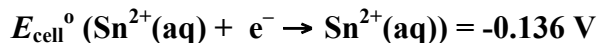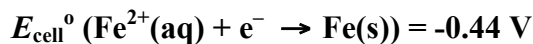- An electrochemical cell consists of an Fe^{2+}/Fe half cell with unknown $[Fe^{2+}]$ and a Sn^{2+}/Sn half-cell with $[Sn^{2+}] = 1.10$ M. The electromotive force (electrical potential) of the cell was measured at 25 °C to be 0.35 V. What is the concentration of Fe^{2+} in the Fe^{2+}/Fe half-cell?

From the reduction potential table,

$$E_{cell}^o \ (Fe^{2+}(aq) + e^- \rightarrow Fe(s)) = \text{-0.44 V}$$

$$E_{cell}^o \ (Sn^{2+}(aq) + e^- \rightarrow Sn^{2+}(aq)) = \text{-0.136 V}$$

The Fe^{2+}/Fe half cell has the more negative reduction potential so it is the half cell that is turned around to act as the oxidation half cell:

$$E_{cell}^o \ (Fe(s) \rightarrow Fe^{2+}(aq) + e^- \ ) = \text{+0.44 V}$$
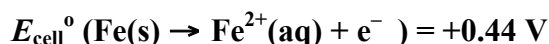
In combination with the Sn^{2+}/Sn reduction half cell, this gives an overall reaction and cell potential of:

$$Fe(s) + Sn^{2+}(aq) \rightarrow Fe^{2+}(aq) + Sn(s) \qquad E^o = ((+0.44) + (-0.136)) \text{ V} = 0.30 \text{ V}$$

For this reaction with $[Sn^{2+}(aq)] = 1.10$ M:

$$Q = \frac{[Fe^{2+}(aq)]}{[Sn^{2+}(aq)]} = \frac{[Fe^{2+}(aq)]}{(1.10)}$$

For the 2e⁻ reaction, the Nernst equation gives the cell potential as:

$$E_{cell} = E^o - \frac{RT}{nF} \ln Q$$

$$= (0.30 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(2 \times 96485 \text{ C mol}^{-1})} \ln \frac{[Fe^{2+}(aq)]}{(1.10)} = 0.35 \text{ V}$$

Solving this gives, $[Fe^{2+}(aq)] = 0.031$ M.

Answer: **0.031 M**

Calculate the equilibrium constant for the reaction at 25 °C.

Using $E^o = (RT/nF) \ln K$:

$$0.30 \text{ V} = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(2 \times 96485 \text{ C mol}^{-1})} \ln K$$

Solving this gives $K = 1.9 \times 10^{10}$

Answer: **1.9×10^{10}**

Calculate the standard Gibbs free energy change for the reaction at 25 °C.

Using $\Delta G^o = -nFE^o$:

$\Delta G^o = -2 \times (96485 \text{ C mol}^{-1}) \times (0.30 \text{ V}) = -59 \text{ kJ mol}^{-1}$

Answer: **-59 kJ mol^{-1}**

	Marks
• A concentration cell is constructed from two beakers containing 1 M $NiCl_2$ and 0.002 M $NiCl_2$. Describe the overall change that occurs as the concentration cell runs.	**3**

$[Ni^{2+}(aq)]$ will reduce in the more concentrated solution and Ni(s) will be deposited on the electrode.

Simultaneously, $[Ni^{2+}(aq)]$ will increase in the less concentrated solution and the Ni(s) electrode will dissolve.

What would be the major driving force for the overall reaction, enthalpy or entropy? Explain your answer.
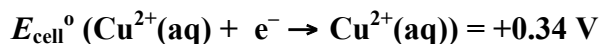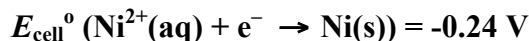
Entropy

The overall enthalpy change of the reaction is zero. Maximum entropy is reached when the concentrations of the two cells are equal.

**THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.**

- An electrochemical cell consisting of a Ni^{2+}/Ni half-cell with unknown $[Ni^{2+}]$ and a Cu^{2+}/Cu half-cell with $[Cu^{2+}] = 2.5$ M has a cell voltage of 0.64 V at 298 K. What is the initial concentration of Ni^{2+} in the Ni^{2+}/Ni half-cell?

