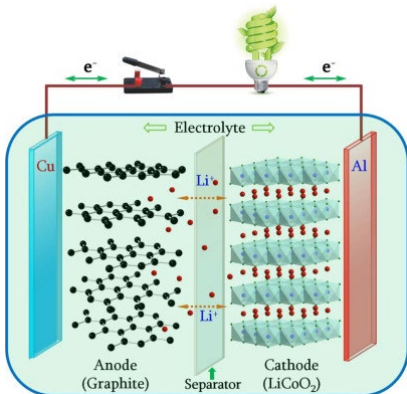


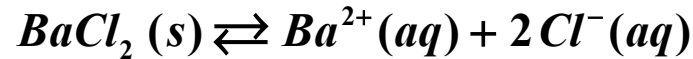
Lectures 24-25 Winter 2020

Chemistry 163B

Electrochemistry



activity coefficients for ions (HW8 #58)



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

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

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

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

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

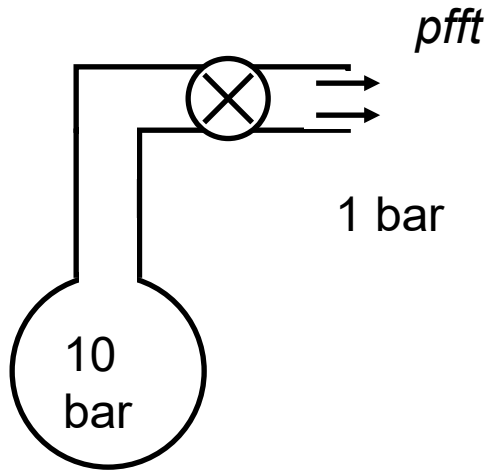
but only $\gamma_{\text{Ba}^{2+}} = \gamma_{\text{Cl}^-} = \gamma_{\pm}$ ($\gamma_{+} = \gamma_{-} \equiv \gamma_{\pm}$)

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

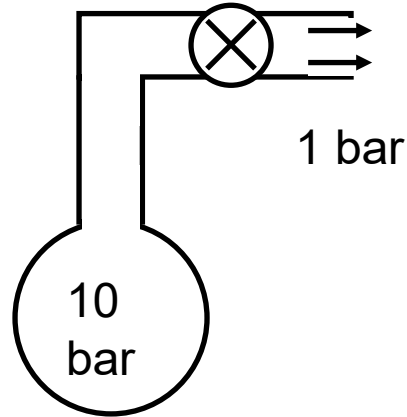
$$K_{sp} = (\gamma_{\pm})^3 \left[\text{Ba}^{2+} \right] \left[\text{Cl}^- \right]^2$$

work of expansion

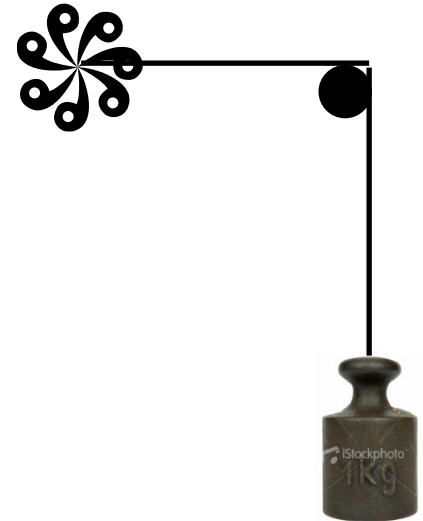
$H_2 (10 \text{ bar}) \rightarrow H_2(1 \text{ bar})$



