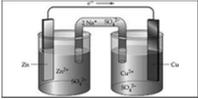


# Chemistry 163B W2020

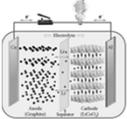
## Lectures 24-25- Electrochemistry Quickie



**Lectures 24-25 Winter 2020**

**Chemistry 163B**

**Electrochemistry**



1

**activity coefficients for ions (HW8 #58)**

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

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

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

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

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

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

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

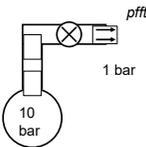
$$K_{sp} = (\gamma_{\pm})^3 [Ba^{2+}] [Cl^-]^2$$

2

**work of expansion**

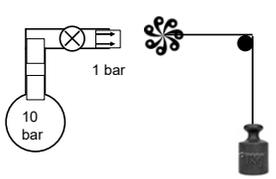
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$H_2(10 \text{ bar}) \rightarrow H_2(1 \text{ bar})$



10 bar

only P-V  
useless?



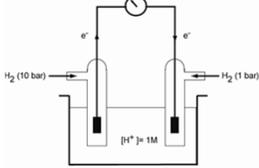
10 bar

real  $w_{other}$   
useful?

3

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

---



$$H_2(10 \text{ bar}) \rightarrow 2H^+ + 2e^-$$

$$2H^+ + 2e^- \rightarrow H_2(1 \text{ bar})$$

$$H_2(10 \text{ bar}) \rightarrow H_2(1 \text{ bar})$$

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

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

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

4

**$d\mu$  and work-other (previously done for dG)**

---


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

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

$\leq 0$  by 2nd law

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

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

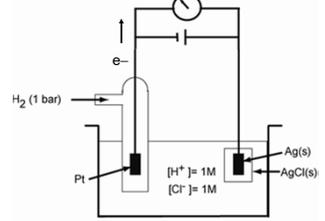
REVERSIBILITY

$w_{other}$  (p. 292<sub>4th</sub>) p. 292<sub>4th</sub>  $\bar{\mu}$  vs  $\mu$  'perhaps' more rigorous if you like

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

---



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

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

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

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# Chemistry 163B W2020

## Lectures 24-25- Electrochemistry Quickie

**$\Delta\mu$  for the reaction**  
(see Appendix A, Table 4.1 for data; additional decimal places from other tables)

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

$\Delta\mu_f^\circ \approx \Delta G_f^\circ$ (kJ)	0	-109.79	0	-131.23	0	kJ/mol
---	---	---------	---	---------	---	--------

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

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

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

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

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

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**and FINALLY  $w_{other}$  !!! (p. 324th)**

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.	$- \int_{V_i}^{V_f} P_{ext} dV$	$\text{Pa m}^3 = \text{J}$
Spring stretching and compression	Force ( $F$ ), distance ( $x$ ) The spring is the system.	$w = \int_{x_i}^{x_f} F \cdot dx$	$\text{N m} = \text{J}$
Bubble expansion and contraction	Surface tension ( $\gamma$ ), surface area ( $a$ ) The content of the bubble is the system.	$w = - \int_{a_i}^{a_f} \gamma da$	$(\text{N m}^{-1})(\text{m}^2) = \text{J}$
Current passes through conductor	Electrical potential difference ( $\Phi$ ), electrical charge ( $Q$ ) The conductor is the system.	$w = \int_0^Q \Phi dQ'$	$\text{V C} = \text{J}$

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**$w_{other}$  (p. 2924th)** BUT

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

electric potential      charge transfer

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

from negative charge on e      moles of e's transferred

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

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

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

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

E&R<sub>9th</sub> p260  $z = -n$

UNITS:  $[w] = [Q][\Phi]$   
joule = coulomb  $\times$  volt

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**sign of  $\Phi$  and spontaneity**

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

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

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

$\Delta\mu_{T,P} < 0$  spontaneous  $\Rightarrow \Phi > 0$  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  $-n\mathcal{F} \mathcal{E}_{mf} \approx \Delta\mu$  even if the reactants and products are not at equilibrium conditions, in the absence of reverse potential.

