

- A voltaic cell is constructed with a  $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$  (in acidic solution) half cell and a  $\text{Sn}/\text{Sn}^{2+}$  half cell. Measurement shows that the Sn electrode is negative. Write the balanced half equations and the overall spontaneous reaction.

**Marks**  
**3**

reduction half equation	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$ (reduction always occurs at the cathode which is positively charged)
oxidation half equation	$\text{Sn}(\text{s}) \rightarrow \text{Sn}^{2+}(\text{aq}) + 2\text{e}^-$ (oxidation always occurs at the anode which is negatively charged)
overall reaction	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 3\text{Sn}(\text{s}) \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l}) + 3\text{Sn}^{2+}(\text{aq})$

**3**

- How many hours will it take to produce 1.00 kg of aluminium metal from a molten  $\text{Al}^{3+}$  salt, using a current of 100 A?

**Production to Al requires reduction of  $\text{Al}^{3+}$ :  $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$ .**

**Thus, production of 1 mol of Al requires 3 mol of electrons.**

**The atomic mass of Al is 26.98 so 1.00 kg corresponds to:**

$$\text{number of moles of Al} = n = \frac{\text{mass}}{\text{atomic mass}} = \frac{(1.00 \times 10^3 \text{ g})}{(26.98 \text{ g mol}^{-1})} = 37.1 \text{ mol}$$

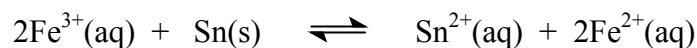
**Hence,  $(3 \times 37.1) \text{ mol} = 111 \text{ mol}$  of electrons are required. As number of moles of electrons delivered by a current is given by  $\frac{I \times t}{F}$ , the time taken to deliver this amount using a current of 100 A is:**

$$t = \frac{nF}{I} = \frac{(111 \text{ mol} \times 96485 \text{ C mol}^{-1})}{(100 \text{ A})} = 107000 \text{ seconds} = \frac{10700}{(60 \times 60)} = 29.8 \text{ hours}$$

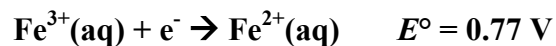
**Answer: 29.8 hours**

**Marks**  
**2**

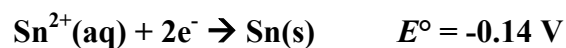
- What is the value of the equilibrium constant for the following reaction at 298 K?



**The half cell reduction reactions and standard potentials are:**



**and**



**The  $\text{Sn}^{2+} / \text{Sn}(\text{s})$  is operating in reverse so:**

$$E_{\text{cell}}^{\circ} = ((0.77) - (-0.14) \text{ V}) = 0.91 \text{ V}$$

**Using  $E_{\text{cell}}^{\circ} = \frac{RT}{nF} \ln K$ , the equilibrium constant for this  $2\text{e}^{-}$  process is:**

$$\ln K = \frac{(2) \times (96485 \text{ C mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} \times (0.91) = 70.9$$

$$K = e^{70.9} = 6.05 \times 10^{30}$$

Answer:  $6.05 \times 10^{30}$

- The physiological properties of chromium depend on its oxidation state. Consider the half reaction in which Cr(VI) is reduced to Cr(III).



Calculate the potential for this half reaction at 25 °C, where pH = 7.40 and  $[\text{CrO}_4^{2-}(\text{aq})] = 1.0 \times 10^{-6} \text{ M}$ .

