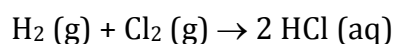# 16

Electrochemistry

Answers to worked examples

WE 16.1 Drawing a cell diagram (on p. 739 in *Chemistry*³)

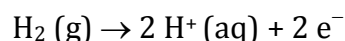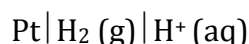Draw a cell diagram for an electrochemical cell with the overall reaction:

H_2 (g) + Cl_2 (g) $\rightarrow$ 2 HCl (aq)

Strategy

Write the two half-cell reactions and identify the oxidation and reduction reactions.

Solution

The half-cell process

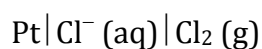$$H_2 \text{ (g)} \rightarrow 2 \text{ H}^+ \text{ (aq)} + 2 \text{ e}^-$$

represents an *oxidation* process as the H_2 (g) loses electrons, and may be written as

$$Pt \mid H_2 \text{ (g)} \mid H^+ \text{ (aq)}$$

where the vertical lines represent a boundary between solid, aqueous or gas phases and the components are written with the reduced species first. The half-cell process

$$Cl_2 \text{ (g)} + 2 \text{ e}^- \rightarrow 2 \text{ Cl}^- \text{ (aq)}$$
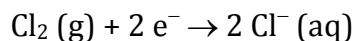
is a reduction because the Cl_2 (g) gains electrons and may be written

$$Pt \mid Cl^- \text{ (aq)} \mid Cl_2 \text{ (g)}$$

By convention, the anode, at which oxidation occurs, is written as the left-hand electrode, and the cathode, at which reduction occurs, as the right-hand

electrode. The two half cells may then be combined using a vertical double lines to denote a junction where the junction potential has been eliminated, perhaps by the use of a salt bridge. It is also conventional to write the components in the order that they appear in the overall equation

$$\text{Pt} | \text{H}_2 \text{ (g)} | \text{H}^+ \text{(aq)} \parallel \text{Cl}_2 \text{ (g)} | \text{Cl}^- \text{ (aq)} | \text{Pt}$$

WE 16.2   Interpreting a cell diagram (on p. 740 in *Chemistry*³)

What is the overall reaction occurring in the cell

$$\text{Pt (s)} | \text{V}^{2+} \text{(aq)}, \text{V}^{3+} \text{(aq)} \parallel \text{Fe}^{3+} \text{(aq)}, \text{Fe}^{2+} \text{(aq)} | \text{Pt (s)}$$
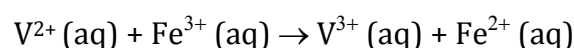
Strategy

Identify the two half cells and write out their reactions. Combine the two half-cell reactions, remembering the convention that oxidation is assumed to occur in the left-hand cell and reduction in the right-hand cell.

Solution

The two half-cell reactions are

Left (oxidation) $\text{V}^{2+} \text{(aq)} \rightarrow \text{V}^{3+} \text{(aq)} + \text{e}^-$

Right (reduction) $\text{Fe}^{3+} \text{(aq)} + \text{e}^- \rightarrow \text{Fe}^{2+} \text{(aq)}$

Then, adding the two half-cell reactions to get the overall cell reaction.

$$\text{V}^{2+} \text{(aq)} + \text{Fe}^{3+} \text{(aq)} \rightarrow \text{V}^{3+} \text{(aq)} + \text{Fe}^{2+} \text{(aq)}$$

**WE 16.3   Predicting the direction of redox reactions (on p. 743 in *Chemistry*³)**

Predict whether acidified aqueous potassium permanganate ($KMnO_4$) could be used to oxidise Fe^{2+} to Fe^{3+} under standard conditions.

Strategy

Write equations for the possible half reactions and find their standard reduction potentials from Table 16.2. Calculate the cell potential for the overall cell potential, remembering to use the conventions given in Equation 16.10.
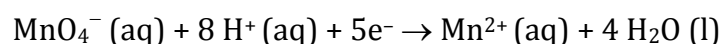
Solution

The appropriate half-cell reaction for the Fe^2/Fe^{3+} reduction/oxidation couple is

$$Fe^{3+} (aq) + e^- \rightarrow Fe^{2+} (aq)$$
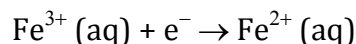
for which $E^\ominus = +0.77$ V. The corresponding oxidation process is just the reverse of this process

$$Fe^{2+} (aq) \rightarrow Fe^{3+} (aq) + e^-$$
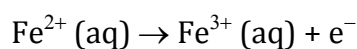
for which $E^\ominus = -0.77$ V. The half cell corresponding to reduction of permanganate ions is

$$MnO_4^- (aq) + 8 H^+ (aq) + 5e^- \rightarrow Mn^{2+} (aq) + 4 H_2O (l)$$

for which $E^\ominus = +1.52$ V. Combining these two equations therefore gives

$$5 Fe^{2+} (aq) + MnO_4^- (aq) + 8 H^+ (aq) \rightarrow 5 Fe^{3+} (aq) + Mn^{2+} (aq) + 4 H_2O (l)$$
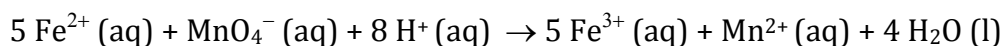
with a cell potential from Equation 16.11 of

$$E^\ominus_{cell} = E^\ominus_R - E^\ominus_L = +1.52 \text{ V} - 0.77 \text{ V} = +0.75 \text{ V}$$

A positive value for the cell potential indicates that the reaction is spontaneous in the direction written, implying that potassium permanganate can be used to oxidise $Fe^{2+}(aq)$ ions to $Fe^{3+}(aq)$ ions.

**WE 16.4 Calculating cell potentials (on p. 744 in *Chemistry*[3])**

Use values of standard reduction potentials from Table 16.2 to calculate $E^\ominus_{cell}$ for the following electrochemical cell

$$Fe (s) \mid Fe^{2+} (aq) \parallel Fe^{3+} (aq), Fe^{2+} (aq) \mid Pt (s)$$
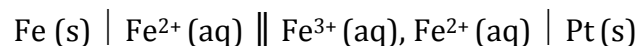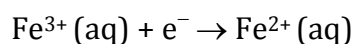
Strategy

Use the cell diagram to write half reactions for the oxidation reaction and the reduction reaction. Calculate the cell potential using Equation 16.11.

Solution

The left-hand cell is, by convention, the anode and represents an oxidation

$$Fe (s) \rightarrow Fe^{2+} (aq) + 2 e^-$$
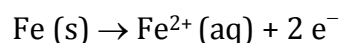
whilst the right-hand cell is the cathode and represents a reduction

$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$$

The overall cell potential is therefore

$$E_{cell}^{\ominus} = E_R^{\ominus} - E_L^{\ominus}$$

Consulting Table 16.2, shows that the standard reduction potential for the left-hand $Fe/Fe^{2+}(aq)$ cell is –0.44 V and for the right-hand $Fe^{2+}(aq)/Fe^{3+}(aq)$ cell is +0.77 V. Thus

$$E_{cell}^{\ominus} = E_R^{\ominus} - E_L^{\ominus} = +0.77 \text{ V} - (-0.44 \text{ V}) = +1.21 \text{ V}$$

WE 16.5 **Gibbs energy changes from electrochemistry (on p. 748 in *Chemistry*³)**

Calculate the standard Gibbs energy change at 298 K for the reaction in the Daniell cell

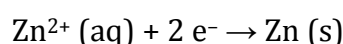$$Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$$
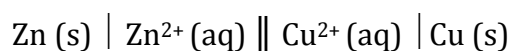
Strategy

Identify the two half-cell reactions and determine the standard cell potential using Equation 16.11 and the appropriate values in Table 16.2. Use Equation 16.14 to calculate the standard Gibbs energy change.

Solution

The reduction half reaction for the left-hand cell is

$$Zn^{2+}(aq) + 2 e^- \rightarrow Zn(s)$$

for which $E_L^{\ominus} = -0.76$ V and for the right-hand cell is

$$Cu^{2+}(aq) + 2 e^- \rightarrow Cu(s)$$
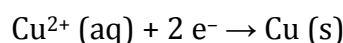
for which $E_L^{\ominus} = +0.34$ V. By convention, the left-hand cell is assumed to be the anode and is therefore an oxidation rather than reduction reaction. Thus, the overall cell potential is therefore

$$E_{cell}^{\ominus} = E_R^{\ominus} - E_L^{\ominus} = +0.34 \text{ V} - (-0.76 \text{ V}) = +1.10 \text{ V}$$

The standard Gibbs energy of reaction is, from Equation 16.14,

$$\Delta_r G^{\ominus} = -zFE^{\ominus}$$

As written, the two half-cell reactions are both two-electron processes, so that
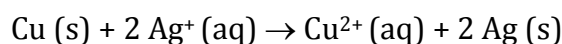
$$z = 2$$

and therefore

$$\Delta_r G^{\ominus} = -2 \times 96485 \text{ C mol}^{-1} \times +1.10 \text{ V}$$
$$= -212 \times 10^3 \text{ CV mol}^{-1} = -212 \text{ kJ mol}^{-1}$$

because

$$10^3 \text{ CV} \equiv 1 \text{ kJ}$$

WE 16.6 Calculating a thermodynamic equilibrium constant (on p. 749 in
**   *Chemistry*³)**

Calculate the thermodynamic equilibrium constant at 298 K for the reaction

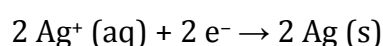Cu (s) + 2 Ag⁺ (aq) → Cu²⁺ (aq) + 2 Ag (s)

Strategy

Determine the standard cell potential from Equation 16.11 by identifying the
appropriate half cells and consulting Table 16.2. Use Equation 16.15 to
determine the corresponding equilibrium constant.

Solution

The reaction may be broken down into two half-cell reactions. The standard
reduction potential of the first,

2 Ag⁺ (aq) + 2 e⁻ → 2 Ag (s)

is $E^{\ominus}$ =+0.80 V. This is a reduction process, because the Ag⁺ (aq) ions gain
electrons, so forms the cathode. The second reaction is

Cu (s) → Cu²⁺ (aq) + 2 e⁻
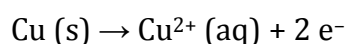
which is the reverse of the reduction half reaction

Cu²⁺ (aq) + 2 e⁻ → Cu (s)
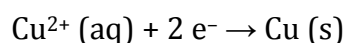
for which $E^{\ominus}$ =+0.34 V. This is an oxidation process, because the Cu (s) loses
electrons, and so forms the anode. The overall cell potential is thus, from
Equation 16.10,

$$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode} = +0.80 \text{ V} - 0.34 \text{V} = +0.46 \text{ V}$$

As written, both reactions are two-electron processes, so that $z = 2$. Then, using Equation 16.15 and substituting in the values,

$$\ln K = \frac{zF}{RT} E^{\ominus}_{cell} = \frac{2 \times 96485 \text{ C mol}^{-1}}{8.3145 \text{ J K}^{-1}\text{mol}^{-1} \times 298 \text{ K}} \times 0.46 \text{ V} = 35.8$$
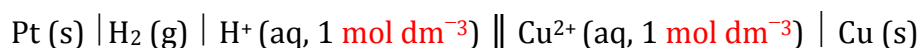
so that

$$K = e^{35.8} = 3.62 \times 10^{15}$$

The equilibrium therefore lies in favour of the products, which is to be expected for a cell whichhas a positive cell potential.
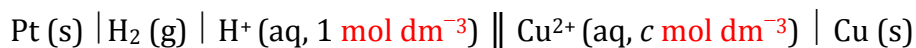
WE 16.7 **Using the Nernst equation (on p. 751 in *Chemistry*[3])**

(a) Write an equation for the overall reaction that occurs in the following cell.

Pt (s) $|$ H₂ (g) $|$ H⁺ (aq, 1 mol dm⁻³) $\|$ Cu²⁺ (aq, 1 mol dm⁻³) $|$ Cu (s)

(b) Calculate the value of $E^{\ominus}_{cell}$.

(c) The potential, $E^{\ominus}_{cell}$, for the cell below is measured and found to be +0.25 V.

Pt (s) $|$ H₂ (g) $|$ H⁺ (aq, 1 mol dm⁻³) $\|$ Cu²⁺ (aq, c mol dm⁻³) $|$ Cu (s)

What is the concentration, c, of the Cu²⁺ (aq) solution?

