Write your name here

Surname	Other names

Edexcel GCE

Centre Number	Candidate Number

Chemistry
Advanced
Unit 5: General Principles of Chemistry II – Transition Metals and Organic Nitrogen Chemistry (including synoptic assessment)

Wednesday 1 February 2012 – Morning
Time: 1 hour 40 minutes

Paper Reference
6CH05/01

You must have: Data Booklet

Candidates may use a calculator.

Total Marks

Instructions

- Use **black** ink or ball-point pen.
- **Fill in the boxes** at the top of this page with your name, centre number and candidate number.
- Answer **all** questions.
- Answer the questions in the spaces provided – *there may be more space than you need.*

Information

- The total mark for this paper is 90.
- The marks for **each** question are shown in brackets – *use this as a guide as to how much time to spend on each question.*
- Questions labelled with an **asterisk** (*) are ones where the quality of your written communication will be assessed – *you should take particular care with your spelling, punctuation and grammar, as well as the clarity of expression, on these questions.*
- A Periodic Table is printed on the back cover of this paper.

Advice

- Read each question carefully before you start to answer it.
- Keep an eye on the time.
- Try to answer every question.
- Check your answers if you have time at the end.

Turn over ▶

PEARSON

SECTION A

Answer ALL the questions in this section. You should aim to spend no more than 20 minutes on this section. For each question, select one answer from A to D and put a cross in the box ☒. If you change your mind, put a line through the box ☒ and then mark your new answer with a cross ☒.

1 An electrochemical cell consists of a standard hydrogen electrode and a $Cu^{2+}(aq)|Cu(s)$ electrode which uses copper(II) sulfate solution. Which one of the following does **not** affect the e.m.f. of the cell?

☒ **A** The volume of the copper(II) sulfate solution.

☒ **B** The temperature.

☒ **C** The pressure of the hydrogen.

☒ **D** The concentration of the copper(II) sulfate solution.

(Total for Question 1 = 1 mark)

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2 Which answer corresponds to the correct value of $E^{\ominus}_{cell}$ for the oxidation of hydrogen peroxide by manganate(VII) ions? The half-reactions are

$$2H^+ + O_2 + 2e^- \rightleftharpoons H_2O_2 \qquad E^{\ominus} = +0.68\ V$$

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O \qquad E^{\ominus} = +1.51\ V$$

The overall equation is

$$2MnO_4^- + 6H^+ + 5H_2O_2 \rightleftharpoons 2Mn^{2+} + 8H_2O + 5O_2$$

☒ **A** $E^{\ominus}_{cell} = +2.19\ V$

☒ **B** $E^{\ominus}_{cell} = -0.83\ V$

☒ **C** $E^{\ominus}_{cell} = -0.38\ V$

☒ **D** $E^{\ominus}_{cell} = +0.83\ V$

(Total for Question 2 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.

3 The transition metal complex $Pt(NH_3)_2Cl_2$ exists as two geometric isomers. This is because the complex

☒ **A** is square-planar.

☒ **B** is tetrahedral.

☒ **C** contains a double bond.

☒ **D** is octahedral.

(Total for Question 3 = 1 mark)

4 Hydrogen peroxide, H_2O_2, can be analysed by titration. The hydrogen peroxide solution is treated with acidified potassium iodide solution, and the liberated iodine is titrated with a standard solution of sodium thiosulfate, $Na_2S_2O_3$. The products are iodide ions and tetrathionate ions, $S_4O_6^{2-}$.

Which of the following applies to this reaction?

		Action of H_2O_2	Action of $S_2O_3^{2-}$
☒	**A**	oxidizing agent	oxidizing agent
☒	**B**	oxidizing agent	reducing agent
☒	**C**	reducing agent	oxidizing agent
☒	**D**	reducing agent	reducing agent

(Total for Question 4 = 1 mark)

5 A hydrated transition metal ion is colourless. Which of the following could be the electronic configuration of this ion?

