

Problem Set #12, Chem 340, Fall 2013

– Due Wednesday, Dec 4, 2013

Please show all work for credit

To hand in:

Ionic equilibria:

1. Calculate the value of m_{\pm} in 5.0×10^{-4} molal solutions of (a) KCl, (b) $\text{Ca}(\text{NO}_3)_2$, and (c) ZnSO_4 . Assume complete dissociation.

a) KCl

$$m_{\pm} = (v_+^{v_+} v_-^{v_-})^{1/v} m$$

$$m_{\pm} = \sqrt{1} m = 5.0 \times 10^{-4} \text{ mol kg}^{-1}$$

b) $\text{Ca}(\text{NO}_3)_2$

$$m_{\pm} = (v_+^{v_+} v_-^{v_-})^{1/v} m$$

$$m_{\pm} = (4)^{1/3} m = (4)^{1/3} \times 5.0 \times 10^{-4} \text{ mol kg}^{-1} = 7.9 \times 10^{-4} \text{ mol kg}^{-1}$$

c) ZnSO_4

$$m_{\pm} = (v_+^{v_+} v_-^{v_-})^{1/v} m$$

$$m_{\pm} = (1)^{1/2} m = 5.0 \times 10^{-4} \text{ mol kg}^{-1}$$

2. Calculate γ_{\pm} , and a_{\pm} for a 0.0325 m solution of $\text{K}_4\text{Fe}(\text{CN})_6$ at 298 K.

$$I = \frac{m}{2} (v_+ z_+^2 + v_- z_-^2) = \frac{1}{2} (m_+ z_+^2 + m_- z_-^2)$$

$$I = \frac{1}{2} (4 \times 0.0325 \text{ mol kg}^{-1} + 4^2 \times 0.0325 \text{ mol kg}^{-1}) = 0.325 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 |z_+ z_-| \sqrt{\frac{I}{\text{mol kg}^{-1}}} = -1.173 \times 4 \times \sqrt{0.325} = -2.6749$$

$$\gamma_{\pm} = 0.069$$

$$m_{\pm} = (v_+^{v_+} v_-^{v_-})^{1/v} m = (4^4)^{1/5} \times 0.0325 \text{ mol kg}^{-1} = 0.099 \text{ mol kg}^{-1}$$

$$a_{\pm} = \left(\frac{m_{\pm}}{m^{\circ}} \right) \gamma_{\pm} = 0.099 \times 0.069 = 0.0068$$

3. Chloroacetic acid has a dissociation constant of $K_a = 1.38 \times 10^{-3}$. (a) Calculate the degree of dissociation for a 0.0825 *m* solution of this acid using the Debye–Hückel limiting law. (b) Calculate the degree of dissociation for a 0.0825 *m* solution of this acid that is also 0.022 *m* in KCl using the Debye–Hückel limiting law.

a) $K_a = 1.38 \times 10^{-3}$
0.0825 *m*

$$K_a = \frac{(m_+ \gamma_+)(m_- \gamma_-)}{m} = \frac{m^2 \gamma_{\pm}^2}{0.0825 - m} = 1.38 \times 10^{-3}$$

when $\gamma_{\pm} = 1$

$$m^2 = 1.1385 \times 10^{-4} - 1.38 \times 10^{-3} m$$

$$m^2 + 1.38 \times 10^{-3} m - 1.1385 \times 10^{-4} = 0$$

$$m = \frac{-1.38 \times 10^{-3} \pm \sqrt{(1.38 \times 10^{-3})^2 - 4(1)(-1.1385 \times 10^{-4})}}{2} = 0.0100 \text{ mol kg}^{-1}$$

$$I = \frac{m}{2}(2) = m = 0.0100 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{0.0100} = -0.1173$$

$$\gamma_{\pm} = 0.8893$$

when $\gamma_{\pm} = 0.8893$

$$m^2 = 1.43956 \times 10^{-4} - 1.7449 \times 10^{-3} m$$

$$m^2 + 1.7449 \times 10^{-3} m - 1.43956 \times 10^{-4} = 0$$

$$m = \frac{-1.7449 \times 10^{-3} \pm \sqrt{(1.7449 \times 10^{-3})^2 - 4(1)(-1.43956 \times 10^{-4})}}{2} = 0.0112 \text{ mol kg}^{-1}$$

$$I = \frac{m}{2}(2) = m = 0.0112 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{0.0112} = -0.1239$$

$$\gamma_{\pm} = 0.8835$$

when $\gamma_{\pm} = 0.8835$

$$m^2 = 1.4587 \times 10^{-4} - 1.7681 \times 10^{-3} m$$

$$m^2 + 1.7681 \times 10^{-3} m - 1.4587 \times 10^{-4} = 0$$

$$m = \frac{-1.7681 \times 10^{-3} \pm \sqrt{(1.7681 \times 10^{-3})^2 - 4(1)(-1.4587 \times 10^{-4})}}{2} = 0.0112 \text{ mol kg}^{-1}$$

$$I = 0.0112 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{0.0112} = -0.1239$$

The degree of dissociation is $\frac{0.0112}{0.0825} \times 100\% = 13.6\%$

Same value, done!

b)

$$\begin{array}{l} \text{K}^+ \text{Cl}^- \quad \nu_+ = \nu_- = 1 \quad 1 \\ \quad \quad \quad z_+ = 1 \quad z_- = 1 \end{array}$$

$$I = 0.022 \text{ mol kg}^{-1} \text{ from the KCl alone.}$$

We first calculate the activity coefficient using this value.

$$I = \frac{0.022}{2} (+1) = 0.022 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{0.022} = -0.1740$$

$$\gamma_{\pm} = 0.8403$$

We next calculate the concentration of the ions produced through the dissociation of the acid in the solution.

$$\frac{m^2 (0.8403)^2}{0.0825 - m} = 1.38 \times 10^{-3}$$

$$\frac{m^2}{0.0825 - m} = 1.9544 \times 10^{-3}$$

$$m^2 = 1.6124 \times 10^{-4} - 1.9544 \times 10^{-3} m$$

$$m^2 = 1.9544 \times 10^{-3} m - 1.6124 \times 10^{-4} = 0$$

$$m = \frac{-1.9544 \times 10^{-3} \pm \sqrt{(1.9544 \times 10^{-3})^2 - 4(1)(-1.6124 \times 10^{-4})}}{2} = 0.01176 \text{ mol kg}^{-1}$$

The ionic strength is the sum of that due to the chloroacetic acid and the KCl or

$$I = 0.022 + 0.012 = 0.034 \text{ mol kg}^{-1}.$$

We recalculate γ_{\pm} using this value for the ionic strength.

$$\ln \gamma_{\pm} = -1.173 \times 1 \times \sqrt{0.034} = -0.2163$$

$$\gamma_{\pm} = 0.8055$$

and recalculate m

$$\frac{m^2 (0.8055)^2}{0.0825 - m} = 1.38 \times 10^{-3} \text{ giving}$$

$$m = 0.01222 \text{ mol kg}^{-1}$$

Given the fact that the concentration of KCl is only known to 2 significant figures, this value of m is sufficiently close to the previous value that a further iteration is not

necessary. The degree of dissociation is $\frac{0.01222}{0.0825} = 14.8\%$.