Strategy

Write the chemical equation for the cell reaction and hence determine the standard cell potential. Devise an expression for the reaction quotient and use the Nernst equation, Equation 16.17, to write an expression for the cell potential in terms of the unknown concentration.

Solution

(a) As written, the cell represents the reaction

Cu²⁺ (aq, 1 mol dm⁻³) + H₂ (g) → Cu (s) + 2 H⁺ (aq, 1 mol dm⁻³)
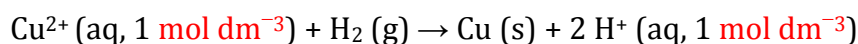
The cathodic standard half cell, which corresponds to reduction, is

Cu²⁺ (aq) + 2 e⁻ → Cu (s)
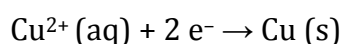
so that $E^{\ominus}_{cathode} = +0.34$ V and the anodic half cell, which corresponds to oxidation is

$$H_2 \text{ (g)} \rightarrow 2 \text{ H}^+ \text{ (aq)} + 2 \text{ e}^-$$
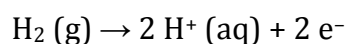
so that $E^{\ominus}_{\text{anode}} = 0$ V.

(b) Hence, from Equation 16.10,

$$E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{cathode}} - E^{\ominus}_{\text{anode}} = +0.34 \text{ V} - 0 \text{ V} = +0.34 \text{ V}$$

(c) The Nernst equation, Equation 16.16, is

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{zF} \ln Q$$

As written, the reaction is a two electron process, so that $z = 2$. The reaction quotient is, using Equations 15.2 and 14.19

$$Q = \frac{a_{\text{Cu(s)}} a^2_{\text{H}^+(\text{aq})}}{a_{\text{Cu}^{2+}(\text{aq})} a_{\text{H}_2(\text{g})}} = \frac{[\text{H}^+(\text{aq})]^2}{[\text{Cu}^{2+}(\text{aq})] \times p_{\text{H}_2(\text{g})}} \times (p^{\ominus}/c^{\ominus})$$

and if it is assumed that the partial pressure of H_2 is

$$p_{\text{H}_2(\text{g})} = p^{\ominus} = 1 \text{ bar}$$

and the concentration of hydrogen ions is

$$[\text{H}^+(\text{aq})] = c^{\ominus} = 1 \text{ mol dm}^{-3}$$

then

$$Q = c^{\ominus}/[\text{Cu}^{2+}(\text{aq})]$$

if

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{zF} \ln Q$$

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{zF} \ln(c^{\ominus}/c)$$

and

$$-\ln(c^{\ominus}/c) = zF(E_{\text{cell}} - E^{\ominus}_{\text{cell}})/RT$$

$$\ln(c/c^{\ominus}) = zF(E_{\text{cell}} - E^{\ominus}_{\text{cell}})/RT$$

Thus,

$$c = e^{zF(E_{\text{cell}} - E^{\ominus}_{\text{cell}})/RT} c^{\ominus}$$

$$= e^{2 \times 96485 \text{ C mol}^{-1} \times (0.25 \text{ V} - 0.34 \text{ V})/8.3145 \text{ J K}^{-1}\text{mol}^{-1} \times 298 \text{ K}} \text{ mol dm}^{-3}$$

$$= 9.0 \times 10^{-4} \text{ mol dm}^{-3}$$

WE 16.8 Reacting quantities in electrolysis (on p. 759 in *Chemistry³*)

In the electrolysis of Na_2SO_4, O_2 (g) is produced at the anode. For how long would a current of 10 A need to pass in order to produce 0.50 g of O_2 (g) at the anode?

<u>Strategy</u>

Calculate the number of moles of O_2 (g) produced, and from the balanced equation calculate the number of moles of electrons needed. Use Faraday's constant to work out the charge of these electrons, and hence the time needed to pass this much charge with the stated current.

<u>Solution</u>

The number of moles of O_2 (g) in 0.50 g is given by

$$\frac{0.50 \text{ g}}{31.998 \text{ g mol}^{-1}} = 0.0156 \text{ mol}$$

One mole of O_2 (g) occurs with the passage of 4 electrons, according to the equation:

$$2H_2O \rightarrow O_2 + 4H^+ + 4 \text{ e}^-$$
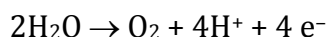
Therefore, the number of moles of electrons is

$$0.0156 \text{ mol} \times 4 = 0.0625 \text{ mol}$$

1 mol of electrons carries 96485 C of charge, therefore 0.0625 mol is equivalent to:

$$96485 \text{ C mol}^{-1} \times 0.0625 \text{ mol} = 6030 \text{ C}.$$

1 A = 1 C s^{-1}, therefore the time taken to pass this much charge is

$$\frac{6030 \text{ C}}{10 \text{ A}} = 603 \text{ s (approx. 10 min)}$$

Answers to boxes

Box 16.1 Ultrapure water and conductivity (on p. 733 in *Chemistry*³)

(a) Calculate the concentrations of $H^+(aq)$ and $OH^-(aq)$ in pure water.

(b) From data in Table 16.1, predict the molar conductivity, $\Lambda_m°$, of pure water.

(c) Calculate the conductivity, κ, of pure water in $\mu S\ cm^{-1}$.

(d) Assuming that the conductivity of a sample of water is all due to dissolved sodium chloride, calculate the concentration needed to give a solution with $\kappa = 100\ \mu S\ cm^{-1}$.

Strategy

Write an expression for the self-ionization constant of water in terms of the concentrations of the ions. Use Equation 16.8, the law of independent migration of ions, to determine the molar conductivity using the limiting values from Table 16.1. Rearrange Equation 16.7 to determine the concentration.

Solution

(a) The self-ionization constant

$$K_w = [H^+(aq)][OH^-(aq)] = 1 \times 10^{-14}\ mol^2 dm^{-6}$$

But, in water

$$[H^+(aq)] = [OH^-(aq)]$$

so that

$$K_w = [H^+(aq)]^2 = [OH^-(aq)]^2 = 1 \times 10^{-14}\ mol^2 dm^{-6}$$

and therefore

$$[H^+(aq)] = [OH^-(aq)] = \sqrt{1 \times 10^{-14}\ mol^2 dm^{-6}} = 1 \times 10^{-7} mol\ dm^{-3}$$

Remembering that

$$1\ m^3 = 10^3\ dm^3$$

then

$$[H^+(aq)] = [OH^-(aq)] = 1 \times 10^{-4} mol\ m^{-3}$$

(b) The concentrations of the ions are so low that it is reasonable to use the limiting molar conductivities, $\Lambda_m = \Lambda_m^o$, which are strictly only valid for infinite dilution. Thus, using Equation 16.8, and noting that the stoichiometric coefficients of the ions are $\nu_+ = 1$ and $\nu_- = 1$,

$$\Lambda_m^o = \nu_+\lambda_+ + \nu_-\lambda_-$$
$$= (1 \times 35.0 \times 10^{-3}\ \mathrm{S\ m^2\ mol^{-1}}) + (1 \times 19.9 \times 10^{-3}\ \mathrm{S\ m^2\ mol^{-1}})$$
$$= 54.9 \times 10^{-3}\ \ \mathrm{S\ m^2\ mol^{-1}}$$

(c) Rearranging Equation 16.7,

$$K = \Lambda \times c = 54.9 \times 10^{-3}\ \ \mathrm{S\ m^2\ mol^{-1}} \times 1 \times 10^{-4}\ \mathrm{mol\ m^{-3}}$$
$$= 5.49 \times 10^{-6}\ \mathrm{S\ m^{-1}} = 5.49\ \mu\mathrm{S\ m^{-1}} = 0.0549\ \mu\mathrm{S\ cm^{-1}}$$

(d) For NaCl, $\nu_+ = \nu_- = 1$ and assuming that the concentrations are sufficiently low that it is reasonable to use the limiting molar conductivities,

$$\Lambda_m \approx \Lambda_m^o = \nu_+\lambda_+ + \nu_-\lambda_-$$
$$= (\lambda_{Na^+} + \lambda_{Cl^-})$$
$$= 5.0 \times 10^{-3}\ \mathrm{S\ m^2\ mol^{-1}} + 7.6 \times 10^{-3}\ \mathrm{S\ m^2\ mol^{-1}}$$
$$= 12.6 \times 10^{-3}\ \mathrm{S\ m^2\ mol^{-1}}$$

Rearranging Equation 16.7, and noting that

$$100\ \mu\mathrm{S\ cm^{-1}} = 10^2 \times 10^{-6}\ \mathrm{S\ cm^{-1}} = 10^{-4}\ \mathrm{S\ cm^{-1}} = 1 \times 10^{-2}\ \mathrm{S\ m^{-1}}$$

then

$$c = K/\Lambda_m = 1 \times 10^{-2}\ \mu\mathrm{S\ cm^{-1}}/12.6 \times 10^{-3}\ \mathrm{S\ m^2\ mol^{-1}}$$
$$= 0.79\ \mathrm{mol\ m^{-3}} = 7.9 \times 10^{-4}\ \mathrm{mol\ dm^{-3}}$$

Box 16.3 Practical measurement of $E^\ominus$ values (on p. 745 in *Chemistry³*)

Calculate the cell potentials, $E^\ominus_{cell}$, at 25°C for the electrochemical cells

$$\mathrm{Zn\ (s) \mid Zn^{2+}\ (aq) \parallel reference\ half\ cell}$$

and

$$\mathrm{reference\ half\ cell \parallel Cu^{2+}\ (aq) \mid Cu\ (s)}$$
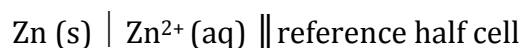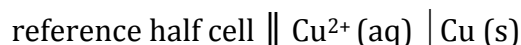
where the reference half cell is: (a) the standard hydrogen electrode; (b) the silver-silver chloride electrode. (c) Work out the *difference* between the values of $E^{\ominus}_{cell}$ for the two cells in (a) and the two cells in (b).

Strategy

Write the full form of the cells and use Equation 16.11, together with the data for the standard reduction potentials in Table 16.2, to determine the cell potentials.

Solution

(a) The potential of the cell is the difference between the cell potential of the two half cells. By convention, we denote the left-hand cell as the anode and the right-hand cell as the cathode. For the standard hydrogen electrode, $E^{\ominus}_{H^+,H_2} = 0$ V, so that, combining Equations 16.10 and 16.11, for the cell

$$Zn(s) \mid Zn^{2+} (aq) \parallel H^+(aq), H_2(g) \mid Pt\ (s)$$

$$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode} = E^{\ominus}_R - E^{\ominus}_L = E^{\ominus}_{H^+,H_2} - E^{\ominus}_{Zn^{2+},Zn}$$

$$= 0.00\ V - (-0.76\ V) = +0.76\ V$$

and

$$Pt(s) \mid H^+(aq), H_2(g) \parallel Cu^{2+}(aq) \mid Cu(s)$$

$$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode} = E^{\ominus}_R - E^{\ominus}_L = E^{\ominus}_{Cu^{2+},Cu} - E^{\ominus}_{H^+,H_2}$$

$$= +0.34\ V - 0.00\ V = +0.34\ V$$

so that the difference between the cell potentials is 0.42 V.

(b) In the same way, using a silver–silver chloride reference, for which $E^{\ominus}_{AgCl,Ag} = +0.22$ V

$$Zn(s) \mid Zn^{2+} (aq) \parallel Ag(s) \mid AgCl(s) \mid Cl^-(aq)$$

$$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode} = E^{\ominus}_R - E^{\ominus}_L = E^{\ominus}_{H^+,H_2} - E^{\ominus}_{Zn^{2+},Zn}$$

$$= 0.22\ V - (-0.76\ V) = +0.54\ V$$

and

$$Ag(s) \mid AgCl(s) \mid Cl^-(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$$

$$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode} = E^{\ominus}_R - E^{\ominus}_L = E^{\ominus}_{Cu^{2+},Cu} - E^{\ominus}_{H^+,H_2}$$

$$= +0.34\ V - 0.22\ V = +0.12\ V$$

so that the difference between the cell potentials is, as before, 0.42 V.

