

Write your name here

Surname

Other names

Centre Number

Candidate Number

Edexcel GCE

Chemistry

Advanced

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

Wednesday 19 June 2013 – Morning

Time: 1 hour 40 minutes

Paper Reference

6CH05/01R

You must have: Data Booklet

Total Marks

Candidates may use a calculator.

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 ►

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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 nitric(V) acid, HNO_3 , the oxidation number of the nitrogen is +5. This means that the **nitrogen** in nitric acid
- A has five electrons in its outer shell.
 - B is an ion with a charge of +5.
 - C would have a charge of +5 if its bonding electrons were transferred completely.
 - D forms five covalent bonds in total.

(Total for Question 1 = 1 mark)

- 2 What are the components of the half-cell required to measure the standard reduction potential of the following system?



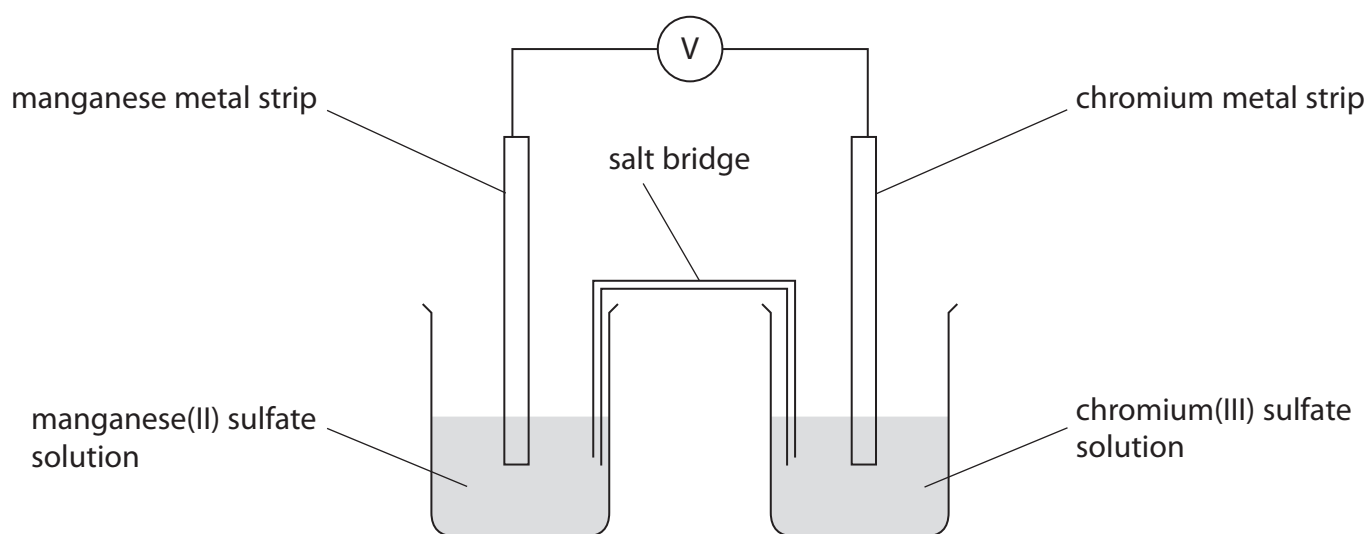
	Ion(s) in the solution	Metal electrode
<input type="checkbox"/> A	Fe^{2+}	iron
<input type="checkbox"/> B	Fe^{3+}	iron
<input type="checkbox"/> C	Fe^{2+} and Fe^{3+}	iron
<input type="checkbox"/> D	Fe^{2+} and Fe^{3+}	platinum

(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 following cell is set up:

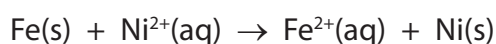


The standard electrode potential of the chromium(III)/chromium half cell is -0.74 V and that of the manganese(II)/manganese half cell is -1.19 V . Thus the emf of the cell, as shown in the diagram, under standard conditions is

- A $+1.93\text{ V}$
- B $+0.45\text{ V}$
- C -0.45 V
- D -1.93 V

(Total for Question 3 = 1 mark)

