Oxford Cambridge and RSA

Tuesday 4 June 2019 – Afternoon

A Level Chemistry A

H432/01 Periodic table, elements and physical chemistry

Time allowed: 2 hours 15 minutes

You must have:
- the Data Sheet for Chemistry A (sent with general stationery)

You may use:
- a scientific or graphical calculator

Please write clearly in black ink. **Do not write in the barcodes.**

Centre number | | | | | | Candidate number | | | | |

First name(s) _____

Last name StemUp Model Solution

INSTRUCTIONS
- Use black ink. You may use an HB pencil for graphs and diagrams.
- Answer **all** the questions.
- Where appropriate, your answers should be supported with working. Marks may be given for a correct method even if the answer is incorrect.
- Write your answer to each question in the space provided. If additional space is required, use the lined page(s) at the end of this booklet. The question number(s) must be clearly shown.

INFORMATION
- The total mark for this paper is **100**.
- The marks for each question are shown in brackets **[ ]**.
- Quality of extended responses will be assessed in questions marked with an asterisk (*).
- This document consists of **32** pages.

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SECTION A

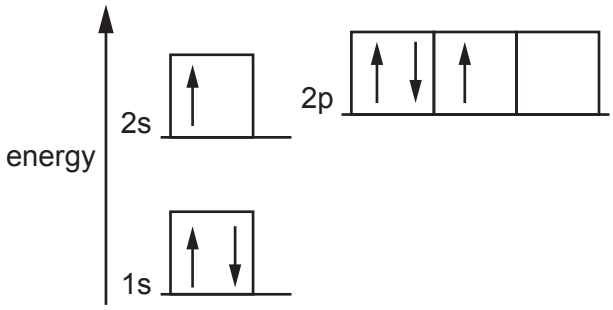
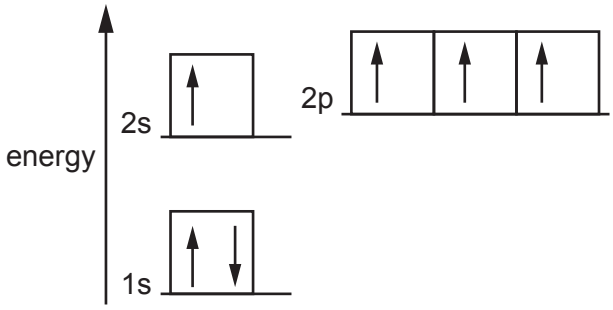
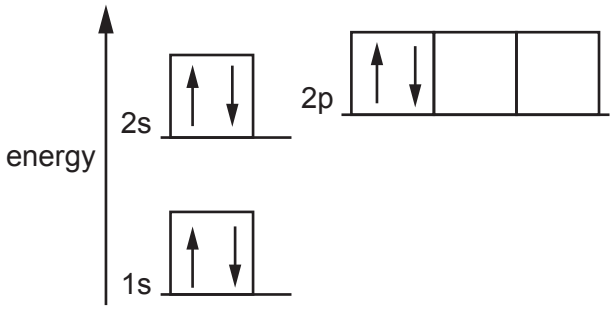
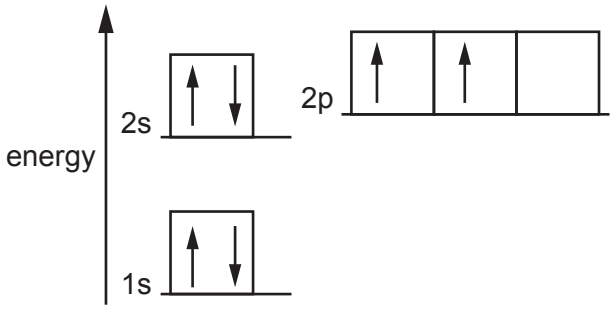
You should spend a maximum of 20 minutes on this section.

Write your answer to each question in the box provided.

Answer **all** the questions.

1 In the diagrams below, each box represents an orbital and each electron is shown as an arrow.

Which diagram shows the correct arrangement of electrons in an atom of carbon?

A	
B	
C	
D	

Your answer D **[1]**

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2 Which statement about the reactions of halogens with halide ions is correct?

A I_2(aq) can oxidise Br^-(aq).

B Cl_2(aq) can reduce Br^-(aq).

C Br^-(aq) can reduce Cl_2(aq).

D Cl^-(aq) can oxidise I_2(aq).

Your answer C **[1]**

3 One molecule of a gas has a mass of 2.658×10^{-23} g.

What is a possible formula of the gas?

A CH_4

B O_2

C SO_2

D SO_3

Your answer A **[1]**

4 In the laboratory, acid spills can be cleaned up and made safe by spreading anhydrous sodium carbonate over the spill to neutralise the acid.

A student accidentally spills 50.0 cm^3 of 2.00 mol dm^{-3} HCl(aq) on the bench.

What is the minimum mass of anhydrous sodium carbonate required to neutralise the acid?

A 4.15 g

B 5.30 g

C 8.30 g

D 10.6 g

Your answer B **[1]**

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5 What is the oxidation number of N in $Mg(NO_2)_2 \cdot 3H_2O$?

A +2

B +3

C +4

D +5

Your answer B **[1]**

6 Which reaction is a redox reaction?

A $NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$

B $NaNO_2 + HCl \rightarrow NaCl + HNO_2$

C $CaSO_3 + 2HCl \rightarrow CaCl_2 + H_2O + SO_2$

D $3CuO + 2NH_3 \rightarrow 3Cu + 3H_2O + N_2$

Your answer D **[1]**

7 Which set of elements in the solid state contain a simple molecular lattice, a giant covalent lattice and a giant metallic lattice?