☒ **A** $[Ar]\ 3d^5 4s^2$

☒ **B** $[Ar]\ 3d^8$

☒ **C** $[Ar]\ 3d^{10} 4s^2$

☒ **D** $[Ar]\ 3d^{10}$

(Total for Question 5 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.

6 Which of the following reagents would enable you to separate iron(III) hydroxide from a mixture of iron(III) hydroxide and copper(II) hydroxide?

☒ **A** Dilute hydrochloric acid

☒ **B** Aqueous ammonia

☒ **C** Dilute nitric acid

☒ **D** Sodium hydroxide solution

(Total for Question 6 = 1 mark)

7 When a solution containing 0.10 mol of chromium(III) chloride, $CrCl_3.6H_2O$, is treated with excess silver nitrate solution, 0.20 mol of silver chloride, AgCl, is immediately precipitated. The formula of the complex ion in the solution is

☒ **A** $[Cr(OH)_6]^{3-}$

☒ **B** $[Cr(H_2O)_6]^{3+}$

☒ **C** $[CrCl(H_2O)_5]^{2+}$

☒ **D** $[CrCl_2(H_2O)_4]^{+}$

(Total for Question 7 = 1 mark)

8 Which of the following species is **not** able to act as a ligand in the formation of transition metal complexes?

☒ **A** $C_6H_5NH_2$

☒ **B** NH_3

☒ **C** $NH_2CH_2CH_2CH_2NH_2$

☒ **D** NH_4^+

(Total for Question 8 = 1 mark)

9 The element zinc, with electronic configuration $1s^22s^22p^63s^23p^63d^{10}4s^2$, is **not** regarded as a transition element because

☒ **A** the oxide of zinc is amphoteric.

☒ **B** none of its ions has an unpaired electron in the *d*-subshell.

☒ **C** it does not readily form complex ions.

☒ **D** it has a boiling temperature low enough for it to be easily distilled.

(Total for Question 9 = 1 mark)

10 The compounds below were heated with aqueous sodium hydroxide solution. Which one of them did **not** give sodium ethanoate, CH_3COONa, as one of the products?

☒ **A** CH_3COOCH_3

☒ **B** CH_3COCH_3

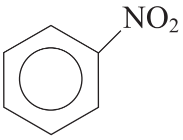
☒ **C** CH_3COOH

☒ **D** CH_3COCl

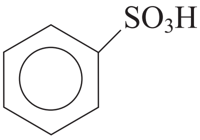
(Total for Question 10 = 1 mark)

11 Which of the following products is formed when phenylamine (aniline) is reacted with **dilute** sulfuric acid?

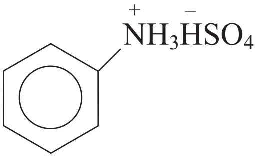
☒ **A**



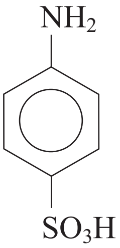
☒ **B**



☒ **C**



☒ **D**



(Total for Question 11 = 1 mark)

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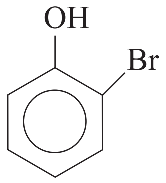
12 For the nitration of phenol, which is the most suitable set of conditions and the reason for its use?

		Conditions	Reactivity of phenol to electrophiles compared with benzene
☒	**A**	dilute nitric acid at room temperature	more reactive
☒	**B**	concentrated nitric and sulfuric acid at room temperature	more reactive
☒	**C**	concentrated nitric and sulfuric acid at 55 °C	the same
☒	**D**	dilute nitric acid and dilute sulfuric acid at room temperature	less reactive

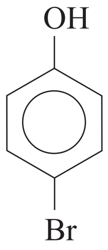
(Total for Question 12 = 1 mark)