Box 16.4 Corrosion as an electrochemical process (on p. 751 in *Chemistry*[3])

(a) Suggest why rusting occurs much more readily in solutions containing dissolved electrolytes, for example in sea-water or in cars during the winter months when salt is spread onto roads?

(b) Which of the following: sodium, copper, tin, zinc, graphite could be used as sacrificial anodes for an iron structure?

Strategy

(a) Consider the effect of increasing the number of ions in solution on the conductivity and hence the reactivity of the solution.

(b) Use Table 16.2 to write the systems in the order in which they appear in the electrochemical series and hence determine which of the materials would be more reactive than iron.

Solution

(a) The presence of other ions from the sodium chloride in either sea water or during the winter months on roads increases the number of ions in solution. The increased ionic strength of the solution increases conductivity and allows a higher rate of reaction.

(b) Considering the standard reduction potentials in Table 16.2

$$E^{\ominus}_{Cu^{2+}/Cu} > E^{\ominus}_{Sn^{2+}/Sn} > E^{\ominus}_{Fe^{2+}/Fe} > E^{\ominus}_{Zn^{2+}/Zn} > E^{\ominus}_{Na^+/Na}$$

Thus, since both zinc and sodium are below iron in the electrochemical series, either could be used as a sacrificial electrode. In practice, the highly reactive nature of sodium makes its use difficult, so that zinc is most commonly used.

Box 16.5 Bioelectrochemistry: nerve cells and ion channels (on p. 754 in *Chemistry*[3])

(a) The intracellular concentration of Cl^- ions is 7 mmol dm^{-3}. If the membrane potential due to Cl^- is +76 mV, calculate the extracellular concentration of Cl^-.

(b) Calculate the Gibbs energy changes for the transport of K^+ ions and Na^+ ions

against the membrane potentials. Compare these with the energy available from the hydrolysis of ATP described in Box 14.8.

Strategy

(a) Rearrange the special form of the Nernst equation for concentration cells, Equation 16.18 and use it to determine the unknown concentration. Remember to use the physiological temperature, 37 °C = 310 K.

(b) Use the membrane potentials for transport of the ions across the cell membranes in Equation 16.14.

Solution

(a) For a concentration cell such as this, the standard cell potential, which is the cell potential when the cell is at equilibrium and the concentrations across the membrane are equal, is $E_{cell}^{\ominus} = 0$ V. The Nernst equation, Equation 16.17, therefore reduces to Equation 16.18

$$\Delta E_{Cl^-} = \frac{RT}{zF} \ln \frac{[Cl^-]_{outside}}{[Cl^-]_{inside}}$$

so that

$$\ln \frac{[Cl^-]_{outside}}{[Cl^-]_{inside}} = \ln([Cl^-]_{outside}/c^{\ominus}) - (\ln[Cl^-]_{inside}/c^{\ominus}) = \frac{zF\Delta E_{Cl^-}}{RT}$$

and therefore

$$\ln([Cl^-]_{outside}/c^{\ominus}) = \frac{zF\Delta E_{Cl^-}}{RT} + \ln([Cl^-]_{inside}/c^{\ominus})$$

$$= \frac{1 \times 96485 \text{ C mol}^{-1} \times +76.0 \times 10^{-3} \text{ V}}{8.3145 \text{ J K}^{-1}\text{mol}^{-1} \times 310 \text{ K}} + \ln(7 \times 10^{-3})$$

$$= -2.11$$

Thus

$$[Cl^-]_{outside} = e^{-2.11} c^{\ominus} = 0.120 \text{ mol dm}^{-3} = 120 \text{ mmol dm}^{-3}$$

(b) Using Equation 16.4 on p.725,

$$\Delta G_{K^+} = -zF\Delta E_{K^+} = -1 \times 96485 \text{ C mol}^{-1} \times (-0.090 \text{ V})$$

$$= +8.7 \times 10^3 \text{ J mol}^{-1} = +8.7 \text{ kJ mol}^{-1}$$

and

$$\Delta G_{Na^+} = -zF\Delta E_{Na^+} = -1 \times 96485 \text{ C mol}^{-1} \times (+0.062 \text{ V})$$
$$= -6.0 \times 10^3 \text{ J mol}^{-1} = -6.0 \text{ kJ mol}^{-1}$$

Box 16.6 Electrolysis and rechargeable batteries (on p. 759 in *Chemistry*[3])

(a) Draw cell diagrams for (i) the lead-acid battery and (ii) the nickel–metal hydride battery.
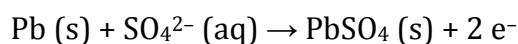
(b) What is the balanced equation for the overall cell reaction for the nickel–metal hydride battery?
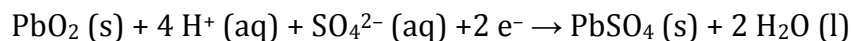
Strategy

Use the principles outlines on p. 734 to write the chemical reactions as electrochemical cell diagrams.
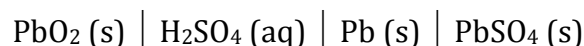
Solution

(a) The reaction at the anode, which, by convention, is the left-hand cell

$$\text{Pb (s) + SO}_4{}^{2-} \text{ (aq)} \rightarrow \text{PbSO}_4 \text{ (s) + 2 e}^-$$

and at the cathode, which forms the right-hand cell

$$\text{PbO}_2 \text{ (s) + 4 H}^+ \text{ (aq) + SO}_4{}^{2-} \text{ (aq) +2 e}^- \rightarrow \text{PbSO}_4 \text{ (s) + 2 H}_2\text{O (l)}$$

so that the cell may be written

$$\text{PbO}_2 \text{ (s)} \mid \text{H}_2\text{SO}_4 \text{ (aq)} \mid \text{Pb (s)} \mid \text{PbSO}_4 \text{ (s)}$$

with the H^+ (aq) and $SO_4{}^{2-}$ (aq) ions combined as H_2SO_4 (aq).

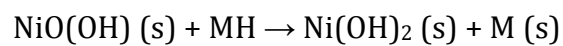In the same way, for the nickel–metal hydride system, the reaction at the anode is

$$\text{OH}^- \text{ (aq) + MH} \rightarrow \text{H}_2\text{O (l) + M (s) +e}^-$$

and at the cathode

$$\text{NiO(OH) (s) + H}_2\text{O (l) + e}^- \rightarrow \text{Ni(OH)}_2 \text{ (s) + OH}^-\text{(aq)}$$
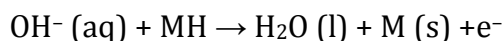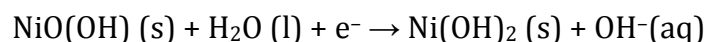
so that the combined cell may be written

$$\text{MH (s), M (s)} \mid \text{OH}^- \text{ (aq)} \mid \text{OH}^- \text{ (aq)} \mid \text{Ni (s), NiO(OH) (s), Ni(OH)}_2 \text{ (s)}$$
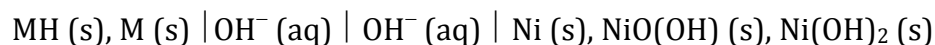
(b) Combing the two half reactions for the nickel–nickel metal hydride cell into a single chemical equation gives

$$NiO(OH) \text{ (s)} + MH \rightarrow Ni(OH)_2 \text{ (s)} + M \text{ (s)}$$

Answers to end of chapter questions

(You will need to use standard reduction potentials, $E^{\ominus}$, from Table 16.2 on p.738)

1. (a) Use the data in Table 16.1 to calculate the limiting molar conductivities of magnesium sulfate and sodium carbonate in water.

(b) Estimate the conductivity of a solution of magnesium sulfate with a concentration of 1×10^{-5} mol dm^{-3}. (Section 16.2)

Strategy

From the chemical formulae of the compounds, you can work out how many of each type of ion forms when it dissolves in water and multiply these by the values of Λ° taken from Table 16.1.

Solution

(a) Find the number of ions formed when the salt dissolves.

Magnesium sulfate:

$MgSO_4$ forms one Mg^{2+} (aq) cation and one $SO_4{}^{2-}$ (aq) anion. $\nu_+ = 1$; $\nu_- = 1$.

Sodium carbonate:

Na_2CO_3 forms two Na^+ (aq) cations and one $CO_3{}^{2-}$ (aq) anion. $\nu_+ = 2$; $\nu_- = 1$.

Multiply by the ionic conductivities from Table 16.1

$$\Lambda_m{}^{\circ} = \nu_+ \times \lambda_+ + \nu_- \times \lambda_-$$

$MgSO_4$: $\Lambda_m{}^{\circ} = (1 \times 10.6 \text{ mS m}^2 \text{ mol}^{-1}) + (1 \times 13.9 \text{ mS m}^2 \text{ mol}^{-1})$

$$\Lambda_m{}^{\circ} = 24.5 \text{ mS m}^2 \text{ mol}^{-1}$$

Na_2CO_3 : $\Lambda_m{}^{\circ} = (2 \times 5.0 \text{ mS m}^2 \text{ mol}^{-1}) + (1 \times 17.0 \text{ mS m}^2 \text{ mol}^{-1})$

$$\Lambda_m{}^{\circ} = 27.0 \text{ mS m}^2 \text{ mol}^{-1}$$

(b) Calculate the conductivity using Equation 16.7. The solution is dilute so that it may be assumed that the molar conductivity is given by its limiting infinite dilution value.

$$\Lambda_m = \frac{\kappa}{c} \quad \text{so that conductivity,} \quad \kappa = \Lambda_m{}^{\circ} \times c$$

SI units are needed so the concentration must be converted using 1 $mol\ dm^{-3}$ = 1 × 10^3 $mol\ m^{-3}$.

$$\kappa = \Lambda_m° \times c\ = 24.5\ mS\ m^2\ mol^{-1} \times 1 \times 10^{-2}\ mol\ m^{-3}$$

$$\kappa = 24.5 \times 10^{-2}\ mS\ m^{-1} = 0.245\ S\ m^{-1}$$

2. The conductivity of a saturated solution of silver chloride at 25°C is 1.89 × 10^{-4} S m^{-1}. Given that the molar conductivities at infinite dilution of KCl(aq), KNO_3(aq) and $AgNO_3$(aq) are 15.0 $mS\ m^2\ mol^{-1}$, 14.6 $mS\ m^2\ mol^{-1}$ and 13.4 $mS\ m^2\ mol^{-1}$, calculate the solubility product of AgCl in water at 25°C. (Section 16.2)

Strategy

AgCl is sparingly soluble, so that you can assume that the molar conductivity is given by its value at infinite dilution. $\Lambda_{AgCl} = \Lambda°_{AgCl}$. From the molar conductivity you can find the concentration of Ag^+ and Cl^-, then use these to find the solubility product.

Solution

(1) $\Lambda°_{KCl} = \lambda_{K+} + \lambda_{Cl-} = 15.0\ mS\ m^2\ mol^{-1}$

(2) $\Lambda°_{KNO3} = \lambda_{K+} + \lambda_{NO3-} = 14.6\ mS\ m^2\ mol^{-1}$

(3) $\Lambda°_{AgNO3} = \lambda_{Ag+} + \lambda_{NO3-} = 13.4\ mS\ m^2\ mol^{-1}$

You need the value for AgCl. This can be found by eliminating the values for K^+ and NO_3^-.

(1) + (3) − (2):

$(\cancel{\lambda_{K+}} + \lambda_{Cl-}) + (\lambda_{Ag+} + \cancel{\lambda_{NO3-}}) - (\cancel{\lambda_{K+}} + \cancel{\lambda_{NO3-}}) = (\lambda_{Ag+} \lambda_{Cl-}) = \Lambda°_{AgCl}$

$\Lambda°_{AgCl}$ = (15.0 + 13.4 − 14.6) $mS\ m^2\ mol^{-1}$ = 13.8 $mS\ m^2\ mol^{-1}$

You can find the concentration of the saturated solution of AgCl from the conductivity, κ.

$$\Lambda_m = \frac{\kappa}{c} \quad \text{or} \quad c = \frac{\kappa}{\Lambda_m}$$

$$c = \frac{\kappa}{\Lambda_m} = \frac{1.89 \times 10^{-4}\,\text{S m}^{-1}}{13.8 \times 10^{-3}\,\text{S m}^2\,\text{mol}^{-1}}$$

$c = 0.0137$ mol m^{-3} = 1.37×10^{-5} mol dm^{-3}. This is the concentration of

both Ag$^+$ and Cl$^-$.

$$K_s = a_{\text{Ag}^+} \times a_{\text{Cl}^-} = [\text{Ag}^+]/1 \text{ mol dm}^{-3} \times [\text{Cl}^-] / 1 \text{ mol dm}^{-3} = (1.37 \times 10^{-5})^2$$

$K_s = (1.37 \times 10^{-5})^2 = 1.88 \times 10^{-10}$

3. Consider the cell

Al(s)|Al^{3+}(aq)||Au^{3+}(aq)|Au(s)

(a) At which electrode does reduction occur?