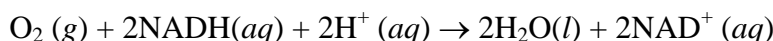
4. The principal ions of human blood plasma and their molar concentrations are

$m_{Na^+} = 0.14 m$, $m_{Cl^-} = 0.10 m$, $m_{HCO_3^-} = 0.025 m$. Calculate the ionic strength of blood plasma.

Note: obviously something missing, pos-neg imbalance

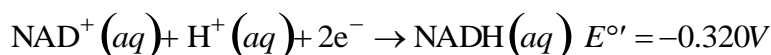
$$I = \frac{1}{2} \sum_i m_i z_i^2 = \frac{1}{2} [(0.14 m \times 1^2) + (0.10 m \times 1^2) + (0.025 m \times 1^2)] = 0.1325 m$$

5. The oxidation of NADH by molecular oxygen occurs in the cellular respiratory system:

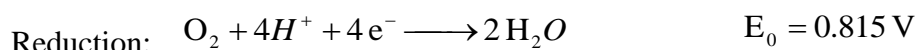


Using the information in Table 9.7, calculate the standard Gibbs energy change that results from the oxidation of NADH by molecular oxygen.

The standard reduction potential for nicotine adenine dinucleotide is



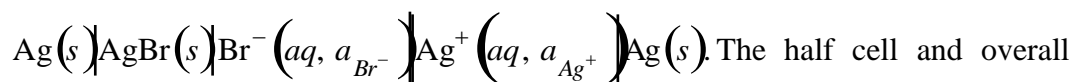
Using the half cell reactions:



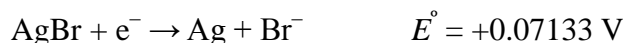
$$E_{\text{cell}} = E_{\text{red}} + E_{\text{ox}} = 1.135V$$

$$\Delta G^\circ_{\text{reaction}} = -nF\Delta\phi = (4) \times (96485 \text{ C mol}^{-1}) \times (1.135V) = -438.0 \text{ kJ mol}^{-1}$$

6. Determine K_{sp} for AgBr at 298.15 K using the electrochemical cell described by



reactions are



$$\log_{10} K_{sp} = -\frac{nE^\circ}{0.05916} = -\frac{0.729V}{0.05916V} = -12.310$$

$$K_{sp} = 4.90 \times 10^{-13}$$

7. For a given overall cell reaction, $\Delta S^\circ_R = 17.5 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta H^\circ_R = -225.0 \text{ kJ mol}^{-1}$.

Calculate E° and $\left(\frac{\partial E^\circ}{\partial T}\right)_P$.

$$E^\circ = -\frac{\Delta G^\circ_R}{nF} = -\frac{\Delta H^\circ_R - T\Delta S^\circ_R}{nF} = -\frac{-225000 \text{ J mol}^{-1} - 298.15 \text{ K} \times 17.5 \text{ J K}^{-1} \text{ mol}^{-1}}{1 \times 96485 \text{ C mol}^{-1}} = 2.38V$$

$$\left(\frac{\partial E^\circ}{\partial T}\right)_P = \frac{\Delta S^\circ_R}{nF} = \frac{17.5 \text{ J K}^{-1} \text{ mol}^{-1}}{1 \times 96485 \text{ C mol}^{-1}} = 1.81 \times 10^{-4} \text{ V K}^{-1}$$

8. The following data have been obtained for the potential of the cell

Pt(s) | H₂(g, f = 1 atm) | HCl(aq, m) | AgCl(s) | Ag(s) as a function of *m* at 25°C.

<i>m</i> (mol kg ⁻¹)	<i>E</i> (V)	<i>m</i> (mol kg ⁻¹)	<i>E</i> (V)	<i>m</i> (mol kg ⁻¹)	<i>E</i> (V)
0.00100	0.597915	0.0200	0.43024	0.500	0.27231
0.00200	0.54425	0.0500	0.38588	1.000	0.23328
0.00500	0.49846	0.100	0.35241	1.500	0.20719
0.0100	0.46417	0.200	0.31874	2.000	0.18631

Calculate E° and γ_{\pm} for HCl at $m = 0.00100, 0.0100, 0.100,$ and 1.000 .

Cell reaction: $2\text{AgCl}(s) + \text{H}_2(g) \rightarrow 2\text{Ag}(s) + 2\text{H}^+(aq) + 2\text{Cl}^-(aq)$

$$E = E^\circ - \frac{RT}{2F} \ln(a_{\text{H}^+} a_{\text{Cl}^-})^2 = E^\circ - \frac{RT}{F} \ln(a_{\text{H}^+} a_{\text{Cl}^-})$$

$$a_{\text{H}^+} a_{\text{Cl}^-} = a_{\pm}^2 = \gamma_{\pm}^2 m_{\pm}^2$$

$$E = E^\circ - \frac{2RT}{F} \left(\ln \frac{m}{m^\circ} \right) - \frac{2RT}{F} (\ln \gamma_{\pm})$$

In the low concentration limit we can use the Debye-Hückel result

$$\ln \gamma_{\pm} = -0.50926 \log_{10} \sqrt{\frac{m}{m^\circ}} = -1.172614 \ln \sqrt{\frac{m}{m^\circ}}$$

Therefore, for dilute solutions

$$E + \frac{2RT}{F} \ln \left(\frac{m}{m^\circ} \right) = E^\circ + \frac{2RT}{F} \times 1.172614 \times \sqrt{\frac{m}{m^\circ}}$$

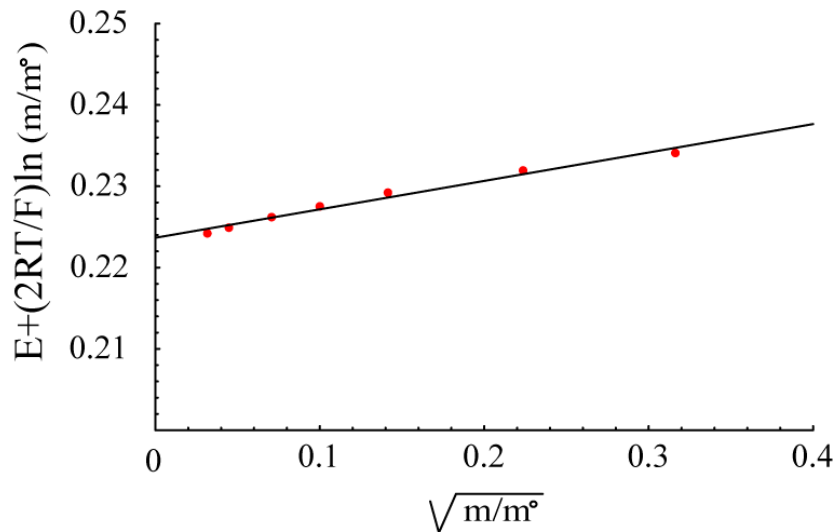
Using this result, a plot of $E + \frac{2RT}{F} \ln \left(\frac{m}{m^\circ} \right)$ (y axis) vs. $\sqrt{\frac{m}{m^\circ}}$ (x axis) will have an

intercept of E° . We use the data up to $m = 0.100$, as the Debye-Hückel model is not valid for more concentrated solutions.