A S, Si, Al

B P, Si, C

C S, P, Si

D Mg, P, S

Your answer A **[1]**

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8 3.528 g of a Group 2 metal, **M**, is reacted with an excess of chlorine.
The reaction forms 9.775 g of a chloride.

What is metal **M**?

A magnesium

B calcium

C strontium

D barium

Your answer B **[1]**

9 Which statement is **not** correct for Group 2 hydroxides?

A $Mg(OH)_2$ can be used to treat indigestion.

B $Ca(OH)_2$ is used in agriculture to neutralise alkaline soils.

C The anion in $Sr(OH)_2$ contains 10 electrons.

D $Ba(OH)_2$ is a product from the reaction of barium and water.

Your answer B **[1]**

10 Radical reactions are responsible for the catalysed breakdown of the ozone layer.

The overall equation is shown below.

$2O_3 \rightarrow 3O_2 \qquad \Delta_r H = -284\,kJ\,mol^{-1}$

The molar gas volume in the ozone layer is approximately $2.5\,m^3\,mol^{-1}$.

What is the energy released, in kJ, during the breakdown of $1.0\,m^3$ of ozone in the ozone layer?

A 56.8

B 113.6

C 355

D 710

Your answer A **[1]**

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11 A graph of ln k against $\frac{1}{T}$ (T in K) for a reaction has a gradient with the numerical value of −4420.

What is the activation energy, in kJ mol^{-1}, for this reaction?

A −532

B −36.7

C +36.7

D $+5.32 \times 10^5$

Your answer C **[1]**

12 The equation shows the dissociation of the acid H_3AsO_4 in water.

$$H_3AsO_4 + H_2O \rightleftharpoons H_2AsO_4^- + H_3O^+$$

Which pair is a conjugate acid–base pair?

A H_3AsO_4 and H_2O

B $H_2AsO_4^-$ and H_3O^+

C H_3AsO_4 and H_3O^+

D H_3O^+ and H_2O

Your answer D **[1]**

13 What is the number of stereoisomers that $Ni(H_2NCH_2CH_2NH_2)_2Cl_2$ can form?

A 2

B 3

C 4

D 6

Your answer B **[1]**

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14 Which property/properties is/are correct for a transition element?

1 The element has atoms with a partially filled d sub-shell.

2 The existence of more than one oxidation state in its compounds.

3 The formation of coloured ions.

A 1, 2 and 3

B Only 1 and 2

C Only 2 and 3

D Only 1

Your answer C **[1]**

15 Four redox systems relevant to hydrogen–oxygen fuel cells are shown below.

			$E^{\ominus}$ / V
$H_2O(l) + e^-$	$\rightleftharpoons$	$OH^-(aq) + \frac{1}{2}H_2(g)$	−0.83
$H^+(aq) + e^-$	$\rightleftharpoons$	$\frac{1}{2}H_2(g)$	0.00
$\frac{1}{2}O_2(g) + H_2O(l) + 2e^-$	$\rightleftharpoons$	$2OH^-(aq)$	+0.40
$\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$	$\rightleftharpoons$	$H_2O(l)$	+1.23

Which statement(s) is/are correct for an alkaline hydrogen–oxygen fuel cell?

1 The reaction at the positive electrode is: $\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O(l)$.

2 The overall cell reaction is: $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$.

3 The cell potential is 1.23 V.

A 1, 2 and 3

B Only 1 and 2

C Only 2 and 3

D Only 1

Your answer C **[1]**

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SECTION B

Answer **all** the questions.

16 Sir Humphry Davy discovered several elements including sodium, potassium, magnesium, calcium and strontium.

(a) Explain which block in the Periodic Table sodium and magnesium belong to.

s-block, because the highest energy (outer) electron is in an s sub-shell (s orbital). **[1]**

(b) A sample of magnesium, A_r = 24.305, is found to consist of three isotopes. The accurate relative isotopic masses and % abundances of two of the isotopes are shown in the table.

Isotope	Relative isotopic mass	% abundance
^{24}Mg	23.985	78.99%
^{25}Mg	24.986	10.00%

Determine the relative isotopic mass of the third isotope of magnesium in the sample.

Give your answer to **5** significant figures.

$(78.99 \times 23.985 + 10.00 \times 24.986 + 11.01 \times m) \div 100 = 24.305$

$11.01m = 2430.5 - 1894.575 - 249.86 = 286.065$

$m = 286.065 \div 11.01 = 25.982$

relative isotopic mass = 25.982 **[2]**

(c) A student adds an excess of calcium oxide to water in a test tube.
In a separate test tube, the student adds an excess of strontium oxide to water.

(i) Write the equation for the reaction of calcium oxide with water.

State symbols are **not** required.

$CaO + H_2O \rightarrow Ca(OH)_2$ **[1]**

(ii) Suggest the approximate pH of the two solutions formed in the test tubes.

pH with calcium oxide about 12

pH with strontium oxide about 13

[1]