From the reduction potential table,

$$E_{cell}^{o} \ (Ni^{2+}(aq) + e^- \rightarrow Ni(s)) = \text{-0.24 V}$$

$$E_{cell}^{o} \ (Cu^{2+}(aq) + e^- \rightarrow Cu^{2+}(aq)) = \text{+0.34 V}$$

The Ni^{2+}/Ni half cell has the more negative reduction potential so it is the half cell that is turned around to act as the oxidation half cell:

$$E_{cell}^{o} \ (Ni(s) \rightarrow Ni^{2+}(aq) + e^- \ ) = \text{+0.24 V}$$
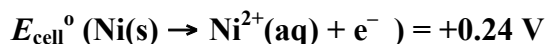
In combination with the Cu^{2+}/Cu reduction half cell, this gives an overall reaction and cell potential of:

$$Ni(s) + Cu^{2+}(aq) \rightarrow Ni^{2+}(aq) + Cu(s) \qquad E^o = ((+0.24) + (0.34)) \text{ V} = 0.58 \text{ V}$$
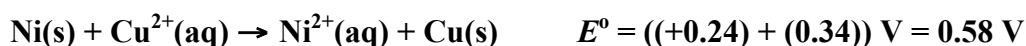
For this reaction with $[Cu^{2+}(aq)] = 2.5$ M:

$$Q = \frac{[Ni^{2+}(aq)]}{[Cu^{2+}(aq)]} = \frac{[Ni^{2+}(aq)]}{(2.5)}$$

For the 2e⁻ reaction, the Nernst equation gives the cell potential as:

$$E_{cell} = E^o - \frac{RT}{nF} \ln Q$$

$$= (0.58 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(2 \times 96485 \text{ C mol}^{-1})} \ln \frac{[Ni^{2+}(aq)]}{(2.5)} = 0.64 \text{ V}$$

Solving this gives, $[Ni^{2+}(aq)] = 0.023$ M.

Answer: **0.023 M**

Calculate the equilibrium constant for the reaction at 25 °C.

Using $E^o = \dfrac{RT}{nF} \ln K$:

$$0.58 \text{ V} = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(2 \times 96485 \text{ C mol}^{-1})} \ln K$$

$$K = 4.2 \times 10^{19}$$

Answer: **4.2×10^{19}**

ANSWER CONTINUES ON THE NEXT PAGE

Calculate the standard Gibbs free energy change for the reaction at 25 °C.

Using $\Delta G^o = -nFE^o$:

$\Delta G^o = -2 \times (96485 \text{ C mol}^{-1}) \times (0.58 \text{ V}) = -110 \text{ kJ mol}^{-1}$

Answer: **+110 kJ mol⁻¹**

|	**Marks**
• What is the voltage of a concentration cell constructed from two beakers containing 2.5 M $CuSO_4$ and 0.025 M $CuSO_4$ at 298 K?	**3**

Answer:

Explain the changes necessary for the cell to reach equilibrium.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

• Balance the following redox reaction, which is carried out in an acidic solution.

$$I^- + IO_3^- \rightarrow I_2$$

**Marks
3**

Working

$$IO_3^-(aq) + 6H^+(aq) + 5I^-(aq) \rightarrow 3I_2(aq) + 3H_2O(l)$$
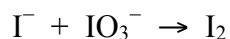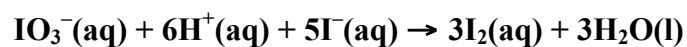
- **The unbalanced has I^- being oxidised to I_2. This involves 1 e^- as the oxidation number is changing from -1 in I^- to 0 in I_2.**
- **The unbalanced equation has IO_3^- being reduced to I_2. This involves 5 e^- as the oxidation number is changing from +5 in IO_3^- to 0 in I_2.**
- **To balance the oxidation and reduction processes, $5I^-$ are therefore required.**
- **This gives a total charge of -6 on the left hand side (from IO_3^- and $5I^-$) and no charged species on the right hand side.**
- **To balance the charges, $6H^+$ are added to the left hand side. Note that the solution is acidic so there are H^+ in the solution.**
- **Lastly, there are now 6H and 3O on the left hand side so $3H_2O$ is added to the right hand side to ensure atom balance.**
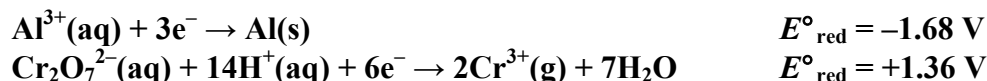
Marks
7

- The following redox reaction occurs in a voltaic cell:

    $2Al(s) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 2Al^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$
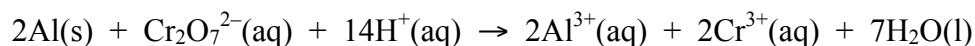
Calculate the standard cell potential, $E°_{cell}$, for the cell at 25 °C.

From the standard reduction potentials table:

$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$ $E°_{red} = -1.68$ V
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(g) + 7H_2O$ $E°_{red} = +1.36$ V

In the reaction, the Al^{3+} / Al half cell is reversed and is acting as the oxidation half cell with $E°_{ox} = +1.68$ V. Hence:

$E°_{cell} = E°_{ox} + E°_{red} = (+1.68$ V$) + (1.36$ V$) = +3.04$ V

Answer: **+3.04 V**

Calculate the cell potential, E_{cell}, at 25 °C when $[Cr_2O_7^{2-}(aq)] = 7.2 \times 10^{-5}$ M, $[Al^{3+}(aq)] = 0.55$ M, $[Cr^{3+}(aq)] = 0.75$ M and the pH is 2.35.

As pH = $-\log_{10}[H^+(aq)]$, when pH = 2.35, $[H^+(aq)] = 10^{-2.35}$.