(b) Which electrode is the anode?

(c) Which electrode will lose mass in the cell reaction?

(d) To which electrode will cations migrate?

(e) Which substance is acting as a reducing agent?

(f) Write the half reaction for the gold half cell.

(g) Calculate a value for $E^\ominus_{\text{cell.}}$

(Section 16.3)

Strategy

Apply the cell conventions given.

Solution

(a) Reduction, i.e. gain of electrons, occurs at the cathode which is the right-hand

side of the cell diagram, which in this case is the Au^{3+} (aq) / Au (s) system.

(b) The left-hand electrode which in this example is the Al^{3+} (aq) / Al (s) system

is, by convention, the anode, which is where oxidation occurs.

(c) At the anode, aluminium metal, Al (s) is converted to aqueous aluminium (III) ions, Al^{3+} (aq), and so loses mass. In contrast, at the cathode, gold ions from solution, Au^{3+} (aq), are deposited at the electrode to form more gold metal, Au (s).

(d) Cations migrate toward the cathode i.e. to the gold electrode.

(e) The gold ions, Au^{3+} (aq) gain electrons to become gold metal, Au (s) and so being reduced

$$Au^{3+} \text{ (aq)} + 3 \text{ e}^- \rightarrow Au \text{ (s)}$$
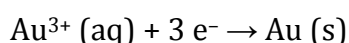
The solid aluminium, Al (s), which loses the electrons

$$Al \text{ (s)} \rightarrow Al^{3+} \text{ (aq)} + 3 \text{ e}^-$$
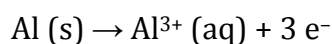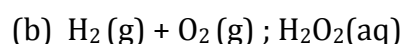
is therefore acting as a reducing agent.

(f) $\qquad\qquad\qquad\qquad Au^{3+} \text{ (aq)} + 3 \text{ e}^- \rightarrow Au \text{ (s)}$

(g) Using Equations 16.10 and 16.11

$$E_{cell}^{\ominus} = E_{cathode}^{\ominus} - E_{anode}^{\ominus} = E_R^{\ominus} - E_L^{\ominus} = E_{Au^{3+},Au}^{\ominus} - E_{Al^{3+},Al}^{\ominus}$$
$$= +1.50 \text{ V} - (-1.66 \text{ V}) = +3.16 \text{ V}$$

4.   Draw cell diagrams for electrochemical cells that use the following reactions:

(a) Cd(s) + Sn^{2+} (aq) ; Sn(s) + Cd^{2+}(aq)

(b) H_2 (g) + O_2 (g) ; H_2O_2(aq)

(c) Br_2 (aq) + Sn^{2+}(aq) ; Sn^{4+}(aq) + $2Br^-$ (aq)

(d) Cu^{2+} (aq) + 2Ag(s) + $2Br^-$ (aq) ; Cu(s) + 2AgBr(s)

(e) MnO_4^-(aq) + $8H^+$ (aq) + $5Fe^{2+}$ (aq) ; Mn^{2+} (aq) + $4H_2O$(l) + $5Fe^{3+}$(aq)
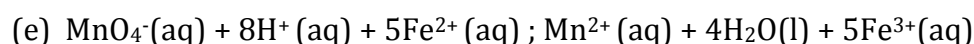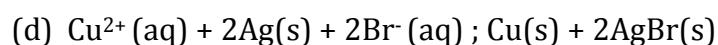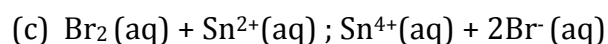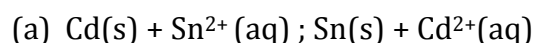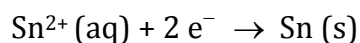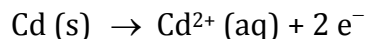
(Section 16.3)

Strategy

Write the two half cell reactions and use Table 16.2 to identify the oxidation and reduction reactions. Remember that the half cell with the most negative standard reduction potential will be the oxidation process and that with the most positive standard reduction potential the reduction process. Write the oxidation

reaction, which forms the anode, as the left-hand cell, and the reduction reactions, which is the cathode as the right-hand cell.

Solution

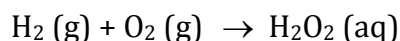(a) $\qquad$ Cd (s) + Sn²⁺ (aq) $\rightarrow$ Sn (s) + Cd²⁺ (aq)
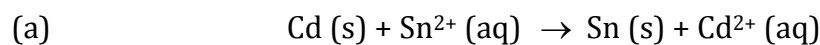
The two half-cell reactions are

$$Cd \text{ (s)} \rightarrow Cd^{2+} \text{ (aq)} + 2 \ e^-$$

$$Sn^{2+} \text{ (aq)} + 2 \ e^- \rightarrow Sn \text{ (s)}$$

Consulting Table 16.2, $E^{\ominus}_{Sn^{2+}/Sn} > E^{\ominus}_{Cd^{2+}/Cd}$ so that the cadmium system, Cd (s) $|$ Cd²⁺ (aq), must be the anode, where oxidation occurs, and the tin system, Sn²⁺ (aq) $|$ Sn (s), the cathode, where reduction occurs. Putting the two halves together, joined by a salt bridge, gives

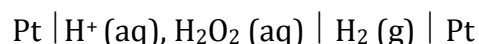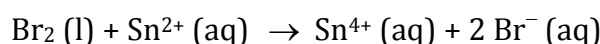$$Cd \text{ (s)} \mid Cd^{2+} \text{ (aq)} \parallel Sn^{2+} \text{ (aq)} \mid Sn \text{ (s)}$$

(b) In the same way for

$$H_2 \text{ (g)} + O_2 \text{ (g)} \rightarrow H_2O_2 \text{ (aq)}$$

then the two half cell reactions are

$$2 \ H_2O \text{ (l)} \rightarrow 2 \ H^+ \text{ (aq)} + 2 \ e^- + H_2O_2 \text{ (aq)}$$

$$2 \ H^+ \text{ (aq)} + 2 \ e^- \rightarrow H_2 \text{ (g)}$$
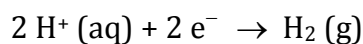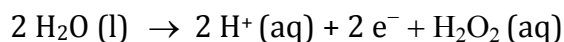
so that, because $E^{\ominus}_{H^+/H_2} > E^{\ominus}_{H^+/H_2O_2}$, so that the Pt $|$ H₂O (l), H⁺ (aq), H₂O₂ (aq) system forms the anode, and the 2 H⁺ (aq) $|$ H₂ (g) $|$ Pt the cathode. Combining then gives

$$Pt \mid H^+ \text{ (aq)}, H_2O_2 \text{ (aq)} \mid H_2 \text{ (g)} \mid Pt$$

(c) For

$$Br_2 \text{ (l)} + Sn^{2+} \text{ (aq)} \rightarrow Sn^{4+} \text{ (aq)} + 2 \ Br^- \text{ (aq)}$$

so that the two half cells are

$$Sn^{2+} \text{ (aq)} \rightarrow Sn^{4+} \text{ (aq)} + 2 \ e^-$$

$$Br_2 \text{ (l)} + 2 \ e^- \rightarrow 2 \ Br^- \text{ (aq)}$$
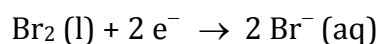
and, because $E^{\ominus}_{Br_2/Br^-} > E^{\ominus}_{Sn^{2+}/Sn}$, then the Pt $|$ Sn²⁺ (aq), Sn⁴⁺ (aq) system must be the left-hand anode, where oxidation occurs and the Br₂ (l), Br⁻ (aq)$|$Pt system the right-hand cathode where reduction occurs. Thus, putting the two halves together, joined by a salt bridge

$$Pt \mid Sn^{2+} (aq), Sn^{4+} (aq) \parallel Br_2 (l), Br^- (aq) \mid Pt$$

(d) For

$$Cu^{2+} (aq) + 2 Ag (s) + 2 Br^- (aq) \rightarrow Cu (s) + 2 AgBr (s)$$

then the two half cells are

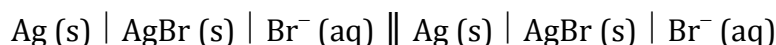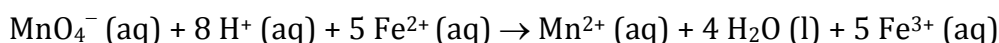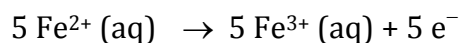$$2 Ag (s) + 2 Br^- (aq) \rightarrow 2 AgBr (s) + 2 e^-$$

$$Cu^{2+} (aq) + 2 e^- \rightarrow Cu (s)$$
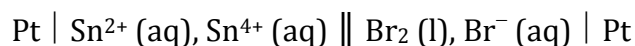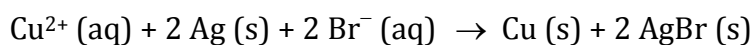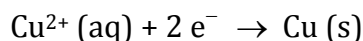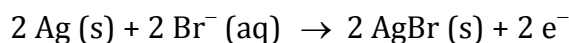
with, since $E^{\ominus}_{Cu^{2+}/Cu} > E^{\ominus}_{AgBr/Ag}$, the Ag (s) $\mid$ AgBr (s) $\mid$ Br$^-$ (aq) cell the left-hand anode

and the Ag (s) $\mid$ AgBr (s) $\mid$ Br$^-$ (aq) cell the right-hand cathode. Thus, combining the

two hal;f cells using a salt bridge,

$$Ag (s) \mid AgBr (s) \mid Br^- (aq) \parallel Ag (s) \mid AgBr (s) \mid Br^- (aq)$$

(e) For the cell,

$$MnO_4^- (aq) + 8 H^+ (aq) + 5 Fe^{2+} (aq) \rightarrow Mn^{2+} (aq) + 4 H_2O (l) + 5 Fe^{3+} (aq)$$

then the half cells are

$$MnO_4^- (aq) + 8 H^+ (aq) + 5 e^- \rightarrow Mn^{2+} (aq) + 4 H_2O (l)$$

$$5 Fe^{2+} (aq) \rightarrow 5 Fe^{3+} (aq) + 5 e^-$$
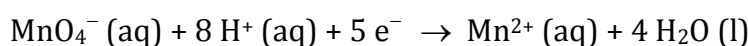
Because $E^{\ominus}_{MnO_4^-/Mn^{2+}} > E^{\ominus}_{Fe^{3+}/Fe^{2+}}$, then the anode, where oxidation occurs is the

Pt $\mid$ Fe^{2+} (aq), Fe^{3+} (aq) system and the cathode, where reduction occurs is

MnO$_4^-$ (aq), H$^+$ (aq), Mn^{2+} (aq) $\mid$ Pt. Putting the two halves together, joined by a salt

bridge,

$$Pt \mid Fe^{2+} (aq), Fe^{3+} (aq) \parallel MnO_4^- (aq), H^+ (aq), Mn^{2+} (aq) \mid Pt$$
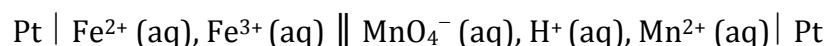
5. For each of the following electrochemical cells:

(i) write the half cell reactions; (ii) calculate $E^{\ominus}_{cell}$.

