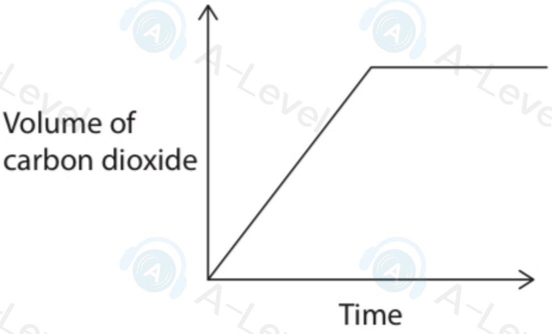
**14** The formation of carbon dioxide from the reaction between manganate(VII) ions and ethanedioate ions is autocatalysed by manganese(II) ions.

The equation for this reaction is shown.

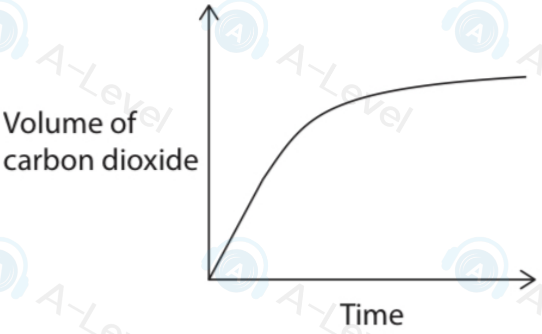
$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

Which graph for the complete reaction shows the autocatalysis of this reaction by the manganese(II) ions?