The reaction involves transfer of 6 e⁻: $n = 6$. Using the Nernst equation for this reaction:

$$E_{cell} = E° - \frac{RT}{nF}\ln Q = E° - \frac{RT}{nF}\ln\frac{[Al^{3+}(aq)]^2[Cr^{3+}(aq)]^2}{[Cr_2O_7^{2-}(aq)][H^+(aq)]^{14}}$$

$$= (+3.04) - \frac{(8.314)(298\ K)}{(6)(96485)}\ln\frac{(0.55)^2(0.75)^2}{(7.2\times10^{-5})(10^{-2.35})^{14}} = +2.68\ V$$

Answer: **+2.68 V**

What is the effect on the E_{cell} of decreasing the concentration of $Cr_2O_7^{2-}$ in the cathode compartment?

From the Nernst equation, decreasing $[Cr_2O_7^{2-}]$ will increase Q and decrease E_{cell}. In the concentration of this reactant is decreased, the reaction will shift slightly towards reactants and E_{cell} will decrease.

What is the effect on the E_{cell} of adding a 0.35 M solution of $Al(NO_3)_3$ to the anode compartment?

Adding a 0.35 M solution of Al^{3+} to a 0.55 M solution of Al^{3+} will increase the number of moles of Al^{3+} but *decrease* the concentration. It is a dilution.

This will reduce Q and increase E_{cell}. In the concentration of this product is decreased, the reaction will shift slightly towards products and E_{cell} will increase.

		Marks
• Consider a voltaic cell in which oxidation of Cr to Cr^{3+} by O_2 in the presence of acid occurs. Write the half-reaction that occurs at each electrode and the overall balanced redox reaction.		**3**

Reaction at anode	**$Cr(s) \rightarrow Cr^{3+}(aq) + 3e^-$**
Reaction at cathode	**$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$**
Overall balanced reaction	**$4Cr(s) + 3O_2(g) + 12H^+(aq) \rightarrow 4Cr^{3+}(aq) + 6H_2O(l)$**

• Is O_2 a stronger oxidizing agent under acidic or basic conditions? Give reasons for your answer.	**2**

Acidic. Increasing the concentration of $H^+(aq)$ will favour the products in the reaction.

At standard conditions, $[H^+(aq)] = 1$ M. From the Nernst equation, the potential depends on the $H^+(aq)$ as

$$E_{cell} = E° - \frac{RT}{nF}\ln Q = E° - \frac{RT}{12F}\ln\frac{1}{[H^+(aq)]^{12}}$$

where $[Cr^{3+}(aq)]$ and $P(O_2)$ have been taken to be standard conditions for simplicity.

At low pH, $[H^+(aq)]$ is high so Q is small. The reduction potential is *decreased* so the oxidation potential is *increased*.

At high pH, $[H^+(aq)]$ is low so Q is large. The reduction potential is *increased* so the oxidation potential is *decreased*.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

		Marks
• The CrO_4^{2-} ion can oxidise the I_3^- ion in acidic solution. The products of the reaction are Cr^{3+} and I_2. Show the separate balanced half-equations for the oxidation and reduction as well as the net balanced redox equation.		3

Oxidation half-equation	$2I_3^-(aq) \rightarrow 3I_2(aq) + 2e^-$
Reduction half-equation	$CrO_4^{2-}(aq) + 8H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O(l)$
Balanced redox equation	$2CrO_4^{2-}(aq) + 16H^+ + 6I_3^-(aq) \rightarrow 2Cr^{3+} + 8H_2O(l) + 9I_2(aq)$

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

	Marks
• Hydrogen peroxide, H_2O_2, can decompose to water and oxygen. Using the following redox potentials, determine whether this decomposition reaction is spontaneous or not.	**2**

$$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O \qquad E° = 1.76 \text{ V}$$

$$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2 \qquad E° = 0.70 \text{ V}$$

The decomposition reaction is:
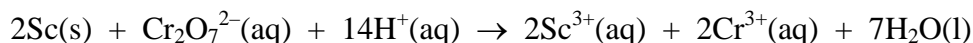
$2H_2O_2$(l) → $2H_2O$(l) + O_2(g)

This is combines the first half cell as the reduction half cell and the second half cell as the oxidation half cell:

$E° = (+1.76 \text{ V}) + (-0.70 \text{ V}) = +1.06 \text{ V}$

As $E° > 0$, the reaction is spontaneous.

- The following redox reaction occurs in a voltaic cell:

$$2Sc(s) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 2Sc^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$$

Calculate the cell potential, E_{cell}, at 25 °C when $[Cr_2O_7^{2-}(aq)] = 6.2 \times 10^{-5}$ M, $[Sc^{3+}(aq)] = 0.35$ M, $[Cr^{3+}(aq)] = 0.75$ M and the pH is 1.85. The standard cell potential, $E°_{cell}$, for this cell is 3.70 V.

Using pH = -log$_{10}$[H$^+$(aq), [H$^+$(aq)] = 10$^{-1.85}$ M.