4 The equation for the reaction of iron and nickel(II) ions in aqueous solution is



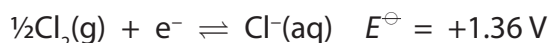
Under standard conditions the value of the equilibrium constant, K_c , for this reaction is greater than 1. Hence, for this reaction,

- A $\Delta S_{\text{total}}^{\ominus}$ and $E_{\text{reaction}}^{\ominus}$ are both positive.
- B $\Delta S_{\text{total}}^{\ominus}$ is positive and $E_{\text{reaction}}^{\ominus}$ is negative.
- C $\Delta S_{\text{total}}^{\ominus}$ is negative and $E_{\text{reaction}}^{\ominus}$ is positive.
- D $\Delta S_{\text{total}}^{\ominus}$ and $E_{\text{reaction}}^{\ominus}$ are both negative.

(Total for Question 4 = 1 mark)



- 5 Chlorine is prepared in the laboratory by the reaction of potassium manganate(VII) with concentrated hydrochloric acid. The ionic half-equations and their standard electrode potentials are



- (a) Concentrated hydrochloric acid is preferred to 1 mol dm⁻³ hydrochloric acid because

- A it lowers the activation energy of the reaction.
- B the reaction is thermodynamically unfavourable under standard conditions.
- C it increases the rate of reaction.
- D it increases the equilibrium constant, K_c , for the overall reaction.

- (b) From the half-equations it may be deduced that

- A 1 mol of manganate(VII) ions reacts with 5 mol of chloride ions.
- B 5 mol of manganate(VII) ions reacts with 1 mol of chloride ions.
- C 1 mol of manganate(VII) ions reacts with 2.5 mol of chlorine.
- D 2.5 mol of manganate(VII) ions reacts with 1 mol of chlorine.

(Total for Question 5 = 2 marks)

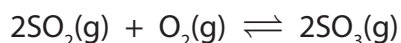
- 6 The electronic structure of the chromium(III) ion, Cr³⁺, is

- | | | 3d | | | | 4s |
|----------------------------|------|----|---|---|--|----|
| <input type="checkbox"/> A | [Ar] | ↑ | | | | ↑↓ |
| <input type="checkbox"/> B | [Ar] | ↑ | ↑ | | | ↑ |
| <input type="checkbox"/> C | [Ar] | ↑ | ↑ | ↑ | | |
| <input type="checkbox"/> D | [Ar] | ↑↓ | ↑ | | | |

(Total for Question 6 = 1 mark)



- 7 In the manufacture of sulfuric acid, sulfur dioxide is converted to sulfur trioxide using a catalyst of vanadium(V) oxide:



The electronic configuration of vanadium is $[\text{Ar}] 3\text{d}^3 4\text{s}^2$, so the mechanism for this reaction is most likely to involve a sequence in which vanadium(V) is converted to

- A vanadium(VI) by oxygen then back to vanadium(V) by sulfur dioxide.
- B vanadium(VI) by sulfur dioxide then back to vanadium(V) by oxygen.
- C vanadium(IV) by oxygen then back to vanadium(V) by sulfur dioxide.
- D vanadium(IV) by sulfur dioxide then back to vanadium(V) by oxygen.

(Total for Question 7 = 1 mark)

- 8 Titanium has the electronic structure $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^6 3\text{d}^2 4\text{s}^2$. Which of the following compounds is **unlikely** to exist?

