Write your name here

Surname	Other names

Pearson Edexcel
International Advanced Level

Centre Number

Candidate Number

Chemistry

Advanced

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

Tuesday 21 January 2014 – Afternoon
Time: 1 hour 40 minutes

Paper Reference
WCH05/01

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

6/6/6/6/2/

P 4 2 9 9 3 A 0 1 2 8

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 In which of the following compounds does iron have the highest oxidation number?

☒ **A** Fe_3O_4

☒ **B** K_2FeO_4

☒ **C** $Na_4Fe(CN)_6$

☒ **D** $Na_3Fe(CN)_6$

(Total for Question 1 = 1 mark)

2 Which of the following is **not** a redox reaction?

☒ **A** $3CrCl_2 + Na_2CrO_4 + 8HCl \rightarrow 4CrCl_3 + 4H_2O + 2NaCl$

☒ **B** $2MnO_4^{2-} + C_8H_7O_3^- + 2OH^- \rightarrow 2MnO_4^{3-} + C_8H_5O_3^- + 2H_2O$

☒ **C** $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$

☒ **D** $MnO_4^- + 3H_2SO_4 \rightarrow MnO_3^+ + H_3O^+ + 3HSO_4^-$

(Total for Question 2 = 1 mark)

3 The standard reduction potentials of two systems are given below.

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E^{\ominus} = +0.34\ V$$

$$Ag^+(aq) + e^- \rightleftharpoons Ag(s) \qquad E^{\ominus} = +0.80\ V$$

What is $E^{\ominus}_{cell}$ for the reaction between copper and silver nitrate?

$$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

☒ **A** −1.26 V

☒ **B** −0.46 V

☒ **C** +0.46 V

☒ **D** +1.26 V

(Total for Question 3 = 1 mark)

4 A cell is set up with two metal-metal ion half cells and the digital voltmeter reads zero. Given that all the components of the cell have been included and are working properly, what is the most likely explanation for the zero reading?

☒ **A** The cell has been set up the wrong way round.

☒ **B** The entropy change, $\Delta S_{system} = 0$.

☒ **C** The activation energy for the reaction is very high.

☒ **D** The reaction system is at equilibrium.

(Total for Question 4 = 1 mark)

5 What is the electronic configuration of the Fe^{3+} ion?

		3d					4s
☒ **A**	[Ar]	↑	↑	↑	↑	↑	
☒ **B**	[Ar]	↑↓	↑↓	↑			
☒ **C**	[Ar]	↑	↑	↑	↑		↑
☒ **D**	[Ar]	↑	↑	↑			↑↓

(Total for Question 5 = 1 mark)

6 Ammonia gas is formed in the combustion of biomass fuels and is a significant pollutant when it is released directly into the atmosphere. One method of removing this ammonia involves its oxidation using a titanium(IV) oxide catalyst.

The **best** explanation for the use of titanium(IV) oxide is that the titanium

☒ **A** contains many active sites on which the reaction can occur.

☒ **B** is readily oxidized to a higher oxidation state which can then be reduced back to oxidation state +4.

☒ **C** is readily reduced to a lower oxidation state which can then be oxidized back to oxidation state +4.

☒ **D** has partially filled d orbitals in its +4 oxidation state.

(Total for Question 6 = 1 mark)

7 A transition metal ion, M, forms a complex with a bidentate ligand, B. The formula of the complex is MB_3 so the shape of the complex is most likely to be

☒ **A** trigonal planar.

☒ **B** pyramidal.

☒ **C** trigonal bipyramidal.

☒ **D** octahedral.

(Total for Question 7 = 1 mark)

8 Which of the following lists **all** the types of bond that are present in a crystalline sample of the compound tetraamminecopper(II) sulfate?

☒ **A** Ionic, covalent and dative covalent

☒ **B** Ionic and dative covalent

☒ **C** Ionic and covalent

☒ **D** Covalent and dative covalent

(Total for Question 8 = 1 mark)

9 A compound, **X**, is dissolved in water. Sodium hydroxide solution and dilute aqueous ammonia were added to different samples of this solution of **X**. In both, a precipitate formed which dissolved in excess reagent. Compound **X** could be

☒ **A** copper(II) sulfate.