$\frac{m}{m^\circ}$	$\sqrt{\frac{m}{m^\circ}}$	<i>E</i>	$E + \frac{2RT}{F} \ln \left(\frac{m}{m^\circ} \right)$
0.001	0.031623	0.57915	0.224212
0.002	0.044721	0.54425	0.224909
0.005	0.070711	0.49846	0.226203
0.010	0.1	0.46417	0.227531
0.020	0.141421	0.43024	0.229218
0.050	0.223607	0.38588	0.231943
0.100	0.316228	0.35241	0.234090

The data in the table is graphed below. The best fit line gives a value for E° of

0.223665 V.



Given E° we can now find γ_\pm from

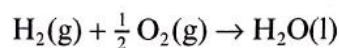
$$\ln \gamma_\pm = \frac{F}{RT} (E^\circ - E) - \ln \left(\frac{m}{m^\circ} \right)$$

$$E^\circ = 0.223655 \text{ V}$$

m/m°	$\ln \gamma_\pm$	γ_\pm
0.001	-0.010654	0.989
0.010	-0.0755112	0.927
0.100	-0.203036	0.816

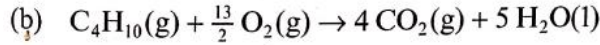
9. A fuel cell develops an electric potential from the chemical reaction between reagents supplied from an outside source. What is the cell potential of a cell fuelled by (a) hydrogen and oxygen, (b) the combustion of butane at 1.0 bar and 298 K?

(a) The cell reaction is



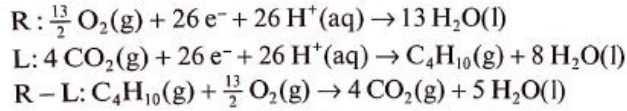
$$\Delta_r G^\circ = \Delta_f G^\circ(\text{H}_2\text{O}, \text{l}) = -237.13 \text{ kJ mol}^{-1} \text{ [data table]}$$

$$E_{\text{cell}}^\circ = -\frac{\Delta_r G^\circ}{\nu F} [6.26] = \frac{+237.13 \text{ kJ mol}^{-1}}{(2) \times (96.485 \text{ kC mol}^{-1})} = \boxed{+1.23 \text{ V}}$$



$$\begin{aligned} \Delta_r G^\circ &= 4\Delta_f G^\circ(CO_2, g) + 5\Delta_f G^\circ(H_2O, l) - \Delta_f G^\circ(C_4H_{10}, g) \\ &= [(4) \times (-394.36) + (5) \times (-237.13) - (-17.03)] \text{ kJ mol}^{-1} \text{ [data tables]} \\ &= -2746.06 \text{ kJ mol}^{-1} \end{aligned}$$

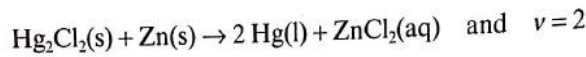
In this reaction the number of electrons transferred, ν , is not immediately apparent, as in part (a). To find ν we break the cell reaction down into half-reactions as follows:



Hence, $\nu = 26$.

$$\text{Therefore, } E = \frac{-\Delta G^\circ}{\nu F} = \frac{+2746.06 \text{ kJ mol}^{-1}}{(26) \times (96.485 \text{ kC mol}^{-1})} = \boxed{+1.09 \text{ V}}$$

- 10.** Consider the cell, $Zn(s)|ZnCl_2(0.0050 \text{ mol kg}^{-1})|Hg_2Cl_2(s)|Hg(l)$, for which the cell reaction is $Hg_2Cl_2(s) + Zn(s) \rightarrow 2 Hg(l) + 2 Cl^-(aq) + Zn^{2+}(aq)$. Given that $E^\circ(Zn^{2+}, Zn) = -0.7628 \text{ V}$, $E^\circ(Hg_2Cl_2, Hg) = +0.2676 \text{ V}$, and that the cell potential is $+1.2272 \text{ V}$, (a) write the Nernst equation for the cell. Determine (b) the standard cell potential, (c) $\Delta_r G$, $\Delta_r G^\circ$, and K for the cell reaction, (d) the mean ionic activity and activity coefficient of $ZnCl_2$ from the measured cell potential, and (e) the mean ionic activity coefficient of $ZnCl_2$ from the Debye - Hückel limiting law. (f) Given that $(\partial E_{\text{cell}} / \partial T)_p = -4.52 \times 10^{-4} \text{ V K}^{-1}$, calculate $\Delta_r S$ and $\Delta_r H$.



$$(a) \quad E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{25.693 \text{ mV}}{\nu} \ln Q [6.27, 25^\circ\text{C}]$$

$$\begin{aligned} Q &= a(Zn^{2+})a^2(Cl^-) \\ &= \{\gamma_+ b(Zn^{2+})/b^\circ\} \times \gamma_-^2 \{b(Cl^-)/b^\circ\}^2, \quad \text{where } b(Zn^{2+}) = b, b(Cl^-) = 2b, \text{ and } \gamma_+ \gamma_-^2 = \gamma_\pm^3 \end{aligned}$$

Therefore, $Q = \gamma_\pm^3 \times 4b^3$ [$b \equiv b/b^\circ$ here and below]

$$\text{and } E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{25.693 \text{ mV}}{2} \ln(4b^3 \gamma_\pm^3) = E_{\text{cell}}^\circ - \frac{3}{2} \times (25.693 \text{ mV}) \times \ln(4^{1/3} b \gamma_\pm)$$

$$= \boxed{E_{\text{cell}}^\circ - (38.54 \text{ mV}) \times \ln(4^{1/3} b) - (38.54 \text{ mV}) \ln(\gamma_\pm)}$$

$$(b) E_{\text{cell}}^{\circ} = E^{\circ}(\text{Hg}_2^{2+}/\text{Hg}) - E^{\circ}(\text{Zn}^{2+}/\text{Zn}) = +0.2676 \text{ V} - (-0.7628 \text{ V}) = \boxed{1.0304 \text{ V}}$$

$$(c) \Delta_r G = -vFE_{\text{cell}} = -(2) \times (9.6485 \times 10^4 \text{ C mol}^{-1}) \times (1.2272 \text{ V}) = \boxed{-236.81 \text{ kJ mol}^{-1}}$$

$$\Delta_r G^{\circ} = -vFE_{\text{cell}}^{\circ} = -(2) \times (9.6485 \times 10^4 \text{ C mol}^{-1}) \times (1.0304 \text{ V}) = \boxed{-198.84 \text{ kJ mol}^{-1}}$$

$$\ln K = -\frac{\Delta_r G^{\circ}}{RT} = \frac{1.9884 \times 10^5 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})} = 80.211 \quad \text{so} \quad K = \boxed{6.84 \times 10^{34}}$$

