TJC 2022 H2 Chemistry Paper 1 Answer Key

1	2	3	4	5		6	7	8	9	10
D	**C**	**A**	**B**	**D**		**B**	**B**	**C**	**A**	**A**
11	12	13	14	15		16	17	18	19	20
D	**C**	**B**	**D**	**B**		**A**	**C**	**A**	**B**	**D**
21	22	23	24	25		26	27	28	29	30
C	**B**	**D**	**C**	**A**		**D**	**C**	**B**	**C**	**A**

1 Answer: **D**

Worked Solution:

Number of neutrons in $^{31}P^{3-}$ = 31 – 15 = 16

Number of neutrons in $^{32}S^{2-}$ = 32 – 16 = 16

Thus, $^{31}P^{3-}$ are $^{32}S^{2-}$ are isotonic.

Angle of deflection of species in electric field $\propto \frac{charge}{mass}$

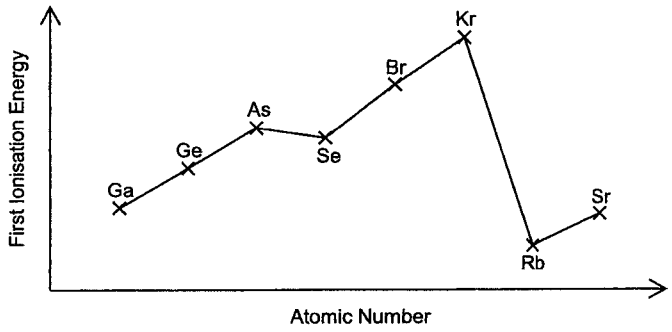
$^{31}P^{3-}$ has a higher charge and a smaller mass than $^{32}S^{2-}$. The angle of deflection of $^{31}P^{3-}$ will be greater than that for $^{32}S^{2-}$.

2 Answer: **C**

Worked Solution: 3rd electron of B comes from an inner shell, B has 3 valence electron and is from Group 13. C is from Group 15.

3 Answer: **A**

Worked Solution:



1: correct, from diagram, IE of Ga < Ge < As

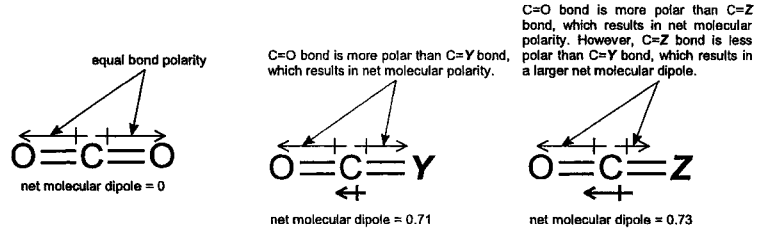
2: wrong, Se < As < Br

3: correct, Se < Br < Kr

4: wrong, Sb < As < P

4 Answer: **B**

Worked Solution:



×	**A**	O is the most electronegative element in Group 16. Thus, the C=O bond is the most polar amongst the three bonds.
✓	**B**	O is the most electronegative element in Group 16. Since C=***Z*** bond is less polar than C=***Y*** bond, this suggests that ***Y*** is more electronegative than ***Z***. *(See diagrams above.)*
×	**C**	While this statement is true, it does not explain the observed trend.
×	**D**	Bond length has little bearing on net molecular dipole.

5 Answer: **D**

Worked Solution:

SO_2 has bent shape, bond angle < 120°. SO_3 has trigonal planar shape, bond angle is 120°.

6 Answer: **B**

Worked Solution: PV= nRT

A. Incorrect. The number of moles of L is greater than number of moles of M

B. Correct. At constant T, PV= n x constant

C. Incorrect. At constant T, V = nRT/P, straight line pass through origin, different gradient for L & M

D. Incorrect. At constant P, V = (nR)/p x T = constant x T

More papers at www.testpapersfree.com

BP~581

7 Answer: **B**

Worked Solution:

element		pH of solution when oxide of element is added to water	pH of solution when chloride of element is added to water
X	Na	$Na_2O + H_2O \rightarrow 2NaOH$ pH = 13	$NaCl(aq)$, pH = 7
Y	P	$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$ pH = 2	$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$ pH = 2
Z	Al	Al_2O_3 is insoluble in water pH = 7	$AlCl_3$ undergoes hydration and hydrolysis. pH of solution is about 3.

8 Answer: **C**

Worked Solution: Ionic radii of group 2 cations increases down the group. Charge density and polarising power decrease down the group, thermal stability increases down the group.

9 Answer: **A**

A. Incorrect statement - Chlorine has a greater reducing strength than bromine. Bromine will not be able to displace chloride.

B. $AgCl$ is insoluble in nitric acid.

C. Chlorine oxidises thiosulfate to sulfate, which forms white ppt of barium sulfate.

D. Chlorine displaces iodide, brown iodine solution is formed.

10 Answer: **A**

Worked Solution:

Let V_{CH_4} cm^3 be the volume of CH_4 in mixture.

$\Rightarrow$ Volume of CO in mixture = $(15 - V_{CH_4})$ cm^3

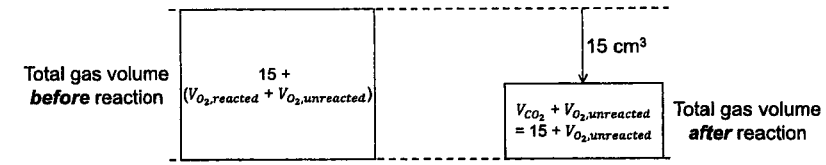
	CH_4	:	O_2	:	CO_2
mole ratio	1	:	2	:	1
volume ratio	V_{CH_4}	:	$2\,V_{CH_4}$		V_{CH_4}

	CO	:	O_2	:	CO_2
mole ratio	1	:	$\frac{1}{2}$	:	1
volume ratio	$15 - V_{CH_4}$	:	$\frac{1}{2}(15 - V_{CH_4})$	:	$15 - V_{CH_4}$

Since total volume of CH_4 and CO combusted = 15 cm^3, and equimolar ratios of CH_4 to CO_2, and of CO to CO_2 are formed, total volume of CO_2 formed = 15 cm^3

Total volume of O_2 added into reaction vessel = $(V_{O_2,reacted} + V_{O_2,unreacted})$ cm^3

$$CH_4 + CO + \frac{5}{2}O_2 \longrightarrow 2CO_2 + 2H_2O$$



$15 + V_{O_2,reacted} + V_{O_2,unreacted} = 15 + (15 + V_{O_2,unreacted})$

$\Rightarrow V_{O_2,reacted} = 15$ cm^3

$\Rightarrow 2\,V_{CH_4} + \frac{1}{2}(15 - V_{CH_4}) = 15$

$\Rightarrow V_{CH_4} = 5$ cm^3, which is $\frac{5}{15} \times 100 =$ **33.3 %** of the mixture

11 Answer: **D**

Worked Solution:

$\Delta H_r^\ominus = \sum m\Delta H_f^\ominus(pdts) - \sum n\Delta H_f^\ominus(rxts)$

$\Delta H_f^\ominus(MgCl_2) = \Delta H_r^\ominus + \Delta H_f^\ominus(HCl)$

The standard enthalpy change of formation of elements in their standard states at 298 K and 1 bar is, by definition, ***zero***

12 Answer: **C**

Worked Solution:

The rate of the reaction depends on the rate of the slow step, i.e.

$$\text{rate} = k'[B][C]$$

However, the rate equation for the overall reaction should be in terms of reactant concentrations only. (Note that **C** and **D** are reaction intermediates.)

Since step 1 of the mechanism is an equilibrium, 2**A** ⇌ **C**, we can write an expression for its equilibrium constant,

$$K_{step\ 1} = \frac{[C]}{[A]^2}$$

Rearranging, $[C] = K_{step\ 1}[A]^2$

The rate equation then becomes

$$\text{Rate} = k'[B](K_{step\ 1}[A]^2) = k[A]^2[B]$$

where $k = k' \times K_{step\ 1}$

More papers at www.testpapersfree.com

13 Answer: **B**

Worked Solution:

Graph of **[W]** against time is a downward-sloping straight line with constant gradient.

⇒ Rate of reaction is independent of **[W]**.

⇒ Reaction is zero order wrt **[W]**.

[W] / mol dm^{-3}	[V] / mol dm^{-3}	Rate of reaction / mol dm^{-3} min^{-1}
0.10	1.0	$\frac{0.10}{20} = 0.0050$
0.10	2.0	$\frac{0.10}{10} = 0.010$

When **[V]** × 2, while **[W]** is unchanged, rate of reaction × 2

⇒ Reaction is first order wrt **[V]**.

Order of reaction wrt **[X]** cannot be determined from the graph.

∴ Only Statements 1 & 2 are correct.

14 Answer: **D**

Worked Solution:

	$BiCl_3(aq)$	+	$H_2O(l)$	⇌	$BiOCl(s)$	+	$2HCl(aq)$
Initial amt / mol	0.1		–		–		0
Change in amt / mol	−0.02		–		+0.02		+2(0.02)
Eqm amt / mol	0.08		–		0.02		2(0.02)

$$K_c = \frac{[HCl]^2}{[BiCl_3]} = \frac{(\frac{2 \times 0.02}{2})^2}{\frac{0.08}{2}}$$

15 Answer: **B**

Worked Solution: When temp increases, by LCP, position of eqm shifts to the right to favour the endothermic reaction to absorb heat. So K_a increases. Since $K_a = \alpha^2 c$, degree of dissociation also increases.

16 Answer: **A**

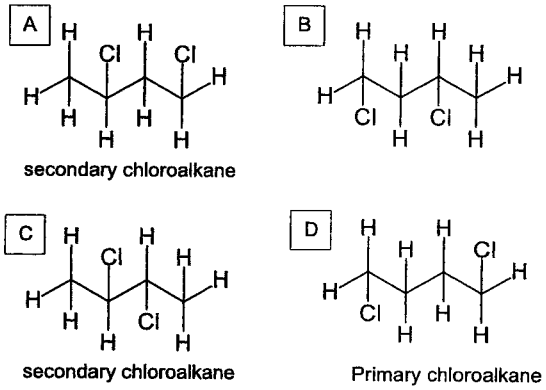
Worked Solution:

Solubility product is only affected by changes in temperature.

17 Answer: **C**

Worked Solution:

Products formed:



Isomer A and B are the same.

No. of constitutional isomers: 3

18 Answer: **A**

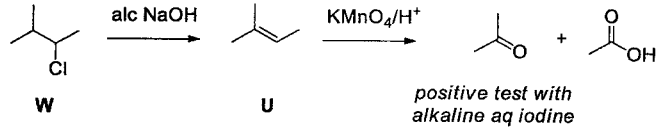
Worked Solution:

Due to the delocalisation of π electrons, the π electron cloud in benzene is less susceptible to an electrophilic attack than a localised π electron cloud in cyclohexene.

Thus, cyclohexene reacts readily with a weak electrophile like a polarised Br_2, while benzene requires a Lewis acid catalyst to generate a stronger electrophile, Br^+, before a reaction with bromine can occur.

19 Answer: **B**

Worked Solution:



More papers at www.testpapersfree.com

BP~583

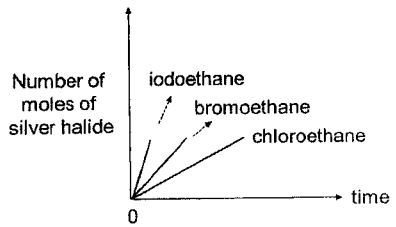
BP~584

20 Answer: **D**

Worked Solution:

Each mole of dichloroethane provides 2x the amount of AgC*l* as chloroethane, for the same amount of time of the experiment.

For bromoethane and iodoethane, the rate of reaction is faster due to weaker C–X bond, but the amount of AgX produced is the same as chloroethane, so the graph should be:



21 Answer: **C**

Worked Solution:

	$-OH \equiv Na \equiv \frac{1}{2}H_2$	$-CO_2H \equiv NaHCO_3 \equiv CO_2$
alcohol	√	X
phenol	√	X
acid	√	√

Option	H_2 from Na	CO_2 from $NaHCO_3$
A	1	0
B	1	0
C	1	1
D	1	2

22 Answer: **B**

Worked Solution:

A × **2,4-DNPH:** positive test for carbonyl group in vanillin and cinnamaldehyde

B √ **Fehling's solution:** positive test for aliphatic aldehyde group in cinnamaldehyde and negative for benzaldehyde in vanillin

C × **Hot acidified $K_2Cr_2O_7$:** positive test for aldehyde group in vanillin and cinnamaldehyde.

D × **Tollens' reagent:** positive test for both

23 Answer: **D**

Worked Solution:

Order of decreasing acidity: carboxylic acids > phenols > alcohols

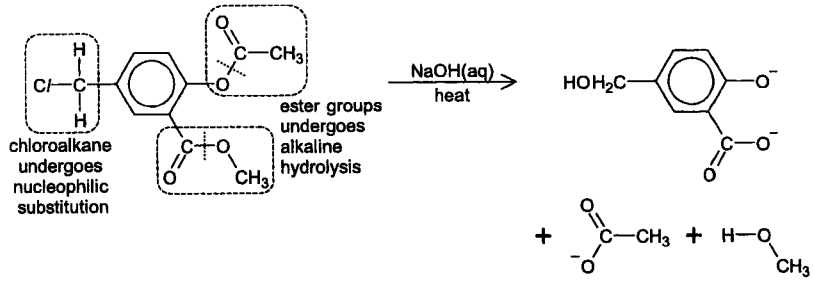
[Refer to page 5, Section 3.1 (Comparison of Acid strength between RCOOH, phenol and alcohols) in the Carboxylic Acids lecture notes.]

2-chlorobenzoic acid is more acidic than benzoic acid. 2-chlorobenzoic acid has an electron-withdrawing C*l* atom which disperses the negative charge on the 2-chlorobenzoate ion and helps to stabilise it to a larger extent than the benzoate ion.

∴ Order of decreasing acidity: 3 > 2 > 1 > 4

24 Answer: **C**

Worked Solution:



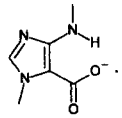
25 Answer: **A**

Worked Solution:

1 N^2 is the less basic as it is an amide where the lone pair of electrons on N is delocalised over the O–C–N bond and hence is not available for dative bonding with a proton.

N^1 is the more basic as the lone pair of electrons on N is in an orbital that is perpendicular to the C=C and hence cannot be delocalised. The lone pair of electrons is available for dative bonding to H^+.

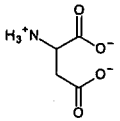
2 Caffeine does not react with ethanoyl chloride as there are no H attached to N^1 and N^2.

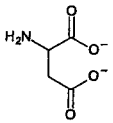
3 Caffeine undergo alkaline hydrolysis to form only one mole of methylamine and  .

More papers at www.testpapersfree.com

26 Answer: **D**

Worked Solution:

At pH = 4, the major species of aspartic acid present is  . Since it has a net charge of −1, it will migrate to the positive electrode (anode).

At pH = 11, the major species is  . Since it is doubly charged, it would migrate faster than if the pH = 4.

27 Answer: **C**

Worked Solution:

Hexacyanoferrate(III) is an oxidising agent, NOT an reducing agent.

The stronger the reducing agent, the more likely it will undergo oxidation, the less positive/more negative the $E^{\ominus}$ will be.

$E^{\ominus}(NO_3^-/NO_2) = +0.81\ V < E^{\ominus}(VO_2^+/VO^{2+}) = +1.00\ V < E^{\ominus}(MnO_2/Mn^{2+}) = +1.23V$

28 Answer: **B**

Electrode half-equation	$E^{\ominus}$ / V
Co^{3+} (aq) + e^- → Co^{2+}(aq)	+1.82
Cu^{2+} (aq) + $2e^-$ ⇌ Cu (s)	+0.34
Fe^{3+} (aq) + e^- → Fe^{2+}(aq)	+0.77
I_2 (s) + $2e^-$ → $2I^-$ (aq)	+0.54
$S_2O_8^{2-}$ (aq) + $2e^-$ → $2SO_4^{2-}$ (aq)	+2.01

Worked Solution:

An ion is deemed suitable to catalyse the reaction if it is able to be consumed and regenerated, i.e. the $E^{\ominus}$ value is in between that of 0.54V and +2.01V.

Cu^{2+} cannot oxidise iodide in the first place due to non-spontaneous reaction (0.34 – 0.54 < 0), so it cannot be consumed and is not a suitable catalyst.

Co^{2+}: reacts with peroxydisulfate to form SO_4^{2-} and Co^{3+} ($E^{\ominus}_{cell}$ = 2.01 – 1.82 > 0) and Co^{3+} then reacts with iodide to give iodine and regenerates Co^{2+} ($E^{\ominus}_{cell}$ = 1.82 – 0.54 > 0).

Fe^{2+}: reacts with peroxydisulfate to form SO_4^{2-} and Fe^{3+} ($E^{\ominus}_{cell}$ = 2.01 – 0.77 > 0) and Fe^{3+} then reacts with iodide to give iodine and regenerates Co^{2+} ($E^{\ominus}_{cell}$ = 0.77 – 0.54 > 0).

Fe^{3+}: reacts with iodide to give iodine and Fe^{2+} ($E^{\ominus}_{cell}$ = 0.77 – 0.54 > 0) and Fe^{2+} then reacts with peroxydisulfate to form SO_4^{2-} and regenerates Fe^{3+} ($E^{\ominus}_{cell}$ = 2.01 – 0.77 > 0).

29 Answer: **C**

Worked Solution:

The maximum oxidation state of vanadium is found in VO_2^+

Finely divided Fe is used as a catalyst in the manufacture of ammonia

$E^{\ominus}_{Zn2+/Zn} = -0.76V$; $E^{\ominus}_{V3+/V2+} = -0.26V$; $E^{\ominus}_{V2+/V} = -1.20V$

Vanadium is denser than calcium.

30 Answer: **A**

Worked Solution:

ethylenediamine (en) > $H_2NCH_2CO_2^-$ (gly^-) > $C_2O_4^{2-}$

$[Co(gly)_3]$ complex is violet, the complex absorbs yellow light (560–590 nm)

$[Co(C_2O_4)_3]^{3-}$(aq) a smaller energy gap between the two sets of d-orbitals in a transition metal complex, the complex absorbs a longer wavelength of light (590–700 nm), colour of complex should be **blue or green**

and $[Co(en)_3]^{3+}$(aq), a larger energy gap between the two sets of d-orbitals in a transition metal complex, the complex absorbs a shorter wavelength light (400–590 nm), colour of complex should be **yellow, orange, red**

More papers at www.testpapersfree.com

BP~585

More papers at www.testpapersfree.com

TEMASEK JUNIOR COLLEGE

2022 JC2 PRELIMINARY EXAMINATION

Higher 2

TEMASEK JUNIOR COLLEGE

CANDIDATE NAME: WORKED SOLUTIONS

CENTRE NUMBER: S

INDEX NUMBER

Chemistry **9729/02**

Paper 2 Structured Questions **25 August 2022**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number and name in the spaces at the top of this page.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** the questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use		
Paper 1		/30
Paper 2	Q1	/9
	Q2	/14
	Q3	/10
	Q4	/8
	Q5	/20
	Q6	/14
	Total	/75
Paper 3		/80
TOTAL (%)		/100

This document consists of **23** printed pages and **1** blank page.

More papers at www.testpapersfree.com

Answer **all** the questions in the space provided.