☒ **B** iron(II) sulfate.

☒ **C** manganese(II) sulfate.

☒ **D** zinc(II) sulfate.

(Total for Question 9 = 1 mark)

10 The carbon-carbon bonds in benzene are all the same length. The best evidence for this comes from

☒ **A** high resolution proton nmr spectroscopy.

☒ **B** X-ray diffraction.

☒ **C** mass spectrometry.

☒ **D** bomb calorimetry.

(Total for Question 10 = 1 mark)

11 Benzene reacts very slowly with chlorine but the reaction speeds up when finely divided iron is added. This is because

☒ **A** the chlorine molecule donates an electron pair to the iron producing an electrophile.

☒ **B** the iron reacts with chlorine to form iron(III) chloride which then acts as an electrophile in its reaction with benzene.

☒ **C** the iron reacts with chlorine to form iron(III) chloride which then acts as an electron pair acceptor.

☒ **D** iron is a transition metal and acts as a heterogeneous catalyst in the reaction.

(Total for Question 11 = 1 mark)

12 It is calculated that, as a result of delocalization, benzene has a stabilization energy of 150 kJ mol^{-1}. This means that

☒ **A** the enthalpy change for the conversion of benzene to cyclohexa-1,3,5-triene would be +150 kJ mol^{-1}.

☒ **B** the enthalpy change for the conversion of cyclohexa-1,3,5-triene to benzene would be +150 kJ mol^{-1}.

☒ **C** the enthalpy change for the conversion of cyclohexane to benzene is +150 kJ mol^{-1}.

☒ **D** the enthalpy change for the conversion of benzene to cyclohexane is +150 kJ mol^{-1}.

(Total for Question 12 = 1 mark)

13 When a gas jar containing methylamine is opened near an open bottle of concentrated hydrochloric acid, white smoke is seen. The chemical formula of the white smoke is

☒ **A** CH_3NH_4Cl

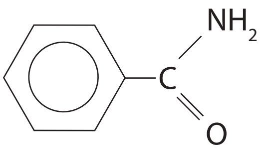
☒ **B** CH_3NH_3Cl

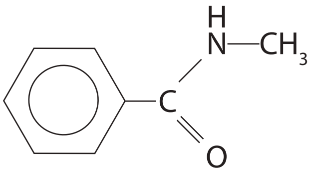
☒ **C** CH_3NH_2Cl

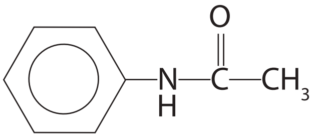
☒ **D** NH_4Cl

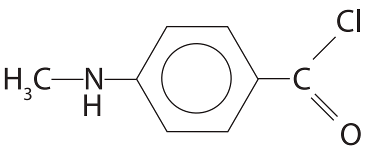
(Total for Question 13 = 1 mark)

14 When benzoyl chloride, C_6H_5COCl, is added to methylamine at room temperature, the main organic product of the reaction is

☒ **A** 

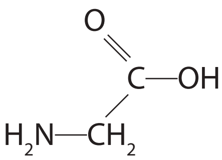
☒ **B** 

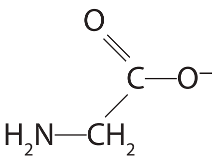
☒ **C** 

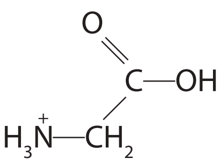
☒ **D** 

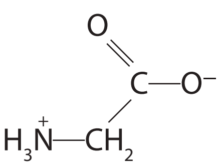
(Total for Question 14 = 1 mark)

15 In an aqueous solution with a pH of 3, the amino acid glycine exists mainly as

☒ **A** 

☒ **B** 

☒ **C** 

☒ **D** 

(Total for Question 15 = 1 mark)

16 What is the total number of peaks due to singly charged ions in the **complete** mass spectrum of chlorine, Cl_2?

☒ **A** Two

☒ **B** Three

☒ **C** Four

☒ **D** Five

(Total for Question 16 = 1 mark)

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17 The low resolution proton nmr spectrum of a compound contains two peaks. Which of the following compounds could **not** give this spectrum?