- A K_3TiF_6
- B K_2TiF_6
- C $\text{K}_2\text{Ti}_2\text{O}_5$
- D K_2TiO_4

(Total for Question 8 = 1 mark)

- 9 All metal hydroxides dissolve in acid. When aqueous solutions of sodium hydroxide and ammonia are added separately to samples of chromium(III) hydroxide, in both cases the solid dissolves to form a green solution. How should these reactions be classified?

	sodium hydroxide	ammonia
<input type="checkbox"/> A	amphoteric	amphoteric
<input type="checkbox"/> B	amphoteric	ligand exchange
<input type="checkbox"/> C	ligand exchange	amphoteric
<input type="checkbox"/> D	ligand exchange	ligand exchange

(Total for Question 9 = 1 mark)



10 The ligands that form complex ions are either neutral, like NH_3 , or negatively charged, like CN^- . Nickel(II) ions, Ni^{2+} , form complexes with both these ligands. The bonding between Ni^{2+} and the ligands in these complexes is

	NH_3	CN^-
<input type="checkbox"/> A	dative covalent	dative covalent
<input type="checkbox"/> B	ionic	dative covalent
<input type="checkbox"/> C	dative covalent	ionic
<input type="checkbox"/> D	ionic	ionic

(Total for Question 10 = 1 mark)

11 When excess aqueous ammonia is added to a solution containing $\text{Zn}^{2+}(\text{aq})$ ions, a colourless solution is formed. This solution is colourless because

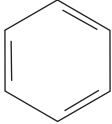
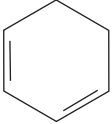
- A zinc does not form complex ions.
- B the d orbitals of Zn^{2+} in the complex formed are not split into different energy levels.
- C the energy difference between the d orbitals of Zn^{2+} in the complex formed does not correspond to the visible region of the spectrum.
- D the d orbitals of Zn^{2+} in the complex formed are full.

(Total for Question 11 = 1 mark)

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



12 Bromine reacts with benzene on heating in the presence of a catalyst and with cyclohexa-1,3-diene in the cold. The types of reaction involved are

	bromine with benzene 	bromine with cyclohexa-1,3-diene 
<input type="checkbox"/> A	addition	addition
<input type="checkbox"/> B	addition	substitution
<input type="checkbox"/> C	substitution	addition
<input type="checkbox"/> D	substitution	substitution

(Total for Question 12 = 1 mark)

13 Phenylamine, $C_6H_5NH_2$, and benzene react with bromine in a similar way, but phenylamine reacts much faster. This increased rate of reaction is most likely due to the effect that the

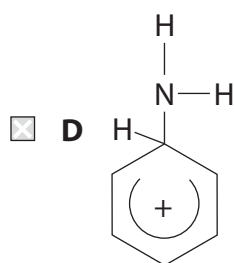
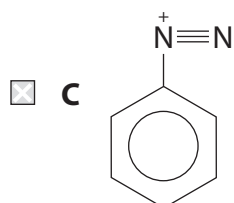
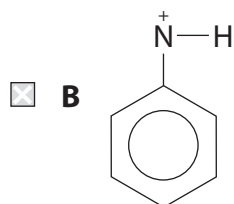
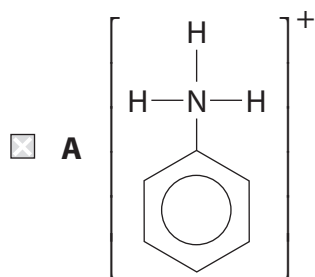
- A electronegativity of the nitrogen has on the benzene ring.
- B electronegativity of the nitrogen has on the bromine molecule.
- C lone pair of electrons of the nitrogen has on the benzene ring.
- D lone pair of electrons of the nitrogen has on the bromine molecule.

(Total for Question 13 = 1 mark)

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



14 When dilute nitric(V) acid, HNO_3 , reacts with phenylamine, the ion formed is



(Total for Question 14 = 1 mark)

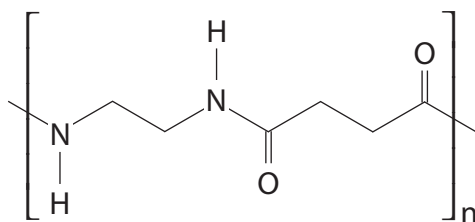
15 Methylamine, CH_3NH_2 , is **very** soluble in water. This is because it

- A forms hydrogen bonds with water.
- B forms London forces with water.
- C exists mainly as ions in aqueous solution.
- D exists as a zwitterion.

