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Pearson Edexcel International Advanced Level	Centre Number		Candidate Number
Chemistry	•		
Advanced Unit 5: General Principles and Organic Nitro (including synopt	s of Chemistry gen Chemistr	у	nsition Metals
Advanced Unit 5: General Principles and Organic Nitro (including synopt Friday 20 January 2017 – N	s of Chemistry gen Chemistr ic assessment	у	Paper Reference
Advanced Unit 5: General Principles and Organic Nitro (including synopt	s of Chemistry gen Chemistr ic assessment	у	

Instructions

- Use **black** ink or **black** 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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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 Which set of successive ionisation energies, in kJ mol^{-1} , could **not** be for a transition element?
 - ☑ A 653 1592 2987 4740
 - **B** 658 1310 2653 4175
 - **C** 759 1561 2958 5290
 - **□ D** 900 1757 14849 21007

(Total for Question 1 = 1 mark)

- **2** The bonding **within** the complex ion, $[Cu(H_2O)_6]^{2+}$ is
 - A covalent and dative covalent only.
 - **B** covalent, dative covalent and ionic.
 - **C** covalent only.
 - **D** dative covalent only.

(Total for Question 2 = 1 mark)

3 An aqueous solution of a transition metal ion formed a green precipitate with both ammonia and sodium hydroxide solutions.

The green precipitate dissolved to form a blue solution with excess ammonia, but was insoluble in excess sodium hydroxide.

Which of these is the transition metal ion?

- A Cr³⁺
- B Cu²⁺
- **C** Fe²⁺
- **D** Ni²⁺

(Total for Question 3 = 1 mark)

4 When aqueous sodium hydroxide is added to a solution containing manganese(II) ions, an off-white precipitate of manganese(II) hydroxide forms. The precipitate then gradually turns brown.

What type of reaction causes this precipitate to change colour?

- A Deprotonation
- B Disproportionation
- □ C Ligand exchange
- D Oxidation

(Total for Question 4 = 1 mark)

5 Aluminium oxide reacts as shown in the equations.

$$AI_2O_3 + 6H^+ \rightarrow 2AI^{3+} + 3H_2O$$

$$Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2AI(OH)_4^-$$

These two reactions show that aluminium oxide is

- **A** acidic.
- **B** amphoteric.
- C basic.
- **D** an oxidising agent.

(Total for Question 5 = 1 mark)

6 What is the molecular formula of the compound below?

- A C₉H₉O
- B C₉H₁₀O
- \square **D** $C_9H_{12}O$

(Total for Question 6 = 1 mark)

7 When excess bromine reacts with benzene in the presence of ultraviolet radiation, the product below is formed.

The type of reaction occurring is

- **A** free radical addition.
- **B** free radical substitution.
- **C** electrophilic addition.
- **D** electrophilic substitution.

(Total for Question 7 = 1 mark)

8 Phenol, C_6H_5OH , has a K_a value of 1.28×10^{-10} mol dm⁻³.

What is the pH of a 0.10 mol dm⁻³ solution of phenol?

- **■ B** 5.45
- **C** 9.89
- ☑ D 10.89

(Total for Question 8 = 1 mark)

9 Phenylamine, C₆H₅NH₂, is a weak base.

$$C_6H_5NH_2(aq) + H_2O(I) \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)$$

The equilibrium constant for this reaction is 5.0×10^{-10} mol dm⁻³.

What is the concentration of OH⁻ ions, in mol dm⁻³, in a 0.10 mol dm⁻³ solution of phenylamine?

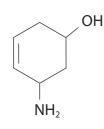
- \triangle **A** 2.2 × 10⁻⁵
- **B** 7.1×10^{-6}
- lacktriangle C 5.0 × 10⁻¹⁰
- \triangle **D** 5.0 × 10⁻¹¹

(Total for Question 9 = 1 mark)

10 An organic compound **X** reacted with bromine water to give a white precipitate. **X** gave a deep blue solution with an aqueous solution containing Cu²⁺ ions.

