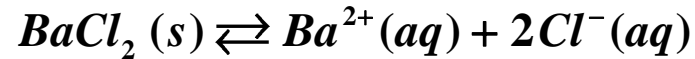


Chemistry 163B

Electrochemistry

activity coefficients for ions (HW9 #58)



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

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

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

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

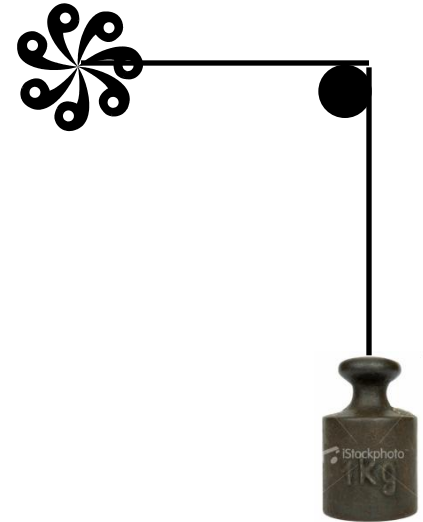
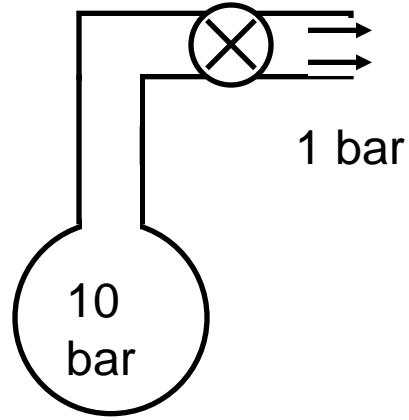
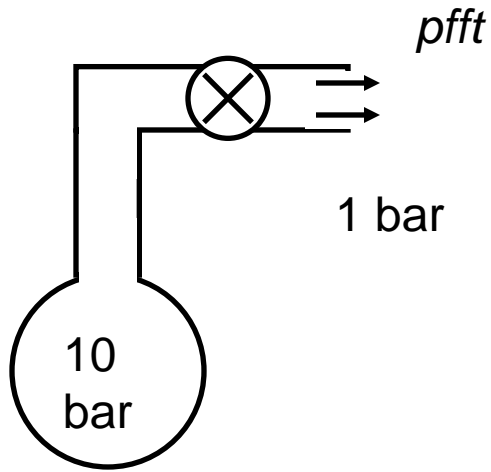
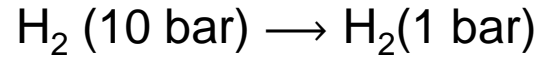
cannot determine $\gamma_{\text{Ba}^{2+}}$ and γ_{Cl^-} independently

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

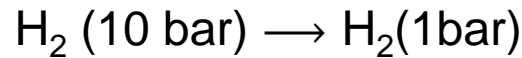
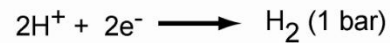
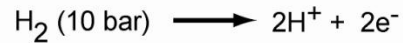
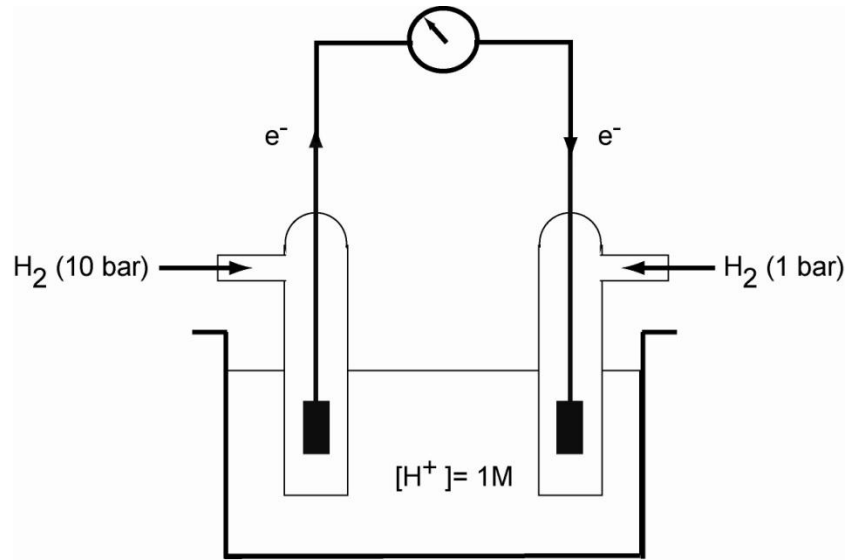
$$K_{sp} = \frac{(\gamma_{\pm})^3 \left(\frac{[\text{Ba}^{2+}]}{1M}\right) \left(\frac{[\text{Cl}^-]}{1M}\right)^2}{1} \quad (1)$$

