Chemistry 163B

Electrochemistry

activity coefficients for ions (HW8 #58)

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

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

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

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

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

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

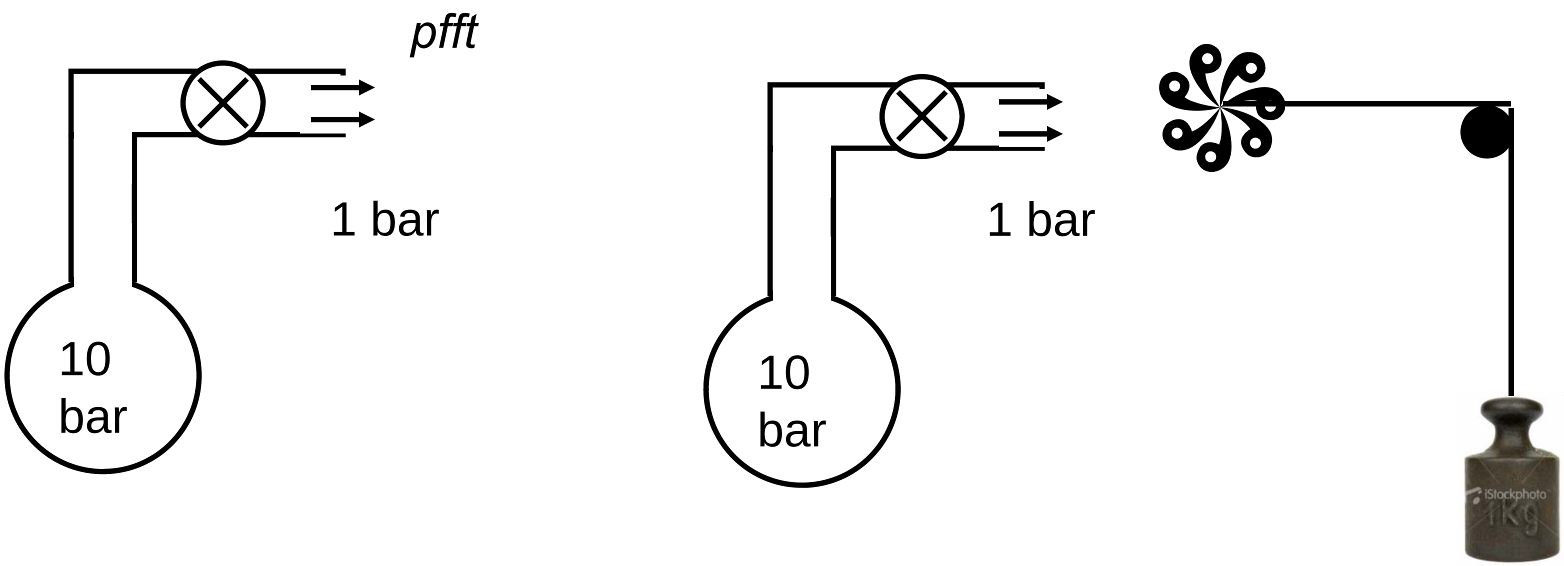
but only $\gamma_{Ba^{2+}} = \gamma_{Cl^-} = \gamma_\pm \quad \left(\gamma_+ = \gamma_- \equiv \gamma_\pm\right)$