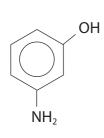
Which of the following could be the structure of X?

⊠ A

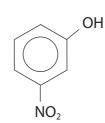


 \boxtimes B

⊠ C



 \boxtimes D



(Total for Question 10 = 1 mark)

- 11 Which of these compounds cannot form an amide in a reaction with ethanoyl chloride?
 - A NH₃
 - B CH₃NH₂

 - \square **D** CH₃CH₂N(CH₃)₂

(Total for Question 11 = 1 mark)

12 What is the minimum volume, in cm³, of oxygen needed for the complete combustion of 10 cm³ of hexane gas, $C_6H_{14}(g)$?

All gas volumes are measured at the same temperature and pressure.

- **B** 95
- ☑ D 190

(Total for Question 12 = 1 mark)

C D nich	0.072 0.324 0.648 (Total for Question 13 = 1 mark) is the most important advantage of combinatorial chemistry over traditional
D nich	0.648 (Total for Question 13 = 1 mark)
nich etho	(Total for Question 13 = 1 mark)
etho	
etho	is the most important advantage of combinatorial chemistry ever traditional
Λ	ds for developing pharmaceuticals?
A	Many more compounds can be made in a given time.
В	Only stereo-specific compounds are formed.
C	The compounds formed have fewer impurities.
D	The compounds formed have fewer side effects.
	(Total for Question 14 = 1 mark)
e lav	render flowers and stalks are crushed and mixed with water.
nich	is the correct order of practical techniques to extract linalool from this mixture?
A	refluxing, distilling, drying, decanting
В	steam distilling, purifying by washing, drying, decanting
C	steam distilling, using a separating funnel, drying, decanting
D	using a separating funnel, drying, decanting, distilling
	(Total for Question 15 = 1 mark)
a me	ethanol-oxygen fuel cell, methanol is
	oxidised at the anode.
В	oxidised at the cathode.
_	reduced at the anode.
C	. Canada at the unique
	D aloca boil e lav nich A B C D



17 Copper(II) ions oxidise titanium(II) ions.

The relevant half-equations are

Half-equation **1**
$$Ti^{3+} + e^- \rightleftharpoons Ti^{2+}$$

Half-equation 2
$$Cu^{2+} + 2e^{-} \rightleftharpoons Cu$$
 $E^{\ominus} = +0.34 \text{ V}$

$$E_{\text{cell}}^{\ominus}$$
 for the reaction = + 0.71 V.

The standard electrode potential for half-equation 1 is

- ☑ B -1.05 V
- ☑ D +1.05 V

(Total for Question 17 = 1 mark)

18 This question is about the following reactions.

$$\mathbf{P}$$
 2Fe²⁺(aq) + Br₂(aq) \rightarrow 2Fe³⁺(aq) + 2Br⁻(aq)

$$\mathbf{Q}$$
 2Fe²⁺(aq) + I₂(aq) \rightarrow 2Fe³⁺(aq) + 2I⁻(aq)

$$\mathbf{R}$$
 2Fe³⁺(aq) + 2Br⁻(aq) \rightarrow 2Fe²⁺(aq) + Br₂(aq)

Relevant standard electrode potentials are shown in the table.

Electrode reaction	E [⊕] /V
$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$2Fe^{3+}(aq) + 2e^{-} \rightleftharpoons 2Fe^{2+}(aq)$	+0.77
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.09

Which reactions are thermodynamically feasible under standard conditions?

- A P and Q
- B P and S
- C Q and R
- D Q and S

(Total for Question 18 = 1 mark)

19 A titration experiment was used to find the percentage of iron in iron tablets. The volumes used and measurement uncertainty for each reading of the burette and pipette are shown.

Apparatus	Volume used /cm³	Measurement uncertainty / cm ³
burette	21.80	±0.05
pipette	25.0	±0.06

What are the total percentage uncertainties, to 2 decimal places?