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

work of expansion



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



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

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

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

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

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

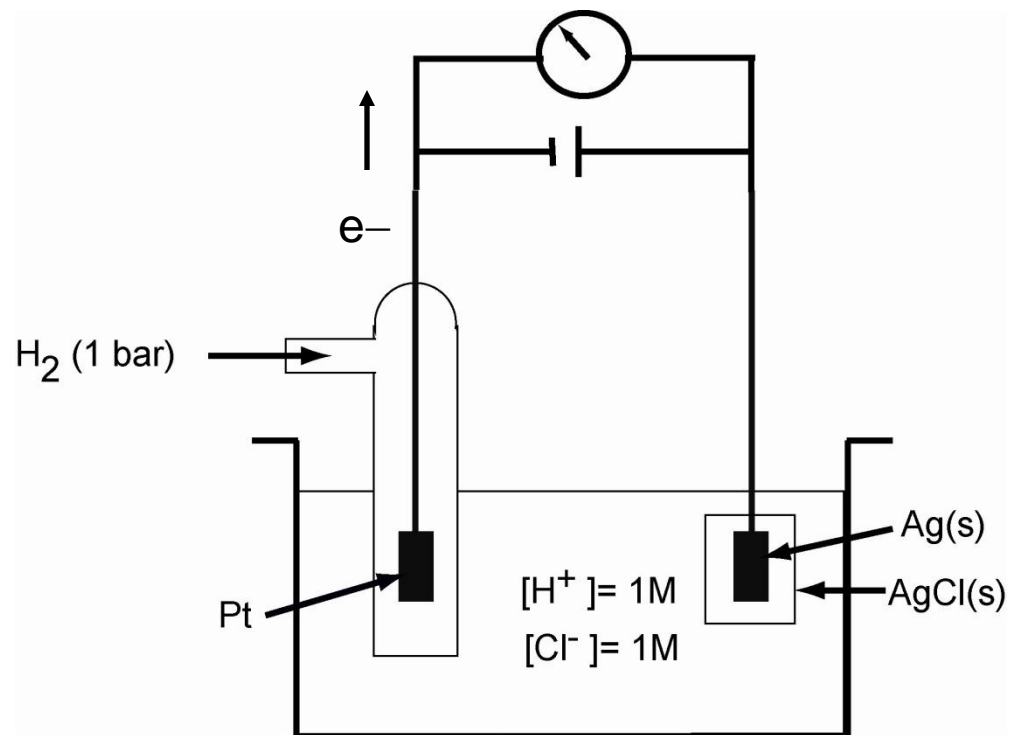
$$d\mu = \underbrace{d\bar{q} - Td\bar{S}}_{\leq 0 \text{ by 2nd law}} - \bar{S}dT + VdP + d\bar{w}_{other} \quad (\text{very general})$$

