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### FOREWORD

This booklet contains reports written by Examiners on the work of candidates in certain papers. Its contents are primarily for the information of the subject teachers concerned.

## CHEMISTRY

### GCE Advanced Level and GCE Advanced Subsidiary Level

Paper 9701/01 Multiple Choice

Question Number	Key	Question Number	Key
1	С	21	D
2	С	22	С
3	С	23	D
4	D	24	В
5	В	25	D
6	D	26	В
7	В	27	D
8	D	28	В
9	В	29	D
10	D	30	D
11	Α	31	D
12	В	32	С
13	D	33	D
14	С	34	Α
15	D	35	D
16	В	36	С
17	D	37	Α
18	С	38	Α
19	D	39	D
20	Α	40	Α

#### **General comments**

For this paper, the mean score was 23.2 (58.2%), very near the targeted value of 60%, and the standard deviation of the scores was 6.58 (16.5%), indicating that overall the paper performed satisfactorily.

The first thirty questions were simple completion items, while **Questions 31** to **40** were three-statement multiple completion items.

#### Comments on individual questions

Questions 2, 13, 16, 29 and 32 had a high facility, representing areas of the syllabus that are widely understood.

Two questions did not distinguish between the more able and less able candidates as well as expected.

#### **Question 7**

This asked candidates to estimate the bond angles in the  $PH_3$  molecule: some 42% of candidates, including some of the more able candidates, gave the tetrahedral answer of 109°, whereas only 31% gave the correct answer of (about) 104°. The Examiners had anticipated that this question would have scored well, but clearly a significant proportion of candidates had not understood that within the electron-pair repulsion model a lone pair of electrons is deemed to have greater repulsion than a bond pair.

#### **Question 9**

Candidates were given four compounds –  $CH_3CH_2CH_3$  and three of its oxidation products,  $CH_3CH_2CH_2OH$ ,  $CH_3COCH_3$  and  $CH_3CH_2CO_2H$  – and asked which would release the greatest amount of energy on complete combustion. 40% of candidates gave the correct answer (propane itself), the others presumably not appreciating that every stage in the oxidation process would be exothermic, and that therefore the earliest point in a sequence of oxidations would yield the highest energy release. An alternative approach to this question would have been to make use of the table of bond energies within the *Data Booklet*, leading to the same conclusion.

Rather surprisingly four questions had a facility below the design limit of 25%, i.e. below the 'guessing level', and the reasons for this were clearly very varied.

#### Question 10

There was a lack of understanding of how to calculate a partial pressure within an equilibrium mixture of gases.

#### **Question 23**

The estimation of the number of different substitution products obtainable by the attack of bromine on ethane proved too difficult for many candidates.

#### Question 38

The results of this question were contradictory: candidates were asked which of three compounds would be hydrolysed by aqueous NaOH more rapidly than  $CH_3CH_2Cl$ . The three compounds were  $ClCH_2CH_2Cl$  (1),  $CH_3CH_2Br$  (2) and  $CH_3CH_2I$  (3). 40% gave the answer **C**, that **2** and **3** did but not **1**; 36% gave the answer **D**, that **1** did but not **2** and **3** – exactly the reverse. Only 17% of candidates appreciated that all did, **1** because there are twice the number of chlorine atoms in the compound to be released, and **2** and **3** because in each case the carbon-halogen bond undergoes heterolytic fission more readily.

#### Question 39

A total of 78% of candidates believed that pentaerythritol,  $C(CH_2OH)_4$ , can be dehydrated by concentrated sulphuric acid to yield an alkene.

All other questions performed within the design limits, but one deserves further comment.

#### **Question 37**

Examiners are well aware that the free radical mechanism of substitution of methyl groups by chlorine, especially in its stages of initiation, propagation and termination, is widely understood: when set as a straightforward question of recall this always scores highly. As termination can theoretically come about by the combination of any two free radicals, this question asked candidates to identify three possible final products from ethane and chlorine –  $CH_3CH_2Cl$ ,  $CH_3CH_2CH_2CH_3$ , and  $CH_3CHClCHClCH_3$ . Only 25% realised that all three are possibilities: 59% rejected the last two.

Paper 9701/02

Theory 1

#### General comments

There were a pleasing number of candidates who made very good attempts to answer all of the questions. There appears to be a definite improvement in the understanding of the subject matter on the part of many candidates. On the other hand, there are still some candidates whose knowledge is poor.

There were fewer candidates who failed to read the specific instructions contained in some questions such as 'Write equations ..... giving state symbols.' Failure to include state symbols in this case resulted in a loss of marks.

#### **Comments on specific questions**

#### Question 1

There were many good answers to this question, although a significant number of candidates struggled with the second calculation.

- (a) Most candidates were able to give the correct expression for  $K_c$ . The most common error was to give the expression for the reverse reaction i.e.  $K_c$  was upside down.
- (b) The majority of candidates were able to substitute the data in the question in their expression for  $K_c$  correctly and obtain the following answer:  $K_c = \frac{0.274 \times 0.274}{(1.47)^2} = 0.035$  (no units).
- (c) Many candidates struggled to answer this part because they mistakenly tried to apply le Chatelier's principle to the equilibrium at the lower temperature. At room temperature, iodine would be a solid and the concentration of gaseous iodine would be very small. The other effect of the low temperature would be that the rate of attainment of the equilibrium would be slow. For both these reasons, the determination of  $K_c$  would be more difficult at room temperature.
- (d)(i) A significant number of candidates found it difficult to explain clearly how  $\Delta H$  values can be calculated from bond energy values. The most common error was to subtract the total bond energy of the reactants from the total bond energy of the products. Strangely, many candidates who made this mistake then carried out the calculation in part (d)(ii) correctly. Candidates should appreciate that bond breaking is an endothermic process while bond making is exothermic.
  - (ii) Most candidates correctly looked up the data required and there were many correct answers to this part. However, there were also many candidates who were unable to carry out the calculation correctly. Common errors were to omit to multiply the value of the energy of the H-I bond by two, or to state that the dissociation of hydrogen iodide, is exothermic.