	Total percentage uncertainty on volume measured by burette	Total percentage uncertainty on volume measured by pipette
⋈ A	0.23	0.24
⋈ B	0.23	0.48
⊠ c	0.46	0.24
⊠ D	0.46	0.48

(Total for Question 19 = 1 mark)

20 Sulfuryl chloride, SO₂Cl₂, reacts with water to give a mixture of sulfuric acid, H₂SO₄, and hydrochloric acid, HCl.

How many moles of sodium hydroxide, NaOH, are needed to neutralise the solution formed by adding 1 mol of sulfuryl chloride to excess water?

- Δ 1
- B 2
- **⊠** C 3
- □ 4

(Total for Question 20 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

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SECTION B

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

- 21 Compounds derived from benzene have many uses, including as dyes and drugs.
 - (a) Sudan I is an intense orange-red azo dye that is used to colour waxes, oils and polishes.

It can be prepared from benzene using the reaction scheme shown.

(i) Give the mechanism of the reaction taking place in Step 1, including an equation for the formation of the electrophile.

(4)

(ii) Identify the reagents needed in Step 2 .	(1)
(ii	i) Explain why, in Step 3 , the temperature should not be higher than 10°C.	(1)
(iv	v) Draw the structure of benzenediazonium chloride, showing all the bonds in the side-chain and any charges.	(1)
(v) Draw the structure of the organic compound needed to produce Sudan I from benzenediazonium chloride in Step 4 .	(1)

(b) Sudan IV is another azo dye.	
The first step of a suggested synthesis of Sudan IV involved the preparation of methylbenzene from benzene.	
Give the reagent and conditions to prepare methylbenzene from benzene.	(2)

*(c) Benzyl benzoate is present in many asthma drugs.

benzyl benzoate

Outline how a chemist could synthesise a sample of benzyl benzoate in three or four steps, using benzaldehyde, C_6H_5CHO , as the **only** organic compound.

Include the reagents and conditions for the steps in the synthesis and draw the structures of the intermediates.

(5)

(Total for Question 21 = 15 marks)



- **22** The elements from scandium to zinc belong to the d-block. Most of these elements are transition elements.
 - (a) (i) Complete the electronic configurations of a scandium atom, a manganese(III) ion and an iron(II) ion.

(2)

	30			45
		30		

(ii) Scandium, iron and manganese are **d-block elements**, but only iron and manganese are **transition elements**.

Explain the meaning of these terms.

d-block elements

(2)

transition elements

(iii) Explain, in terms of electronic configurations, why Fe ²⁺ ions are readily oxidised to Fe ³⁺ ions but Mn ²⁺ ions are not readily oxidised to Mn ³⁺ ions.	(2)
(iv) Explain why the Fe ²⁺ and Fe ³⁺ ions have different colours in aqueous solution	ı.
A detailed explanation of why transition metal ions are coloured is not requir	red. (2)
(b) The concentration of a solution of potassium manganate(VII), KMnO ₄ , can be found by titration with arsenic(III) oxide, As ₂ O ₃ .	
In this reaction, arsenic(III) oxide is oxidised to arsenic(V) oxide, As_2O_5 , and the mole ratio of As_2O_3 to MnO_4^- is 5:4.	
Deduce the final oxidation number of the manganese. Explain your reasoning.	(3)



(c) Oxaliplatin is a drug used for the treatment of cancer. It consists of a platinum **ion** linked to two different bidentate ligands. The complex can be represented by the structure shown.

(i) State the meaning of the term **bidentate ligand**.

(1)

(ii) Draw the structures of the two bidentate ligands in oxaliplatin.

(2)

(iii) State the oxidation number of platinum in this complex.

(1)

(Total for Question 22 = 15 marks)



- 23 Amino acids contain both amine and carboxylic acid functional groups.
 - (a) The amino acid alanine can be synthesised from ammonia and ethanal in three steps.

$$O = C + NH_3 + Step 1 + H_2C$$

$$CH_3 + CH_3 + H_2C$$

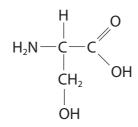
- (i) Suggest the reagent for Step 2.
- (ii) Identify, by name or formula, the reagent for Step **3**.
- (iii) Use your knowledge of amine chemistry to suggest the **displayed** formula of the organic product formed when alanine reacts with chloroethane.