$$d\mu_{T,P} \leq d\bar{w}_{other}$$

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

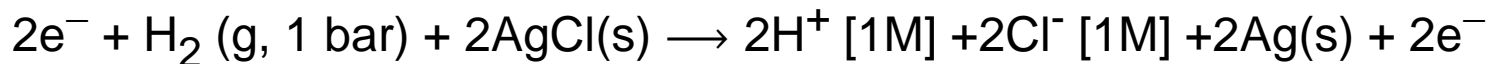
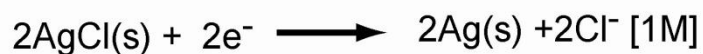
responsible for 3 redox reactions; here's II (HW9, prob #60)



oxidation *anode*

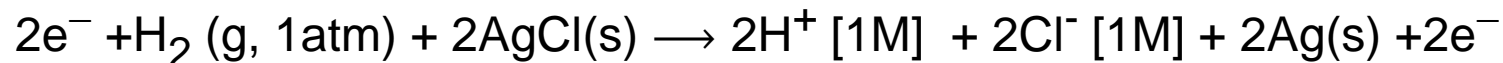


reduction *cathode*



$\Delta\mu$ for the reaction

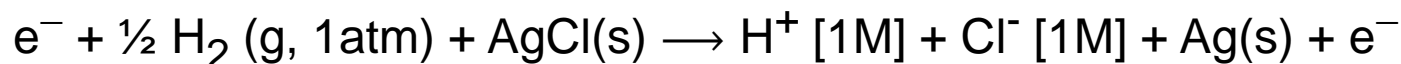
(see Appendix A, Table 4.1 for data; additional decimal places from other tables)



$$\Delta\mu_f \approx \Delta G_f \text{ (kJ)} \quad 0 \quad -109.79 \quad 0 \quad -131.23 \quad 0$$

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

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



$$\Delta\mu \approx \Delta G = -21.44 \text{ kJ per } \frac{1}{2} \text{ mole H}_2$$

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

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)	$w = - \int_{V_i}^{V_f} P_{\text{external}} dV$	$\text{Pa m}^3 = \text{J}$
Stretching	Force (F), length (l)	$w = \int_{x_i}^{x_f} \mathbf{F} \cdot d\mathbf{l}$	$\text{N m} = \text{J}$
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)	$w = \int_0^Q \phi dQ'$	$\text{V C} = \text{J}$