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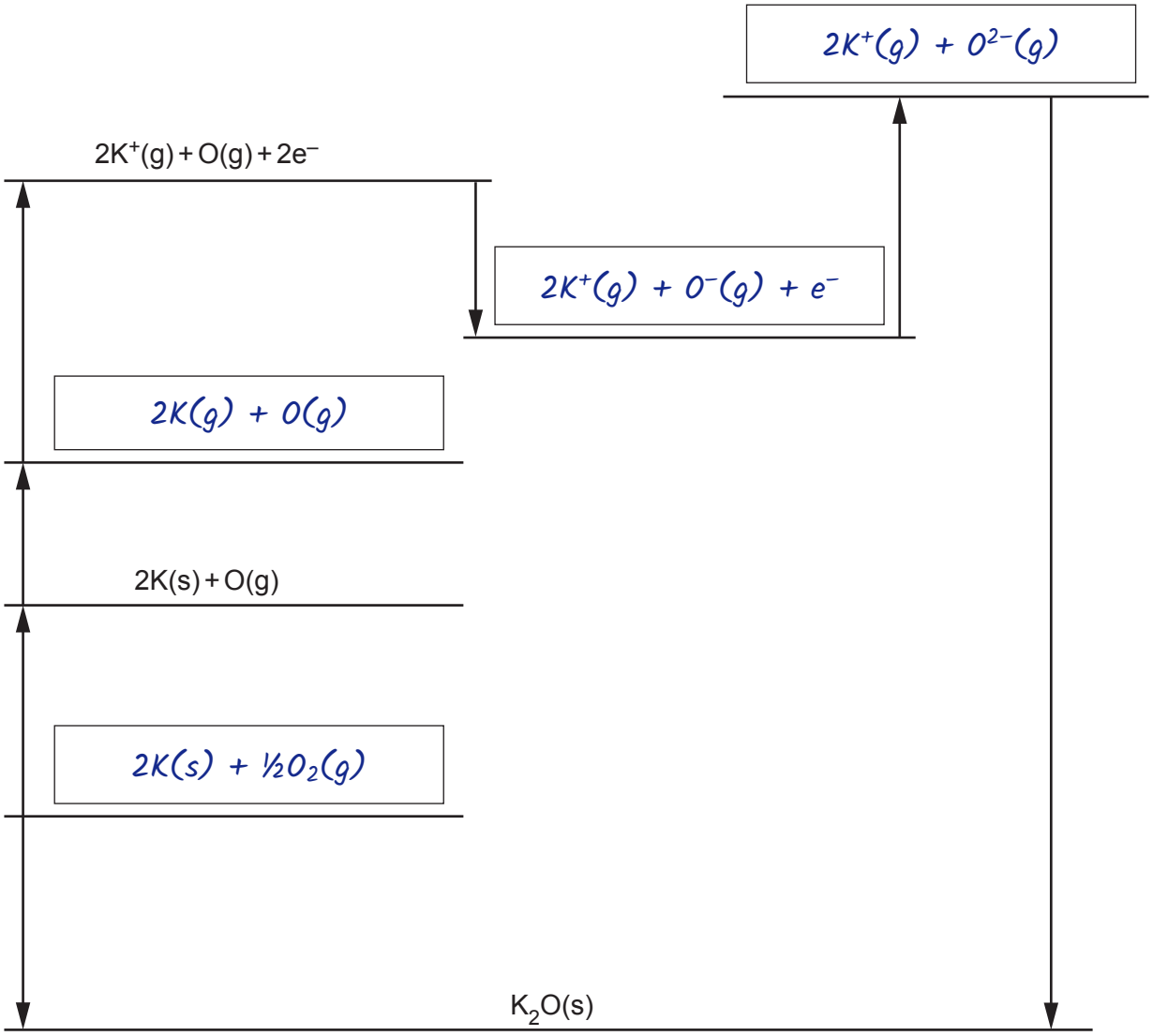
(d) The table below shows enthalpy changes involving potassium, oxygen and potassium oxide, K_2O.

	Enthalpy change / kJ mol^{-1}
formation of potassium oxide	–363
1st electron affinity of oxygen	–141
2nd electron affinity of oxygen	+790
1st ionisation energy of potassium	+419
atomisation of oxygen	+249
atomisation of potassium	+89

(i) The incomplete Born–Haber cycle below can be used to determine the lattice enthalpy of potassium oxide.

In the boxes, complete the species present in the cycle.
Include state symbols for the species.



[4]

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(ii) Calculate the lattice enthalpy of potassium oxide.

lattice enthalpy = ΔfH − (2ΔatH(K) + ΔatH(O) + 2IE(K) + EA1 + EA2)

= −363 − (2 × 89 + 249 + 2 × 419 − 141 + 790)

= −363 − 1914 = −2277

lattice enthalpy = ...−2277.... kJ mol^{-1} **[2]**

(e) A similar Born–Haber cycle to potassium oxide in **(d)** can be constructed for sodium oxide.

(i) The first ionisation energy of sodium is more endothermic than that of potassium.

Explain why.

Sodium atoms have a smaller atomic radius (fewer shells) than potassium atoms, so there is less shielding of the outer electron. So the nuclear attraction on the outer electron is stronger (the outer electron experiences more attraction).

[2]

(ii) The lattice enthalpy of sodium oxide is more exothermic than that of potassium oxide.

Explain why.

Na^+ ions have a smaller ionic radius than K^+ ions (Na^+ has a greater charge density). So there is a stronger attraction between the Na^+ ions and the O^{2-} ions (stronger attraction between the oppositely charged ions).

[2]

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17 Healthy human blood needs to be maintained at a pH of 7.40 for the body to function normally.

(a)* Carbonic acid, H_2CO_3, is a weak acid which, together with hydrogencarbonate ions, HCO_3^-, acts as a buffer to maintain the pH of blood.

The pK_a value for the dissociation of carbonic acid is 6.38.

Explain, in terms of equilibrium, how the carbonic acid–hydrogencarbonate mixture acts as a buffer in the control of blood pH, and calculate the $[HCO_3^-] : [H_2CO_3]$ ratio in healthy blood. **[6]**

Carbonic acid is a weak acid and partially dissociates: $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$. The buffer contains large amounts of both the weak acid, H_2CO_3, and its conjugate base, HCO_3^-.

If acid is added, $[H^+]$ increases and the added H^+ reacts with the conjugate base: $H^+ + HCO_3^- \rightarrow H_2CO_3$. The equilibrium shifts to the left, removing most of the added H^+, so the pH stays almost constant.