The reaction involves transfer of 6 e$^-$, as 2Sc → 2Sc^{3+}, so n = 6.

For the reaction,

$$Q = \frac{[Sc^{3+}(aq)]^2[Cr^{3+}(aq)]^2}{[Cr_2O_7(aq)^{2-}][H^+(aq)]^{14}} = \frac{(0.35)^2(0.75)^2}{(6.2 \times 10^{-5})(10^{-1.85})^{14}} = 8.83 \times 10^{28}$$

The cell potential is given by the Nernst equation:

$$E_{cell} = E° - \frac{RT}{nF}\ln Q = (3.70 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(6 \times 96485 \text{ C mol}^{-1})}\ln(8.83 \times 10^{28})$$

$$= +3.41 \text{ V}$$

Answer: **+3.41 V**

What is the effect on the E_{cell} of decreasing the concentration of $Cr_2O_7^{2-}$ in the cathode compartment?

This change will increase the value of Q and so E_{cell} decreases.

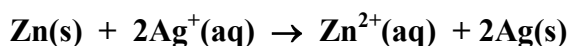What is the effect on the E_{cell} of adding a 0.35 M solution of $Sc(NO_3)_3$ to the anode compartment?

This will not change $[Sc^{3+}(aq)]$ so there is no effect on the value of E_{cell}.

**Marks
6**

- Consider the galvanic cell $Zn(s) \,|\, Zn^{2+}(aq) \,||\, Ag^+(aq) \,|\, Ag(s)$ with initial concentrations of $[Zn^{2+}] = 1.00$ M and $[Ag^+] = 0.50$ M. Draw the cell and clearly label which electrode is the anode and which electrode is the cathode.
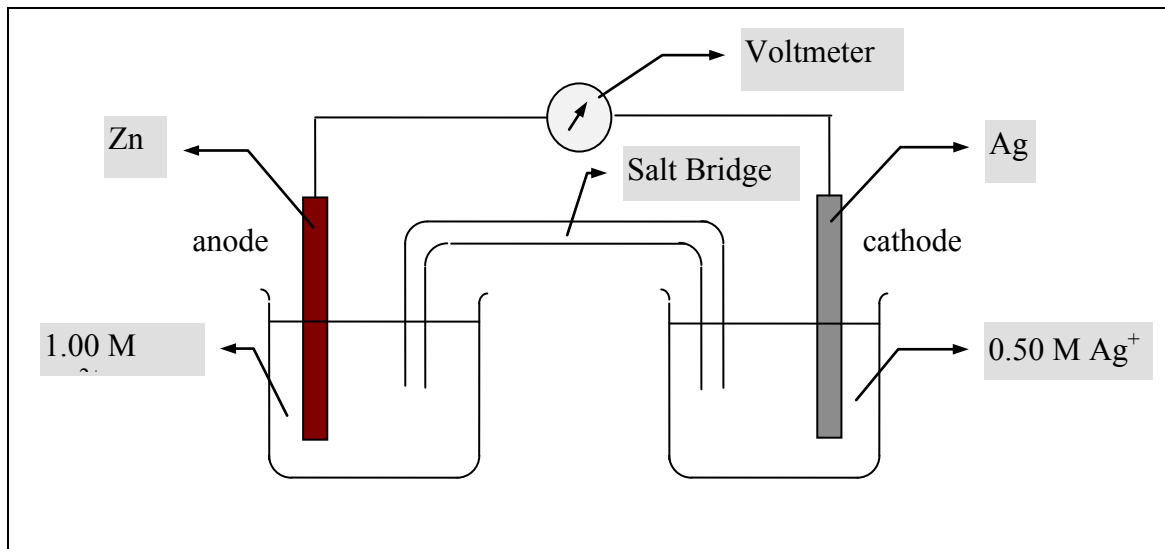
Write the equation for the reaction.
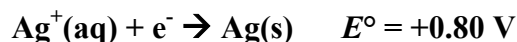
$Zn(s) \ + \ 2Ag^+(aq) \ \rightarrow \ Zn^{2+}(aq) \ + 2Ag(s)$

Calculate the cell potential at 298 K.

The two half cells are:

   $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $E° = +0.76$ V (reversed from reduction potential)

   $Ag^+(aq) + e^- \rightarrow Ag(s)$ $E° = +0.80$ V

The standard cell potential is therefore, $E° = (+0.76 + 0.80)$ V $= 1.56$ V

As the cell is working at non-standard concentrations, the Nernst equation must be used to work out the cell potential:

   $E_{cell} = E° - 2.303 \times \dfrac{RT}{nF} \log Q$

The reaction is a 2 electron process, $n = 2$, with $Q = \dfrac{[Zn^{2+}(aq)]}{[Ag^+(aq)]^2}$.