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

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

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

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

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

$$E \ \& \ R \ p260 \ z \equiv -n$$

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

sign of Φ and spontaneity

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

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

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

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

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

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

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

$$T = 298\text{K}$$

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

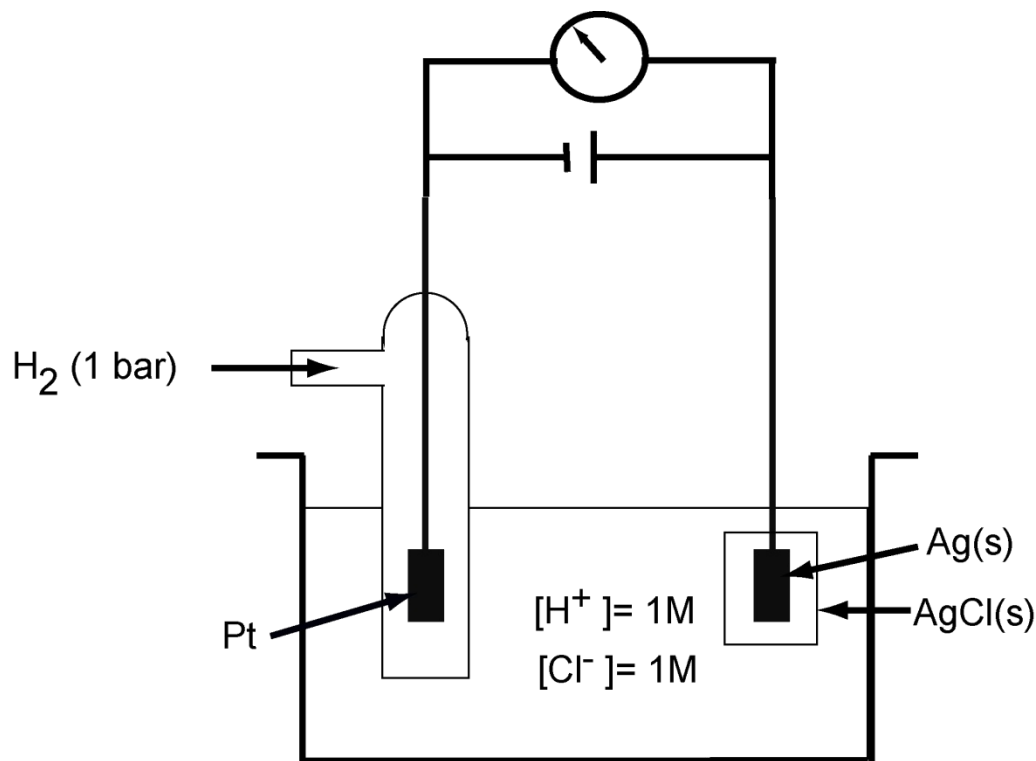
n = moles electrons transferred

$[n]$ = mol

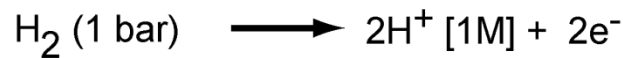
$\bar{n} = n \times \text{mol}^{-1}$

$[\bar{n}] = \textit{unitless}$

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

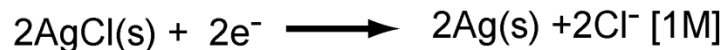


oxidation *anode*

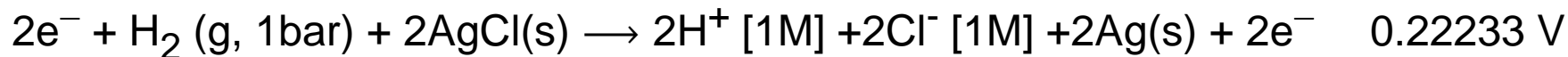


$$\Phi_0$$

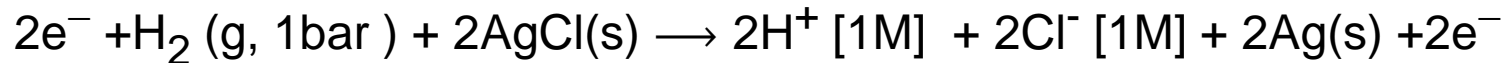
reduction *cathode*



$$0.22233 \text{ V}$$



example incorporating activities



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

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

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

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

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

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

example incorporating activities

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

0.22233 V $2 \text{ e}'\text{s}$

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

unitless; have dropped
standard state concs
and pressure from
denominators

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

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

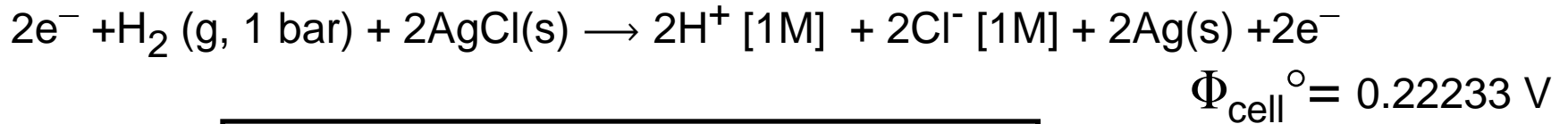
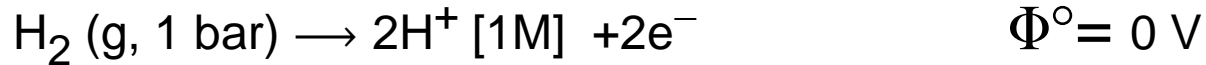
$$\Delta\mu = -n\mathcal{F}\Phi$$

