ}$$

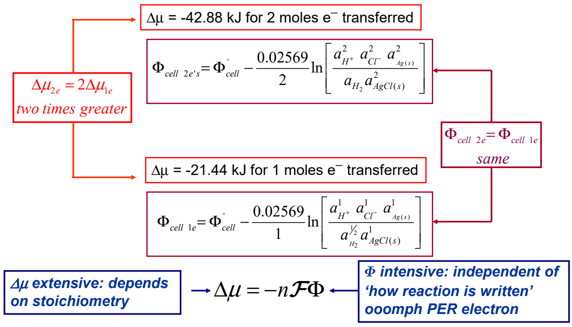
$\boxed{\Delta\mu^{\circ} = \text{-21.44 kJ for 1 moles } e^{-} \text{ transferred}}$

e^{-} +½H_2 (g, P_{H2}) + AgCl(s) → H^{+} [H^{+}] + Cl^{-} [Cl^{-}] + Ag(s) +e^{-}

$\Phi_{cell\ 1e}$

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

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



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

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

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

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

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

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

$\Delta\mu$ extensive: depends on stoichiometry

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

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

$2e^- + \quad 2CytC(Fe^{3+}) \rightarrow 2CytC(Fe^{2+})$ 0.25

$2e^- + ½O_2(g) + 2H^+(aq) \rightarrow H_2O\ (\ell)$ 0.816

reaction: the oxidation of CytC(Fe^{2+})

$\Phi^{\circ\prime}$(V)

oxidation $2CytC(Fe^{2+}) \rightarrow 2CytC(Fe^{3+}) + 2e–$ - 0.25

reduction $2e^- + ½O_2(g) + 2H^+(aq) \rightarrow H_2O\ (\ell)$ 0.816

$½O_2(g) + 2H^+(aq) + 2CytC(Fe^{2+}) \rightarrow 2CytC(Fe^{3+}) + H_2O\ (\ell)$ **?=** $\Phi^{\circ\prime}_{cell}$

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

biological example (redox equation III)

$½O_2(g) + 2H^+(aq) + 2CytC(Fe^{2+}) \rightarrow 2CytC(Fe^{3+}) + H_2O\ (\ell)$

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

standard state '

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

Φ and thermodynamic derivatives, etc. (HW8, prob #59)

$$\boxed{\begin{gathered}\Delta\mu = -n\mathcal{F}\Phi \\ \Phi = -\frac{\Delta\mu}{n\mathcal{F}}\end{gathered}}$$

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

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

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

ΔC_p from Φ

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

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

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

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

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

relationships on final

Electrochemistry:

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

$$\Phi = \Phi^{\circ} - \frac{\underline{R}T}{n\mathcal{F}}\ln Q$$

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

batteries and fuel cells

battery -
- nicely package electrochemical cell
- closed system
- runs irreversibly (Φ < 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
$\Delta G=-377\ \text{kJ mol}^{-1}$, $\Delta H=-228\ \text{kJ mol}^{-1}$

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

the winner:

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

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types of batteries

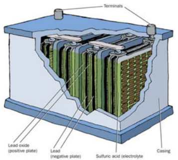
Lead storage
Pb(s) oxidized to Pb^{2+} PbO_2 reduced to Pb^{2+}

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

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

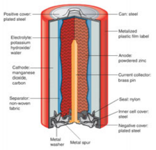
respectively, and the overall reaction is

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



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

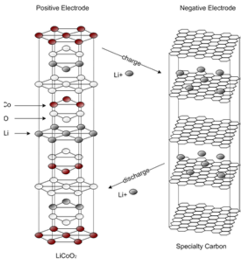
H_2O + M + e$^-$→OH$^-$ + MH
$Ni(OH)_2$ + OH$^-$ →NiO(OH) + H_2O + e$^-$

High power Ni-MH battery of Toyota NHW20 Prius

Li-ion batteries

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

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



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.