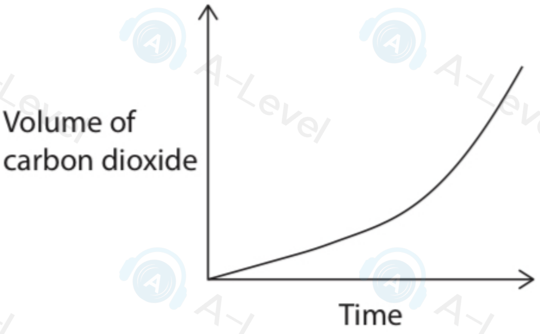
☒ **A**



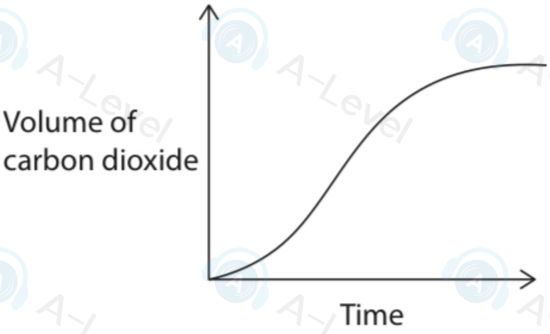
☒ **B**



☒ **C**



☒ **D**



**(Total for Question 14 = 1 mark)**

**TOTAL FOR SECTION A = 20 MARKS**

**14** What is the sequence of oxidation number changes for vanadium when $V_2O_5$ is used in the contact process?

☒ **A** +2 → +1 → +2

☒ **B** +2 → +5 → +2

☒ **C** +5 → +4 → +5

☒ **D** +5 → +6 → +5

**10** Which ion is **not** blue?

☒ **A** $VO^{2+}$

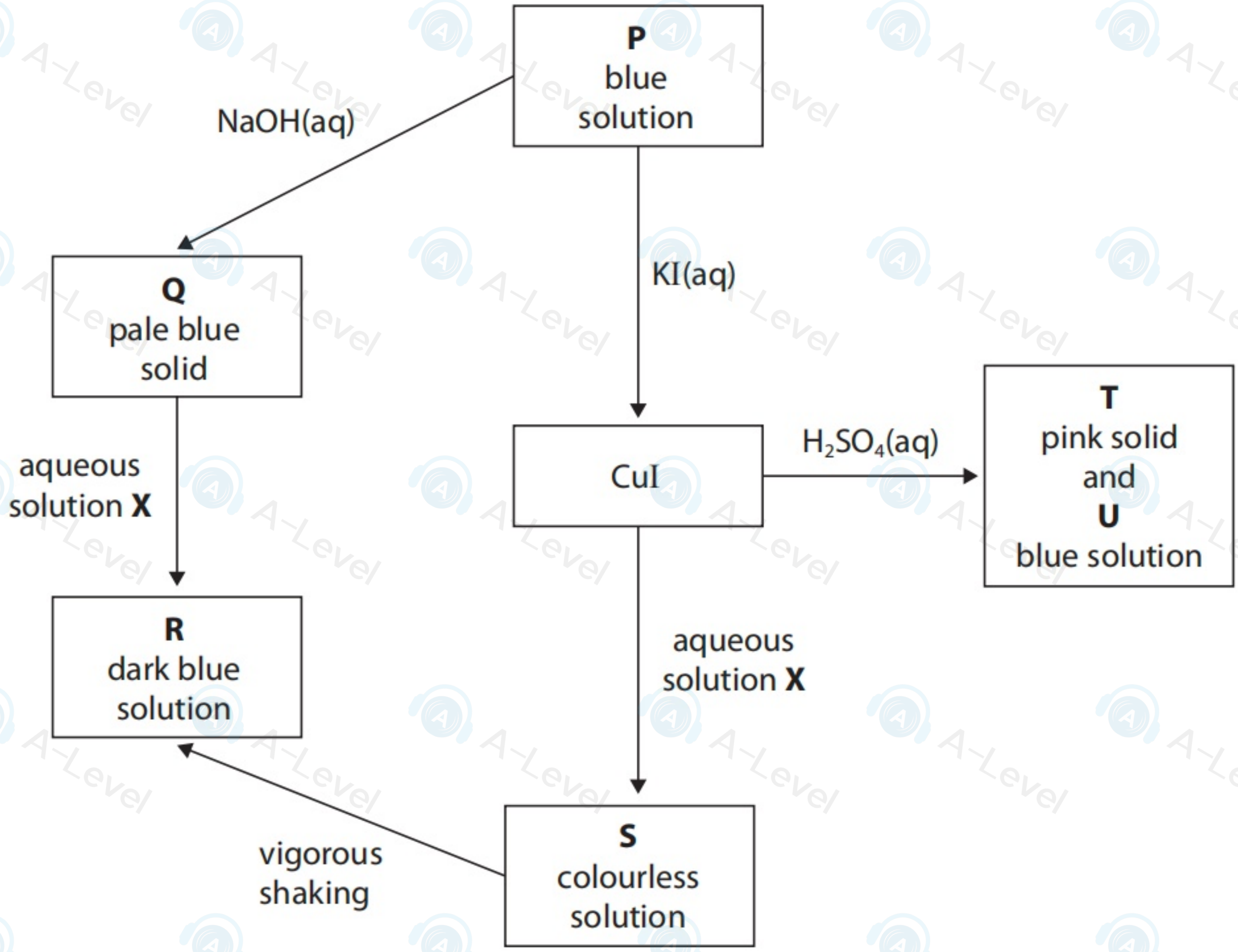
☒ **B** $[Co(H_2O)_6]^{2+}$

☒ **C** $[Cr(H_2O)_6]^{2+}$

☒ **D** $[Cu(H_2O)_6]^{2+}$

**5** This question concerns the chemistry of copper.

In the reaction sequence, the substances P, Q, R, S, T and U contain copper in various oxidation states.



(a) What are the electronic structures of the three copper species?