If alkali is added, the OH^- reacts with H^+: $H^+ + OH^- \rightarrow H_2O$ (or $H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$). As $[H^+]$ falls, H_2CO_3 dissociates and the equilibrium shifts to the right, replacing the H^+, so the pH stays almost constant.

Ratio: $K_a = 10^{-6.38} = 4.17 \times 10^{-7}$ mol dm^{-3} and $[H^+] = 10^{-7.40} = 3.98 \times 10^{-8}$ mol dm^{-3}.

$K_a = [H^+][HCO_3^-] / [H_2CO_3]$, so $[HCO_3^-] / [H_2CO_3] = K_a / [H^+] = 4.17 \times 10^{-7} / 3.98 \times 10^{-8} = 10.47$

$[HCO_3^-] : [H_2CO_3] = 10.47 : 1$

Additional answer space if required

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(b) Red blood cells contain haemoglobin.

Explain using ligand substitutions:

- how haemoglobin transports oxygen around the body
- why carbon monoxide is toxic.

Haemoglobin contains Fe^{2+}. In the lungs O_2 bonds to the Fe^{2+} by a coordinate (dative) bond, replacing a H_2O ligand (ligand substitution). Oxygen is carried round the body and, in the tissues where it is needed, the O_2 is released and replaced by H_2O (or CO_2). CO is toxic because it replaces the O_2 on the Fe^{2+} and forms a much stronger coordinate bond than O_2 does (CO is a stronger ligand), so it binds almost irreversibly and less O_2 is transported. **[3]**

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18 This question is about reactions of ions and compounds of transition elements.

(a) A student carries out two experiments on a solution containing $[Cr(H_2O)_6]^{3+}(aq)$.

Experiment 1
The student adds an excess of aqueous ammonia to a solution containing $[Cr(H_2O)_6]^{3+}(aq)$ until a purple solution is formed.

Experiment 2
The student carries out the following reaction sequence.

Step 1 NaOH(aq) is added slowly to a solution containing $[Cr(H_2O)_6]^{3+}(aq)$ in a boiling tube.
A grey–green precipitate forms.

Step 2 An excess of NaOH(aq) is added to the boiling tube.
The precipitate dissolves and a green solution forms containing a 6 coordinate complex ion.

Step 3 H_2O_2 is added to the mixture and the boiling tube is heated.
A yellow solution forms.

Step 4 The solution in the boiling tube is acidified.
The solution now contains $Cr_2O_7^{2-}(aq)$.

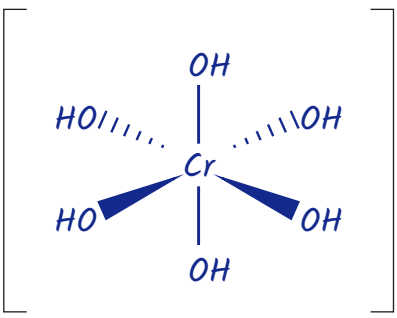
(i) What is the formula of the complex ion in the purple solution that forms in **Experiment 1**?

$[Cr(NH_3)_6]^{3+}$ ..... **[1]**

(ii) Suggest an equation for the reaction in **Experiment 2**, **Step 1**.
Include state symbols.

$Cr^{3+}(aq) + 3OH^-(aq) \rightarrow Cr(OH)_3(s)$ ..... **[1]**

(iii) Draw a 3-D diagram for the shape of the complex ion that forms in **Experiment 2**, **Step 2**.
Include the charge of the ion.



3– .....

[2]

(iv) What is the formula of the **ion** that causes the yellow colour in **Experiment 2**, **Step 3**?

CrO_4^{2-} ..... **[1]**

(v) State the colour of the solution that forms in **Experiment 2**, **Step 4**.

orange ..... **[1]**

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(b) Vanadium ions have four common oxidation states. **Table 18.1** shows the colours of the ions in aqueous solution.

Oxidation state of vanadium	Vanadium ion	Colour
+5	$VO_2^+(aq)$	yellow
+4	$VO^{2+}(aq)$	blue
+3	$V^{3+}(aq)$	green
+2	$V^{2+}(aq)$	violet

Table 18.1

(i) Complete the electron configuration of a V^{3+} ion.

$1s^2$ $2s^2 2p^6 3s^2 3p^6 3d^2$ ..... **[1]**

(ii) The student adds excess iron to a solution containing $VO^{2+}(aq)$ ions, and observes that the colour of the solution changes from blue to green and then to violet.

Use the relevant standard electrode potentials shown in **Table 18.2** to explain these observations.

	Redox system			$E^\ominus$/V
1	$V^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$V(s)$	−1.18
2	$Fe^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Fe(s)$	−0.44
3	$V^{3+}(aq) + e^-$	$\rightleftharpoons$	$V^{2+}(aq)$	−0.26
4	$VO^{2+}(aq) + 2H^+ + e^-$	$\rightleftharpoons$	$V^{3+}(aq) + H_2O(l)$	+0.34
5	$Fe^{3+}(aq) + e^-$	$\rightleftharpoons$	$Fe^{2+}(aq)$	+0.77
6	$VO_2^+(aq) + 2H^+ + e^-$	$\rightleftharpoons$	$VO^{2+}(aq) + H_2O(l)$	+1.00

Table 18.2

VO^{2+} is reduced to V^{3+} (green), then V^{3+} is reduced to V^{2+} (violet).

$E^\ominus$ of system 4 (+0.34 V) is more positive than system 2 (Fe^{2+}/Fe, −0.44 V), so system 4 shifts right (VO^{2+} gains electrons): E_{cell} = +0.78 V.

$E^\ominus$ of system 3 (−0.26 V) is also more positive than system 2, so system 3 shifts right (V^{3+} gains electrons): E_{cell} = +0.18 V. ..... **[3]**

(iii) Construct an equation for the **first** colour change from blue to green.

