

21 Electrochemistry

Physical constants: $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$, $F = 96,485 \text{ C mol}^{-1}$.

- 21.1 For each of the following cells: (a) write the cell using the notation described in section 21.1.2 on page 794, (b) determine the conventional cell reaction, stating the number of electrons involved, (c) write down the Nernst equation for the cell, (d) using the data in Table 21.1 on page 805 determine the standard cell potential, (e) hence determine the spontaneous cell reaction when all of the species are present in their standard states.

In the following table it can be assumed that: (i) all ions are in aqueous solution; (ii) H_2O is in its liquid form; (iii) O_2 , H_2 , and Cl_2 are gases; (iv) the solutions in the right- and left-hand sides are separated by a salt bridge; (v) an inert platinum electrode can be used as required.

	left-hand half-cell reaction	right-hand half-cell reaction
1	$\text{H}^+ + e^- \rightarrow \frac{1}{2}\text{H}_2$	$\text{Cu}^+ + e^- \rightarrow \text{Cu(m)}$
2	$\text{H}^+ + e^- \rightarrow \frac{1}{2}\text{H}_2$	$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe(m)}$
3	$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe(m)}$	$\text{H}^+ + e^- \rightarrow \frac{1}{2}\text{H}_2$
4	$\text{Mn}^{2+} + 2e^- \rightarrow \text{Mn(m)}$	$\text{Au}^{3+} + 3e^- \rightarrow \text{Au(m)}$
5	$\text{AgCl(s)} + e^- \rightarrow \text{Ag(m)} + \text{Cl}^-$	$\text{H}^+ + e^- \rightarrow \frac{1}{2}\text{H}_2$
6	$\text{AgI(s)} + e^- \rightarrow \text{Ag(m)} + \text{I}^-$	$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn(m)}$
7	$\text{AgCl(s)} + e^- \rightarrow \text{Ag(m)} + \text{Cl}^-$	$\text{Hg}_2\text{Cl}_2\text{(s)} + 2e^- \rightarrow 2\text{Hg(l)} + 2\text{Cl}^-$
8	$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$	$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$
9	$\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$	$\text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
10	$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$	$\text{PbO(s)} + \text{H}_2\text{O} + 2e^- \rightarrow \text{Pb(m)} + 2\text{OH}^-$

- 21.2 For each of the following cells: (a) write down the right- and left-hand half-cell reactions (as reductions); (b) determine the conventional cell reaction, stating the number of electrons involved, (c) write down the Nernst equation for the cell, (d) using the data in Table 21.1 on page 805 determine the standard cell potential, (e) hence for cells 1–9 hence determine the spontaneous cell reaction when all of the species are present in their standard states.

- $\text{Zn(m)} \mid \text{Zn}^{2+}(\text{aq}) \parallel \text{Mg}^{2+}(\text{aq}) \mid \text{Mg(m)}$
- $\text{Pt(m)} \mid \text{H}_2(\text{g}) \mid \text{H}^+(\text{aq}) \parallel \text{Fe}^{3+}(\text{aq}) \mid \text{Fe(m)}$
- $\text{Pt(m)} \mid \text{Sn}^{4+}(\text{aq}), \text{Sn}^{2+}(\text{aq}) \parallel \text{Cu}^{2+}(\text{aq}) \mid \text{Cu(m)}$
- $\text{Ag(m)}, \text{AgI(s)} \mid \text{HI(aq)} \mid \text{H}_2(\text{g}) \mid \text{Pt(m)}$
- $\text{Pt(m)} \mid \text{H}_2(\text{g}) \mid \text{H}^+(\text{aq}) \mid \text{O}_2(\text{g}) \mid \text{Pt(m)}$
- $\text{Pt(m)} \mid \text{H}_2(\text{g}) \mid \text{OH}^-(\text{aq}) \mid \text{O}_2(\text{g}) \mid \text{Pt(m)}$
- $\text{Ag(m)}, \text{AgBr(s)} \mid \text{Br}^-(\text{aq}), \text{Br}_2(\text{aq}) \mid \text{Pt(m)}$
- $\text{Pb(m)}, \text{PbO(s)} \mid \text{OH}^-(\text{aq}) \mid \text{H}_2(\text{g}) \mid \text{Pt(m)}$
- $\text{Pt(m)} \mid \text{Cr}_2\text{O}_7^{2-}(\text{aq}), \text{Cr}^{3+}(\text{aq}), \text{H}^+(\text{aq}) \parallel \text{Cl}^-(\text{aq}) \mid \text{AgCl(s)}, \text{Ag(m)}$
- $\text{Ag(m)}, \text{AgCl(s)} \mid \text{Cl}^-(\text{aq}, [\text{Cl}^-] = c_L) \parallel \text{Cl}^-(\text{aq}, [\text{Cl}^-] = c_R) \mid \text{AgCl(s)}, \text{Ag(m)}$

21.3 Devise cells which have the following conventional cell reactions. In each case: (a) write the cell in the way described in section 21.1.2 on page 794; (b) write the right- and left-hand side half-cell reactions (as reductions); (c) determine the cell potential when all of the species are present in their standard states; (d) hence determine the direction of the spontaneous cell reaction when all of the species are present in their standard states.