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**$\Phi$  vs concentration**

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

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

$\Phi^\circ$

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

$T = 298K$

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

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

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

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

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

$2e^- + H_2(g, 1\text{ bar}) + 2AgCl(s) \rightarrow 2H^+[1M] + 2Cl^-[1M] + 2Ag(s) + 2e^-$	$\Phi_0$ 0 0.22233
---	--------------------------

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# Chemistry 163B W2020

## Lectures 24-25- Electrochemistry Quickie

**example incorporating activities**

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

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

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

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

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**example incorporating activities**

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

0.22233 V

$$\Phi = 0.22233 - \frac{0.02569}{2} \ln \left[ \frac{\gamma_{\pm}^4 [H^+]^2 [Cl^-]^2}{\gamma_{H_2} (P_{H_2(g)})} \right]$$

unless; have dropped standard state conc's and pressure from denominators

• Calculate  $\gamma$ 's from observed  $\Phi$  (HW#8, prob 60)

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**calculate  $\Delta\mu$  from  $\Phi$**

$\Delta\mu^\circ$  from  $\Phi^\circ$  ( $\gamma_s=1$ )

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

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

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

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

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

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

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

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

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

$\Phi_{\text{cell}}^\circ = 0.22233 \text{ V}$

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

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

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

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

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

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

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

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

$\Phi_{\text{cell}}^\circ = 0.22233 \text{ V}$

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

$$= -(1 \text{ mol } e^-s)(96485 \text{ C mol}^{-1})(0.22233 \text{ V})$$

$$= 2.145 \times 10^4 \text{ C V} = 21.45 \text{ kJ}$$

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

$\Phi$  intensive same as for 2 mole  $e^-$ 's  
 $\Phi$  is oomph per electron

$$e^- + \frac{1}{2}H_2(g, P_{H_2}) + AgCl(s) \rightarrow H^+[H^+] + Cl^-[Cl^-] + Ag(s) + e^- \quad \Phi_{\text{cell } 1e}$$

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

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

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

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

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

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

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

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

$\Delta\mu$  extensive: depends on stoichiometry

$\Phi$  intensive: independent of 'how reaction is written' oomph PER electron

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

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# Chemistry 163B W2020

## Lectures 24-25- Electrochemistry Quickie

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

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

<b>standard REDUCTION potentials</b>	$\Phi^{\circ'}_{red}(V)$
	pH7
$2e^- + 2CytC(Fe^{3+}) \rightarrow 2CytC(Fe^{2+})$	0.25
$2e^- + \frac{1}{2}O_2(g) + 2H^+(aq) \rightarrow H_2O(l)$	0.816

<b>reaction: the oxidation of CytC(<math>Fe^{2+}</math>)</b>	$\Phi^{\circ'}(V)$
oxidation $2CytC(Fe^{2+}) \rightarrow 2CytC(Fe^{3+}) + 2e^-$	- 0.25
reduction $2e^- + \frac{1}{2}O_2(g) + 2H^+(aq) \rightarrow H_2O(l)$	0.816

$\frac{1}{2}O_2(g) + 2H^+(aq) + 2CytC(Fe^{2+}) \rightarrow 2CytC(Fe^{3+}) + H_2O(l)$      $? = \Phi^{\circ'}_{cell}$

↑  
standard state  $[H^+]=10^{-7}$

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**biological example (redox equation III)**

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

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

standard state'

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



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**$\Phi$  and thermodynamic derivatives, etc. (HW8, prob #59)**

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

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

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

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

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

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**$\Delta C_p$  from  $\Phi$**

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

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

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

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

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

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**relationships on final**

Electrochemistry:

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

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

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

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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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# Chemistry 163B W2020