The correct answer is  $+11 \text{ kJ mol}^{-1}$ .

- (e)(i) Many candidates were able to state that a strong acid is one that is completely dissociated into ions.
  - (ii) Fewer candidates were able to complete the equation correctly. Examiners expected  $H_3O^+$  and  $I^-$  to be stated as the ions formed.
  - (iii) This part was poorly answered. Many candidates who had given a correct equation in part (ii) then quoted  $H_3O^+$  as their answer. A conjugate base must be a proton acceptor and only  $I^-$  can do this.  $H_3O^+$  can only be a proton donor, i.e. the conjugate acid.

There were many good answers to this question. However, there were also many candidates who wrote very muddled answers in part (b), making contradictory statements such as  $(SO_3)$  is simple molecular with strong covalent bonds between the molecules.' Candidates are strongly advised to keep their answers simple and to indicate clearly what type of bonding they are discussing and what particles – atoms, molecules, or ions – the bonds are holding together. Although the question suggested candidates might use diagrams in their answers, there were very few good clear diagrams.

- (a) The majority of candidates answered this correctly.
- (b)(i) Whilst there were many good answers to this part, there were also many candidates who contradicted themselves. What Examiners expected was a discussion about the giant lattice present in aluminium oxide and the great strength of the bonds present in the lattice.
  - (ii) Again there were many good answers but too many candidates who correctly stated that van der Waals' forces exist between the SO<sub>3</sub> molecules, omitted to state that these forces of attraction are weak.
  - (iii) This part was generally well answered and a few candidates presented clearly drawn structures.
- (c) The majority of candidates gave correct equations to both parts of this question. The most common error was for the equations to be unbalanced.

#### **Question 3**

In recent years, knowledge of the chemistry of chlorine has often been poor. This year there were many good answers with a significant number of candidates scoring high marks on this question.

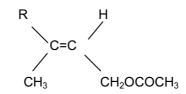
(a)(i) Compared with previous years, there were many excellent diagrams. Most candidates knew that the anode is made of titanium and the cathode of steel. Some candidates, who clearly understood the processes involved, failed to identify the diaphragm or failed to label the inlets and outlets correctly and were penalised as a result.

There was still a significant number of candidates who drew the mercury cathode cell which the syllabus no longer requires – see Syllabus Sections 6 (b)(i) and 9.4 (g).

- (ii) Most candidates gave correct half equations. The most common error was to omit the state symbols which the question clearly asked for.
- (iii) Although the question specifically asked for an explanation of redox changes occurring at the electrodes 'in terms of changes in oxidation number', there were many candidates who simply stated at which electrode oxidation and reduction occurred.
- (iv) Most candidates were able to state that the chemical produced in solution by the electrolysis is sodium hydroxide.
- (v) The large-scale uses of sodium hydroxide were not so well known. Examiners expected answers such as the manufacture of bleach, sodium chlorate(I), or of soap. They did not accept 'used in school laboratories' as a large-scale use.
- (b) The majority of candidates were able to give correct equations for both parts of this section. There were, however, many answers to part (ii) which explained the change in bonding in terms of covalent bonds becoming hydrogen bonds. This was not accepted.
- (c) The reactions of aqueous chloride ions with aqueous silver ions, followed by aqueous ammonia, continue to be poorly known and understood. Examiners expected candidates to state in part (i) that a white precipitate of silver chloride would be formed. Candidates were than expected to state in part (ii) that this precipitate would dissolve in an excess of aqueous ammonia forming the colourless complex [Ag(NH<sub>3</sub>)<sub>2</sub>]C*I*. Many candidates struggled to write the correct equations for these two reactions and there were many equations with incorrect state symbols.

Although the molecules referred to in this question were large and apparently complicated, there were many candidates who simply concentrated their answers on the functional groups concerned – and scored good marks in the process.

- (a) The correct molecular formula,  $C_{10}H_{20}O$ , and  $M_r$  of 156 were quoted by most candidates. The most common error was to give the molecular formula as  $C_{10}H_{19}OH$ . This was not given any credit as it is not a molecular formula.
- (b) The majority of candidates were able to state that citronellol and geraniol both contain alcohol and alkene functional groups. Very few candidates gained the third mark in this section by stating that the alcohol was a primary alcohol.
- (c) This section was very well answered with most candidates identifying carbon atom number 6 in the citronellol molecule as being chiral.
- (d)(i) Many candidates sensibly used the advice in the question and used R- to represent the long hydrocarbon chain. Most of these candidates answered this part correctly by exchanging their R- group and the CH<sub>3</sub> group on the left of the carbon-carbon double bond. A significant number of candidates however, mistakenly placed either their R- group or the CH<sub>3</sub> group on the right hand side of the double bond and received no credit.
  - (ii) Many candidates understood that geraniol has no optical isomers because the molecule does not contain a chiral carbon atom.
- (e) Although many candidates knew that aqueous bromine would be decolourised when reacted with citronellol, a surprising number did not answer the question as it was set. Instead of describing what they 'would expect to see' they discussed what would happen to the bromine molecule or the carbon-carbon double bond. Such answers received no credit.
- (f)(i) Many candidates knew that acidified dichromate(VI) is an oxidising agent that would oxidise the -CH<sub>2</sub>OH group of geraniol to -CO<sub>2</sub>H. Unfortunately, a significant number of candidates also thought that the C=C bond would be oxidised to a dihydroxy compound or even split by the oxidising agent. Only acidified manganate(VII) ions will carry out either of these reactions, depending on the conditions used.
  - (ii) Geraniol will react with ethanoic acid in the presence of an acidic catalyst to produce an ester. While many candidates understood this, a significant number of them gave the wrong structure for the ester formed. The required structure was



which is clearly an ester of ethanoic acid.