- 1 $\text{Zn(m)} + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(m)}$
- 2 $2\text{Ag(m)} + \text{Sn}^{4+}(\text{aq}) \longrightarrow \text{Sn}^{2+}(\text{aq}) + 2\text{Ag}^+(\text{aq})$
- 3 $\text{AgCl(m)} + \frac{1}{2}\text{H}_2(\text{g}) \longrightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{Ag(m)}$
- 4 $\text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{Ag(m)} \longrightarrow \text{AgCl(m)} + \frac{1}{2}\text{H}_2(\text{g})$
- 5 $2\text{AgCl(m)} + \text{H}_2(\text{g}) \longrightarrow 2\text{H}^+(\text{aq}) + 2\text{Cl}^-(\text{aq}) + 2\text{Ag(m)}$
- 6 $2\text{AgCl(m)} + 2\text{Hg(l)} \longrightarrow \text{Hg}_2\text{Cl}_2(\text{m}) + 2\text{Ag(m)}$
- 7 $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{Cl}^-(\text{aq}) + 4\text{Ag(m)} \longrightarrow 2\text{H}_2\text{O(l)} + 4\text{AgCl(m)}$
- 8 $\text{H}_2\text{O(l)} + \text{Pb(m)} \longrightarrow \text{H}_2(\text{g}) + \text{PbO(s)}$
- 9 $\text{AgBr(m)} \longrightarrow \text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq})$
- 10 $\text{Al(m)} + 3\text{Ce}^{4+}(\text{aq}) \longrightarrow \text{Al}^{3+}(\text{aq}) + 3\text{Ce}^{3+}(\text{aq})$

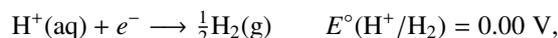
21.4 Consider the following cell (at 298 K)



- (a) Determine the conventional cell reaction and hence write down the Nernst equation for the cell in terms of the concentrations c_1 and c_2 .
 - (b) Determine the cell potential when all of the species are present in their standard states (i.e. $c_1 = c_2 = 1 \text{ mol dm}^{-3}$), and hence state the spontaneous cell reaction.
 - (c) By considering the Nernst equation, determine the value of the ratio c_1/c_2 which will reduce the cell potential to zero.
 - (d) Hence state what range of values of c_1/c_2 will lead to the spontaneous cell reaction being the *opposite* of that determined in (b).
- 21.5 Use the data in Table 21.1 on page 805 to determine whether or not the following processes are thermodynamically feasible when all of the species are present in their standard states and at 298 K (all ions are in aqueous solution).
- (a) The oxidation of Cu(m) to Cu^{2+} by Fe^{3+} (assume that the Fe^{3+} is reduced to Fe^{2+})
 - (b) The oxidation of Fe^{2+} to Fe^{3+} by $\text{Cl}_2(\text{g})$
 - (c) The oxidation of $\text{H}_2\text{O(l)}$ to $\text{O}_2(\text{g})$ by Fe^{3+} (under acidic conditions)
 - (d) The reduction of Cu^{2+} to Cu^+ by Ag(m)
 - (e) The reduction of Fe^{3+} to Fe(m) by Zn(m)
 - (f) The reduction of Mn^{2+} to Mn(m) by Tl .

21.6 The potential produced by the hydrogen electrode is dependent on concentration of $\text{H}^+(\text{aq})$ and the partial pressure of H_2 .

(a) Given that the half-cell reaction is



write down the Nernst equation for the half-cell potential.

(b) Assuming that the partial pressure of H_2 is 1 bar (i.e. the standard pressure) show that the half-cell potential is given by

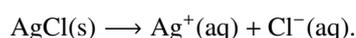
$$E = \frac{RT}{F} \ln [\text{H}^+].$$

(c) Hence show that the half-cell potential is related to the pH in the following way [hint $\ln x \equiv \ln 10 \times \log x$]

$$E = -\ln 10 \times \frac{RT}{F} \times \text{pH}.$$

(d) Does it become easier or more difficult for a reducing agent to reduce H^+ to H_2 as the pH increases?