☒ **A** Propane

☒ **B** Butane

☒ **C** 2-methylpropane

☒ **D** 2,2-dimethylpropane

(Total for Question 17 = 1 mark)

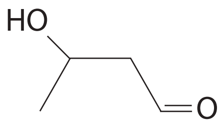
Use this space for any rough working. Anything you write in this space will gain no credit.

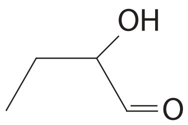
18 A compound, **P**, has the following properties:

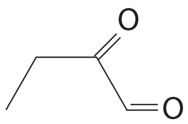
P forms a red precipitate when heated with Fehling's or Benedict's solution.

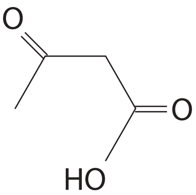
P forms a pale yellow precipitate when warmed with iodine dissolved in aqueous sodium hydroxide.

P could be

☒ **A** 

☒ **B** 

☒ **C** 

☒ **D** 

(Total for Question 18 = 1 mark)

19 10 cm^3 of a gaseous hydrocarbon was mixed with excess oxygen and ignited. The gas volumes were measured at room temperature and pressure before and after combustion and it was found that the total gas volume had contracted by 20 cm^3. Given that combustion was complete, the formula of the hydrocarbon was

☒ **A** C_4H_4

☒ **B** C_4H_6

☒ **C** C_4H_8

☒ **D** C_4H_{10}

(Total for Question 19 = 1 mark)

20 Steam distillation may be used in the purification of some compounds. The use of this technique depends on the compound

☒ **A** forming a single layer with water.

☒ **B** forming two layers with water.

☒ **C** having a lower boiling temperature than water.

☒ **D** being flammable.

(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 Potassium manganate(VII) can be used in redox titrations to determine the concentration of iron(II) ions and ethanedioate ions in aqueous solution. Aqueous solutions of potassium manganate(VII) are unstable, so it is often standardized using solutions of iron(II) ammonium sulfate, freshly prepared from Mohr's salt, $Fe(NH_4)_2(SO_4)_2.6H_2O$.

(a) Use the relevant ionic half-equations, and standard reduction potentials on page 17 of the Data Booklet, to answer the following questions. State symbols are not required in the equations.

(i) Write the ionic half-equation for the reduction of manganate(VII) ions in acid solution.

(1)

(ii) Write the ionic half-equation for the oxidation of water to form oxygen and hydrogen ions.

(1)

(iii) Combine your answers to (a)(i) and (a)(ii) to derive an equation to show the production of oxygen in acidified manganate(VII) solution.

(1)

(iv) Calculate $E^{\ominus}_{cell}$ for the reaction in (a)(iii) and hence explain why aqueous solutions of potassium manganate(VII) are unstable.

(2)

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(b) 250 cm^3 of a solution containing 10.00 g of Mohr's salt was prepared. Separate 25.0 cm^3 samples of this solution were pipetted into conical flasks, excess sulfuric acid added and then each mixture was titrated against potassium manganate(VII) solution.

The mean titre was 25.85 cm^3.

*(i) Describe in outline how you would prepare the 250 cm^3 of Mohr's salt solution, given 10.00 g of the solid.

(4)

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(ii) State what you would see at the end-point of the titration.

(1)

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(iii) Write the ionic equation showing that 1 mol of manganate(VII) ions reacts with 5 mol of iron(II) ions in acid conditions. State symbols are not required.

