ANSWERS TO PRACTICE QUESTIONS

4 Cell (1)

(a) (i) $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$ $\quad E^\ominus = +1.33$ V ... (1)
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $\quad E^\ominus = +0.34$ V ... (2)

Reduction: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
Cathode: **Pt electrode** in $Cr_2O_7^{2-}(aq)$ / $Cr^{3+}(aq)$ half–cell

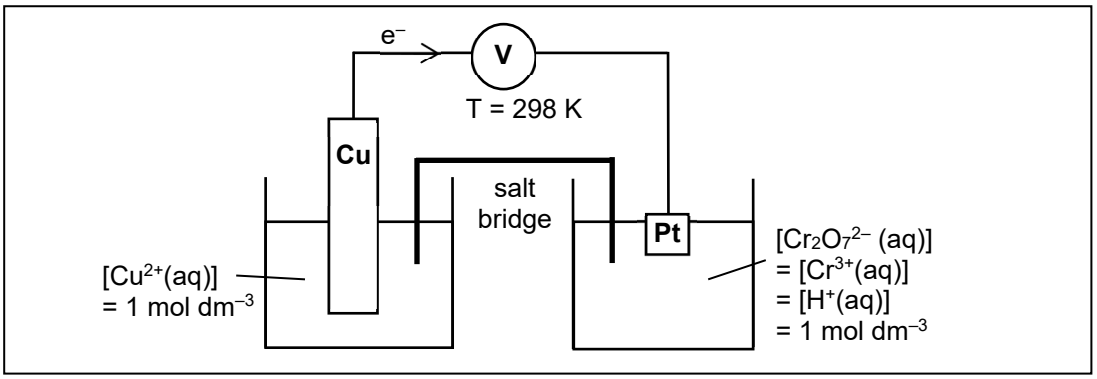
Oxidation: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
Anode: **Copper electrode** in $Cu^{2+}(aq)$ / $Cu(s)$ half–cell

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

Note: Students are to note that both the half and full equations are written with → instead of ⇌ seen in the Data Booklet.

(ii) $E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode} = +1.33 - (+0.34) = +0.99$ V

(iii)



Cell (2)

(a) (i) $H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$ $\quad E^\ominus = +1.77$ V
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$ $\quad E^\ominus = +0.68$ V

Reduction: $H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$
Cathode: **Pt electrode** in $H_2O_2(aq)$ / $H_2O(l)$ half–cell

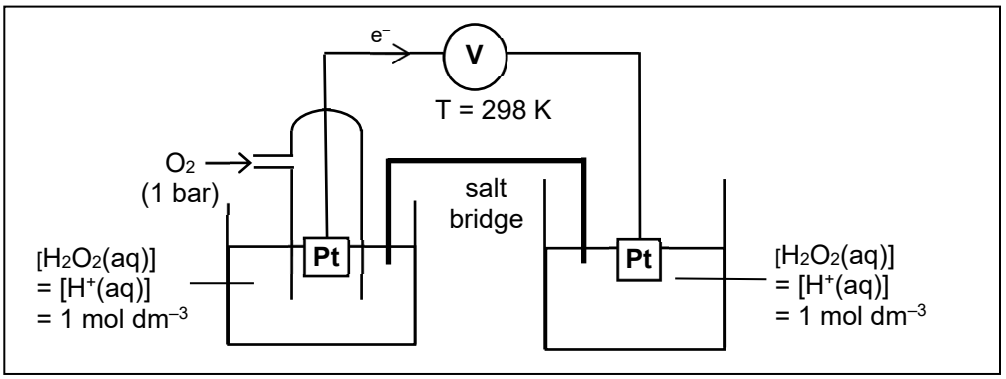
Oxidation: $H_2O_2(aq) \rightarrow O_2(g) + 2H^+(aq) + 2e^-$
Anode: **Pt electrode** in $O_2(g)$ / $H_2O_2(aq)$ half–cell

Overall**:** $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

Note: Students are to note that both the half and full equations are written with → instead of ⇌ seen in the Data Booklet.

(iii) $E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode} = +1.77 - (+0.68) = +1.09$ V

(iv)



(b) **(i)** Cu^{2+} precipitates out as $CuCO_3$ and so <u>$[Cu^{2+}(aq)]$ decreases</u>.

This shifts the position of equilibrium of (2) to the left so that $E(Cu^{2+}/Cu)$ becomes <u>less positive</u>. Hence, E_{cell} becomes <u>more positive</u> (i.e. $E_{cell} > E^{\ominus}_{cell}$).