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

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

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

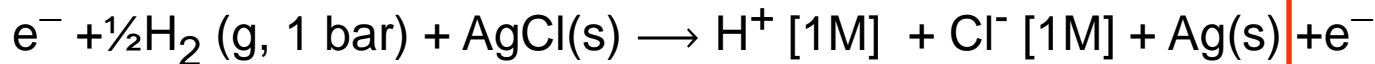
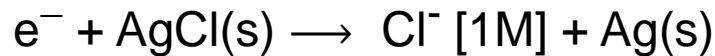
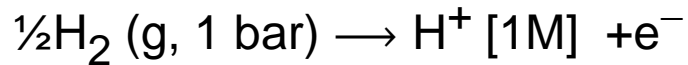
intensive Φ vs extensive $\Delta\mu$ $\Phi = - (\Delta\mu / n\mathcal{F})$



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

$$\Phi_{\text{cell } 2\text{e}'\text{s}} = \Phi_{\text{cell}}^\circ - \frac{0.02569 \text{ V}}{2} \ln \left[\frac{a_{\text{H}^+}^2 a_{\text{Cl}^-}^2 a_{\text{Ag}(\text{s})}^2}{a_{\text{H}_2} a_{\text{AgCl}(\text{s})}^2} \right]$$

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



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

$$\Phi^\circ = 0 \text{ V}$$

$$\Phi^\circ = 0.22233 \text{ V}$$

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

Φ° intensive

same as for 2 mole e^- 's

Φ is oomph per electron

$$\Phi_{\text{cell } 1\text{e}} = \Phi_{\text{cell}}^\circ - \frac{0.02569 \text{ V}}{1} \ln \left[\frac{a_{\text{H}^+}^1 a_{\text{Cl}^-}^1 a_{\text{Ag}(\text{s})}^1}{a_{\text{H}_2}^{1/2} a_{\text{AgCl}(\text{s})}^1} \right]$$

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

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

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

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

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

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

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

$\Delta\mu$ *extensive: depends on stoichiometry*

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

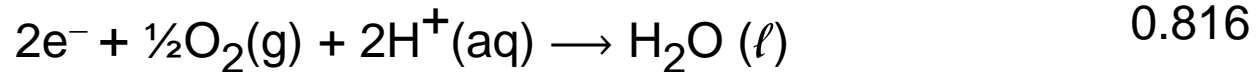
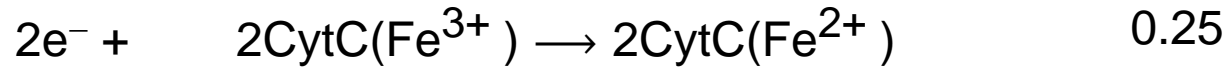
Φ *intensive: independent of 'how reaction is written' oomph PER electron*

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

CytC=cytochrome C
 standard state pH=7, [H⁺]=10⁻⁷

standard REDUCTION potentials

Φ^{o'}_{red}(V)
 pH7



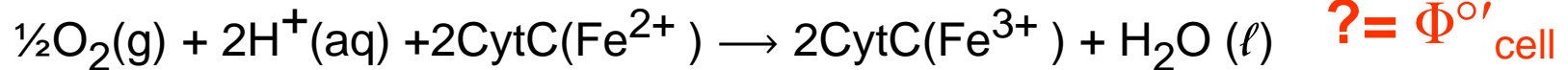
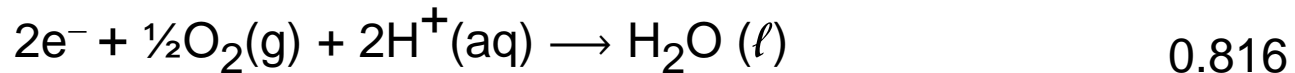
reaction: the oxidation of CytC(Fe²⁺)

Φ^{o'}(V)

oxidation

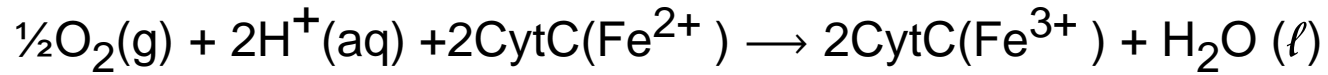


reduction



↑
 standard state [H⁺]=10⁻⁷

biological example (redox equation III)



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

standard state'

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

what's Q ?

what's n ?