The cell potential is thus:

   $E_{cell} = 1.56 \text{ V} - 2.303 \times \dfrac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{2 \times 96485 \text{ C mol}^{-1}} \log \dfrac{(1.00)}{(0.50)^2} = 1.54 \text{ V}$

Answer: **+1.54 V**

ANSWER CONTINUES ON THE NEXT PAGE

Is this a spontaneous voltaic cell? Give a reason for your answer.
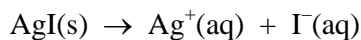
The cell is spontaneous as $E > 0$.

As $\Delta G = -nFE$, if E is positive then ΔG must be negative.

Reactions in which $\Delta G < 0$ are spontaneous.

Marks

4

- The measured potential of the following cell is –0.742 V at 298 K.
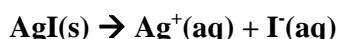
    Ag(s) | AgNO$_3$ (0.010 M) || NaI (0.030 M) | AgI(s) | Ag(s)

Calculate the standard cell potential and determine the equilibrium constant, K_{sp}, for the following reaction at 298K.

$$AgI(s) \rightarrow Ag^+(aq) + I^-(aq)$$

The two half cell reactions are:

   Ag(s) → Ag$^+$(aq) + e$^-$ and   AgI(s) + e$^-$ → Ag(s) + I$^-$(aq)

The overall cell reaction is:

   AgI(s) → Ag$^+$(aq) + I$^-$(aq)

The cell potential is given by the Nernst equation:

$$E_{cell} = E° - 2.303 \times \frac{RT}{nF} \log Q$$

The reaction is a 1 electron process, $n = 1$, with $Q = Q_{sp} = [Ag^+(aq)][I^-(aq)]$

As E_{cell} = -0.742 V, [Ag$^+$(aq)] = 0.010 M and [I$^-$(aq)] = 0.030 M:

$$-0.742 \text{ V} = E° - 2.303 \times \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{1 \times 96485 \text{ C mol}^{-1}} \log(0.010 \times 0.030)$$

$$E° = \text{-0.95 V}$$

At equilibrium, $E = 0$ and $E° = 2.303 \times \frac{RT}{nF} \log K_{sp}$:

$$-0.95 = 2.303 \times \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{1 \times 96485 \text{ C mol}^{-1}} \log K_{sp}$$

$$K_{sp} = 8.5 \times 10^{-17}$$

$E°_{cell}$ = **-0.95 V**	K_{sp} = **8.5 × 10^{-17}**

- Circle the molecule in the following pairs that has the stronger intermolecular forces. Identify the types of forces present for the species selected.

2

molecule pair	types of intermolecular forces
H$_2$ or **N$_2$**	**dispersion (more electrons in N$_2$)**
CH$_3$Cl or CH$_4$	**dipole-dipole and dispersion (dipole present and more electrons in CH$_3$Cl)**
SO$_2$ or CO$_2$	**dipole-dipole and dispersion (dipole present and more electrons in SO$_2$)**
H$_2$O or H$_2$S	**hydrogen bonding (only present in H$_2$O)**

Marks
2

- How does nitric oxide, NO(g), form in a car engine? What happens to the NO once emitted from the tailpipe? Make sure you include the appropriate chemical reactions in your answer.
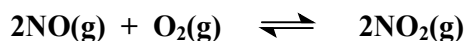
> **NO(g) forms from the reaction of $N_2(g)$ with $O_2(g)$:**
>
> $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\Delta H = +180$ kJ mol^{-1}
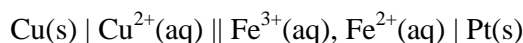>
> **The formation of NO(g) is endothermic, so it is favoured at the high temperatures that exist in the car engine. The high temperatures also speed up the reaction.**
>
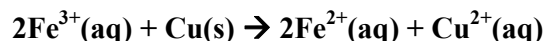> **NO(g) reacts with oxygen in the atmosphere to give $NO_2(g)$.**
>
> $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

- Calculate the standard potential at 298 K of the following electrochemical cell.

5

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

Data:

	$\Delta_f H^\circ$ / (kJ mol^{-1})	S° / (J K^{-1} mol^{-1})
Fe^{3+}(aq)	–49	–316
Fe^{2+}(aq)	–89	–138
Cu^{2+}(aq)	65	–100
Cu(s)	0	33

> **The reaction is:**
>
> $2Fe^{3+}(aq) + Cu(s) \rightarrow 2Fe^{2+}(aq) + Cu^{2+}(aq)$
>
> **Using $\Delta_{rxn}H^\circ = \Sigma m \Delta_f H^\circ(products) - \Sigma n \Delta_f H^\circ(reactants)$,**
>
> $\Delta_{rxn}H^\circ = [(2 \times -89 + 65) - (2 \times -49 + 0)]$ kJ mol^{-1} = -15 kJ mol^{-1}
>
> **Using $\Delta_{rxn}S^\circ = \Sigma S^\circ(products) - \Sigma S^\circ(reactants)$,**
>
> $\Delta_{rxn}S^\circ = [(2 \times -138 + -100) - (2 \times -316 + 33)]$ J K^{-1} mol^{-1} = 223 J K^{-1} mol^{-1}
>
> **As $\Delta_{rxn}G^\circ = \Delta_{rxn}H^\circ - T\Delta_{rxn}S^\circ$, at T = 298 K:**
>
> $\Delta_{rxn}G^\circ = (-15 \times 10^3$ J mol$^{-1}) - (298$ K$)(223$ J K^{-1} mol$^{-1}) = -81454$ J mol^{-1}
>
> **The reaction is a 2 electron process as it involves Cu^{2+}(aq) + 2e$^-$ $\rightarrow$ Cu(s) and as $\Delta_{rxn}G^\circ = -nFE^\circ$:**
>
> -81454 J mol^{-1} = -2 × (96485 C mol^{-1}) × E°
>
> E° = +0.422 V