(a) Fe(s)|Fe^{2+}(aq)||Zn^{2+}(aq)|Zn(s)

(b) Pt(s)|H$_2$(g), H$^+$(aq)||Cl$^-$(aq), AgCl(s)|Ag(s)

(c) Hg(l)|Hg$_2$Cl$_2$(s), Cl$^-$(aq)||Cl$^-$(aq), AgCl(s)|Ag(s)

(d) Pt(s)|Fe^{2+}(aq), Fe^{3+}(aq)||Sn^{4+}(aq), Sn^{2+}(aq)|Pt(s)
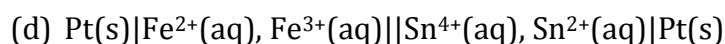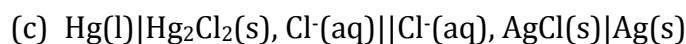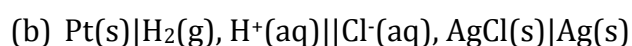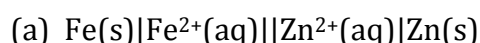
(Section 16.3)

Strategy

Identify the half-cell reactions and use Table 16.2 to find the appropriate standard reduction potential. Calculate the standard potential for the complete cell by subtracting the standard reduction potential for the left-hand cell from that for the right-hand cell according to Equation 16.11.

Solution

(a) The two half cells are

Left, oxidation, anode

$$\text{Fe (s)} \rightarrow \text{Fe}^{2+} \text{ (aq)} + 2 \text{ e}^- \qquad E_L^\ominus = -0.44 \text{ V}$$

Right, reduction, cathode

$$\text{Zn}^{2+} \text{ (aq)} + 2 \text{ e}^- \rightarrow \text{Zn (s)} \qquad E_R^\ominus = -0.76 \text{ V}$$

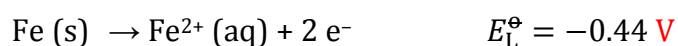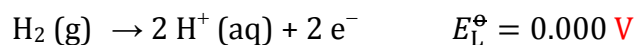so that, using Equation 16.11,

$$E_{cell}^\ominus = E_R^\ominus - E_L^\ominus = -0.76 \text{ V} - (-0.44 \text{ V}) = -0.32 \text{ V}$$

(b) The two half cells are

Left, oxidation, anode

$$\text{H}_2 \text{ (g)} \rightarrow 2 \text{ H}^+ \text{ (aq)} + 2 \text{ e}^- \qquad E_L^\ominus = 0.000 \text{ V}$$

Right, reduction, cathode

$$2 \text{ AgCl (s)} + 2 \text{ e}^- \rightarrow 2 \text{ Ag (s)} + 2 \text{ Cl}^- \text{ (aq)} \quad E_R^\ominus = +0.22 \text{ V}$$
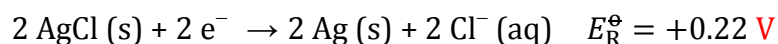
so that, using Equation 16.11,

$$E_{cell}^\ominus = E_R^\ominus - E_L^\ominus = +0.22 \text{ V} - 0 \text{ V} = +0.22 \text{ V}$$

(c) The two half cells are

Left, oxidation, anode

$$2 \text{ Hg (l)} + 2 \text{ Cl}^- \text{ (aq)} \rightarrow \text{Hg}_2\text{Cl}_2 \text{ (s)} + 2 \text{ e}^- \qquad E_L^\ominus = +0.27 \text{ V}$$

Right, reduction, cathode

$$2 \text{ AgCl (s)} + 2 \text{ e}^- \rightarrow 2 \text{ Ag (s)} + 2 \text{ Cl}^- \text{ (aq)} \quad E_R^\ominus = +0.22 \text{ V}$$
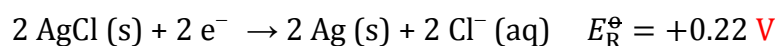
so that, using Equation 16.11,
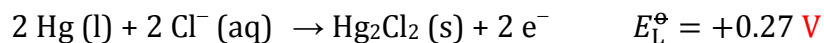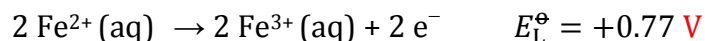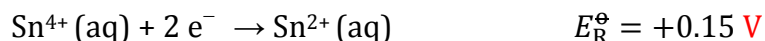
$$E_{cell}^\ominus = E_R^\ominus - E_L^\ominus = +0.22 \text{ V} - 0.27 \text{ V} = -0.05 \text{ V}$$

(d) The two half cells are

Left, oxidation, anode

$$2\ Fe^{2+}\,(aq)\ \rightarrow 2\ Fe^{3+}\,(aq) + 2\ e^- \qquad E_L^\ominus = +0.77\ V$$

Right, reduction, cathode

$$Sn^{4+}\,(aq) + 2\ e^-\ \rightarrow Sn^{2+}\,(aq) \qquad\qquad E_R^\ominus = +0.15\ V$$

so that, using Equation 16.11,

$$E_{cell}^\ominus = E_R^\ominus - E_L^\ominus = +0.15\ V - 0.77\ V = -0.62\ V$$

6. Which of the following is the strongest oxidising agent?

(a) H_2O_2 in acid solution

(b) H_2O_2 in basic solution

(c) MnO_4^- in acid solution

(d) MnO_4^- in basic solution

(e) CrO_4^{2-} in acid solution.

(Section 16.3)

Strategy

The relative ability of a system as an oxidising agent is measured by its E^o value.
The more positive the E^o value, the better the oxidising agent.

Solution

Examine the E^o values and find the most positive value.

(a) $H_2O_2 + 2\ H^+ + 2\ e^- \rightleftharpoons 2\ H_2O$	E^o = 1.77 V
(b) $H_2O_2 + 2\ e^- \rightleftharpoons 2\ OH^-$	E^o = 0.88 V
(c) $MnO_4^- + 8\ H^+ + 5\ e^- \rightleftharpoons Mn^{2+} + 4\ H_2O$	E^o = 1.52 V
(d) $MnO_4^- + 2\ H_2O + 3\ e^- \rightleftharpoons MnO_2 + 4\ OH^-$	E^o = 0.59 V
(e) $CrO_4^{2-} + 8\ H^+ + 3\ e^- \rightleftharpoons Cr^{3+} + 4\ H_2O$	E^o = 1.20 V
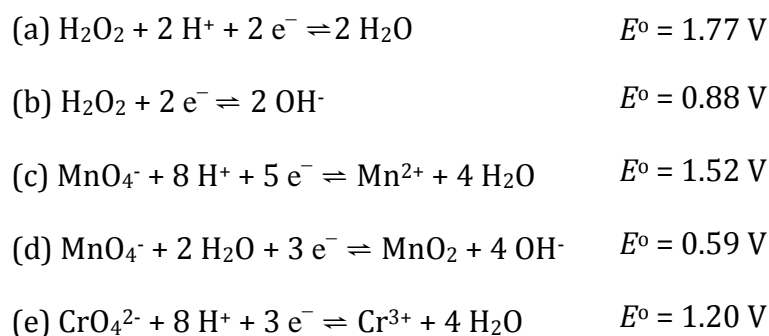
From these data, the strongest oxidising agent is H_2O_2 in acid.

7. Using standard reduction potentials, explain why copper metal does not dissolve in 1 mol dm^{-3} hydrochloric acid (HCl (aq)) but does dissolve in 1 mol dm^{-3} nitric acid (HNO$_3$(aq)). (Section 16.3)

<u>Strategy</u>

You need to write the half-reactions that might occur for the species involved. Then consider their $E^\ominus$ values and decide which reactions will take place under standard conditions.
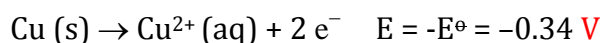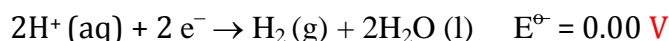
<u>Solution</u>

For copper to dissolve, the following reaction has to proceed.

$$Cu\ (s) \rightarrow Cu^{2+}\ (aq) + 2\ e^- \quad E = -E^\ominus = -0.34\ V$$

In hydrochloric acid, the reaction to consume the electrons produced is:

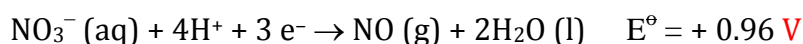$$2H^+\ (aq) + 2\ e^- \rightarrow H_2\ (g) + 2H_2O\ (l) \quad E^\ominus = 0.00\ V$$

The overall cell potential is therefore

$$E^\ominus{}_{cell} = (-0.34\ V) + 0.00\ V = -0.034\ V$$

The cell potential is negative so that the **reaction is not spontaneous**.

However, in nitric acid, an alternative reaction is possible

$$NO_3{}^-\ (aq) + 4H^+ + 3\ e^- \rightarrow NO\ (g) + 2H_2O\ (l) \quad E^\ominus = +0.96\ V$$

The overall reaction here is:

$$3Cu\ (s) + 2NO_3{}^-\ (aq) + 8H^+ + 6\ e^- \rightarrow 3Cu^{2+}\ (aq) + 6\ e^- + 2NO\ (g) + 4H_2O\ (l)$$
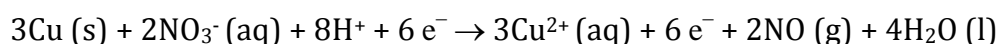
For which the overall cell potential is given by:
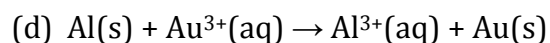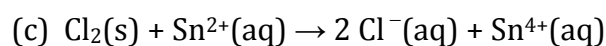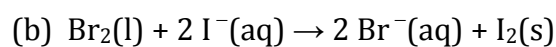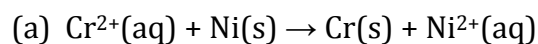
$$E^\ominus{}_{cell} = (-0.34\ V) + 0.96\ V = +0.62\ V$$

Here, the cell potential is positive so that the **reaction is spontaneous**. The reduction of $NO_3{}^-$ to NO gas is sufficient to oxidise the copper metal.

8. Use values of standard reduction potentials, $E^{\ominus}$ in Table 16.2, to decide whether the following reactions occur spontaneously.

(a) $Cr^{2+}(aq) + Ni(s) \rightarrow Cr(s) + Ni^{2+}(aq)$

(b) $Br_2(l) + 2\,I^-(aq) \rightarrow 2\,Br^-(aq) + I_2(s)$

(c) $Cl_2(s) + Sn^{2+}(aq) \rightarrow 2\,Cl^-(aq) + Sn^{4+}(aq)$

(d) $Al(s) + Au^{3+}(aq) \rightarrow Al^{3+}(aq) + Au(s)$
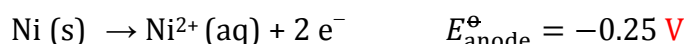
(Section 16.3)

<u>Strategy</u>

Identify the two half-cell reactions from the chemical equation. Use Table 16.2 to find the standard reduction potentials for the half cells and use Equation 16.11 to determine the cell potential, with a positive standard cell potential indicating that the reaction as written will be spontaneous.

<u>Solution</u>

(a) The reaction

$$Cr^{2+}(aq) + Ni\,(s) \rightarrow Cr\,(s) + Ni^{2+}(aq)$$
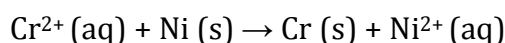
may be written as two half reactions. The first half reaction is an oxidation process, so may be designated as the conventional anode, whilst the second is a reduction and so forms at the cathode.

$$Ni\,(s) \rightarrow Ni^{2+}(aq) + 2\,e^- \qquad E^{\ominus}_{anode} = -0.25\text{ V}$$
$$Cr^{2+}(aq) + 2\,e^- \rightarrow Cr\,(s) \qquad E^{\ominus}_{cathode} = -0.91\text{ V}$$

so that the cell potential for the combined cell is

$$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode} = -0.91\text{ V} - (-0.25\text{ V}) = -0.66\text{ V}$$

Since $E^{\ominus}_{cell} < 0$, the reaction will not be spontaneous, because, according to Equation 16.14, a negative cell potential implies a positive standard Gibbs energy change for the reaction.

(b) In the same way,

$$Br_2\,(l) + 2\,I^-(aq) \rightarrow 2\,Br^-(aq) + I_2\,(s)$$

may be written as

$$2\,I^-\,(aq)\ \rightarrow I_2\,(s) + 2\,e^- \qquad\qquad E^{\ominus}_{anode} = +0.54\ V$$

$$Br_2\,(l) + 2\,e^-\ \rightarrow 2\,Br^-\,(aq) \qquad\qquad E^{\ominus}_{cathode} = +1.08\ V$$
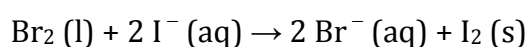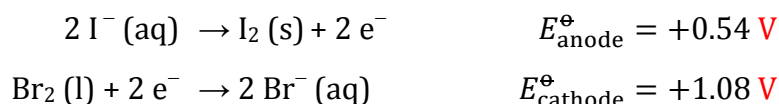
with

$$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode} = +1.08\ V - 0.54\ V = +0.54\ V$$

The standard cell potential is positive, so the reaction is spontaneous as written.