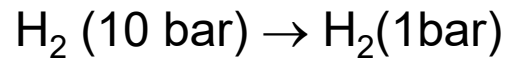
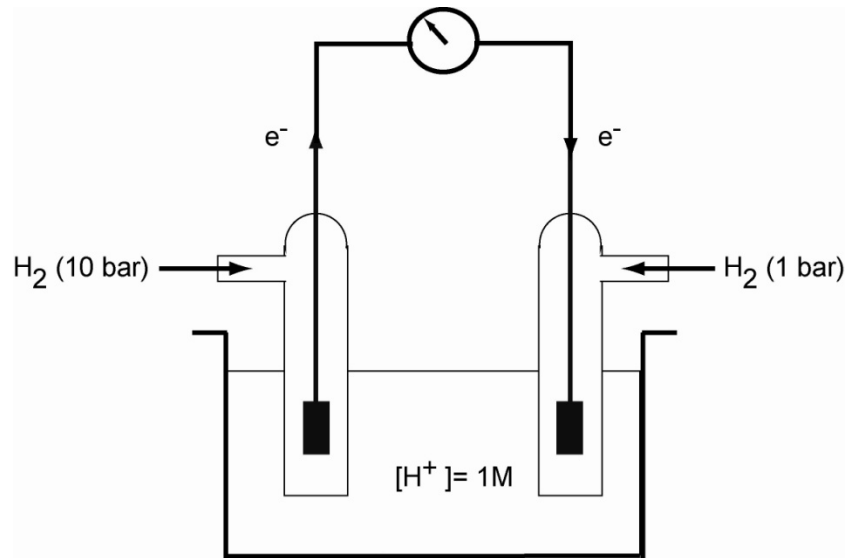
only P-V
useless?



real w_{other}
useful?



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



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

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

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

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


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

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

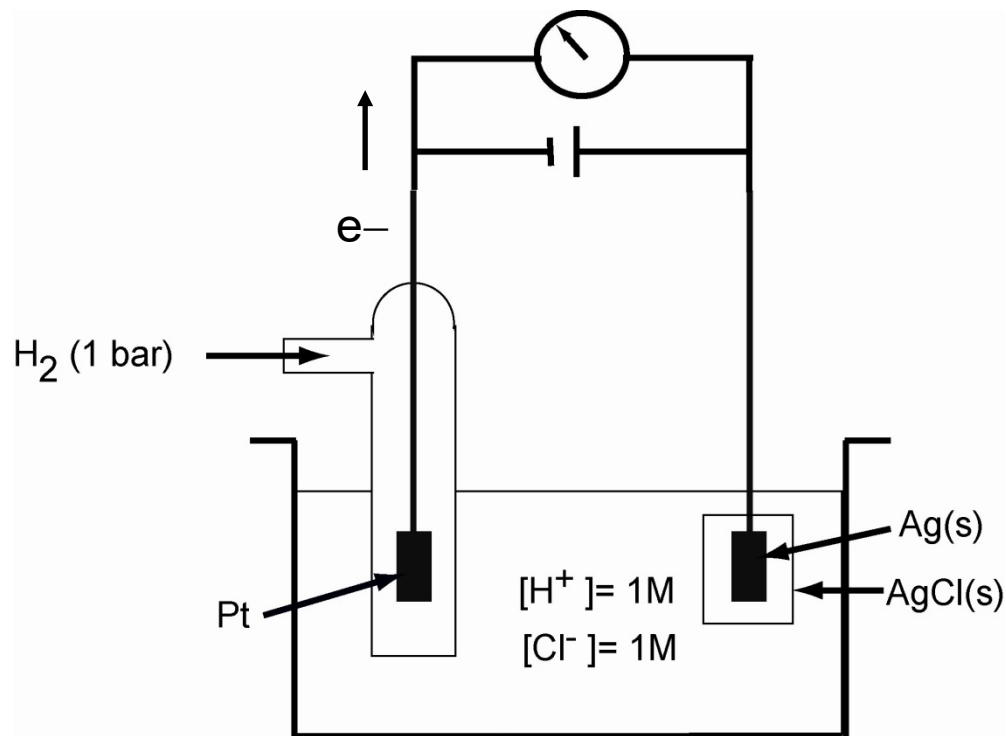
$$\Delta\mu_{T,P} \leq w_{other}$$

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

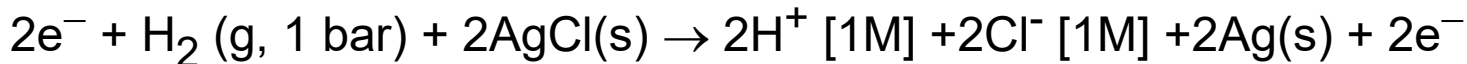
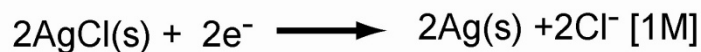
responsible for 3 redox reactions; here's II (HW8, prob #60)