As  $\text{pH} + \text{pOH} = 14.00$  and  $\text{pOH} = -\log_{10}([\text{OH}^-(\text{aq})])$ , at  $\text{pH} = 7.40$ ,

$$\text{pOH} = 14.00 - 7.40 = 6.60 = -\log_{10}([\text{OH}^-(\text{aq})])$$

$$[\text{OH}^-(\text{aq})] = 10^{-6.60}$$

The reaction quotient for the half-cell reaction is,

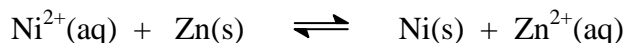
$$Q = \frac{[\text{OH}^-(\text{aq})]^5}{[\text{CrO}_4^{2-}(\text{aq})]} = \frac{(10^{-6.60})^5}{(1.0 \times 10^{-6})} = 1.0 \times 10^{-27}$$

Using the Nernst equation for this three electron process,

$$E = E^\circ - \frac{RT}{nF} \ln Q = (-0.13) - \frac{8.314 \times (25+273)}{3 \times 96485} \ln(1.0 \times 10^{-27}) = +0.40 \text{ V}$$

Answer:  $E = +0.40 \text{ V}$

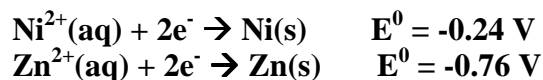
- Consider the following reaction at 298 K.



Calculate  $\Delta G^{\circ}$  for the cell. (Relevant electrode potentials can be found on the data page.)

**Marks**  
**5**

The half-cell reduction reactions and potentials are:



In the reaction above, the Zn is undergoing oxidation so its potential is reversed and the overall cell potential is:

$$E_{\text{cell}}^{\circ} = (-0.24) - (-0.76) = +0.52 \text{ V}$$

Using  $\Delta G^{\circ} = -nFE^{\circ}$  for this two electron reaction:

$$\Delta G^{\circ} = -(2) \times (96485) \times (+0.52) = -100000 \text{ J mol}^{-1} = -100 \text{ kJ mol}^{-1}$$

Answer:  $-100 \text{ kJ mol}^{-1}$

What is the value of the equilibrium constant for the reaction at 298 K?

$$\text{Using } E^{\circ} = \frac{RT}{nF} \ln K,$$

$$+0.52 = \frac{(8.314) \times (298)}{(2) \times (96485)} \ln K \quad \text{so } K = 3.89 \times 10^{17}$$

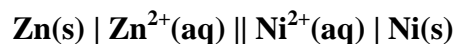
Alternatively, using  $\Delta G^{\circ} = -RT \ln K$ ,

$$-100 \times 10^3 = -(8.314) \times (298) \times \ln K \quad \text{so } K = 3.89 \times 10^{17}$$

Answer:  $3.89 \times 10^{17}$

Express the overall reaction in voltaic cell notation.

In the reaction, Zn is being oxidized and hence is the anode.  $\text{Ni}^{2+}$  is being reduced and so Ni is the cathode. In the standard cell notation, the anode is written on the left and the cathode on the right:



ANSWER CONTINUES ON THE NEXT PAGE

- Using a current of 2.00 A, how long (in minutes) will it take to plate out all of the silver from 0.250 L of a  $1.14 \times 10^{-2}$  M  $\text{Ag}^+(\text{aq})$  solution?

**The number of moles of  $\text{Ag}^+(\text{aq})$  in a 0.250 L of a  $1.14 \times 10^{-2}$  M solution is,**

$$\text{number of moles} = \text{volume} \times \text{concentration} = 0.250 \times 1.14 \times 10^{-2} = 2.85 \times 10^{-3} \text{ mol}$$

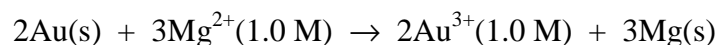
**The reduction of  $\text{Ag}^+(\text{aq})$  is a one electron process,  $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$ , so this number of moles of electrons are required.**

**As the number of moles of electrons delivered by a current  $I$  in a time  $t$  is,**

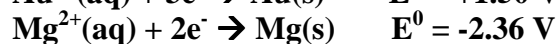
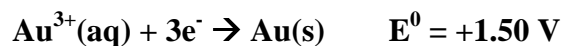
$$\text{number of moles of electrons} = \frac{It}{F} = \frac{2.00 \times t}{96485} = 2.85 \times 10^{-3}$$

$$t = 137 \text{ s} = 2.29 \text{ minutes}$$

- Calculate the standard free-energy change for the following reaction at 298 K.