(ii) $Br_2 + 2e^- \rightleftharpoons 2Br^-$ $\quad E^{\ominus} = +1.07$ V

Br^- reduces $Cr_2O_7^{2-}$ to Cr^{3+}. Note: $E^{\ominus}_{cell} = +1.33 - (+1.07) = +0.26$ V > 0 (feasible)

This <u>decreases $[Cr_2O_7^{2-}(aq)]$ but increases $[Cr^{3+}(aq)]$</u> so that the position of equilibrium of (1) shifts to the left and so $E(Cr_2O_7^{2-}/Cr^{3+})$ becomes <u>less positive</u>. Hence E_{cell} becomes <u>less positive</u> (i.e. $E_{cell} < E^{\ominus}_{cell}$).

(c) To decrease E_{cell}, either (1) decrease $E(H_2O_2/H_2O)$ or (2) increase $E(O_2/H_2O_2)$.

Change (1): $E(H_2O_2/H_2O)$ can be decreased by using <u>H_2O_2 or H^+ of a lower concentration (i.e. < 1 mol dm^{-3})</u> the H_2O_2/H_2O half–cell.

Change (2): $E(O_2/H_2O_2)$ can be increased by using <u>O_2 of a higher pressure (i.e. > 1 bar)</u>, <u>H^+ of a higher concentration (i.e. > 1 mol dm^{-3})</u> <u>or H_2O_2 of a lower concentration (i.e. < 1 mol dm^{-3})</u> in the O_2 / H_2O_2 half–cell.

5 From *Data Booklet*, $E^{\ominus}(H^+/H_2) = 0.00$ V; $E^{\ominus}(Ag^+/Ag) = +0.80$ V

In the reaction $2H^+(aq) + Cd(s) \rightarrow Cd^{2+}(aq) + H_2(g)$, Cd is oxidised.

Thus $E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode} = E^{\ominus}(H^+/H_2) - E^{\ominus}(Cd^{2+}/Cd) = 0.00 - E^{\ominus}(Cd^{2+}/Cd) = +0.40$ V

$\Rightarrow E^{\ominus}(Cd^{2+}/Cd) = -0.40$ V

In the reaction $Pd^{2+}(aq) + 2Ag(s) \rightarrow 2Ag^+(aq) + Pd(s)$, Pd^{2+} is reduced.

Thus $E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode} = E^{\ominus}(Pd^{2+}/Pd) - E^{\ominus}(Ag^+/Ag) = E^{\ominus}(Pd^{2+}/Pd) - 0.80 = +0.19$ V

$\Rightarrow E^{\ominus}(Pd^{2+}/Pd) = +0.99$ V

Therefore, potential of Pd relative to Cd is $+0.99 - (-0.40) =$ <u>+1.39 V</u>

6 (a) (i) $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
Note: This half-equation can be found in the Data Booklet.

(ii) Reduction: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ ($\times$ 3)
Oxidation: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ ($\times$ 2)
Overall: $2CH_3OH + 3O_2 \rightarrow 4H_2O + 2CO_2$

(iii) From *Data Booklet*, $E^\ominus(O_2/H_2O) = +1.23$ V
$E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode}$
Thus, $+1.18 = +1.23 - E^\ominus(CO_2/CH_3OH)$
$E^\ominus(CO_2/CH_3OH) = +1.23 - (+1.18) = +0.05$ V

(iv) Any <u>one</u> of the following:
- Methanol has a more efficient storage (by volume or by weight since it is a liquid) compared to compressed hydrogen gas.
- Hydrogen gas is more volatile and explosive, thus requires high pressure storage system but not methanol (less explosive).

(b) (i) $CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

(ii) $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$
$\Delta G^\ominus = (-1367 \times 10^3) - (298)(-140) = -1.33 \times 10^6$ J mol^{-1} $= -1330$ kJ mol^{-1}

(iii) $E^\ominus_{cell} = \dfrac{-(-1.33 \times 10^6 \text{ J mol}^{-1})}{12\ (96500 \text{ C mol}^{-1})} = +1.15$ V

7 (a) (i) A saturated KCl solution is used to keep the concentration Cl^- constant in the reference electrode.

Examiner Comments
- This question was poorly done. The hint was given in the question regarding the nature of a reference electrode (fixed composition and constant potential).

(ii) The $E^\ominus$ value is <u>more positive</u> than +0.241 V. At standard conditions, the <u>KCl concentration</u> is 1.00 mol dm^{-3}, which is <u>lower than the saturated</u> KCl solution. Therefore, the equilibrium position of the half-equation <u>lies more to the right</u>, resulting in a more positive $E^\ominus$ value.

Note: Concentration of a saturated solution of KCl is 4.55 mol dm^{-3} at 20 ºC.