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

$$\begin{aligned}\Delta\mu &= -n\mathcal{F}\Phi \\ \Phi &= -\frac{\Delta\mu}{n\mathcal{F}}\end{aligned}$$

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

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

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

ΔC_p from Φ

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

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

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

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

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

Electrochemistry:

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

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

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

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)

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: $T_u = 600\text{K}$, $T_L = 300\text{K}$

$$\epsilon = (600 - 300) / 600 = 0.5$$

$$w_{P-V} = (0.5) * 228 \text{ kJ mol}^{-1} = 114 \text{ kJ mol}^{-1}$$

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

$$w_{\text{electrical}} = -\Delta G = 377 \text{ kJ mol}^{-1}$$

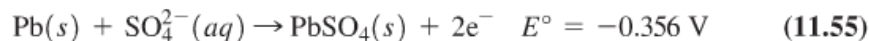
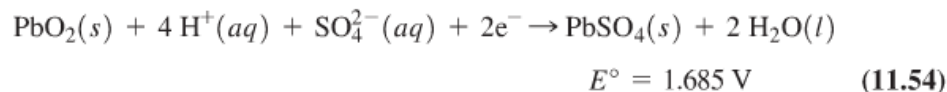
the winner:

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

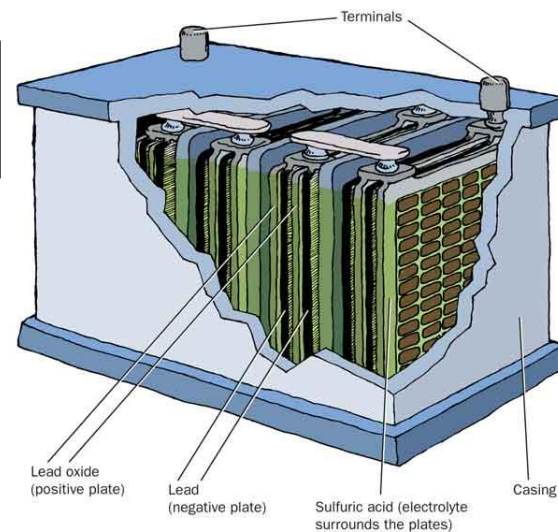
types of batteries

Lead storage

Pb(s) oxidized to Pb²⁺ PbO₂ reduced to Pb²⁺

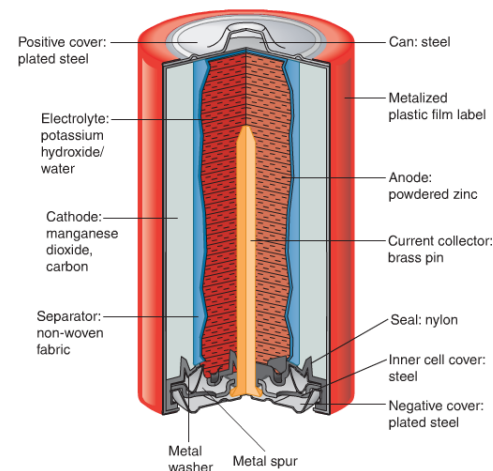
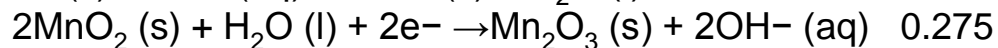
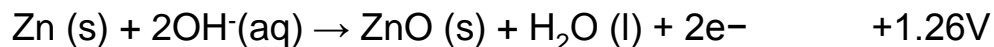


respectively, and the overall reaction is



Alkaline storage (no liquids)