oxidation *anode*

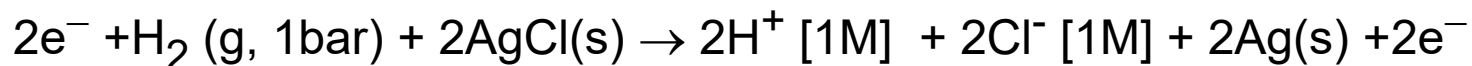


reduction *cathode*



$\Delta\mu$ for the reaction

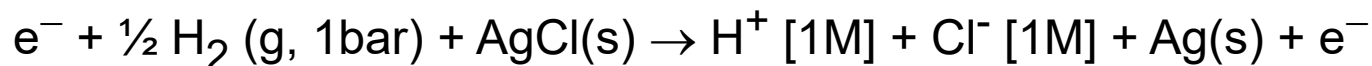
(see Appendix A, Table 4.1 for data; additional decimal places from other tables)



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

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

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



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

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

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

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

electric potential

charge transfer

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

from negative
charge on e

\mathcal{F} is Faraday constant
96,458 coulomb (mole e)⁻¹

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

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

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

$$E\&R_{4th} \text{ p260 } z \equiv -n$$

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

sign of Φ and spontaneity

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

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

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

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

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

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

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

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

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

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

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

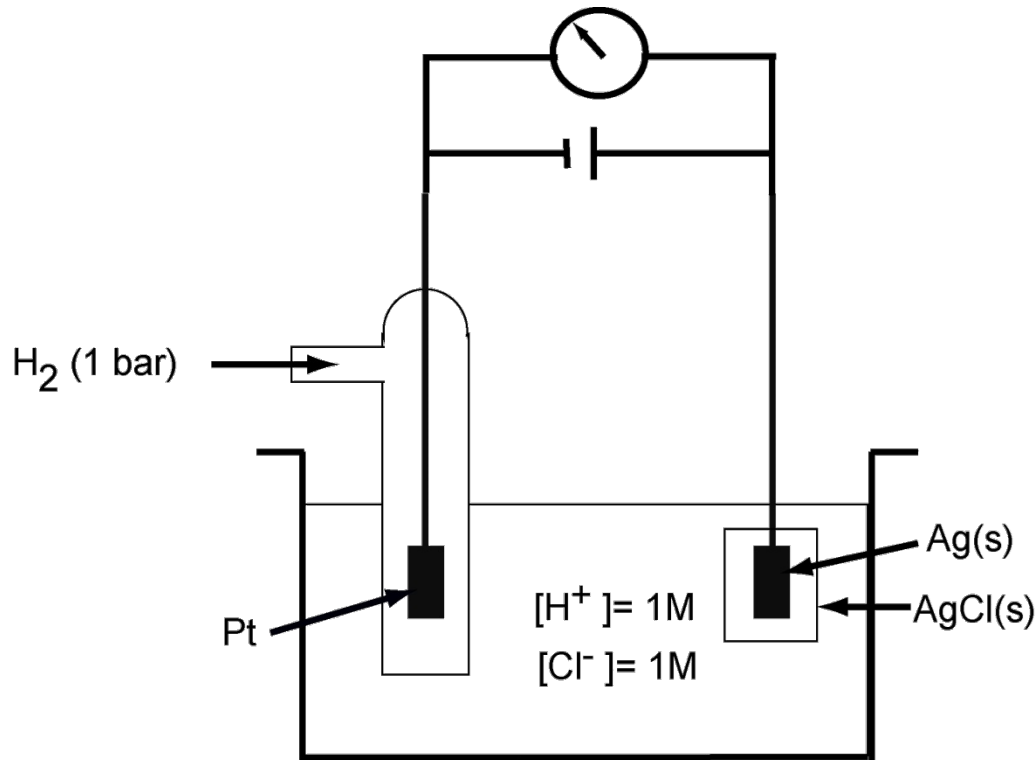
n = moles electrons transferred

$[n] = \text{mol}$

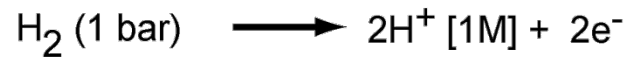