13 Phenol reacts with excess bromine water to give as the organic product(s)

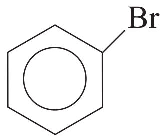
☒ **A**



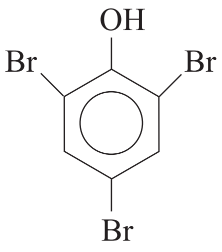
and



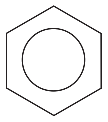
☒ **B**



☒ **C**



☒ **D**



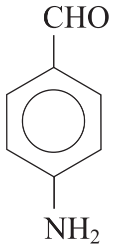
(Total for Question 13 = 1 mark)

14 An organic compound, **X**, shows the following properties:

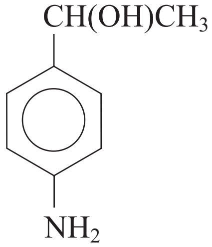
- Oxidation of compound **X** produces a substance that reacts with 2,4-dinitrophenylhydrazine to give a yellow precipitate but does **not** react with Fehling's or Benedict's solution.
- Compound **X** reacts with ice-cold nitrous acid to form a compound that gives a yellow precipitate with an alkaline solution of phenol.

What is the formula of compound **X**?

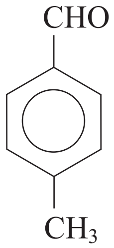
☒ **A**



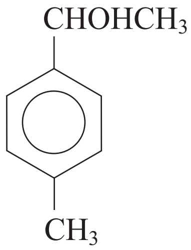
☒ **B**



☒ **C**



☒ **D**



(Total for Question 14 = 1 mark)

15 Which sequence shows the bases in order of decreasing strength?

☒ **A** $C_6H_5NH_2 > CH_3NH_2 > NH_3$

☒ **B** $NH_3 > CH_3NH_2 > C_6H_5NH_2$

☒ **C** $CH_3NH_2 > NH_3 > C_6H_5NH_2$

☒ **D** $NH_3 > C_6H_5NH_2 > CH_3NH_2$

(Total for Question 15 = 1 mark)

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16 Bromoethane can be made by heating ethanol under reflux with 50% sulfuric acid and sodium bromide. When the mixture is distilled, the products include sulfur dioxide, bromine, hydrogen bromide and water as well as bromoethane.

The product mixture is shaken with sodium carbonate solution and later with anhydrous sodium sulfate before being re-distilled. Which of the following shows the correct list of impurities removed at each step?

		Aqueous sodium carbonate wash	Addition of sodium sulfate
☒	**A**	HBr	SO_2, Br_2, water
☒	**B**	SO_2, Br_2	HBr, water
☒	**C**	SO_2, HBr	Br_2, water
☒	**D**	SO_2, Br_2, HBr	water

(Total for Question 16 = 1 mark)

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17 A compound is known to have either the structure $H_2NCH_2CH_2NH_2$ or H_2NCH_2COOH. Which of the following tests would best distinguish between the two compounds?

☒ **A** Reaction with concentrated aqueous sodium hydroxide.

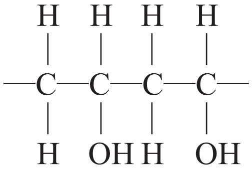
☒ **B** Reaction with nitrous acid.

☒ **C** Reaction with aqueous sodium hydrogencarbonate.

☒ **D** Reaction with ethanoyl chloride.

(Total for Question 17 = 1 mark)

18 Poly(ethenol) is a water-soluble polymer. A section of the chain has the structure shown below.



The polymer is used for making hospital laundry bags so that laundry can be loaded directly into washing machines without it having to be handled.

Poly(ethenol) is water soluble because the polymer

☒ **A** is broken down by the water into monomers.

☒ **B** is broken down by the washing detergent.

☒ **C** breaks into monomers at the temperature of the wash.

☒ **D** forms many strong hydrogen bonds with the water.

(Total for Question 18 = 1 mark)

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19 Which of the following substances is capable of damaging the ozone layer?