(iii) Hydrogen bromide can have two different reactions with geraniol. There will be addition across the C=C bond and the –OH group will undergo substitution by bromine. The former reaction was much better understood than the latter. Candidates were not expected to know which way the HBr would add across the C=C bond.

This question was the most poorly answered on the paper. Only a minority of candidates knew the required mechanism in detail, although it is specified in Syllabus Section 10.5(b). Relatively few candidates were able to complete the calculation in part (c).

- (a)(i) Although most candidates knew the equation that was required, very few gave the displayed formula of the product as required by the question. The most common error was to fail to show the triple bond between the C and N atoms of the  $-C \equiv N$  group. Details of how Examiners expect candidates to draw a displayed formula are given in Syllabus Section 10.1.
  - (ii) The majority of candidates knew that this reaction is a nucleophilic addition.
  - (iii) Many candidates understood that the mechanism involves an attack by the nucleophile CN<sup>-</sup> on the carbon atom of the carbonyl group. Fewer candidates explained clearly that the carbonyl group is polarised with the oxygen atom attracting the bonding electrons from the carbon atom of the C=O group, leaving it with a d+ charge. The structure of the intermediate alkoxide anion was generally well drawn although a significant number of candidates omitted the negative charge on the oxygen atom. Very few candidates completed the mechanism by showing the reaction between the alkoxide anion and a molecule of HCN which results in the re-formation of the CN<sup>-</sup> anion.
- (b)(i) Many candidates struggled with this equation which is

 $CH_3CH(OH)CN + 2H_2O \rightarrow CH_3CH(OH)CO_2H + NH_3.$ 

- (ii) Few candidates were able to identify the reaction as a hydrolysis.
- (c) A large number of candidates struggled with this calculation. Common mistakes were to calculate wrongly the  $M_r$  values of ethanal (44) and of lactic acid (90) and to fail to appreciate that, in theory, one mole of ethanal gives one mole of lactic acid. Since 0.1 mol of ethanal gave 0.06 mol of lactic acid, the percentage yield was given by the following expression.

% yield = 
$$\frac{0.06 \times 100}{0.1}$$
 = 60%

Paper 9701/03 Practical Test

#### General comments

The Examiners again thank Supervisors who provided titration results for **Question 1**. Accuracy marks were awarded from a comparison of the candidate and Supervisor titres. It was very important that Examiners were able to place a particular candidate within a session *and* individual laboratory as titres can vary between sessions/laboratories if different batches of solution are provided.

Centres are reminded of the wording of the Confidential Instructions:

Large volumes of solutions should not be bulked (thirty candidate maximum for any one solution).

Separate results should be provided for each Session and Laboratory.

**Seating plans** should be provided. (It is often possible to spot and resolve solution/titre problems for a small group of candidates in one part of a laboratory if the seating plan is provided).

Whenever inadequate information is supplied there is a risk that candidates will be disadvantaged.

The Examiners observed a generally high standard of practical titration work. Most candidates were able to process the results of the titration.

In the observation/deduction tests, a large number of candidates ignored the rubric:

The names of gases evolved and details of the test used to identify each one.

Candidates should indicate clearly at what stage in a test a change occurs.

#### **Comments on specific questions**

#### **Question 1**

#### Titration

In this question, the accuracy marks available were increased by two and a maximum deduction (of two marks) made from this accuracy mark for errors in recording titres or selecting an appropriate "average".

The majority of candidates recorded consistent titres that were close to those obtained by the Supervisor. Most candidates had no deductions made for the poor recording of the burette data.

The Examiners noted that where a deduction was made for reading a burette to only one decimal place, the error was repeated by many candidates within a group.

The calculations were generally correct but some common errors were as follows:

(b) Candidates used 158 instead of 158.2 when calculating the moles of sodium thiosulphate. Where the  $A_r$  is given in the question it should be used.

Some candidates calculated the moles of sodium thiosulphate present in 1 dm<sup>3</sup> of solution but omitted the step calculating the volume run from the burette.

- (e) Some candidates introduced 5.15 g dm<sup>-3</sup> at this stage instead of in (f).
- (f) One mark was awarded for the evaluation of a fully correct answer to within 1% of the value calculated by the Examiner from the candidate's experimental results. Candidates who had fully correct answers in (a) to (e) and who did not gain this mark had rounded each section to one or at best two significant figures and carried these answers from part to part.

Where an answer to a section is rounded it is recommended that rounding is to three or four significant figures, and that the non-rounded value is carried in the calculator.

#### Question 2

#### Observation and Deduction

The solution provided contained ammonium iron(II) sulphate. Candidates are no longer expected to make a deduction against each observation but to make a final deduction as to the ions present and give supporting evidence for their deductions.

In marking **Question 2** the Examiners were looking for complete observations in each stage of a test. Attention is drawn to the rubric for the question. Comments on individual sections are as follows:

- (a) The solution was prepared and left for a time the observation being made in (f).
- (b) Most candidates recorded a green precipitate, insoluble in excess sodium hydroxide and turning brown in the filter paper. A small number of candidates incorrectly recorded a grey-green precipitate but still observed the precipitate turning brown on exposure to the air. Using the notes provided this observation should have prompted the connection with Fe<sup>2+</sup> rather than Cr<sup>3+</sup>.
- (c) No change should have been observed but many candidates recorded a white precipitate. Silver nitrate is very sensitive to the presence of chloride ion in the distilled water used to prepare solutions. The Examiners ignored reference to any haziness in this test but not reference to a precipitate.
- (d) Many candidates recorded a white precipitate but gave no indication as to when it was formed (see rubric to the question). To gain the mark there had to be reference to the precipitate forming with barium chloride. Many candidates who missed this mark by simply recording a white precipitate in (d) were awarded the mark retrospectively from their 'support evidence' where they stated that a sulphate was present as a white precipitate formed with barium chloride in (d).
- (e) Some candidates failed to describe the test used to identify the gas evolved (see rubric to the question). Once again a retrospective mark was available from the supporting evidence. A candidate who had stated ammonia or gas was evolved in (e) but had not described the test could gain the observation mark from the supporting evidence by stating that the ammonia/gas turned red litmus blue (or equivalent test).