$\bar{n} = n \times \text{mol}^{-1}$

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

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

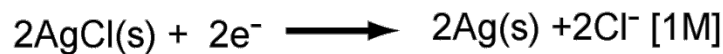


oxidation *anode*



$$\Phi_0$$

reduction *cathode*

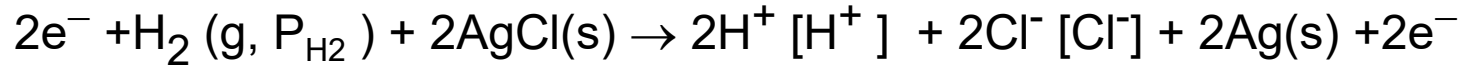


$$0.22233$$



$$0.22233$$

example incorporating activities



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

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

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

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

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

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

example incorporating activities

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

\nearrow
0.22233 V

\bar{n}
 \uparrow
2 e's

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

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° ($\gamma'_s=1$)

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

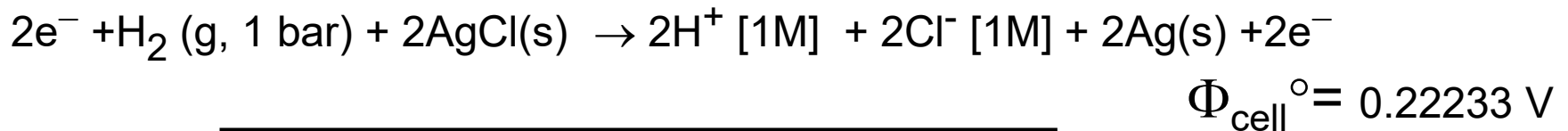
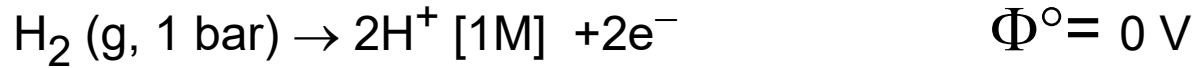
$$\Delta\mu^\circ = -n\mathcal{F}\Phi^\circ$$

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

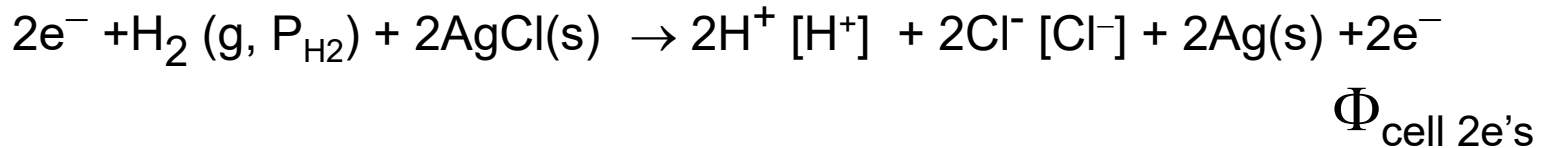
$$\Delta\mu^\circ = -4.290 \times 10^4 \text{ CV} = -42.90 \text{ kJ}$$

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

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

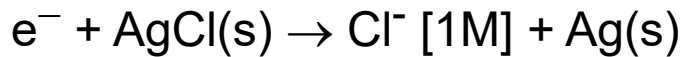
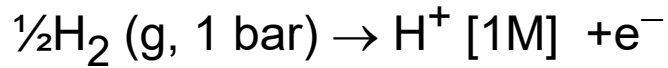


$\Delta\mu^\circ = -42.88 \text{ kJ for 2 moles e}^- \text{ transferred}$



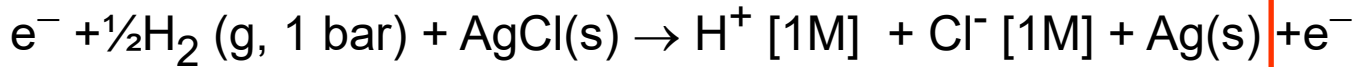
$$\Phi_{\text{cell } 2\text{e}'\text{s}} = \Phi_{\text{cell}}^\circ - \frac{0.02569}{2} \ln \left[\frac{a_{\text{H}^+}^2 a_{\text{Cl}^-}^2 a_{\text{Ag}(\text{s})}^2}{a_{\text{H}_2} a_{\text{AgCl}(\text{s})}^2} \right]$$