(1)

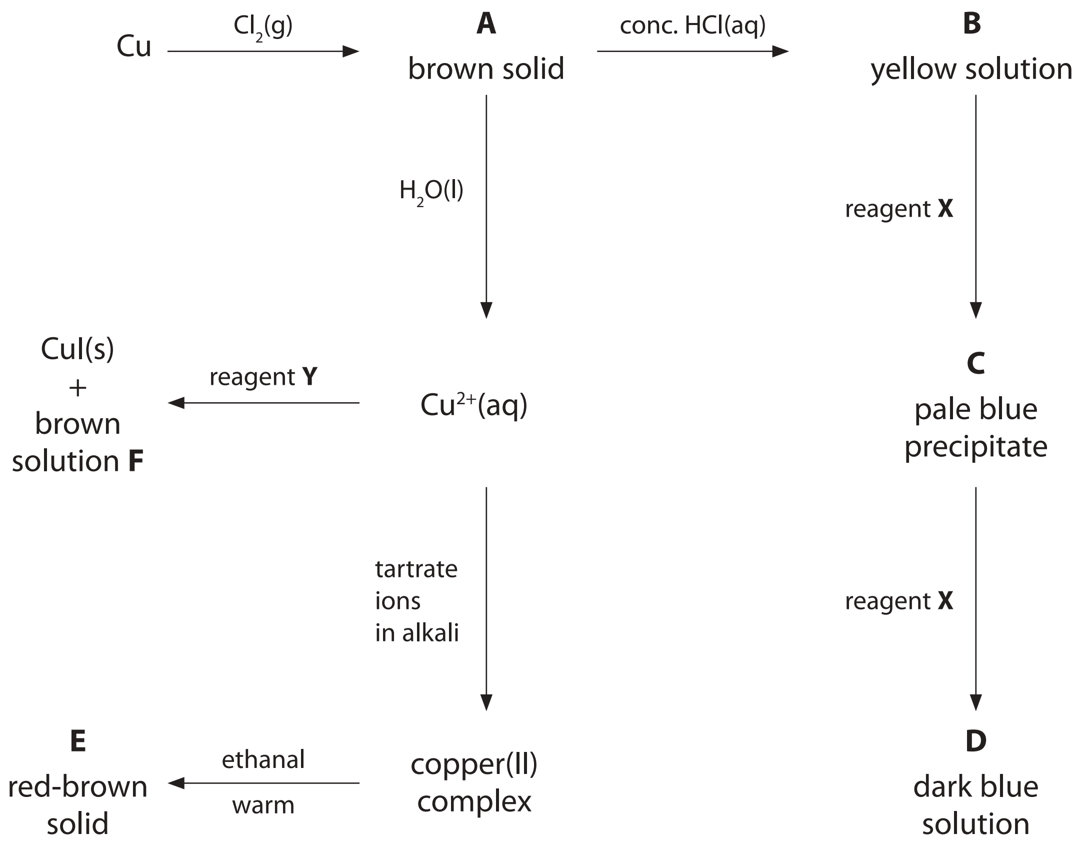
(iv) The concentration of the potassium manganate(VII) solution was stated to be 0.0200 mol dm^{-3}. Calculate the percentage of the potassium manganate(VII) that had reacted between its preparation and the titration.

The molar mass of Mohr's salt is 392 g mol^{-1}.

(4)

(Total for Question 21 = 15 marks)

22 The scheme below summarises some reactions of copper and its compounds.



(a) (i) Identify the copper containing species **A** to **E** either by name, including the oxidation number, or by formula. Also, identify the brown solution, **F**.

(6)

A ....

B ....

C ....

D ....

E ....

F ....

(ii) Identify the reagents **X** and **Y**.

(2)

X ....

Y ....

(iii) Identify the **organic** product of the reaction between the copper(II) complex and ethanal. Hence explain the role of ethanal in the reaction.

(2)

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(iv) The reaction between $Cu^{2+}(aq)$ and reagent **Y** forms CuI(s) and a brown solution, **F**. This reaction is the first stage in a method for the determination of the concentration of $Cu^{2+}(aq)$.

Outline briefly how this method is used. Practical details are **not** required.

(1)

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*(b) (i) Explain why **B** is coloured.

(4)

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(ii) Explain why **B** and **D** have different colours.