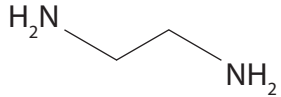
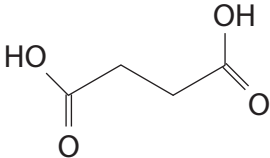
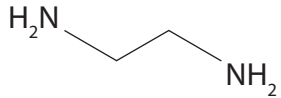
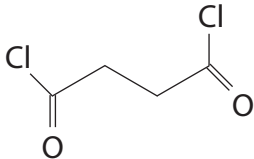
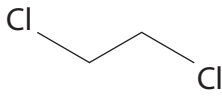
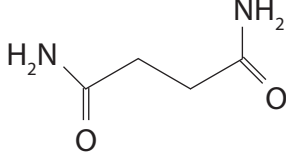
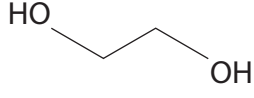
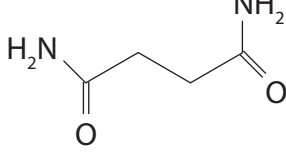
(Total for Question 15 = 1 mark)



16 The structure below shows the repeating pattern of a polymer.



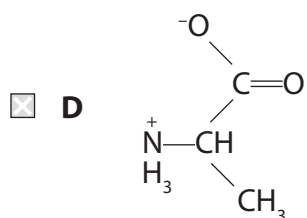
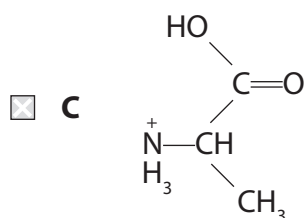
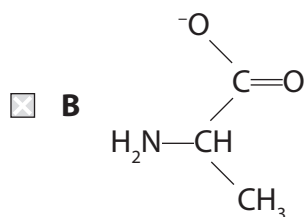
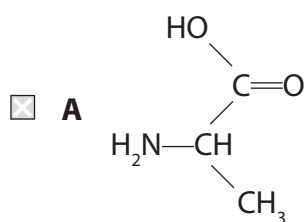
Which of the following pairs of compounds could react **rapidly** to form this polymer?

<input type="checkbox"/> A		
<input type="checkbox"/> B		
<input type="checkbox"/> C		
<input type="checkbox"/> D		

(Total for Question 16 = 1 mark)



17 Which of the following structures best represents the amino acid, alanine, in an aqueous solution with a pH of 12?



(Total for Question 17 = 1 mark)

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



18 Which of the following is true for **all** amino acids?

All amino acids

- A** exist as optical isomers.
- B** are neutral in solution.
- C** are essential to life.
- D** are crystalline solids at room temperature.

(Total for Question 18 = 1 mark)

19 Which of the following physical methods of chemical analysis is used in modern breathalysers?

- A** Infrared spectroscopy
- B** Mass spectrometry
- C** Nuclear magnetic resonance
- D** Ultraviolet spectroscopy

(Total for Question 19 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS



(iii) Identify reagent **X**

(1)

(iv) Write an **ionic** equation for the conversion of solution **C** to $\text{Na}_2\text{Cr}_2\text{O}_7$. State symbols are not required.

(1)

(b) Chromium also exists in a +2 oxidation state. Use the Data booklet to determine the feasibility of the disproportionation of chromium(III) in aqueous solution into chromium(II) and dichromate(VI).

In your answer, show both half equations and the overall equation for the proposed disproportionation. Calculate $E_{\text{cell}}^{\ominus}$ for this reaction and use this value to predict the feasibility of this reaction.

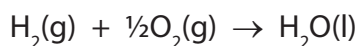
(4)

(Total for Question 20 = 11 marks)



P 4 2 9 8 5 A 0 1 3 2 8

21 Hydrogen combines rapidly with oxygen in the presence of a platinum catalyst:



The reaction is highly exothermic.

(a) Use the thermochemical data from the data booklet to obtain the enthalpy change for this reaction under standard conditions.

(1)

..... kJ mol⁻¹

(b) The same reaction occurs, also with a platinum catalyst, in a fuel cell.