1 **(a)** Element **W** is from Period 5 of the Periodic Table. The first eight ionisation energies of element **W**, in kJ mol^{-1}, are

869 1800 2690 3610 5720 6670 12000 13800

(i) Identify element **W** and explain your answer. [2]

✓ Element W is Tellurium/ Te. Electronic configuration: [Kr]4d^{10}5s^{2}5p^4.

✓ There is a large difference between the 6th and 7th ionisation energies of **W**.

✓ The 7th electron is from an inner electronic shell.

✓ W has 6 valence electrons, hence it is from Group 16.

2 ticks – 1 mark

(ii) Explain the difference between the first ionisation energy of element **W** compared to the element to its left on the Periodic Table. [2]

✓ 1st ionisation energy of Te involves the removal of paired 5p electrons

✓ which experiences inter-electronic repulsion.

✓ Less energy is needed to remove the electron from W/ Te than the valence electron/ unpaired 5p electron in Sb/ element to its left.

✓ IE of element W is lower.

2 ticks – 1 mark

(b) The chlorides of elements in Period 3 of the Periodic Table show different behaviours on addition to water.

(i) Describe and explain the reactions of aluminium chloride, $AlCl_3$, and phosphorus pentachloride, PCl_5, with excess water.

Write equations for any reactions that occur. [3]

$AlCl_3$ undergoes hydration and hydrolysis.

✓ Hydrolysis take place as Al^{3+} has a high charge density hence a high polarising power.

✓ Al^{3+} draws electrons from its surrounding water molecules and weakens the O-H bond. It is easier for a H^+ ion to leave the water molecule.

✓ $AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$

✓ $[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H_3O^+$

✓ PCl_5 undergoes hydrolysis in water due to the presence of energetically accessible vacant 3d orbitals in P for dative bonding with water molecules.

✓ $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

2 ticks – 1 mark

(ii) The reaction of PCl_5 with limited amount of water involves step-wise substitution of –Cl with –OH.

DO NOT WRITE IN THIS MARGIN
DO NOT WRITE IN THIS MARGIN
BP~587

Write the overall balanced equation for the reaction of PCl_5 with limited amount of water. Hence, suggest a three-step reaction sequence for this reaction.

✓ Balanced equation: $PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$

✓ Step 1: $PCl_5 + H_2O \rightarrow PCl_4OH + HCl$

✓ Step 2: $PCl_4OH + H_2O \rightarrow PCl_3(OH)_2 + HCl$

✓ Step 3: $PCl_3(OH)_2 \rightarrow POCl_3 + H_2O$

[Total: 9]

2 Boron trifluoride, BF_3, and aluminium fluoride, AlF_3, differ markedly in their physical properties.

compound	melting point / °C
BF_3	–127
AlF_3	1291

(a) (i) State the type of bonding present in each of these compounds and draw 'dot-and-cross' diagrams in the boxes below to illustrate this bonding.

✓ Type of bonding: ✓ covalent bonding	✓ Type of bonding: ✓ ionic bonding
BF_3	AlF_3

4 ticks – **[2]**

2 to 3 ticks – **[1]**

[2]

(ii) Outline the principles of the Valence Shell Electron Pair Repulsion theory.

Electron pairs in the valence shell of the central atom arrange themselves as far as possible to minimise repulsion and maximise stability. **[1]**

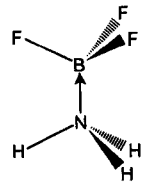
Strength of repulsion between electron pairs decreases in the order:

Lone pair – lone pair repulsion > lone pair – bond pair repulsion > bond pair – bond pair repulsion **[1]**

[2]

(iii) Boron trifluoride forms a compound with ammonia.

Use the Valence Shell Electron Pair Repulsion theory to predict and draw the likely shape of the product formed from this reaction.



[1]

Shape of product: tetrahedral around B *OR* N atom **[1]**
(Dative covalent bond must be clearly shown with an arrow from N to B atom.)

[2]

Cyclobutane is an example of a cyclic alkane. While itself has no commercial or biological significance, more complex derivatives of cyclobutane are important in biology and biotechnology.

Cyclobutane decomposes to ethene as shown by the following equation.

$$\square(g) \rightarrow 2CH_2{=}CH_2(g) \qquad \Delta H^{\ominus}_{decomp}$$

A student planned to determine $\Delta H^{\ominus}_{decomp}$ by using the standard enthalpy changes of combustion of cyclobutane and ethene, represented by $\Delta H^{\ominus}_c$(cyclobutane) and $\Delta H^{\ominus}_c$(ethene) respectively. Both substances are gases at 298 K.

$\Delta H^{\ominus}_c$(ethene) was previously determined to be –1411 kJ mol^{-1} in a flame calorimetric experiment.

To determine $\Delta H^{\ominus}_c$ (cyclobutane), the student decided to conduct another flame calorimetric experiment under the same conditions.

There are two stages to this experiment.

Stage I : Calibration of calorimeter (i.e. copper can, water and other components in the calorimeter)

In the experiment, the calorimeter must first be calibrated by determining its heat capacity, ***C***, which is the amount of heat required to raise the temperature of the calorimeter by 1 K.

Stage II : Determination of $\Delta H^{\ominus}_c$(cyclobutane) using the calibrated calorimeter.

The student carried out the flame calorimetric experiment using the calorimeter. Part of his results is shown below.

Stage I, using ethene as the fuel,

- change in temperature of water = 33.8 °C
- mass of gaseous ethene burnt = 1.00 g

Stage II, using cyclobutane as the fuel,

More papers at www.testpapersfree.com

- change in temperature of water = 32.9 °C
- mass of gaseous cyclobutane burnt = 1.00 g

(b) (i) Use the above information and experimental results to calculate the heat capacity, ***C***, of the calorimeter.

heat produced from combustion of ethene = heat gained by calorimeter

amount of ethene burnt × $|\Delta H_c^\ominus(\text{ethene})|$ = $C \times |\Delta T|$

$\frac{1.00}{28.0} \times 1411 = C \times 33.8$

$C = 1.4909 \approx$ **1.49** kJ K^{-1}

Working – **[1]**

Answer – **[1]**

[2]

(ii) Use your answer to **(b)(i)** to determine $\Delta H_c^\ominus$(cyclobutane).

heat produced from combustion of cyclobutane = heat gained by calorimeter

amount of cyclobutane burnt × $|\Delta H_c^\ominus(\text{cyclobutane})|$ = $C \times |\Delta T|$

$\frac{1.00}{56.0} \times |\Delta H_c^\ominus(\text{cyclobutane})| = 1.4909 \times 32.9$

$\therefore \Delta H_c^\ominus(\text{cyclobutane}) = -2746.9 \approx$ **–2750 kJ mol^{-1}**

Working – **[1]**

Answer (with correct sign) – **[1]**

[2]

(iii) Hence, calculate the standard enthalpy change of decomposition of cyclobutane to ethene, $\Delta H_{decomp}^\ominus$.

$\Delta H_{decomp}^\ominus = \Delta H_c^\ominus(\text{cyclobutane}) - 2\,\Delta H_c^\ominus(\text{ethene})$

$= (-2746.9) - 2(-1411)$

$=$ **+75.1 kJ mol^{-1}**

Working + Answer – **[1]**

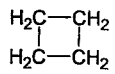
[1]

[Turn over

More papers at www.testpapersfree.com
DO NOT WRITE IN THIS MARGIN

(c) (i) Use data from the *Data Booklet* and the $\Delta H_{decomp}^\ominus$ obtained in **(b)(iii)** to calculate the actual C–C bond energy in cyclobutane.

[You may assume that the difference between the C–H bond energy in cyclobutane and in ethene, and the difference between the C=C bond energy from the *Data Booklet* and in ethene are insignificant.]



(g) → $2CH_2{=}CH_2$(g) $\Delta H_{decomp} = +75.2$ kJ mol^{-1}

bonds broken	bonds formed
4 C–C in cyclobutane 8 C–H	2 C=C 8 C–H

$\Delta H_{decomp} = 4\,BE(C{-}C)_{cyclobutane} - 2\,BE(C{=}C)$

$75.1 = 4\,BE(C{-}C)_{cyclobutane} - 2(610)$

$BE(C{-}C)_{cyclobutane} = \frac{75.1 + 2(610)}{4}$

$= 323.8 \approx$ **324 kJ mol^{-1}**

Working – **[1]**

Answer – **[1]**

[2]

(ii) Suggest an explanation for the difference between the average C–C bond energy from the *Data Booklet* and the actual value calculated in **(c)(i)**.

From Data Booklet, $BE(C{-}C)_{average} = 350$ kJ mol^{-1}

$BE(C{-}C)_{cyclobutane} < BE(C{-}C)_{average}$

C–C bonds in cyclobutane experience **ring** *OR* **angle strain** and are thus **weaker** than the average C–C bond. **[1]**

[1]

[Total: 14]

3 (a) SO_2 gas is found in air near volcanoes. 213 cm^3 of SO_2 collected at r.t.p. near a volcano required 25.0 cm^3 of 0.120 mol dm^{-3} acidified potassium dichromate(VI) solution for complete reaction.

Calculate the final oxidation state of sulfur in the product mixture.

[R] $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$n_{Cr_2O_7^{2-}} = \frac{25.0}{1000} \times 0.120 =$ **3.00 x 10^{-3} mol**

BP~589

n_e = **3.00 x 10^{-3} × 6 = 1.80 x 10^{-2} mol**

n_{SO_2} = **213/ 24000 = 8.88 x 10^{-3} mol**

$\frac{n_e}{n_{SO_2}} = \frac{1.80\times10^{-2}}{8.88\times10^{-3}}$ **=2.03 ≈ 2 [1]**

Initial O.N. of S: +4

Final O.N. of S = +4 + (+2) = +6 [1]

[2]

(b) The Contact process is an important industrial method of manufacturing sulfuric acid.

The key stage of the Contact process is the reaction between sulfur dioxide and oxygen:

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g) \quad \text{-------- Equation 1}$$

Table 3.1 shows how the percentage of sulfur trioxide in the equilibrium mixtures varies with temperature as well as the volume of the reaction vessels.

Table 3.1

Temperature /°C	Percentage of sulfur trioxide in the equilibrium mixture for vessel		
	A	B	C
800	1.68	0.009	0.88
700	2.98	0.016	1.54
600	5.70	0.032	3.02
500	11.9	0.077	6.71

Using the data in Table 3.1,

(i) explain whether the forward reaction is exothermic or endothermic.

- ✓ **As <u>temperature decreases</u>, the percentage of SO_3 increased i.e. <u>position of equilibrium shifted right</u>.**
- ✓ **By Le Chaterlier's Principle, when temperature decreases, <u>system responds by favouring the exothermic reaction to release heat</u>.**
- ✓ **Therefore the forward reaction is <u>exothermic</u>.**

3 ticks = 2m; 2 ticks = 1m

[2]

(ii) explain and rank the three vessels in order of decreasing volume.

At the same temperature, as volume decreases, <u>total pressure increases</u>, <u>position of equilibrium</u> would <u>shift right</u> to <u>decrease the number of moles of gas</u>, hence <u>decreasing pressure</u>. [1]

Order of decreasing volume: <u>B > C > A</u> [1]

[2]

A mixture containing 2 moles of SO_2 and 1 mole of O_2 was heated in a closed 3.60 dm^3 flask at 500 °C and allowed to reach equilibrium. The flask was then rapidly cooled to liquefy SO_3.

After removing gaseous SO_2 and O_2, excess water was carefully added to the liquid SO_3, causing the following reaction to occur:

$$SO_3(l) + H_2O(l) \rightarrow H_2SO_4(aq) \quad \text{-------- Equation 2}$$

The resulting solution was made up to 250 cm^3 in a standard volumetric flask. 25.0 cm^3 of this solution was titrated with 5.00 mol dm^{-3} NaOH and required 38.50 cm^3 for complete neutralisation.

(iii) Calculate the equilibrium amount of SO_3 at 500 °C.

$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

Amount of H^+ in 25.0 cm^3 of solution = Amount of OH^-

= 5.00 x (38.5 / 1000)

= 0.1925 mol

Amount of SO_3, y = amount of H_2SO_4 = ½ x amount of H^+ in 250 cm^3 solution

= ½ x 0.1925 [1] x (250 / 25.0)

= 0.9625 mol [1]

[2]

(iv) Hence, calculate a value for the equilibrium constant, K_c, of equation 1.

	$2SO_2(g)$ +	$O_2(g)$ ⇌	$2SO_3(g)$
Initial amount/ mol	**2**	**1**	**0**
Change in amount/ mol	**– y**	**– ½y**	**+ y**
Equilibrium amount/ mol	**2–y**	**1–½y**	**y**

Amount of SO_2 = 2 – y = 2 – 0.9625 = 1.0375 = 1.04 mol

Amount of O_2 = 1 – (y/2) = 1 – (0.9625 / 2) = 0.51875 = 0.519 mol [1]

Amount of SO_3 = y = 0.9625 = 0.963 mol

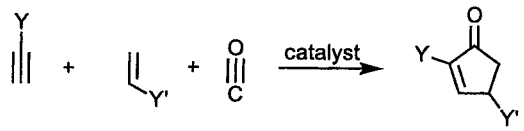
$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{\left(\frac{0.9625}{3.60}\right)^2}{\left(\frac{1.0375}{3.60}\right)^2\left(\frac{0.51875}{3.60}\right)} = 5.97\ mol^{-1}\ dm^3\ [1]$$

[2]

[Total: 10]

More papers at www.testpapersfree.com

4 **(a)** The Pauson-Khand reaction is a gas phase reaction between an alkyne, an alkene and carbon monoxide to form a cyclic carbonyl compound, as shown in Fig. 4.1.



where Y and Y' can be C*l* or H.

Fig. 4.1

An organic compound **A** was produced from the Pauson-Khand reaction. The compound has the following composition by mass; 51.5 % C, 13.7% O, 30.5% C*l* and 4.3% H. The relative molecular mass of **A** is 116.5.
Upon heating with ethanolic $AgNO_3$, **A** gave a white precipitate.

(i) Determine the molecular formula of **A** and draw its structural formula. [2]

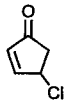
	C	O	C*l*	H
% by mass	51.5	13.7	30.5	4.3
Relative amount / mol	4.29	0.856	0.859	4.3
Simplest ratio	5	1	1	5

Empirical formula of **A**: C_5H_5OCl

Let molecular formula of **A** be $(C_5H_5OCl)_n$

$\therefore$ n(12.0 x 5 + 1.0 x 5 + 16.0 + 35.5) = 116.5

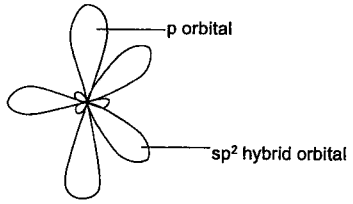
n = 1



Molecular formula of **A** = C_5H_5OCl **[1]** **[1]**

Note: white ppt of AgCl is formed, implies chloroalkane present, so Cl cannot be on the alkene (stronger C-Cl bond due to partial double bond character, similar to chlorobenzene)

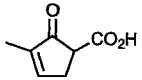
(ii) Draw a diagram to show the orbitals of the carbonyl carbon in compound **A**. State the type of hybridisation involved. [1]



More papers at www.testpapersfree.com
DO NOT WRITE IN THIS MARGIN

sp^2 hybridisation

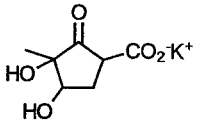
(b) Another possible product of the Pauson-Khand reaction is shown below:



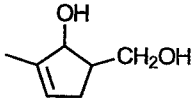
B

Draw the organic product formed when **B** reacts with each of the following.

(i) cold $KMnO_4$(aq) in KOH(aq)



(ii) $LiAlH_4$



[2]

(c) A flask with a volume of 100 cm^3 was first weighed with air filling the flask, and then with another gas **Z**, filling the flask. The results, measured at 26 °C and 1.00 x 10^5 Pa are shown.

Mass of flask containing air	= 47.930 g
Mass of flask containing **Z**	= 47.989 g
Density of air	= 0.00118 g cm^{-3}

Calculate the relative molecular mass of **Z**. [3]

Mass of air	= 100 x 0.00118	= 0.118 g
Mass of flask	= 47.930 – 0.118	= 47.812 g
Mass of Z	= 47.989 – 47.812	= 0.177 g [1]

$$pV = nRT = \frac{m}{M_r}RT$$

$$M_r = \frac{m}{pV}RT = \frac{0.177 \times 8.31 \times 299}{1 \times 10^5 \times 100 \times 10^{-6}}$$ [1]correct *working*

$= 44.0$ [1]correct answer

[Total:8]

BP~591

5 (a) The 'bromine clock' involves a reaction between bromide ions and bromate(V) ions in acid solution:

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

The reaction can be monitored by adding phenol and a constant volume of methyl red to all the experiments.

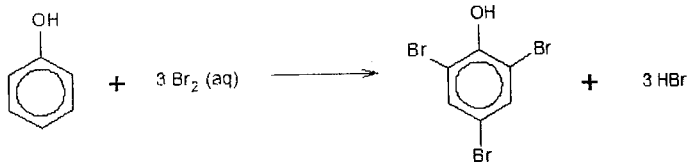
Phenol reacts immediately with the bromine as it is produced. Once all the phenol added has reacted, the bromine that is subsequently produced will oxidise the methyl red causing the disappearance of the red colour in the reaction mixture.

A series of experiments were carried out to investigate the order of reaction with respect to $[BrO_3^-]$ and the results obtained are shown in Table 5.1.

Table 5.1

Expt	Volume of BrO_3^- / cm^3	Volume of Br^- / cm^3	Volume of H^+ / cm^3	Volume of phenol / cm^3	Volume of deionised water / cm^3	Time taken for the colour of methyl red to disappear /s
1	5.0	5.0	10.0	1.0	11.0	82
2	10.0	5.0	10.0	1.0	6.0	42
3	10.0	5.0	10.0	2.0	5.0	x

(i) Write an equation for the reaction between phenol and bromine water.



[1]

(ii) Deduce the order of reaction with respect to $[BrO_3^-]$. Explain your reasoning.

Expt	Volume of BrO_3^- / cm^3	Time taken for the colour of methyl red to disappear /s	Relative rate / $cm^3\ s^{-1}$
1	5.0	82	1/82 = 0.0122
2	10.0	42	1/42 = 0.0238

Comparing expts 1 and 2 where the $[Br^-]$ and $[H^+]$ are constant, the rate is doubled when $[BrO_3^-]$ is doubled. Thus, the reaction is first order w.r.t $[BrO_3^-]$.

[1]

(iii) Using your answer in **(a)(ii)**, calculate the value of x.

The volume and amount of phenol will affect the amount of bromine that it would react with. Hence, the time taken for the colour of methyl red to disappear would also be different.

rate $\propto \frac{Vol\ of\ phenol}{time}$

Comparing expt 1 and 3,

$\frac{\frac{1}{82}}{\frac{2}{x}} = (\frac{5}{10})$

x = 82 s [1]

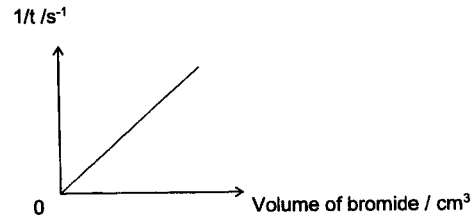
Alternative answer:

Comparing expt 2 and 3

$\frac{\frac{1}{42}}{\frac{2}{x}} = (\frac{10}{10})$

x = 84 s

(iv) Another series of experiments were conducted with varying volumes of bromide ions and large excess of BrO_3^- and H^+. The total volume of the mixture was kept constant. The results obtained were used to plot a graph of 1/t against the volume of bromide.