(d) From part (a):

$$1.2272 \text{ V} = 1.0304 \text{ V} - (38.54 \text{ mV}) \times \ln(4^{1/3} \times 0.0050) - (38.54 \text{ mV}) \times \ln \gamma_{\pm}$$

$$\ln \gamma_{\pm} = -\frac{(1.2272 \text{ V}) - (1.0304 \text{ V}) - (0.1864 \text{ V})}{0.03854 \text{ V}} = -0.2698 \quad \text{so} \quad \gamma_{\pm} = \boxed{0.763}$$

(e) $\log \gamma_{\pm} = -|z_{-}z_{+}| AI^{1/2}$ [5.75]

$$I = \frac{1}{2} \sum_i z_i^2 (b_i/b^{\circ}) \quad [5.76]$$

where $b(\text{Zn}^{2+}) = b = 0.0050 \text{ mol kg}^{-1}$ and $b(\text{Cl}^{-}) = 2b = 0.010 \text{ mol kg}^{-1}$

Thus, $I = \frac{1}{2}[(4) \times (0.0050) + (0.010)] = 0.015$

$$\log \gamma_{\pm} = -(2) \times (0.509) \times (0.015)^{1/2} = -0.125 \quad \text{so} \quad \gamma_{\pm} = \boxed{0.75}$$

This compares remarkably well to the value obtained from experimental data in part (d).

$$(f) \Delta_r S = -\left(\frac{\partial \Delta_r G}{\partial T}\right)_p$$

$$= vF \left(\frac{\partial E}{\partial T}\right)_p \quad [6.36] = (2) \times (9.6485 \times 10^4 \text{ C mol}^{-1}) \times (-4.52 \times 10^{-4} \text{ V K}^{-1})$$

$$= \boxed{-87.2 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$\Delta_r H = \Delta_r G + T\Delta_r S = (-236.81 \text{ kJ mol}^{-1}) + (298.15 \text{ K}) \times (-87.2 \text{ J K}^{-1} \text{ mol}^{-1})$$

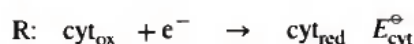
$$= \boxed{-262.4 \text{ kJ mol}^{-1}}$$

11. The standard potentials of proteins are not commonly measured by the methods described in this chapter because proteins often lose their native structure and function when they react on the surfaces of electrodes. In an alternative method, the oxidized protein is allowed to react with an appropriate electron donor in solution. The standard potential of the protein is then determined from the Nernst equation, the equilibrium concentrations of all species in solution, and the known standard potential of the electron donor. We illustrate this method with the protein cytochrome *c*. The one-electron reaction between cytochrome *c*, cyt, and 2,6-dichloroindophenol, D, can be followed spectrophotometrically because each of the four species in solution has a distinct absorption spectrum. We write the reaction as $\text{cyt}_{\text{ox}} + \text{D}_{\text{red}} \rightarrow \text{cyt}_{\text{red}} + \text{D}_{\text{ox}}$, where the subscripts 'ox' and 'red' refer to oxidized and reduced states, respectively. (a) Consider E_{cyt}° and E_{D}° to be the standard potentials of cytochrome *c* and D, respectively. Show that, at equilibrium, a plot of $\ln([\text{D}_{\text{ox}}]_{\text{eq}}/[\text{D}_{\text{red}}]_{\text{eq}})$ versus $\ln([\text{cyt}_{\text{ox}}]_{\text{eq}}/[\text{cyt}_{\text{red}}]_{\text{eq}})$ is linear with slope of 1 and y-intercept $F(E_{\text{cyt}}^{\circ} - E_{\text{D}}^{\circ})/RT$, where equilibrium activities are

replaced by the numerical values of equilibrium molar concentrations. (b) The following data were obtained for the reaction between oxidized cytochrome *c* and reduced D in a pH 6.5 buffer at 298 K. The ratios $[D_{ox}]_{eq}/[D_{red}]_{eq}$ and $[cyt_{ox}]_{eq}/[cyt_{red}]_{eq}$ were adjusted by titrating a solution containing oxidized cytochrome *c* and reduced D with a solution of sodium ascorbate, which is a strong reductant. From the data and the standard potential of D of 0.237 V, determine the standard potential cytochrome *c* at pH 6.5 and 298K.

$[D_{ox}]_{eq}/[D_{red}]_{eq}$	0.00279	0.00843	0.0257	0.0497	0.0748	0.238	0.534
$[cyt_{ox}]_{eq}/[cyt_{red}]_{eq}$	0.0106	0.0230	0.0894	0.197	0.335	0.809	1.39

The half-reactions involved are:



The overall cell reaction is:



(a) The Nernst equation for the cell reaction is

$$E = E^\ominus - \frac{RT}{F} \ln \frac{[cyt_{red}][D_{ox}]}{[cyt_{ox}][D_{red}]}$$

At equilibrium, $E = 0$; therefore

$$\ln \frac{[cyt_{red}]_{eq} [D_{ox}]_{eq}}{[cyt_{ox}]_{eq} [D_{red}]_{eq}} = \frac{F}{RT} (E_{cyt}^\ominus - E_D^\ominus)$$

$$\ln \left(\frac{[D_{ox}]_{eq}}{[D_{red}]_{eq}} \right) = \ln \left(\frac{[cyt]_{ox}}{[cyt]_{red}} \right) + \frac{F}{RT} (E_{cyt}^\ominus - E_D^\ominus)$$

Therefore a plot of $\ln \left(\frac{[D_{ox}]_{eq}}{[D_{red}]_{eq}} \right)$ against $\ln \left(\frac{[cyt]_{ox}}{[cyt]_{red}} \right)$ is linear with a slope of one and an intercept of $\frac{F}{RT} (E_{cyt}^\ominus - E_D^\ominus)$.

(b) Draw up the following table.