(2)

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(c) Aqueous copper(I) ions undergo a disproportionation reaction.

(i) Write the ionic equation for this reaction. Include state symbols in your answer.

(1)

(ii) Explain, stating the relevant oxidation numbers, why the reaction in (c)(i) is classified as a disproportionation.

(1)

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(iii) Use the standard reduction potentials on page 17 of the Data Booklet to calculate $E^{\ominus}_{cell}$ for this disproportionation. Hence show that this reaction is thermodynamically feasible.

(2)

(Total for Question 22 = 21 marks)

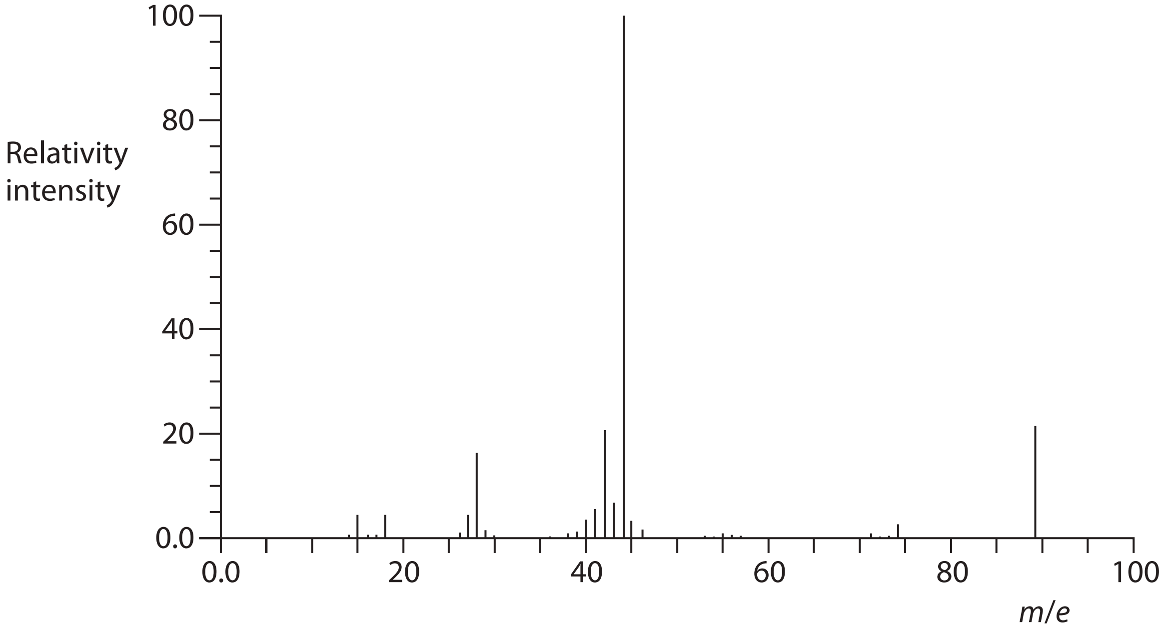
23 Compound **P** is a white crystalline solid with the following percentage composition by mass.

Element	**% composition by mass**
carbon	40.44
hydrogen	7.87
oxygen	35.96
nitrogen	15.73

(a) Calculate the empirical formula of **P**. You **must** show your working.

(3)

(b) The mass spectrum of **P** is shown below.



(i) Label the molecular ion on the mass spectrum using the symbol M^+.

(1)

(ii) Deduce the molecular formula of **P**.

(1)

(c) **P** was dissolved in sodium carbonate solution and, on heating, a colourless gas, which turned lime water cloudy, was very slowly evolved. When an aqueous solution of **P** was mixed with an aqueous solution of copper(II) sulfate, the blue colour of the copper(II) sulfate solution darkened.

(i) Use the results of these two experiments to deduce the functional groups that are present in **P**. Explain your answers.

