To hand in: Ionic equilibria - (m = b, molality, M = c_A = [A], molarity):

1. Calculate the value of $m_\pm$ in $5.0 \times 10^{-4}$ molal solutions of (a) KCl, (b) Ca(NO$_3$)$_2$, and (c) ZnSO$_4$. Assume complete dissociation.

2. Calculate $\gamma_\pm$ and $a_\pm$ for a 0.0325 $m$ solution of K$_4$Fe(CN)$_6$ at 298 K.

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.

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.

5. The oxidation of NADH by molecular oxygen occurs in the cellular respiratory system:
   \[ \text{O}_2 (g) + 2\text{NADH}(aq) + 2\text{H}^+ (aq) \rightarrow 2\text{H}_2\text{O}(l) + 2\text{NAD}^+ (aq) \]
   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
   \[ \text{NAD}^+ (aq) + \text{H}^+ (aq) + 2\text{e}^- \rightarrow \text{NADH}(aq) \quad E^\circ = -0.320V \]

6. Determine $K_{sp}$ for AgBr at 298.15 K using the electrochemical cell described by
   \[ \text{Ag(s)} | \text{AgBr(s)} | \text{Br}^- (aq, a_{Br^-}) | \text{Ag}^+ (aq, a_{Ag^+}) | \text{Ag(s)} \]

7. For a given overall cell reaction, $\Delta S_R^\circ = 17.5 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta H_R^\circ = -225.0 \text{ kJ mol}^{-1}$.
   Calculate $E^\circ$ and \( \left( \frac{\partial E^\circ}{\partial T} \right)_P \).
8. The following data have been obtained for the potential of the cell
\[ \text{Pt}(s)\mid H_2(g, f = 1 \text{ atm})\mid HCl(aq, m)\mid AgCl(s)\mid Ag(s) \] as a function of \( m \) at 25°C.

<table>
<thead>
<tr>
<th>( m ) (mol kg(^{-1}))</th>
<th>( E ) (V)</th>
<th>( m ) (mol kg(^{-1}))</th>
<th>( E ) (V)</th>
<th>( m ) (mol kg(^{-1}))</th>
<th>( E ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00100</td>
<td>0.597915</td>
<td>0.0200</td>
<td>0.43024</td>
<td>0.500</td>
<td>0.27231</td>
</tr>
<tr>
<td>0.00200</td>
<td>0.54425</td>
<td>0.0500</td>
<td>0.38588</td>
<td>1.000</td>
<td>0.23328</td>
</tr>
<tr>
<td>0.00500</td>
<td>0.49846</td>
<td>0.1000</td>
<td>0.35241</td>
<td>1.500</td>
<td>0.20719</td>
</tr>
<tr>
<td>0.0100</td>
<td>0.46417</td>
<td>0.2000</td>
<td>0.31874</td>
<td>2.000</td>
<td>0.18631</td>
</tr>
</tbody>
</table>

Calculate \( E^\circ \) and \( \gamma \) for HCl at \( m = 0.00100, 0.0100, 0.100, \) and 1.000.

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?

10. Consider the cell, \( \text{Zn}(s)\mid \text{ZnCl}_2 (0.0050 \text{ mol kg}^{-1})\mid \text{Hg}_2\text{Cl}_2(s)\mid \text{Hg}(l) \), for which the cell reaction is \( \text{Hg}_2\text{Cl}_2(s) + \text{Zn}(s) \rightarrow 2 \text{Hg}(l) + 2 \text{Cl}^-(aq) + \text{Zn}^{2+}(aq) \).

Given that \( E^\circ(\text{Zn}^{2+}, \text{Zn}) = -0.7628 \text{ V} \), \( E^\circ(\text{Hg}_2\text{Cl}_2, \text{Hg}) = +0.2676 \text{ V} \), and that the cell potential is +1.2272 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 \( \text{ZnCl}_2 \) from the measured cell potential, and (e) the mean ionic activity coefficient of \( \text{ZnCl}_2 \) from the Debye–Hückel limiting law. (f) Given \( \left( \frac{\partial E_{\text{cell}}}{\partial T} \right)_p = -4.52 \times 10^{-4} \text{ V K}^{-1} \), calculate \( \Delta_r S \) and \( \Delta_r H \).

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 \( E^\circ_{\text{cyt}} \) and \( E^\circ_{\text{D}} \) 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 \( \ln([\text{cyt}_{\text{ox}}]_{\text{eq}}) \)
$/text{cyt}_{\text{red}}$/eq is linear with slope of 1 and y-intercept $F(E'_{\text{cyt}} - E'_{\text{D}})/RT$, 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 $[D_{\text{ox}}]$/eq$/[D_{\text{red}}]$/eq and $[\text{cyt}_{\text{ox}}]$/eq$/[\text{cyt}_{\text{red}}]$/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 for cytochrome c at pH 6.5 and 298K.

\[
\begin{array}{cccccccccc}
[D_{\text{ox}}]/[D_{\text{red}}]$/eq & 0.00279 & 0.00843 & 0.0257 & 0.0497 & 0.0748 & 0.238 & 0.534 \\
[\text{cyt}_{\text{ox}}]/[\text{cyt}_{\text{red}}]$/eq & 0.0106 & 0.0230 & 0.0894 & 0.197 & 0.335 & 0.809 & 1.39 \\
\end{array}
\]

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$_2^\cdot$. The reaction can be written

$$\text{Fe}^{2+}$-$\text{Mb} + \text{O}_2 \rightarrow \text{Fe}^{3+}$-$\text{Mb} + \text{O}_2^\cdot, \quad \varepsilon' = -0.971 \text{ V}.$$ 

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

$$\text{Fe}^{3+}$-$\text{Mb} + e^- \rightarrow \text{Fe}^{2+}$-$\text{Mb}, \quad \varepsilon' = +0.046 \text{ V}.$$ 

O$_2$ can be electrochemically reduced to hydrogen superoxide, a weak acid (pK$_\text{a}$~4.9):

$$\text{O}_2 + \text{H}^+ + e^- \rightarrow \text{HO}_2^- \quad \varepsilon' = -1.215 \text{ V}.$$ 

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

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.