**(1)**

| | | Cu | $Cu^+$ | $Cu^{2+}$ |
|---|---|---|---|---|
| ☒ | **A** | [Ar] $3d^9\ 4s^2$ | [Ar] $3d^9\ 4s^1$ | [Ar] $3d^9$ |
| ☒ | **B** | [Ar] $3d^9\ 4s^2$ | [Ar] $3d^8\ 4s^2$ | [Ar] $3d^7\ 4s^2$ |
| ☒ | **C** | [Ar] $3d^{10}\ 4s^1$ | [Ar] $3d^9\ 4s^1$ | [Ar] $3d^8\ 4s^1$ |
| ☒ | **D** | [Ar] $3d^{10}\ 4s^1$ | [Ar] $3d^{10}$ | [Ar] $3d^9$ |

(b) Which rows show the substances with their correct oxidation states?

**(1)**

| | | Cu(0) | Cu(I) | Cu(II) |
|---|---|---|---|---|
| ☒ | **A** | S | U | P |
| ☒ | **B** | S | R | Q |
| ☒ | **C** | T | S | P |

4 Which metal hydroxide precipitate is soluble in **both** excess aqueous ammonia and excess aqueous sodium hydroxide?

☒ **A** $Cu(OH)_2$

☒ **B** $Fe(OH)_2$

☒ **C** $Ni(OH)_2$

☒ **D** $Zn(OH)_2$

6 Acidified manganate(VII) ions react with ethanedioate ions.

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

The rate of this reaction increases then decreases.

What are the reasons for these changes in rate of reaction?

| | | Reason rate increases | Reason rate decreases |
|---|---|---|---|
| ☒ | **A** | $Mn^{2+}$ acts as a catalyst | kinetic energy of particles decreases |
| ☒ | **B** | $Mn^{2+}$ acts as a catalyst | concentration of reactants decreases |
| ☒ | **C** | $MnO_4^-$ acts as a catalyst | kinetic energy of particles decreases |
| ☒ | **D** | $MnO_4^-$ acts as a catalyst | concentration of reactants decreases |

**4** Aqueous sodium hydroxide and aqueous ammonia are added, until they are in excess, to separate portions of a pale green aqueous solution **E**.

| Test | Observations |
|---|---|
| Aqueous sodium hydroxide is added to **E** | Green precipitate forms<br>No further change in excess |
| Aqueous ammonia is added to **E** | Green precipitate forms<br>Green precipitate dissolves in excess to form a pale blue solution |

Which ion is present in **E**?

☒ **A** $Cu^{2+}$

☒ **B** $Fe^{2+}$

☒ **C** $Ni^{2+}$

☒ **D** $V^{2+}$

**2** An oxide of vanadium is the catalyst in one step of the contact process for the manufacture of sulfuric acid.

Which reaction involves the vanadium oxide catalyst and how does the oxidation number of vanadium change during the process?

| | | Reaction | Oxidation number changes for vanadium |
|---|---|---|---|
| ☒ | **A** | $S + O_2 \rightarrow SO_2$ | $+5 \rightarrow +4 \rightarrow +5$ |
| ☒ | **B** | $SO_2 \rightarrow SO_3$ | $+4 \rightarrow +5 \rightarrow +4$ |
| ☒ | **C** | $SO_2 \rightarrow SO_3$ | $+5 \rightarrow +4 \rightarrow +5$ |
| ☒ | **D** | $SO_3 + H_2O \rightarrow H_2SO_4$ | $+4 \rightarrow +5 \rightarrow +4$ |

**5** Chromium(III) hydroxide, $Cr(OH)_3(H_2O)_3$, is amphoteric.

This means that chromium(III) hydroxide dissolves in

☒ **A** water

☒ **B** strong acid only

☒ **C** strong alkali only

☒ **D** strong acid and strong alkali

**3** Which complex ion is colourless?

☒ **A** $[Al(H_2O)_6]^{3+}$

☒ **B** $[Cu(H_2O)_6]^{2+}$

☒ **C** $[Fe(H_2O)_6]^{3+}$

☒ **D** $[Ni(H_2O)_6]^{2+}$

**9** The half-equation for the reaction taking place at the positive electrode in an **alkaline** hydrogen-oxygen fuel cell is

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

What is the half-equation for the reaction taking place at the negative electrode?