(i) Write the two ionic half equations which occur in an **alkaline** fuel cell. Include state symbols.

(3)

Equation 1

Equation 2

(ii) The alkali in an alkaline fuel cell serves the same purpose as the acid in an acid fuel cell. State this purpose.

(1)

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*(iii) Platinum catalyses both the direct combination of hydrogen with oxygen and the reactions in the fuel cell. By considering the way in which the catalyst lowers the activation energy, suggest two **similarities** in these processes.

(2)

Similarity 1

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.....

Similarity 2

.....

.....

(c) The use of hydrogen as a fuel, both in fuel cells and in direct combustion reactions, is seen as an important potential alternative to fossil fuels.

(i) State what is considered to be the main advantage of hydrogen compared with fossil fuels, bearing in mind that most hydrogen is obtained from fossil fuels.

(1)

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*(ii) Explain the main advantage of using a fuel cell over direct combustion of hydrogen.

(2)

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(iii) State a disadvantage of using a hydrogen fuel cell compared with direct combustion of hydrogen.

(1)

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(iv) Suggest **two** advantages of using an ethanol fuel cell rather than a hydrogen fuel cell.

(2)

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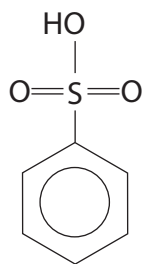
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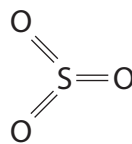
(Total for Question 21 = 13 marks)



22 (a) Benzenesulfonic acid (structure I) may be prepared from benzene. The reaction is a typical electrophilic substitution in which the electrophile is sulfur trioxide (structure II).



Structure I



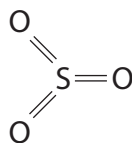
Structure II

(i) Identify the reagent used as the source of sulfur trioxide in this preparation.

(1)

(ii) On the formula of sulfur trioxide below, show the partial charges on each atom and explain how they arise.

(2)



Structure II

(iii) Suggest why sulfur trioxide is an effective electrophile.

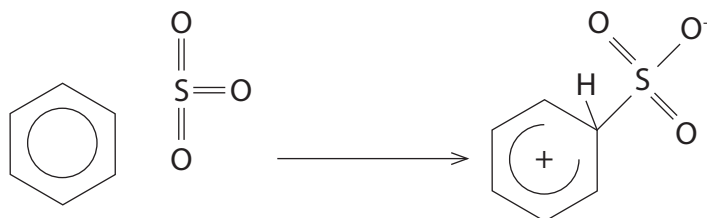
(1)



(b) The mechanism for the electrophilic substitution reaction between benzene and sulfur trioxide to form benzenesulfonic acid is similar to that for the nitration of benzene.

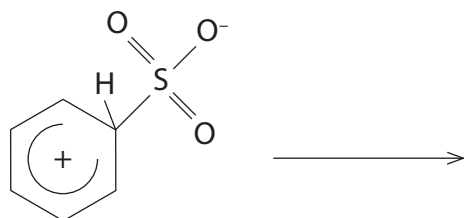
(i) Complete the first step of this mechanism by adding two curly arrows.

(2)



(ii) The mechanism for the formation of benzenesulfonic acid has two further steps. Complete the mechanism, showing curly arrows where appropriate.

(3)

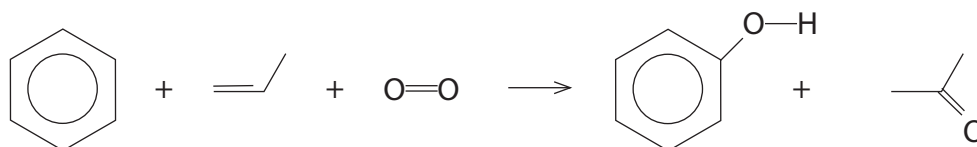


(c) At one time the main industrial use for benzenesulfonic acid was in the manufacture of phenol in a two-stage process. In the first stage, benzenesulfonic acid was reacted with sodium hydroxide forming an intermediate organic compound along with sodium sulfite, Na_2SO_3 , and water. In the second stage, the intermediate organic compound was reacted with hydrochloric acid to form phenol.