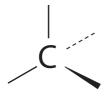


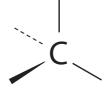
(b) Tyrosine and serine are amino acids that contain an additional OH group.

(i) Draw the structure of the zwitterion of tyrosine.

(ii) Complete the diagrams to show the two optical isomers of serine.







(2)



(iii) Tyrosine and serine can form different types of condensation polymers.

Draw **two** repeat units of the polyamide formed from tyrosine only and **two** repeat units of the polyester formed from serine only.

The polymer linkages must be displayed.

(4)

serine

Polyamide formed from tyrosine only

Polyester formed from serine only				

(c) Amino acids are detected using ninhydrin.

Ninhydrin reacts with most amino acids to give a purple colour. The reaction can be summarised as

(i) Draw the structure of the aldehyde formed when tyrosine reacts with ninhydrin.

OH

+ RCHO + CO₂ + 3H₂O

(ii) Draw the structure of the amino acid that reacts with ninhydrin to form 2-methylpropanal, (CH ₃) ₂ CHCHO.	(1)
(d) Explain whether or not tyrosine and serine can be distinguished by their infrared absorbance in the 4000 to 2000 cm ⁻¹ range. Justify your answer by quoting information from the Data Booklet.	(1)

(e) This question is about the high resolution proton nmr spectrum of the amino acid valine.

(i) State the total number of different proton environments in valine.

(1)

(ii) Use the Data Booklet, and your knowledge of nmr spectra, to complete the table for the protons in valine shown in **bold** in the structure.

(3)

Protons in valine	Chemical shift / ppm from TMS	Splitting pattern
CH ₃	0.1–1.9	
C H	0.1–1.9	
ОН		singlet

(Total for Question 23 = 17 marks)

TOTAL FOR SECTION B = 47 MARKS

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SECTION C

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

24

The +6 oxidation state

There are many compounds that contain an element in the +6 oxidation state, when six of the element's electrons are used in bonding.

Similarities exist between sulfur(VI) compounds and chromium(VI) compounds. For example, sulfur forms sulfate(VI) ions, SO_4^{2-} , and disulfate(VI) ions, $S_2O_7^{2-}$, while chromium forms chromate(VI) ions, CrO_4^{2-} , and dichromate(VI) ions, $Cr_2O_7^{2-}$. The ions with corresponding formulae have the same shape.

Other transition metal compounds exist with the metal in oxidation state +6. Potassium manganate(VI), K_2MnO_4 , can be prepared in alkaline solution but it readily disproportionates in neutral or acidic solution. Potassium ferrate(VI), K_2FeO_4 , is obtained by heating iron filings with potassium nitrate and then pouring the cooled mixture into water.

(a) (i) Draw a dot and cross diagram for a sulfate(VI) ion, SO₄²⁻.

(2)

(ii) State the shape of a sulfate(VI) ion, SO₄²⁻.



(iii) Many sulfate(VI) compounds are soluble in water. However, lead(II) sulfate(VI) is sparingly soluble.

0.0500 g of lead(II) sulfate(VI), PbSO₄, was mixed with 250.0 cm³ of water. Calculate the mass of undissolved lead(II) sulfate(VI) in this mixture.

Data:

solubility of lead(II) sulfate(VI) = $1.26 \times 10^{-4} \text{ mol dm}^{-3}$ molar mass of PbSO₄ = 303.3 g mol^{-1}

(2)

(b) (i) Sodium disulfate(VI) decomposes on heating to form only two products: sodium sulfate(VI) and an oxide of sulfur in oxidation state +6.

Write the equation for this decomposition. State symbols are not required.

(1)

(ii) Ammonium dichromate(VI) decomposes on heating to form chromium(III) oxide, nitrogen and water.