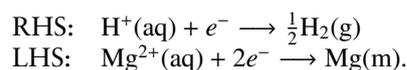
21.7 (a) Devise a cell whose conventional cell reaction is



(b) Using tabulated data, determine the standard potential of this cell at 298 K and hence find $\Delta_r G_{\text{cell}}^\circ$.

(c) Hence determine the solubility product of AgCl, and the concentration of dissolved Ag^+ ions in a saturated solution of AgCl.

21.8 In this question we will use data on cell potentials to compute some thermodynamic parameters for Mg^{2+} in a way very similar to that illustrated in section 21.9.2 on page 817 for Ag^+ . The cell we need to consider in this case is the following



At 298 K the standard potential for this cell is +2.360 V, and the temperature dependence of the standard cell potential is $dE^\circ/dT = -1.99 \times 10^{-4} \text{ V K}^{-1}$.

(a) Determine the conventional cell reaction.

(b) Determine $\Delta_r G_{\text{cell}}^\circ$, $\Delta_r S_{\text{cell}}^\circ$ and $\Delta_r H_{\text{cell}}^\circ$ (all at 298 K) for this reaction.

(c) Hence, assuming the usual conventions that $\Delta_r G^\circ(\text{H}^+(\text{aq})) = 0$, $\Delta_r H^\circ(\text{H}^+(\text{aq})) = 0$ and $\Delta_r S^\circ(\text{H}^+(\text{aq})) = 0$, find the standard Gibbs energy, enthalpy and entropy of formation of $\text{Mg}^{2+}(\text{aq})$.

(d) Dissect the conventional cell reaction found in (a) into a Hess's Law cycle of the same form as that in Fig. 21.12 on page 819. [continued over]

- (e) Use the following data, along with your value of $\Delta_f H^\circ(\text{Mg}^{2+}(\text{aq}))$, to determine the *absolute* enthalpy of hydration of Mg^{2+} , $\Delta H_{\text{hyd}}^\circ(\text{Mg}^{2+})$:



[Be very careful to make sure that you use the $\Delta_r H^\circ$ value for the *direction* of reaction specified in the Hess's Law cycle.]

- 21.9 Use the following data to construct an oxidation state diagram for cobalt. Comment on any features of interest which are revealed by your diagram.

half-cell reaction	E° / V (298K)
$\text{Co}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Co}(\text{m})$	-0.282
$\text{Co}^{3+}(\text{aq}) + e^- \rightarrow \text{Co}^{2+}(\text{aq})$	+1.92
$\text{CoO}_2(\text{s}) + 4\text{H}^+ + e^- \rightarrow \text{Co}^{3+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$	+1.4

- 21.10 Before an ion-selective electrode can be used to make measurements, the potential it generates (when forming a cell with a suitable external reference electrode) needs to be calibrated as a function of the concentration of the ions. This is normally done by measuring the potential for a series of solutions of known concentration and then constructing a calibration curve. For the greatest accuracy, it is best to calibrate the electrode over the range of concentrations likely to be encountered in the measurements.

Low concentrations of ions are usually specified in parts per million (ppm) by weight. For example, if a solution contains 5 ppm of fluoride it means that

$$\frac{\text{mass of F}^-}{\text{mass of solvent}} = 5 \times 10^{-6}.$$

It follows that 1 dm³ of water, which would weigh 1000 g, will contain 5.0×10^{-3} g of F⁻. Given that the RMM of F is 18.998, this corresponds to a concentration of 2.63×10^{-4} mol dm⁻³. For these very dilute solutions, the concentration expressed in ppm is directly proportional to the concentration in mol dm⁻³.

Measurements on a series of solutions of known concentration gave the following data

ppm F ⁻	5	4	3	2	1.5	1	0.5
E / V	0.288	0.282	0.276	0.264	0.258	0.246	0.229

The expected variation of the cell potential with concentration is of the form

$$E = A + B \ln [\text{F}^-],$$

where A and B are constants; in this expression, $[\text{F}^-]$ can be expressed in ppm. By plotting a suitable straight-line graph, show that these data fit this equation; determine the values of A and B .

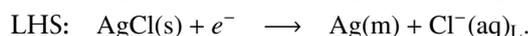
The electrode was then used to measure the fluoride concentration in drinking water. Over a series of measurements the average potential was found to be 0.255 V, with a spread of measurements between 0.254 V and 0.256 V. Determine the concentration (in ppm) of F⁻ in the water, and the likely error on the measurement.