☒ **A** $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$

☒ **B** $H_2 + OH^- \rightarrow H_2O + H^+ + 2e^-$

☒ **C** $H_2 \rightarrow 2H^+ + 2e^-$

☒ **D** $H_2 + H_2O \rightarrow 3H^+ + OH^- + 2e^-$

**8** Which complex contains **only** monodentate ligands?

☒ **A** $[Fe(CN)_6]^{4-}$

☒ **B** $[Cr(C_2O_4)_3]^{3-}$

☒ **C** $[Ni(EDTA)]^{2-}$

☒ **D** $[Co(NH_2CH_2CH_2NH_2)_2Cl_2]$

**5** The formula of hydrated copper(II) bromide is $CuBr_2{\cdot}4H_2O$.

What is the percentage, by mass, of water of crystallisation in this compound?

☒ **A** 6.10%

☒ **B** 8.06%

☒ **C** 24.4%

☒ **D** 32.2%

**1** Which of these is a d-block element but is not a transition element?

☒ **A** cobalt

☒ **B** copper

☒ **C** nickel

☒ **D** zinc

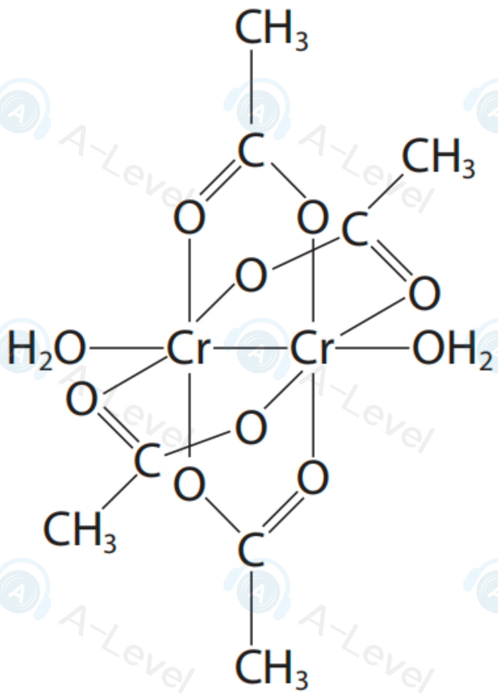
**10** The emf, $E^{\ominus}_{cell}$, of a cell is +0.57 V.

The numerical values of the standard electrode potentials of the two half-cells joined in this cell are 0.17 V and 0.40 V.

What are the signs of the standard electrode potentials of the right-hand half-cell and the left-hand half-cell?

| | | Sign of standard electrode potential | |
|---|---|---|---|
| | | in left-hand half-cell | in right-hand half-cell |
| ☒ | **A** | negative | negative |
| ☒ | **B** | negative | positive |
| ☒ | **C** | positive | negative |
| ☒ | **D** | positive | positive |

**7** The structure of the complex $Cr_2(CH_3CO_2)_4(H_2O)_2$ is shown.



What is the coordination number of chromium in this complex?

☒ **A** two

☒ **B** four

☒ **C** six

☒ **D** twelve

**8** Standard electrode potentials can also be given an alternative name.
The electrochemical series lists standard electrode potentials in order.

Which of these is correct?

| | | Alternative name for standard electrode potential | Order of standard electrode potentials in the electrochemical series |
|---|---|---|---|
| ☒ | **A** | standard reduction potential | most negative to most positive |
| ☒ | **B** | standard reduction potential | most positive to most negative |
| ☒ | **C** | standard cell potential | most negative to most positive |
| ☒ | **D** | standard cell potential | most positive to most negative |