Deduce the order with respect to $[Br^-]$, explain your reasoning.

The order of reaction with respect to $[Br^-]$ is 1 as the graph shows a line passing through origin i.e. rate of reaction is directly proportional to $[Br^-]$. [1]

(v) Given that the unit of the rate constant is $mol^{-3}\ dm^9\ s^{-1}$, deduce the order with respect to $[H^+]$.

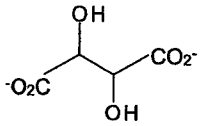
rate = k $[Br^-][BrO_3^-][H^+]^y$

(mol $dm^{-3}\ s^{-1}$) = ($mol^{-3}\ dm^9\ s^{-1}$)(mol dm^{-3})(mol dm^{-3})(mol dm^{-3})^y

y = 2 [1]

DO NOT WRITE IN THIS MARGIN
More papers at www.testpapersfree.com

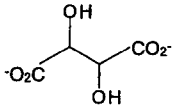
(b) The reaction between $S_2O_8^{2-}$ and tartrate ions is catalysed by iron(III) ions and the overall equation is as shown.



$+ 3S_2O_8^{2-} + 2H_2O \rightarrow 2CO_2 + 2HCO_2^- + 6H^+ + 6SO_4^{2-}$

Tartrate ions

Write equations to illustrate how iron(III) ions catalyses the reaction.



$6Fe^{3+} +$ $+ 2H_2O \rightarrow 6Fe^{2+} + 2CO_2 + 2HCO_2^- + 6H^+$ [1]

$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$ [1]

(c) Methyl red is a pH indicator. It is red when the pH is less than 4.4 and yellow when the pH is above 6.2.

In microbiology, methyl red is used to identify bacteria that produces acids from the metabolism of glucose. The type of acid produced depends on the specific enzymatic pathways present in the bacteria.

All the bacteria initially metabolise glucose to pyruvic acid, CH_3COCO_2H. After which, some bacteria use the mixed acid pathway to metabolise pyruvic acid while other bacteria use the butanediol fermentation pathway. The products formed and the colour of methyl red are shown in Table 5.2.

Table 5.2

Metabolism pathway	Products formed per mole of glucose	Colour of methyl red
Mixed acid pathway	4 mol of acids (mainly lactic acid, $CH_3CH(OH)CO_2H$, and ethanoic acid), 1 mol of ethanol, 1 mol of CO_2 1 mol of H_2	Red
Butanediol fermentation pathway	1 mol of acid	Yellow

(i) Explain the colours of methyl red shown in Table 5.2.

For the mixed acid metabolism pathway, the <u>larger amount</u> of acids produced <u>lower the pH to below 4.4</u> resulting in methyl red turning red.

For the butanediol fermentation pathway, less acid is produced so the pH is <u>not lowered to less than 6.2 / is more than 6.2</u> (and less than 7) hence it appeared as yellow. [1]

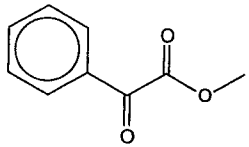
More papers at www.testpapersfree.com

(ii) State the reagent and condition to obtain lactic acid from pyruvic acid.

pyruvic acid lactic acid

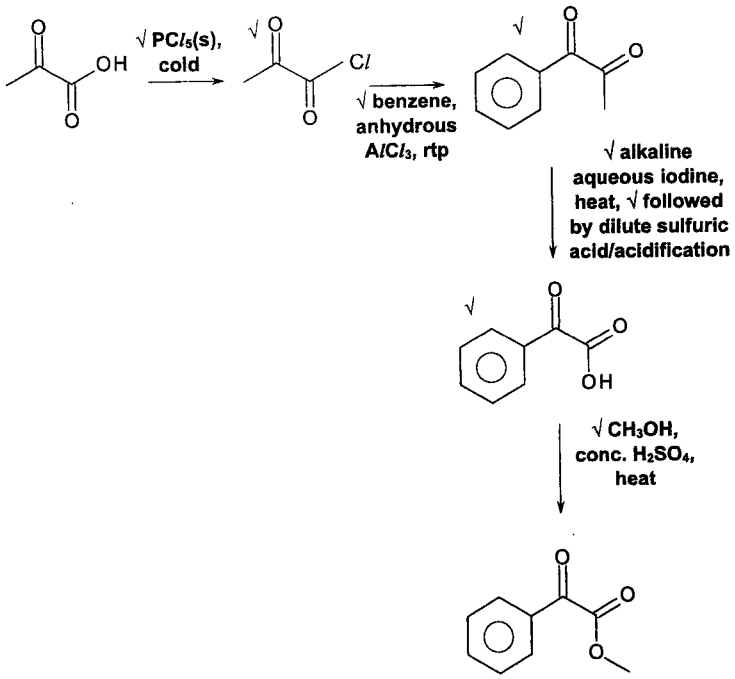
$NaBH_4$ in alcohol, rtp [1]

(iii) Suggest the reagents and conditions, including the structures of the intermediates, for the synthesis of compound **Y** from pyruvic acid.



compound **Y**

BP~593



(steps 2 and 3 can be swapped)

(d) Table 5.3 shows the pK_a values of some compounds, including phenol.

Table 5.3

Compound	pK_a
Phenol	10.0
Phenylmethanol, $C_6H_5CH_2OH$	15.4
Phenylmethanethiol, $C_6H_5CH_2SH$	9.93

(i) Suggest how the acidities of phenol and phenylmethanol compare with each other.

The lower the pK_a, the stronger the acid. Hence, the acid strength is

C_6H_5OH > $C_6H_5CH_2OH$

The more stable the anion formed, the stronger the acid.

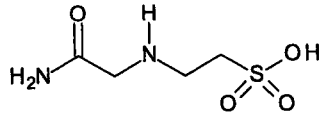
C_6H_5OH is the stronger acid because the lone pair of electrons on the oxygen atom of $C_6H_5O^-$ ion is delocalised into the benzene ring. This disperses the negative charge on the oxygen atom, stabilising the $C_6H_5O^-$ ion. [1]

The electron-donating $C_6H_5CH_2$- group intensifies the negative charge on the $C_6H_5CH_2O^-$ ion, destabilising the anion. The negative charge is also localised on the O atom of the $C_6H_5CH_2O^-$. Therefore, $C_6H_5CH_2OH$ is the weaker acid and has the less tendency to dissociate to give H^+ than C_6H_5OH [1]

(ii) Suggest a reason why the pK_a for $C_6H_5CH_2SH$ is much lower than that for $C_6H_5CH_2OH$.

$C_6H_5CH_2SH$ is a much stronger acid than $C_6H_5CH_2OH$ because the size of S atom is larger than O atom, which leads to less effective atomic orbital overlap and weaker S – H bond. Hence, $C_6H_5CH_2SH$ dissociates more readily to give H^+. [1]

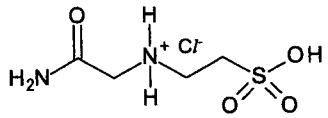
(e) ACES, $C_4H_{10}N_2O_4S$, is another compound containing sulfur.



ACES

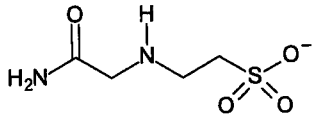
ACES has a pK_a value of 6.88.

(i) Draw the structure of the product formed when dilute hydrochloric acid is added to ACES at room temperature.



[1]

(ii) Draw the structure of the conjugate base of ACES.



[1]

(iii) The pH of a solution of ACES is 2.2.

Calculate the ratio of [conjugate base of ACES] to [ACES].

More papers at www.testpapersfree.com

$K_a = \frac{[C_4H_9N_2O_4S^-][H^+]}{[C_4H_{10}N_2O_4S]}$

$10^{-6.88} = \frac{[C_4H_9N_2O_4S^-]10^{-2.2}}{[C_4H_{10}N_2O_4S]}$

$\frac{[C_4H_9N_2O_4S^-]}{[C_4H_{10}N_2O_4S]} = 2.09 \times 10^{-5}$ **[1]**

Alternative method: use buffer equation.

(iv) 0.0200 mol of the conjugate base of ACES is dissolved in 100 cm^3 of deionised water. 50 cm^3 of 0.300 mol dm^{-3} of hydrochloric acid was added to the solution.

Given that the conjugate base reacts with hydrochloric acid in a 1:1 stoichiometry, calculate the pH of the solution.

	$C_4H_9N_2O_4S^-$	+ HCl	→ $C_4H_{10}N_2O_4S$	+ NaCl
Initial no. of moles /mol	0.0200	$\frac{50}{1000} \times 0.3$	0	0
Final no. of moles / mol	0.020 – 0.015 = 0.005	0	0.015	

correct calculation of the amount of salt and acid [1]

$pH = pK_a + \log \frac{[C_4H_9N_2O_4S^-]}{[C_4H_{10}N_2O_4S]}$

$= 6.88 + \log \frac{(0.005)/\frac{150}{1000}}{(0.015)/\frac{150}{1000}}$

$= 6.40$ **[1]**

[Total: 20]

More papers at www.testpapersfree.com
DO NOT WRITE IN THIS MARGIN

6 The Gabriel synthesis is a 3-step approach to synthesis amines. Phthalimide is used as the main reactant, which has a nitrogen atom flanked by two carbonyl groups.

Propylamine is obtained from the Gabriel synthesis method as shown in Fig. 6.1.

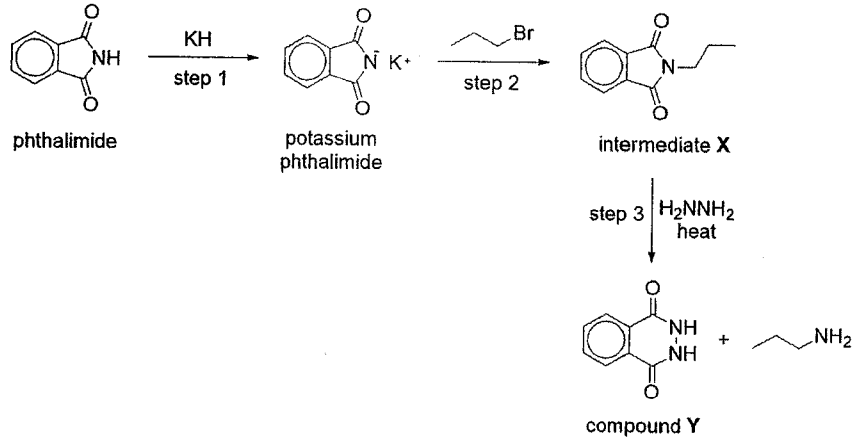


Fig. 6.1

(a) (i) State the role of phthalimide in the above reaction in step 1. [1]

• Bronsted acid

(ii) With reference to the product formed in step 1, explain why phthalimide is able to function as the role identified in **(a)(i)**. [1]

Phthalimide can function as an acid as after deprotonation, the <u>lone pair of electrons on the nitrogen atom can be delocalised over the 2 C=O groups, resulting in resonance stabilised anion</u>. Hence, phthalimide can dissociate H^+ in water easily.

(b) Step 2 of Gabriel synthesis is a nucleophilic substitution reaction.

With reference to the structures of relevant reactants, explain why potassium phthalimide does not react with 2-bromo-2-methylpropane at all. [2]

✓ For S_N2 reaction, the <u>nucleophile approach is blocked by the bulky alkyl groups behind the C-Br bond</u>.

✓ For S_N1 reaction, the <u>bulky benzene ring in potassium phthalimide makes it difficult for it to approach the carbocation</u>.

Hence, there is • <u>high steric hindrance around both potassium phthalimide and 2-bromo-2-methylpropane</u>, hence it is difficult for the nucleophile to react with 2-bromo-2-methylpropane.

Every 2 ✓ = 1 mark

DO NOT WRITE IN THIS MARGIN
BP~595

BP~596

(c) Suggest another reagent and condition used to liberate the free amine from intermediate **X** in the last step.

Construct a balanced equation for this reaction, showing the structures of all reactants and products. [2]

• **Dilute NaOH / KOH, heat.**

•

(d) A sample contains both propylamine and compound **Y** after the Gabriel synthesis shown in Fig. 6.1. A student decides to purify propylamine from the impure sample and starts by adding an equal volume of dilute hydrochloric acid, with stirring, to the sample.

Some physical data for various compounds are given in Table 6.1.

Table 6.1

	propylamine	water	compound **Y**
Density / g cm^{-3}	0.719	1.0	1.3
Boiling point / °C	47.8	100.0	523.5

(i) With reference to structure and bonding, explain the purpose of the addition of dilute hydrochloric acid in the purification process. [3]

Propylamine reacts with hydrochloric acid to form a ✓ salt, which has ionic bonds between the cations and anions. ✓ Water is a polar solvent with hydrogen bonds between the solvent molecules. The ✓ formation of ion-dipole interactions between the ions and water molecules releases ✓ sufficient energy to overcome both the ionic bonds in the salt and hydrogen bond between water molecules. Hence the ✓ salt of propylamine will be more soluble in aqueous medium and hence ✓ extracted out as a separate layer from organic compound Y.

Every 2 ✓ = 1 mark

(ii) Starting with the mixture from **(d)(i)**, plan an experiment to purify propylamine from the impure mixture. [3]

Your plan should include details of:

• how propylamine is obtained in its anhydrous liquid form; and

• suitable apparatus used.

Pour the mixture from (d)(i) into a ✓ separatory funnel. ✓ Stopper and shake the separatory funnel, occasionally opening the tap to prevent pressure build-up.

✓ Collect the upper aqueous layer (containing salt of propylamine) from the separatory funnel into a conical flask. ✓ Add dilute NaOH, with stirring, until the solution is just made alkaline by occasionally testing with red litmus paper. Transfer the mixture to a round bottom flask and add boiling chips.

✓ Connect the round bottom flask to a distillation setup with a thermometer. Propylamine will be the first distillate to be collected when the thermometer reads 47.8 °C.

DO NOT WRITE IN THIS MARGIN

✓ Add anhydrous $MgSO_4$ / Na_2SO_4 / $CaCl_2$ / $CaSO_4$, with stirring, to dry the distillate. Filter the suspension into a dry conical flask to obtain anhydrous propylamine.

Every 2 ✓ = 1 mark

(e) A student made the following statement in his journal

"Using a 2:1 mole ratio of bromomethane and potassium phthalimide in the Gabriel synthesis method will produce a dimethylamine."

Comment on the validity of the student's statement. [2]

The student's statement is • incorrect / invalid / wrong.

The • lone pair of electrons on the nitrogen atom on intermediate X is delocalised over the 2 neighbouring C=O groups, hence it is no longer available to act as nucleophile to attack the electron deficient C of a second equivalent of bromomethane. Bromomethane and potassium phthalimide will only react in a 1:1 mole ratio.

[Total: 14]

DO NOT WRITE IN THIS MARGIN

More papers at www.testpapersfree.com

TEMASEK JUNIOR COLLEGE

2022 JC2 PRELIMINARY EXAMINATION

Higher 2

TEMASEK JUNIOR COLLEGE

CANDIDATE NAME **WORKED SOLUTIONS**

CENTRE NUMBER S

INDEX NUMBER

Chemistry **9729/03**

Paper 3 Free Response Questions **14 September 2022**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do **NOT** open this booklet until you are told to do so.

Write your name, civics class, centre number and index number on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

The number of marks is given in brackets [ ] at the end of each question or part question

For Examiner's Use		
Paper 3	Q1	/18
	Q2	/20
	Q3	/22
	Q4	/20
	Q5	/20
	Total	/80

This document consists of **23** printed pages and **1** blank page.

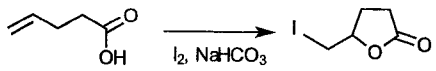
More papers at www.testpapersfree.com

Section A

Answer **all** the questions in this section.

1 **(a)** Iodolactonisation reaction was first reported by M. J. Bougalt in 1904 and has since become one of the most effective ways to synthesise lactones.

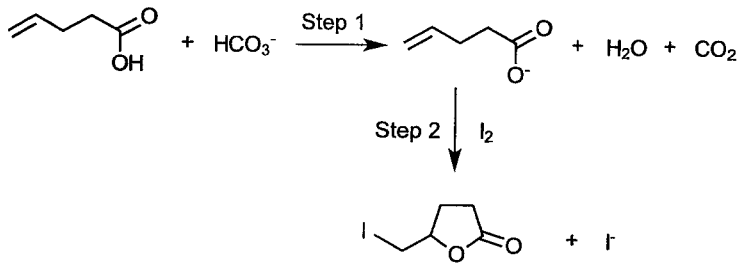
An example of the iodolactonisation is the reaction of 4-pentenoic acid as shown in Fig 1.1.



Compound X

Fig 1.1

Two simplified steps in the iodolactonisation mechanism are given in Fig 1.2.



Compound X

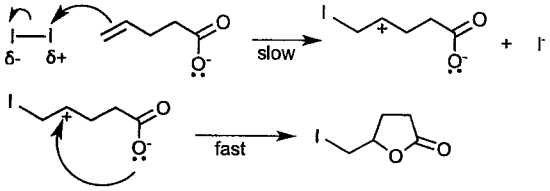
Fig 1.2

(i) Suggest the role of HCO_3^- in step **1**. [1]

It acts as a Bronsted-Lowry <u>base</u> to abstract H^+ from the carboxylic acid.[1]

(ii) Suggest the mechanism for reaction taking place in **Step 2.** Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [3]

- **Electrophilic addition**



Name of mechanism [1]

Mechanism [2]

BP~597

(iii) Sketch a well-labelled reaction pathway diagram for the reaction in **Step 2**, given that the reaction is exothermic. [2]

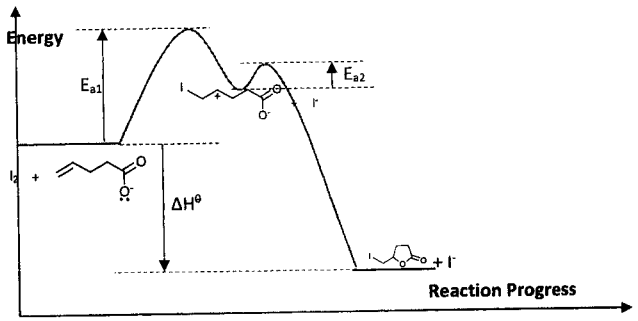
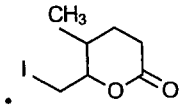


Diagram & labelling:[1]

E_{a1}, E_{a2} & $\Delta H^{\ominus}$: [1]

(iv) Suggest the structural formulae of the final organic product formed when $CH_2{=}CHCH(CH_3)CH_2CH_2COOH$ undergoes iodolactonisation in a similar process in Fig 1.1. [1]



(b) Carbon monoxide is one of the most widespread and dangerous industrial hazards. The formation of carboxyhaemoglobin, $Hb(CO)_4$, takes place much more readily than the formation of oxyhaemoglobin, $Hb(O_2)_4$.

$Hb(aq) + 4O_2(aq) \rightleftharpoons Hb(O_2)_4(aq)$ ... **(1)**

$Hb(aq) + 4CO(aq) \rightleftharpoons Hb(CO)_4(aq)$ ... **(2)**

A treatment method for carbon monoxide poisoning is to provide the patient with pure oxygen gas over a period of time.