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



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

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



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

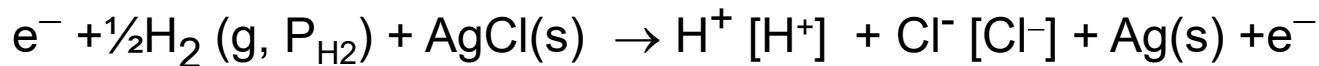
$$\Delta\mu^\circ = -n\mathcal{F}\Phi^\circ$$

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

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

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

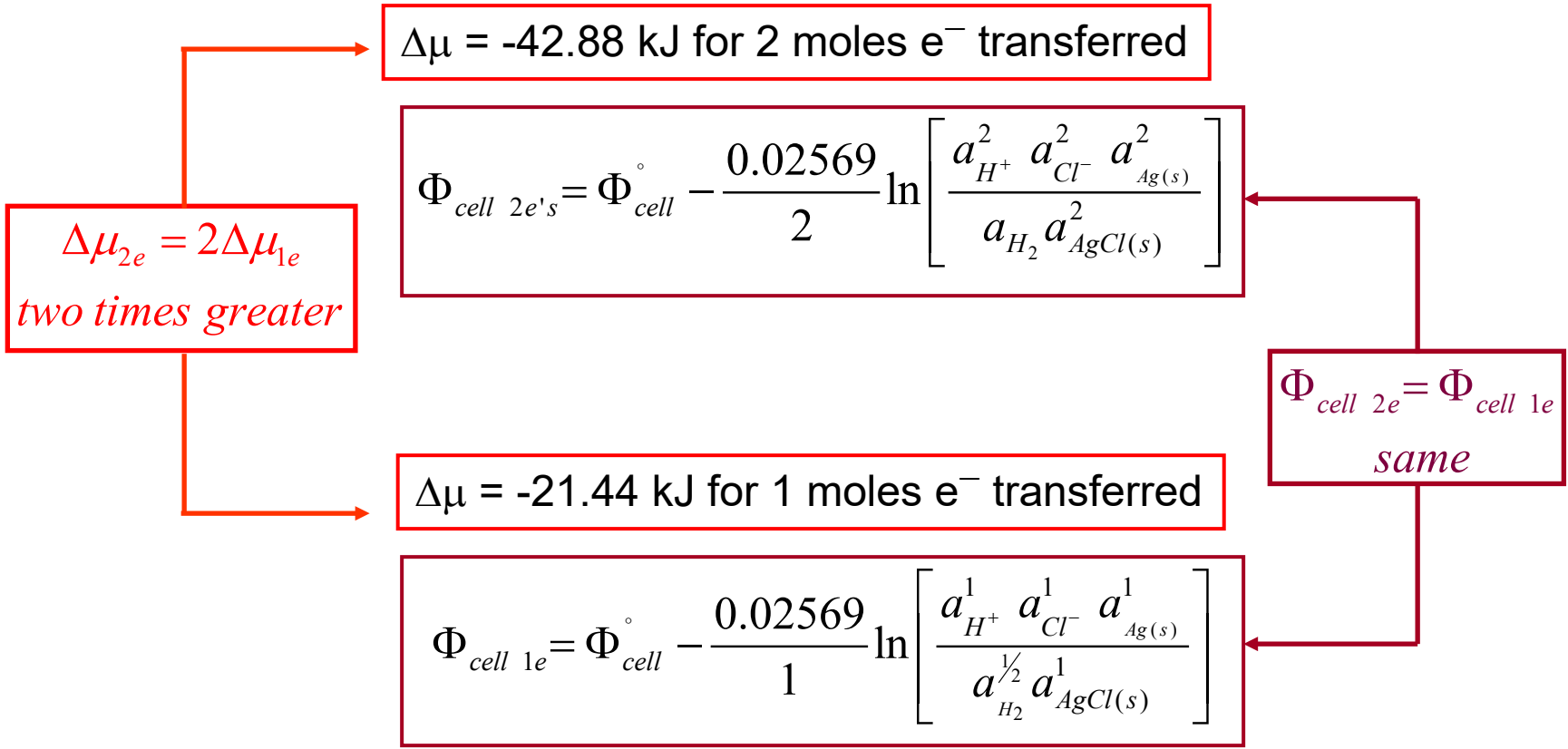
↑
 Φ° intensive
 same as for 2 mole e⁻
 Φ is oomph per electron



