

Chemistry 163B

Lectures 24-25- Electrochemistry Quickie W2013

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Electrochemistry

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activity coefficients for ions (HW8 #58)

$$\text{BaCl}_2(s) \rightleftharpoons \text{Ba}^{2+}(aq) + 2\text{Cl}^-(aq)$$

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

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

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

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

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

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

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

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work of expansion

$\text{H}_2(10 \text{ bar}) \rightarrow \text{H}_2(1 \text{ bar})$

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

$\text{H}_2(10 \text{ bar}) \rightarrow 2\text{H}^+ + 2\text{e}^-$
 $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(1 \text{ bar})$

$\text{H}_2(10 \text{ bar}) \rightarrow \text{H}_2(1 \text{ bar})$

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

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

$\Delta\mu = \Delta\mu^\circ + RT \ln \frac{P(1 \text{ bar})}{P(10 \text{ bar})} = -5.706 \text{ kJ per mole H}_2$ 4

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

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

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

≤ 0 by 2nd law

$$d\mu_{T,P} \leq \bar{d}w_{\text{other}}$$

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

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

oxidation anode $\text{H}_2(1 \text{ bar}) \rightarrow 2\text{H}^+[1M] + 2\text{e}^-$
reduction cathode $2\text{AgCl}(s) + 2\text{e}^- \rightarrow 2\text{Ag}(s) + 2\text{Cl}^-[1M]$

$2\text{e}^- + \text{H}_2(\text{g}, 1 \text{ bar}) + 2\text{AgCl}(s) \rightarrow 2\text{H}^+[1M] + 2\text{Cl}^-[1M] + 2\text{Ag}(s) + 2\text{e}^-$ 6

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

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

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

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

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

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

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

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

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

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

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

electric potential charge transfer

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

from negative charge on e \mathcal{F} is Faraday constant
96,458 coulomb (mole e^-)⁻¹

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

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

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

E & R p260 z ≡ -n

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

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sign of Φ and spontaneity

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

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

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

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

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$\Delta\mu$ vs Φ

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

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

Φ°

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

$T = 298 \text{ K}$

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

$n = \text{moles electrons transferred}$

$[\bar{n}] = \text{mol}$

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

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

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

Φ_0

0.22233

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

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example incorporating activities

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

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

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

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

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example incorporating activities

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

0.22233 V 2 e's

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

unless, 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

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

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

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

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

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

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

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

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

$$2e^- + H_2(g, 1\text{ bar}) + 2AgCl(s) \rightarrow 2H^+[1M] + 2Cl^-[1M] + 2Ag(s) + 2e^- \quad \Phi_{\text{cell}}^\circ = 0.22233\text{ V}$$

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

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

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

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

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

$$e^- + \frac{1}{2}H_2(g, 1\text{ bar}) + AgCl(s) \rightarrow H^+[1M] + Cl^-[1M] + Ag(s) + e^- \quad \Phi_{\text{cell}}^\circ = 0.22233\text{ V}$$

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

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

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

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

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

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

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

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

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

$\Delta\mu$ extensive: depends on stoichiometry

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

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

	$\Phi^{\circ'}_{red}(V)$ pH7
standard REDUCTION potentials	
$2e^- + 2CytC(Fe^{3+}) \rightarrow 2CytC(Fe^{2+})$	0.25
$2e^- + \frac{1}{2}O_2(g) + 2H^+(aq) \rightarrow H_2O(l)$	0.816
reaction: the oxidation of CytC(Fe²⁺)	$\Phi^{\circ'}(V)$
<i>oxidation</i> $2CytC(Fe^{2+}) \rightarrow 2CytC(Fe^{3+}) + 2e^-$	- 0.25
<i>reduction</i> $2e^- + \frac{1}{2}O_2(g) + 2H^+(aq) \rightarrow H_2O(l)$	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)

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

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

standard state'

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



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

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

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

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

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

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

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ΔC_p from Φ

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

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

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

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

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

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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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End of Lecture

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