**The half-cell reduction reactions and potentials are:**



**In the reaction above, the Au is undergoing oxidation so its potential is reversed and the overall cell potential is:**

$$E_{\text{cell}}^{\circ} = (-2.36) - (+1.50) = -3.86\text{ V}$$

**Using  $\Delta G^{\circ} = -nFE^{\circ}$  for this six electron reaction:**

$$\Delta G^{\circ} = -(6) \times (96485) \times (-3.86) = +2.23 \times 10^6\text{ J mol}^{-1} = +2.23 \times 10^3\text{ kJ mol}^{-1}$$

Answer:  $+2.23 \times 10^3\text{ kJ mol}^{-1}$

**Marks**  
**6**

- The solubility product constant of AgCl is  $K_{sp} = 1.8 \times 10^{-10} \text{ M}^2$ . Using the relevant electrode potentials found on the data page, calculate the reduction potential at 298 K of a half-cell formed by:
  - an Ag electrode immersed in a saturated solution of AgCl.

**The standard electrode potential for  $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$  is  $E^\circ = +0.80 \text{ V}$ . This refers to the potential with  $[\text{Ag}^+(\text{aq})] = 1 \text{ M}$ .**

**For the dissolution of  $\text{AgCl}(\text{s}) \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ ,  $K_{sp} = [\text{Ag}^+(\text{aq})][\text{Cl}^-(\text{aq})]$ . As  $[\text{Ag}^+(\text{aq})] = [\text{Cl}^-(\text{aq})]$ ,**

$$[\text{Ag}^+(\text{aq})] = \sqrt{K_{sp}} = \sqrt{1.8 \times 10^{-10}} = 1.3 \times 10^{-5} \text{ M}$$

**Using the Nernst equation, the cell potential at 298 K (25 °C) is,**

$$E = E^\circ - \frac{0.0592}{n} \log Q$$

**The  $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$  half cell involves one electron and so  $n = 1$ . The reaction quotient is  $\frac{1}{[\text{Ag}^+(\text{aq})]}$ . Hence,**

$$E = (+0.80) - \frac{0.0592}{1} \log \left( \frac{1}{1.3 \times 10^{-5}} \right) = +0.52 \text{ V}$$

Answer:  $E = +0.52 \text{ V}$

- an Ag electrode immersed in a 0.5 M solution of KCl containing some AgCl precipitate.

**$[\text{Cl}^-(\text{aq})] = 0.5 \text{ M}$  and as  $K_{sp} = [\text{Ag}^+(\text{aq})][\text{Cl}^-(\text{aq})]$ ,**

$$[\text{Ag}^+(\text{aq})] = \frac{K_{sp}}{[\text{Cl}^-(\text{aq})]} = \frac{1.8 \times 10^{-10} \text{ M}^2}{0.5 \text{ M}} = 3.6 \times 10^{-10} \text{ M}$$

**The electrode potential is now,**

$$E = (+0.80) - \frac{0.0592}{1} \log \left( \frac{1}{3.6 \times 10^{-10}} \right) = +0.24 \text{ V}$$