## Lectures 24-25- Electrochemistry Quickie

**efficiency of  $w_{\text{electrical}}$  vs  $w_{p,v}$**

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

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

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

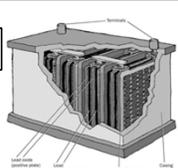
**the winner:**

$\frac{w_{\text{electrical}}}{w_{p,v}} = \frac{377}{114} = 3.31$
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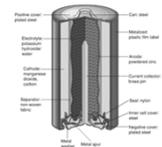
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**types of batteries**

**Lead storage**  
**Pb(s) oxidized to  $\text{Pb}^{2+}$   $\text{PbO}_2$  reduced to  $\text{Pb}^{2+}$**   
 $\text{PbO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2\text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2 \text{H}_2\text{O}(\text{l})$   $E^\circ = 1.685 \text{ V}$  (11.54)  
 $\text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^-$   $E^\circ = -0.356 \text{ V}$  (11.55)  
 respectively, and the overall reaction is  
 $\text{PbO}_2(\text{s}) + \text{Pb}(\text{s}) + 2 \text{H}_2\text{SO}_4(\text{aq}) \rightleftharpoons 2 \text{PbSO}_4(\text{s}) + 2 \text{H}_2\text{O}(\text{l})$   $E^\circ = 2.04 \text{ V}$  (11.56)



**Alkaline storage (no liquids)**  
**Zn(s) oxidized to  $\text{Zn}^{2+}$   $\text{MnO}_2$  reduced to  $\text{Mn}_2\text{O}_3$**   
 $\text{Zn}(\text{s}) + 2\text{OH}(\text{aq}) \rightarrow \text{ZnO}(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^-$   $+1.26 \text{ V}$   
 $2\text{MnO}_2(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3(\text{s}) + 2\text{OH}^-(\text{aq})$   $0.275 \text{ V}$   
**Zn(s) + 2MnO<sub>2</sub>(s) → ZnO(s) + Mn<sub>2</sub>O<sub>3</sub>(s) +1.5 V**



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**types of batteries**

**NiMH- Nickel Metal Hydride**  
 M="intermetallic compound", e.g.  $\text{M} = \text{AB}_5$ ,  
 A is a rare earth mixture of lanthanum, cerium, neodymium, praseodymium  
 B is nickel, cobalt, manganese, and/or aluminum

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

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



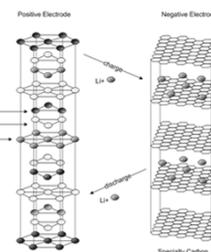
High power Ni-MH battery of Toyota NHW20 Prius

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**Li-ion batteries**

$\text{LiCoO}_2 \rightleftharpoons \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^-$   
 $x\text{Li}^+ + xe^- + 6\text{C} \rightleftharpoons \text{Li}_x\text{C}_6$

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**

<b>Zinc</b>	<b>1.5V</b>	<b>Non-rechargeable</b> —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](http://batteryuniversity.com/learn/article/whats_the_best_battery)

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**battery property comparison**

<b>Zinc</b>	<b>1.5V</b>	<b>Non-rechargeable</b> —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.
<b>Alkaline</b>	<b>1.5V</b>	<b>Rechargeable</b> —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.
<b>Nickel-Metal Hydride (NiMH)</b>	<b>1.25V</b>	<b>Rechargeable</b> —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.
<b>Lithium ion</b>	<b>3.6V</b>	<b>Rechargeable</b> —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](http://batteryuniversity.com/learn/article/whats_the_best_battery)

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# Chemistry 163B W2020

## Lectures 24-25- Electrochemistry Quickie

**fuel cells**

PEM- proton exchange membrane

Electric Current

Fuel In Air In

Excess Fuel Unused Gases Out

Anode Electrolyte Cathode

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

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

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

$$dG = -SdT + VdP + \sum_{i \neq e^-} \mu_i^{(\gamma)} dn_i^{(\gamma)} \leq \tilde{d}w_{elec}$$

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

VS

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

$$(\Delta G)_{T,P} = \sum_{i \neq e^-} \nu_i^{(\gamma)} \tilde{\mu}_i^{(\gamma)} \leq 0$$