$\ln \left(\frac{[D_{ox}]_{eq}}{[D_{red}]_{eq}} \right)$	-5.882	-4.776	-3.661	-3.002	-2.593	-1.436	-0.6274
$\ln \left(\frac{[cyt_{ox}]_{eq}}{[cyt_{red}]_{eq}} \right)$	-4.547	-3.772	-2.415	-1.625	-1.094	-0.2120	-0.3293

The plot of $\ln\left(\frac{[D_{ox}]_{eq}}{[D_{red}]_{eq}}\right)$ against $\ln\left(\frac{[cyt_{ox}]_{eq}}{[cyt_{red}]_{eq}}\right)$ is shown in Fig. 7.6. The intercept is -1.2124 . Hence

$$\begin{aligned} E_{cyt}^{\ominus} &= \frac{RT}{F} \times (-1.2124) + 0.237 \text{ V} \\ &= 0.0257 \text{ V} \times (-1.2124) + 0.237 \text{ V} \\ &= \boxed{+0.206 \text{ V}} \end{aligned}$$

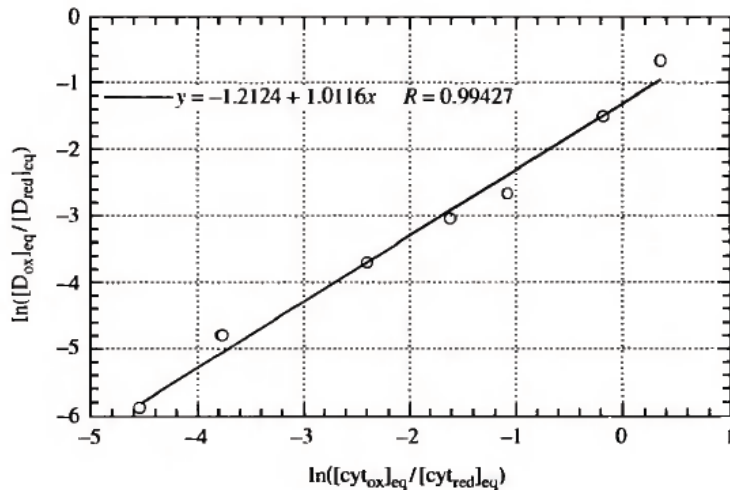
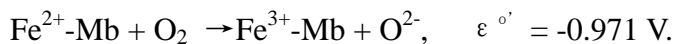
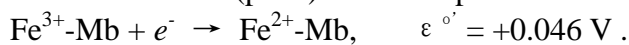


Figure 7.6

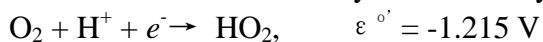
12. Fe^{2+} -myoglobin (Fe^{2+} -Mb) is spontaneously oxidized by molecular oxygen in a one-electron process to give Fe^{3+} -Mb and superoxide, O^{2-} . The reaction can be written



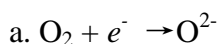
The biochemists' (pH 7) reduction potential of Fe^{3+} -Mb is



O_2 can be electrochemically reduced to hydrogen superoxide, a weak acid ($\text{pK}_a \sim 4.9$):



- Calculate the pH 7 reduction potential for oxygen to superoxide.
- Calculate the potential for the one-electron oxidation of myoglobin by oxygen at an oxygen pressure of 0.02 bar and pH 7.



$$\varepsilon^{\circ'} = -0.971 \text{ V} + 0.046 \text{ V} = -0.925 \text{ V}$$

b. $Q = 1/0.02 = 50$, the number of electrons transferred $\nu_e = 1$,

$$\varepsilon' = \varepsilon^{\circ'} - (0.0591 \text{ V} / \nu_e) \cdot \log Q = -0.971 \text{ V} - 0.0591 \text{ V} \cdot \log 50 = -1.071 \text{ V}$$

13. Lysozyme (m.w. 14.3 kD) is a rather basic protein; at pH 7, it has a net positive charge of +18. If we dissolve 5 g of lysozyme in 100 mL of 0.1 M KCl, and dialyze against 0.1 M KCl, calculate the Donnan potential and the concentration of K^+ and Cl^- inside the membrane.

$$Z_M = 18, c_M = (5 \text{ g} / 14300 \text{ g mol}^{-1}) / 0.1 \text{ L} = 3.50 \times 10^{-3} \text{ M}, c = 0.1,$$

$$\text{The ratio of } c_{K,in} \text{ to } c_{K,out} \text{ is } r = \frac{-Z_M c_M}{2c} + \sqrt{\left(\frac{Z_M c_M}{2c}\right)^2 + 1} = 0.733.$$

$$c_{K,in} = c_{Cl,in} = 0.73 \times 0.1 \text{ M} = 0.073 \text{ M}$$

If assume the Lysozyme is associated with Cl^- for charge balance (not specified), then

$$c_{Cl,in} = c_{K,in} + Z_M c_M = 0.073 + 18 \times 3.50 \times 10^{-3} \text{ M} = 0.136 \text{ M}.$$

$$\text{Donnan potential is } V = (RT/F) \ln r = 0.0257 \ln 0.733 = -0.00798 \text{ V} = -7.98 \text{ mV}$$

14. Ferredoxins (Fd) are iron- and sulfur-containing proteins that undergo redox reactions in a variety of microorganisms. A particular ferredoxin is oxidized in a one-electron reaction, independent of pH, according to the equation:



To determine the standard potential of Fd_{red}/Fd_{ox} a known amount was placed in a buffer at pH 7.0 and bubbled with H_2 at 1 bar pressure. (Finely divided platinum catalyst was present to ensure reversibility.) At equilibrium, the ferredoxin was found spectrophotometrically to be exactly one-third in the reduced form and two-thirds in the oxidized form.

a. Calculate K' , the equilibrium constant, for the system $1/2 H_2 + Fd_{ox} \rightarrow Fd_{red} + H^+$.

b. Calculate $\varepsilon^{\circ'}$ for the Fd_{red}/Fd_{ox} half-reaction at 25°C.

$$\begin{aligned} \text{a)} \quad K &= [H^+][Fd_{red}]/([H_2]^{1/2}[Fd_{ox}]) \\ &= (10^{-7})(1/3)(2/3) = \underline{5 \times 10^{-8}} \end{aligned}$$

b) $E^{\circ'}$ refers to standard states at pH7, so H^+ is not included in the equilibrium expression

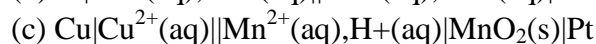
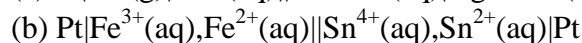
$$K'(pH7) = [Fd_{red}]/([H_2]^{1/2}[Fd_{ox}]) = \underline{0.5}$$

$$E^{\circ'} = (RT/nF) \ln K' = 0.0591 \log_{10} 0.5 = -0.0178 \text{ V}$$

$$Fd_{ox} + e^- \rightarrow Fd_{red}; \quad E^{\circ'} = -0.0178 - 0.421 = \underline{-0.439 \text{ V}}$$