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

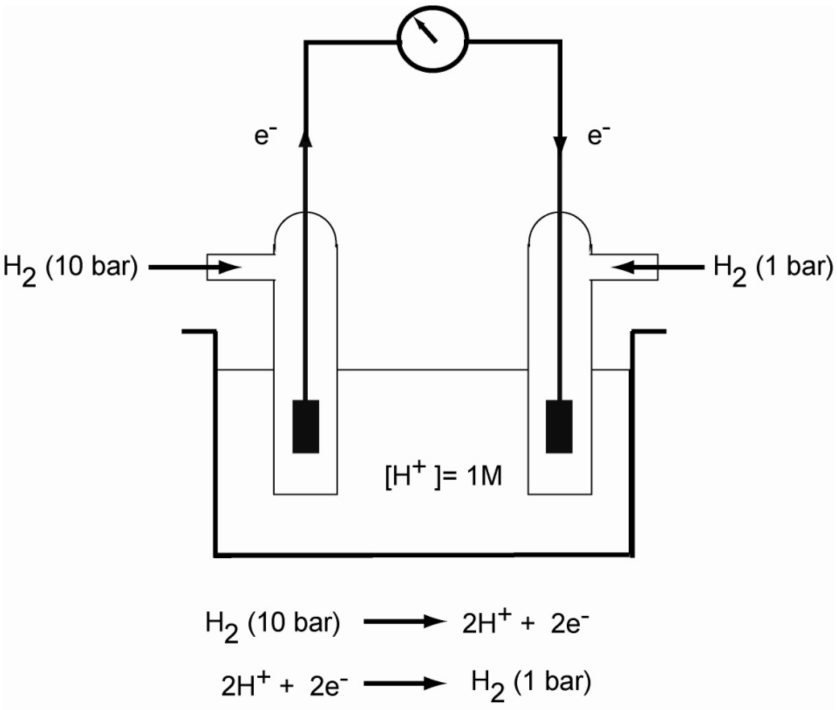
$$K_{sp} = (\gamma\pm)^3\left[Ba^{2+}\right]\left[Cl^-\right]^2$$

work of expansion

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



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



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

$$\Delta\mu = \Delta\mu^\circ + \underline{\boldsymbol{R}}\boldsymbol{T}\,\mathbf{ln}\,\boldsymbol{Q}_{reaction}$$

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

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

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

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

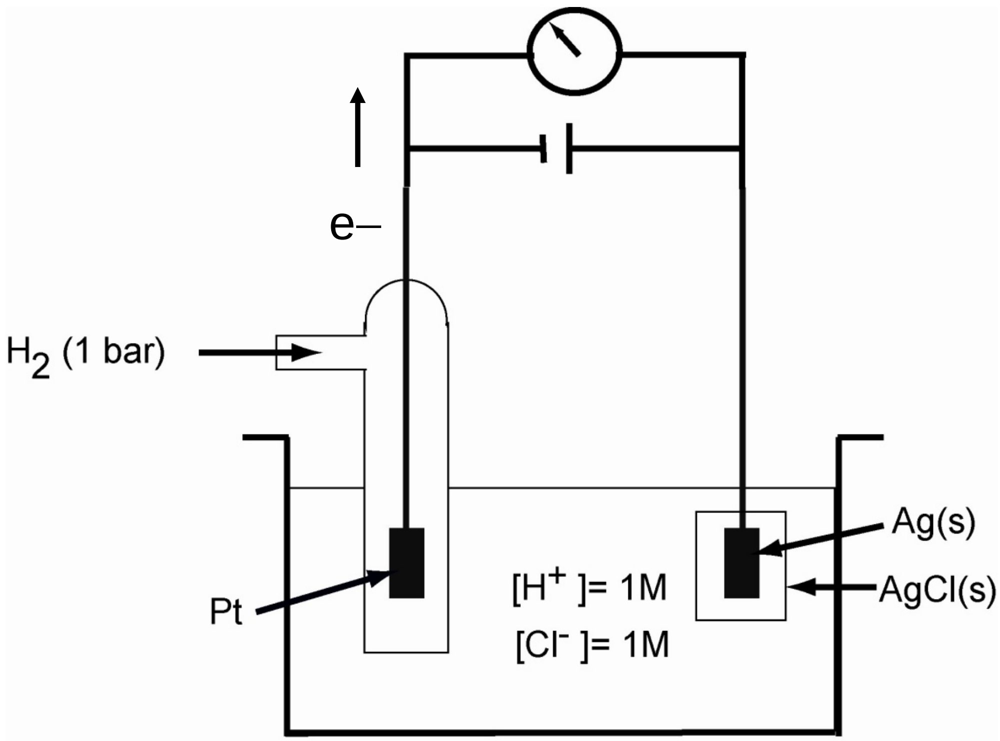
$$d\mu = \underbrace{đq - Td\bar{S}}_{\leq 0 \text{ by 2nd law}} - \bar{S}dT + VdP + đw_{other} \quad \text{(very general)}$$

$$d\mu_{T,P} \leq đw_{other}$$

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 (HW8, prob #60)



oxidation *anode* H_2 (1 bar) $\longrightarrow$ $2H^+$ [1M] + $2e^-$

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

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

$\Delta\mu^\circ$ for the reaction

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

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

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

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

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

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

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

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

and FINALLY w_{other} !!! (p. 20 [18]$_{2nd}$)