☒ **A** NaCl

☒ **B** CO_2

☒ **C** C_2HF_5

☒ **D** $C_2F_3Cl_3$

(Total for Question 19 = 1 mark)

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20 Analysis suggests that a particular organic synthesis produces a medicine that contains trace impurities that may be hazardous. What is the best way for this discovery to be reported and evaluated?

☒ **A** In a scientific journal which subjects its articles to peer review.

☒ **B** On the Internet in an article on a website.

☒ **C** In a newspaper article in several broadsheet newspapers.

☒ **D** In a widely circulated magazine.

(Total for Question 20 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

Answer ALL the questions. Write your answers in the spaces provided.

21 (a) Chromium is a typical transition metal, although its electronic configuration does **not** fit the general trend found in the first transition series.

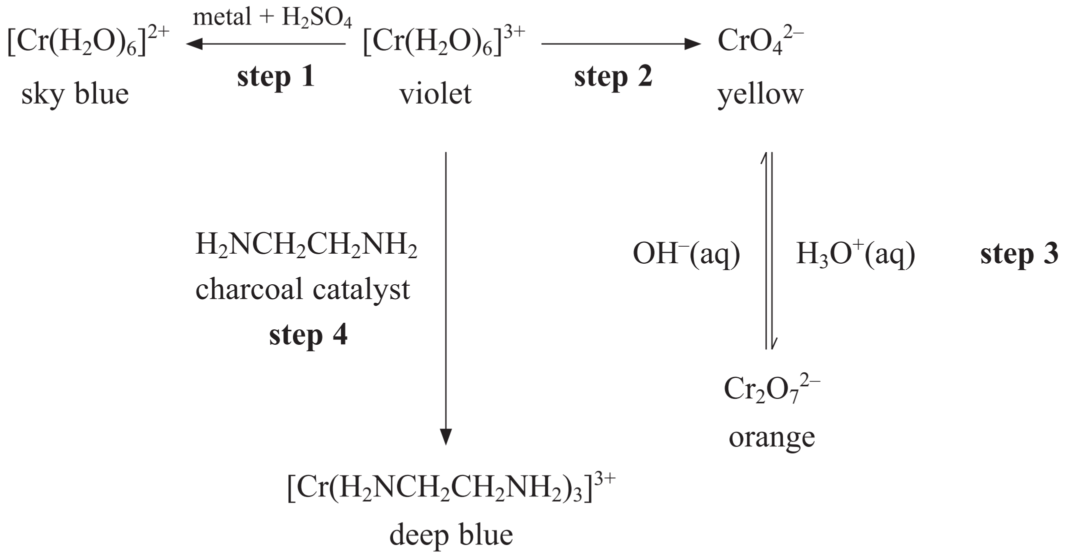
Complete the electronic configurations in *s,p,d* notation for vanadium and chromium.

(1)

Vanadium: [Ar] ....

Chromium: [Ar] ....

(b) Some interconversions found in the chemistry of chromium are shown below. Use this information to answer the questions that follow.



(i) State **two** typical properties of transition metals, other than the formation of coloured ions, which are shown in the diagram above.

(2)

....

....

....

(ii) Use $E^\ominus$ values from your data booklet to suggest a metal that could be used for **step 1**. Justify your answer by calculating $E^\ominus$ for your cell.

(2)

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....

....

....

(iii) Explain, using oxidation numbers, whether or not the conversion in **step 3** is a redox reaction.

(2)

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....

....

....

(iv) The organic compound $H_2NCH_2CH_2NH_2$ that is used in **step 4** is 1,2-diaminoethane, often called ethylenediamine.
It is a **bidentate ligand**. Explain the meaning of this term.

(1)

....

....

(v) Explain, in terms of its structure, how $H_2NCH_2CH_2NH_2$ can act as a bidentate ligand whereas H_2NNH_2 cannot.

(2)

....

....