(i) Write the two equations for the manufacture of phenol by this method. State symbols are not required.

(2)

(ii) Nowadays, phenol is manufactured using the Hock process which is summarised below.



Suggest why the Hock process is preferred.

(2)

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(Total for Question 22 = 13 marks)



23 (a) The following data were obtained from experiments on solutions of aqueous amines of the same concentration.

Amine	Formula	pH of solution
Butylamine	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	11.9
Dibutylamine	$(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{NH}$	12.1
Phenylamine (aniline)	$\text{C}_6\text{H}_5\text{NH}_2$	8.8

(i) Identify the feature of the amine molecules that causes the solutions to be alkaline.

(1)

(ii) Write the equation for the reaction that occurs when butylamine is dissolved in water. State symbols are not required.

(1)

*(iii) Suggest why the dibutylamine solution is more alkaline than the butylamine solution.

(2)



*(iv) Suggest why the phenylamine solution is much less alkaline than the butylamine solution.

(2)

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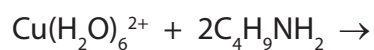
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(b) When butylamine is added to an aqueous solution of copper(II) sulfate, initially a pale blue precipitate is formed. When excess butylamine is added, the precipitate dissolves to form a deep blue solution.

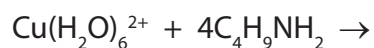
Complete the equations below. State symbols are not required.

(4)

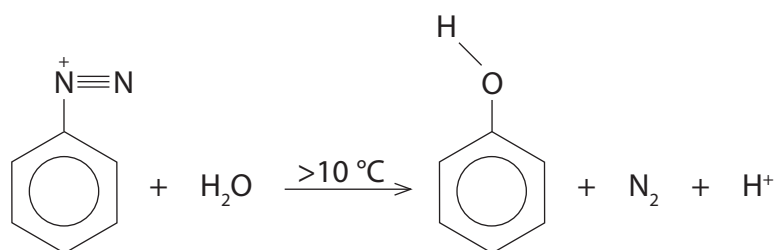
I Formation of the pale blue precipitate



II The overall equation for the formation of the deep blue solution



*(c) When phenylamine is treated with a mixture of sodium nitrite, NaNO_2 , and hydrochloric acid at about 5°C , the resulting solution contains the benzenediazonium ion. If the temperature of this solution is allowed to rise above 10°C , the benzenediazonium ion reacts to form phenol:



By considering the role of the water molecule in this reaction, state the type and mechanism occurring and explain why it is unusual in benzene chemistry.

(2)

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(Total for Question 23 = 12 marks)

TOTAL FOR SECTION B = 49 MARKS

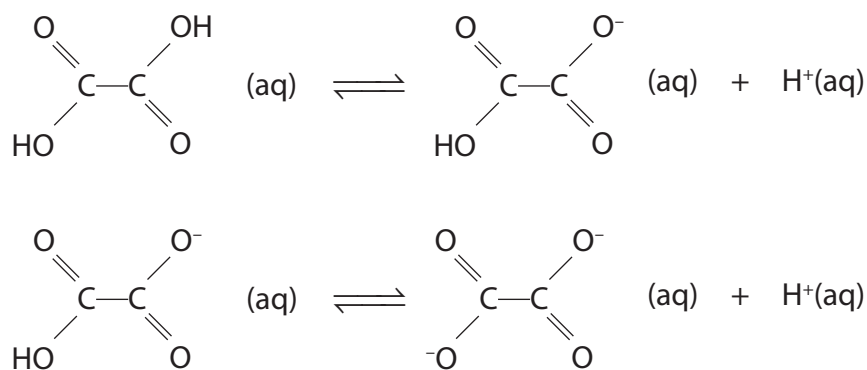


SECTION C

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

24

Ethanedioic acid (also known as oxalic acid) is a dicarboxylic acid. Like sulfuric acid, it has two replaceable hydrogen atoms so it dissociates in two stages which are shown below. Acids like these are called 'dibasic'.