$Fe + 4H^+ + 2VO^{2+} \rightarrow Fe^{2+} + 2H_2O + 2V^{3+}$ ..... **[1]**

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(c) Iron(II) gluconate, $C_{12}H_{22}FeO_{14}$, is the active ingredient in some brands of iron supplements.

A student carries out an experiment to determine the mass of iron(II) gluconate in one tablet of an iron supplement, using the method below.

Stage 1 The student crushes two tablets and dissolves the powdered tablets in dilute sulfuric acid.

Stage 2 The student makes up the solution from **Stage 1** to 250.0 cm^3 in a volumetric flask.

Stage 3 The student then titrates 25.0 cm^3 portions of the solution obtained in **Stage 2** with 0.00200 mol dm^{-3} potassium manganate(VII).

The student obtains a mean titre of 13.50 cm^3.

In this titration, 1 mol of manganate(VII) ions reacts with 5 mol of iron(II) ions.

(i) Explain why the student used 0.00200 mol dm^{-3} potassium manganate(VII) solution for this titration, rather than the more usual concentration of 0.0200 mol dm^{-3} used in manganate(VII) titrations.

The dilute solution gives a large titre (13.50 cm^3, not 1.35 cm^3), so the percentage error (uncertainty) in the titre is smaller. **[1]**

(ii) Use the student's results to determine the mass, in mg, of iron(II) gluconate in **one** tablet.

Give your answer to **3** significant figures.

$n(MnO_4^-) = 0.00200 \times 13.50 \div 1000 = 2.70 \times 10^{-5}$ mol

$n(Fe^{2+})$ in 25.0 cm^3 $= 5 \times 2.70 \times 10^{-5} = 1.35 \times 10^{-4}$ mol

$n(Fe^{2+})$ in 250.0 cm^3 $= 1.35 \times 10^{-4} \times 10 = 1.35 \times 10^{-3}$ mol

$M_r(C_{12}H_{22}FeO_{14}) = 445.8$

mass in 2 tablets $= 1.35 \times 10^{-3} \times 445.8 = 0.6018$ g

mass in 1 tablet $= 0.6018 \div 2 = 0.3009$ g $= 301$ mg

mass of iron(II) gluconate in one tablet = 301 mg **[5]**

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(iii) Some iron supplements contain iron(II) sulfate or iron(II) fumarate.

The information in **Table 18.3** is taken from the labels of two iron supplements, **A** and **B**.

Iron supplement	Iron compound	Mass of iron compound in one tablet / mg
A	iron(II) sulfate, $FeSO_4$	180
B	iron(II) fumarate, $C_4H_2FeO_4$	210

Table 18.3

Choose which iron supplement, **A** or **B**, would provide the greater mass of iron per tablet.

A: mass of Fe = 180 × 55.8 ÷ 151.9 = 66.1 mg

B: mass of Fe = 210 × 55.8 ÷ 169.8 = 69.0 mg

iron supplement: .....B (iron(II) fumarate)..... **[1]**

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19 Sulfuric acid is an important chemical used to make detergents, fertilisers and dyes. It is manufactured in a multi-step process.

(a) In the first step of the manufacture of sulfuric acid, sulfur dioxide, SO_2, can be made from the combustion of hydrogen sulfide, H_2S, shown in **Reaction 1**.

$2H_2S(g) + 3O_2(g) \rightarrow 2SO_2(g) + 2H_2O(l)$ $\Delta_r H = -1125\,kJ\,mol^{-1}$ **Reaction 1**

(i) Explain why the enthalpy change for **Reaction 1** has a negative value.

Use ideas about enthalpy changes associated with bond breaking and bond making.

Bond breaking is endothermic and bond making is exothermic; more energy is released forming the new bonds (in SO_2 and H_2O) than is needed to break the bonds (in H_2S and O_2). **[1]**

(ii) Some standard entropy values are given below.

Substance	$H_2S(g)$	$O_2(g)$	$SO_2(g)$	$H_2O(l)$
$S^{\ominus}$ / $J\,K^{-1}\,mol^{-1}$	206	205	248	70

Using calculations, explain whether **Reaction 1** is feasible at 20 °C.

Calculations

$\Delta S = \Sigma S(products) - \Sigma S(reactants)$

$= (2 \times 248 + 2 \times 70) - (2 \times 206 + 3 \times 205)$

$= 636 - 1027 = -391\ J\ K^{-1}\ mol^{-1} = -0.391\ kJ\ K^{-1}\ mol^{-1}$

$T = 20 + 273 = 293\ K$

$\Delta G = \Delta H - T\Delta S = -1125 - (293 \times -0.391)$

$\Delta G = -1010\ kJ\ mol^{-1}$

Explanation for feasible or non feasible Feasible, because $\Delta G < 0$ (ΔG is negative) at 20 °C. **[4]**

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(iii) Calculate the standard enthalpy change of formation, $\Delta_f H^\ominus$, of hydrogen sulfide using the enthalpy change for **Reaction 1**, and the standard enthalpy changes of combustion below.

Substance	$\Delta_c H^\ominus$ / kJ mol^{-1}
S(s)	−296.8
H_2(g)	−285.8

$2H_2S(g) + 3O_2(g) \rightarrow 2SO_2(g) + 2H_2O(l)$ $\Delta_r H = -1125\,kJ\,mol^{-1}$ **Reaction 1**

$2\Delta fH(H_2S) + \Delta rH = 2\Delta cH(S) + 2\Delta cH(H_2)$

$2\Delta fH(H_2S) = 2 \times (-296.8) + 2 \times (-285.8) - (-1125)$

$= -593.6 + (-571.6) + 1125 = -1165.2 + 1125 = -40.2$

$\Delta fH(H_2S) = -40.2 \div 2 = -20.1\ kJ\ mol^{-1}$

$\Delta_f H^\ominus$ of hydrogen sulfide = ...−20.1..... kJ mol^{-1} **[3]**

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(b) The second step in the manufacture of sulfuric acid is the conversion of SO_2 into sulfur trioxide, SO_3, using **Equilibrium 1**.