(f) A mark was given for the colour of the precipitate formed (white, off-white, grey) and a mark for the colour of the solution (pale yellow to yellow). Most candidates commented on the colour of the precipitate but made no comment about the solution.

The majority of candidates recorded a white precipitate when hydrochloric acid was added to the solution made by dissolving the precipitate in nitric acid.

#### Identification of the lons

Most candidates were able to correctly identify the ions present. Credit was given if the Examiners saw appropriate, if incomplete observations for the relevant tests.

#### Supporting Evidence

Many candidates gave supporting evidence for only one or two of the ions present. The Examiners expected to see, and did see regularly, evidence for all three ions. Listing tests (b), (d) and (e) was sufficient if observation marks had been awarded for those tests.

Where observations were incomplete, the minimum acceptable were:

- for Fe<sup>2+</sup> a green precipitate or a precipitate turning brown in (b)
- for NH<sub>4</sub><sup>+</sup> reference to ammonia in (e)
- for  $SO_4^{2-}$  reference to a white precipitate in (d).

#### The Identity of the solid formed in (f)

This proved to be a very difficult part of the question. The presence of silver in the solid was realised by a number of candidates from the white precipitate with hydrochloric acid. Very few candidates were able to work out that the solid was metallic silver formed in a redox reaction:

 $Ag^{+}(aq) + Fe^{2+}(aq) \Rightarrow Ag(s) + Fe^{3+}(aq)$ 

The solution changing to a pale yellow/yellow in colour indicated the oxidation of the iron(II) to iron(III).

Some candidates suggested silver sulphate as the precipitate but this compound is relatively soluble in water and would not have formed as a precipitate.

**Question 2** carried a total of eleven marking points with a maximum of ten marks for the question. A few answers were seen where eleven marks were gained and the maximum of ten marks awarded. Good candidates regularly scored seven to eight marks for the question, losing marks for the final part and some incomplete observations.

Paper 9701/04 Paper 4

#### **General comments**

The general standard of answers was much the same as last year's. For the most part, candidates continue to show a good general knowledge of trends, properties and reactions, but their detailed knowledge is often less secure. In the mathematical answers, fewer now quote their answers to the same number of significant figures that their calculators give them (which is good), but there seems to be a trend in the opposite direction: the premature rounding-off of intermediate values in calculations can cause the final answer to be outside the accepted limits. As a general rule, intermediate values should be kept to 4 or 5 significant figures, and the final value quoted to 3 significant figures.

Most candidates finished the whole paper, with little sign of being rushed to complete it – the extra quarter of an hour has helped them here. In general answers were well expressed, and sufficient working was shown in calculations to allow the awarding of error-carried-forward marks for incorrect answers where appropriate.

#### Comments on specific questions

#### Question 1

- (a)(i) There was some confusion between "strong" and "concentrated" in some candidates' minds. Others thought that because it was an organic base, guanidine had to be weak. They were expected to deduce from the final pH (between 13 and 14) that guanidine was a strong base.
  - (ii) Most candidates could carry out this calculation, although several confused base-e with base-10 on their calculators, and calculated  $[H^+]$  to be  $e^{-0.7} = 0.5$  mol dm<sup>-3</sup> or even  $e^{+0.7} = 2.0$  mol dm<sup>-3</sup>. Allowance could be made for this initial error in the marking of later parts of the calculation. Many more candidates thought that  $[H_2SO_4] = 2 \times [H^+]$  rather than =  $[H^+]/2$ .
  - (iii) Accurate reading of the graph would give the end-point volume as  $34.0 \pm 0.5 \text{ cm}^3$ , but some candidates used  $35 \text{ cm}^3$ . Several others thought [guanidine] = [H<sub>2</sub>SO<sub>4</sub>]
  - (iv) An error-carried forward mark could be allowed here if the concentration had been calculated incorrectly in part (iii). Many candidates multiplied 8.68 by their answer to part (iii) rather than dividing.
- (b)(i) Most candidates balanced the equation correctly:  $\rightarrow$  7CaSO<sub>4</sub> + 3Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> + 2HF.
  - (ii) The use of the ratio 7/3 was important here. Several candidates inverted it during their calculations. Others misread the question, and thought it asked them to calculate the mass of  $H_2SO_4$  that was needed to react with 1.0 kg of phosphate rock.
- (c)(i) The key points Examiners looked for here were: a realisation that buffers are only effective when *small* quantities of acid or base are added, and that the pH does not remain *unchanged* when acid or base is added, but only changes to a *small extent*. A phrase such as "resists a change in pH" is acceptable.
  - (ii) Most candidates scored this mark. The most common mistake was to add 0.3 to the  $pK_a$  (7.2) rather than subtract it.
- Answers: (a)(ii)  $[H^+] = 0.2 \text{ mol } dm^{-3}$ ,  $[H_2SO_4] = 0.1 \text{mol } dm^{-3}$ , (iii) [guanidine] = 0.147 mol<sup>-3</sup>, (iv)  $M_r = 59$ ; (b)(ii) 0.98 kg; (c)(ii) pH = 6.9.

#### **Question 2**

- (a) Some candidates extracted the wrong equation from the *Data Booklet*. Of the three equations involving the reduction of oxygen;  $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ ,  $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$  and  $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$  only the last one is appropriate in this instance. (Although not penalised, the use of an equilibrium arrow is not appropriate is this case, since the drawing of current from the cell would cause the reduction to go to completion)
- (b) Most candidates scored the mark here (polarity =  $\oplus$ ).
- (c) The correct voltage (1.23 V) was quoted by all candidates who used the correct equation in (a), but only by some of those who used the  $O_2/OH^-$  equation. In this case the  $E^{\theta}$  value for the oxidation of H<sub>2</sub> should have been the one for  $2H_2O + 2e^- \rightarrow 2OH^- + H_2$  (-0.83V). Hence:

 $E_{cell} = 0.40 - (-0.83) = 1.23V$ . An error-carried-forward mark was allowed for the  $O_2/H_2O_2$  value.