With reference to the equations given above, explain why this is a suitable treatment method. [2]

Providing O_2 forms $Hb(O_2)_4(aq)$, which ✓ **shifts the position of 1st equilibrium to the right,** ✓ **removing Hb(aq)** from the bloodstream.

By Le Chatelier's Principle, the ✓ **position of 2nd equilibrium will shift left to** ✓ **increase amount of Hb(aq),** thus reducing the amount of $Hb(CO)_4(aq)$ in the body.

2✓: [1]

(c) The water-gas shift reaction is used to produce hydrogen gas industrially by reacting carbon monoxide with water vapour.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

An evacuated tank was initially filled with 0.0197 atm of CO and 0.0394 atm of H_2O at 600 K. It was sealed and left to stand. At equilibrium, the partial pressure of CO_2 was found to be 0.0191 atm.

(i) Calculate the value of K_p at 600 K. [2]

	CO (g)	+ H_2O (g)	⇌ CO_2 (g)	+ H_2 (g)
Initial P / atm	0.0197	0.0394	0	0
Δ in P / atm	–0.0191	–0.0191	+0.0191	+0.0191
Eqm P / atm	**0.0006**	**0.0203**	**0.0191**	**0.0191**

Working [1]

$$K_p = \frac{(0.0191)(0.0191)}{(0.0006)(0.0203)} = 30.0$$

Answer [1]

Table 1.1 shows how the value of K_p varies with temperature.

Table 1.1

T / K	300	900	1500
value of K_p	1.170×10^5	1.978	0.2195

(ii) The Gibbs free energy, $\Delta G^{\ominus}$ (in J mol^{-1}), and the equilibrium constant, K_p, of a reaction are related by the following equation:

$$\Delta G^{\ominus} = -RT \ln K_p,$$

where R is the molar gas constant and T is the temperature in Kelvins.

Using the given values of K_p, calculate the values of $\Delta G^{\ominus}$ at 300 K and 900 K. Hence, determine the value of $\Delta S^{\ominus}$ for the water-gas shift reaction.

(Assume that both $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ are independent of temperature.) [3]

$\Delta G^{\ominus}_{(300)} = -RT \ln K_{p(300)}$

$= -(8.31)(300) \ln (117000) = -29090$ J mol^{-1} [√]

$\Delta G^{\ominus}_{(900)} = -RT \ln K_{p(900)}$

$= -(8.31)(900) \ln (1.978) = -5101$ J mol^{-1} [√]

$\Delta G^{\ominus}_{(300)} = \Delta H^{\ominus} - (300)\Delta S^{\ominus} = -29090$ J mol^{-1} ----- (1) **allow ecf [√]**

$\Delta G^{\ominus}_{(900)} = \Delta H^{\ominus} - (900)\Delta S^{\ominus} = -5101$ J mol^{-1} ----- (2) **allow ecf [√]**

(1) – (2): $\Delta S^{\ominus} = -40.0$ J K^{-1} mol^{-1} (3 sf) **allow ecf [1] include unit**

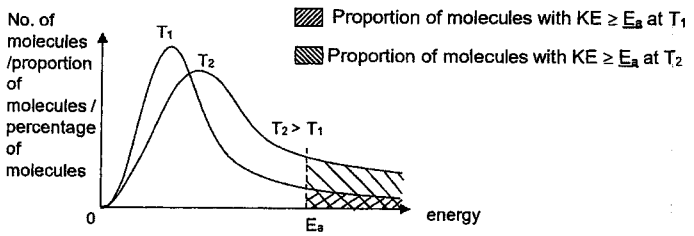
(iii) Comment on the magnitude of the calculated value of $\Delta S^{\ominus}$. [1]

More papers at www.testpapersfree.com

The magnitude is **small** as there is **no change in the amount of gaseous molecules** when reactants changed to products. Hence, there is little change in the number of ways that energy can be distributed over the molecules.

(iv) With the aid of a sketch of the Boltzmann distribution, explain how an increase in temperature affects the rate of water-gas shift reaction. [3]

Boltzmann distribution diagram: **[1]**



At higher temperatures, **the proportion of molecules with kinetic energy greater than or equal to activation energy increases** [√].

Frequency of effective collision increases [√],

rate constant increases [√],

rate increases [√].

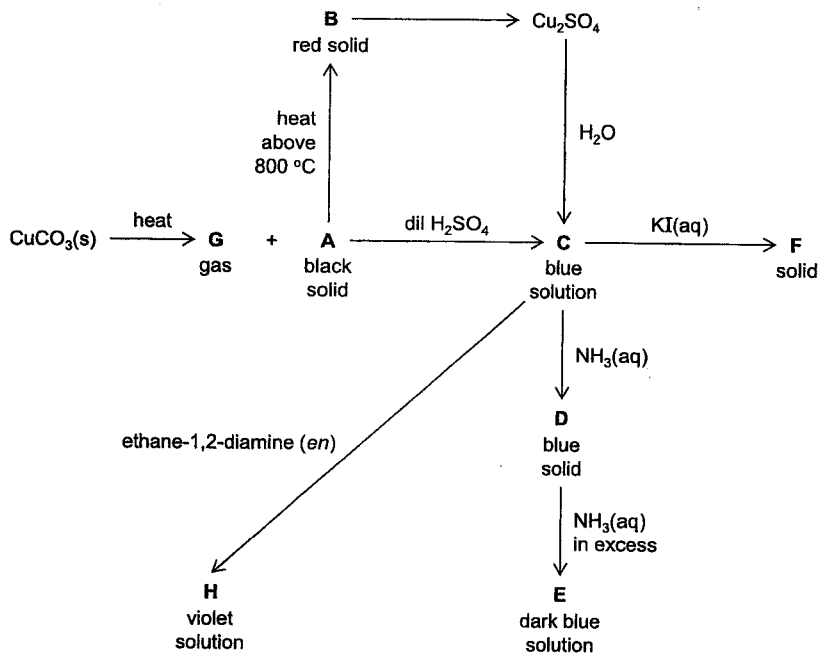
2√: [1]

[Total:18]

More papers at www.testpapersfree.com
DO NOT WRITE IN THIS MARGIN

2 Copper is a typical transition element with more than one oxidation state. Many of its compounds have colours in the blue-green-yellow part of the visible spectrum.

The following reaction scheme shows the chemistry of some copper-containing species.



(a) **(i)** **A** and **B** are both compounds of copper and oxygen only.

Cu_2SO_4 can be made from **B** under certain anhydrous conditions. The oxidation number of copper in **B** is the same as in Cu_2SO_4.

Identify gas **G**, and write the formula of the copper-containing species in **A** to **C**. [2]

G: CO_2 **A**: CuO **B**: Cu_2O **C**: $[Cu(H_2O)_6]^{2+}$

1 tick for each answer.

4 ticks – [2]

2 to 3 ticks – [1]

(ii) Suggest, with reason, the colour of solid **F**. [2]

Oxidation of copper in **F**, CuI = +1

Electronic configuration of Cu^+: [Ar] $3d^{10}$

The d orbitals of Cu^+ ion are **fully filled**.

DO NOT WRITE IN THIS MARGIN
DO NOT WRITE IN THIS MARGIN
BP~599

No electrons can undergo d-d transition from the lower energy group of d orbitals to the higher energy group. *OR* **No d-d electronic transition can occur**. **[1]**

Thus, solid **F** is expected to be **white** *OR* **grey-white**. **[1]**

(b) Explain the transformations from **C** to **E** in terms of the competing equilibria and the type of reaction that has occurred. Include equations and the formulae of all copper-containing species. [4]

- ✓ When $NH_3(aq)$ is added dropwise to **C**, a blue precipitate **D**, **$Cu(OH)_2(H_2O)_4$** *OR* **$Cu(OH)_2$**, is formed. **NH_3 acts as a base**.
- ✓ $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
- ✓ When excess $NH_3(aq)$ is added, **E**, which contains the dark blue complex, **$[Cu(NH_3)_4(H_2O)_2]^{2+}$**, is formed **$NH_3$ acts as a ligand** here.
- ✓ By Le Chatelier's Principle, **concentration of $[Cu(H_2O)_6]^{2+}$ decreases**, and **position of equilibrium (1) shifts left**, causing **D** to dissolve.

4 ticks – [2]

2 to 3 ticks – [1]

$[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(H_2O)_4(s) + 2H_2O(l)$ ----- (1)

OR $Cu^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s)$ ----- (1) **[1]**

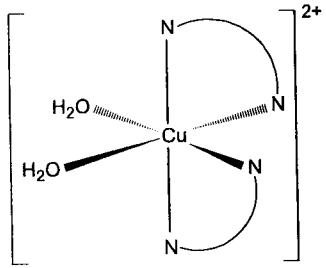
$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$ **[1]**

(Note: equation does not start with $Cu(OH)_2(H_2O)_4$)

(c) Like many organic compounds, transition metal complexes also exhibit stereoisomerism, namely *cis-trans* isomerism and enantiomerism.

For example, $[Cu(en)_2(H_2O)_2]^{2+}$, the complex ion present in **H**, has three stereoisomers, **X**, **Y** and **Z**. One of these stereoisomers, **X**, is shown below.

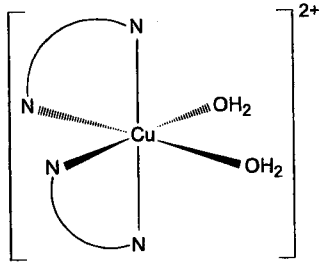
(N⌒N represents the *en* ligand.)



X

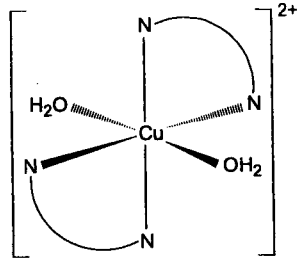
X and **Z** are *cis-trans* isomers, while **Y** is an enantiomer of **X**.

Draw and label clearly the three-dimensional diagrams of **Y** and **Z**. You should use N⌒N to represent the *en* ligand. [3]



[1]

Y



[1]

Z
(*trans*-isomer of X)

Correct labels for Y and Z – [1]

(d) Selective precipitation is a technique of separating ions in an aqueous solution by using a reagent that precipitates one or more of the ions, while leaving other ions in solution. In the case of Cu^{2+} ions, the separation is achieved by adjusting the pH so that only Cu^{2+} ions are precipitated.

In an experiment, a student adds sodium hydroxide gradually to a solution containing 0.100 mol dm^{-3} Cu^{2+} ions and 0.100 mol dm^{-3} Fe^{2+} ions.

Relevant K_{sp} values are given in Table 2.1.

Table 2.1

metal hydroxide	K_{sp} / mol^3 dm^{-9}
$Cu(OH)_2$	2.2×10^{-20}
$Fe(OH)_2$	8.0×10^{-16}

Determine the pH at which maximum separation of the two cations is achieved. [2]

$$K_{sp}\ of\ Fe(OH)_2 = [Fe^{2+}][OH^-]^2$$
$$8.0 \times 10^{-16} = (0.100)[OH^-]^2$$
$$[OH^-] = 8.944 \times 10^{-8}\ mol\ dm^{-3}$$

Calculation of $[OH^-]$ at max separation – [1]

∴ pH at maximum separation = $14 - [-\log_{10}(8.944 \times 10^{-8})]$ = **6.95** **[1]**

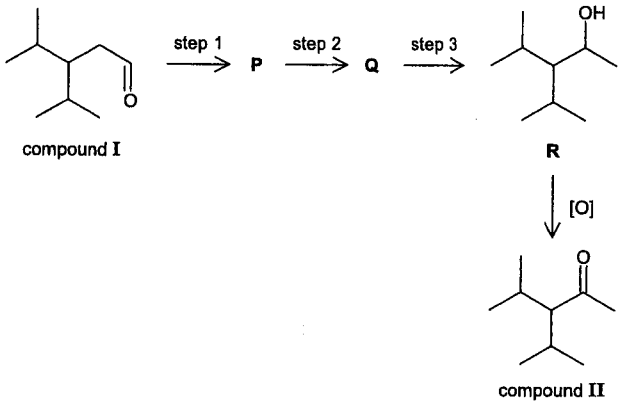
Explanation:

$Cu(OH)_2$ would first be precipitated as a lower concentration of OH^- is needed for precipitation. Maximum separation is achieved when the *maximum amount of $Cu(OH)_2$ has precipitated i.e.* just before $Fe(OH)_2$ is precipitated i.e. a saturated solution of $Fe(OH)_2$.

BP~600
DO NOT WRITE IN THIS MARGIN
More papers at www.testpapersfree.com

(e) **(i)** Compound **II** can be converted from compound **I** in four steps.

State the reagents and conditions you would use for steps 1–3 and give the structures of compounds **P** and **Q**.



[5]

step	reagents & conditions	compound
1	$LiAlH_4$ in dry ether, r.t.p. *OR* $NaBH_4$ in ethanol, r.t.p. *OR* H_2, Ni, high temperature and pressure *OR* H_2, Pd or Pt, r.t.p. [1]	OH [1] P
2	excess conc H_2SO_4, 170 °C *OR* Al_2O_3, 400 °C [1]	[1] Q
3	cold, conc H_2SO_4, followed by $H_2O(l)$, heat *OR* $H_2O(g)$, conc H_3PO_4, high temperature and pressure [1]	–

(ii) Suggest how compounds **II** and **R** could be distinguished from one another by means of a simple chemical test. [2]

Appropriate chemical test: [1]

Observation for both compounds: [1]

Possible Tests:

		Observations

More papers at www.testpapersfree.com

	To each compound separately, add	II (ketone)	R (secondary alcohol)
1	**2,4-dinitrophenylhydrazine.** **Accept 2,4-DNPH *OR* Brady's reagent.**	**Orange ppt**	**No ppt**
2	solid **PCl_5**	**No white fumes**	**White fumes** (of HCl)
3	**Na(s)**	**No effervescence**	**Effervescence.** H_2 gas evolved "pops" with a lighted splint
4	**$K_2Cr_2O_7$(aq), dil H_2SO_4** and **heat** in a water bath. **Accept acidified $K_2Cr_2O_7$.**	**Orange** solution does **not turn green.**	**Orange** solution **turns green.**
5	**$KMnO_4$(aq), dil H_2SO_4** and **heat** in a water bath. **Accept acidified $KMnO_4$.**	**Purple** solution is **not decolourised.**	**Purple** solution is **decolourised.**

[Total: 20]

3 **(a)** The reaction of $SiBr_4$ with moist ethoxyethane produces two oxybromides with the formula $Si_3O_2Br_8$ (M_r = 755.5) and Si_2OBr_6 (M_r = 551.6).

When 0.192 g of one of the oxybromides reacts with excess water, all the bromine atoms are converted to bromide ions. Excess silver nitrate is added and 0.392 g of cream precipitate is obtained.

(i) Determine, with the aid of calculations, the identity of the oxybromide which reacted with excess water. [2]

Cream ppt is AgBr, M_r = 187.8

Amt of ppt formed = 0.392/187.8 = 0.002087 mol

Amt of $Si_3O_2Br_8$ used = 0.192/755.5 = 2.541 x 10^{-4} mol (8.2 Br atoms)

Amt of Si_2OBr_6 used = 0.192/551.6 = 3.481 x 10^{-4} mol (5.99 Br atoms)

Hence, the oxybromide is Si_2OBr_6 [1]

working [1]

(ii) The cream precipitate was only sparingly soluble in excess aqueous ammonia. However, on addition of aqueous sodium cyanide, the precipitate completely dissolves.

The numerical values of the stability constant, K_{stab}, for the relevant complex ions are given below.

Complex	Stability constant / K_{stab}
$[Ag(NH_3)_2]^+$	1.7 x 10^7

BP~601

$[Ag(CN)_2]^-$	1.0×10^{21}

With reference to the table above, briefly explain the observations above as fully as you can. [3]

Cream ppt AgBr is sparingly soluble in water and exists in equilibrium with its aqueous ions

$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$ ... (1)

In the presence of aqueous NH_3, free Ag^+ forms a complex ion, $[Ag(NH_3)_2]^+$. However since AgBr has moderate K_{sp} value, ionic product $[Ag^+][Br^-]$ decreases but remains larger than K_{sp}(AgBr), so the ppt is remains insoluble. [1]

When cyanide ions are added, ✓ Ag^+ forms a more stable complex due to larger K_{stab} value. Hence ✓ conc of Ag^+ decrease to a greater extent. [1]

By Le Chatelier's principle, ✓ position of equilibrium (1) shifts to right to increase conc of Ag^+ ions. ✓ Ionic product decreases below K_{sp}, hence cream ppt dissolves. [1]

(b) Polypeptide chain **Y** has a sequence of 8 α-amino acids. 2 enzymes, **E1** and **E2**, are added to separate samples of **Y** and the following fragments are obtained.

Fragments after reaction with **E1**	Fragments after reaction with **E2**
val-gln-phe	cys-phe-val
cys-phe	gln-lys-asp
gln-lys-asp	gln-phe

E1 hydrolyse the peptide bond at the carboxylic acid end of phenylalanine (phe) while **E2** hydrolyse the peptide bond at the amino end of glutamine (gln).

(i) Under specific conditions, the dipeptide cys-phe exists as a zwitterion. Explain

- the term "zwitterion"; and
- one physical property of the cys-phe dipeptide to support its existence as a zwitterion. [2]

• A zwitterion is a dipolar compound that contains both cationic and anionic groups and is electrically neutral. [1]

1 physical property **[1]**:

High melting point: in the solid state, dipeptide exist as zwitterions in which both the anion and cation are held in the same unit (an internal salt). A large amount of energy is required to overcome the strong electrostatic forces of attraction or ionic bonds between the zwitterions.

Soluble in water: formation of ion-dipole interactions between water and zwitterions release sufficient energy to overcome the ionic bonds between the zwitterions and hydrogen bonds between water molecules.

The table below shows the R group of some α-amino acids and the pK_a values of respective functional groups.

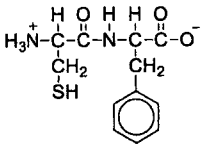
Amino acid	Structure of R-group	pK_a of α-amino group	pK_a of α-carboxylic group	pK_a of R group
cys	$-CH_2SH$	10.28	1.91	8.14
phe	$-CH_2-$	9.09	2.18	-

(ii) Draw the zwitterion of cys-phe and determine a pH at which the cys-phe exists as a zwitterion as the predominant species. [2]

At 1st equivalence point, the α-COOH of Phe is deprotonated, giving a zwitterion

Hence isoelectric point, pI = ½ (2.18+8.14) = 5.16 [1] (accept between 2.18 and 8.14)

Structure of zwitterion is



[1]

(iii) Deduce the sequence of the amino acids in polypeptide chain **Y**. [2]

E1 hydrolyse the peptide bond at the carboxylic acid end of phe, so 2 possible structures are:

val-gln-phe-cys-phe-gln-lys-asp

cys-phe-val-gln-phe-gln-lys-asp

E2 hydrolyse the peptide bond at the amino end of gln, so 2 possible structure are:

cys-phe-val-gln-lys-asp-gln-phe

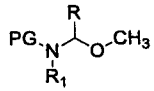
cys-phe-val-gln-phe-gln-lys-asp

logical reasoning / working **[1]**

Hence the correct sequence of amino acids in Y is

• cys-phe-val-gln-phe-gln-lys-asp [1]

Compound **A** is formed from the electrolysis from α-amino acids in methanol solvent,

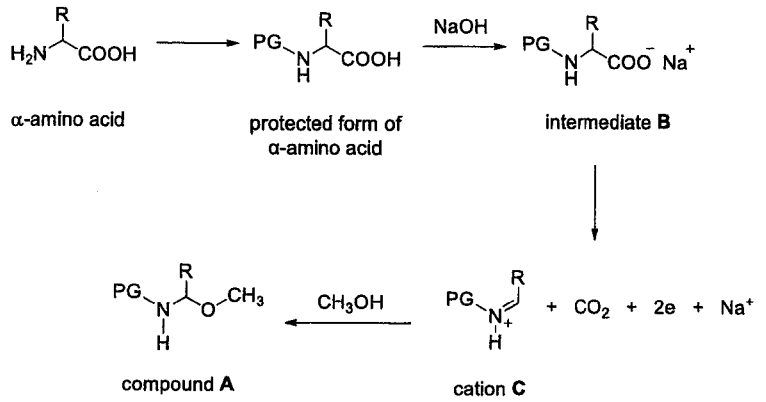


compound **A**

where R is alkyl, R_1 is alkyl or hydrogen and PG is the protecting group, CH_3CO–.