(c) The reaction

$$Cl_2\,(s) + Sn^{2+}\,(aq) \rightarrow 2\,Cl^-\,(aq) + Sn^{4+}\,(aq)$$

may be written as

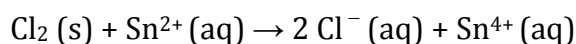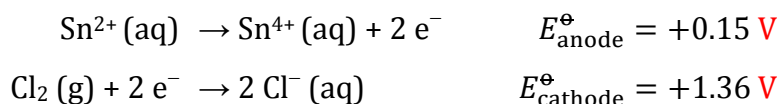$$Sn^{2+}\,(aq)\ \rightarrow Sn^{4+}\,(aq) + 2\,e^- \qquad\qquad E^{\ominus}_{anode} = +0.15\ V$$

$$Cl_2\,(g) + 2\,e^-\ \rightarrow 2\,Cl^-\,(aq) \qquad\qquad E^{\ominus}_{cathode} = +1.36\ V$$

with

$$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode} = +1.36\ V - 0.15\ V = +1.21\ V$$

The standard cell potential is positive, so the reaction is spontaneous as written.

(d) The reaction

$$Al\,(s) + Au^{3+}\,(aq) \rightarrow Al^{3+}\,(aq) + Au\,(s)$$

may be written as

$$Al\,(s)\ \rightarrow Al^{3+}\,(aq) + 3\,e^- \qquad\qquad E^{\ominus}_{anode} = -1.66\ V$$

$$Au^{3+}\,(aq) + 3\,e^-\ \rightarrow Au\,(s) \qquad\qquad E^{\ominus}_{cathode} = +1.50\ V$$
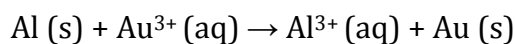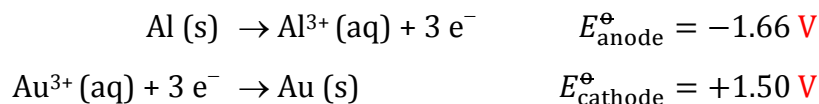
with

$$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode} = +1.50\ V - (-1.66\ V) = +3.16\ V$$

The standard cell potential is positive, so the reaction is spontaneous as written.

9. Silver articles sometimes become tarnished with a black coating of Ag_2S. The tarnish can be removed by placing the silverware in an aluminium pan and covering it with a solution of an inert electrolyte such as NaCl. Explain the electrochemical basis for this procedure. (Section 16.3)

Strategy

Consider the relative positions of the Al(s)/Al³⁺ (aq) and Ag₂S(s)/Ag⁺ (aq) in the electrochemical series.

Solution

The Al(s)/Al³⁺(aq) half cell has $E^{\ominus}_{cell}$ = 1.66 V so it is quite highly reducing. It can reduce Ag₂S to Ag⁺ (aq), for which the standard electrode potential is $E^{\ominus}_{cell}$ = − 0.64 V and so dissolve the tarnish. The silver and aluminium establish an electrochemical cell with the electrolyte solution as the salt bridge.

10. Use data from Table 16.2 to calculate the standard Gibbs energy change $\Delta_r G^{\ominus}$, and the thermodynamic equilibrium constant, K, at 298 K for the reactions:

(a) Mg (s) + Zn²⁺ (aq) → Zn (s) + Mg²⁺ (aq)

(b) Cl₂ (g) + 2 I⁻ (aq) → I₂ (s) + 2 Cl⁻ (aq)

(c) Cr₂O₇²⁻(aq) + 3 Fe(s) + 14 H₃O⁺ (aq) → 2 Cr³⁺(aq) + 3 Fe²⁺(aq) + 21 H₂O(l)

(d) 2 Br⁻ (aq) + Cl₂ (g) → Br₂ (l) + 2 Cl⁻ (aq)

(Section 16.4)

Strategy

Identify the half reactions and use Table 16.2 to calculate the cell potential for the overall reaction. Then use Equation 16.14 to determine the standard Gibbs energy change and Equation 16.15 the equilibrium constant at 298 K.

Solution

(a) The reaction

$$Mg\ (s) + Zn^{2+}\ (aq) \rightarrow Zn\ (s) + Mg^{2+}\ (aq)$$

may be written as

$$Mg\ (s) \rightarrow Mg^{2+}\ (aq) + 2\ e^{-} \qquad E^{\ominus}_{anode} = -2.37\ V$$
$$Zn^{2+}\ (aq) + 2\ e^{-} \rightarrow Zn\ (s) \qquad E^{\ominus}_{cathode} = -0.76\ V$$
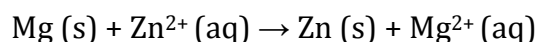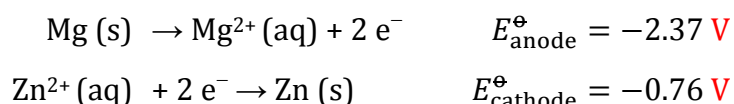
where the Mg²⁺/Mg half cell is the anode, because the magnesium metal loses electrons and so is oxidised. Thus,
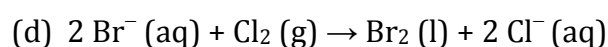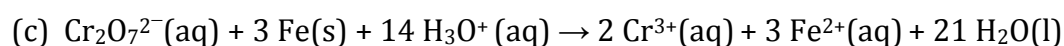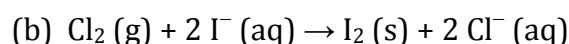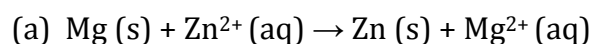
$$E_{cell}^{\ominus} = E_{cathode}^{\ominus} - E_{anode}^{\ominus} = -0.76 \text{ V} - (-2.37 \text{ V}) = +1.61 \text{ V}$$

Using Equation 16.14 to calculate the standard Gibbs energy change, and noting that the half-cell reactions are two-electron processes, so that $z = 2$,

$$\Delta_r G^{\ominus} = -zFE_{cell}^{\ominus}$$
$$= -2 \times 96485 \text{ C mol}^{-1} \times +1.61 \text{ V}$$
$$= -310.7 \times 10^3 \text{ J mol}^{-1} = -310.7 \text{ kJ mol}^{-1}$$

The equilibrium constant is then, from Equation 16.15,

$$\ln K = \frac{zF}{RT} E_{cell}^{\ominus} = \frac{2 \times 96485 \text{ C mol}^{-1}}{8.3145 \text{ J K}^{-1}\text{mol}^{-1} \times 298 \text{ K}} \times 1.61 \text{ V} = 125$$

so that

$$K = e^{125} = 2.9 \times 10^{54}$$

(b) In the same way, the reaction

$$\text{Cl}_2 \text{ (g)} + 2 \text{ I}^- \text{ (aq)} \rightarrow \text{I}_2 \text{ (s)} + 2 \text{ Cl}^- \text{ (aq)}$$

may be written as

$$\text{Cl}_2 \text{ (g)} \rightarrow 2 \text{ Cl}^- \text{ (aq)} + 2 \text{ e}^- \qquad E_{anode}^{\ominus} = +1.36 \text{ V}$$
$$2 \text{ I}^- \text{ (aq)} + 2 \text{ e}^- \rightarrow \text{I}_2 \text{ (s)} \qquad E_{cathode}^{\ominus} = +0.54 \text{ V}$$

where the Cl_2/Cl^- half cell is the anode, because the chloride ions lose electrons and so are oxidised. Thus,

$$E_{cell}^{\ominus} = E_{cathode}^{\ominus} - E_{anode}^{\ominus} = +0.54 \text{ V} - 1.36 \text{ V} = -0.82 \text{ V}$$

Using Equation 16.14 to calculate the standard Gibbs energy change, and noting that the half-cell reactions are two-electron processes, so that $z = 2$,

$$\Delta_r G^{\ominus} = -zFE_{cell}^{\ominus}$$
$$= -2 \times 96485 \text{ C mol}^{-1} \times -0.82 \text{ V}$$
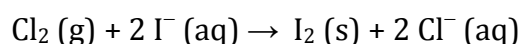$$= +158.2 \times 10^3 \text{ J mol}^{-1} = +158.2 \text{ kJ mol}^{-1}$$

The equilibrium constant is then, from Equation 16.15,

$$\ln K = \frac{zF}{RT} E_{cell}^{\ominus} = \frac{2 \times 96485 \text{ C mol}^{-1}}{8.3145 \text{ J K}^{-1}\text{mol}^{-1} \times 298 \text{ K}} \times -0.82 \text{ V} = -64$$
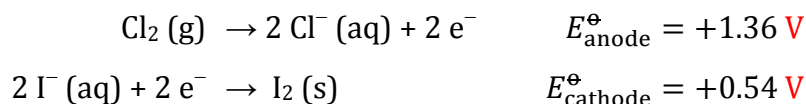
so that

$$K = e^{-64} = 1.8 \times 10^{-28}$$

The position of equilibrium therefore favours the formation of Cl_2 (g) and I^-(aq) ions.

(c) The reaction

$Cr_2O_7{}^{2-}$ (aq) + 3 Fe(s) + 14 H_3O^+ (aq) $\rightarrow$ 2 Cr^{3+} (aq) + 3 Fe^{2+} (aq) + 21 H_2O

may be written as

$$3 \text{ Fe(s)} \rightarrow 3 \text{ Fe}^{2+} \text{(aq)} + 6 \text{ e}^- \qquad E_{anode}^{\ominus} = -0.44 \text{ V}$$

$$Cr_2O_7{}^{2-} \text{ (aq)} + 14 \text{ H}_3O^+ \text{(aq)} + 6e^- \rightarrow 2 \text{ Cr}^{3+} \text{(aq)} + 21 \text{ H}_2O \text{ (l)} \quad E_{cathode}^{\ominus} = +1.33 \text{ V}$$

where the Fe^{2+}/Fe half cell is the anode, because the iron loses electrons and so is oxidised. Thus,

$$E_{cell}^{\ominus} = E_{cathode}^{\ominus} - E_{anode}^{\ominus} = +1.33 \text{ V} - (-0.44 \text{ V}) = +1.77 \text{ V}$$

Using Equation 16.14 to calculate the standard Gibbs energy change, and noting that the half-cell reactions are six-electron processes, so that $z = 6$,

$$\Delta_r G^{\ominus} = -zFE_{cell}^{\ominus}$$
$$= -6 \times 96485 \text{ C mol}^{-1} \times 1.77 \text{ V}$$
$$= -1024.7 \times 10^3 \text{J mol}^{-1} = -1024.7 \text{ kJ mol}^{-1}$$
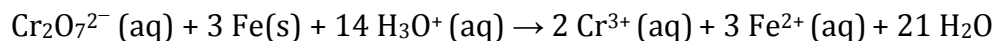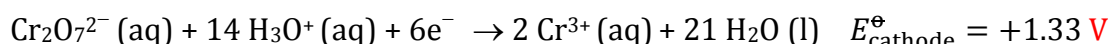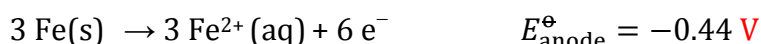
The equilibrium constant is then, from Equation 16.15,

$$\ln K = \frac{zF}{RT}E_{cell}^{\ominus} = \frac{6 \times 96485 \text{ C mol}^{-1}}{8.3145 \text{ J K}^{-1}\text{mol}^{-1} \times 298 \text{ K}} \times 1.77 \text{ V} = 414$$

so that

$$K = e^{414} > 1 \times 10^{100}$$

The equilibrium constant is so large that its value cannot be displayed on a standard calculator. The thermodynamics therefore favour the production of products.