Examiner Comments
- Students who lost marks here were careless in their reading of the question. The E value (+0.241 V) given is <u>not</u> at standard conditions.
- When answering questions, students should be clear in referring to E or $E^\ominus$. E is used to represent the potential at any conditions that are not standard.

(b) (i) $Ag^+(aq) + e^- \rightleftharpoons Ag(s)$ $\quad E^\ominus = +0.80$ V

Since the Ag^+/Ag electrode has the more positive $E^\ominus$, it is the cathode. The <u>S.C.E. is the anode</u>.

(ii) E_{cell} = +0.80 – 0.241 = +0.559 V

Examiner Comments

- This question was generally well done.
- Students are reminded to express their answers in 3 s.f. and with units.

(iii) At very low concentrations of Ag^+, small increases in $[Ag^+]$ result in an exponential/ large increase in E_{cell} as shown by the steep gradient of the graph.

Examiner Comments

- Some students described the shape of the graph in terms of rate, e.g. increased rapidly, increased at a greater rate, etc. This is not accepted as there is no time scale on the graph.
- A number of students discussed the gentle gradient at relatively higher $[Ag^+]$. This is not accepted as it doesn't answer the question.

8 **(a)** $E^{\ominus}_{cell}$ = +0.80 – (+0.34) = +0.46 V (spontaneous)

(b) $E^{\ominus}_{cell}$ = +1.07 – (+0.77) = +0.30 V (spontaneous)

(c) $E^{\ominus}_{cell}$ = –1.66 – (+1.36) = –3.02 V (not spontaneous)

(d) $E^{\ominus}_{cell}$ = –0.43 – (–0.83) = +0.40 V (spontaneous)

(e) $E^{\ominus}_{cell}$ = +1.52 – (+0.68) = +0.84 V (spontaneous)

(f) They are both oxidising agents hence they cannot react with each other.

(g)

$Zn^{2+} + 2e^- \rightleftharpoons Zn$	$E^{\ominus}$ = –0.76 V ..... (1)
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	$E^{\ominus}$ = +1.33 V ..... (2)
$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	$E^{\ominus}$ = –0.41 V ..... (3)
$Cr^{2+} + 2e^- \rightleftharpoons Cr$	$E^{\ominus}$ = –0.91 V ..... (4)
$Cr^{3+} + 3e^- \rightleftharpoons Cr$	$E^{\ominus}$ = –0.74 V ..... (5)

Combining half reactions (1) and (2), $E^{\ominus}_{cell}$ = +1.33 – (–0.76) = +2.09 V (spontaneous)
Combining half reactions (1) and (3), $E^{\ominus}_{cell}$ = –0.41 – (–0.76) = +0.35 V (spontaneous)
Combining half reactions (1) and (4), $E^{\ominus}_{cell}$ = –0.91 – (–0.76) = –0.15 V (not spontaneous)

Thus, Zn will reduce $Cr_2O_7^{2-}$ to Cr^{3+} and further reduce Cr^{3+} to Cr^{2+}.

9 **(a)**

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	$E^{\ominus}$ = +1.52 V
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	$E^{\ominus}$ = +1.36 V
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	$E^{\ominus}$ = +1.33 V

Under standard conditions, MnO_4^- can oxidise Cl^- to Cl_2,
i.e. $E^{\ominus}_{cell}$ = +1.52 – (+1.36) = +0.16 V > 0

In the titration determination of iron(II) ions, the amount of Fe^{2+} ions present is determined by the amount of oxidant it reacts with.

If MnO_4^- were used, some MnO_4^- will be consumed by Cl^- instead of reacting solely with Fe^{2+}. This would result in a larger amount of MnO_4^- used than required i.e. the results would be inaccurate.

On the other hand, under standard conditions, $Cr_2O_7^{2-}$ cannot oxidise Cl^- to Cl_2,
i.e. $E^\ominus_{cell} = +1.33 - (+1.36) = -0.03\ V < 0$

Hence all $Cr_2O_7^{2-}$ will be solely used to react with Fe^{2+} ions and thus $K_2Cr_2O_7(aq)$ can be used for the titration determination of iron(II) ions in the presence of dilute HCl(aq).

(b) $H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$ $\quad E^\ominus = +1.77\ V$
$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$ $\quad E^\ominus = +0.68\ V$

Hydrogen peroxide can spontaneously itself undergo simultaneous oxidation and reduction under standard conditions. This reaction is called disproportionation.

$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$
$E^\ominus_{cell} = +1.77 - (+0.68)\ V = +1.09\ V > 0$
$\Rightarrow$ reaction is thermodynamically feasible under standard conditions.

Hence bubbles of oxygen are given off by a solution of hydrogen peroxide on standing.