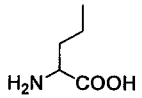
More papers at www.testpapersfree.com

The α-amino acids are first converted to its protected form, followed by reaction with sodium hydroxide to form an intermediate, **B**.



At the anode, the anion in intermediate **B** undergoes decarboxylation to form cation **C**. No other reactions occur at the anode.

Norvaline is an α-amino acid which is used in dietary supplement for bodybuilding. It undergoes the electrolysis reaction above.



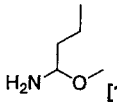
norvaline

(c) State the reagent and condition to convert norvaline to its protected form. [1]

CH_3COCl, room temp [1]

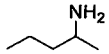
(d) Compound **A** undergoes hydrolysis to form amine **X**.

(i) Draw the structure of amine **X**, when norvaline undergoes the electrolysis reaction above, followed by hydrolysis. [1]



[1]

(ii) Explain the difference in basicity of amine **X** and 2-aminopentane. [2]



2-aminopentane

Amine X is <u>less basic</u> than 2-aminopentane. [1]

More papers at www.testpapersfree.com
DO NOT WRITE IN THIS MARGIN

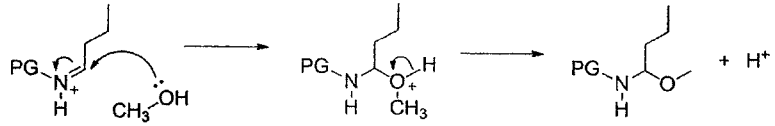
The presence of the <u>electron withdrawing oxygen atom reduces the electron density on the nitrogen atom in amine X</u>. The <u>lone pair electrons are less available to accept / dative bond with H^+</u>.[1]

(e) Cation **C** subsequently reacts with methanol, as a nucleophile to give **A** in 2 steps.

Step 1: methanol attacks the electron deficient carbon in cation **C**, to form another cation intermediate.

Step 2: the intermediate undergoes deprotonation to give **A**.

Starting with the appropriate structure of **C** which is produced from norvaline, use appropriate curly arrows to show how the **A** is formed at the anode. Show clearly the charges and lone pair of electrons as well as structure of intermediate formed. [2]



1 mark for each step + charges + lone pair e and curly arrows

(f) **(i)** The standard reduction potential of CO_2/CH_3OH is +0.45 V, measured against the standard hydrogen electrode.

Write the ion-electron half reaction for the complete oxidation of methanol. [1]

$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e$

(ii) With reference to the reaction occurring at the anode for the electrolysis, suggest a suitable standard reduction potential value for (cation **C**)/(compound **B**) and explain your answer. [2]

• **+0.40 V** *(any value less positive than +0.45 V. Accept only 1 value, reject if range is given instead)*

At the anode, both CH_3OH and anion intermediate B can be oxidised. Since <u>B</u> • <u>is preferentially oxidised at the anode</u> instead of CH_3OH, its <u>E° value has to be less positive</u>, implying that <u>B is more easily oxidised</u> than CH_3OH at the anode.

(g) The efficiency of the electrolysis reaction of compound **A** is around 95%.

A current of 0.1 A was applied to the electrolytic cell consisting of *N*-protected norvaline for 1 hour.

Calculate the mass of compound **A** produced at the anode when norvaline undergoes the electrolysis reaction. [M_r of **A**: 145.0] [2]

[Total: 22]

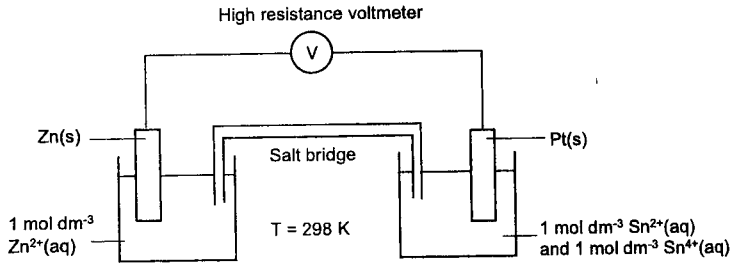
DO NOT WRITE IN THIS MARGIN
BP~603

Section B

Answer **one** question from this section.

4 **(a)** An electrochemical cell consists of a half-cell containing Sn^{4+}/Sn^{2+} and another half-cell containing Zn^{2+}/Zn.

(i) Draw a fully labelled diagram of the experimental setup used to measure the standard potential of this cell. [2]



- ✓ **voltmeter labelled (or circled V)**
- ✓ **Zn electrode and Pt electrode**
- ✓ **1 mol dm^{-3} Zn^{2+}**
- ✓ **1 mol dm^{-3} each for Sn^{2+} and Sn^{4+}**
- ✓ **298 K**

Note: Salt bridge must be labelled (must touch solution)

(ii) Use data from the Data Booklet to calculate a value for the standard cell potential. [1]

$E^{\ominus}_{Zn^{2+}/Zn}$ **= -0.76V =** $E^{\ominus}_{oxid}$

$E^{\ominus}_{Sn^{4+}/Sn^{2+}}$ **= +0.15V =** $E^{\ominus}_{red}$

$E^{\ominus}_{cell} = E^{\ominus}_{red} - E^{\ominus}_{oxid}$

= +0.15 – (-0.76)

= + 0.91 V [1]

E values either quoted or shown in working. Sign must be shown.

(iii) Explain how the cell potential will change when a small amount of sodium carbonate is added to the Zn^{2+}/Zn half-cell. [2]

Formation of insoluble zinc carbonate causes the $[Zn^{2+}]$ to decrease. The position of equilibrium of $Zn^{2+} + 2e^- \rightleftharpoons Zn$ shifts to the left, favouring oxidation. [1]

$E_{Zn^{2+}/Zn}$ or E_{oxid} becomes more negative, hence E_{cell} becomes more positive. [1]

(iv) Thermal decomposition of zinc carbonate is an endothermic reaction. Explain why the decomposition reaction is spontaneous at high temperature. [1]

$ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$

ΔH is positive for endothermic reaction.

ΔS is positive due to the increase in number of moles of gases, hence greater disorder.

ΔG = ΔH – TΔS is negative at high temperature. [1]

(v) Using relevant data from the *Data Booklet*, explain the relative thermal stability of zinc carbonate and calcium carbonate. [2]

- ✓ **Ionic radii: Zn^{2+} - 0.074nm, Ca^{2+} - 0.099nm**
- ✓ **Order of thermal stability $ZnCO_3 < CaCO_3$**

2 points [1]

Zn^{2+} has the highest charge density. Zn^{2+} polarises the carbonate ion and weakens the C-O bond to the greater extent. Less energy is needed to break the C-O bond. [1]

(b) An oxide of tin, **G**, contains the metal in both oxidation states II and IV. **G** was dissolved in excess $H_2SO_4(aq)$ to produce solution **H**, which contains a mixture of tin(II) sulfate and tin(IV) sulfate. Solution **H** was divided into two portions.

A 25.0 cm^3 of one potion required 17.40 cm^3 of 0.0150 mol dm^{-3} $KMnO_4$ to reach the end-point.

An excess of powdered zinc was added to another portion of **H**. The mixture was stirred until the reaction was complete, and then filtered. 25.0 cm^3 of the filtrate required 26.10 cm^3 of 0.0150 mol dm^{-3} $KMnO_4$ to reach the end-point.

The equation for the titration reaction is as follows.

$$2MnO_4^- + 16H^+ + 5Sn^{2+} \rightarrow 2Mn^{2+} + 8H_2O + 5Sn^{4+}$$

(i) Deduce the Sn^{2+}/Sn^{4+} ratio in the oxide **G**, and hence suggest the formula of **G**. [3]

No. of moles of MnO_4^- reacted with Sn^{2+} = $\frac{17.40}{1000} \times 0.015$ = 2.61 x 10^{-4} mol

No. of moles of Sn^{2+} = $\frac{5}{2} \times 2.61 \times 10^{-4}$ = 6.53 x 10^{-4} mol

No. of moles of MnO_4^- reacted with Sn^{2+} reduced from Sn^{4+}

= $\frac{26.10}{1000} \times 0.015$ - 2.61 x 10^{-4}

= 1.31 x 10^{-4} mol

No. of moles of Sn^{4+} = = $\frac{5}{2} \times 1.31 \times 10^{-4}$ = 3.28 x 10^{-4} mol

working [1]

Alternative

volume of MnO^{4-} reacted with Sn^{2+} originally present : Sn^{2+} reduced from Sn^{4+}

= 17.40 : (26.10 – 17.40)

= 17.40 : 8.70 [1]

More papers at www.testpapersfree.com

$Sn^{2+}/Sn^{4+} = \frac{6.53 \times 10^{-4}}{3.28 \times 10^{-4}} = \frac{2}{1}$ [1] or use volume ratio

Formula of G is Sn_3O_4 [1]

(ii) Tin(IV) oxide, SnO_2, reacts separately with both acids and alkalis. Write separate equations for the reaction of tin(IV) oxide with

- hydrochloric acid
- sodium hydroxide [2]

$SnO_2 + 4HCl \rightarrow SnCl_4 + 2H_2O$ [1]

$SnO_2 + 2NaOH \rightarrow Na_2SnO_3 + H_2O$ [1]

(c) Halogenoalkanes react with lithium to give organolithium compounds.

These organolithium compounds can react with carbonyl compounds to form alcohols, as shown in Fig. 4.1.

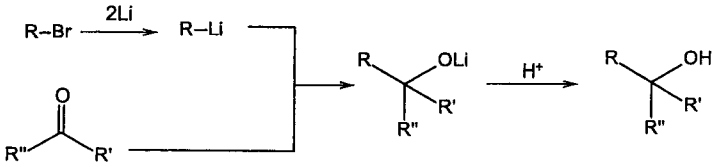
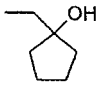


Fig. 4.1

(R is alkyl, R' and R'' are either alkyl or H)

(i) Draw the skeletal formula of the organic product formed when bromoethane is reacted with lithium, followed by cyclopentanone in a similar synthetic route as shown in Fig. 4.1. [1]



[1]

(ii) Compound **J**, $C_{10}H_{14}NBr$, decolourises aqueous bromine to give a white precipitate **K**, $C_{10}H_{12}NBr_3$.

J reacts with hot alcoholic NaOH to form isomers **L** and **M**, with the formula $C_{10}H_{13}N$. When heated with acidified $KMnO_4$, **L** gives effervescence, whereas **M** gives **N** as one of the products. Reacting the **N** with bromomethane according to the sequence in Fig. 4.1 gives 2-methylpropan-2-ol.

Heating **J** gives **P**, $C_{10}H_{13}N$ as the organic product.

Suggest the possible structures of **J**, **K**, **L**, **M** and **P**. For each reaction, state the *type of reaction* described and explain what the information tells you about the functional groups present in each compound. [6]

✓ **J has a high C:H ratio, J contains benzene.**

✓ **J undergoes <u>electrophilic substitution</u> with aqueous bromine to form K. J is a <u>phenylamine</u> (not phenol since J does not contain O).**

More papers at www.testpapersfree.com
DO NOT WRITE IN THIS MARGIN

✓ **<u>1 of the 2,4,6 positions</u> of the phenylamine contains a substituent and is <u>not available</u> for substitution by Br.**

✓ **J undergoes <u>elimination</u> with alcoholic NaOH to form L and M which are <u>alkenes</u>.**

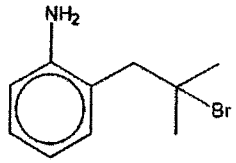
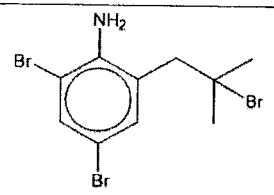
✓ **L and M undergoes <u>oxidation</u>/ oxidative cleavage with $KMnO_4$. L contains a <u>terminal alkene</u>.**

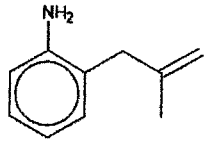
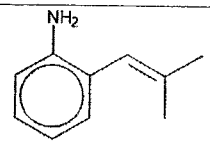
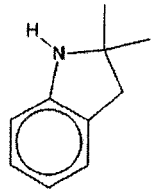
✓ **Following the reaction scheme in Fig. 4.1, <u>N is propanone</u>.**

✓ **J undergoes <u>nucleophilic substitution</u> to form P, $-NH_2$ and the bromoalkyl substituents should be adjacent to each other on the benzene.**

Every 2 √ [1]

max [3]

J √	K √
	

L √	M √	P [1]
		

structures [3]

DO NOT WRITE IN THIS MARGIN
BP~605

5 (a) In 1944, T. Ellingham published plots of Gibbs free energy change, ΔG, against temperature, T, for several reactions. Today, such plots are called Ellingham diagrams.

At present, titanium is more commonly produced by reducing titanium tetrachloride with magnesium. Titanium tetrachloride is a colourless liquid that boils at 400 K. To optimise this reduction process, it is necessary to know how ΔG of the reaction changes with T.

Fig. 5.1 shows the variation in ΔG with T for the following reactions:

Reaction 1: $\frac{1}{2}Ti + Cl_2 \longrightarrow \frac{1}{2}TiCl_4$

Reaction 2: $Mg + Cl_2 \longrightarrow MgCl_2$

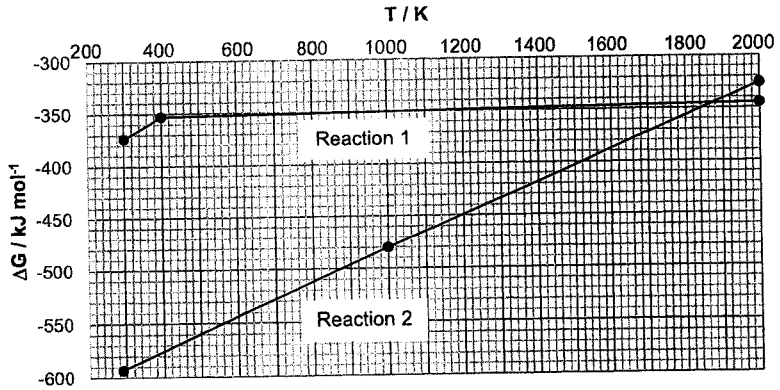


Fig. 5.1

(i) With reference to the gradient of the graph for Reaction 2, deduce the sign of ΔS.

Hence, explain why the graph for Reaction 2 becomes more positive with increasing temperature. [2]

√ **For graph of ΔG against T, y–intercept gives ΔH and the gradient gives $-\Delta S$. Since the gradient for reaction 2 is positive, ΔS is** negative.

√ This is because there is a decrease in disorder due to decrease in the number of moles of gas molecules from 1 to 0.

√ **Since ΔH and ΔS are both negative, $-T\Delta S$ becomes more positive with increasing temperature and hence the graph for reaction 2 becomes more positive**

3 √ = 2m; 2 √ = 1m

Industrially, the reduction of titanium tetrachloride by magnesium is carried out at 1100 K in an atmosphere of argon:

$$\frac{1}{2}TiCl_4 + Mg \longrightarrow \frac{1}{2}Ti + MgCl_2$$

(ii) Suggest a reason for the reduction to be carried out in an atmosphere of argon. [1]

To prevent the hot titanium extracted from oxidising to TiO_2

Note: traces of oxygen in the titanium tend to make the metal brittle.

Similar to enthalpy change of reaction, the Gibbs free energy, ΔG, of a reaction can be calculated using the following expression.

$$\Delta G = \sum \Delta G \text{ (products)} - \sum \Delta G \text{ (reactants)}$$

With reference to Figure 5.1,

(iii) evaluate ΔG for the reduction of $TiCl_4$ by Mg at 1100 K. [1]

$\frac{1}{2}Ti + Cl_2 \longrightarrow \frac{1}{2}TiCl_4$ ΔG at 1110 K = –350

$Mg + Cl_2 \longrightarrow MgCl_2$ ΔG at 1110 K = –465

ΔG = –465 – (–350)

= –115 kJ mol^{-1}

(iv) state the temperature above which it is **not** feasible to reduce $TiCl_4$ with Mg. [1]

1870 K (at T higher than 1870 K, $\Delta G > 0$)

Accept 1860-1880 K

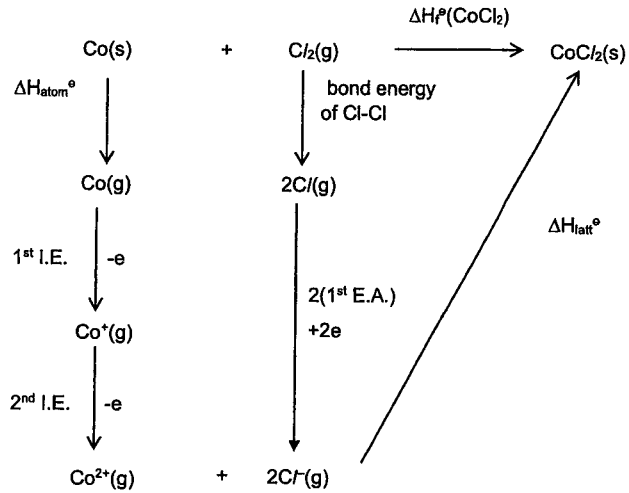
Cobalt(II) chloride has been extensively used as a catalyst for various organic transformations.