TABLE 2.1 TYPES OF WORK

Types of Work	Variables	Equation for Work	Conventional Units
Volume expansion	Pressure (P), volume (V)	$w = -\int P_{external}\, dV$	$\mathrm{Pa\ m^3 = J}$
Stretching	Force (F), length (l)	$w = -\int F\, dl$	$\mathrm{N\ m = J}$
Surface expansion	Surface tension (γ), area (σ)	$w = -\int \gamma\, d\sigma$	$\mathrm{(N\ m^{-1})(m^2) = J}$
Electrical	Electrical potential (ϕ), electrical charge (Q)	$w = \int \phi\, dQ$	$\mathrm{V\ C = J}$

w_{other} (p. 260 [255]$_{2nd}$) *p. 260 $\tilde{\mu}$ vs μ is overcomplicated*

$$đ w_{electrical} = \Phi\, dQ$$

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)$^{-1}$

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

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

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

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

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

sign of Φ and spontaneity

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

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

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

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

$\Delta\mu$ vs Φ

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

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

$$\boxed{\begin{array}{l} \Phi = \Phi^\circ - \dfrac{\underline{R}T}{n\mathcal{F}}\ln Q_{reaction} \\ T = 298K \\ \Phi = \Phi^\circ - \dfrac{0.02569}{\bar{n}}\ln Q_{reaction} \end{array}}$$