(c) The half-equations relating the interconversion of the species $Cr^{2+}(aq)$, $Cr^{3+}(aq)$ and $Cr_2O_7^{2-}(aq)$ are given below.

Half-equation I: $Cr^{3+}(aq) + e^- \rightarrow Cr^{2+}(aq)$

Half-equation II: $Cr_2O_7^{2-}(aq) + 6e^- + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

(i) Use your data booklet to find $E^\ominus$ for each of the above half-equations.

(1)

Half-equation I .... Volts

Half-equation II .... Volts

*(ii) Write the overall equation for the disproportionation of Cr^{3+} into Cr^{2+} and $Cr_2O_7^{2-}$.

Use the $E^\ominus$ values you have obtained in (c)(i) to show whether or not this disproportionation is feasible under standard conditions.

(4)

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(Total for Question 21 = 15 marks)

22 (a) Tiglic acid is a compound that is used as a defensive agent by some beetles.

(i) Tiglic acid contains, by mass, 60% carbon, 8% hydrogen, with the remainder being oxygen. Show that these data are consistent with the formula $C_5H_8O_2$.

(1)

(ii) Tiglic acid contains a carbon-carbon double bond and a carboxylic acid group.

Suggest **one** test for each of these groups in tiglic acid. State what you would do and what you would see as a positive result for the tests.

(4)

Test for C═C ....

....

....

....

Test for —COOH ....

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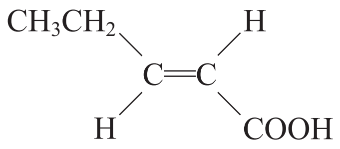
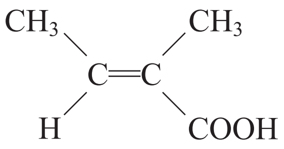
....

....

(b) It is suggested that the structure of tiglic acid is either that of **A** or **B**.



A



B

(i) State, with a reason, whether **B** is the *E*- or *Z*- isomer.

(2)

....

....

....

(ii) The mass spectrum of tiglic acid shows two prominent peaks at mass/charge ratios 45 and 55. Write the formulae of the fragments giving rise to each of these peaks.

(2)

45 ....

55 ....

(iii) Does this data from the mass spectrum **alone** enable you to decide which of **A** or **B** is the structure of tiglic acid? Explain your answer.

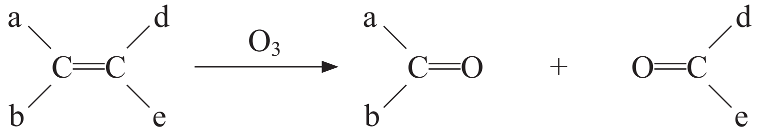
(1)

....

....

....

(c) The position of a C═C double bond in a molecule can be determined by ozonolysis. The compound is reacted with ozone and then dilute acid, two carbonyl compounds being produced as shown below.



Ozonolysis of tiglic acid gives two carbonyl compounds, **C** and **D**.

Compound **C** gives a silver mirror with Tollens' reagent and gives iodoform with iodine in alkali.

Compound **D** does **not** give a silver mirror with Tollens' reagent, but does give iodoform with iodine in alkali.

*(i) From the results of the experiments, deduce the functional groups present in **C** and **D**. By considering the two possible structures for tiglic acid, give the structural formulae of **C** and **D**.

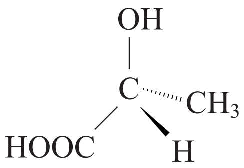
From the structures you have drawn, state which of the structures **A** or **B** could represent tiglic acid.

(6)

(ii) Explain whether or not these tests show definitely that your answer to (c)(i) represents tiglic acid.

