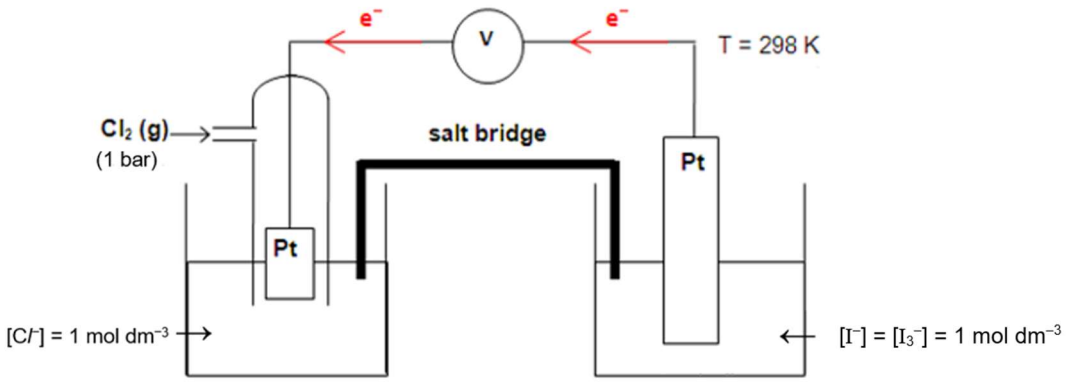
## ANSWERS TO SELF-CHECK QUESTIONS

**1 (a)** The ***standard electrode potential***, $E^{\ominus}$, of a half–cell is the electromotive force, measured at **298 K**, between the **half–cell** and the **standard hydrogen electrode**, in which the concentration of any reacting species in solution is **1 mol dm$^{-3}$** and any gaseous species is at a pressure of **1 bar**.

**(b)** The **standard cell potential** ($E^{\ominus}_{cell}$) is the **potential difference** between two half–cells under **standard conditions**.

**2 (a)**




*Checklist for the general labels to include when drawing the setup:*

| in each half-cell | connecting 2 half-cells |
|---|---|
| ☐ identity of electrode | ☐ external wire with voltmeter |
| ☐ identity and concentration of electrolyte | ☐ direction of electron flow |
| ☐ gas jar, identity and partial pressure of gas (if any) | ☐ salt bridge |
| | ☐ temperature |

*Note: Question may also ask for the labelling of anode (–) or cathode (+).*

**(b)** Set up the electrochemical cell as shown above. Read off the $E^{\theta}_{cell}$ value on the voltmeter. The greater the $E^{\theta}_{cell}$ value, the greater the difference in electrode potentials of the two half-cells. Monitor the direction of the flow of electrons to identify the electrode that is positively charged (the one to which electrons are flowing towards). The electrode that is positively charged contains the stronger oxidising agent which is preferentially reduced.

**(c)** $Cl_2\,(g) + 2I^-(aq) \rightarrow I_2\,(aq) + 2Cl^-(aq)$

**3 (a)** reduction half cell: $Cl_2 / Cl^-$

**(b)** $Cl_2 + Co \rightarrow 2Cl^- + Co^{2+}$

**(c)** $E^{\ominus}_{cell} = +1.36 - (-0.28) = +1.64$ V

**ANSWERS TO PRACTICE QUESTIONS**

**4 Cell (1)**

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

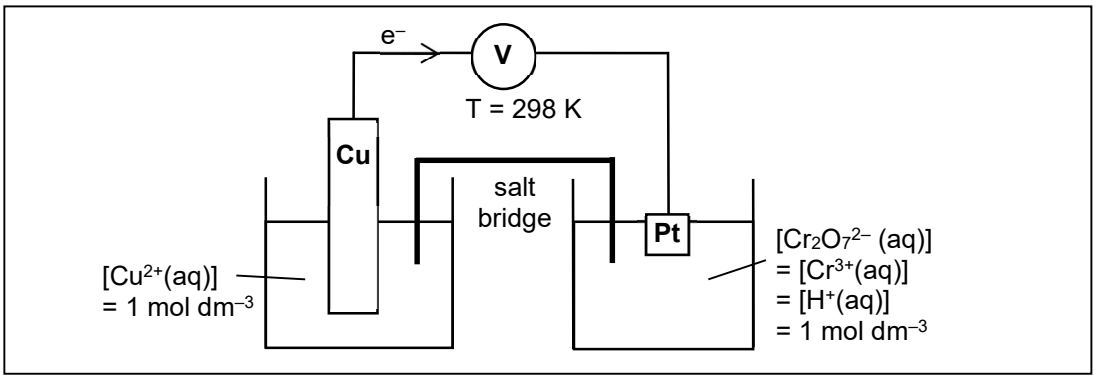
Oxidation: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
Anode: **Copper electrode** in $Cu^{2+}(aq)$ / Cu(s) half–cell