**6:** Which is **incorrect** for $H_2O$, $OH^-$ and $NH_3$?

☒ **A** all can act as bidentate ligands

☒ **B** all can act as electron pair donors

☒ **C** all can form dative covalent bonds

☒ **D** all can take part in complex ion formation

**(Total for Question 6 = 1 mark)**

**7** What are the shapes of the complexes $[CuCl_4]^{2-}$ and $Pt(NH_3)_2Cl_2$?

| | | $[CuCl_4]^{2-}$ | $Pt(NH_3)_2Cl_2$ |
|---|---|---|---|
| ☒ | **A** | square planar | square planar |
| ☒ | **B** | square planar | tetrahedral |
| ☒ | **C** | tetrahedral | square planar |
| ☒ | **D** | tetrahedral | tetrahedral |

**(Total for Question 7 = 1 mark)**

**2** The half-equations for a hydrogen-oxygen fuel cell in **alkaline** solution are shown.

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E^\ominus = -0.83\,V$$

$$\tfrac{1}{2}O_2(g) + H_2O(l) + 2e^- \rightarrow 2OH^-(aq) \qquad E^\ominus = +0.40\,V$$

(a) The equation for the overall cell reaction is

**(1)**

☒ **A** $3H_2O(l) + \tfrac{1}{2}O_2(g) \rightarrow H_2(g) + 4OH^-(aq)$

☒ **B** $H_2(g) + 4OH^-(aq) \rightarrow 3H_2O(l) + \tfrac{1}{2}O_2(g)$

☒ **C** $H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l)$

☒ **D** $H_2O(l) \rightarrow H_2(g) + \tfrac{1}{2}O_2(g)$

(b) Calculate $E^\ominus_{cell}$ for the reaction occurring in the hydrogen-oxygen fuel cell, under alkaline conditions.

**(1)**

☒ **A** −1.23 V

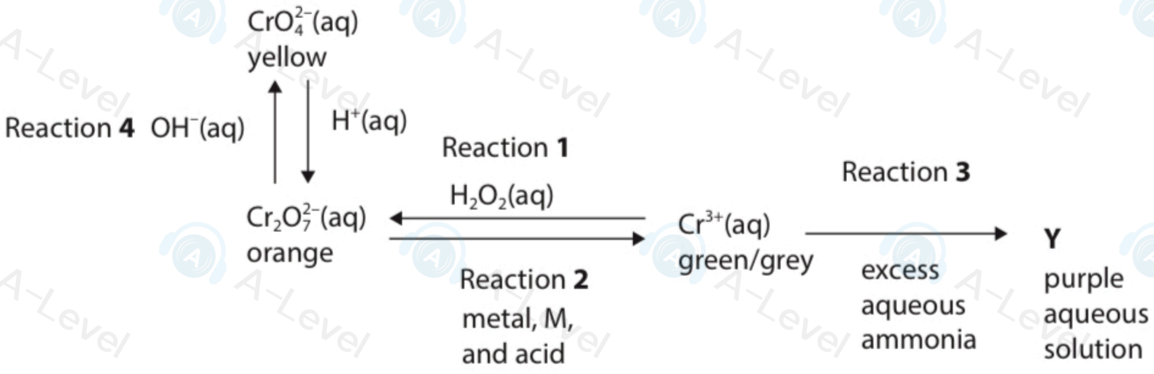
☒ **B** −0.43 V

☒ **C** +0.43 V

☒ **D** +1.23 V

**20** This question is about some chromium compounds.

(a) Some reactions of chromium compounds are shown.



(i) Write the equation for Reaction **1**. Use the half-equations from page 10 of your Data Booklet. State symbols are **not** required.

**(2)**

(ii) In Reaction **2**, $Cr_2O_7^{2-}$ reacts with a metal, M, in acid conditions forming $Cr^{3+}$ and $M^{2+}$.

Identify a possible metal, M, calculating $E^{\ominus}_{cell}$ for its reaction with $Cr_2O_7^{2-}$.

Use information from page 10 of your Data Booklet.