(4)

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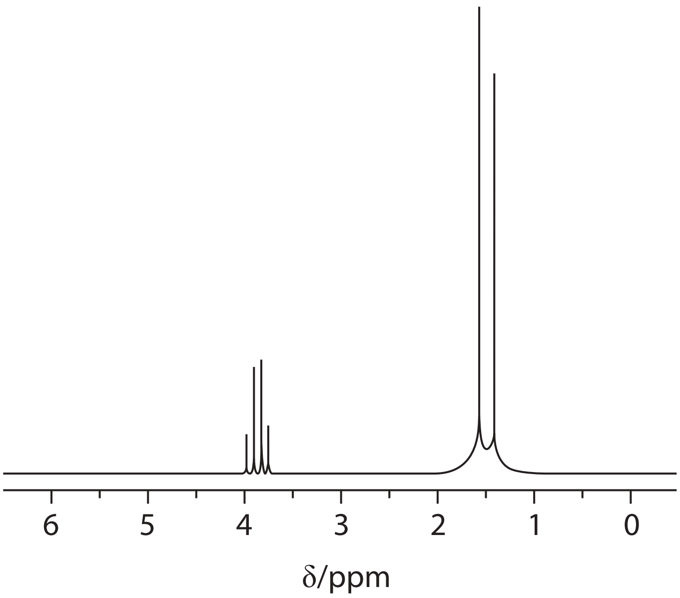
(ii) There are several compounds which have the formula you have deduced in (b)(ii) and contain the two functional groups you have identified in (c)(i).

Draw the structural or displayed formulae of **two** of these compounds.

(2)

(iii) The nuclear magnetic resonance spectrum of compound **P** is shown below.



This part of the spectrum only shows the peaks due to the hydrogen atoms which are attached directly to carbon atoms.

Use this spectrum to deduce the structure of **P**. Justify your answer.

(2)

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(d) Explain why **P** is a solid at room temperature and pressure.

(1)

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(Total for Question 23 = 14 marks)

TOTAL FOR SECTION B = 50 MARKS

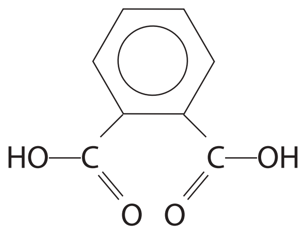
SECTION C

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

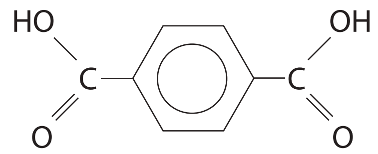
24

Phthalates

The benzene dicarboxylic acids and their esters are important industrial compounds. The structures of two of these acids are shown below.

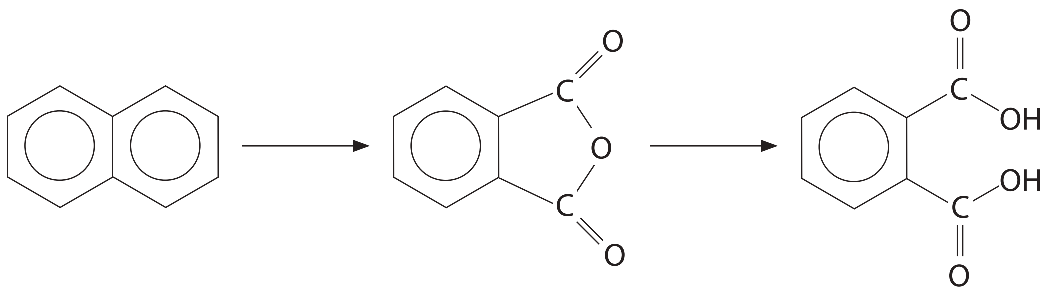


benzene-1,2-dicarboxylic acid



benzene-1,4-dicarboxylic acid

Benzene-1,2-dicarboxylic acid is manufactured by the catalytic oxidation of naphthalene to phthalic anhydride which is then hydrolysed. This reaction sequence is summarised below.