(d) For the reaction

$$2 \text{ Br}^- \text{ (aq)} + Cl_2 \text{ (g)} \rightarrow Br_2 \text{ (l)} + 2 \text{ Cl}^- \text{ (aq)}$$

then the two half reactions are

$$Cl_2\text{ (g)} \rightarrow 2\text{ Cl}^-\text{ (aq)} + 2\text{ e}^- \qquad E^{\ominus}_{anode} = +1.36\text{ V}$$

$$2\text{ Br}^-\text{ (aq)} + 2\text{ e}^- \rightarrow Br_2\text{ (s)} \qquad E^{\ominus}_{cathode} = +1.08\text{ V}$$

where the Cl_2/Cl^- half cell is the anode, because the chloride ions lose electrons and so are oxidised. Thus,

$$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode} = +1.08\text{ V} - 1.36\text{ V} = -0.28\text{ V}$$

Using Equation 16.14 to calculate the standard Gibbs energy change, and noting that the half-cell reactions are two-electron processes, so that $z = 2$,

$$\Delta_r G^{\ominus} = -zFE^{\ominus}_{cell}$$

$$= -2 \times 96485\text{ C mol}^{-1} \times -0.28\text{ V}$$

$$= +54.03 \times 10^3\text{ J mol}^{-1} = +54.03\text{ kJ mol}^{-1}$$
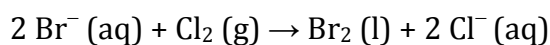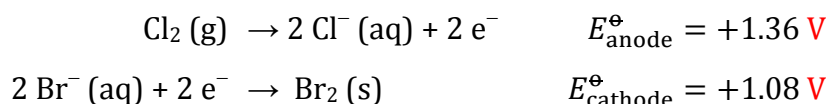
The equilibrium constant is then, from Equation 16.15,

$$\ln K = \frac{zF}{RT}E^{\ominus}_{cell} = \frac{2 \times 96485\text{ C mol}^{-1}}{8.3145\text{ J K}^{-1}\text{mol}^{-1} \times 298\text{ K}} \times -0.28\text{ V} = -22$$

so that

$$K = e^{-22} = 3.4 \times 10^{-10}$$

The position of equilibrium therefore favours the formation of Cl_2 (g) and Br^-(aq) ions.

11. Calculate $E^{\ominus}_{cell}$ for Co (s) | Co^{2+} (aq) || Ni^{2+} (aq) | Ni (s) when:

(a) $[Ni^{2+}] = 1.0$ mol dm^{-3}, $\quad [Co^{2+}] = 0.10$ mol dm^{-3};

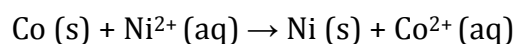(b) $[Ni^{2+}] = 0.01$ mol dm^{-3}, $\quad [Co^{2+}] = 1.0$ mol dm^{-3};
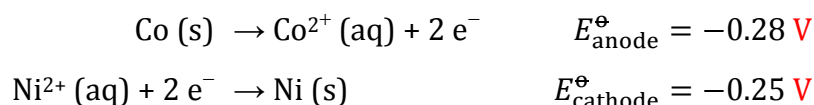
(Section 16.4)

Strategy

Identify the overall and the two half reactions and calculate the standard cell potential using the data in Table 16.2. Write the appropriate Nernst equation, using Equation 16.16, and substitute in the values for the standard cell potential and concentrations.

Solution

(a) The overall cell reaction is

$$Co\ (s) + Ni^{2+}\ (aq) \rightarrow Ni\ (s) + Co^{2+}\ (aq)$$

with half reactions

$$Co\ (s)\ \rightarrow Co^{2+}\ (aq) + 2\ e^- \qquad E^\ominus_{anode} = -0.28\ V$$

$$Ni^{2+}\ (aq) + 2\ e^-\ \rightarrow Ni\ (s) \qquad E^\ominus_{cathode} = -0.25\ V$$

with

$$E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode} = -0.25\ V - (-0.28\ V) = +0.03\ V$$

The Nernst equation is then

$$E_{cell} = E^\ominus_{cell} - \frac{RT}{zF}\ln Q$$

where Q is the reaction quotient, Q, which was defined in Equation 15.2. For this cell,

$$Q = \frac{a_{Ni(s)}a_{Co^{2+}(aq)}}{a_{Ni^{2+}(aq)}a_{Co(s)}} = \frac{[Co^{2+}(aq)]}{[Ni^{2+}(aq)]}$$

because the activity of a pure solid is

$$a_{J(s)} = 1$$

and that of a component in dilute solution is

$$a_{J(aq)} = [J]/c^\ominus$$

Thus

$$E_{cell} = E^\ominus_{cell} - \frac{RT}{zF}\ln\frac{[Co^{2+}(aq)]}{[Ni^{2+}(aq)]}$$

$$= +0.03\ V - \frac{8.3145\ J\ K^{-1}mol^{-1} \times 298\ K}{2 \times 96485\ C\ mol^{-1}}\ln\frac{1.0\ mol\ dm^{-3}}{0.10\ mol\ dm^{-3}}$$

$$= 0\ V$$

(b) Using the same approach,

$$E_{cell} = E^\ominus_{cell} - \frac{RT}{zF}\ln\frac{[Co^{2+}(aq)]}{[Ni^{2+}(aq)]}$$

$$= +0.03\ V - \frac{8.3145\ J\ K^{-1}mol^{-1} \times 298\ K}{2 \times 96485\ C\ mol^{-1}}\ln\frac{0.01\ mol\ dm^{-3}}{1.00\ mol\ dm^{-3}}$$

$$= +0.089\ V$$

12. Given the following half cell reactions, calculate the solubility product (see Box 15.1, p.699) of silver bromide at 298 K. (Section 16.4)

$$AgBr \text{ (s)} + e^- \rightarrow Ag \text{ (s)} + Br^- \text{ (aq)} \quad E^\ominus = +0.07 \text{ V}$$

$$Ag^+ \text{ (aq)} + e^- \rightarrow Ag \text{ (s)} \quad\quad\quad E^\ominus = +0.80 \text{ V}$$
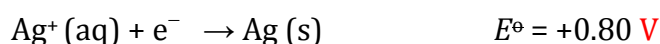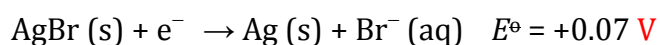
Strategy

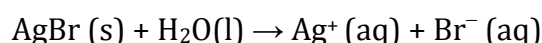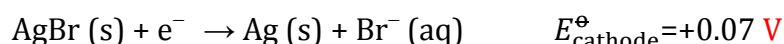Combine the two half-cell reactions to produce a chemical equation for the dissolution of silver bromide. Calculate the standard cell potential for the process and use Equation 16.15 to determine the corresponding equilibrium constant, which is the solubility product for silver bromide.

Solution

The dissolution of silver bromide

$$AgBr \text{ (s)} + H_2O(l) \rightarrow Ag^+ \text{ (aq)} + Br^- \text{ (aq)}$$

may be expressed in the form of two half-cell reactions

$$Ag \text{ (s)} \rightarrow Ag^+ \text{ (aq)} + e^- \quad\quad\quad E^\ominus_{anode} = +0.80 \text{ V}$$

$$AgBr \text{ (s)} + e^- \rightarrow Ag \text{ (s)} + Br^- \text{ (aq)} \quad E^\ominus_{cathode} = +0.07 \text{ V}$$

where the Ag^+/Ag system is designated the anode because the silver is oxidised as electrons are removed to form the silver ions. Thus

$$E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode} = +0.07 \text{ V} - 0.80 \text{ V} = -0.73 \text{ V}$$

Then, using Equation 16.15, to determine the corresponding equilibrium constant for the reaction, where because the reactions are one-electron processes, $z = 1$,

$$\ln K = \frac{zF}{RT} E^\ominus_{cell} = \frac{1 \times 96485 \text{ C mol}^{-1}}{8.3145 \text{ J K}^{-1}\text{mol}^{-1} \times 298 \text{ K}} \times -0.73 \text{ V} = -28$$

so that

$$K = e^{-28} = 4.5 \times 10^{-13}$$

13. Calculate E_{cell} and the Gibbs energy change for the following cells:

(a) $Ag \text{ (s)}|Ag^+(aq, 1.0 \text{ mol dm}^{-3}) \| Cu^{2+} \text{ (aq, 1.0 mol dm}^{-3})|Cu \text{ (s)}$

(b) Ag (s)|Ag$^+$(aq, 0.1 mol dm^{-3}) || Cu^{2+} (aq, 0.1 mol dm^{-3})|Cu (s)

(c) Ag (s)|Ag$^+$(aq, 1.0 mol dm^{-3}) || Cu^{2+} (aq, 0.1 mol dm^{-3})|Cu (s)
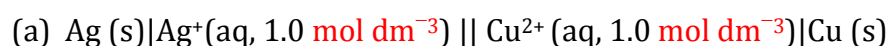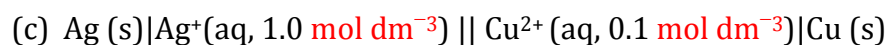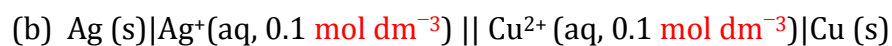
(Section 16.4)

Strategy

Write the chemical equations for the overall reaction and for the two separate half cells. Use Table 16.2 to determine the standard cell potential and the Nernst equation, Equation 16.16, to calculate the cell potential for each of the sets of conditions. Determine the Gibbs energy change using Equation 16.17.

Solution

(a) The overall reaction may be written

$$2 \text{ Ag (s)} + \text{Cu}^{2+} \text{ (aq)} \rightarrow 2 \text{ Ag}^+ \text{ (aq)} + \text{Cu (s)}$$

and may be expressed in the form of two half-cell reactions

$$2 \text{ Ag (s)} \rightarrow 2 \text{ Ag}^+ \text{ (aq)} + 2 \text{ e}^- \qquad E^{\ominus}_{\text{anode}} = +0.80 \text{ V}$$

$$\text{Cu}^{2+} \text{ (aq)} + 2 \text{ e}^- \rightarrow \text{Cu (s)} \qquad E^{\ominus}_{\text{cathode}} = +0.34 \text{ V}$$

where the Ag$^+$/Ag system is designated the anode because the silver is oxidised as electrons are removed to form the silver ions. Thus

$$E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{cathode}} - E^{\ominus}_{\text{anode}} = +0.34 \text{ V} - 0.80 \text{ V} = -0.46 \text{ V}$$
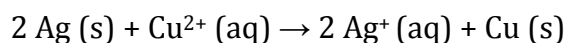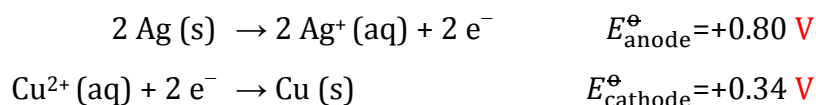
The Nernst equation, Equation 16.16 has the form

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{zF} \ln Q$$

where Q is the reaction quotient, Q, which was defined in Equation 15.2. For this cell,

$$Q = \frac{a_{\text{Cu(s)}} a^2_{\text{Ag}^+(\text{aq})}}{a_{\text{Cu}^{2+}(\text{aq})} a^2_{\text{Ag(s)}}} = \frac{[\text{Ag}^+(\text{aq})]^2}{[\text{Cu}^{2+}(\text{aq})]}$$

because the activity of a pure solid is

$$a_{\text{J(s)}} = 1$$

and that of a component in dilute solution is

$$a_{\text{J(aq)}} = [\text{J}]/c^{\ominus}$$

Thus

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{RT}{zF} \ln \frac{[Ag^+(aq)]^2}{[Cu^{2+}(aq)]}$$

Since the concentration of the aqueous solutions is 1.0 mol dm⁻³ in each case,

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus}$$

The reaction involves the transfer of 2 electrons, so $z = 2$, so, using Equation 16.14 to calculate the Gibbs energy change,

$$\Delta_r G = -zFE_{\text{cell}}$$
$$= -2 \times 96485 \text{ C mol}^{-1} \times -0.46 \text{ V}$$
$$= +89 \times 10^3 \text{ J mol}^{-1} = +89 \text{ kJ mol}^{-1}$$