- (d) Examiners were looking for one of the following suggestions: a larger salt bridge, or replacing it with a diaphragm to allow a larger current to pass; larger surface areas for the electrodes; an increase in the concentrations of the electrolytes; increasing the pressures of the gases. Several candidates wanted to change the system completely, replacing oxygen by a more powerful oxidant such as fluorine.
- (e) Many candidates came unstuck in the last stage of this relatively straightforward calculation. Either they did not use the value of the Faraday correctly (multiplying rather than dividing) or they thought that 1 Faraday would produce 2 g of hydrogen, rather than 1 g. A few candidates thought there were 12 hours in a day, rather than 24. Some even thought a day contained 60 hours!

(f) Apart from a few candidates who seemed to have read the question the wrong way round, and gave advantages and disadvantages for hydrocarbon fuels, most scored 1 or 2 marks for this part. The advantages looked for could have included less pollution; cleaner by-products; less dependence of finite resources. Disadvantages were the greater expense to develop or to produce (Pt being an expensive metal); more space required for the power unit; not so much power produced per unit volume; the difficulty of storing and transporting hydrogen. The flammability or explosive properties of hydrogen were not accepted – petrol is also flammable, and has been the cause of many explosions both in storage and in vehicles.

Answers: (c) E<sub>cell</sub> = 1.23V; (e) 3.6 g.

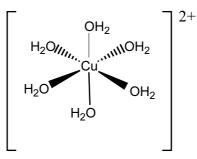
#### Question 3

For candidates who had studied this topic, and had revised it thoroughly, this was a straightforward 4 marks. Most knew that the solubilities decreased down the group, and that lattice and hydration energies were important, but fewer were able to explain that although both decrease as one goes down the group, the lattice energies do so to only a small extent, due to the larger size of the sulphate ion swamping the effect of increasing cationic radius on the ( $r_{+} + r_{-}$ ) value. Hence towards the bottom of the group, the (exothermic) hydration energy can no longer compensate for the (endothermic) reverse lattice energy, making  $\Delta H_{solution}$  too endothermic. Some candidates were confused and discussed the thermal stabilities of the sulphates instead.

#### Question 4

- (a) Many candidates gave various properties of transition elements (coloured ions, variable oxidation states etc.), but fewer gave the required definition. The syllabus defines a transition element as one that forms *at least one ion with a partially filled d-shell*. This excluded scandium (d<sup>0</sup> in all its compounds) and zinc (d<sup>10</sup> in all compounds).
- (b)(i) Compared to the variation across a period, the atomic radii show very little change across the transition element group. Examiners accepted a description of a *slight* decrease (e.g. from Cr to Ni) or a *slight* increase (e.g. to Cu).
  - (ii) Candidates were expected to appreciate that due the relatively invariant atomic radius, and hence size, the densities would show an increase in accordance with the increase in atomic mass (assuming the packing ratio/coordination number was the same). Arguments based on numbers of electrons or protons were not relevant.
- (c) Most candidates scored a mark for  $....3d^9$ , although some incorrectly wrote  $....3d^84s^1$  or  $....3d^74s^2$ . A few misread the question, and thought it asked for the configuration of the Cu atom. Some gave it correctly as  $...3d^{10}4s^1$ , whereas others wrote  $...3d^94s^2$ . Neither scored the mark.
- (d)(i) Three points were looked for here: a complex ion is one in which:
  - a *ligand/ion/group* is
  - *datively bonded* to a
  - (central) *metal ion/atom*.
  - (ii) Three points were also looked for here:
    - the charge (2+) either on the copper atom, or (better) at the right of the formula
    - all six water molecules bonded to the copper ion *via* their oxygen atoms (rather than hydrogen)
    - a convincing diagram showing an octahedral arrangement (wedge bonds not absolutely necessary, but they help).

The following diagram includes all these points:



Unfortunately some candidates thought they were required to draw the formula of the tetra-ammine (or even the hexa-ammine).

- (e)(i) Acceptable colours were dark/deep/navy/royal blue or purple. Examiners even allowed Oxford blue (!). Prussian blue was not accepted, however, as it was felt that this is specific for the iron-cyanide complex of that name.
  - (ii) Candidates were expected to know that the cuprammonium complex contained 4 ammonia molecules. Thus the following was acceptable:

$$4NH_{3} + [Cu(H_{2}O)_{6}]^{2+} \longrightarrow [Cu(NH_{3})_{4}(H_{2}O)_{2}]^{2+} + 4H_{2}O$$
$$\longrightarrow [Cu(NH_{3})_{4}]^{2+} + 6H_{2}O$$

(f) In general candidates were not good at explaining the shifting of the reversible equilibrium:

 $[Cu(H_2O)_6]^{2+} + 4CT = [CuCl_4]^{2-} + 6H_2O$ 

according to the changing conditions, as a result of the *exchange* of  $H_2O$  by CI ligands and *vice versa*. Marks were awarded for the formula of the chloro complex; the balanced equation; the mention of ligand replacement or exchange, and the concept of reversibility.

#### **Question 5**

- (a)(i) Acceptable catalysts included A*l*, Fe,  $AlCl_3$ , FeC $l_3$ , I<sub>2</sub> (but not FeBr<sub>3</sub> or  $AlBr_3$  the chlorine would oxidise Br<sup>-</sup> to Br<sub>2</sub>.) The general term *halogen carrier* was not accepted in the absence of an identified compound.
  - (ii) UV light *or* sunlight is needed. One or two candidates suggested that *ultra-violent* light was needed! (They were given credit for this spelling error.) If aqueous chlorine was mentioned either here or in part (i) one mark was deducted.
- (b) Various non-metal chlorides would achieve this transformation:  $PCl_3$ ,  $PCl_5$  and  $SOCl_2$  were the most commonly used. Once again, the mention of (aq) negated the mark.