**(2)**

(iii) Give the formula of the species responsible for the purple colour formed in Reaction **3**, naming the type of reaction that occurs.

**(2)**

(c) We require small amounts of chromium(III) ions, $Cr^{3+}$, in our diet as they are important in the breakdown of fats, and many other body processes. However, too high a concentration of $Cr^{3+}$ is toxic.

Blood should not contain more than 4 parts per billion by mass of $Cr^{3+}$.

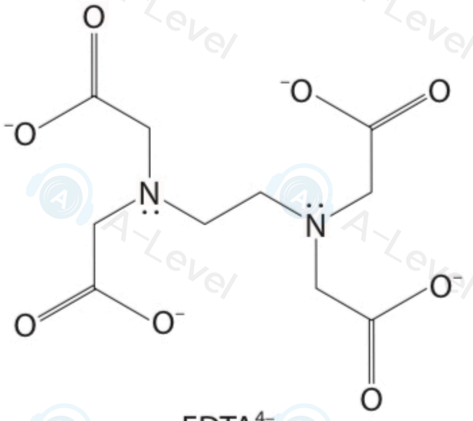
The concentration of $Cr^{3+}$ in a blood sample was $1.345 \times 10^{-7}\,mol\,dm^{-3}$.

(i) Show, by calculation, that the $Cr^{3+}$ level in this blood sample exceeds the safe limit.

[1 billion = $1 \times 10^{9}$ Assume the density of blood is $1.0\,g\,cm^{-3}$]

**(2)**

(ii) $EDTA^{4-}$ has been considered as a potential treatment for $Cr^{3+}$ poisoning.



$EDTA^{4-}$

Suggest how $EDTA^{4-}$ would act to treat $Cr^{3+}$ poisoning, giving a reason why $EDTA^{4-}$ would be preferred to other reagents such as 1,2-diaminoethane, $NH_2CH_2CH_2NH_2$.

**(2)**

**(Total for Question 20 = 17 marks)**

## Manganese and some of its compounds

Manganese is the twelfth most abundant element in the Earth's crust and it is an essential element for all living organisms.

Manganese is a transition metal and it can form compounds with oxidation states +2, +3, +4, +5, +6 and +7, although not all these are stable and some readily undergo disproportionation.

Some compounds and ions containing manganese are effective heterogeneous and homogeneous catalysts.

Alkaline batteries have a manganese(IV) oxide cathode and are used in digital cameras and toys. They have a similar voltage to traditional zinc-carbon batteries but have a higher energy density and last longer.

(a) Some of the properties of manganese and its compounds depend on electronic configurations.

(i) Complete the electronic configurations for a manganese atom and a manganese(II) ion, using the electron-in-boxes notation.

**(1)**

Mn atom: [Ar] ☐☐☐☐☐ (3d) ☐ (4s)

$Mn^{2+}$ ion: [Ar] ☐☐☐☐☐ (3d) ☐ (4s)

(ii) The standard electrode potentials, $E^\ominus$, for the half-cells involving the oxidation states +3 and +2 for manganese and iron are shown.

$$Mn^{3+}(aq) + e^- \rightleftharpoons Mn^{2+}(aq) \qquad E^\ominus = +1.49\,V$$

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \qquad E^\ominus = +0.77\,V$$

Explain, in terms of electronic configurations, why the $E^\ominus$ value for the $Mn^{2+}/Mn^{3+}$ half-cell is significantly higher than that for the $Fe^{2+}/Fe^{3+}$ half-cell.

**(3)**

(ii) Manganese(IV) oxide catalyses the decomposition of hydrogen peroxide.

$$2H_2O_2(aq) \rightarrow 2H_2O(aq) + O_2(g)$$

$100\,cm^3$ of a solution of hydrogen peroxide decomposed to produce $86.0\,cm^3$ of oxygen gas, measured at room temperature and pressure (r.t.p.).

Calculate the concentration of the hydrogen peroxide solution in $mol\,dm^{-3}$.