Write the equation for this decomposition. State symbols are not required.



(c) Use these standard electrode potentials to answer the following questions.

Electrode reaction	E [⊕] /V
$SO_4^{2-}(aq) + H_2O(I) + 2e^- \implies SO_3^{2-}(aq) + 2OH^-(aq)$	-0.93
CrO ₄ ²⁻ (aq) +	
$MnO_4^-(aq) + e^- \rightleftharpoons MnO_4^{2-}(aq)$	+0.56
$MnO_4^{2-}(aq) + 2H_2O(l) + 2e^- \implies MnO_2(s) + 4OH^-(aq)$	+0.59
$2H^+(aq) + O_2(g) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.68
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \Rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$MnO_{4}^{-}(aq) + 8H^{+}(aq) + 5e^{-} \rightleftharpoons Mn^{2+}(aq) + 4H_{2}O(l)$	+1.51
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(I)$	+1.77
$FeO_4^{2-}(aq) + 8H^+(aq) + 3e^- \rightleftharpoons Fe^{3+} + 4H_2O(I)$	+2.20

(i) Complete the table using information from page 14 of the Data Booklet.

(1)

(ii) Give the formula of the species which, under standard conditions, is the strongest oxidising agent.

(1)

(iii) Write the equation for the disproportionation of the manganate(VI) ion. Include state symbols.

(iv) Calculate the standard cell potential, E_{cell}^{\oplus} , for the following reaction.

$$2MnO_4^-(aq) + 6H^+(aq) + 5H_2O_2(aq) \rightarrow 2Mn^{2+}(aq) + 5O_2(g) + 8H_2O(l)$$
 (1)

(v) Draw a fully labelled diagram of the apparatus you would use to determine the standard electrode potential of the dichromate(VI)/chromium(III) electrode at 298 K, using a standard hydrogen electrode.

(5)

- (d) The mass of ethanol in 5.00 cm³ of white wine is found by oxidising the ethanol to ethanoic acid using acidified potassium dichromate(VI) solution. The excess acidified potassium dichromate(VI) solution is then determined.
 - Step 1 5.00 cm³ of white wine was diluted to 100.0 cm³ with distilled water.
 - Step 2 10.0 cm³ of acidified potassium dichromate(VI) solution, of concentration 0.0150 mol dm⁻³, was placed in a conical flask with 1.00 cm³ of the diluted white wine and left until all the ethanol had been completely oxidised.
 - Step 3 10 cm³ (an excess) of potassium iodide solution was added to the flask to react with the remaining potassium dichromate(VI) solution.
 - Step 4 The iodine produced was titrated with 0.0300 mol dm⁻³ sodium thiosulfate solution.
 - Step 5 The procedure was repeated twice more.

The mean titre of sodium thiosulfate solution was 9.20 cm³.

The equations for the reactions taking place are

$$2Cr_2O_7^{2-} + 16H^+ + 3C_2H_5OH \rightarrow 4Cr^{3+} + 11H_2O + 3CH_3COOH$$

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

(i) Use the equations to determine the mole ratio of $S_2O_3^{2-}$ to $Cr_2O_7^{2-}$ in this series of reactions.

*(ii) Calculate the mass of ethanol in 5.00 cm³ of the original white wine.

(6)

(Total for Question 24 = 23 marks)

TOTAL FOR SECTION C = 23 MARKS TOTAL FOR PAPER = 90 MARKS



5 5 0 8 - 5	Key stromic symbol name nic (proton) number (5) (6) 50.9 52.0 V Cr V Cr Nb Mo nnoblum neyborum 41 Ta W ntantalum tungsten 73 74 73 74 106 Db Sg bun dubnium seaborgum 105
Cr 24 24 95.9 Mo nesystem te 42 183.8 W tungstem r 74 [266] Sg seeborgium b	titanium vanadium chromium 22 23 24 24 25 25 24 25 24 25 25 25 24 25 25 25 25 25 25 25 25 25 25 25 25 25