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

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

↑ back ↓ more  
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free energy of charged species in the presence of electrostatic potential

$$d\tilde{\mu}_i^{(\gamma)} = d\mu_i^{(\gamma)} + (dw_i^{(\gamma)})_{other} = -\tilde{S}_i^{(\gamma)} dT + \tilde{V}_i^{(\gamma)} dP + \phi^{(\gamma)} dQ_{elec}^{(\gamma)}$$

Faraday  
96,485 Coulombs mole<sup>-1</sup>

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

integer (signed) charge      electrostatic potential in phase  $\gamma$        $\mu_i^{(a)} = \mu_i^{(b)}$

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a charge in two phases (different potential  $\phi$ ; otherwise same)

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

$\mu_i^{(a)}$  is escaping tendency from phase (a),  $\mu_i^{(b)}$  from phase  $\beta$   
+ charge ( $z_i > 0$ ): ion 'escapes' to phase of lower (more negative) potential  $\phi$   
- charge ( $z_i < 0$ ): ion 'escapes' to phase of higher (more positive) potential  $\phi_{ad}$

$\tilde{\mu}_i$  electrochemical potential

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

$$\Delta G_{reaction} = \sum_{i \neq e^-} \nu_i^{(\gamma)} \tilde{\mu}_i^{(\gamma)} \quad \text{where } \nu_i^{(\gamma)} \text{ are the stoichiometric coefficients}$$

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 solution phase  $\alpha$       for any neutral species  $z_i = 0$

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

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

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

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 detrons at metal electrodes

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$\tilde{\mu}_i$  electrochemical potential

$$\Delta G_{reaction} = \sum_{i \neq e^-} \nu_i^{(\gamma)} \tilde{\mu}_i^{(\gamma)} \quad \text{where } \nu_i^{(\gamma)} \text{ are the stoichiometric coefficients}$$

thus:  $\Delta G_{reaction} = \sum_{i \neq e^-} \nu_i^{(\gamma)} \mu_i^{(\gamma)} + \sum_e \nu_e^{(oxidation)} z_e \mathcal{F} \phi^{(oxidation electrode)} + \sum_e \nu_e^{(reduction)} z_e \mathcal{F} \phi^{(reduction electrode)}$

$\nu_e^{(oxidation)} = +N_{transferred electrons}$  and  $\nu_e^{(oxidation)} = -N_{transferred electrons}$

and  $(\mu^{(reactant electrode)})_e^0 = (\mu^{(product electrode)})_e^0$

$$\Delta G_{reaction} = \sum_{\gamma, i \neq e^-} \nu_i^{(\gamma)} \mu_i^{(\gamma)} - n \mathcal{F} (\phi^{(reduction electrode)} - \phi^{(oxidation electrode)})$$

$emf \equiv \mathcal{E} \equiv (\phi^{(oxidation electrode)} - \phi^{(reduction electrode)})$  (IUPAC convention)

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

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# Chemistry 163B W2020

## Lectures 24-25- Electrochemistry Quickie

**so it boils down to**

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from  
 $\tilde{\mu}_i$

$$\Delta G_{\text{reaction}} = \sum_{\substack{\gamma, i = \text{species} \\ \text{other than } e^-}} \nu_i^{(\gamma)} \mu_i^{(\gamma)} + nF\mathcal{E} \leq 0$$

$$\Delta G_{\text{reaction 'regular'}} = \sum_{\substack{\gamma, i = \text{species} \\ \text{other than } e^-}} \nu_i^{(\gamma)} \mu_i^{(\gamma)} \leq -nF\mathcal{E}$$

**VS**

from  
 $\mu_i$   
 $\Delta\mu_{\text{electron}} \approx \Delta G_{\text{reaction}}$

$$(\Delta G_{\text{reaction 'regular'}})_{T,P} \leq W_{\text{electrical}}$$

$$(\Delta G_{\text{reaction 'regular'}})_{T,P} \leq -n_{\text{electrons transferred}} F\mathcal{E}$$

'regular'  $\Rightarrow$  not including  $\mu_{e^-}$

RETURN TO  
SANITY

■■■■►

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