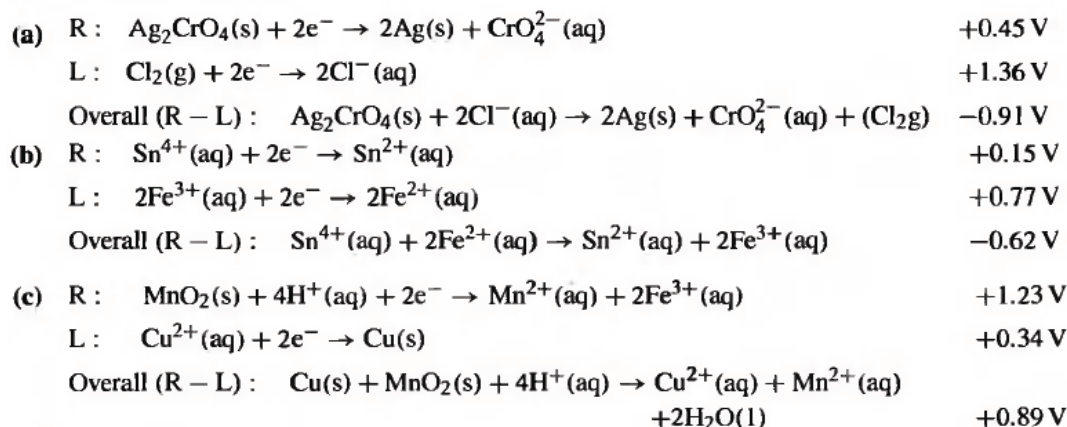
Extra, practice for test:

15. Write the cell reaction and electrode half-reactions and calculate the standard potential of each of the following cells:



The cell notation specifies the right and left electrodes. Note that for proper cancellation we must equalize the number of electrons in half-reactions being combined.

For the calculation of the standard emfs of the cells we have used $E^\ominus = E_R^\ominus - E_L^\ominus$, with standard electrode potentials from Table 7.2.



COMMENT. Those cells for which $E^\ominus > 0$ may operate as spontaneous galvanic cells under standard conditions. Those for which $E^\ominus < 0$ may operate as nonspontaneous electrolytic cells. Recall that E^\ominus informs us of the spontaneity of a cell under standard conditions only. For other conditions we require E .

16. Consider the cell $\text{Pt}|\text{H}_2(\text{g},p^\ominus)|\text{HCl}(\text{aq})|\text{AgCl}(\text{s})|\text{Ag}$, for which the cell reaction is $2\text{AgCl}(\text{s}) + \text{H}_2(\text{g}) \rightarrow 2\text{Ag}(\text{s}) + 2\text{HCl}(\text{aq})$. At 25°C and a molality of HCl of 0.010 mol kg^{-1} , $E_{\text{cell}} = +0.4658\text{ V}$. (a) Write the Nernst equation for the cell reaction. (b) Calculate $\Delta_r G$ for the cell reaction. (c) Assuming that the Debye - Hückel limiting law holds at this concentration, calculate $E^\ominus(\text{Cl}^-, \text{AgCl}, \text{Ag})$.

(a)
$$E = E^\ominus - \frac{RT}{\nu F} \ln Q \quad \nu = 2$$

$$Q = \prod_j a_j^{\nu_j} = a_{\text{H}^+}^2 a_{\text{Cl}^-}^2 \quad [\text{all other activities} = 1]$$

$$= a_+^2 a_-^2 = (\gamma_+ b_+)^2 \times (\gamma_- b_-)^2 \quad \left[b \equiv \frac{b}{b^\ominus} \text{ here and below} \right]$$

$$= (\gamma_+ \gamma_-)^2 \times (b_+ b_-)^2 = \gamma_\pm^4 b^4 \quad [5.66. b_+ = b, b_- = b]$$

$$\text{Hence, } E = E^\ominus - \frac{RT}{2F} \ln (\gamma_\pm^4 b^4) = \boxed{E^\ominus - \frac{2RT}{F} \ln (\gamma_\pm b)}$$

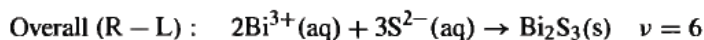
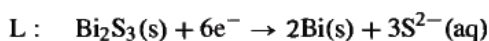
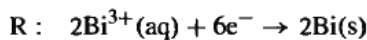
(b) $\Delta_r G = -\nu FE [7.27] = -(2) \times (9.6485 \times 10^4 \text{ C mol}^{-1}) \times (0.4658 \text{ V}) = \boxed{-89.89 \text{ kJ mol}^{-1}}$

$$(c) \quad \log \gamma_{\pm} = -|z_+z_-|AI^{1/2}[5.69] = -(0.509) \times (0.010)^{1/2} [I = b \text{ for HCl(aq)}] = -0.0509$$

$$\gamma_{\pm} = 0.889$$

$$E^{\ominus} = E + \frac{2RT}{F} \ln(\gamma_{\pm}b) = (0.4658 \text{ V}) + (2) \times (25.693 \times 10^{-3} \text{ V}) \times \ln(0.889 \times 0.010) \\ = \boxed{+0.223 \text{ V}}$$

17. The potential of the cell Bi |Bi₂S₃(s)|Bi₂S₃(aq)|Bi is 0.96 V at 25° C. Calculate (a) the solubility product of Bi₂S₃ and (b) its solubility.



$$\ln K = \frac{\nu FE^{\ominus}}{RT} = \frac{6(0.96 \text{ V})}{(25.693 \times 10^{-3} \text{ V})} = 22\bar{4}$$

$$K = e^{22\bar{4}}$$

$$(a) \quad K = \frac{a_{\text{Bi}_2\text{S}_3(\text{s})}}{a_{\text{Bi}^{3+}(\text{aq})}^2 a_{\text{S}^{2-}(\text{aq})}^3} = \frac{M^5}{[\text{Bi}^{3+}]^2 [\text{S}^{2-}]^3} = e^{22\bar{4}}$$

In the above equation the activity of the solid equals 1 and, since the solution is extremely dilute, the activity coefficients of dissolved ions also equals 1. Substituting $[\text{S}^{2-}] = 1.5[\text{Bi}^{3+}]$ and solving for $[\text{Bi}^{3+}]$ gives $[\text{Bi}^{3+}] = 2.7 \times 10^{-20} \text{ M}$. Bi₂S₃ has a solubility equal $\boxed{\text{to } 1.4 \times 10^{-20} \text{ M}}$.

(b) The solubility equilibrium is written as the reverse of the cell reaction. Therefore,

$$K_S = K^{-1} = 1/e^{22\bar{4}} = \boxed{5.2 \times 10^{-98}}$$

18. The potential of the cell Pt |H₂(g, p°)|HCl(aq, b)|Hg₂Cl₂(s)|Hg(l) has been measured with high precision with the following results at 25° C:

$b/(\text{mmol kg}^{-1})$	1.6077	3.0769	5.0403	7.6938	10.9474
E/V	0.60080	0.56825	0.54366	0.52267	0.50532

Determine the standard cell potential and the mean activity coefficient of HCl at these molalities. (Make a least-squares fit of the data to the best straight line.)



$$E = E^{\ominus} - \frac{RT}{F} \ln a(\text{H}^+)a(\text{Cl}^-) \text{ [Section 7.8].}$$

$$a(\text{H}^+) = \gamma_+ b_+ = \gamma_+ b; \quad a(\text{Cl}^-) = \gamma_- b_- = \gamma_- b \left[b = \frac{b}{b^{\ominus}} \text{ here and below} \right].$$

$$a(\text{H}^+)a(\text{Cl}^-) = \gamma_+ \gamma_- b^2 = \gamma_{\pm}^2 b^2.$$

$$E = E^{\ominus} - \frac{2RT}{F} \ln b - \frac{2RT}{F} \ln \gamma_{\pm}. \quad (a)$$