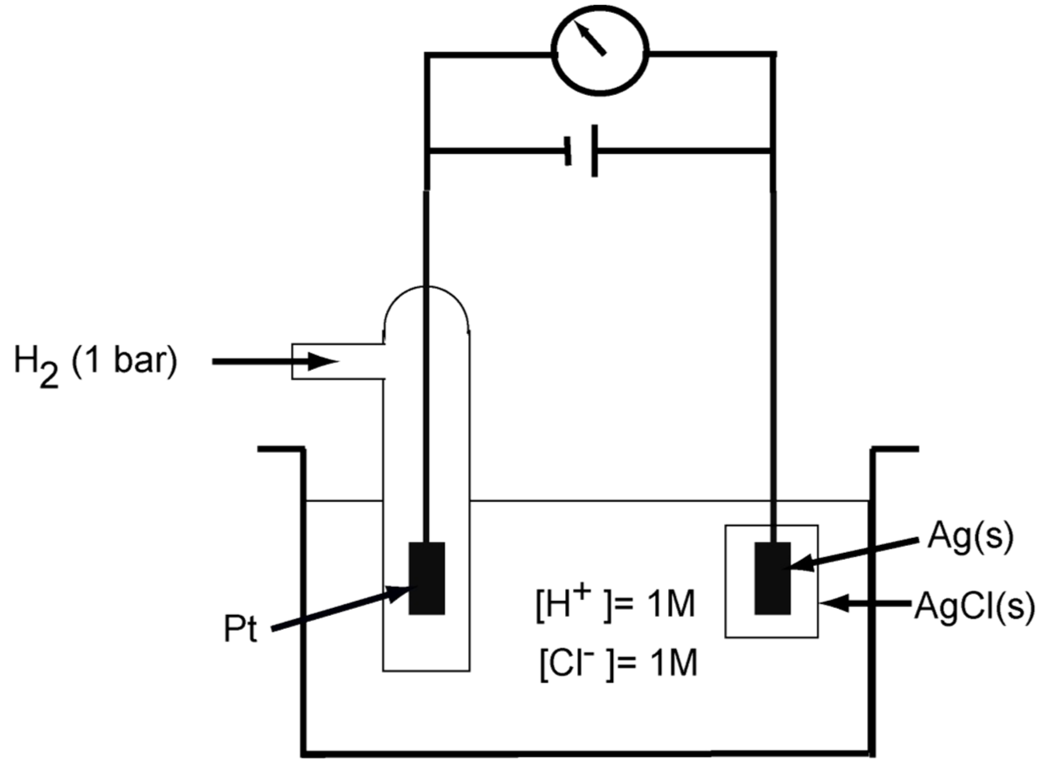
n = moles electrons transferred

$[\mathrm{n}]=\mathrm{mol}$

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

$[\bar{\mathrm{n}}] =$ ***unitless***

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



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

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

example incorporating activities

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

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

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

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

can't independently meansure 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

$$\Phi = \underset{\text{0.22233 V}}{\Phi^\circ} - \frac{0.02569}{\underset{\text{2 e's}}{\bar{n}}} \ln\left[\frac{\gamma_\pm^4 [H^+]^2 [Cl^-]^2}{\gamma_{H_2} P_{H_2}}\right]$$

$$\Phi = 0.22233 - \frac{0.02569}{2} \ln \underbrace{\left[\frac{\gamma_\pm^4 [1M]^2 [1M]^2}{\gamma_{H_2} (1\text{ bar})}\right]}_{\text{unitless; have dropped standard state concs and pressure from denominators}}$$

example incorporating activities

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

- Calculate γ's from observed Φ (HW8, prob 60)
- If γ's =1

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

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

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

$$\Delta\mu = -4.290\times10^{4}\ CV = -42.90\ kJ$$

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

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

H_2 (g, 1 bar) $\longrightarrow$ $2H^+$ [1M] $+2e^-$ $\Phi° = 0$ V

$2e^- + 2AgCl(s) \longrightarrow 2Cl^-$ [1M] + 2Ag(s) $\Phi° = 0.22233$ V

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

$\Phi_{cell}° = 0.22233$ V

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

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

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

$$\tfrac{1}{2}H_2\ (g,\ 1\ bar) \longrightarrow H^+\ [1M]\ + e^-$$

$$e^- + AgCl(s) \longrightarrow Cl^-\ [1M] + Ag(s)$$

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

$\Phi° = 0\ V$

$\Phi° = 0.22233\ V$

$\Phi_{cell}° = 0.22233\ V$

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

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

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

intensive Φ vs extensive Δμ   *Φ = - (Δμ /nℱ)*

$$\Delta\mu_{2e} = 2\Delta\mu_{1e}$$

two times greater

Δμ = -42.88 kJ for 2 moles e⁻ transferred

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

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

same

Δμ = -21.44 kJ for 1 moles e⁻ transferred

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

Δμ extensive: depends on stoichiometry

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

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

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

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

standard REDUCTION potentials	$\Phi^{\circ\prime}_{red}$(V) pH7
$2e^- + 2CytC(Fe^{3+}) \longrightarrow 2CytC(Fe^{2+})$	0.25
$2e^- + \frac{1}{2}O_2(g) + 2H^+(aq) \longrightarrow H_2O(\ell)$	0.816

	reaction: the oxidation of $CytC(Fe^{2+})$	$\Phi^{\circ\prime}$(V)
oxidation	$2CytC(Fe^{2+}) \longrightarrow 2CytC(Fe^{3+}) + 2e-$	- 0.25
reduction	$2e^- + \frac{1}{2}O_2(g) + 2H^+(aq) \longrightarrow H_2O(\ell)$	0.816

$\frac{1}{2}O_2(g) + 2H^+(aq) + 2CytC(Fe^{2+}) \longrightarrow 2CytC(Fe^{3+}) + H_2O(\ell)$ **?=** $\Phi^{\circ\prime}_{cell}$

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

biological example (redox equation III)

$$\tfrac{1}{2}O_2(g) + 2H^+(aq) + 2CytC(Fe^{2+}) \longrightarrow 2CytC(Fe^{3+}) + H_2O(\ell)$$

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

standard state '

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

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

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

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

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

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

ΔC_p from Φ

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

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

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

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

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

Electrochemistry:

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

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

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

End of Lecture