Answer: **+0.422 V**

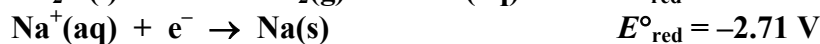|	**Marks**
• In the chlor-alkali process, three useful products are formed, including two of the "top ten" chemicals. Write the overall reaction, identify the two "top ten" chemicals, and propose why the third useful product is not usually harnessed in this process.	**3**

$2Cl^-(aq) + 2H_2O(l) \rightarrow Cl_2(g) + H_2(g) + 2OH^-(aq)$
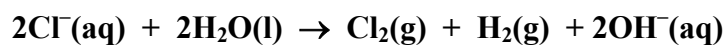
The two "top ten" chemicals produced are NaOH and Cl_2.

H_2 is not harnessed as it is produced more cheaply in other ways.

Explain why the $Na^+(aq)$ is not reduced to Na(s) in this process.

**Water is reduced preferentially. The reduction potentials are:**

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E°_{red} = -0.83$ V
$Na^+(aq) + e^- \rightarrow Na(s)$ $E°_{red} = -2.71$ V

Even with an overpotential, it is much easier to reduce water than $Na^+(aq)$.

**(An equivalent explanation is that if Na(s) were produced, it would react very readily with H_2O to produce $H_2(g)$ and $OH^-(aq)$.)**

	Marks
	6

- The standard dry cell (battery) has the following shorthand notation:

$$Zn(s) \mid Zn^{2+}(aq) \parallel MnO_2(s), Mn_2O_3(s) \mid graphite(s)$$
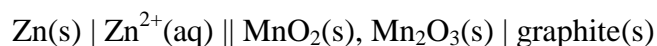
Which component of the battery is the anode?

Zn is being oxidized and hence this is the anode.

Give the balanced half equation that takes place at the anode.

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
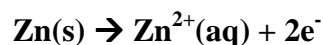
Which component of the battery is the cathode? | **Graphite (an inert electrode).**

Give the balanced half equation that takes place at the cathode.
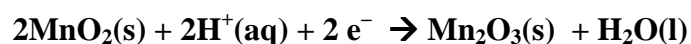
$2MnO_2(s) + 2H^+(aq) + 2 e^- \rightarrow Mn_2O_3(s) + H_2O(l)$

What is the role of the salt bridge in a voltaic cell and how is this accomplished?

The salt bridge completes the circuit and thus allows electrical neutrality to be maintained. The flow of electrons from anode to cathode is countered by the flow of anions to the anode and the flow of cations to the cathode.

This is accomplished by the ions in solution carrying the current. In a standard dry cell, NH_4Cl is used: $NH_4^+(aq)$ is the cation and $Cl^-(aq)$ is the anion.

|	Marks
• Give balanced ionic equations for the reactions that occur in each of the following cases.	**3**

Potassium metal is added to excess water.

When added to water, potassium produces an alkaline solution and hydrogen gas which is ignited by the exothermicity of the reaction:

$2K(s) + 2H_2O(l) \rightarrow 2K^+(aq) + 2OH^-(aq) + H_2(g)$
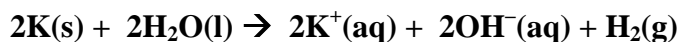
Solutions of zinc nitrate and sodium phosphate are mixed.

A white precipitate is produced (Table E2-3 in the Laboratory Manual). The zinc ion has a +2 charge and phosphate, PO_4^{3-}, has a -2 charge:
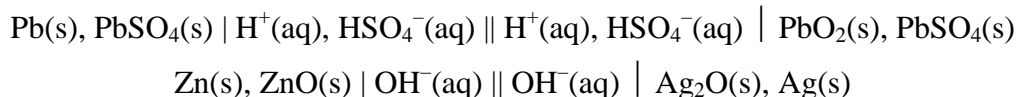
$3Zn^{2+}(aq) + 2PO_4^{3-}(aq) \rightarrow Zn_3(PO_4)_2(s)$
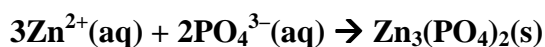
Solid strontium carbonate is dissolved in dilute nitric acid.