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H = -197\,kJ\,mol^{-1}$ **Equilibrium 1**

An industrial chemist carries out some research into **Equilibrium 1**.

- The chemist fills a $10.2\,dm^3$ container with $SO_2(g)$ at RTP, and then adds 12.0 g of $O_2(g)$.
- The chemist adds the vanadium(V) oxide catalyst, and heats the mixture. The mixture is allowed to reach equilibrium at a pressure of 2.50 atm and a temperature of 1000 K.
- A sample of the equilibrium mixture is analysed, and found to contain 0.350 mol of SO_3.

(i) Write an expression for K_p for **Equilibrium 1**.

Include the units.

$$K_p = \frac{p(SO_3)^2}{p(SO_2)^2 \times p(O_2)}$$

units = ...atm^{-1}.... **[2]**

(ii) Determine the value of K_p for **Equilibrium 1** at 1000 K.

Show all your working.

Give your answer to **3** significant figures.

initial: $n(SO_2) = 10.2 \div 24.0 = 0.425$ mol; $n(O_2) = 12.0 \div 32.0 = 0.375$ mol

equilibrium: $n(SO_3) = 0.350$ mol; $n(SO_2) = 0.425 - 0.350 = 0.075$ mol

$n(O_2) = 0.375 - 0.350 \div 2 = 0.200$ mol; total moles = 0.625 mol

$p(SO_2) = 0.075 \div 0.625 \times 2.50 = 0.300$ atm

$p(O_2) = 0.200 \div 0.625 \times 2.50 = 0.800$ atm

$p(SO_3) = 0.350 \div 0.625 \times 2.50 = 1.40$ atm

$K_p = 1.40^2 \div (0.300^2 \times 0.800) = 27.2\ atm^{-1}$

K_p = ...27.2.... **[5]**

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(iii) The chemist repeats the experiment in **(b)** at a different temperature.

The chemist finds that the value of K_p is greater than the answer to **(b)(ii)**.

Explain whether the temperature in the second experiment is higher or lower than 1000 K.

A greater K_p means the equilibrium position has shifted to the right (more SO_3). Lower temperature than 1000 K, because the forward reaction is exothermic, so lowering the temperature shifts the equilibrium to the right. **[2]**

(iv) Explain the significance of the expression: $K_p \gg 1$.

The equilibrium position lies far to the right; the forward reaction is greatly favoured, giving a very high yield of products (SO_3). **[1]**

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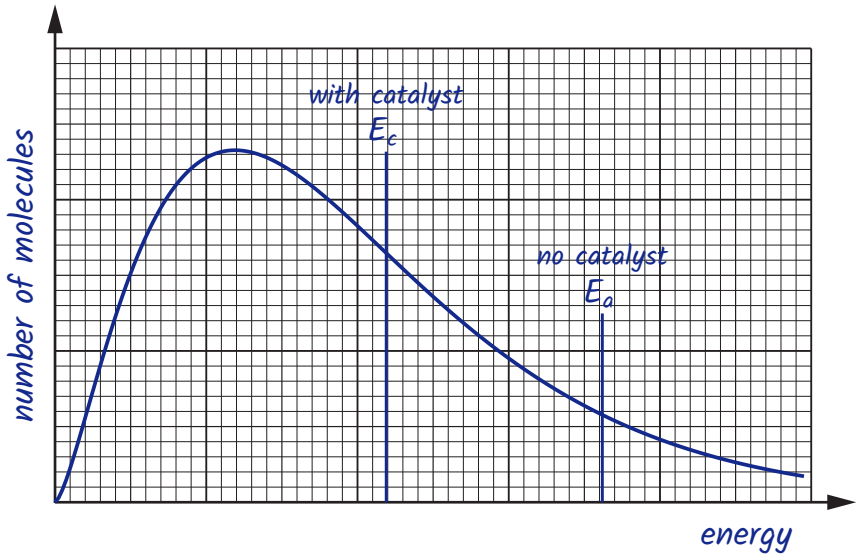
(c) Vanadium(V) oxide, $V_2O_5(s)$, is used as a catalyst in **equilibrium 1**.

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H = -197\,kJ\,mol^{-1}$ **Equilibrium 1**

(i) Explain how the presence of $V_2O_5(s)$ increases the rate of reaction.

Include a labelled sketch of the Boltzmann distribution, on the grid below.

Label the axes.



V_2O_5 provides an alternative reaction route with a lower activation energy, E_c (to the left of E_a on the distribution).
So a greater proportion of molecules have energy above the activation energy (more molecules have enough energy to react; greater area under the curve above E_c), so the rate increases. **[4]**

(ii) Explain whether vanadium(V) oxide is acting as a homogeneous or heterogeneous catalyst.

Heterogeneous; the V_2O_5 catalyst is a solid, in a different phase (state) from the gaseous reactants. **[1]**

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20 This question is about weak acids.

The K_a values of three weak acids are shown in **Table 20.1**.

Weak acid	K_a / mol dm^{-3}
iodic(V) acid, HIO_3(aq)	1.78×10^{-1}
propanoic acid, C_2H_5COOH(aq)	1.35×10^{-5}
hydrocyanic acid, HCN(aq)	6.17×10^{-10}

Table 20.1

(a) Calculate the pH of 0.0800 mol dm^{-3} C_2H_5COOH(aq).

Give your answer to **2** decimal places.

