Chemistry 163B

Electrochemistry

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

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

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

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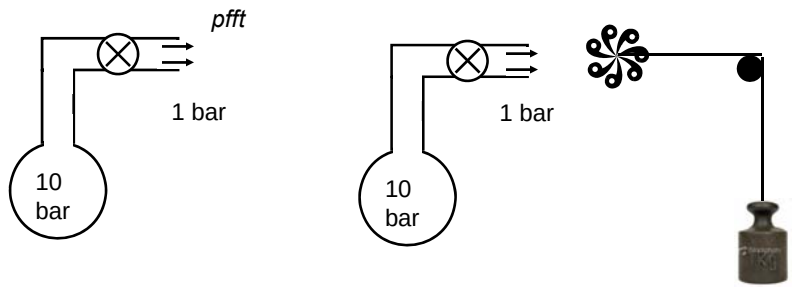
work of expansion

H_2 (10 bar) ⟶ H_2(1 bar)



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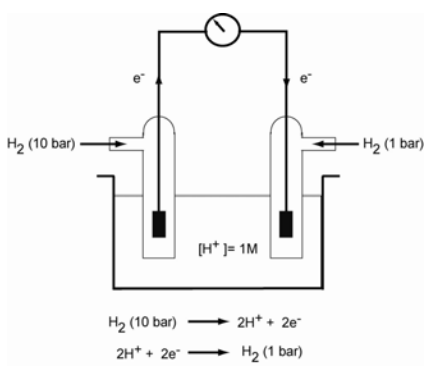
hydrogen pressure ['concentration'] cell *(reaction I of III)*



H_2 (10 bar) ⟶ H_2(1bar)

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

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

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

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dμ and work-other (did before for dG)

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

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

$$d\mu_{T,P} \leq đw_{other}$$

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

REVERSIBILITY

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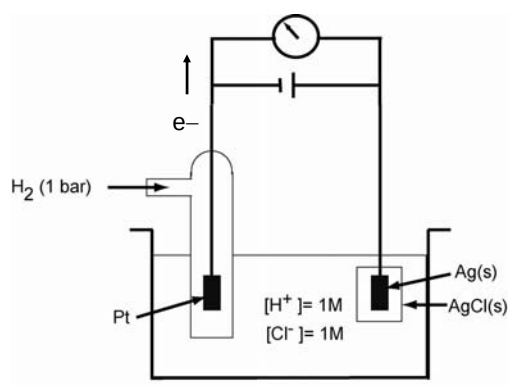
responsible for 3 redox reactions; here's II (HW8, prob #60)



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

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

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

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

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

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

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

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

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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)	$w = -\int P_{external}\,dV$	Pa m^3 = J
Stretching	Force (F), length (l)	$w = -\int F\,dl$	N m = J
Surface expansion	Surface tension (γ), area (σ)	$w = -\int \gamma\,d\sigma$	(N m^{-1})(m^2) = J
Electrical	Electrical potential (ϕ), electrical charge (Q)	$w = \int \phi\,dQ$	V C = J

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

$$đw_{electrical} = \Phi\, dQ$$

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)$^{-1}$

$$đw_{electrical} = -\Phi\mathcal{F}dn$$

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

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

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

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

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sign of Φ and spontaneity

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

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

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

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

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Δμ vs Φ

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

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

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

$$T = 298K$$

$$\Phi = \Phi^{\circ} - \frac{0.02569}{\overline{n}}\ln Q_{reaction}$$

n = moles electrons transferred

$[n]$=mol

$\overline{n}$= n × mol^{-1}

$[\overline{n}]$ = ***unitless***

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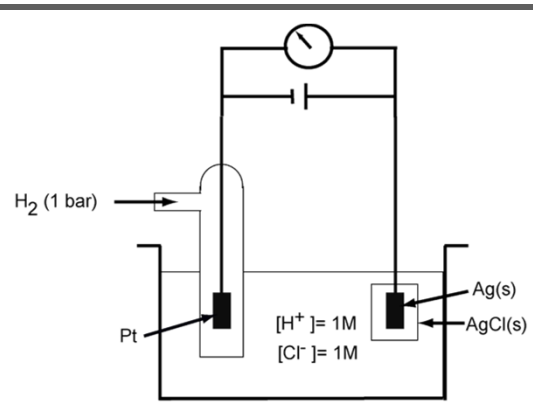
responsible for 3 redox reactions; here's II (HW8, prob #60)



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

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

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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^-}

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

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

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example incorporating activities

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

0.22233 V 2 e's

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

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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]

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

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

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

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

Φ_{cell}°= 0.22233 V

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

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

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

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

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

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

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

Δμ = -21.44 kJ for 1 moles e^- transferred

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

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

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

Δμ = -42.88 kJ for 2 moles e^- transferred

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

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

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

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

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

standard REDUCTION potentials	$\Phi^{o\prime}_{red}$(V) pH7
$2e^- + 2CytC(Fe^{3+}) \longrightarrow 2CytC(Fe^{2+})$	0.25
$2e^- + ½O_2(g) + 2H^+(aq) \longrightarrow H_2O(\ell)$	0.816

	reaction: the oxidation of CytC(Fe^{2+})	$\Phi^{o\prime}$(V)
oxidation	$2CytC(Fe^{2+}) \longrightarrow 2CytC(Fe^{3+}) + 2e^-$	- 0.25
reduction	$2e^- + ½O_2(g) + 2H^+(aq) \longrightarrow H_2O(\ell)$	0.816
	$½O_2(g) + 2H^+(aq) + 2CytC(Fe^{2+}) \longrightarrow 2CytC(Fe^{3+}) + H_2O(\ell)$	?= $\Phi^{o\prime}_{cell}$

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

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biological example (redox equation III)

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

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

standard state '

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

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

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

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

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

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

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ΔC_p from Φ

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

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

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

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

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

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relationships on final

Electrochemistry:

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

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

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

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End of Lecture

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