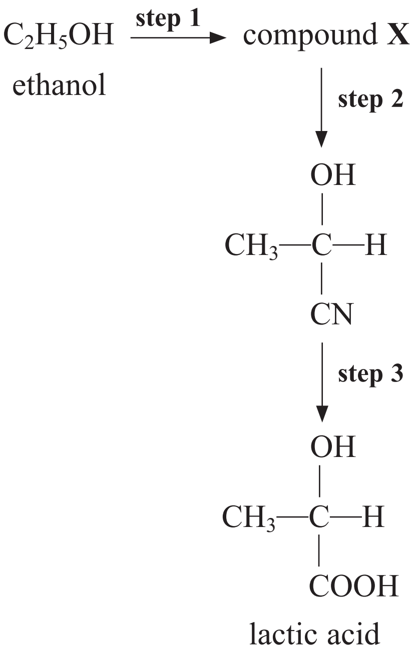
(1)

(d) Lactic acid is a chiral molecule that is found in sweat as the (–) isomer only. Its structural formula is



(–) - lactic acid

(i) Lactic acid can be made from ethanol in three steps.



Give the structural formula of the intermediate **X** and the reagents and conditions required for **steps 1** and **2**.

(4)

Step 1 ....

....

Step 2 ....

....

(ii) Classify the type and mechanism of the reaction that occurs in **step 2**.

(1)

....

*(iii) By considering the stereochemistry of the mechanism in **step 2**, explain why this synthesis would **not** give a single optical isomer of lactic acid.

(2)

....

....

....

....

(iv) Suggest why synthetic pathways for the manufacture of pharmaceuticals may require reactions that are highly stereospecific.

(1)

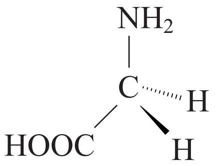
....

....

....

(Total for Question 22 = 25 marks)

23 Proteins are polymers of α-amino acids, the simplest of which is glycine.



(a) (i) Draw the **structural** formula for the zwitterion of glycine in the solid state.

(1)

(ii) Explain, on the basis of your answer to (a)(i), why glycine has a relatively high melting temperature for such a small molecule.

(2)

....

....

....

....

(iii) Draw the structure of the protein chain that would be formed if glycine alone were to be polymerized. Show part of the chain containing two glycine residues.

(2)

*(b) A solution of hydrolysed protein contains the individual amino acids that make up the protein. Briefly state how you would use chromatography, together with known samples of amino acids, to show which amino acids the protein contained. Do **not** give detailed experimental instructions.

(5)

(Total for Question 23 = 10 marks)

TOTAL FOR SECTION B = 50 MARKS

SECTION C

Answer ALL the questions. Write your answers in the spaces provided.

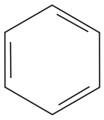
24 Read the passage below carefully and answer the questions which follow.

Molecular structure and colour chemistry

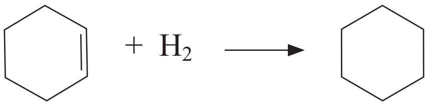
The sight of tubes of paint or of coloured pencils in an artists' supply shop is something that most people enjoy; we love colour.

The ability to synthesise brightly-coloured compounds coincides with the rapid growth of the organic chemicals industry. Synthetic organic dyes started to appear in the mid-19th century when William Perkin synthesised Mauve in 1856 at the age of 18. He was trying to synthesise quinine even though he did not know the structure of the molecule.

In the 19th century many chemists did not believe that molecules existed. The work of Butlerov, Couper, and notably Kekulé showed that molecules not only exist but have specific structures. In 1865 Kekulé suggested a ring structure for the aromatic compound benzene which he represented as



Kekulé knew that benzene does not react with bromine water. Later work showed that the enthalpy change of hydrogenation of the compound is $-205\ \text{kJ mol}^{-1}$, rather than the value of $-360\ \text{kJ mol}^{-1}$ that would be expected if the structure was exactly as shown above, given that the enthalpy change of hydrogenation for cyclohexene to cyclohexane



is $-120\ \text{kJ mol}^{-1}$.