(b) Using the data in Table 5.1 and relevant data from the *Data Booklet*, construct a Born–Haber cycle to determine the standard enthalpy change of formation of cobalt(II) chloride. [3]

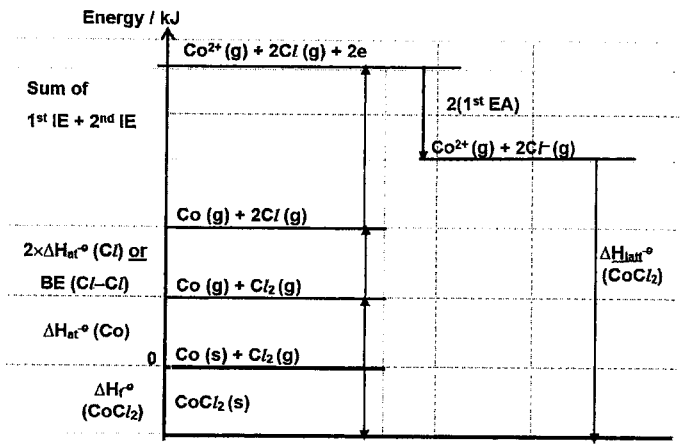
Table 5.1

Enthalpy term	ΔH / kJ mol^{-1}
Lattice energy of $CoCl_2$	-2624
Standard enthalpy change of atomisation of cobalt	+427
First electron affinity for chlorine	-364

BP~606
DO NOT WRITE IN THIS MARGIN
More papers at www.testpapersfree.com



OR



By Hess' Law,

$\Delta H_f^{\ominus}(CoCl_2) = +427 + 244 + 757 + 1640 + 2(-364) + (-2624)$

$= \underline{-284\ kJ\ mol^{-1}}$

1m – labelled Born-Haber cycle (axis, zero point, all enthalpy terms/value)

1m – balanced equations with state symbols

1m – calculated value with sign and units *(do not award if no units/sign)*

More papers at www.testpapersfree.com
DO NOT WRITE IN THIS MARGIN

(c) Cobalt(II) chloride is known to be a useful catalyst for the synthesis of α-aminonitriles by a one-pot 3-component condensation as shown:

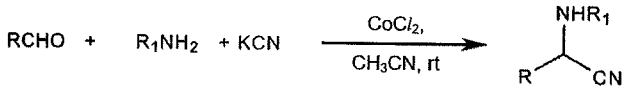
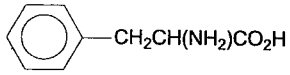


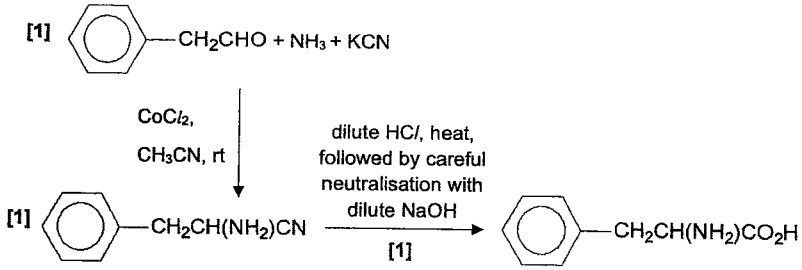
Fig. 5.2

Using the information in Fig. 5.2, propose a pathway to synthesize the following α–amino acid:



phenylalanine

Suggest the structures of the aldehyde that can be used as starting material and the intermediate. State the reagents and conditions for each step clearly. [3]



(d) Compound **Q**, $C_5H_{10}O_3$, does not react with 2,4–DNPH but reacts with warm alkaline aqueous iodine to give a yellow precipitate.

On treatment with hot concentrated sulfuric acid, compound **Q** forms a mixture of three isomeric compounds **R, S** and **T**, with the formula $C_5H_8O_2$, two of which are cis-trans isomers of each other.

Compound **R** is a sweet-smelling liquid. Both **S** and **T** undergo reaction with acidified potassium manganate (VII) to give **U**, $C_3H_4O_4$, and ethanoic acid. 1 mole of **U** liberates 1 mole of CO_2 on reaction with excess sodium carbonate.

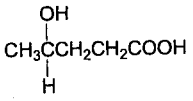
Identify the five compounds **Q** – **U**, explaining the chemistry of the reactions described.

[9]

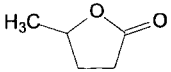
Observation	Type of reaction	Deduction
Q does not react with 2,4–DNPH.	√ does not undergo condensation	√ **Q** does not contain aldehyde or ketone functional group.
Q reacts with alkaline I_2(aq) to give yellow ppt.	√ oxidation	√ **Q** contains $CH_3CH(OH)$– *(reject if answer suggested methyl ketone structure)*

BP~607

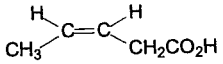
Q reacts with concentrated H_2SO_4 to give **R**, which is a sweet–smelling liquid	√ (Intramolecular) condensation	√ **R** is an **ester.** √ **Q** contains both the –OH and –COOH group
Q reacts with concentrated H_2SO_4 to give **S** and **T**, with the formula $C_5H_8O_2$	√ elimination	√ **S** and **T** contains C=C with √ two different substituents about each sp^2 C (**S** and **T** exhibits cis-trans isomerism)
S and **T** reacts with $KMnO_4$ to give **U**, $C_3H_4O_4$ and ethanoic acid	√ oxidation	√ The C=C in **S/T** is cleaved, there is no terminal C=C as no CO_2 is produced.
1 mole of **U** reacts with excess Na_2CO_3 to give 1 mole of CO_2.	√ acid–base reaction	**U** contains **2** √ **U** is a dicarboxylic acid.



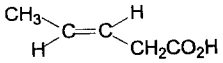
Q



R



S



T

$HOOCCH_2COOH$

U

Structures: [1] each for **Q**, **R**, and **U**; [1] for both **S** and **T** (120° about sp^2 C)

Deductions:

[5]: 13 – 14 √

[4]: 10 – 12 √

[3]: 7 – 9 √

[2]: 4 – 6 √

[1]: 2 – 3 √

[Total: 20]

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN

More papers at www.testpapersfree.com

TEMASEK JUNIOR COLLEGE

2022 JC2 PRELIMINARY EXAMINATIONS
HIGHER 2

CANDIDATE NAME	
CIVICS GROUP	/
CENTRE NO. / INDEX NO.	/

CHEMISTRY **9729/04**
Paper 4 Practical **29 August 2022**
2 hours 30 minutes

Candidates answer on the Question Paper.

READ THESE INSTRUCTIONS FIRST

Write your Civics Group and name on all the work you hand in.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 23 and 24.
At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
1	/ 12
2	/ 19
3	/ 14
4	/ 10
Total	/ 55

This document consists of 22 printed pages and 2 blank pages.

DO NOT WRITE IN THIS MARGIN
More papers at www.testpapersfree.com

Answer **all** the questions in the spaces provided.

1 Determination of the percentage by mass of water of crystallisation in $FeSO_4 \cdot nH_2O$

Read through the whole method before starting any practical work. Where appropriate, prepare a table for your results in the space provided.

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

The amount of Fe^{2+} ions can be determined quantitatively by a titration against a standard solution of potassium manganate(VII), $KMnO_4$. The reaction is shown below.

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

In this experiment, you will determine the percentage by mass of water of crystallisation in $FeSO_4 \cdot nH_2O$. You will titrate a solution of **FA 1** against **FA 3**.

You are provided with

FA 1, contains 26.07 g dm^{-3} of hydrated iron(II) sulfate, $FeSO_4 \cdot nH_2O$, where n is an integer.

FA 2, 1.0 mol dm^{-3} dilute sulfuric acid, H_2SO_4.

FA 3, 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$,

You are to keep **FA 2** and **FA 3** for questions 2 and 3.

(a) (i) Titration of FA 1 against FA 3

1. Fill a burette, labelled **FA 3**, with **FA 3**.
2. Use a pipette to transfer 10.0 cm^3 of **FA 1** into a 250 cm^3 conical flask.
3. Use a measuring cylinder to add about 10 cm^3 of **FA 2** to this flask.
4. Titrate **FA 1** with **FA 3** from the burette until the appearance of the first permanent pale-pink colour.
5. Record your titration results, to an appropriate level of precision, in the space on Page 3.
6. Repeat steps 1 to 4 until consistent results are obtained.

DO NOT WRITE IN THIS MARGIN
BP~609

Titration Results

Final burette reading / cm³	**9.20**	**9.30**
Initial burette reading / cm³	**0.00**	**0.00**
Volume of FA 3 used / cm³	**9.20**	**9.30**
	√	√

Tables have correct headers and units [1]
Note: Mark is lost if any final and initial burette readings are inverted or 50 is used as the initial burette reading.

All burette readings & volume used for all accurate titres in the titration table are recorded to 2dp and at least two uncorrected titres for end-point within ±0.10 cm³. [1]

[2]

(ii) From your titrations, obtain a suitable volume of **FA 3**, $V_{FA\ 3}$, to be used in your calculations. Show clearly how you obtained this volume.

Average titre = $\frac{9.20 + 9.30}{2}$

= 9.25 cm³ [1]

Answer should be recorded to 2.d.p

Mark is lost if there are arithmetic errors in the table.

Mark is lost if the titres used are not identified either in the table (by, for example, a tick) or in a calculation.

Accuracy
2 marks: If difference is ≤ 0.20cm³

1 mark: If difference is ≤ 0.40 cm³

0 mark: For a difference > 0.40 cm³

Volume of **FA 3** = ...[3]

(b) (i) Calculate the amount of Fe^{2+} in 10.0 cm³ of **FA 1**.

$5Fe^{2+} \equiv MnO_4^-$

No. of moles of Fe^{2+} = 9.25/1000 × 0.020 × 5

= • 9.25 x 10^{-4} mol [1]

amount of Fe^{2+} in 10.0 cm³ of **FA 1** = ... [1]

DO NOT WRITE IN THIS MARGIN
[Turn over

DO NOT WRITE IN THIS MARGIN

(ii) Calculate the amount of Fe^{2+} in 1 dm³ of **FA 1**.

No. of moles of Fe^{2+} = 9.25 x 10^{-4} x $\frac{1000}{10}$

= • 0.0925 mol [1]

amount of Fe^{2+} in 1 dm³ of **FA 1** = ... [1]

(iii) Calculate the M_r of the hydrated iron(II) sulfate, $FeSO_4.nH_2O$, in **FA 1**.

M_r of $Fe(SO_4).nH_2O$ = 26.07 / 0.0925

= 281.8 [1]

M_r of the hydrated iron(II) sulfate = ...

Hence, deduce the value of *n*, the water of crystallisation in the hydrated iron(II) sulfate.

[A_r: Fe, 55.8; S, 32.1; O, 16.0; H, 1.0]

n = {281.8 – [(55.8) + (32.1) + 4(16.0)]} ÷ 18.0

= 7.22

= 7 (nearest whole number) [1]

Note: This answer must be a positive integer.

n = ...

[2]

(iv) Hence, determine the percentage by mass of water of crystallisation in $FeSO_4 \cdot nH_2O$.
Show your working.

percentage by mass of water of crystallisation in $FeSO_4 \cdot nH_2O$.

= $\frac{7.22 \times 18}{281.8}$ x100%

= 46.1% [1]

Note for marker: If student uses the rounded off integer, need to re-calculate the M_r. otherwise, penalise.

Percentage by mass of water of crystallisation = ...

DO NOT WRITE IN THIS MARGIN
[Turn over

DO NOT WRITE IN THIS MARGIN

More papers at www.testpapersfree.com

[1]

(v) Iron(II) sulfate in solution is readily oxidised by air to form iron(III) sulfate.

State the effect, on the value of *n* calculated in **(b)(iii)**, if some of your sample of **FA 1** had oxidised before you carried out the titration. Explain your answer.

Amount /Volume of MnO_4^- used is smaller OR mass/amount of Fe^{2+} used is smaller [1]

mass/moles/amount water larger so (mole) ratio larger so n increases [1]

Allow difference in titre/moles of MnO_4^- / Fe^{2+} will be too small to change the (integer) value of n for 1 mark.
Allow for 1 mark: less MnO_4^- / Fe^{2+} and n increases

[2]

[Total: 12]

2 To investigate the reaction between manganate(VII) ions and $C_2O_4^{2-}$ ions.

In this experiment, you will investigate the kinetics of the reaction between MnO_4^- and $C_2O_4^{2-}$.

FA 4 is 0.0100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$

FA 5 is 0.200 mol dm^{-3} sodium ethanedioate, $Na_2C_2O_4$

FA 6 is 0.100 mol dm^{-3} potassium iodide, KI

FA 2 and **FA 3** are solutions from question 1.

You are to keep **FA 5** for question 3.

You are also provided with a starch indicator.

Acidified potassium manganate(VII) ions oxidises $C_2O_4^{2-}$ ions to produce Mn^{2+} ions which act as an autocatalyst for the reaction.

$$2\,MnO_4^-(aq) + 5\,C_2O_4^{2-}(aq) + 16\,H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

Acidified potassium manganate(VII) ions also oxidises I^- ions according to the following reaction:

$$2MnO_4^-(aq) + 10I^-(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5I_2(aq) + 8H_2O(l)$$

You will add a solution of acidified potassium manganate(VII) to a mixture containing **FA 2** and **FA 5**. At timed intervals, you will draw 10 cm^3 aliquots of the reaction mixture. The

More papers at www.testpapersfree.com
DO NOT WRITE IN THIS MARGIN

concentration of MnO_4^- ions in each aliquot will be determined after adding the aliquot to an excess of I^- solution and titrating the iodine produced against $S_2O_3^{2-}$ solution.

The reaction between iodine from the reaction mixture and $S_2O_3^{2-}$ solution is given below.

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

Each titration can only be performed once, so you must work very carefully.

Note: $C_2O_4^{2-}$ does not react with I^- in the reaction mixture.

In an appropriate format in the space provided on page 8, draw a table to record your

- transfer time (in minutes and seconds, to the nearest second) when half of the reaction mixture has emptied from the pipette,
- the decimal time, t_d, in minutes, to 0.1 min, for example, if t = 3 min 20 s then t_d = 3 min + 20/60 = 3.3 min,
- titration results for each of your aliquots. Make certain that your recorded results show the precision of your working.

Procedure

Note: Read all instructions in the procedure before you start performing the experiment.

1. Label each of the large test-tubes **1** to **6**. Using a measuring cylinder, add approximately 10 cm^3 of **FA 6** to each of these test-tubes.
2. Using appropriate measuring cylinders, transfer 50.0 cm^3 of **FA 5**, 5.0 cm^3 of **FA 2** and 45.0 cm^3 of deionised water into a conical flask labelled **reaction mixture**.
3. Using an appropriate measuring cylinder, transfer 25.0 cm^3 of **FA 3** to the conical flask labelled **reaction mixture**. Start the stopwatch and swirl the mixture thoroughly to mix its contents.
4. At approximately 1 minute, use a 10 cm^3 pipette to remove a 10.0 cm^3 aliquot of the reaction mixture. **Immediately** transfer this aliquot into the test-tube labelled **1** and swirl the mixture. Note and record the transfer time (in minutes and seconds, to the nearest second) when half of the reaction mixture has emptied from the pipette.
5. At approximately 2 minutes, repeat step 4. Transfer this aliquot into the large test-tube labelled **2**.
6. Repeat step 4 four more times at about three minute intervals, transferring the aliquots into test-tubes labelled **3** to **6**.

Note: Performing all of the titrations only after all the aliquots have been collected may affect time management.

DO NOT WRITE IN THIS MARGIN
DO NOT WRITE IN THIS MARGIN
BP~611

BP~612

Titrations

7. Pour the contents of test-tube labelled **1** into a clean 250 cm^3 conical flask. Rinse the test-tube and add the washings to the conical flask.

8. Titrate the iodine in this solution with **FA 4**. When the colour of the solution turns pale yellow, add about 1 cm^3 of starch indicator. The solution will turn dark blue/black. The end-point is reached when the dark blue/black colour just disappears. Record your results.

9. Repeat steps **8** to **9** for each of the remaining test-tubes labelled **2** to **6**.

(a) Experimental results

Specified Time	1 min	2 min	5 min	8 min	11 min	14 min
Transfer Time (in minutes and seconds)	**1 min 4 s**	**2 min 2 s**	**5 min 2 s**	**8 min 8 s**	**11 min 2 s**	**14 min 8 s**
Decimal Time, t_d /min	**1.1**	**2.0**	**5.0**	**8.1**	**11.0**	**14.1**
Final Burette Reading /cm^3	**19.70**	**19.70**	**17.35**	**27.30**	**30.80**	**32.60**
Initial Burette Reading /cm^3	**0.00**	**0.00**	**0.00**	**17.50**	**27.50**	**31.00**
Volume of **FA 4** added /cm^3	**19.70**	**19.70**	**17.35**	**9.80**	**3.30**	**1.60**

[3]

Table with correct headers and units **[1]**

6 sets of results of correctly calculated values and interval for transfer time **[1]**

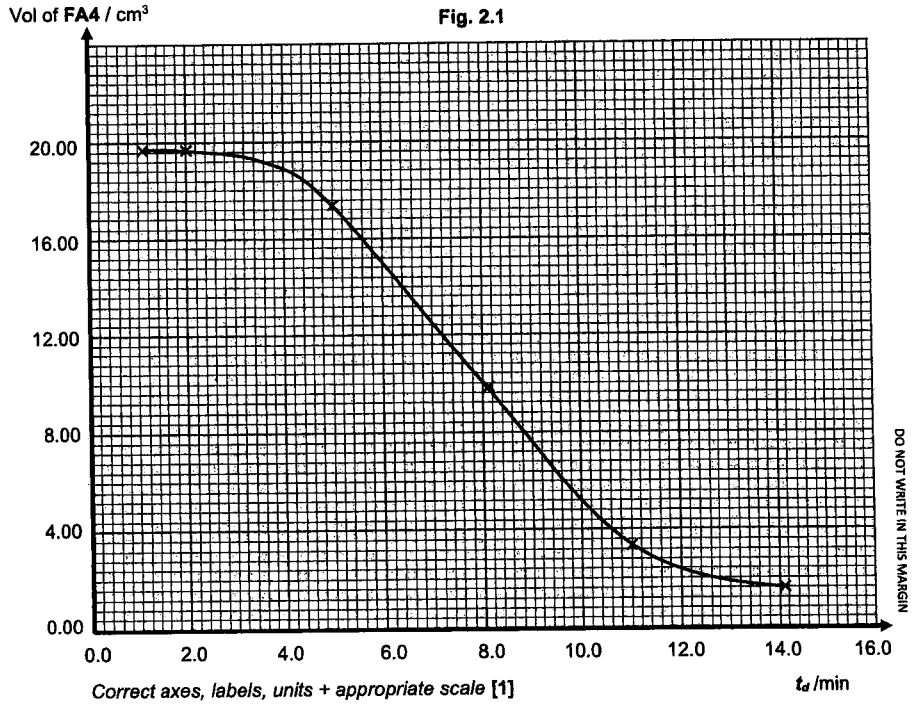
Note: results should be within 30 s of specified time

1 dp for decimal time **[1]**

DO NOT WRITE IN THIS MARGIN

(b) **(i)** On the grid in **Fig. 2.1**, plot a graph of **volume of sodium thiosulfate, FA 4**, on the *y*-axis, against time, t_d, on the *x*-axis. You should draw the most suitable line that takes into account all of your plotted points.

Fig. 2.1



Correct axes, labels, units + appropriate scale **[1]**

All points correctly plotted **[1]**

Smooth curve and correct shape showing a gentler gradient at the start, gradient becomes steeper with time **[1]**

(ii) Consider the **shape** of the graph in **Fig.2.1.**

Describe the shape and explain how it relates to the rate of reaction between MnO_4^- and $C_2O_4^{2-}$.