10 From the *Data Booklet*,

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	$E^\ominus = +1.36\ V$
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	$E^\ominus = +1.07\ V$
$I_2 + 2e^- \rightleftharpoons 2I^-$	$E^\ominus = +0.54\ V$
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	$E^\ominus = -0.44\ V$
$Fe^{3+} + 3e^- \rightleftharpoons Fe$	$E^\ominus = -0.04\ V$
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	$E^\ominus = +0.77\ V$

Let X = Cl, Br or I.
For the reaction between X_2 and Fe,
$E^\ominus_{cell} = E^\ominus(X_2/X^-) - E^\ominus(Fe^{2+}/Fe)$
Since $E^\ominus_{cell} > 0$ for X = Cl, Br and I
$\Rightarrow$ the reaction between X_2 and Fe is spontaneous and Fe is oxidised by X_2 to Fe^{2+}.

Note: $E^\ominus(Fe^{2+}/Fe)$ is more negative than $E^\ominus(Fe^{3+}/Fe) \Rightarrow$ there is a higher tendency for Fe to be oxidised to Fe^{2+} than to Fe^{3+}.

For the reaction between X_2 and Fe^{2+},
$E^\ominus_{cell} = E^\ominus(X_2/X^-) - E^\ominus(Fe^{3+}/Fe^{2+})$
Since $E^\ominus_{cell} > 0$ only for X = Cl and Br
$\Rightarrow$ the reactions between Cl_2 and Fe^{2+} & Br_2 and Fe^{2+} are spontaneous. Hence, Fe^{2+} is further oxidised by Cl_2 and Br_2 to Fe^{3+}.
However, $E^\ominus_{cell} < 0$ for X = I.
$\Rightarrow$ the reaction between I_2 and Fe^{2+} is not spontaneous and Fe^{2+} is not further oxidised by I_2.

Hence when iron is heated separately with Cl_2, Br_2 and I_2, the products are $FeCl_3$, $FeBr_3$ and FeI_2 respectively. (Ans C).

11 **(a)** $E^\ominus_{cell} = +0.22 - (+0.80) = -0.58\ V$

(b) $\Delta G^\ominus = -nFE^\ominus = -(1)(96500)(-0.58) = +55970\ J\ mol^{-1} = +56.0\ kJ\ mol^{-1}$

(c) $\Delta G^\ominus = -RT \ln K_{sp}$

$+56.0 \times 10^3 = -(8.31)(298) \ln K_{sp}$
$K_{sp} = 1.53 \times 10^{-10}$ mol^2 dm^{-6}

Note: Units for K not required for this calculation.

12 **(a)** $E^{\ominus} = +0.77 - (-0.25) = +1.02$ V
$2Fe^{3+}(aq) + Ni(s) \rightarrow 2Fe^{2+}(aq) + Ni^{2+}(aq)$

(b) For Fe^{3+}/ Fe^{2+} half-cell – solution turns from greenish-yellow to green
For $Ni^{2+}/$ Ni half-cell – anode decreases in size (Note: Ni^{2+} is green)

(c) $\Delta G^{\ominus} = -nFE^{\ominus} = -(2)(96500)(1.02) = -1.97 \times 10^5$ J mol^{-1} = –197 kJ mol^{-1}

(d) $[Ni^{2+}]$ after 10 h = 1 + 0.373 = 1.373 mol dm^{-3}

$$E_{Ni^{2+}/Ni} = E^{\ominus}_{Ni^{2+}/Ni} - (9.916 \times 10^{-5})T \; log \; \frac{1}{[Ni^{2+}]}$$

$E_{Ni2+/Ni} = -0.25 - (9.916 \times 10^{-5})(298) \log(1/1.373) = -0.246$ V

(e) $$E_{cell} = E^{\ominus}_{cell} - (9.916 \times 10^{-5})T \; log \left(\frac{[Ni^{2+}]\,[Fe^{2+}]^2}{[Fe^{3+}]^2} \right)$$

$E_{cell} = +1.02 - (9.916 \times 10^{-5})(273 + 35) \; log \; (0.20) = +1.04$ V

(f)

$$K_c = \frac{\left[Fe^{2+}\right]^2 \left[Ni^{2+}\right]}{\left[Fe^{3+}\right]^2}$$

At equilibrium, $E_{cell} = 0$ (cell stops working)

$$0 = +1.02 - (9.916 \times 10^{-5})\,(273 + 35) \; log \; \frac{\left[Fe^{2+}\right]^2 \left[Ni^{2+}\right]}{\left[Fe^{3+}\right]^2}$$

$$K_c = \frac{\left[Fe^{2+}\right]^2 \left[Ni^{2+}\right]}{\left[Fe^{3+}\right]^2} = 2.50 \times 10^{33} \text{ mol dm}^{-3}$$

Note: units for K not required for this calculation.