Carbonates produce $CO_2(g)$ when treated with acid:

$SrCO_3(s) + 2H^+(aq) \rightarrow Sr^{2+}(aq) + CO_2(g) + H_2O(l)$

• Explain why the voltage of the lead acid battery ($E° = 2.05$ V) decreases when it discharges, whereas the zinc/silver button battery ($E° = 1.6$ V) does not.	**2**

Pb(s), $PbSO_4(s)$ | $H^+(aq)$, $HSO_4^-(aq)$ || $H^+(aq)$, $HSO_4^-(aq)$ | $PbO_2(s)$, $PbSO_4(s)$

Zn(s), ZnO(s) | $OH^-(aq)$ || $OH^-(aq)$ | $Ag_2O(s)$, Ag(s)

The overall reaction for the zinc/silver button battery is:

$Zn(s) + Ag_2O(s) \rightarrow ZnO(s) + 2Ag(s)$

All components are solids and hence do not enter in to equilibrium constant expression for the reaction or into the Nernst equation for the cell. The voltage will remain constant as concentrations of all products and reactants remains constant.

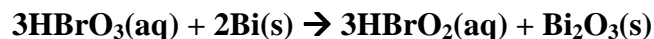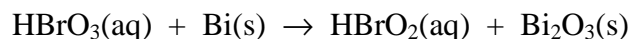**In contrast, the overall reaction for the lead acid battery is:**

$PbO_2(s) + Pb(s) + 2H^+(aq) + 2HSO_4^-(aq) \rightarrow 2PbSO_4(s) + 2H_2O$

Here the concentrations of $H^+(aq)$ and $HSO_4^-(aq)$ decrease as the battery discharges and hence the voltage drops.

	Marks
• Balance the following redox equation in acidic medium.	**4**

$$HBrO_3(aq) \; + \; Bi(s) \; \rightarrow \; HBrO_2(aq) \; + \; Bi_2O_3(s)$$

$3HBrO_3(aq) + 2Bi(s) \rightarrow 3HBrO_2(aq) + Bi_2O_3(s)$

In an acidic medium, the $HBrO_3(aq)$ will be the pre-dominant species rather than the conjugate base $BrO_3^-(aq)$.

Which species is the oxidizing agent?	**$HBrO_3$**
Which element is reduced?	**Br**
What is the oxidation number of Br before the reaction?	**+V**
How many electrons does each Bi gain or lose?	**it loses 3 e⁻**

4

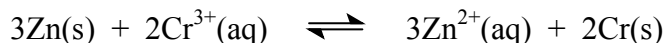• What is the role of the salt bridge in a voltaic cell and how is this accomplished?

The salt bridge completes the circuit by allowing electrical neutrality to be maintained via the movement of ions.

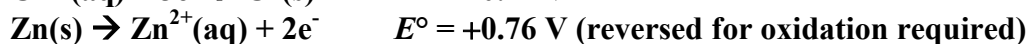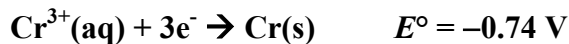How is this role achieved in the lead acid battery?

The sulfuric acid solution provides H^+ and HSO_4^- ions to conduct the current. The reactants (Pb and PbO_2) and products ($PbSO_4$) are all solids so no physical separation other than initial placement is required.

Marks
3

- Calculate the standard electrochemical potential for the following reaction.

$$3Zn(s) + 2Cr^{3+}(aq) \rightleftharpoons 3Zn^{2+}(aq) + 2Cr(s)$$

The half reactions and potentials are:

$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$ $E° = -0.74$ V
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $E° = +0.76$ V (reversed for oxidation required)

Hence, $E° = ((-0.74) + (+0.76))$ V = +0.02 V

Answer: **+0.02 V**

Use the Nernst equation to calculate the relative cation concentrations at 298 K for which the cell potential, $E = 0$.

The Nernst equation gives $E_{cell} = E^0 - 2.303 \times \dfrac{RT}{nF} \log(Q)$. $E_{cell} = 0$ **when:**

$$E^0 = 2.303 \times \frac{RT}{nF} \log(Q) = 2.303 \times \frac{RT}{nF} \log(K_{eq})$$

The ratio of cation concentrations is just $Q = \dfrac{[Zn^{2+}(aq)]^3}{[Cr^{2+}(aq)]^2}$. **The process involves**

$6e^-$ **so n = 6 and Q can be obtained using the $E° = +0.02$ V:**

$$Q = 10^{nFE°/2.303RT} = 10^{(6 \times 96485 \times +0.02)/(2.303 \times 8.314 \times 298)} = 100$$

Answer: **100**

2

- Fluorine and chlorine are both in Group 17. Briefly explain why HF exhibits hydrogen bonding but HCl does not.

Fluorine is more electronegative than chlorine so the H-F molecule is much more polar; the partial negative charge on F in HF is larger than that on Cl in HCl, as is the partial positive charge on H. This leads to a stronger H-bonding interaction.

In addition, the smaller size of F allows closer approach between HF molecules and stronger interactions.