[Molar volume of gas at r.t.p. = $24.0\,dm^3\,mol^{-1}$]

**(2)**

(c) Potassium manganate(VI), $K_2MnO_4$, is a green solid.
In acidic solution, the manganate(VI) ions disproportionate to form manganate(VII) ions and manganese(IV) oxide.

Write the **ionic** equation for this disproportionation.
State symbols are not required.

**(1)**

(d) Manganate(VII) ions react with ethanedioate ions in acidic solution.

$$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$$

Two experiments were carried out:

**Experiment 1**
Aqueous potassium manganate(VII) was added to a mixture of excess ethanedioic acid and sulfuric acid. The concentration of the manganate(VII) ions was determined as the reaction progressed.

**Experiment 2**

(e) Methylbenzene is oxidised to benzoic acid by heating under reflux with an alkaline solution of potassium manganate(VII).

In an experiment, 1.73 g of methylbenzene was mixed with 7.00 g of potassium manganate(VII) and excess potassium hydroxide solution.

The overall equation is

$$2MnO_4^- + C_6H_5CH_3 \rightarrow 2MnO_2 + C_6H_5COO^- + OH^- + H_2O$$

(i) Show that the potassium manganate(VII) is in excess.

[Molar masses / g mol$^{-1}$: $C_6H_5CH_3 = 92$ $KMnO_4 = 158$]

**(3)**

(ii) State how the benzoate ions, $C_6H_5COO^-$, can be converted into benzoic acid.

**(1)**

(f) Alkaline batteries consist of an anode made of a zinc alloy, a cathode made of manganese(IV) oxide and an electrolyte of aqueous potassium hydroxide.

The overall equation for the reaction in the cell is

$$2MnO_2(s) + Zn(s) \rightleftharpoons Mn_2O_3(s) + ZnO(s) \qquad E^{\ominus}_{cell} = +1.43\,V$$

(i) Write the half-equations for the reactions at the anode and the cathode.

**18** Vanadium forms compounds with oxidation states +2, +3, +4 and +5.

(a) State the oxidation number of vanadium in $Na_3VO_4$.

**(1)**

(b) In aqueous solution, vanadium(II) exists as $[V(H_2O)_6]^{2+}$ but vanadium(V) exists as $[VO_2(H_2O)_4]^{+}$.

Explain why vanadium(V) does **not** exist as $[V(H_2O)_6]^{5+}$.

**(3)**

(c) Hydrated potassium vanadium(III) sulfate contains 7.9 % potassium, 10.2 % vanadium, 12.9% sulfur, 4.8% hydrogen and 64.2% oxygen.

Calculate the empirical formula of this compound and hence write the overall formula showing the potassium ($K^+$), vanadium ($V^{3+}$) and sulfate ($SO_4^{2-}$) ions and the water of crystallisation.

**(3)**

(d) An acidified aqueous solution of potassium manganate(VII) oxidises vanadium(III) ions.

In an experiment, 10.0 $cm^3$ portions of a solution containing 0.132 mol $dm^{-3}$ vanadium(III) ions are titrated against 0.0200 mol $dm^{-3}$ potassium manganate(VII) in acidic conditions.

The mean titre is 26.40 $cm^3$.

(i) Calculate the ratio of the number of moles of manganate(VII) ions, $MnO_4^-$, to the number of moles of vanadium(III) ions, $V^{3+}$, in this oxidation.

You **must** show all your working.

**(3)**

(ii) Write the equation for the reaction between manganate(VII) ions and vanadium(III) ions in acidic solution.
State symbols are not required.

**(2)**

*(e) Vanadium(V) ions, $VO_2^+$, in acidic solution may be reduced step by step through its oxidation states.

Compare and contrast the use of iron and tin in this reduction process.
Include equations and $E^\ominus_{cell}$ values for any reactions that occur.
State symbols are not required.

**(6)**

Use only data from these tables.