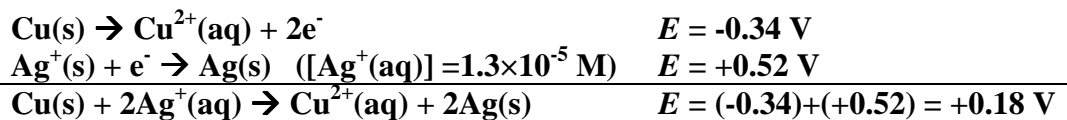
Answer:  $E^\circ = +0.24 \text{ V}$

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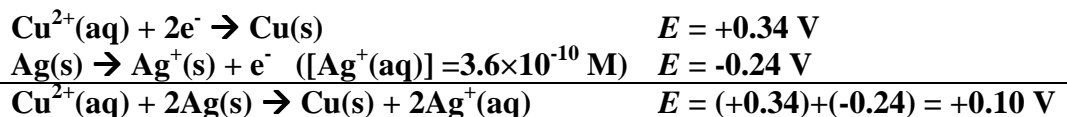
Each of these half-cells is connected to a standard  $\text{Cu}^{2+}(1\text{ M})/\text{Cu}(\text{s})$  half-cell. In which half-cell, (a) or (b), will clear evidence of a reaction be seen? Describe the change(s) observed.

**For the  $\text{Cu}^{2+}(1\text{ M})/\text{Cu}(\text{s})$  half cell, the reduction potential is  $E^\circ = +0.34\text{ V}$ .**

**If the half cell is combined with half cell (a), the former has the least positive cell potential and is reversed:**



**If the half cell is combined with half cell (b), the latter has the least positive cell potential and is reversed:**



**Although both reactions have  $E > 0\text{ V}$  and so are spontaneous, only the second reaction will give clear evidence of a reaction. The  $\text{Ag}^+(\text{aq})$  ions produced will react with the excess  $\text{Cl}^-(\text{aq})$  present to give a white precipitate of  $\text{AgCl}$  around the electrode**

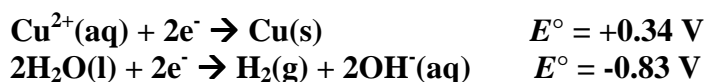


- An aqueous solution of  $\text{CuSO}_4$  is electrolysed with a current of 1.00 A for 60 minutes. Calculate the mass of the products that are formed at the two electrodes.

If a current of 1.00 A is passed for 60 minutes, the number of electrons delivered is,

$$\text{moles of } e^- = \frac{It}{F} = \frac{(1.00 \text{ A}) \times (60 \times 60 \text{ s})}{(96485 \text{ C mol}^{-1})} = 0.037 \text{ mol}$$

At the cathode, the two possible reduction reactions are:



The reduction of  $\text{Cu}^{2+}(\text{aq})$  is much easier ( $E$  is less negative) so  $\text{Cu}(\text{s})$  is formed on the cathode.

[This potential for the reduction of water corresponds to  $[\text{H}^+(\text{aq})] = 1 \text{ M}$ . Using the Nernst equation gives  $E = -0.42 \text{ V}$  for a pH 7 solution. An overpotential of 0.4 to 0.6 V must be added so that the reduction potential is actually  $\sim 1 \text{ V}$ . Thus it is even more difficult to reduce water than the  $E^\circ$  value suggests.]

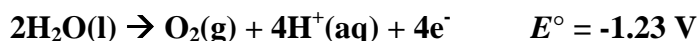
Each mole of  $\text{Cu}(\text{s})$  requires 2 moles of electrons so,

$$\text{number of moles of Cu(s)} = \frac{1}{2} \times 0.037 \text{ mol} = 0.019 \text{ mol}$$

The atomic mass of Cu is  $63.55 \text{ g mol}^{-1}$  so the mass of copper deposited is,

$$\begin{aligned} \text{mass of Cu(s)} &= \text{number of moles} \times \text{molar mass} \\ &= 0.019 \text{ mol} \times 63.55 \text{ g mol}^{-1} = 1.2 \text{ g} \end{aligned}$$

At the anode, oxidation of  $\text{H}_2\text{O}$  occurs to produce  $\text{O}_2(\text{g})$ .



As  $\text{SO}_4^{2-}$  contains S(VI), further oxidation is very difficult.