When Greiss in 1856 discovered diazotisation and the azo dyes, he used a reaction characteristic of aromatic amines. Witt, in 1876, found the functional groups in the dye molecule that make it water-soluble and enable it to attach to the cloth fibres. Graebe, Liebermann and Perkin in 1869 patented the synthesis of alizarin, found in madder root grown in Holland and Von Baeyer synthesised indigo in 1880, until then grown in India. Synthetic dyes were made available in large quantities and were cheaper than the sources from plants.

Now the organic chemical industry produces a vast range of pigments and dyestuffs for use in paints and for fabrics, inks and other materials, making our world the most colourful that it has ever been.

(a) (i) Explain why Perkin's attempted synthesis of quinine was almost certain to fail.

(1)

(ii) Suggest the effect that the growth of the organic chemicals industry in the late 19th century had on Holland and India in particular.

(2)

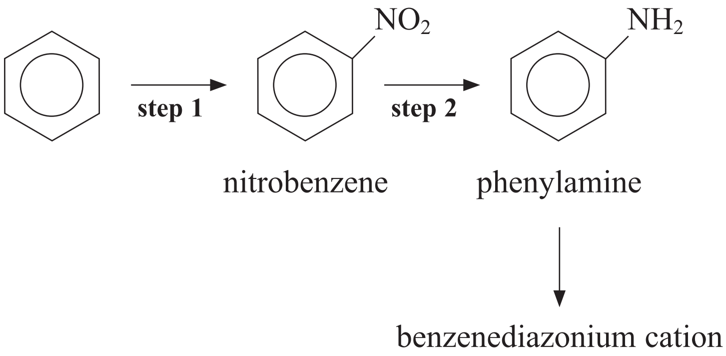
(b) (i) What observation did Kekulé make to show that benzene does **not** react with bromine water? Explain the significance of this with reference to his representation of the molecule.

(2)

(ii) Explain, in terms of the bonding in the benzene ring, why the enthalpy of hydrogenation is less exothermic than would be expected from a molecule with three double bonds.

(3)

(c) The first steps in the preparation of an azo dye from benzene are shown below.



Give the mechanism for the reaction in **step 1**, including the equation for the formation of the electrophile.

(4)

Equation for formation of electrophile

Mechanism

(d) (i) Phenylamine is converted into the benzenediazonium cation using sodium nitrite and hydrochloric acid at a temperature between 0 °C and 10 °C.

Explain why the temperature must **not** be lower or higher than these limits if a good yield is to be obtained.

(2)

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....

....

....

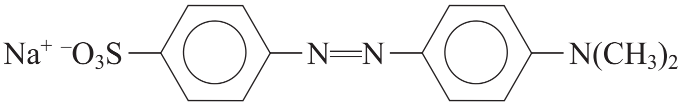
(ii) Draw the structural formula of the benzenediazonium cation showing all the bonds and the charge.

(1)

(iii) Suggest how you could convert a sample of the benzenediazonium cation into an azo dye. Give the name of the other compound you would use and the skeletal formula of the azo dye you would obtain.

(3)

(e) The structural formula of methyl orange is given below.



Suggest the main features of methyl orange which make it water-soluble, giving your reasons.

(2)

(Total for Question 24 = 20 marks)

TOTAL FOR SECTION C = 20 MARKS
TOTAL FOR PAPER = 90 MARKS

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The Periodic Table of Elements