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:

$$\text{Fd}_{\text{red}} \rightarrow \text{Fd}_{\text{ox}} + e^-.$$ 

To determine the standard potential of Fd$_{\text{red}}$/Fd$_{\text{ox}}$ 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$_2 + \text{Fd}_{\text{ox}} \rightarrow \text{Fd}_{\text{red}} + \text{H}^+$. 
b. Calculate $\varepsilon'$ for the Fd$_{\text{red}}$/Fd$_{\text{ox}}$ half-reaction at 25°C.
15. Write the cell reaction and electrode half-reactions and calculate the standard potential of each of the following cells:

(a) \[ \text{Pt} | \text{Cl}_2(g) | \text{HCl}(aq) | \text{Ag}_2\text{CrO}_4(s) | \text{Ag} \]
(b) \[ \text{Pt} | \text{Fe}^{3+}(aq) | \text{Fe}^{2+}(aq) | \text{Sn}^4+(aq) | \text{Sn}^2+(aq) | \text{Pt} \]
(c) \[ \text{Cu} | \text{Cu}^{2+}(aq) | \text{Mn}^{2+}(aq) | H^+(aq) | \text{MnO}_2(s) | \text{Pt} \]

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

17. The potential of the cell \[ \text{Bi} | \text{Bi}_2\text{S}_3(s) | \text{Bi}_2\text{S}_3(aq) | \text{Bi} \] is 0.96 V at 25° C. Calculate (a) the solubility product of \( \text{Bi}_2\text{S}_3 \) and (b) its solubility.

18. The potential of the cell \[ \text{Pt} | \text{H}_2(g,p^o) | \text{HCl}(aq,b) | \text{Hg}_2\text{Cl}_2(s) | \text{Hg}(l) \] 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 \( \text{HCl} \) at these molalities. (Make a least-squares fit of the data to the best straight line.)

19. Express \( a_± \) in terms of \( a_+ \) and \( a_- \) for (a) \( \text{Li}_2\text{CO}_3 \), (b) \( \text{CaCl}_2 \), (c) \( \text{Na}_3\text{PO}_4 \), and (d) \( \text{K}_4\text{Fe(CN)}_6 \). Assume complete dissociation.

20. Express \( \gamma_± \) in terms of \( \gamma_+ \) and \( \gamma_- \) for (a) \( \text{SrSO}_4 \), (b) \( \text{MgBr}_2 \), (c) \( \text{K}_3\text{PO}_4 \), and (d) \( \text{Ca(NO}_3)_2 \). Assume complete dissociation.

21. Using the Debye–Hückel limiting law, calculate the value of \( \gamma_± \) in \( 5.0 \times 10^{-3} \text{ m} \) solutions of (a) \( \text{KCl} \), (b) \( \text{Ca(NO}_3)_2 \), and (c) \( \text{ZnSO}_4 \). Assume complete dissociation.

22. Calculate \( I, \gamma_±, \) and \( a_± \) for a 0.0250 \( \text{ m} \) solution of \( \text{K}_2\text{SO}_4 \) at 298 K. Assume complete dissociation. How confident are you that your calculated results will agree with experimental results?
23. Calculate the ionic strength of each of the solutions in 0.0500 $m$ solutions of (a) Ca(NO$_3$)$_2$, (b) NaOH, (c) MgSO$_4$, and (d) AlCl$_3$.

24. By finding appropriate half-cell reactions, calculate the equilibrium constant at 298.15 K for the following reactions:
   a. $4\text{NiOOH} + 2\text{H}_2\text{O} \rightarrow 4\text{Ni(OH)}_2 + \text{O}_2$
   b. $4\text{NO}_3^- + 4\text{H}^+ \rightarrow 4\text{NO} + 2\text{H}_2\text{O} + 3\text{O}_2$

25. You are given the following half-cell reactions:
   \[
Pd^{2+} (aq) + 2e^- \rightleftharpoons Pd (s) \quad E^\circ = 0.83 \text{ V}
   \]
   \[
PdCl_4^{2-} (aq) + 2e^- \rightleftharpoons Pd (s) + 4Cl^- (aq) \quad E^\circ = 0.64 \text{ V}
   \]
   a. Calculate the equilibrium constant for the reaction
   \[
Pd^{2+} (aq) + 4Cl^- (aq) \rightleftharpoons PdCl_4^{2-} (aq)
   \]
   b. Calculate $\Delta G^\circ$ for this reaction.

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 pH = 7. For concentrations
   \[
c_{\text{NAD}^+} = 1.00 \times 10^{-2} \text{ M}, \quad c_{\text{NADH}} = 2.50 \times 10^{-4} \text{ M},
   \]
   \[
c_{\text{acetaldehyde}} = 3.30 \times 10^{-1} \text{ M}, \quad c_{\text{acetic}} = 3.60 \times 10^{-3} \text{ M}
   \]
   Calculate the reaction quotient $Q$ and the Gibbs energy change.