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

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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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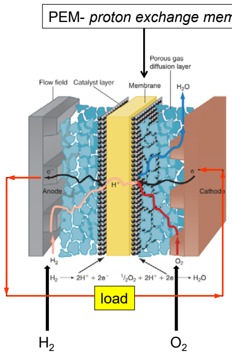
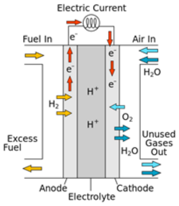
Lectures 24-25- Electrochemistry Quickie

fuel cells





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

End of Lecture

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

$$\boxed{\begin{aligned} dG &= -SdT + VdP + \sum_{i,\gamma} \mu_i^{(\gamma)} dn_i^{(\gamma)} \le đw_{elec} \\ (\Delta G)_{T,P} &= \sum_{i,\gamma} \nu_i^{(\gamma)} \mu_i^{(\gamma)} += (\Delta\mu_{reaction}) \le w_{elec} \end{aligned}}$$

VS

$$\boxed{\begin{aligned} dG &= -SdT + VdP + \sum_{i,\gamma} \tilde{\mu}_i^{(\gamma)} dn_i^{(\gamma)} \\ (\Delta G)_{T,P} &= \sum_{i,\gamma} \nu_i^{(\gamma)} \tilde{\mu}_i^{(\gamma)} \le 0 \end{aligned}}$$

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

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

back more

free energy of charged species in the presence of electrostatic potential

$$d\tilde{\mu}_i^{(\gamma)} = d\mu_i^{(\gamma)} + \left(dw_i^{(\gamma)}\right)_{other} = -\bar{S}_i^{(\gamma)} dT + \bar{V}_i^{(\gamma)} dP + \underbrace{\phi^{(\gamma)}\, dQ_i^{(\gamma)}}_{đw_{other}}$$

Faraday
96,485 Coulombs mole-1

$$\tilde{\mu}_i^{(\gamma)} = \mu_i^{(\gamma)} + z_i \mathcal{F} \phi^{(\gamma)}$$

electrostatic potential in phase γ

$\mu_i^{(\alpha)} = \mu_i^{(b)}$

integer (signed) charge

a charge in two phases (different potential ϕ ; otherwise same)

$$\tilde{\mu}_i^{(\alpha)} - \tilde{\mu}_i^{(\beta)} = z_i \mathcal{F}\left(\phi^{(\alpha)} - \phi^{(\beta)}\right) = z_i \mathcal{F} \Delta\phi$$

$\mu_i^{(\alpha)}$ is escaping tendency from phase (α) , $\mu_i^{(\beta)}$ from phase β

+ charge (z_i >0): ion 'escapes' to phase of lower (more negative) potential ϕ

– charge (z_i < 0): ion 'escapes' to phase of higher (more positive) potential ϕ

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

$$\tilde{\mu}_i^{(\gamma)} = \mu_i^{(\gamma)} + z_i \mathcal{F} \phi^{(\gamma)}$$

$\Delta G_{reaction} = \sum_{i,\gamma} \nu_i^{(\gamma)} \tilde{\mu}_i^{(\gamma)}$ where $\nu_i^{(\gamma)}$ are the stoichiometric coefficients

note: these must now include $\nu_{e^-}^{(\gamma)} \tilde{\mu}_{e^-}^{(\gamma)}$ for electrons involved in stoichiometry

assume the phases are metal electrodes and solutions with ions.

for ions in a given soultion phase α

$$\sum_{i=ions} \nu_i^{(\alpha)} \tilde{\mu}_i^{(\alpha)} = \sum_i \nu_i^{(\alpha)} \mu_i^{(\alpha)} + \sum_i \nu_i^{(\alpha)} z_i \mathcal{F} \phi^{(\alpha)}$$

$$\sum_i \nu_i^{(\alpha)} z_i \mathcal{F} \phi^{(\alpha)} = \mathcal{F} \phi^{(\alpha)} \sum_i \nu_i^{(\alpha)} z_i$$

and $\sum_{i=ions} \nu_i^{(\alpha)} z_i = 0$ *for* charge *neutrality*

for any neutral spcies $z_i = 0$

$$\tilde{\mu}_i^{(\alpha)} = \mu_i^{(\alpha)}$$

thus $\sum_i \nu_i^{(\alpha)} \tilde{\mu}_i^{(\alpha)} = \sum_i \nu_i^{(\alpha)} \mu_i^{(\alpha)}$ **for all reactants and products except**