Production of each mole of  $\text{O}_2(\text{g})$  requires 4 moles of electrons so,

$$\text{number of moles of O}_2(\text{g}) = \frac{1}{4} \times 0.037 \text{ mol} = 0.0093 \text{ mol}$$

The molar mass of  $\text{O}_2$  is  $(2 \times 16.00) = 32.00 \text{ g mol}^{-1}$  so the mass of  $\text{O}_2(\text{g})$  formed is,

$$\begin{aligned} \text{mass of O}_2(\text{g}) &= \text{number of moles} \times \text{molar mass} \\ &= 0.0093 \text{ mol} \times 32.00 \text{ g mol}^{-1} = 0.30 \text{ g} \end{aligned}$$

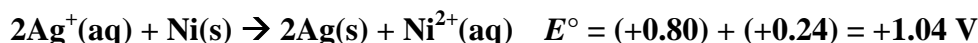
- A galvanic cell consists of a  $\text{Ni}^{2+}/\text{Ni}$  half cell with  $[\text{Ni}^{2+}] = 1.00 \text{ M}$ , and a  $\text{Ag}^+/\text{Ag}$  half cell with  $[\text{Ag}^+] = 1.00 \text{ M}$ . Calculate the electromotive force of the cell at  $25^\circ\text{C}$ .

**Marks**  
**5**

As the concentrations of  $\text{Ni}^{2+}$  and  $\text{Ag}^+$  are both  $1.00 \text{ M}$ , the 'electromotive force' (i.e. the cell potential) refers to standard potentials. The two half-cell reactions and standard reduction potentials are:



The least positive ( $\text{Ni}^{2+}/\text{Ni}$ ) cell is reversed – Ni is oxidized in this reaction and  $\text{Cu}^{2+}$  is reduced. This gives the overall reaction and potential:



Answer: **+1.04 V**

Calculate the equilibrium constant of the reaction at  $25^\circ\text{C}$ .

The equilibrium constant  $K$  and the standard cell potential are related by,

$$E^\circ = \frac{RT}{nF} \ln K$$

The reaction involves two electrons,  $n = 2$ , and so at  $T = 25^\circ\text{C}$ ,

$$+1.04 = \frac{8.314 \times (25 + 273)}{2 \times 96485} \ln K$$

$$\ln K = 81 \quad \text{or} \quad K = e^{81} = 1.5 \times 10^{35}$$

Answer:  **$1.5 \times 10^{35}$**

Calculate the standard free energy change of the reaction at  $25^\circ\text{C}$ .

The standard free energy change is directly related to the standard cell potential,  $\Delta G^\circ = -nFE^\circ$ ,

$$\Delta G^\circ = -2 \times 96485 \times 1.04 = -201 \text{ kJ mol}^{-1}$$

Alternatively, the standard free energy change is related to the equilibrium constant by  $\Delta G^\circ = -RT \ln K$ ,

$$\Delta G^\circ = -(8.314) \times (25 + 273) \times \ln(1.5 \times 10^{35}) = -2.0 \times 10^2 \text{ kJ mol}^{-1}$$

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

**ANSWER CONTINUES ON THE NEXT PAGE**

Is the reaction spontaneous? Give reasons for your answer.

**As  $E^\circ > 0$ , or, equivalently, as  $\Delta G^\circ < 0$ , the reaction is spontaneous (2<sup>nd</sup> Law of Thermodynamics).**

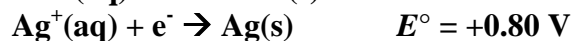
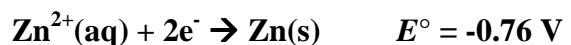
Express the overall reaction in the shorthand voltaic cell notation.

**The oxidation half cell (the anode) is written on the left and the reduction half cell (the cathode) is written on the right. The two half-cells are connected by a salt bridge:**

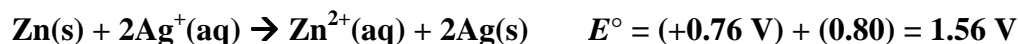


- A galvanic cell is made of a  $\text{Zn}^{2+}/\text{Zn}$  half cell with  $[\text{Zn}^{2+}] = 2.0 \text{ M}$  and an  $\text{Ag}^+/\text{Ag}$  half cell with  $[\text{Ag}^+] = 0.050 \text{ M}$ . Calculate the electromotive force of the cell at  $25^\circ\text{C}$ .

