Marks 4

- Calculate the initial cell potential for the following *unbalanced* reaction at 25 °C from the standard electrode potentials. Assume the concentration of all species is initially 1 M.

$$Fe^{3+}(aq) + Sn^{2+}(aq) \rightarrow Fe^{2+}(aq) + Sn^{4+}(aq)$$

The balanced equation is:

$$2Fe^{3+}(aq) + Sn^{2+}(aq) \rightarrow 2Fe^{2+}(aq) + Sn^{4+}(aq)$$

The relevant half cell reactions and potentials are:

$Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)$ $E^{o} = +0.77$ V
$Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^{-}$ $E^{o} = -0.15$ V **(oxidation so sign changed)**

Hence,

$$E^{o}_{cell} = (+0.77 - 0.15)\text{ V} = +0.62\text{ V}$$

Answer: **+0.62 V**

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

Using $E^{o} = \frac{RT}{nF}\ln K$ **and** $T = (25 + 273)\text{ K} = 298\text{ K}$,

$$0.62\text{ V} = \frac{(8.314\text{ J K}^{-1}\text{ mol}^{-1})(298\text{ K})}{2\times(96485\text{ C mol}^{-1})}\ln K$$

$$K = 9.4 \times 10^{20}$$

Note that the reaction involves 2 electrons (n = 2) as each Sn^{2+} is oxidised to Sn^{4+} and two Fe^{3+} are reduced to two Fe^{2+}.

Answer: $\mathbf{9.4 \times 10^{20}}$

Marks

- Give the oxidation number of carbon in each of the following. **2**

CF_2Cl_2(g)	**+4**
$Na_2C_2O_4$(s)	**+3**
HCO_3^-(aq)	**+4**
C(s)	**0**

- Consider a voltaic cell that uses the following half-reactions: **3**

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

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

Write a balanced equation for the overall reaction.

The two cell potentials are +1.51 V (MnO_4^-/Mn^{2+}) and +0.15 V (Sn^{4+}/Sn^{2+}). The least positive (Sn^{4+}/Sn^{2+}) is reversed so that it is the oxidation reaction. Combining the half cells in this way gives, after balancing:

$$\mathbf{2MnO_4^-(aq) + 16H^+(aq) + 5Sn^{2+}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Sn^{4+}(aq)}$$

Which species is the oxidising agent?	**MnO_4^-(aq)**
Which species is the reducing agent?	**Sn^{2+}(aq)**

Calculate the standard cell potential. (Refer to the table of standard reduction potentials.)

As noted above, the Sn^{4+}/Sn^{2+} half cell is reversed so that its oxidation potential is -0.15 V. Hence, the standard cell potential is:

$$\mathbf{E^o_{cell} = E^o_{red} + E^o_{ox} = (+1.51) + (-0.15) = +1.38\,V}$$

Answer: **+1.38 V**

- A galvanic cell is made of a Ni^{2+}/Ni half cell with $[Ni^{2+}] = 1.00 \times 10^{-3}$ M and a Ag^{+}/Ag half cell with $[Ag^{+}] = 5.00 \times 10^{-2}$ M. Calculate the electromotive force of the cell at 25 °C.

Marks 6

The reduction potentials for the two half cells are (from the data sheet):

$Ni^{2+}(aq) + 2e^{-} \rightarrow Ni(s)$ $\quad E° = -0.24$ V
$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$ $\quad E° = +0.80$ V

The $Ni^{2+}(aq)$ / Ni(s) cell has the lower electrode potential and it is the one that is reversed. Hence, the cell reaction and the standard cell potential are

$2Ag^{+}(aq) + Ni(s) \rightarrow 2Ag(s) + Ni^{2+}(aq)$ $\quad E° = (+0.80\text{ V}) + (+0.24\text{ V}) = 1.04$ V

At non-standard concentrations, the electrode potential is given by the Nernst equation:

$$E = E° - \frac{RT}{nF}\ln Q$$

For this two electron reduction, $n = 2$ and $Q = \frac{[Ni^{2+}(aq)]}{[Ag^{+}(aq)]^2}$

$[Ni^{2+}(aq)] = 1.00 \times 10^{-3}$ M and $[Ag^{+}(aq)] = 5.00 \times 10^{-2}$ M. Hence, at T = 25 °C = (25 + 273) K = 298 K:

$$E = (1.04\text{ V}) - \frac{(8.314\text{ J K}^{-1}\text{ mol}^{-1})(298\text{ K})}{(2 \times 96485\text{ C mol}^{-1})} \ln\left(\frac{1.00 \times 10^{-3}}{(5.00 \times 10^{-2})^2}\right) = 1.06\text{ V}$$