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

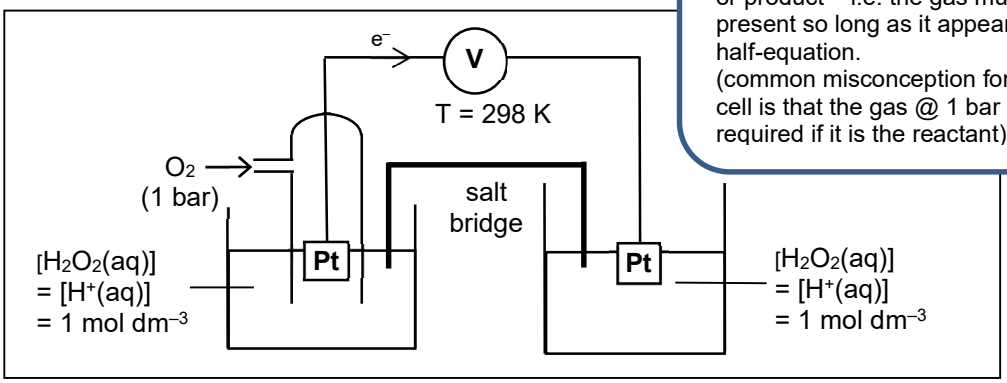
Overall**:** $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

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

Note to tutors:
Highlight during the lesson that the gas (@1 bar) may be the reactant or product – i.e. the gas must be present so long as it appears in the half-equation.
(common misconception for voltaic cell is that the gas @ 1 bar is only required if it is the reactant)

**(iv)**




**(b)** **(i)** $Cu^{2+}$ precipitates out as $CuCO_3$ and so $\underline{[Cu^{2+}(aq)] \text{ decreases}}$.

This shifts the position of equilibrium of (2) to the left so that $E(Cu^{2+}/Cu)$ becomes $\underline{\text{less positive}}$. Hence, $E_{cell}$ becomes $\underline{\text{more positive}}$ (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 $\underline{\text{decreases } [Cr_2O_7^{2-}(aq)] \text{ but increases } [Cr^{3+}(aq)]}$ so that the position of equilibrium of (1) shifts to the left and so $E(Cr_2O_7^{2-}/Cr^{3+})$ becomes $\underline{\text{less positive}}$. Hence $E_{cell}$ becomes $\underline{\text{less positive}}$ (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 $\underline{H_2O_2 \text{ or } H^+ \text{ of a lower concentration (i.e. < 1 mol dm}^{-3}\text{)}}$ the $H_2O_2/H_2O$ half–cell.

Change (2): $E(O_2/H_2O_2)$ can be increased by using $\underline{O_2 \text{ of a higher pressure (i.e. > 1 bar)}}$, $\underline{H^+ \text{ of a higher concentration (i.e. > 1 mol dm}^{-3}\text{)}}$ or $\underline{H_2O_2 \text{ of a lower concentration (i.e. < 1 mol dm}^{-3}\text{)}}$ 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 $+0.99 - (-0.40) = \underline{+1.39 \text{ V}}$

**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 KC$l$ solution is used to keep the concentration C$l^-$ 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>KC$l$ concentration</u> is 1.00 mol dm$^{-3}$, which is <u>lower than the saturated</u> KC$l$ 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 KC$l$ 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) |

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 HC*l*(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 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*,

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

Let X = C*l*, 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 = C*l*, 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 = C*l* 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.

Note to tutors: Highlight to students that the T in this eqn, $\Delta G^{\ominus} = -RT \ln K$, is the T at which eqm is achieved. It may not necessarily be 298 K.

$\Delta G = \Delta G^{\ominus} + RT \ln Q$ (Q is reaction quotient)
At eqm @ T K (need not be 298 K),
$\Delta G = \Delta G^{\ominus} + RT \ln K = 0$
Hence, $\Delta G^{\ominus} = -RT \ln K$

**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.