for eletrons at metal eletrodes

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

$\Delta G_{reaction} = \sum_{i,\gamma} \nu_i^{(\gamma)} \tilde{\mu}_i^{(\gamma)}$ where $\nu_i^{(\gamma)}$ are the stoichiometric coefficients

$$\textit{thus}:\ \Delta G_{reaction} = \sum_{i,\gamma} \nu_i^{(\gamma)} \mu_i^{(\gamma)} + \nu_{e^-}^{(\text{oxidation})} z_{e^-} \mathcal{F} \phi^{(\textit{oxidation electrode})} + \nu_{e^-}^{(\textit{reduction})} z_{e^-} \mathcal{F} \phi^{(\textit{reduction electrode})}$$

$\nu_{e^-}^{(\text{reduction})} = +n_{transferred\ eletrons}$ and $\nu_{e^-}^{(\text{oxidation})} = -n_{transferred\ eletrons}$

$$\textit{and}\ \left(\mu^{(\textbf{reactant electrode})}\right)_{e^-}^0 = \left(\mu^{(\textbf{product electrode})}\right)_{e^-}^0$$

$$\Delta G_{reaction} = \sum_{\substack{\gamma, i = species \\ other\ than\ e^-}} \nu_i^{(\gamma)} \mu_i^{(\gamma)} - n\mathcal{F}\left(\phi^{(\textit{reduction electrode})} - \phi^{(\textit{oxidation electrode})}\right)$$

$$emf \equiv \mathcal{E} \equiv \left(\phi^{(\text{oxidation electrode})} - \phi^{(\textit{reduction electrode})}\right)\ \textbf{(IUPAC convention)}$$

$$\Delta G_{reaction} = \sum_{\substack{\gamma, i = species \\ other\ than\ e^-}} \nu_i^{(\gamma)} \mu_i^{(\gamma)} + n\mathcal{F}\mathcal{E}$$

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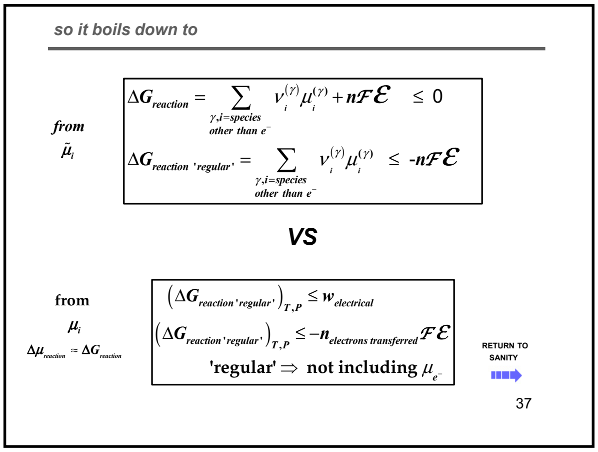

so it boils down to

from $\tilde{\mu}_i$

$$\boxed{\begin{aligned}\Delta G_{reaction} &= \sum_{\substack{\gamma, i = species \\ other\ than\ e^-}} \nu_i^{(\gamma)} \mu_i^{(\gamma)} + n\mathcal{F}\mathcal{E} \quad \leq 0 \\ \Delta G_{reaction\ 'regular'} &= \sum_{\substack{\gamma, i = species \\ other\ than\ e^-}} \nu_i^{(\gamma)} \mu_i^{(\gamma)} \ \leq \ -n\mathcal{F}\mathcal{E}\end{aligned}}$$

VS

from μ_i

$\Delta\mu_{reaction} \approx \Delta G_{reaction}$

$$\boxed{\begin{aligned}&\left(\Delta G_{reaction\ 'regular'}\right)_{T,P} \leq w_{electrical} \\ &\left(\Delta G_{reaction\ 'regular'}\right)_{T,P} \leq -n_{electrons\ transferred}\mathcal{F}\mathcal{E} \\ &\text{'regular'} \Rightarrow \ \text{not including } \mu_{e^-}\end{aligned}}$$

RETURN TO SANITY ➡