Converting from natural logarithms to common logarithms (base 10) in order to introduce the Debye-Hückel expression, we obtain

$$\begin{aligned}
 E &= E^\ominus - \frac{(2.303) \times 2RT}{F} \log b - \frac{(2.303) \times 2RT}{F} \log \gamma_{\pm} \\
 &= E^\ominus - (0.1183 \text{ V}) \log b - (0.1183 \text{ V}) \log \gamma_{\pm} \\
 &= E^\ominus - (0.1183 \text{ V}) \log b - (0.1183 \text{ V}) \left[-|z_+z_-|A I^{1/2} \right] \\
 &= E^\ominus - (0.1183 \text{ V}) \log b + (0.1183 \text{ V}) \times A \times b^{1/2} \quad [I = b].
 \end{aligned}$$

Rearranging,

$$E + (0.1183 \text{ V}) \log b = E^\ominus + \text{constant} \times b^{1/2}.$$

Therefore, plot $E + (0.1183 \text{ V}) \log b$ against $b^{1/2}$, and the intercept at $b = 0$ is E^\ominus/V . Draw up the following table.

$b/(\text{mmol kg}^{-1})$	1.6077	3.0769	5.0403	7.6938	10.9474
$\left(\frac{b}{b^\ominus}\right)^{1/2}$	0.04010	0.05547	0.07100	0.08771	0.1046
$E/V + (0.1183) \log b$	0.27029	0.27109	0.27186	0.27260	0.27337

The points are plotted in Fig. 7.2. The intercept is at 0.26840, so $E^\ominus = +0.26840 \text{ V}$. A least-squares best fit gives $E^\ominus = +0.26843 \text{ V}$ and a coefficient of determination equal to 0.99895.

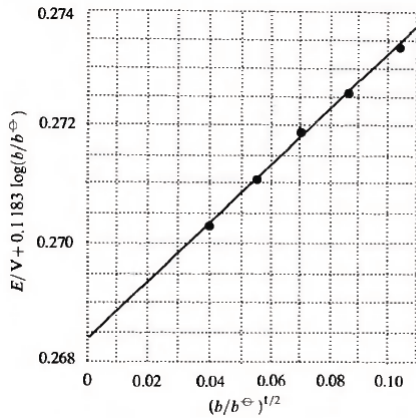


Figure 7.2

For the activity coefficients we obtain from equation (a)

$$\ln \gamma_{\pm} = \frac{E^\ominus - E}{2RT/F} - \ln \frac{b}{b^\ominus} = \frac{0.26843 - E/V}{0.05139} - \ln \frac{b}{b^\ominus}$$

and we draw up the following table.

$b/(\text{mmol kg}^{-1})$	1.6077	3.0769	5.0403	7.6938	10.9474
$\ln \gamma_{\pm}$	-0.3465	-0.05038	-0.6542	-0.07993	-0.09500
γ_{\pm}	0.9659	0.9509	0.9367	0.9232	0.9094

19. Express a_{\pm} in terms of a_+ and a_- for (a) Li_2CO_3 , (b) CaCl_2 , (c) Na_3PO_4 , and (d) $\text{K}_4\text{Fe}(\text{CN})_6$. Assume complete dissociation.

$$\text{a) } \text{Li}_2\text{CO}_3 \quad a_{\pm} = (a_+^{v_+} a_-^{v_-})^{\frac{1}{v}} = (a_+^2 a_-)^{\frac{1}{3}}$$

$$\text{b) } \text{CaCl}_2 \quad a_{\pm} = (a_+^{v_+} a_-^{v_-})^{\frac{1}{v}} = (a_+ a_-^2)^{\frac{1}{3}}$$

$$\text{c) } \text{Na}_3\text{PO}_4 \quad a_{\pm} = (a_+^{v_+} a_-^{v_-})^{\frac{1}{v}} = (a_+^3 a_-)^{\frac{1}{4}}$$

$$\text{d) } \text{K}_4\text{Fe}(\text{CN})_6 \quad a_{\pm} = (a_+^{v_+} a_-^{v_-})^{\frac{1}{v}} = (a_+^4 a_-)^{\frac{1}{5}}$$

20. Express γ_{\pm} in terms of γ_+ and γ_- for (a) SrSO_4 , (b) MgBr_2 , (c) K_3PO_4 , and (d) $\text{Ca}(\text{NO}_3)_2$. Assume complete dissociation.

$$\text{a) } \text{SrSO}_4 \quad \gamma_{\pm} = (\gamma_+ \gamma_-)^{\frac{1}{2}}$$

$$\text{b) } \text{MgBr}_2 \quad \gamma_{\pm} = (\gamma_+ \gamma_-^2)^{\frac{1}{3}}$$

$$\text{c) } \text{K}_3\text{PO}_4 \quad \gamma_{\pm} = (\gamma_+^3 \gamma_-)^{\frac{1}{4}}$$

$$\text{d) } \text{Ca}(\text{NO}_3)_2 \quad \gamma_{\pm} = (\gamma_+ \gamma_-^2)^{\frac{1}{3}}$$

21. Using the Debye–Hückel limiting law, calculate the value of γ_{\pm} in $5.0 \times 10^{-3} \text{ m}$ solutions of (a) KCl , (b) $\text{Ca}(\text{NO}_3)_2$, and (c) ZnSO_4 . Assume complete dissociation.

a) KCl

$$I = \frac{m}{2} (v_+ z_+^2 + v_- z_-^2) = \frac{1}{2} (m_+ z_+^2 + m_- z_-^2)$$

$$I = \frac{1}{2} (0.0050 \text{ mol kg}^{-1} + 0.0050 \text{ mol kg}^{-1}) = 0.0050 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 |z_+ z_-| \sqrt{\frac{I}{\text{mol kg}^{-1}}} = -1.173 \times \sqrt{0.0050} = -0.08294$$

$$\gamma_{\pm} = 0.92$$

b) $\text{Ca}(\text{NO}_3)_2$

$$I = \frac{m}{2} (v_+ z_+^2 + v_- z_-^2) = \frac{1}{2} (m_+ z_+^2 + m_- z_-^2)$$

$$I = \frac{1}{2} (0.0050 \text{ mol kg}^{-1} + 2^2 \times 0.0050 \text{ mol kg}^{-1}) = 0.0125 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 |z_+ z_-| \sqrt{\frac{I}{\text{mol kg}^{-1}}} = -1.173 \times 2 \times \sqrt{0.0125} = -0.26229$$

$$\gamma_{\pm} = 0.77$$

c) ZnSO_4

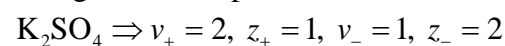
$$I = \frac{m}{2} (v_+ z_+^2 + v_- z_-^2) = \frac{1}{2} (m_+ z_+^2 + m_- z_-^2)$$

$$I = \frac{1}{2} (4 \times 0.0050 \text{ mol kg}^{-1} + 4 \times 0.0050 \text{ mol kg}^{-1}) = 0.020 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 |z_+ z_-| \sqrt{\frac{I}{\text{mol kg}^{-1}}} = -1.173 \times 4 \times \sqrt{0.020} = -0.6635$$

$$\gamma_{\pm} = 0.52$$

22. Calculate I , γ_{\pm} , and a_{\pm} for a 0.0250 m solution of K_2SO_4 at 298 K. Assume complete dissociation. How confident are you that your calculated results will agree with experimental results?