$[H^+] = \sqrt{(K_a \times [C_2H_5COOH])} = \sqrt{(1.35 \times 10^{-5} \times 0.0800)}$

$[H^+] = 1.039 \times 10^{-3}$ mol dm^{-3}

$pH = -\log(1.039 \times 10^{-3}) = 2.98$

pH = ...2.98..... **[2]**

(b) A student adds a total of 45.0 cm^3 of 0.100 mol dm^{-3} NaOH(aq) to 25.0 cm^3 of 0.0800 mol dm^{-3} C_2H_5COOH(aq) and monitors the pH throughout.

(i) Show by calculation that 20.0 cm^3 of NaOH(aq) is required to reach the end point.

$n(C_2H_5COOH) = 0.0800 \times 25.0 \div 1000 = 2.00 \times 10^{-3}$ mol

reacts 1 : 1, so $n(NaOH)$ needed $= 2.00 \times 10^{-3}$ mol

$V(NaOH) = 2.00 \times 10^{-3} \div 0.100 \times 1000 = 20.0$ cm^3

[1]

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(ii) Calculate the pH of the final solution.

Give your answer to **2** decimal places.

$n(NaOH)$ added $= 0.100 \times 45.0 \div 1000 = 4.50 \times 10^{-3}$ mol

$n(OH^-)$ in excess $= 4.50 \times 10^{-3} - 2.00 \times 10^{-3} = 2.50 \times 10^{-3}$ mol

total volume $= 25.0 + 45.0 = 70.0$ cm^3

$[OH^-] = 2.50 \times 10^{-3} \div 0.0700 = 0.0357$ mol dm^{-3}

$[H^+] = K_w \div [OH^-] = 1.00 \times 10^{-14} \div 0.0357 = 2.80 \times 10^{-13}$ mol dm^{-3}

$pH = -\log(2.80 \times 10^{-13}) = 12.55$

pH = ...12.55..... **[4]**

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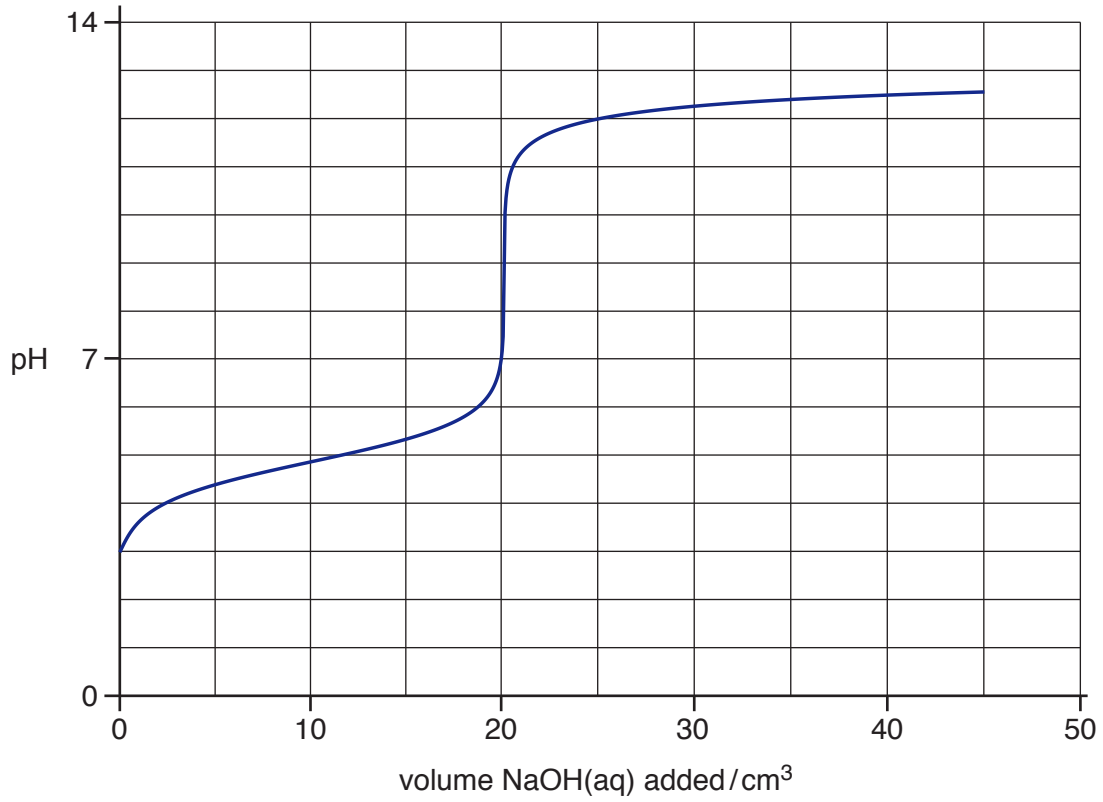
(iii) On the axes below, sketch a pH curve for the pH changes during the addition of 45.0 cm^3 of 0.100 mol dm^{-3} NaOH(aq) to 25.0 cm^3 of 0.0800 mol dm^{-3} C_2H_5COOH(aq).



[3]

(iv) The student considers using the four indicators in **Table 20.2** for the titration.

Indicator	pH range
Cresol red	0.2 – 1.8
Bromophenol blue	3.0 – 4.6
Cresol purple	7.6 – 9.2
Indigo carmine	11.6 – 14.0

Table 20.2

Explain which indicator would be most suitable for the titration.

Cresol purple, because its pH range (7.6 to 9.2) lies within the vertical section (rapid pH change) of the curve, so its colour change matches the equivalence point (about pH 8.7).

[1]

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(v) The student repeats the experiment starting with 25.0 cm^3 of 0.0800 mol dm^{-3} HCN(aq) and adding a total of 45.0 cm^3 of 0.100 mol dm^{-3} NaOH(aq).