- 21.11 Manufacturers of glass electrodes, used to measure pH, warn customers that the accuracy of the results may be reduced if the Na⁺ concentration in the solution under test is high. Why is this?

- 21.12 A *concentration cell* is one in which the RHS and LHS electrodes are identical with the only difference between them being the concentration (or pressure) of the species involved. An example of such a cell is once constructed from two AgCl/Cl⁻ electrodes



in which the concentration of Cl⁻ in the left-hand half-cell is [Cl⁻]_L, and that on the right is [Cl⁻]_R. In writing the half-cell reactions for such a cell, we need to be careful to keep track of which side of the cell the Cl⁻ is in. The half cell reactions are therefore written

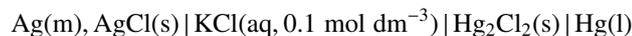


Note the subscripts 'R' and 'L' indicating which half-cell the Cl⁻ belongs to.

- (a) Determine the conventional cell reaction, and hence show that the cell potential is given by

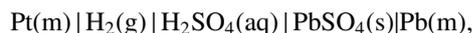
$$E = \frac{RT}{F} \ln \frac{[\text{Cl}^-]_{\text{L}}}{[\text{Cl}^-]_{\text{R}}}$$

- (b) Why does the standard half cell potential of the AgCl/Cl⁻ couple *not* appear in the expression for the cell potential?
- (c) Determine the direction of the spontaneous cell reaction when [Cl⁻]_R > [Cl⁻]_L and when [Cl⁻]_L > [Cl⁻]_R. Rationalize your conclusions.
- (d) From the above expression for the cell potential, compute dE/dT [Hint: all but one of the terms on the right do not depend on T]. Hence find Δ_rS_{cell} and Δ_rH_{cell}. Comment on the results you obtain.
- 21.13 The potential of the following cell was measured at temperatures of 278, 298 and 318 K as +0.0389, +0.0458 and +0.0527 V respectively



- (a) Write down the half cell reactions of the two electrodes and hence determine the conventional cell reaction. Also, write down the Nernst equation for the cell, and comment on why the cell potential does not depend on the concentration of Cl⁻.
- (b) Determine Δ_rG_{cell}^o at 298 K.
- (c) Using Δ_rS_{cell}^o = nF(dE^o/dT), find Δ_rS_{cell}^o and hence Δ_rH_{cell}^o (you will need to plot a graph).
- (d) Hence determine the standard enthalpy of formation of Hg₂Cl₂(s) at 298 K, given that at this temperature the standard enthalpy of formation of AgCl(s) is -126.8 kJ mol⁻¹.

21.14 Consider the cell



whose standard potential is found to be -0.356 V at 298 K .

- Write down the conventional cell reaction.
- Given that the standard half-cell potential of the $\text{Pb}^{2+}(\text{aq})/\text{Pb(m)}$ electrode is -0.126 V at 298 K , determine the solubility product of $\text{PbSO}_4(\text{s})$ at this temperature. What will the concentration of Pb^{2+} ions be in a saturated solution of PbSO_4 at 298 K ?
- Given that the temperature variation of the standard potential of the above cell is given by $dE^\circ/dT = 1.1 \times 10^{-4} \text{ V K}^{-1}$, determine $\Delta_r S_{\text{cell}}^\circ$ and hence $\Delta_r H_{\text{cell}}^\circ$.
- Given that at 298 K the standard enthalpy of formation of $\text{PbSO}_4(\text{s})$ is $-918.4 \text{ kJ mol}^{-1}$, determine the standard enthalpy of formation of $\text{SO}_4^{2-}(\text{aq})$.

- 21.15 (a) Describe carefully what is meant by the term *standard electrode potential*. Explain how tables of standard *half-cell* potentials can be drawn up.
- (b) An electrochemical cell is constructed from two half cells: on the right a silver wire dips into a $0.001 \text{ mol dm}^{-3}$ AgNO_3 solution, and the half cell on left is a hydrogen electrode with hydrogen gas at 1 bar pressure and an HCl solution of variable concentration, m . At 298 K the cell potential was found to vary with m in the following way:

$m / \text{mol dm}^{-3}$	0.6	0.8	1.0	1.2	1.4
E / V	0.6375	0.6304	0.6252	0.6214	0.6182

Determine the Nernst equation for the cell and then, *by plotting a suitable straight-line graph*, test how well the above data fit your equation.

- (c) From your graph, estimate the standard half-cell potential of the Ag^+/Ag couple.