**Marks
4**

- The standard dry cell (battery) has the following shorthand notation:

$$Zn(s) \mid Zn^{2+}(aq) \parallel MnO_2(s), Mn_2O_3(s) \mid graphite(s)$$
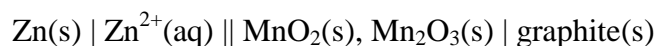
Which component of the battery is the anode? **Zn(s) electrode**

Give the balanced half equation that takes place at the anode.

Oxidation at the anode: Zn(s) → Zn^{2+}(aq) + 2e^{-}

Which component of the battery is the cathode? **Graphite electrode**

Give the balanced half equation that takes place at the cathode.

Reduction at the cathode: 2MnO$_2$(s) + 2H^{+}(aq) + 2e^{-} → Mn$_2$O$_3$ + H$_2$O(l)
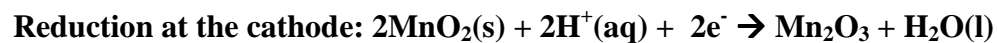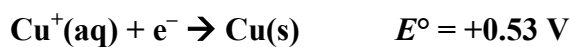
- The mechanism of copper toxicity to aquatic organisms is unknown. Most theories attribute the toxicity to the Cu^{2+} species because Cu^+ is unstable in aqueous solution. Given the half-reactions and half-cell potentials on the data page, show that it is electrochemically favourable for $Cu^+(aq)$ to react with itself to form $Cu^{2+}(aq)$ and $Cu(s)$.

The reaction of interest is:

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

It can be considered as a reduction of $2Cu^+(aq)$ to make $2Cu(s)$, followed by the oxidation of one of the $Cu(s)$ to make $Cu^{2+}(aq)$.

The half cell reactions and potentials are:

$Cu^+(aq) + e^- \rightarrow Cu(s)$ $E° = +0.53$ V

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ $E° = –0.34$ V (reversed as oxidation required)

Hence the reaction:

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

has a cell potential $E° = ((+0.53) + (–0.34))$ V $= +0.19$ V

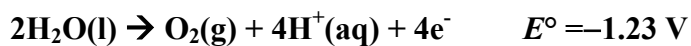**As $E° > 0$, the reaction is spontaneous**

- The Co^{3+} ion is unstable in aqueous solution, but for a different reason to Cu^+ above. Using the table of reduction potentials on the data page, propose the reason why this might be so.
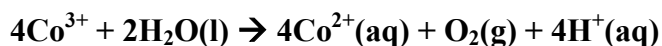
2

The Co^{3+} / Co^{2+} half cell is:

$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$ $E° = +1.82$ V
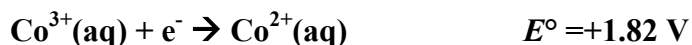
This is sufficiently positive to be able to oxidise water:

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $E° = –1.23$ V

The overall reaction is:

$4Co^{3+} + 2H_2O(l) \rightarrow 4Co^{2+}(aq) + O_2(g) + 4H^+(aq)$

The electrode potential is $E° = ((+1.82) + (–1.23))$ V $= +0.59$ V

As $E° > 0$, the reaction is spontaneous

**Marks
3**

- A concentration cell is constructed of two hydrogen electrodes; one immersed in a solution with $[H^+] = 1.0$ M and the other in hydrochloric acid of unknown concentration. The observed cell potential was 0.25 V. What is the pH of the unknown hydrochloric acid?

> The half cell is $2H^+ + 2e^- \rightarrow H_2$ for both electrodes so $E° = 0$. The cell potential arises from the different $[H^+(aq)]$ concentrations in solutions 'a' and 'b'.
>
> The Nernst equation gives
>
> $$E_{cell} = E^0 - 2.303 \times \frac{RT}{nF}\log(Q) \text{ with } E° = 0,\ Q = \frac{[H^+(aq)]_a^2}{[H^+(aq)]_b^2} \text{ and } n = 2.$$
>
> Hence, $E_{cell} = -2.303 \times \dfrac{(8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K})}{(2 \times 96485\ \text{C mol}^{-1})}\log(\dfrac{[H^+(aq)]_a^2}{(1.0)^2}) = 0.25\ \text{V}$
>
> This gives, $[H^+(aq)]_a = 5.9 \times 10^{-5}$ M.
>
> As pH $= -\log[H^+(aq)]$, the pH $= -\log(5.9 \times 10^{-5}) = 4.2$

Answer: **4.2**

3

- Consider the organic solvents ethanol (CH_3CH_2OH) and ether ($CH_3CH_2OCH_2CH_3$). Which liquid will have the higher vapour pressure? Give a brief reason for your answer.

> **Ether: major intermolecular forces are dispersion forces and dipole-dipole forces.**
>
> **Ethanol: major intermolecular force is H-bonding.**
>
> **Ether has the weaker intermolecular forces and therefore has the lower boiling point and higher vapour pressure.**

Consider the liquids mercury and water. Which liquid will have the higher surface tension? Give a brief reason for your answer.

> **Mercury: major intermolecular forces are metallic bonds.**
>
> **Water: major intermolecular force is H-bonding.**
>
> **Mercury has the stronger intermolecular forces and therefore has the greater surface tension.**