Zn(s) oxidized to Zn²⁺ MnO₂ reduced to Mn₂O₃



types of batteries

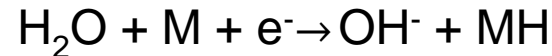
NiMH- Nickel Metal Hydride

M='intermetallic compound', e.g. $M=AB_5$,

A is a rare earth mixture of lanthanum, cerium, neodymium, praseodymium

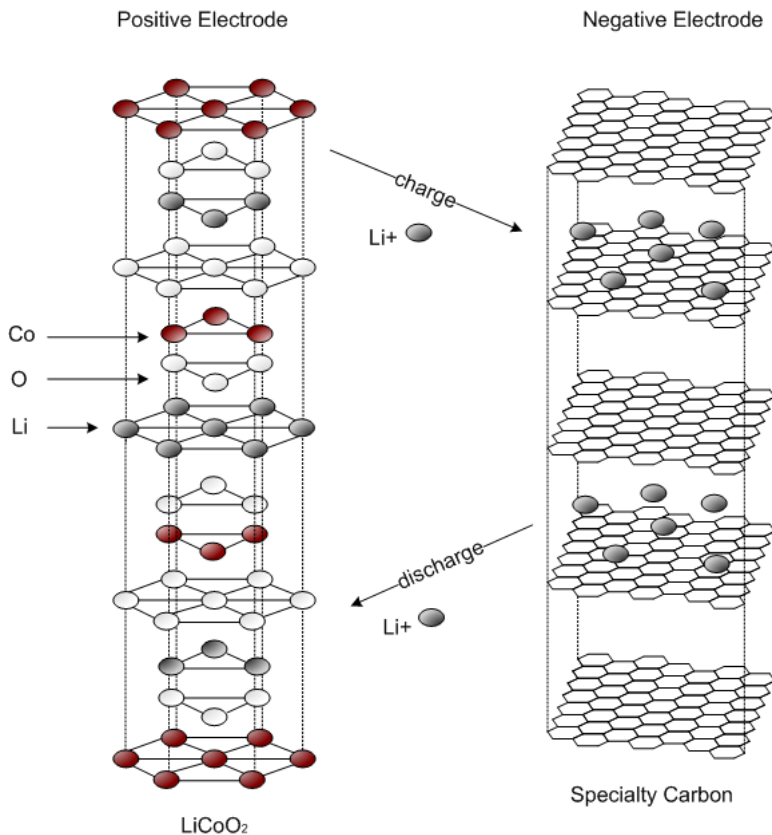
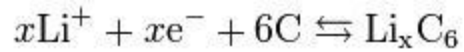
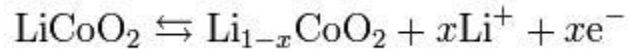
B is nickel, cobalt, manganese, and/or aluminum

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



High power Ni-MH battery of Toyota NHW20 Prius

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.