Vanadium systems

| Electrode system | $E^\ominus$ / V |
|---|---|
| $V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$ | −0.26 |
| $VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{3+}(aq) + H_2O(l)$ | +0.34 |
| $VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$ | +1.00 |

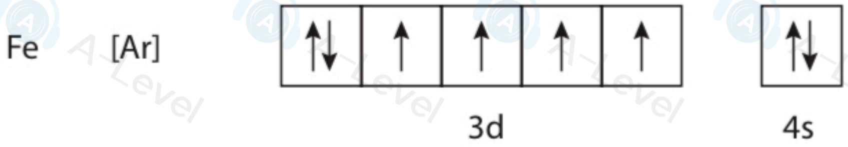
Reducing agents

| Electrode system | $E^\ominus$ / V |
|---|---|
| $Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$ | −0.44 |
| $Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$ | −0.14 |

**21** This question is about iron(II) sulfate, $FeSO_4$.

(a) (i) The electronic configuration for Fe is shown.

**(1)**



Complete the electronic configuration for the $Fe^{2+}$ ion in iron(II) sulfate.

(ii) An aqueous solution of iron(II) sulfate is pale green in colour.
When left exposed to the air the solution turns brown.

Explain why this colour change occurs. In your response refer to your answer from (a)(i).

**(3)**

**19** This question is about compounds and complex ions of iron.

(a) A compound of iron contains, by mass, 39.5% potassium, 28.2% iron and 32.3% oxygen.

Calculate the empirical formula of this compound.

**(2)**

(b) The reaction between iodide ions and persulfate ions is thermodynamically feasible under standard conditions. The reaction is very slow but is catalysed by the presence of $Fe^{2+}$ ions.

$$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(s) + 2SO_4^{2-}(aq)$$

(i) Give a reason why the activation energy for this reaction is high in the absence of a catalyst.

**(1)**

(ii) Write the ionic equations for the reactions that occur when the catalyst of $Fe^{2+}$ ions is added.
State symbols are not required.

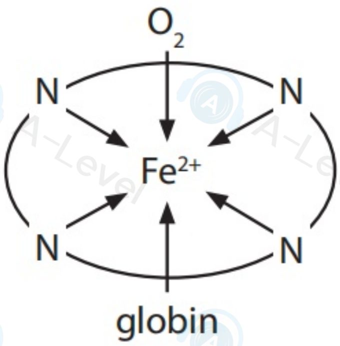
**(2)**

(c) In aqueous solution, iron(II) exists as the complex ion $[Fe(H_2O)_6]^{2+}$.

(i) Explain how water acts as a monodentate ligand.

**(2)**

(d) Haemoglobin is an iron(II) complex which carries oxygen around the body. Part of the structure of oxyhaemoglobin is shown.



The four nitrogen atoms are part of a multidentate ligand in the haem group.

Explain, in terms of the iron(II) complex, why carbon monoxide is toxic.

**(2)**

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(e) Ethanedioate ligands react with iron(II) ions in aqueous solution.

$$[Fe(H_2O)_6]^{2+} + 2C_2O_4^{2-} \rightarrow [Fe(C_2O_4)_2(H_2O)_2]^{2-} + 4H_2O$$

Explain, in terms of entropy, why this reaction is feasible.

**(2)**

(f) Potassium dichromate(VI) oxidises iron(II) ions to iron(III) ions in acid solution.

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Iron(III) ions do not react with acidified potassium dichromate(VI).

A solution **Y** contains 6.28 g dm$^{-3}$ of iron as a mixture of iron(II) ions and iron(III) ions.

50 cm$^3$ of dilute sulfuric acid is added to a 25.0 cm$^3$ portion of **Y** and it is titrated with a solution containing 2.56 g dm$^{-3}$ of dichromate(VI) ions, $Cr_2O_7^{2-}$. The titration is repeated until concordant results are obtained.

The mean titre is 22.55 cm$^3$.