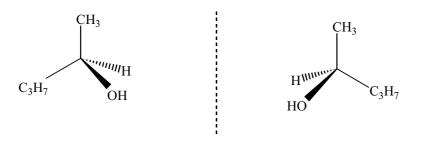
In general candidates knew their reagents/conditions for these reactions fairly well, although fewer scored the mark for part (b).

- (c)(i) Most candidates correctly identified the correct order as C>B>A. Some forfeited the mark by placing more that one tick in the column.
  - (ii) Fewer candidates were able to offer a clear explanation for the order. The points looked for were, for compound A, the delocalisation of the lone pair on the chlorine atom over the aryl ring, causing a stronger C-Cl bond, and for compound C, the realisation that joining the carbon atom to *two* electronegative atoms (chlorine and oxygen) would make it very  $\delta$ +, and hence susceptible to nucleophilic attack. An alternative (and possibly better) explanation in terms of an addition-elimination mechanism being possible for compound C (as in the hydrolysis of SiCl<sub>4</sub>) was allowed for in the mark scheme, and was seen on a few scripts.

(d) Most candidates correctly drew the third structure ( $C_6H_5CO_2H$ ), fewer recognised the amide  $C_6H_5CONHCH_3$  as the second product. Some candidates misread the question, so wrote  $C_6H_5O^-Na^+$  as the product of the first reaction, rather than the ester  $C_6H_5CO_2C_6H_5$ . Candidates should be reminded to draw their structures carefully: the bond from the benzene ring to the organic group (e.g. COOH) should be drawn going to its *carbon* atom, not one of the oxygens or the hydrogen atom.

#### Question 6

- (a)(i) Most candidates correctly identified compound **E** as the one reacting with alkaline aqueous iodine.
  - (ii) Although most scored a mark for  $CHI_3$  as one of the products, some wrote, unthinkingly,  $CH_3I$ . Fewer identified  $CH_3CH_2CH_2CO_2$   $a^+$  (*not* butanoic acid) as the other product.
- (b) Despite the hint of two isomers being formed *in equal amounts* many candidates did not recognise this as an example of optical isomerism. Marks were awarded for stating that the alcohol from E has 4 different groups around a carbon atom; hence it is *chiral* or *asymmetric* and exists as *non-superimposable mirror images*. In addition marks could be gained for stating that *the alcohol* from the reduction of compound D is achiral, or contains two identical groups on its alcohol carbon atom, and for drawing two stereochemical formulae such as the following:



#### **Question 7**

- (a) Many candidates scored two marks here for the two observations: the brown-orange colour would disappear, and a white precipitate would form. Some thought that only one of the two compounds would react, or that one of the two would decolourise the bromine water, whereas the other one would form the white precipitate.
- (b) There were many reactions candidates could have chosen. The following is a selection of the answers that were seen, and which attracted a mark:
  - adding neutral FeCl<sub>3</sub>(aq) produces a violet/purple/lilac colouration with phenol, but not with phenylamine. (N.B. the FeCl<sub>3</sub> had to be both *neutral* and *aqueous*)
  - adding universal indicator to a solution of the compound it would turn orange/red with phenol
  - adding Na metal to the pure compound it would fizz/produce a gas with phenol
  - adding NaOH(aq) to the pure compound phenol would dissolve, whereas phenylamine would not
  - adding H<sup>+</sup>(aq) to the pure compound phenylamine would dissolve
  - adding HNO<sub>2</sub> at room temperature phenylamine would produce gaseous N<sub>2</sub>
  - adding HNO<sub>2</sub> at 5°C, followed by an alkaline solution of phenol phenylamine would produce a coloured (orange) dye.

Note, however, that the production of a colour on adding the unknown (+ NaOH(aq)) to a cold solution of a phenyldiazonium salt would not distinguish them – both phenol and phenylamine give dyes with the phenyldiazonium cation under these conditions.

#### (c) The relevant part of the mark scheme is as follows:

- **IV** KMnO<sub>4</sub> (aq *or* with  $H^+$  or  $OH^-$ ) + heat [1]
- **V**  $HNO_3 + H_2SO_4$  [1] conc at T < 60°C but > 40°C [1]
- **VI** Sn/Fe/Zn + HCl [1]

Although acidified dichromate will oxidise 4-nitromethylbenzene to 4-nitrobenzoic acid, it has no effect on other methyl groups joined to aryl rings – it needs the strong electron-withdrawing effect of the  $NO_2$  group for it to work. The attempted reduction of nitro groups with  $LiA_{H_4}$  or  $NaBH_4$  produces a mixture of azo and hydrazo compound. Catalytic hydrogenation is also unsuccessful. In general candidates showed a good understanding and recall of these reagents.

#### Paper 9701/05

**Practical Test** 

#### General comments

The Examiners thank Supervisors who provided experimental results for **Question 1**. In this paper Supervisors' results were not used in assessing accuracy marks, but they gave an important indication as to the experimental values expected from each candidate.

**Question 2** involved a planning exercise that was not directly related to the syllabus but involved simple practical techniques that were well within the capabilities of an A2 candidate. In the stem of the question, the Examiners presented a definition of solubility and of a saturated solution. Further information was given to amplify each definition and to aid understanding by the candidate. After marking the question, the Examiners were left with the impression that many candidates had not taken note of the information given. Candidates tried a number of ways to prepare a saturated solution and further methods to determine the solubility.

#### Comments on specific questions

#### Question 1

In each experiment candidates were asked to record the times of reaction to the nearest second. The majority of candidates followed this instruction but a significant number gave the full digital display, e.g. 34.67 s. A very small number recorded the digital display in minutes and seconds. A small group of candidates rounded their times to the nearest second but recorded the time as 23.0, 34.0 etc. which is a time to the nearest 0.1 s.