Predict **one** similarity and **one** difference between the pH curve with C_2H_5COOH(aq) and the pH curve with HCN(aq). Use the information in **Table 20.1**, and your answer to **(b)(iii)**.

Similarity Same volume of NaOH (20.0 cm^3) needed to reach the end point; same final pH (12.55).

Difference HCN starts at a higher pH (smaller K_a, weaker acid) and has a shorter vertical section.

[2]

(c) The student calculates the pH of 0.0800 mol dm^{-3} HIO_3(aq). The student assumes that the equilibrium concentration of HIO_3(aq) is the same as the initial concentration of HIO_3(aq).

The student measures the pH, and finds that the measured pH value is different from the calculated pH value.

Explain why the measured pH is different from the calculated pH.

HIO_3 has a large K_a (it is a 'stronger' weak acid), so it dissociates to a significant extent; $[HIO_3]$ at equilibrium is significantly lower than the initial $[HIO_3]$, so the assumption is not valid.

[1]

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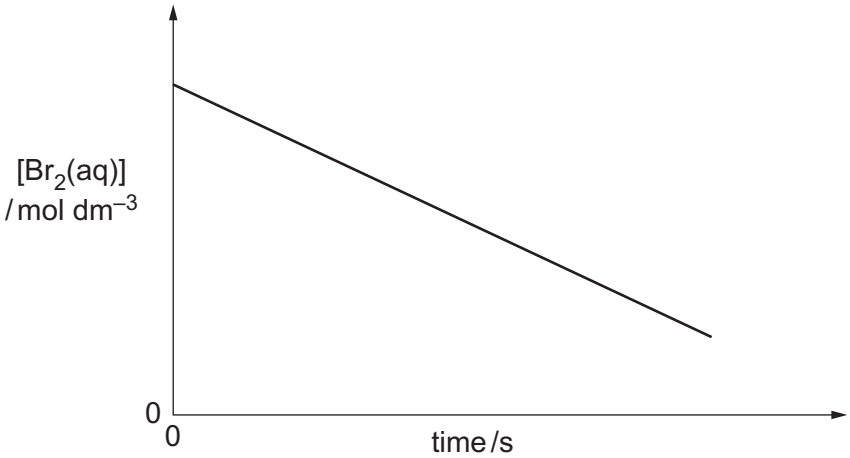
21* Three students carry out a rates investigation on the reaction between bromine and propanone in the presence of hydrochloric acid.

$CH_3COCH_3(aq) + Br_2(aq) \rightarrow CH_3COCH_2Br(aq) + HBr(aq)$

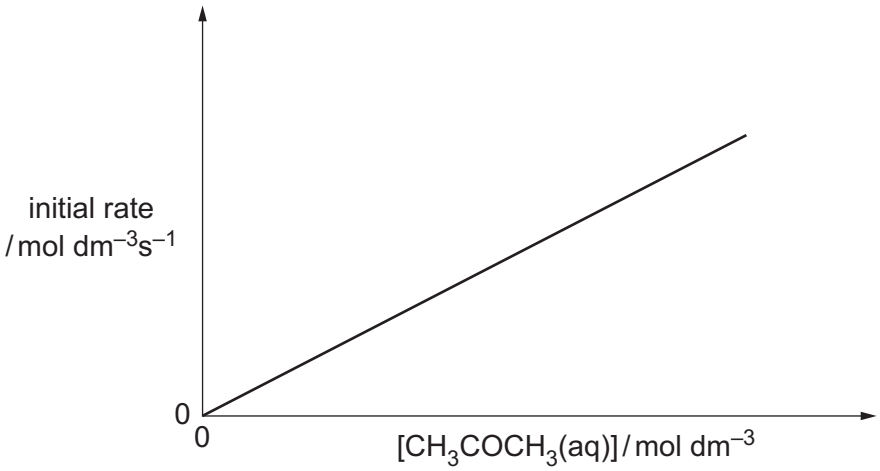
Each student investigates the effect of changing the concentration of one of the reactants whilst keeping the other concentrations constant.

Their results are shown below.

Results of student 1



Results of student 2



Results of student 3

Experiment	$[Br_2(aq)]$ / mol dm^{-3}	$[CH_3COCH_3(aq)]$ / mol dm^{-3}	$[H^+(aq)]$ / mol dm^{-3}	Initial rate / 10^{-5} mol dm^{-3} s^{-1}
1	0.004	1.60	0.20	1.25
2	0.004	1.60	0.40	2.50

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Explain how the reaction orders can be determined from the students' results, and determine the rate equation and rate constant. **[6]**

Student 1: the graph of $[Br_2]$ against time is a straight line with a constant negative gradient, so the rate is constant and does not depend on $[Br_2]$. The reaction is zero order with respect to Br_2.

Student 2: the graph of initial rate against $[CH_3COCH_3]$ is a straight line through the origin, so the rate is directly proportional to $[CH_3COCH_3]$. The reaction is first order with respect to CH_3COCH_3.

Student 3: from experiment 1 to 2, $[H^+]$ doubles (0.20 to 0.40 mol dm^{-3}) with the other concentrations constant, and the rate doubles (1.25 to 2.50 × 10^{-5} mol dm^{-3} s^{-1}). The reaction is first order with respect to H^+.

Rate equation: rate = $k[CH_3COCH_3][H^+]$

k = rate ÷ ($[CH_3COCH_3][H^+]$) = 1.25 × 10^{-5} ÷ (1.60 × 0.20)

$k = 3.91 \times 10^{-5}$ dm^3 mol^{-1} s^{-1}

Additional answer space if required

END OF QUESTION PAPER

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ADDITIONAL ANSWER SPACE

If additional space is required, you should use the following lined page(s). The question number(s) must be clearly shown in the margin(s).

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