Answer: **1.06 V**

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

The equilibrium constant is related to the standard electrode potential:

$$E° = \frac{RT}{nF}\ln K$$

Hence, with $E° = 1.04$ V and $n = 2$:

$$\ln K = E° \times \frac{nF}{RT} = (1.04\text{ V}) \times \frac{(2 \times 96485\text{ C mol}^{-1})}{(8.314\text{ J K}^{-1}\text{ mol}^{-1})(298\text{ K})} = 81.0$$

so,

$$K = 1.51 \times 10^{35}$$

Answer: **1.51×10^{35}**

ANSWER CONTINUES ON THE NEXT PAGE

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

The standard free energy change, $\Delta G°$, is related to the standard electrode potential, $E°$:

$$\Delta G° = -nFE°$$
$$= -(2) \times (96485\ \mathrm{C\ mol^{-1}}) \times (1.04\ \mathrm{V}) = -201000\ \mathrm{J\ mol^{-1}} = 201\ \mathrm{kJ\ mol^{-1}}$$

Alternatively, the free energy change is related to the equilibrium constant, K:

$$\Delta G° = -RTlnK$$
$$= -(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (298\ \mathrm{K}) \times (1.51 \times 10^{35}) = -201\ \mathrm{kJ\ mol^{-1}}$$

Answer: **$-201\ \mathrm{kJ\ mol^{-1}}$**

Indicate whether the reaction is spontaneous or not. Give reasons for your answer.

- **$E°$ > 0 so the reaction is spontaneous.**
- **$\Delta G°$ < 0 so the reaction is spontaneous.**
- **K is much greater than 1 so the reaction is spontaneous.**

Express the overall reaction in the shorthand voltaic cell notation.

$Ni(s)\,|\,Ni^{2+}(aq)\,||\,Ag^{+}(aq)\,|\,Ag(s)$

- Explain why copper dissolves in dilute HNO_3, but not in dilute HCl?

Marks
2

Copper does not dissolve in dilute HCl(aq) it is not oxidized to Cu^{2+}(aq) under these conditions:

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

$$2H^{+}(aq) + 2e^{-} \rightarrow H_2(g) \qquad E°_{red} = 0 \text{ V}$$

The overall cell potential $E° = E°_{ox} + E°_{red}$ = (-0.34 + 0) = -0.34 V. The cell potential is negative and the reaction is not spontaneous.

Copper does dissolve in dilute HNO_3 due to oxidation by the NO_3^{-} ion:

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

$$NO_3^{-}(aq) + 4H^{+}(aq) + 3e^{-} \rightarrow NO(g) + 2H_2O \qquad E°_{red} = 0.96 \text{ V}$$

The overall cell potential $E° = E°_{ox} + E°_{red}$ = (-0.34 + 0.96) = +0.62 V. The cell potential is positive and the reaction is spontaneous.

- Consider the following *unbalanced* reaction at 25 °C: 3

$$Fe^{3+}(aq) + Sn^{2+}(aq) \rightarrow Fe^{2+}(aq) + Sn^{4+}(aq)$$

Calculate the standard cell potential.

The two half cells and the standard reduction potentials are:

$Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)$ $E_{red}° = +0.77$ V
$Sn^{4+}(aq) + 2e^{-} \rightarrow Sn^{2+}(aq)$ $E_{red}° = +0.15$ V

As the Sn^{4+} / Sn^{2+} cell has the least positive reduction potential, it is reversed and becomes the oxidation half cell:

$Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e$ $E_{ox}° = -0.15$ V

Hence, the standard cell potential is:

$E° = (+0.77 \text{ V}) + (-0.15 \text{ V}) = +0.62 \text{ V}$

Answer: **+0.62 V**

Calculate the equilibrium constant, *K*, for the reaction at 25 °C.

Using the half cell reactions above, the balanced equation is:

$2Fe^{3+}(aq) + Sn^{2+}(aq) \rightarrow 2Fe^{2+} + Sn^{4+}(aq)$

It involves the transfer of 2 electrons. The equilibrium constant for this 2 electron reaction is therefore given by:

$E° = (RT/nF)\ln K$

$\ln K = E° \times (nF / RT) = (0.62) \times (2 \times 96485) / (8.314 \times 298) = 48.3$

$K = 9.4 \times 10^{20}$

Answer: 9.4×10^{20}