$$\Phi_{\text{cell } 1\text{e}}$$

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

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



$\Delta\mu$ extensive: depends on stoichiometry

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

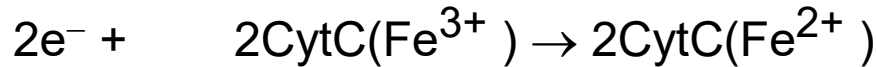
Φ intensive: independent of 'how reaction is written' oomph PER electron

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

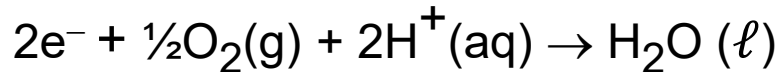
CytC=cytochrome C
 standard state pH=7, $[H^+] = 10^{-7}$

standard REDUCTION potentials

$\Phi^{\circ'}_{red}(V)$
 pH7



0.25



0.816

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

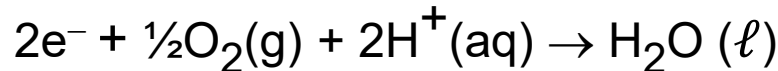
$\Phi^{\circ'}(V)$

oxidation

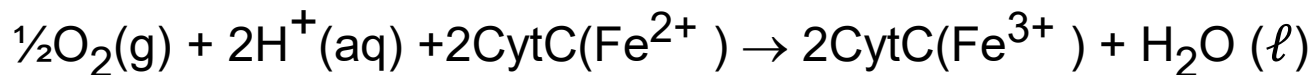


- 0.25

reduction



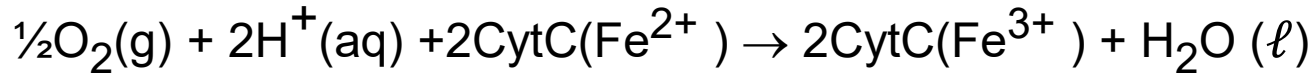
0.816



? = $\Phi^{\circ'}_{cell}$

↑
 standard state $[H^+] = 10^{-7}$

biological example (redox equation III)



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

standard state'

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

what's Q ?

what's n ?



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

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

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

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

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

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:

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

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

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

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

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

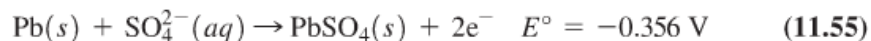
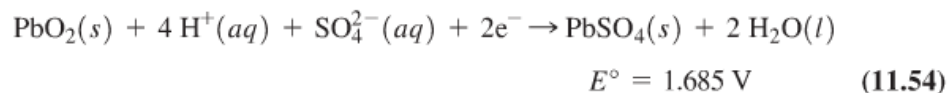
the winner:

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

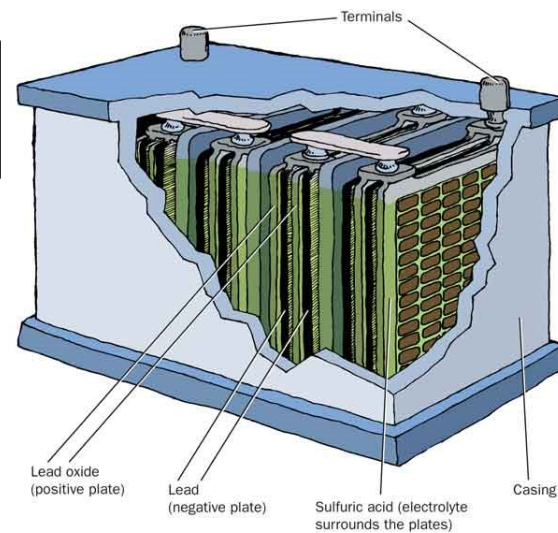
types of batteries

Lead storage

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

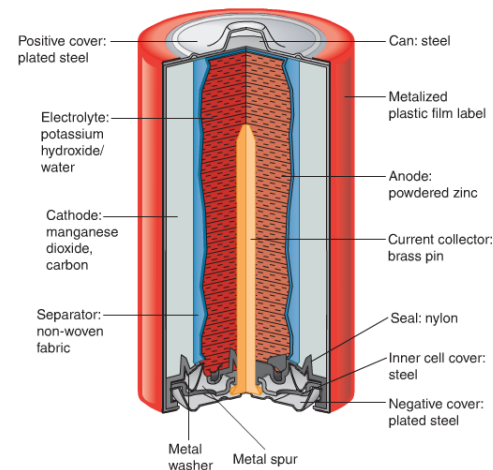
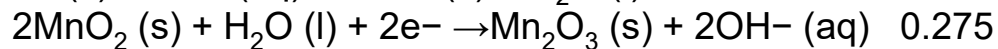
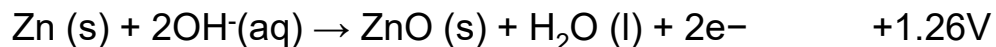


respectively, and the overall reaction is



Alkaline storage (no liquids)

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



types of batteries

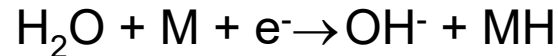
NiMH- Nickel Metal Hydride

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

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

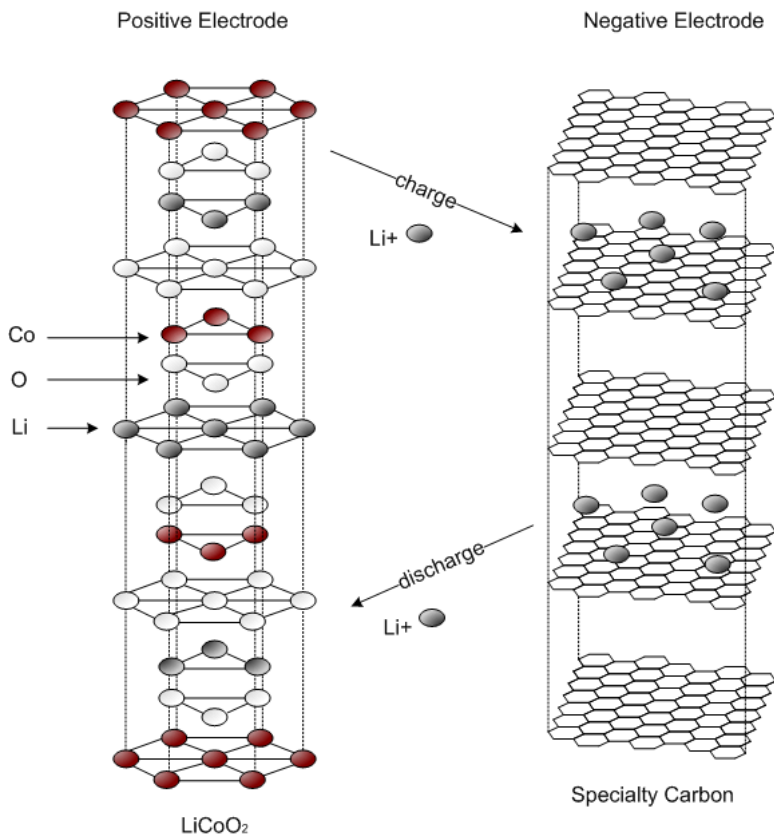
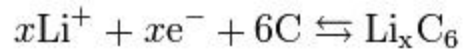
B is nickel, cobalt, manganese, and/or aluminum