Initially, the almost constant gradient shows that the <u>reaction starts slowly</u> as very little Mn^{2+} is formed to catalyse reaction. <u>Rate of reaction then increases</u>, as seen from the steeper gradient, since more Mn^{2+} are produced to catalyse the reaction. Finally, <u>rate of reaction decreases</u> as seen from the less steep gradient since the concentration of reactants decrease as reaction proceeds. [1]

[1]

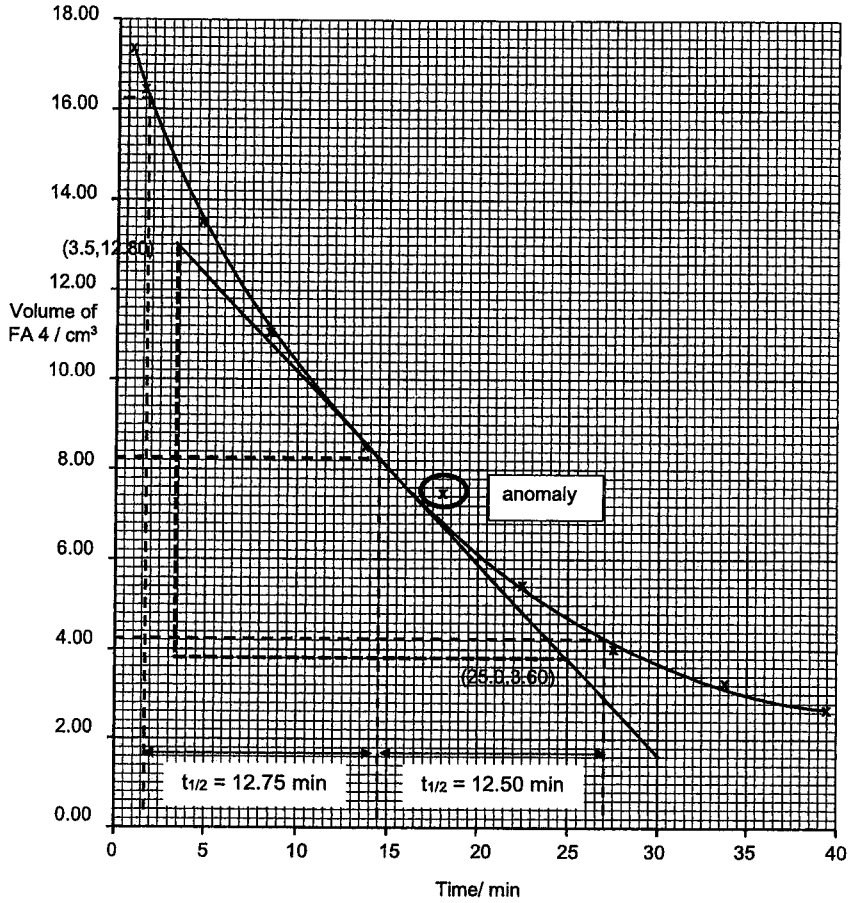
DO NOT WRITE IN THIS MARGIN

More papers at www.testpapersfree.com

2 (c) A student performed a similar experiment under a different temperature. In step **2** of the procedure on page 8, she used the same volumes of **FA 2** and **FA 5** that you used but she also added 5.0 cm^3 of 1.00 mol dm^{-3} manganese(II) sulfate. To keep the total volume of the same as your experiment, she added 40.0 cm^3 of deionised water.

The data from the student's experiment has been plotted in **Fig. 2.2**.

(i) Draw the most appropriate line taking into account all of the plotted points. [1]



Comment: draw a smooth best fit curve, ignoring the anomalous point at 18 min.

More papers at www.testpapersfree.com
DO NOT WRITE IN THIS MARGIN

(ii) Using the graph in **(c)(i)**, calculate the $[MnO_4^-]$ in the reaction mixture at t = 15 min. [2]

Volume of $S_2O_3^{2-}$ = 7.90 cm^3 [1]

Reminder of page 6 procedure:

*At timed intervals, you will draw **10 cm^3 aliquots** of the reaction mixture. The concentration of MnO_4^- ions in **each (10 cm^3) aliquot** will be determined after adding the aliquot to an excess of I^- solution and titrating the iodine produced against $S_2O_3^{2-}$ solution.*

No. of moles of $S_2O_3^{2-}$ = 7.90 x 10^{-3} x 0.0100 = 7.90 x 10^{-5} mol

$MnO_4^- \equiv 5\ S_2O_3^{2-}$

No. of moles of MnO_4^- = 7.90 x 10^{-5} ÷ 5 = 1.58 x 10^{-5} mol

$[MnO_4^-]$ = 1.58 x 10^{-5} ÷ (10 x 10^{-3}) = 1.58 x 10^{-3} mol dm^{-3} [1]

Note: each volume of FA4 sampled is based on only 10 cm^3 solution pipetted out, NOT the whole solution of 100 cm^3.

(iii) Draw a tangent to your graph line in **(c)(i)** at t = 15 min. Calculate the gradient of this line, and hence determine the rate of change of the **amount** of $S_2O_3^{2-}$ ions required in mol min^{-1}. [3]

Gradient = - (12.80-3.60)/(3.5-25.0) = -0.4278 cm^3 min^{-1} [1]

Drawing of tangent on graph and calculation of gradient using co-ordinates that are 3 big squares in both x and y direction [1]

Note: read off coordinates from the graph carefully. Gradient coordinates should be as wide as possible (at least 3 big sq in both x and y direction).

Note: gradient represents rate of change of volume of $S_2O_3^{2-}$ ions

Rate of change of amount of thiosulfate ions = 0.428 x 10^{-3} x 0.0100

= 4.28 x 10^{-6} mol min^{-1} [1]

(iv) Using your answer in **(c)(iii)**, calculate the rate of change of MnO_4^- in mol min^{-1}. [1]

$2\ MnO_4^- \equiv 5\ I_2 \equiv 10\ S_2O_3^{2-}$

DO NOT WRITE IN THIS MARGIN
BP-613

BP~614

$MnO_4^- \equiv 5\ S_2O_3^{2-}$

rate of change of MnO_4^- = $4.28 \times 10^{-6} \div 5 = 8.56 \times 10^{-7}$ mol min^{-1} [1]

(v) Hence, calculate the rate of disappearance of $[MnO_4^-]$ in the reaction mixture, at time t = 15 min. [3]

rate of disappearance of $[MnO_4^-] = 8.56 \times 10^{-7} \div (10 \times 10^{-3})$

$= 8.56 \times 10^{-5}$ mol dm^{-3} min^{-1} [1]

Note: only 10 cm^3 of solution containing $KMnO_4$ is extracted for titration each turn, NOT the whole solution of 100 cm^3.

Shows working in all calculations. All calculations must be relevant although they may not be complete or correct. Any calculation not attempted loses this mark. [1]

Shows appropriate significant figures (3 or 4 sf) and units in all final answers. Any calculation not attempted loses this mark. [1]

(d) Using the graph in (c)(i), show that the reaction between MnO_4^- and $C_2O_4^{2-}$ is first order with respect to $[MnO_4^-]$. [2]

Showing the construction lines for half-life [1] for at least 2 similar half-lives. Do NOT find half-life from t = 0 min as initial volume of FA4 used is not shown.

The volume of FA 4 used is directly proportional to the no. of moles of I_2 liberated by the unreacted MnO_4^- from the reaction. Hence, the volume of FA 1 α $[MnO_4^-]$. Since a constant half-life = 12.50 min, is obtained from the graph, the order of reaction with respect to $[MnO_4^-]$ is 1.

Note: relationship between FA4 and $[KMnO_4]$ must be clearly shown

→ $[KMnO_4]$ ↓ as rxn progresses → $[I_2]$ ↓ → $[S_2O_3^{2-}]$ ↓

explanation [1]

[Total: 19]

DO NOT WRITE IN THIS MARGIN

3 **To explore the chemistry of some compounds of unknown transition elements X and a hydrocarbon.**

FA 7 (MnO_2) is a solid sample of a common dioxide of the unknown transition element **X**

FA 8 (Mn^{2+}, SO_4^{2-}) is a pure solution of compound **Y**, which is the product formed in **3(a)**

FA 9 (cyclohexene) is a hydrocarbon

You will need access to the **FA 2**, **FA 3** and **FA 5** from question 1 and 2.

Perform the tests described in Table 3.1 and record your observations in the table. Test and identify any gases evolved. The observation in **(c)(iii)** has been completed for you. There is no need to carry out this test.

Table 3.1

	tests	observations
(a)	Add 2 cm depth of **FA 2** (H_2SO_4) and 2 cm depth of **FA 5** ($Na_2C_2O_4$) to a test-tube.	√ **Effervescence**
	Using a spatula, add **FA 7** (MnO_2) to the mixture in small portion with swirling until no further change.	√ **Colourless, odourless, acidic gas gave white ppt with limewater**
	Filter the mixture into a test-tube. The filtrate contains compound **Y**.	√ **Pale pink/colourless/pale yellow/ yellow-green filtrate and black residue (remaining unreacted FA 7)**
	Divide the filtrate into two portions. To one portion, add aqueous sodium hydroxide until no further change.	√ **Light brown ppt, insoluble in excess NaOH(aq). Ppt darkens on standing**
	To the other portion, add aqueous ammonia until no further change.	√ **Light brown ppt, insoluble in excess NH_3(aq). Ppt darkens on standing**
(b)(i)	Place 1 cm depth of **FA 8** in a test-tube, add aqueous sodium hydroxide.	√ **Off-White ppt/very light brown ppt, ppt darken on standing / rapidly turning brown on contact with air, insoluble in excess**
(b)(ii)	Place 1 cm depth of **FA 8** in a test-tube, add aqueous ammonia solution.	√ **Off-White ppt/very light brown ppt, ppt darken on standing / rapidly turning brown on contact with air, insoluble in excess** Note: the colour of ppt in (b) is lighter than ppt observed in (a)

DO NOT WRITE IN THIS MARGIN

More papers at www.testpapersfree.com

(c)(i)	Place 5 cm depth of aqueous sodium hydroxide in a test-tube. Add **5 drops** of **FA 9** to this test-tube. Add **FA 3**, dropwise with shaking, until no further change is seen. Allow to stand for 5 minutes, with occasional shaking. Continue with the remaining parts of Question 3.	**√ Solution turns green/blue green** **√ Colour deepens as more FA 3 added** **√ Brown ppt formed**
(c)(ii)	Place 5 cm depth of **FA 2** in a test-tube. Add **5 drops** of **FA 9** to this test-tube. Add **FA 3**, dropwise with shaking, until no further change is seen. Allow to stand for 5 minutes, with occasional shaking. Continue with the remaining parts of Question 3.	**√ Purple $KMnO_4$ decolourises.** **√ Solution turns pink,** **√ then turns brown/ orange/ decolourises.**
(c)(iii)	Place 5 cm depth of water in a test-tube. Add **1 drop** of **FA 9** to this test-tube. Add bromine water, dropwise with shaking.	**Bromine water decolourised**

[6]

[The points are scaled to 6 marks as follows:

12-13 √ = 6; 10 – 11 √ = 5; 8-9 √ = 4; 7-6 √ = 3 ; 5-4 √ = 2; 2-3= 1]

(d) Consider your observations in **(a)** and **(b)**, identify the transition ion formed in **(a)**. Justify your choice by referring to the observations in **(b)**.

Ion present is **Mn^{2+}**

Justification: **off-white ppt formed with both NaOH and NH_3, ppt insoluble in excess and darken on standing**

[1]

DO NOT WRITE IN THIS MARGIN
More papers at www.testpapersfree.com

(e) The anion in **FA 8** is not a nitrate, nitrite or carbonate ion.

You will devise and perform a series of simple tests to identify the anion present in **FA 8**.

Use the Qualitative Analysis Notes on pages 23-24 to deduce the possible anions in **FA 8** and describe **two different** tests, that will allow you to distinguish between the possible anions. You can only use the bench reagents provided.

Perform the tests described and record your observations in the space below. Hence, deduce the identity of the anion in **FA 8**.

Possible anions: [√] **SO_3^{2-}, SO_4^{2-}, I^-, Cl^-, Br^-**

Tests	Observation
To 1 cm depth of FA 8 in a test tube, add $AgNO_3$(aq) followed by dilute HNO_3(aq). [√]	**No ppt formed. [√]**
To 1 cm depth of FA 8 in a test tube, add $Ba(NO_3)_2$(aq) followed by dilute HNO_3(aq). [√]	**White ppt formed** **Insoluble in nitric acid [√]**

Identity of anion: [√] **SO_4^{2-}**

2 √: 1 mark

[3]

(f) Compound **Z** is the main organic product in **(c)(i)** when **FA 9** reacts with **FA 3** under alkaline conditions. The molecular formula of **Z** is $C_6H_{12}O_2$.

(i) Deduce the molecular formula of **FA 9**.

Explain your deduction. Your explanation should be supported by evidence from your observations in **(c)**.

Molecular formula of **FA 9** is **C_6H_{10} [1]**

Explanation: **[1]**

- **Br_2(aq) decolourised, C=C present**
- **Cold alkaline MnO_4^- oxidises C=C to 1,2-diol C(OH)-C(OH)**
- **Only two oxygen atoms in molecular formula of Z, so only one C=C bond**
- **FA 9 is $C_6H_{12}O_2$ – 2OH = C_6H_{10}**

[2]

DO NOT WRITE IN THIS MARGIN
DO NOT WRITE IN THIS MARGIN
BP~615

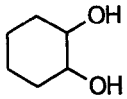
BP~616

(ii) Draw the structural formulae for **FA 9** and compound **Z**.

structure of **FA 9**

[1]

structure of **Z**



[1]

[2]

[Total:14]

4 Planning

You are to plan an experiment to determine the concentration of a solution of $H_2C_2O_4$ and the ΔH_{neut} between ethanedioic acid and sodium hydroxide.

$$\tfrac{1}{2}\,H_2C_2O_4(aq) + NaOH(aq) \rightarrow \tfrac{1}{2}\,Na_2C_2O_4(aq) + H_2O(l) \qquad \Delta H_{neut}$$

You are provided with 2.00 mol dm^{-3} NaOH and a solution of $H_2C_2O_4$ of approximately the same concentration. A series of experiments can be carried out using different volumes of the two solutions. In each experiment, the total volume of the two solutions is to be kept at 50 cm^3 and the increase in temperature, ΔT, is determined.

A graph of ΔT against *volume of $H_2C_2O_4$* can then be used to determine the exact concentration of the $H_2C_2O_4$ solution and ΔH_{neut}.

(a) Determine the volume of $H_2C_2O_4$ and of NaOH to be used such that both solutions will react completely. Show your working clearly and give your answers to the **nearest whole number**.

$$\frac{[H_2C_2O_4] \times \text{Volume } H_2C_2O_4}{[NaOH] \times \text{Volume NaOH}} = \frac{1}{2}$$

Since $[H_2C_2O_4] \approx [NaOH]$,

$\Rightarrow$ Volume $H_2C_2O_4$: Volume NaOH = 1:2

Volume of $H_2C_2O_4$ = 50 × 1/3 = 17 cm^3

Volume of NaOH = 50 × 2/3 = 33 cm^3

OR

No. of moles of $H_2C_2O_4$ = V x $[H_2C_2O_4]$

DO NOT WRITE IN THIS MARGIN

Vol. of NaOH = (2V x $[H_2C_2O_4]$) / [NaOH] = 2V (since $[H_2C_2O_4] \approx [NaOH]$)

2V + V = 50 (since total vol of mixture = 50 cm^3)

V = 16.7 cm^3 (~ 17 cm^3) = vol of $H_2C_2O_4$

Volume of NaOH = 2 x 16.7 = 33.3 cm^3 (~ 33 cm^3)

for both volumes, including working [1]

[1]

(b) Plan a procedure to collect sufficient data to allow a graph of ΔT against *volume of $H_2C_2O_4$* to be drawn.

You are provided with:

- 2.00 mol dm^{-3} NaOH,
- $H_2C_2O_4$ solution of approximately the same concentration,
- the equipment normally found in a school laboratory.

In your plan, you should include the following:

- the procedure, including the apparatus you would use
- a tabulation of the experimental data to be collected, including the volumes of $H_2C_2O_4$ and NaOH

You may assume that the $H_2C_2O_4$ and NaOH solutions have the same initial temperature.

1. **Use a 10 cm^3 measuring cylinder to measure 5 cm^3 of $H_2C_2O_4$ (or use a 50 cm^3 measuring cylinder to measure 45 cm^3 NaOH) and add it into a styrofoam cup. Place this styrofoam cup into a second styrofoam cup, which is then placed in a beaker for support.**
2. **Use a thermometer to measure and record the initial temperature of the solution in the cup.**
3. **Use a second 50 cm^3 measuring cylinder to measure 45 cm^3 of NaOH (or Use a 10 cm^3 measuring cylinder to measure 5 cm^3 $H_2C_2O_4$) and add this second solution to the first solution in the Styrofoam cup.**
4. **Use the thermometer to stir the mixture and measure the highest temperature reached.**
5. **Wash and dry the styrofoam cup and the thermometer.**
6. **Repeat the above steps using the volumes as shown in the table.**

DO NOT WRITE IN THIS MARGIN
More papers at www.testpapersfree.com

Volume of $H_2C_2O_4$ /cm³	Volume of NaOH /cm³	Initial temperature of $H_2C_2O_4$ /°C	Highest temperature after mixing /°C	ΔT /°C
5	45			
10	40			
15	35			
20	30			
30	20			
40	10			

- **overall method [1]**

  Do not award this mark if student added water / uses the same volume of $H_2C_2O_4$ or NaOH / uses a burette to add the second solution to the first solution / planned an experiment to take a temperature readings at 1 min, 2 min, 3 min, 4 min, 5 min etc.

- **suitable choice of apparatus (thermometer, measuring cylinders, Styrofoam cup) [1]**

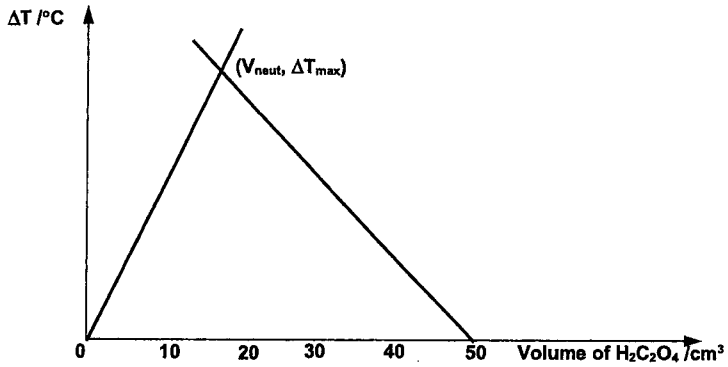
  Note: '10 cm³ measuring cylinder' is not suitable for larger volumes. 50 cm³ measuring cylinders would be more appropriate.

- **suitable volumes of $H_2C_2O_4$ and NaOH (Total volume must be 50 cm³ with at least three $H_2C_2O_4$ volumes < 17 cm³ and at least three > 17 cm³ so that there are at least three plotted points on each line) [1]**

- **table that recorded the initial temperature of $H_2C_2O_4$ (or NaOH) and the highest temperature reached after mixing. [1]**

[4]

(c) Using your answer in **(a)**, sketch, on **Fig. 4.1**, the graph you would expect to obtain from the results.



More papers at www.testpaperstree.com
DO NOT WRITE IN THIS MARGIN

- **two straight lines that intersect, inverted V-shape,**
- **must start from 0 cm³, intersection point shows volume $H_2C_2O_4$ more to the left because it is around 17 cm³ or around 1/3), second line should intersect x-axis if V_{acid} = 50cm³ / should not intersect if V_{acid} < 50cm³**

(d) Suggest a method to minimise heat lost to the surroundings to ensure the results obtained are accurate.

Use a lid for the styrofoam cup / switch off the fans to ensure draft-free environment / using *two* styrofoam cups stacking one into the other [1]

[1]

(e) Another student conducted a similar experiment but used 1.00 mol dm⁻³ of NaOH instead. He obtained the following results:

- Volume of ethanedioic acid needed for complete neutralisation = 15 cm³
- Maximum temperature change = 9.0°C

Calculate the concentration of the $H_2C_2O_4$ solution, in mol dm⁻³ and the ΔH_{neut} in kJ mol⁻¹.