The standard reduction reactions and potentials for the two half cells are:



The least positive ( $\text{Zn}^{2+}/\text{Zn}$ ) couple is reversed giving the overall reaction:



As non-standard concentrations are used, the cell potential is calculated using the Nernst equation. The reaction involves the transfer of  $2\text{e}^-$  so with  $n = 2$  this becomes:

$$E = E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{RT}{nF} \ln \left( \frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Ag}^+(\text{aq})]^2} \right)$$

$$= (+1.56 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(2 \times 96485 \text{ C mol}^{-1})} \ln \left( \frac{2.0}{0.050^2} \right) = +1.47 \text{ V}$$

Answer: +1.47 V

Calculate the equilibrium constant of the reaction at  $25^\circ\text{C}$ .

The equilibrium constant is related to the standard cell potential:

$$E^\circ = \frac{RT}{nF} \ln K$$

Hence,

$$\ln K = E^\circ \times \frac{nF}{RT} = (1.56 \text{ V}) \times \frac{(2 \times 96485 \text{ C mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})} = 121.5$$

$$K = 5.9 \times 10^{52}$$

Answer:  $K = 5.9 \times 10^{52}$

Calculate the standard Gibbs free energy of the reaction at  $25^\circ\text{C}$ .

Using  $\Delta G^\circ = nFE^\circ$ :

$$\Delta G^\circ = -(2 \times 96485 \text{ C mol}^{-1}) \times (+1.56 \text{ V}) = -301 \text{ kJ mol}^{-1}$$

Answer:  $-301 \text{ kJ mol}^{-1}$

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

**As  $E > 0$ ,  $\Delta G^\circ < 0$  and  $K$  is very large: the reaction is spontaneous.**

Express the overall reaction in the shorthand voltaic cell notation.

**$\text{Zn(s)} \mid \text{Zn}^{2+}(\text{aq}) (2.0 \text{ M}) \parallel \text{Ag}^+(\text{aq}) (0.050 \text{ M}) \mid \text{Ag(s)}$**



**Marks**  
**8**

- An Ag electrode immersed in a saturated aqueous solution of AgBr has a reduction potential of 0.437 V at 25 °C with respect to the standard hydrogen electrode. Calculate the solubility product of AgBr at 25 °C.

The standard potential for the reduction  $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$ ,  $E^\circ = +0.80 \text{ V}$ .

The aqueous solution of AgBr will have  $[\text{Ag}^+(\text{aq})]$  equal to the solubility of AgBr. This solution has a non-standard concentration of  $\text{Ag}^+(\text{aq})$  and its potential is given by the Nernst equation with  $n = 1$  for this reduction:

$$E = E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{RT}{F} \ln \left( \frac{1}{[\text{Ag}^+(\text{aq})]} \right)$$

$$E = (+0.80 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(1 \times 96485 \text{ C mol}^{-1})} \ln \left( \frac{1}{[\text{Ag}^+(\text{aq})]} \right) = +0.437 \text{ V}$$

This gives  $[\text{Ag}^+(\text{aq})] = 7.25 \times 10^{-7}$ .

As dissolution of AgBr(s) leads to equal amounts of  $\text{Ag}^+(\text{aq})$  and  $\text{Br}^-(\text{aq})$ , this is also equal to  $[\text{Br}^-(\text{aq})]$ . Thus:

$$K_{\text{sp}} = [\text{Ag}^+(\text{aq})][\text{Br}^-(\text{aq})] = (7.25 \times 10^{-7})^2 = 5.3 \times 10^{-13}$$

Answer:  $K_{\text{sp}} = 5.3 \times 10^{-13}$

A Pd electrode immersed in an aqueous solution containing 0.01 Pd(NO<sub>3</sub>)<sub>2</sub> M and 1.00 M NaCl has a reduction potential of -0.860 V at 25 °C with respect to the Ag electrode above. Calculate the stability constant of the complex ion,  $[\text{PdCl}_4]^{2-}$ , at 25 °C.