$$I = \frac{0.0250}{2} (2 + 4) = 0.0750 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 \times 2 \times \sqrt{0.0750} = -0.6425$$

$$\gamma_{\pm} = 0.523$$

$$a_{\pm} = \left(\frac{m_{\pm}}{m^{\circ}} \right) \gamma_{\pm}$$

$$m_{\pm}^3 = (0.050)^2 (0.0250) = 6.25 \times 10^{-5}$$

$$m_{\pm} = 0.03969 \text{ mol kg}^{-1}$$

$$a_{\pm} = 0.03969 \times 0.5260 = 0.0209$$

Not very confident. Figures 9.5 and 9.6 show significant deviations from predicted behavior for $I > 0.01 \text{ mol kg}^{-1}$.

23. Calculate the ionic strength of each of the solutions in 0.0500 m solutions of (a) $\text{Ca}(\text{NO}_3)_2$, (b) NaOH , (c) MgSO_4 , and (d) AlCl_3 .

$$I = \frac{m}{2} (v_+ z_+^2 + v_- z_-^2)$$

for $\text{Ca}(\text{NO}_3)_2$

$$I = \frac{0.0500}{2} (1 \times 2^2 + 2 \times 1^2) = 0.150 \text{ mol kg}^{-1}$$

for NaOH

$$I = \frac{0.0500}{2} (1 + 1) = 0.0500 \text{ mol kg}^{-1}$$

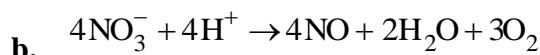
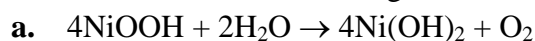
for MgSO_4

$$I = \frac{0.0500}{2} (1 \times 2^2 + 1 \times 2^2) = 0.200 \text{ mol kg}^{-1}$$

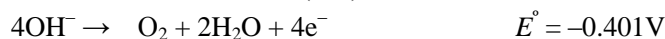
for AlCl_3

$$I = \frac{0.05}{2} (1 \times 3^2 + 3 \times 1^2) = 0.300 \text{ mol kg}^{-1}$$

24. By finding appropriate half-cell reactions, calculate the equilibrium constant at 298.15 K for the following reactions:



a) The half cell reactions are



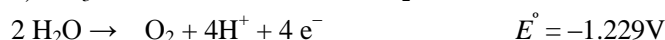
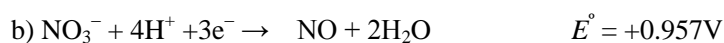
The overall reaction is



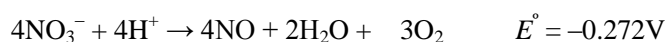
$$\ln K = \frac{nF}{RT} E^\circ = \frac{4 \times 96485 \text{ C mol}^{-1} \times 0.12 \text{ V}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}$$

$$= 18.683$$

$$K = 1.30 \times 10^8$$



The overall reaction is

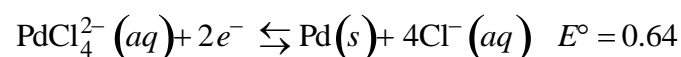
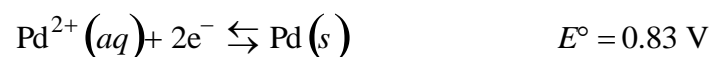


$$\ln K = \frac{nF}{RT} E^\circ = -\frac{12 \times 96485 \text{ C mol}^{-1} \times 0.272 \text{ V}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}$$

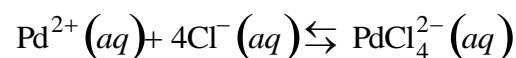
$$= -127.047$$

$$K = 6.67 \times 10^{-56}$$

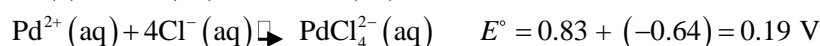
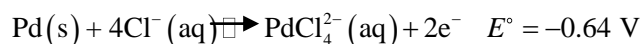
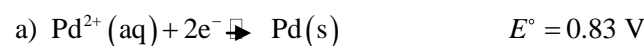
25. You are given the following half-cell reactions:



a. Calculate the equilibrium constant for the reaction



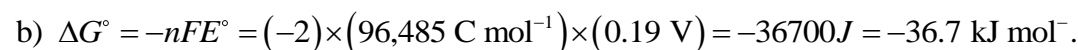
b. Calculate ΔG° for this reaction.



$$E^\circ = \frac{RT}{nF} \ln K$$

$$K = e^{nFE^\circ / RT}$$

$$K = \exp\left(\frac{2(96,485 \text{ C mol}^{-1}) \times (0.19 \text{ V})}{(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) \times (298.15 \text{ K})}\right) = 2.65 \times 10^6$$



26. Using the data in Table 9.7, calculate the standard Gibbs energy change and the equilibrium constant for the oxidation of acetaldehyde to acetic acid by NAD^+ at $\text{pH} = 7$. For concentrations

$$c_{\text{NAD}^+} = 1.00 \times 10^{-2} \text{ M}, c_{\text{NADH}} = 2.50 \times 10^{-4} \text{ M},$$

$$c_{\text{acetaldehyde}} = 3.30 \times 10^{-1} \text{ M}, c_{\text{acetic}} = 3.60 \times 10^{-3} \text{ M}$$

Calculate the reaction quotient Q and the Gibbs energy change.

The equilibrium constant is given:

$$K' = \frac{C_{\text{CH}_3\text{COOH}} C_{\text{NADH}} (C_{\text{H}^+} / 10^{-7})}{C_{\text{CH}_3\text{CHO}} C_{\text{NAD}^+}} = \frac{(3.60 \times 10^{-3} \text{ M}) \times (2.50 \times 10^{-4} \text{ M})}{(1.0 \times 10^{-2} \text{ M}) \times (3.3 \times 10^{-1} \text{ M})} = 2.73 \times 10^{-4}$$

$$\Delta G^{\circ} = R T \ln[K'] = -(8.314472 \text{ J mol}^{-1} \text{ K}^{-1}) \times (298.15 \text{ K}) \times \ln[2.73 \times 10^{-4}] = 20342.4 \text{ J mol}^{-1}$$