The question examined the rates and orders of reaction when bromate ions reacted with bromide ions in the presence of acid. This is a classic experiment, often quoted in text books, where it is stated that the reaction is first order with respect to bromate ion, first order with respect to bromide ion, and second order with respect to hydrogen ion.

In setting the question it was found that the reaction, when bromate ion concentration was varied, produced reliable first order kinetics.

When bromide ion concentration was varied, the reaction approximated to first order kinetics but was not as reliable as that with bromate ion.

When hydrogen ion concentration was varied the reaction did not give second order kinetics but suggested an order of about 1.5.

Experiments 1 and 2 investigated the effect of changing in the concentration of bromate ion.

Experiments 1 and 3 investigated the effect of changing in the concentration of bromide ion.

The Examiners were aware that rates of reaction can be affected by temperature change and that there were likely to be temperature variations across a laboratory. It was assumed that a candidate would complete the experimental work in Experiments 1 to 4 within a short space of time and that change in temperature would not be a major factor for an individual candidate. This was confirmed in a number of Centres where some candidates recorded short times for the reactions but others recorded much longer times – accuracy marks for both groups were comparable.

As the reactions when bromate and bromide ion concentration varied were both first order, the Examiners compared V*t* values for experiments 1 and 2 and the V*t* values for experiments 1 and 3. The % difference between the V*t* values for experiments 1 and 2 was calculated and accuracy marks awarded on a sliding scale for differences between 4% and 10%.

As the reaction involving a change in bromide ion concentration was less reliable, the sliding scale used to award accuracy marks was wider -5% to 20%.

The Examiners were aware that if a candidate obtained poor data in experiment 1 they would be awarded very few accuracy marks. To compensate for this the Vt values for experiments 2 and 3 were also compared and the smaller % difference for experiments 1 and 3, and 2 and 3, used to award the second set of accuracy marks. A number of candidates who obtained poor results to experiment 1 and who would have scored zero marks for accuracy if this experiment had been used in assessing each accuracy mark, were able to gain 50% of the total when experiments 2 and 3 were compared.

No accuracy marks were given for the reaction in which hydrogen ion concentration was varied.

Candidates were asked to calculate  $\frac{1000}{\text{time}}$  for each experiment. A considerable number of candidates

calculated  $\frac{1}{\text{time}}$ . No mark was awarded for this calculation and there was no penalty in the following calculations.

(b) Very few candidates appreciated the reason why the total volume was kept constant in each experiment. Examiners were looking for answers that indicated the volume of an individual reagent was proportional to or a measure of its concentration. Some candidates appreciated that it was necessary to keep the phenol constant and this was given credit.

Many candidates gave maintaining constant depth as the answer – confusion with the acid/thiosulphate reaction in which the formation of colloidal sulphur obscures a marker under the reaction vessel.

#### Calculations

In all three sections the candidates were asked to use experimental data in calculations to arrive at a suggested order of reaction. A number of candidates simply recorded a qualitative statement e.g. 'when the concentration of bromate ion increases the rate increases'. No credit was given for such answers.

In sections (c) and (d) the candidates received credit for:

- comparing in a ratio the volumes used in the experiment
- comparing in a ratio the rates of reaction
- comparing the ratios of volumes and rates to suggest an order of reaction.

The majority of candidates successfully compared  $\frac{R_1}{R_2}$  with  $\frac{V_1}{V_2}$  and gained full marks for each section.

Other candidates adopted a more mathematical approach and produced the expression  $\frac{R_1}{R_2} = \frac{(V_1)^n}{(V_2)^n}$ .

The value of *n* was calculated by inspection of the ratios or by logs.

A small number of candidates inverted one or other of the ratios in determining the order or raised the rates rather than the volume to the power *n*.

Comparison of Vt (and in some cases  $V^2t$  values) enabled other candidates to arrive at first order for these reactions.

In section (e) credit was given for stating that experiments 3 and 4 were involved. If the correct pair of experiments was selected, further credit was given for comparing volumes and comparing rates. Many candidates gained no credit in this section by selecting experiments 1 and 4.

A significant number of candidates obtained high marks in **Question 1**.

#### Question 2

(a) The Examiners anticipated that candidates would read the information given and prepare a solution, saturated at room temperature, by dissolving a maximum amount of solid at an elevated temperature then allowing the solution to return to room temperature when excess solid would precipitate leaving the equilibrium mixture of solid and saturated solution. This method was seldom seen.

The majority of candidates prepared a solution from solid and water at room temperature – adding solid until no more dissolved. This method was allowed but nearly all candidates who prepared their solution in this way missed one marking point. Examiners were looking for an appreciation that such a solution would need to be left for a considerable time (to establish equilibrium).

Another method involved taking 100 g (or 100 cm<sup>3</sup>) of water and adding solid until no more dissolved. The Examiners accepted this as a method with the same missed marking point as above.

Most candidates continued from their saturated solution to determine the solubility but some commenced completely new methods. The instruction in the question stated that the solubility of potassium chlorate in the prepared saturated solution should be determined, but all methods seen received any credit that could be given.

The Examiners saw very few methods where saturated solution was taken and weighed, then evaporated to determine the mass of dissolved solid. Most candidates filtered their saturated solution and weighed the residual solid (with or without drying). Those who had taken an initial 100 g of water filtered the solution and still assumed that 100 g of water was present. Errors in the method such as this were not penalised.

A small number of candidates related potassium chlorate(V) to the potassium bromate(V) used in **Question 1** and its reaction with bromide ions. They reacted the chlorate with iodide ions and carried out a titration with sodium thiosulphate to determine the mass of potassium chlorate in a specified volume of saturated solution.

Another group of candidates clearly had some familiarity with solubility curves and described an experiment where variable masses of water were used with a fixed mass of the potassium chlorate (or vice versa) to find the temperatures at which crystallisation took place. Credit was given provided sufficient readings were indicated to enable a solubility curve to be drawn and the solubility at room temperature, read from the graph, clearly indicated. A very few candidates who started with 100 g of water and saturated with potassium chlorate simply filtered and weighed the filtrate to find the mass of dissolved solid. Again, the solution retained on the filter paper was ignored.