The standard potential for the reduction  $\text{Pd}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pd}(\text{s})$ ,  $E^\circ = +0.92 \text{ V}$ .

The reduction potential of the Pd cell is -0.860 V with respect to the Ag electrode, which has a potential of +0.437 V. Thus,

$$E = (-0.860 + 0.437 \text{ V}) = -0.423 \text{ V}.$$

The aqueous solution will have a non-standard concentration of  $\text{Pd}^{2+}(\text{aq})$  and its potential is given by the Nernst equation with  $n = 2$  for this reduction:

$$E = E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{RT}{2F} \ln \left( \frac{1}{[\text{Pd}^{2+}(\text{aq})]} \right)$$

$$E = (+0.92 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(2 \times 96485 \text{ C mol}^{-1})} \ln \left( \frac{1}{[\text{Pd}^{2+}(\text{aq})]} \right) = -0.423 \text{ V}$$

This gives  $[\text{Pd}^{2+}(\text{aq})] = 3.7 \times 10^{-46}$ .

ANSWER CONTINUES ON THE NEXT PAGE

For the formation of  $[\text{PdCl}_4]^{2-}(\text{aq})$ , the reaction table is:

	$\text{Pd}^{2+}(\text{aq})$	$4\text{Cl}^{-}(\text{aq})$	$\rightleftharpoons$	$[\text{PdCl}_4]^{2-}$
<b>Initial</b>	<b>0.01</b>	<b>1.00</b>		<b>0</b>
<b>Equilibrium</b>	$3.7 \times 10^{-46}$	<b>0.96</b>		<b>0.01</b>

As  $[\text{Pd}^{2+}(\text{aq})]_{\text{eq}}$  is so small, *essentially* all of the initially present  $\text{Pd}^{2+}$  reacts with  $4\text{Cl}^{-}$  to make  $[\text{PdCl}_4]^{2-}$  so  $[\text{Cl}^{-}]_{\text{eq}} = 1.00 - 4 \times 0.01 \text{ M} = 0.96 \text{ M}$  and  $[\text{PdCl}_4]^{2-} = 0.01 \text{ M}$ .

Hence:

$$K_{\text{stab}} = \frac{[\text{PdCl}_4^{2-}]}{[\text{Pd}^{2+}][\text{Cl}^{-}]^4} = \frac{0.01}{(3.7 \times 10^{-46})(0.96)^4} = 3 \times 10^{43}$$

Answer:  $3 \times 10^{43}$



- A melt containing  $\text{Cr}^{3+}$  is electrolysed for exactly 1 hour with a current of 0.54 A. Calculate the quantity of chromium that is deposited in this time at the electrode.

Marks  
2

The number of moles of electrons delivered by a current  $I$  in time  $t$  is equal to  $\frac{It}{F}$ :

$$\text{number of moles of electrons} = \frac{It}{F} = \frac{(0.54 \text{ A}) \times (60 \times 60 \text{ s})}{96485 \text{ C mol}^{-1}} = 0.0201 \text{ mol}$$

The reduction reaction is  $\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$  so 3 mol of electrons are required for each mol of Cr. The number of moles of Cr produced is therefore:

$$\text{number of moles of Cr} = \frac{1}{3} \times 0.0201 \text{ mol} = 0.00672 \text{ mol}$$

This corresponds to:

$$\text{mass of Cr} = \text{number of moles} \times \text{molar mass} =$$

$$(0.00672 \text{ mol}) \times (52.00 \text{ g mol}^{-1}) = 0.35 \text{ g}$$

Answer: 0.35 g

- An Ag electrode immersed in an aqueous solution containing  $\text{AgNO}_3$  (0.010 M) and  $\text{NaCN}$  (1.00 M) has a potential of  $-0.66 \text{ V}$ . Calculate the stability constant of the complex ion,  $[\text{Ag}(\text{CN})_2]^-$ .