As is always the case with dibasic acids, the first dissociation occurs to a far greater extent than the second. Ethanedioic acid is a carboxylic acid but, because there are two carboxyl groups, it is a much stronger acid than ethanoic acid.

Ethanedioic acid is toxic, mainly due to the precipitation of calcium ethanedioate in the kidneys. As it occurs in many plants, the toxicity of ethanedioic acid has caused a number of deaths notably during the First World War when people in England used rhubarb leaves, which contain significant concentrations of the compound, as a vegetable substitute. As it is a reducing agent, the concentration of ethanedioic acid is usually determined by titration with a solution of potassium manganate(VII) of known concentration.

The ethanedioate ion, which is formed when ethanedioic acid dissociates fully, is a bidentate ligand. The ethanedioate ion together with 1,2-diaminocyclohexane, another bidentate ligand, forms a complex with platinum(II) called oxaliplatin which has the same geometry as cisplatin. Oxaliplatin is an anti-cancer drug, which has been used to treat cancers that have become resistant to cisplatin.

Ethanedioic acid has numerous uses, from cleaning and rust removal to the purification of metals. Although it can be prepared from ethene in a two stage process, it is usually manufactured by the oxidation of carbohydrates or glucose using nitric acid, or air, in the presence of vanadium(V) oxide.



(a) (i) Suggest why the presence of the second carboxylic acid group increases the extent of the **first** dissociation of ethanedioic acid compared with the dissociation of ethanoic acid.

(2)

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(ii) Explain, by referring to the equilibria in the passage, why the second dissociation of a dibasic acid occurs to a lesser extent than the first.

(1)

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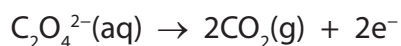
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(b) In an experiment to determine the proportion of ethanedioic acid in rhubarb leaves, 250 g of leaves was crushed and boiled in a solution of sodium carbonate. The resulting mixture was filtered and the filtrate transferred, along with washings from the mixture, to a 250 cm³ volumetric flask. The solution was acidified with sulfuric acid, made up to the mark and mixed thoroughly. 25.0 cm³ portions of the solution were pipetted into a conical flask, about 25 cm³ of sulfuric acid added and the mixture titrated against a solution of potassium manganate(VII) of concentration 0.0200 mol dm⁻³. The mean titre was 28.55 cm³. The relevant ionic half equations for the reaction are



(i) State the colour change that occurs at the end-point of the titration. (1)

*(ii) Calculate the percentage by mass of ethanedioic acid in rhubarb leaves. (5)



(c) (i) Explain the term 'bidentate'.

(1)

(ii) Draw a diagram of the oxaliplatin(II) complex, showing clearly the geometry and charge of the complex and how the ligands are attached to the central ion.

(3)

(d) (i) Suggest a two step **laboratory** synthesis of ethanedioic acid from ethene. Indicate the intermediate compound formed and the reagents required.

(3)



(ii) Suggest why it is preferable from an environmental perspective that ethanedioic acid is manufactured from carbohydrates and glucose rather than from ethene.

(1)

(iii) A sample of ethanedioic acid, manufactured from glucose, was contaminated with a small amount of propanoic acid.

High resolution nmr may be used to distinguish propanoic acid from ethanedioic acid.

Describe the high resolution nmr spectra of both propanoic acid and ethanedioic acid. Do **not** include chemical shift data in your answer.

(4)

(Total for Question 24 = 21 marks)

TOTAL FOR SECTION C = 21 MARKS

TOTAL FOR PAPER = 90 MARKS



The Periodic Table of Elements

	1	2											3	4	5	6	7	0 (8)
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)
	6.9 Li lithium 3	9.0 Be beryllium 4	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	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	4.0 He helium 2
	23.0 Na sodium 11	24.3 Mg magnesium 12	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	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	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	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	101.1 Ru ruthenium 44	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						
				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	
				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	

* Lanthanide series

* Actinide series