naphthalene   phthalic anhydride   benzene-1,2-dicarboxylic acid

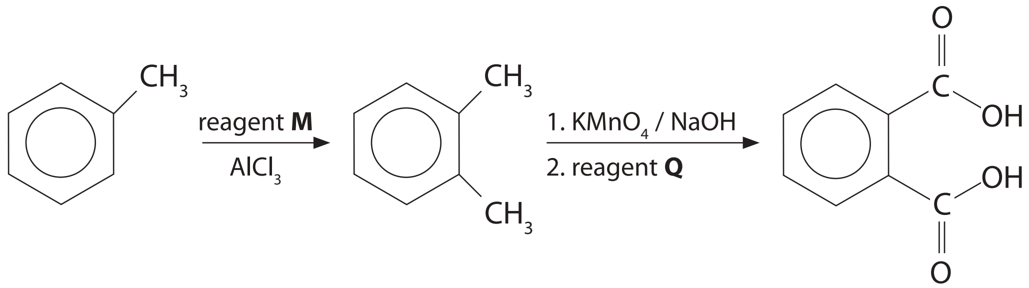
The use of naphthalene as a source of these compounds gave rise to the common names, phthalic acid for benzene-1,2-dicarboxylic acid and terephthalic acid for benzene-1,4-dicarboxylic acid.

The alkyl esters derived from benzene-1,2-dicarboxylic acid are known as phthalates.

Phthalates are used as plasticisers to increase the flexibility of many common plastics. However, some phthalates are known to be endocrine disruptors and recent studies have raised concerns about their role in the fall in human fertility rates. Because phthalates are used in making plastic drinks bottles and leach readily out of the structure, they are easily ingested.

The polyester *Terylene* is derived from benzene-1,4-dicarboxylic acid and ethane-1,2-diol.

(a) One method of preparing benzene dicarboxylic acids in the laboratory is from methylbenzene in the sequence shown below.



(i) Identify reagent **M**, by name or formula.

(1)

....

(ii) Write the equation for the reaction between **M** and $AlCl_3$ to form an electrophile.

(1)

(iii) Give the mechanism for the reaction of methylbenzene with your electrophile in (a)(ii).

(3)

(iv) Suggest why methylbenzene reacts faster than benzene in this type of reaction.

(2)

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(v) In the second step of the synthesis, the potassium manganate(VII) is an oxidizing agent.

Suggest the identity of reagent **Q**, which is added when oxidation is complete.

(1)

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(b) In the oxidation of naphthalene to phthalic anhydride, the catalyst is vanadium(V) oxide. With fresh catalyst, the reaction occurs at 360 °C but, over time, the temperature must be slowly increased as the catalyst activity decreases.

(i) State the property which gives transition metal compounds, such as vanadium(V) oxide, catalytic properties.

(1)

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(ii) Suggest why the catalyst activity decreases over time.

(1)

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....

(c) The simplest phthalate of benzene-1,2-dicarboxylic acid is its dimethyl ester (1,2-dimethyl benzene-1,2-dicarboxylate).

(i) Draw the structure of this phthalate.

(1)

(ii) Suggest and explain what can be deduced about the interactions between the phthalate and the plastic from the fact that phthalates are readily leached from plastic bottles.

(2)

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*(iii) Suggest how a plasticiser works.

(2)

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(d) One way of making *Terylene* is by converting benzene-1,4-dicarboxylic acid into the di-acyl chloride and then reacting it with ethane-1,2-diol.

(i) Suggest a reagent that could be used to convert benzene-1,4-dicarboxylic acid into the di-acyl chloride.

(1)

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(ii) Suggest an advantage of using the di-acyl chloride rather than the dicarboxylic acid to make the polyester.

(1)

....

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....

(iii) Draw the structure of the polyester, *Terylene*, showing two repeat units.

(2)

(iv) In practice, the manufacture of *Terylene* involves a process called ester exchange in which ethane-1,2-diol reacts with the dimethyl ester of benzene-1,4-dicarboxylic acid.

What would be the by-product of this reaction?

(1)

....

....

(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 (1)	2 (2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	3 (13)	4 (14)	5 (15)	6 (16)	7 (17)	0 (8) (18)
1.0 **H** hydrogen 1																	4.0 **He** helium 2
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											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