4

The standard reduction potential,  $E^\circ$ , for the reaction  $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$  is  $+0.80 \text{ V}$ . The Nernst equation can be used to calculate the  $[\text{Ag}^+(\text{aq})]$  after  $\text{CN}^-$  is added. At this point,  $E = -0.66 \text{ V}$ .

Using the Nernst equation for this 1 electron process:

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

$$= (+0.80 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{1 \times 96485 \text{ C mol}^{-1}} \ln \frac{1}{[\text{Ag}^+(\text{aq})]} = -0.66 \text{ V}$$

$$[\text{Ag}^+(\text{aq})] = 2.0 \times 10^{-25} \text{ M}$$

A reaction table can be used to calculate work out the stability constant:

	$\text{Ag}^+(\text{aq})$	$2\text{CN}^-(\text{aq})$	$\rightleftharpoons$	$\text{Ag}(\text{CN})_2^-(\text{aq})$
Initial	0.010	1.00		0
Change	-x	-2x		+x
Equilibrium	$2.0 \times 10^{-25}$	0.98		0.010

Hence,

$$K_{\text{stab}} = \frac{[\text{Ag}(\text{CN})_2^-(\text{aq})]}{[\text{Ag}^+(\text{aq})][\text{CN}^-(\text{aq})]^2} = \frac{(0.010)}{(2.0 \times 10^{-25})(0.98)^2} = 5.1 \times 10^{-22}$$

Answer:  $5.1 \times 10^{-22}$

- Explain the meaning of the terms  $\Delta G$ ,  $n$ , and  $E_{\text{cell}}$  in the equation  $\Delta G = -nFE_{\text{cell}}$ .

**Marks**  
**3**

**$\Delta G$  is the change in free energy due to the completion of a redox reaction. It is the maximum amount of energy that can be extracted from the reaction.**

**$n$  is the number of electrons exchanged.**

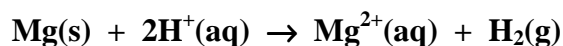
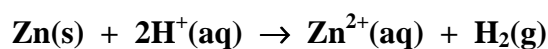
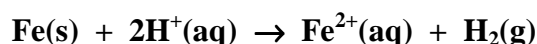
**$E_{\text{cell}}$  is the cell potential as defined in the Nernst equation:**

$$E = E^{\circ} - (RT/nF) \times \ln Q$$

**Marks**  
**4**

- Five strips of different metals were immersed in five different containers with concentrated HCl and the following observations were made.
  1. In the container with the strip of Cu, no change was observed.
  2. In the container with the strip of Sn, no change was observed.
  3. In the container with the strip of Fe, a yellow colour slowly emerged after immersion.
  4. From the container with the strip of Zn, gas started to bubble out.
  5. In the container with the strip of Mg, a vigorous reaction was observed and soon the strip disappeared.

Write down the reactions involved, if any occur.



Explain these experimental observations.

**Cu does not react as the oxidation potential for Cu is negative.**

**Sn would be expected to react as it has a slightly positive oxidation potential. The fact that it does not is due to a high overpotential for the formation of H<sub>2</sub> gas.**

**All the other metals react, evolving H<sub>2</sub>(g) as expected. The higher the oxidation potential (Mg > Zn > Fe), the more vigorous the reaction.**

Explain how cathodic protection can prevent the corrosion of iron.

**Fe, when placed in contact with another metal with a higher oxidation potential (e.g. Zn, Mg) will act as the cathode. The other metal will act as the sacrificial anode and will be oxidised preferentially.**