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

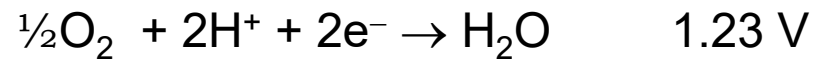
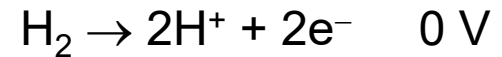
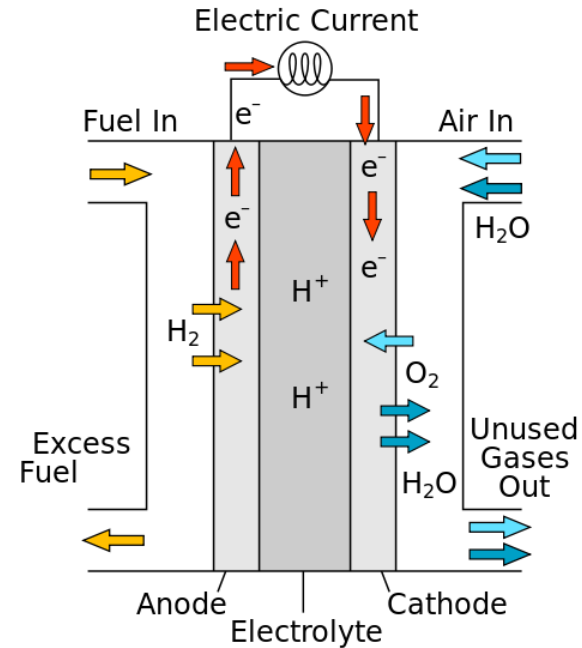
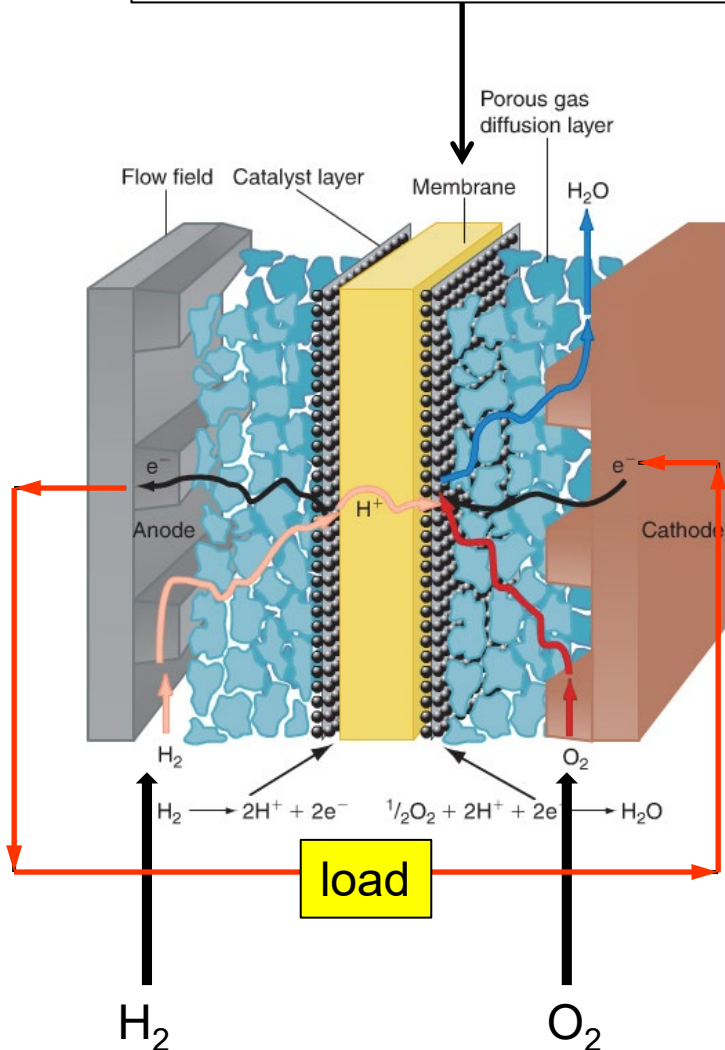
Zinc	1.5V	Non-rechargeable —first the forerunner and later an inexpensive alternative to Alkaline batteries. However, reductions in the price of Alkalines have made both Zinc-Carbon and Zinc-Chloride batteries all but obsolete.
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Zinc	1.5V	Non-rechargeable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

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

VS

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

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

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



back



more

free energy of charged species in the presence of electrostatic potential

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

Faraday
96,485 Coulombs mole⁻¹

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

integer (signed) charge

electrostatic potential in phase γ

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

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

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

$\mu_i^{(\alpha)}$ 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

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

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

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 α

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

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

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

for any neutral species $z_i = 0$

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

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 electrons at metal electrodes

$\tilde{\mu}_i$ electrochemical potential

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

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

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

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

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

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

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

so it boils down to

from

$\tilde{\mu}_i$

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

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

VS

from

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

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

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

'regular' \Rightarrow not including μ_{e^-}

RETURN TO
SANITY