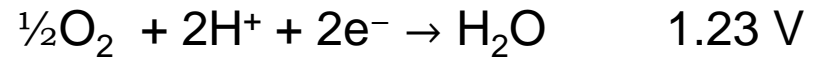
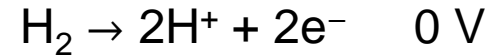
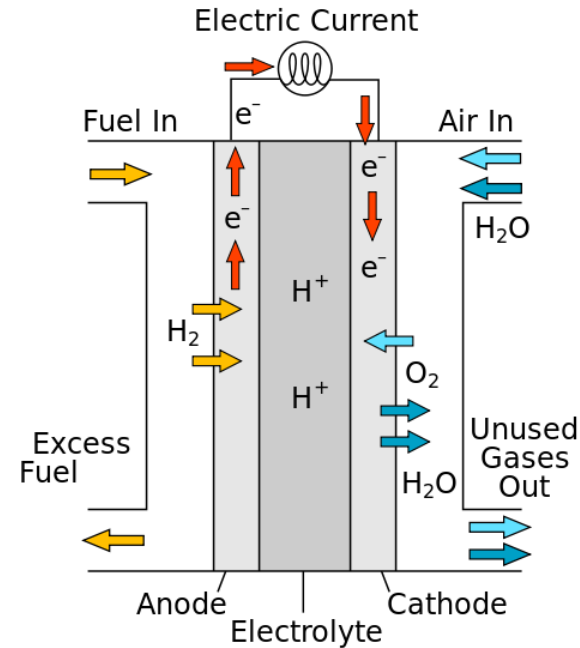
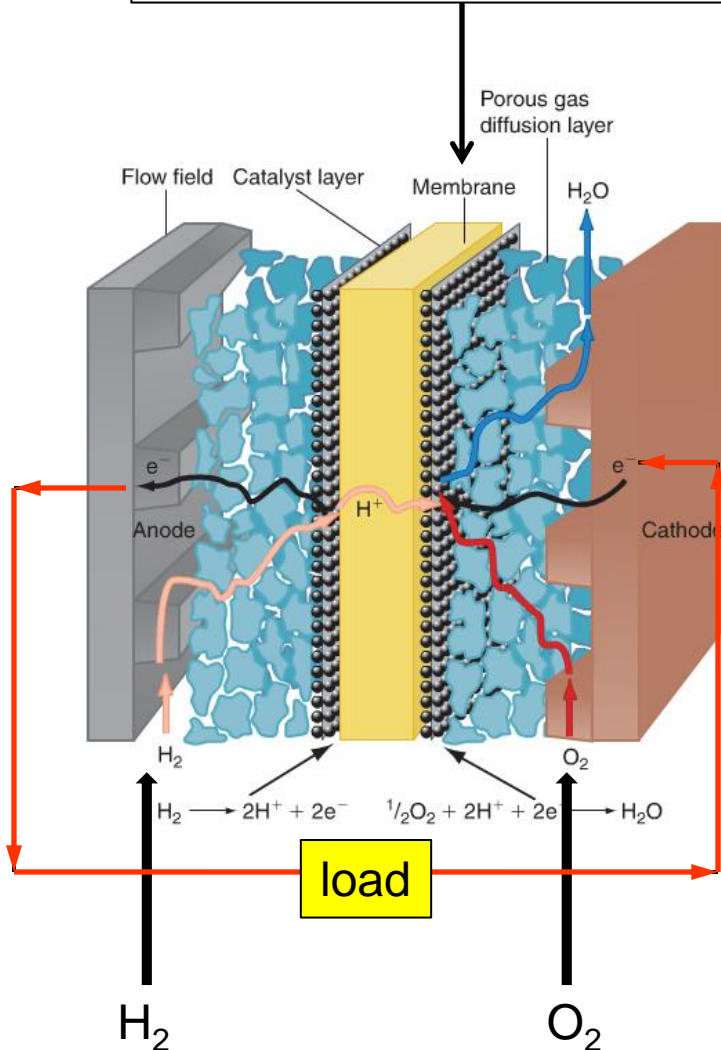
A downside of Li-ion cells, however, is that they contain a flammable electrolyte solution consisting of lithium salts in organic solvents such as ethylene carbonate and ethyl methyl carbonate. This is not the case for other commercial battery types.

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:

fuel cells

PEM- proton exchange membrane



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

$$dG - \bar{d}w_{elec} = -SdT + VdP + \sum_{i,\gamma} \mu_i^{(\gamma)} dn_i^{(\gamma)}$$
$$(\Delta G_{reaction})_{T,P} - w_{elec} = \sum_{i,\gamma} \nu_i^{(\gamma)} \mu_i^{(\gamma)} = (\Delta \mu_{reaction}) \leq 0$$

VS

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

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

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