Key

relative atomic mass
atomic symbol
name
atomic (proton) number

1	2											3	4	5	6	7	0 (8)
							1.0 **H** hydrogen 1										*(18)* 4.0 **He** helium 2
(1)	*(2)*											*(13)*	*(14)*	*(15)*	*(16)*	*(17)*	
6.9 **Li** lithium 3	9.0 **Be** beryllium 4											10.8 **B** boron 5	12.0 **C** carbon 6	14.0 **N** nitrogen 7	16.0 **O** oxygen 8	19.0 **F** fluorine 9	20.2 **Ne** neon 10
23.0 **Na** sodium 11	24.3 **Mg** magnesium 12	*(3)*	*(4)*	*(5)*	*(6)*	*(7)*	*(8)*	*(9)*	*(10)*	*(11)*	*(12)*	27.0 **Al** aluminium 13	28.1 **Si** silicon 14	31.0 **P** phosphorus 15	32.1 **S** sulfur 16	35.5 **Cl** chlorine 17	39.9 **Ar** argon 18
39.1 **K** potassium 19	40.1 **Ca** calcium 20	45.0 **Sc** scandium 21	47.9 **Ti** titanium 22	50.9 **V** vanadium 23	52.0 **Cr** chromium 24	54.9 **Mn** manganese 25	55.8 **Fe** iron 26	58.9 **Co** cobalt 27	58.7 **Ni** nickel 28	63.5 **Cu** copper 29	65.4 **Zn** zinc 30	69.7 **Ga** gallium 31	72.6 **Ge** germanium 32	74.9 **As** arsenic 33	79.0 **Se** selenium 34	79.9 **Br** bromine 35	83.8 **Kr** krypton 36
85.5 **Rb** rubidium 37	87.6 **Sr** strontium 38	88.9 **Y** yttrium 39	91.2 **Zr** zirconium 40	92.9 **Nb** niobium 41	95.9 **Mo** molybdenum 42	[98] **Tc** technetium 43	101.1 **Ru** ruthenium 44	102.9 **Rh** rhodium 45	106.4 **Pd** palladium 46	107.9 **Ag** silver 47	112.4 **Cd** cadmium 48	114.8 **In** indium 49	118.7 **Sn** tin 50	121.8 **Sb** antimony 51	127.6 **Te** tellurium 52	126.9 **I** iodine 53	131.3 **Xe** xenon 54
132.9 **Cs** caesium 55	137.3 **Ba** barium 56	138.9 **La*** lanthanum 57	178.5 **Hf** hafnium 72	180.9 **Ta** tantalum 73	183.8 **W** tungsten 74	186.2 **Re** rhenium 75	190.2 **Os** osmium 76	192.2 **Ir** iridium 77	195.1 **Pt** platinum 78	197.0 **Au** gold 79	200.6 **Hg** mercury 80	204.4 **Tl** thallium 81	207.2 **Pb** lead 82	209.0 **Bi** bismuth 83	[209] **Po** polonium 84	[210] **At** astatine 85	[222] **Rn** radon 86
[223] **Fr** francium 87	[226] **Ra** radium 88	[227] **Ac*** actinium 89	[261] **Rf** rutherfordium 104	[262] **Db** dubnium 105	[266] **Sg** seaborgium 106	[264] **Bh** bohrium 107	[277] **Hs** hassium 108	[268] **Mt** meitnerium 109	[271] **Ds** darmstadtium 110	[272] **Rg** roentgenium 111							

Elements with atomic numbers 112-116 have been reported but not fully authenticated

* Lanthanide series	140 **Ce** cerium 58	141 **Pr** praseodymium 59	144 **Nd** neodymium 60	[147] **Pm** promethium 61	150 **Sm** samarium 62	152 **Eu** europium 63	157 **Gd** gadolinium 64	159 **Tb** terbium 65	163 **Dy** dysprosium 66	165 **Ho** holmium 67	167 **Er** erbium 68	169 **Tm** thulium 69	173 **Yb** ytterbium 70	175 **Lu** lutetium 71
* Actinide series	232 **Th** thorium 90	[231] **Pa** protactinium 91	238 **U** uranium 92	[237] **Np** neptunium 93	[242] **Pu** plutonium 94	[243] **Am** americium 95	[247] **Cm** curium 96	[245] **Bk** berkelium 97	[251] **Cf** californium 98	[254] **Es** einsteinium 99	[253] **Fm** fermium 100	[256] **Md** mendelevium 101	[254] **No** nobelium 102	[257] **Lr** lawrencium 103