(b) If $[Ag^+(aq)] = [Cu^{2+}(aq)] = 0.1$ mol dm⁻³ then

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{RT}{zF} \ln \frac{[Ag^+(aq)]^2}{[Cu^{2+}(aq)]}$$
$$= -0.46 \text{ V} - \frac{8.3145 \text{ J K}^{-1}\text{mol}^{-1} \times 298 \text{ K}}{2 \times 96485 \text{ C mol}^{-1}} \ln \frac{(0.1 \text{ mol dm}^{-3})^2}{0.1 \text{ mol dm}^{-3}}$$
$$= -0.43 \text{ V}$$

and so

$$\Delta_r G = -zFE_{\text{cell}}$$
$$= -2 \times 96485 \text{ C mol}^{-1} \times -0.43 \text{ V}$$
$$= +83 \times 10^3 \text{ J mol}^{-1} = +83 \text{ kJ mol}^{-1}$$

(c) If $[Ag^+(aq)] = [Cu^{2+}(aq)] = 0.1$ mol dm⁻³ then

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{RT}{zF} \ln \frac{[Ag^+(aq)]^2}{[Cu^{2+}(aq)]}$$
$$= -0.46 \text{ V} - \frac{8.3145 \text{ J K}^{-1}\text{mol}^{-1} \times 298 \text{ K}}{2 \times 96485 \text{ C mol}^{-1}} \ln \frac{(1.0 \text{ mol dm}^{-3})^2}{0.1 \text{ mol dm}^{-3}}$$
$$= -0.49 \text{ V}$$

and so

$$\Delta_r G = -zFE_{\text{cell}}$$
$$= -2 \times 96485 \text{ C mol}^{-1} \times -0.49 \text{ V}$$
$$= +95 \times 10^3 \text{ J mol}^{-1} = +95 \text{ kJ mol}^{-1}$$

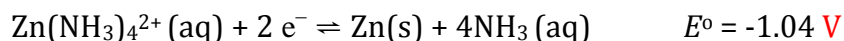**14.** Use the following standard reduction potentials to calculate the equilibrium constant for the formation of the $Zn(NH_3)_4{}^{2+}$ ion. (Section 16.4)

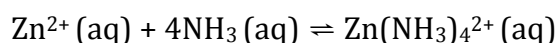$$Zn(NH_3)_4{}^{2+}\,(aq) + 2\ e^- \rightleftharpoons Zn(s) + 4NH_3\,(aq) \qquad E^o = \text{-}1.04\ V$$

$$Zn^{2+}\,(aq) + 2\ e^- \rightleftharpoons Zn(s) \qquad\qquad\qquad\qquad E^o = \text{-}0.76\ V$$
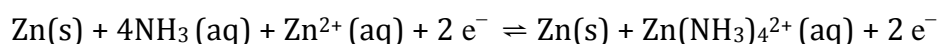
Strategy

Calculate $E^o{}_{cell}$ for the reaction and then use equation 16.15 to calculate the equilibrium constant K.

Solution

The reaction of interest is:

$$Zn^{2+}\,(aq) + 4NH_3\,(aq) \rightleftharpoons Zn(NH_3)_4{}^{2+}\,(aq)$$

This can be obtained by reversing the first half-reaction and adding it to the second.

$$Zn(s) + 4NH_3\,(aq) + Zn^{2+}\,(aq) + 2\ e^- \rightleftharpoons Zn(s) + Zn(NH_3)_4{}^{2+}\,(aq) + 2\ e^-$$

$$E^o{}_{cell} = +1.04\ V - 0.76\ V = +0.28\ V$$

Using $\ln K = \left(\dfrac{nF}{RT}\right)E^o{}_{cell}$

$$\ln K = \left(\frac{2\times 96485\ C\ mol^{-1}}{8.314\ J\ K^{-1}\ mol^{-1} \times\ 298\ K}\right)\times 0.28\ V$$

$$\ln K = 21.8 \quad K = e^{21.8} = 2.9\times 10^9$$

15. Calculate the standard electrode potential for a cell in which the reaction forms 99.99% products at equilibrium under standard conditions at 298 K. Assume $z = 1$ for the reaction. (Section 16.4)

Strategy

Use the given proportions of products and reactants to find the value for K. Then use Equation.16.15 to find the corresponding value for E^o.

Solution

If the reaction forms 99.99% products, there must be 0.01% reactants at equilibrium, so the equilibrium constant, K, is given by:

$$K = \frac{[products]}{[reactants]} = \frac{99.99}{0.01} = 9999$$

Using this value in Equation.16.15, the standard electrode potential can be calculated as follows:

$$\ln K = \left(\frac{nF}{RT}\right) E°_{cell}$$

$E° = $ (8.314 J mol⁻¹ K⁻¹ x 298 K) ln 9999 / (1 x 96485 C mol⁻¹)

$E° = $ +0.236 V

16. A student measured the emf of the following electrochemical cell at 25°C.

Cu(s) | CuSO₄(aq) (0.050 mol dm⁻³) || CuSO₄(aq) (0.500 mol dm⁻³) | Cu(s)

The student connected a piece of copper wire between the electrodes and left the experiment to go for lunch. Some time later the student removed the wire and repeated the emf measurement, recording a value of +0.027 V.

(a) Write the reactions which take place at each electrode

(b) Calculate the emf recorded during the first measurement

(c) Describe briefly what happened in the cell over lunch

(d) Calculate the concentration of copper sulfate in each cell compartment after lunch.

(Section 16.4)

Strategy

From the half cell reactions, use the Nernst equation to calculate emf. Consider what happens to the concentration of copper ions when the cells are connected, and use the Nernst equation again to calculate the change in concentration of each half cell.

Solution

(a) Right hand side: $Cu^{2+}(aq) + 2\ e^- \rightleftharpoons Cu(s)$

Left hand side: $Cu(s) \rightleftharpoons Cu^{2+}(aq) + 2\ e^-$

(b) Using the Nernst equation

$$E_{cell} = E^\circ_{cell} - \frac{RT}{zF} \ln\left(\frac{a_{Cu(s)} \times a_{Cu^{2+}(aq),\ LHS}}{a_{Cu(s)} \times a_{Cu^{2+}(aq),\ RHS}} \right)$$

$$E_{cell} = 0 - \frac{8.314\ J\ K^{-1}\ mol^{-1} \times 298\ K}{2 \times 96485\ C\ mol^{-1}} \ln\left(\frac{(1) \times 0.05}{(1) \times 0.50} \right)$$

E_{cell} = + 0.030 V

(c) If the electrodes are connected by a wire, a current will flow as the cell discharges. Copper metal is deposited on the electrode immersed in the more concentrated solution where the concentration of copper ions decreases. In the other half-cell, copper metal dissolves and the concentration of copper ions in solution increases.

(d) The stoichiometry of the reaction means that the change in concentration in each of the half-cells must be the same. Let the change in concentration be c mol dm^{-3}.

From the Nernst equation, $E_{cell} = E^\circ_{cell} - \frac{RT}{zF} \ln\left(\frac{a_{Cu(s)} \times a_{Cu^{2+}(aq),\ LHS}}{a_{Cu(s)} \times a_{Cu^{2+}(aq),\ RHS}} \right)$

$$0.027\ V = 0 - \frac{RT}{zF} \ln\left(\frac{(0.05 + c)}{(0.50 - c)} \right) \qquad 0.027\ V = -0.013 \ln\left(\frac{(0.05 + c)}{(0.50 - c)} \right)$$

$$\left(\frac{(0.05 + c)}{(0.50 - c)} \right) = \exp{-\left(\frac{0.027}{0.013} \right)} = 0.125$$

$$\left(\frac{(0.05 + c)}{(0.50 - c)} \right) = 0.125$$

$$(0.05 + c) = 0.125 \times (0.50 - c)$$

$$(0.05 + c) = (0.0625 - 0.125c)$$

$$1.125 \, c = 0.0125$$

$$c = 0.011 \text{ mol dm}^{-3}$$

Hence,

Left hand side: $[Cu^{2+} (aq)]$ = (0.05 + 0.011) mol dm^{-3} = 0.06 mol dm^{-3}

Right hand side: $[Cu^{2+} (aq)]$ = (0.50 - 0.011) mol dm^{-3} = 0.49 mol dm^{-3}

17. Electrolysis of a molten chromium salt for 1.5 h with a 5.00 A current deposited 4.835 g of chromium metal. Find the charge on the chromium ion in the salt. (Section 16.5)

Strategy

From the mass of Cr deposited, the number of moles can be calculated. The current and amount of time can be used to find the total amount of charge passed. The charge on the Cr^{n+} ion can be found by comparing these values.

Solution

Find the number of moles of Cr

$$4.835 \text{ g of Cr} = \frac{4.835 \text{ g}}{51.996 \text{ g mol}^{-1}} = 0.093 \text{ mol}$$

Find the number of moles of electrons that flow

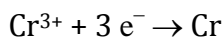Amount of charge passed = 5.00 C s^{-1} × 1.5 h × 60 min h^{-1} × 60 s min^{-1} = 27000 C

1 mol of electrons carries 1 *F*. 1 *F* = 96485 C

$$27000 \text{ C therefore is equivalent to } \frac{27000 \text{ C}}{96485 \text{ C mol}^{-1}} = 0.280 \text{ mol}$$

Hence, 0.280 mol of electrons gave rise to 0.093 mol of Cr

Each mol of Cr therefore required $\dfrac{0.280 \text{ mol}}{0.093 \text{ mol}}$ = 3 electrons.

Hence, salt must contain Cr^{3+} ions.

$$Cr^{3+} + 3\,e^- \rightarrow Cr$$

18. A Leclanche cell (see Section 16.5) produces a current of 0.002 A. If the battery contained 2.5 g of MnO_2, how long will the battery last under these conditions? (Section 16.5)
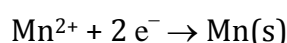
Strategy

Use the half equations for the reaction to calculate the number of moles of electrons produced during the reaction of 2.5 g MnO_2. Work out the charge carried by this many electrons.

Solution

The number of moles of MnO_2 is given by:

$$\frac{2.5 \text{ g}}{86.937 \text{ g mol}^{-1}} = 0.0288 \text{ mol}$$

According to the half equation for the reaction:

$$Mn^{2+} + 2\,e^- \rightarrow Mn(s)$$

it can be seen that 2 moles of electrons are used per mole of MnO_2. Therefore, the amount of electrons passed in the reaction is:

$$2 \times 0.0288 \text{ mol} = 0.0575 \text{ mol}$$

One mole of electrons carries 96485 C, therefore 0.0575 mol is equivalent to:

$$0.0575 \text{ mol} \times 96485 \text{ C mol}^{-1} = 5548 \text{ C}$$

1 A = 1 C s⁻¹, therefore the time needed to pass 5548 C of charge is

$$\frac{5545 \text{ C}}{0.002 \text{ A}} = 2.8 \times 10^6 \text{ s (32 days)}$$

19. Aluminium is manufactured by the electrolysis of molten aluminium oxide, Al_2O_3 (l). If an aluminium plant produces 1000 tonnes of aluminium every 24 hours, what total electric current does it need? (1 tonne = 1000 kg) (Section 16.5)

Strategy

Calculate the number of moles of aluminium produced, and hence the number of moles of electrons needed for this process. Work out the charge passed using Faraday's constant.
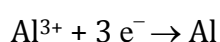
Solution

The number of moles of aluminium is the mass of aluminium in grams divided by its relative mass.

$$1000 \text{ tonnes} = 1 \times 10^6 \text{ kg} = 1 \times 10^9 \text{ g}$$

$$\frac{1 \times 10^9 \text{ g}}{26.981 \text{ g mol}^{-1}} = 3.706 \times 10^7 \text{ mol Al}$$

From the half equation:

$$Al^{3+} + 3 e^- \rightarrow Al$$

it can be seen that 3 moles of electrons are needed to produce one mole of aluminium. Therefore the number of moles of electrons passed is:

$$3.706 \times 10^7 \text{ mol} \times 3 = 1.112 \times 10^8 \text{ mol}$$

One mole of electrons carries 96485 C, therefore 1.112×10^8 mol is equivalent to:

$$1.112 \times 10^8 \text{ mol} \times 96485 \text{ C mol}^{-1} = 1.073 \times 10^{13} \text{ C}$$

1 A = 1 C s⁻¹. Hence:

$$\text{Current} = \frac{1.073 \times 10^{13} \text{ C}}{24 \text{ h} \times 60 \text{ min h}^{-1} \times 60 \text{ s min}^{-1}} = 1.24 \times 10^8 \text{ A}$$