(b) This was a straightforward question, completed to a disappointing standard by the majority of candidates. Full marks were awarded to a small number of candidates.

Many candidates selected inappropriate scales and compressed all of the plotted data into two, or at most three, large squares on the y axis. The Examiners expect to see more than half of each scale used for the plotting of points.

The question asked candidates to plot two curves, one for the solubility of NaBr, the other for the solubility of NaBr.2H<sub>2</sub>O. The Examiners were looking for two distinct smooth curves through the plotted points, intersecting at the transition temperature.

The majority of candidates drew a single line with a point of inflexion or two lines that were 'bent' to meet at 50°C. The expected intersection on a well drawn graph was about 50.7°C.

Question 2 produced a wide range of marks with few candidates at the higher end of the mark range.

Paper 9701/06

Options

#### **General comments**

#### Biochemistry

This continues to be a popular option and candidates were, on the whole, well prepared with no obvious gaps in their knowledge. The increased requirement for calculations in this paper meant that marks were a little lower than in the past.

#### Environmental Chemistry

Although many of the answers were of a good standard, there are still a significant number of candidates who try to answer these questions from general knowledge, and who therefore score low marks.

#### Phase Equilibria

This remains a very popular option and once again produced some very good answers.

#### Spectroscopy

As in previous years, this was one of the less popular options, however there were some very well prepared candidates who scored good marks.

#### Transition Metals

This continues to be a very popular option. Many candidates continue to find the use of half-equations difficult when predicting chemical reactions and balancing equations as in **Question 10 (a)(i)**.

#### Comments on specific questions

#### Question 1

Many candidates were able to write an equation for the hydrolysis of ATP in part (a). Part (b) proved to be more challenging with a significant number of candidates unsure how to plot the graph and use it to determine the Michaelis constant and  $K_m$ . Good candidates coped with the graph, and were then able to make a good attempt at part (c) under conditions of inhibition.

#### Question 2

The first calculation in (a) caused few problems, but writing the equation for the combustion of stearic acid proved more challenging. A significant proportion of candidates also found part (b) tricky, not really thinking in terms of which bonds were being broken. Having said that, the calculations in part (b)(ii) were performed reasonably well. Most candidates could give the use for glucose in animals and one use in plants, but few gave the conversion into cellulose for growth.

#### Question 3

There was some confusion over the role of ozone in the two regions of the atmosphere, and inevitably some candidates got things the wrong way round. That having been said, many candidates had good knowledge of the chemistry of ozone in the atmosphere. Despite the specific references in the syllabus, many candidates lacked knowledge of lean-burn engines and as a result dropped marks. In fact, there were six marking points for a maximum of four marks in part (b).

It was felt that all candidates would have a thorough knowledge of the methods of producing drinking water and of the disposal of solid waste. In fact, knowledge was patchy, and although many candidates scored good marks in part (a), the marks in part (b) were significantly lower. It seemed that many had not been taught the details of landfill and incineration as methods of disposal of solid waste. Despite the fact that there were seven marking points for maximum of five marks, few candidates managed to score three or more.

#### Question 5

Most candidates were able to sketch the melting point/composition diagrams and label them with few problems. In part (c), candidates were required to think about the use in suggesting advantages of aluminium/copper solder, and some found this hard. Part (d) was a little unusual in that candidates were asked to use atomic radius data in order to explain the properties of mixtures of the metals. Once again, well prepared candidates took this in their stride, whilst weak candidates had little idea what to do with the data.

#### **Question 6**

Part (a)(i) was generally well answered, with few losing marks in plotting the data. Some candidates failed to label the liquid and vapour curves, effectively throwing a mark away. The construction lines in (a)(ii) were generally well drawn and the prediction of the composition of the distillate was generally accurate. In part (b), the sketch was generally good, but in part (b)(ii) fewer candidates referred to hydrogen bonding. There was the usual confusion over which fraction was distilled and which left in the vessel in part (b)(ii).

#### **Question 7**

Part (a) of this question was generally well answered, with most candidates able to correctly identify nitromethane and ethene as the two molecules which absorb in the uv/visible region. In part (b), candidates were confident in calculating the number of carbon atoms present in E and many scored both marks. Part (c) proved more challenging, with candidates struggling to identify the different chromophores, and decide which species had the greater conjugation. In part (d), candidates who had practiced identifying compounds from infra-red spectra had little difficulty in identifying the major absorptions and in identifying F as propanoic acid.

#### Question 8

It was felt that part (a) should have been a piece of familiar bookwork for candidates, yet far too many candidates failed to provide sufficient detail to score full marks. By contrast almost every candidate knew the advantages of using n.m.r. spectroscopy as a diagnostic tool in medicine. Although most candidates correctly answered part (c)(i), a much smaller number appreciated that anhydrous copper(II) sulphate has no ligands, and hence the d orbitals are degenerate.

#### Question 9

In part (a), almost all candidates could draw a pair of *cis-trans* isomers but fewer found it easy to draw a pair of optical isomers. Part (b) proved to be much harder, with few candidates scoring more than four of the seven marks available. The major problem appeared to be candidate's recognition of the chemistry taking place in the three reactions, and in turn how to represent this in equations. Many also failed to realise that the reactions were all reversible.

#### Question 10

This proved to be rather easier than **Question 9**, perhaps not surprisingly in that it started with rusting which should have been familiar territory to all who had studied this option. However, as in previous examinations, candidates' use of half-equations was far from secure, and this continues to be a source of lost marks. Candidates were far happier describing and explaining ways in which rusting could be prevented. In part (b), more than half of the candidates correctly calculated the empirical formula of the red solid, although some struggled to work out the oxidation number of iron in it. The balanced equation in (b)(ii) defeated all but the best candidates.