You may assume the following:

- specific heat capacity of all solutions is 4.18 J g⁻¹ °C⁻¹,
- density of all solutions is 1.00 g cm⁻³.

No. of moles of NaOH = $\frac{50-15}{1000}$ x 1

= 0.0350 mol

$H_2C_2O_4 \equiv 2NaOH$,

$[H_2C_2O_4]$ = (½ x 0.035)/(15/1000)

= 1.17 mol dm⁻³ [1]

No. of moles of H_2O produced = no. of moles of NaOH reacted

= 0.0350 mol

$$\Delta H_{neut} = -\frac{(50 \times 4.18 \times 9.0)/1000}{0.0350}$$

= - 53.7 kJ mol⁻¹ [1]

[2]

[Total: 10]

DO NOT WRITE IN THIS MARGIN
DO NOT WRITE IN THIS MARGIN
BP~617

BP~618

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	*reaction with* NaOH(aq)	*reaction with* NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+ (aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq),	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN

(b) Reactions of anions

anion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^- (aq)	NH_3 liberated on heating with OH^-(aq) and *Al* foil
nitrite, NO_2^- (aq)	NH_3 liberated on heating with OH^-(aq) and *Al* foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-} (aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-} (aq)	SO_2 liberated with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colours of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN

More papers at www.testpapersfree.com

TAMPINES MERIDIAN JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

H2 CHEMISTRY **9729/01**

Paper 1 Multiple Choice **22 September 2022**

1 hour

Additional materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Write your name, class and register number on the Answer Sheet in the spaces provided.

There are **thirty** questions in this paper. Answer **all** questions. For each question, there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the use of the Answer Sheet very carefully.

You are advised to fill in the Answer Sheet as you go along. No additional time will be given for the transfer of answers once the examination has ended.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

Use of the Answer Sheet

Ensure you have written your name, class register number and class on the Answer Sheet.

Use a **2B** pencil to shade your answers on the Answer Sheet; erase any mistakes cleanly. Multiple shaded answers to a question will not be accepted.
For **shading of class register number** on the Answer Sheet, please follow the given examples:

If your register number is **1**, then shade **01** in the index number column.
If your register number is **21**, then shade **21** in the index number column.

This document consists of **15** printed pages and **1** blank page.

More papers at www.testpapersfree.com

1 In which species are the numbers of protons, neutrons and electrons **all** different?

A $^{19}_{9}F^-$ **B** $^{23}_{11}Na^+$ **C** $^{31}_{15}P$ **D** $^{32}_{16}S^{2-}$

2 Beams of charged particles are deflected by an electric field. When a beam of protons passes through an electric field of constant strength, the angle of deflection is +12 °.
In another experiment under identical conditions, particle Y is deflected by an angle of – 4 °.

What could be the composition of particle Y?

	protons	neutrons	electrons
1	1	2	2
2	3	3	5
3	4	5	1

A 1, 2 and 3 **B** 1 and 2 **C** 1 only **D** 3 only

3 *Use of the Data Booklet is relevant to this question.*

In which pair of compounds does the first molecule have a smaller bond angle than the second molecule?

A BF_3, NH_3

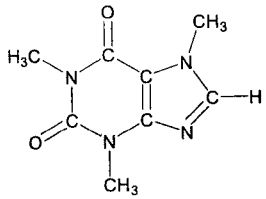
B H_2O, H_2S

C $BeCl_2$, SCl_2

D XeF_4, $SiCl_4$

BP~619

4 To produce decaffeinated coffee, pure liquid CO_2 is sometimes used to extract caffeine from coffee beans.



caffeine

It was discovered that the solubility of caffeine greatly increased when a mixture of ethanol and liquid CO_2 was used.

Which interaction best explains why caffeine is more soluble in the ethanol-CO_2 mixture as compared to liquid CO_2?

A instantaneous dipole - induced dipole interactions

B permanent dipole - permanent dipole interactions

C hydrogen bonding

D dative covalent bond

5 Which graph does **not** share the same general shape as the other three graphs according to the ideal gas law for a fixed mass of gas with pressure *p*, volume V and temperature T in Kelvin?

A *p* against $\frac{1}{V}$ (at constant T)

B *p*V against *p* (at constant T)

C *p*V against V (at constant T)

D $\frac{V}{T}$ against T (at constant *p*)

6 Which statements about Group 2 elements are correct?

1 The charge density of cations increases down the Group.

2 The reducing strength of the elements increases down the Group.

3 The minimum temperature needed for the thermal decomposition of Group 2 carbonates increases down the Group.

4 The melting point of MgO is higher than CaO due to the higher polarising power of Mg^{2+}.

A 1 and 3 **B** 1 and 4 **C** 2 and 3 **D** 2 and 4

7 Due to its radioactive nature, the properties of astatine, At, have to be estimated based on its position in the Periodic Table.

Which prediction concerning At or its compounds is correct?

A Astatine is a weaker oxidising agent than iodine.

B Astatine is a liquid at room temperature.

C Astatine forms diatomic molecules which dissociate into atoms less readily than iodine molecules.

D Hydrogen astatide has a higher decomposition temperature than hydrogen iodide.

8 Sodium thiosulfate ($Na_2S_2O_3$) is used in the textile industry to remove any excess chlorine from bleaching processes by reducing it to chloride ions.

10 cm^3 of 0.20 mol dm^{-3} of sodium thiosulfate requires 192 cm^3 of chlorine gas for complete reaction at room temperature and pressure.

Which of the following is a possible formula of the sulfur-containing product?

A H_2S **B** S **C** SO_2 **D** HSO_4^-

More papers at www.testpapersfree.com

9 Aqueous solutions of **P**, **Q** and **R** react according to the following equation:

$$\mathbf{P} + 3\mathbf{Q} + 2\mathbf{R} \longrightarrow \mathbf{T} + \mathbf{U}$$

The kinetics of the above reaction was studied and the experimental results obtained are shown in the table below.

experiment	volume of **P** / cm³	volume of **Q** / cm³	volume of **R** / cm³	volume of water / cm³	relative initial rate
1	20	20	20	20	16
2	20	10	40	10	32
3	10	10	20	40	4
4	20	10	20	30	8

What is the rate equation for the above reaction?

A Rate = k[**P**][**Q**]

B Rate = k[**P**][**Q**][**R**]

C Rate = k[**P**][**Q**][**R**]^2

D Rate = k[**P**][**Q**]^2[**R**]^2

10 The following data may be useful for this question.

$\Delta H_f^\ominus(N_2H_4(l)) = +50.6$ kJ mol^{-1}

$\Delta H_f^\ominus(N_2O_4(g)) = +9.2$ kJ mol^{-1}

$\Delta H_f^\ominus(H_2O(g)) = -241.8$ kJ mol^{-1}

Hydrazine, $N_2H_4(l)$, reacts with dinitrogen tetroxide, $N_2O_4(g)$, to form nitrogen gas and water vapour.

$$2N_2H_4(l) + N_2O_4(g) \longrightarrow 3N_2(g) + 4H_2O(g)$$

What is the enthalpy change for this reaction?

A +1078 kJ mol^{-1}

B –1078 kJ mol^{-1}

C +1754 kJ mol^{-1}

D –1754 kJ mol^{-1}

More papers at www.testpapersfree.com

11 Travellers to countries with cold climate may sometimes use heat packs to keep warm.

The heat pack is made up of a supersaturated solution of sodium ethanoate and a small metal disc containing very small crystals of sodium ethanoate.

When the disc is broken, small crystals of sodium ethanoate are released into the solution to catalyse the crystallisation reaction of sodium ethanoate.

What are the correct signs for ΔH and ΔS in this reaction?

	ΔH	ΔS
A	+	–
B	+	+
C	–	+
D	–	–

12 When 0.20 mol of hydrogen gas and 0.15 mol of iodine gas are heated at 723 K until equilibrium is established, the equilibrium mixture is found to contain 0.02 mol of iodine gas. The equation for the reaction is as follows:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

What is the correct numerical value for the equilibrium constant, K_c?

A 12.1 **B** 48.3 **C** 92.9 **D** 185.7

13 Which of the following gives the correct relative strengths of the acids and bases in the reaction?

$$HPO_4^{2-}(aq) + H_2BO_3^-(aq) \rightleftharpoons H_2PO_4^-(aq) + HBO_3^{2-}(aq) \qquad K_c > 1$$

	acids	**bases**
A	$H_2PO_4^- > H_2BO_3^-$	$HBO_3^{2-} > HPO_4^{2-}$
B	$H_2PO_4^- > HPO_4^{2-}$	$HBO_3^{2-} > H_2BO_3^-$
C	$H_2BO_3^- > H_2PO_4^-$	$HPO_4^{2-} > HBO_3^{2-}$
D	$H_2BO_3^- > HBO_3^{2-}$	$HPO_4^{2-} > H_2PO_4^-$

BP~621

BP~622

14 The table below shows the values of the ionic product of water, K_w, at two different temperatures.

temperature / °C	K_w / mol^2 dm^{-6}
25	1.00×10^{-14}
62	1.00×10^{-13}

Which statements are correct for pure water?

1 At 62 °C, pH < 7.

2 At 62 °C, pH = 14 – pOH.

3 The ionic dissociation of water is an exothermic process.

A 1 only **B** 2 only **C** 1 and 2 **D** 2 and 3

15 An acidified solution contains 0.10 mol dm^{-3} of $ZnSO_4$ and 0.10 mol dm^{-3} of $CuSO_4$. Hydrogen sulfide gas, H_2S, is blown through the solution until it is saturated with H_2S at 15 °C. The concentration of S^{2-}(aq) in the solution reaches 10^{-35} mol dm^{-3}.

The solubility product of ZnS at 15 °C is 10^{-24} mol^2 dm^{-6} and that of CuS is 10^{-40} mol^2 dm^{-6}.

Which statement describes what happens in the solution?

A No precipitate is formed.

B ZnS only is precipitated.

C CuS only is precipitated.

D Both ZnS and CuS are precipitated.

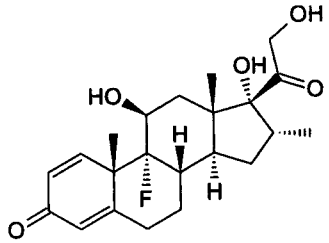
16 $(CH_3CH_2)_3CH$ can react with limited chlorine under *uv* light to produce monochloro-compounds.

How many possible isomers (including stereoisomers) of monochloro-compounds can $(CH_3CH_2)_3CH$ produce?

A 3 **B** 4 **C** 5 **D** 6

[Turn over

17 *Dexamethasone* is a corticosteroid commonly used to treat many inflammatory and autoimmune disorders. It received prominence as it showed high efficacy for patients with severe COVID-19 symptoms who need either mechanical ventilation or supplemental oxygen.



dexamethasone

How many possible stereoisomers exist for *dexamethasone*?

A 2^7 **B** 2^8 **C** 2^9 **D** 2^{10}

18 Which compounds may be a possible product of the reaction of $C_6H_5OCOCHBrCH_3$ with sodium hydroxide under different conditions?

1 $C_6H_5CO_2Na$

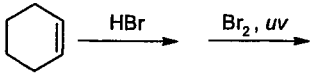
2 $CH_3CH(OH)CO_2Na$

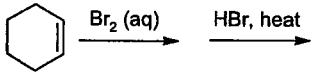
3 $C_6H_5OCOCH{=}CH_2$

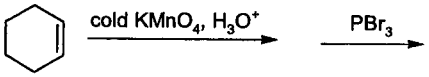
A 1, 2 and 3 **B** 1 and 2 **C** 2 and 3 **D** 3 only

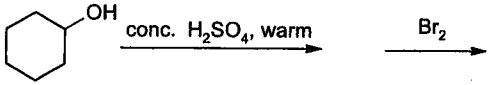
More papers at www.testpapersfree.com

19 Which reaction scheme will **not** give a good yield of 1,2-dibromocyclohexane?

A 

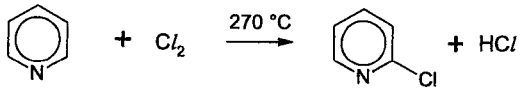
B 

C 

D 

20 Pyridine, like benzene, is an aromatic compound.

In the presence of Cl_2, cyclohexene undergoes an addition reaction at room temperature. However, unlike an alkene, pyridine undergoes a substitution reaction with Cl_2 only at high temperatures.



pyridine

Which statement does **not** help to explain for this observation?

A Pyridine is resonance stabilised.

B Chlorine is not sufficiently electrophilic.

C Pyridine is a weaker nucleophile than cyclohexene.

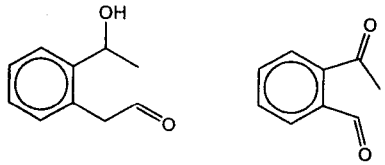
D The lone pair on N atom of pyridine increases the electron density of the π electron cloud.

21 A student carried out an experiment to study the ease of hydrolysis of a series of bromine containing compounds, and recorded the observations based on the addition of acidified silver nitrate solution.

Which of the following gives the expected results?

	time taken for precipitate to appear: shortest →		longest
A	C_6H_5Br	$CH_2BrCONH_2$	CH_3COBr
B	$CH_2BrCONH_2$	C_6H_5Br	CH_3COBr
C	CH_3COBr	C_6H_5Br	$CH_2BrCONH_2$
D	CH_3COBr	$CH_2BrCONH_2$	C_6H_5Br

22 Which reagent could be used to distinguish between compound **X** and compound **Y**?



X **Y**

A 2,4-dinitrophenylhydrazine

B alkaline aqueous iodine

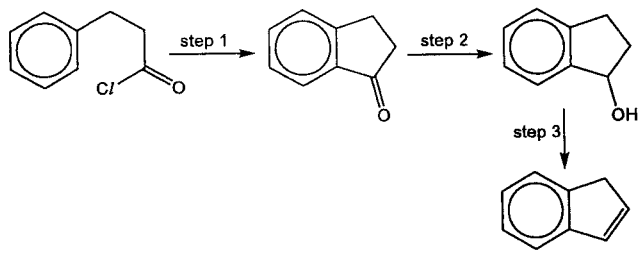
C Tollens' reagent

D Fehling's solution

More papers at www.testpapersfree.com

BP~623

23 A sequence of reactions is shown below.



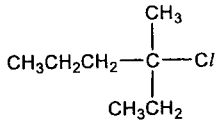
Which is the correct list of reagents and conditions for the sequence?

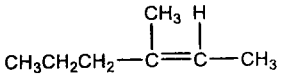
	step 1	step 2	step 3
A	$AlCl_3$(aq)	H_2, Ni	Al_2O_3, heat
B	$AlCl_3$(s)	$LiAlH_4$ in dry ether	conc. H_3PO_4, heat
C	$AlCl_3$(aq)	$NaBH_4$ in methanol	conc. H_3PO_4, heat
D	$AlCl_3$(s)	H_2, Ni	alcoholic KOH, heat

24 Which reaction will **not** form a racemic mixture of products?

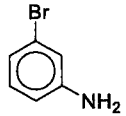
A CH_3CHO with HCN

B CH_3CH_2Br with NaOH(aq)

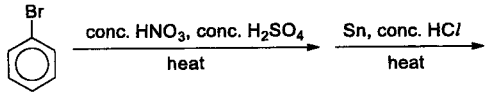
C  with alcoholic KCN

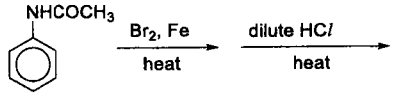
D  with HCl

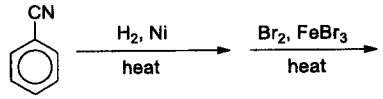
25 Which is the best sequence for synthesising 3-bromophenylamine?

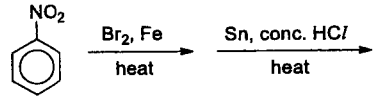


3-bromophenylamine

A 

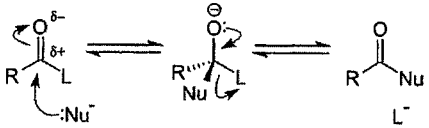
B 

C 

D 

More papers at www.testpapersfree.com

26 Carboxylic acid and their derivatives tend to undergo reactions involving a nucleophile. The mechanism of such a reaction is shown below.



R = alkyl, aryl, H
L = OH, OR, NH_2, Cl, Br, etc
Nu = nucleophile

Which statements concerning the mechanism are correct?

1 One of the steps involves an addition reaction.

2 One of the steps involves an elimination reaction.

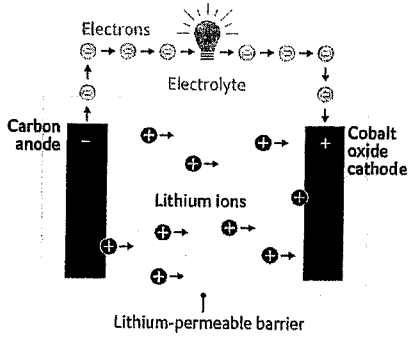
3 The overall reaction is nucleophilic acyl substitution.

A 1, 2 and 3 **B** 1 and 3 **C** 2 and 3 **D** 3 only

More papers at www.testpapersfree.com

27 Electric vehicles are mostly powered by lithium-ion batteries.

The diagram of a typical lithium-ion battery is given below.



The equation at the anode is given as $LiC_6 \rightarrow C_6 + Li^+ + e^-$.

The overall equation of the cell is $LiC_6 + CoO_2 \rightarrow C_6 + LiCoO_2$.

What is the equation at the cathode?

A $CoO_2 + Li^+ + e^- \rightarrow LiCoO_2$

B $Co^{2+} + O_2 + 2e \rightarrow CoO_2$

C $CoO_2 + e^- \rightarrow CoO_2^-$

D $Li^+ + Co + O_2 + e \rightarrow LiCoO_2$

28 An impure copper rod containing zinc and silver is purified by connecting it to the anode of an electrolytic cell. The electrolyte is a 1.0 mol dm^{-3} solution of $CuSO_4$.

A current is passed through the cell for 2 h.

Which observation is **not** correct?

A The anode decreases in mass.

B The cathode increases in mass.

C The blue electrolyte decolourises.

D The Ag impurity deposits at the bottom of the electrolyte.

BP~625

29 Cadmium, Cd, is a Group 12 element in the d-block of the Periodic Table.

What is the main reason why Cd is not classified as a typical transition element?

1 Its complexes are colourless.

2 It has a low melting point of 321 °C.

3 It forms compounds with fully filled 4d orbitals.

4 It does not form compounds with variable oxidation numbers.

A 1, 2, 3 and 4 **B** 1 and 2 **C** 3 only **D** 4 only

30 The Wacker process is an industrial procedure developed to convert ethene to ethanal.

In this reaction, ethene and oxygen gas are bubbled into an aqueous solution of $[PdCl_4]^{2-}$ at high pressure.

The mechanism of the process is given below.

Step 1: $[PdCl_4]^{2-} + CH_2{=}CH_2 + H_2O \rightarrow CH_3CHO + Pd + 2HCl + 2Cl^-$

Step 2: $Pd + 2CuCl_2 + 2Cl^- \rightarrow [PdCl_4]^{2-} + 2CuCl$

Step 3: $2CuCl + \frac{1}{2} O_2 + 2HCl \rightarrow 2CuCl_2 + H_2O$

Which statement concerning the reaction is correct?

A $[PdCl_4]^{2-}$ is a homogeneous catalyst.

B Pd is a heterogeneous catalyst.

C $CuCl_2$ is an intermediate.

D $CuCl$ is a side product.

BLANK PAGE

More papers at www.testpapersfree.com