Victoria Junior College
2022 H2 Chemistry Prelim Exam 9729/1
Suggested Answers

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

1   B

	element	electronic configuration	no. of unpaired e⁻
A	Al	$1s^2 2s^2 2p^6 3s^2 3p^1$	1
	O	$1s^2 2s^2 2p^4$	2
B	B	$1s^2 2s^2 2p^1$	1
	H	$1s^1$	1
C	Cu	$[Ar]3d^{10}4s^1$	1
	I	$[Kr]4d^{10}5s^2 5p^5$	1
D	Fe	$[Ar]3d^6 4s^2$	4
	Cl	$1s^2 2s^2 2p^6 3s^2 3p^5$	1

2   D

Large dip in second I.E. from M to N → second electron removed from an outer shell in N → M is in Group 1 (Na) while N is in Group 2 (Mg).

Option A: True
L is a noble gas (Ne). It has a fully filled valence electron shell and does not form an oxide.

Option B: True
Q is silicon (Si) which has the highest melting point across period 3. Si has a giant molecular structure. Large amount of energy is required to break the strong covalent bonds.

Option C: True
The atomic radius of J (O) is larger than that of K (F). Both O and F are in the same period (similar shielding effect), but F has a greater number of protons (higher nuclear charge), hence higher effective nuclear charge, and valence electrons are pulled closer to the nucleus. So F has a smaller atomic radius than O.

Option D: False
The oxide of N (MgO) has a higher melting point than the oxide of R (P_4O_{10}).

3   B

	molecule	no. of bp	no. of lp	shape	bond angle
A	SO_2	2	1	bent	118°
	OF_2	2	2	bent	105°
B	OCS	2	0	linear	180°
	HCN	2	0	linear	180°
C	CCl_4	4	0	tetrahedral	109.5°
	XeF_4	4	2	square planar	90°
D	CS_2	2	0	linear	180°
	H_2S	2	2	bent	105°

4   A
Statement 1: Correct
In all the three allotropes, each carbon atom is covalently bonded to 3 other carbon atoms. The remaining electron is delocalised and mobile. The p orbitals of the carbon atoms overlap to form a continuous π electron cloud allowing delocalisation of electrons and conduction of electricity.

Statement 2: Incorrect
Unlike graphite, graphene and carbon nanotube do not have layers held together by weak intermolecular forces of attraction. Hence they are not slippery to be used as lubricants.

Statement 3: Incorrect
Note that both carbon allotropes are non-polar. Energy released from the formation of dipole-induced dipole interactions between carbon allotropes and water is insufficient to overcome the strong C-C covalent bonds in the carbon nanotube and graphene as well as the hydrogen bonds between water molecules.

5   A
Since G_A has a higher M_r than G_B, and mass of the two gases is the same, amount of G_A is lower than amount of G_B. For an ideal gas, pV = nRT.

Option A: Correct
At constant p, $V = \frac{nR}{p}T$.
Plotting V against T gives a straight line graph passing through the origin with constant gradient $\frac{nR}{p}$.

Option B: Incorrect
At constant T, pV = nRT = constant.
Plotting pV against V gives a horizontal line.

Option C: Incorrect
At constant T, pV = nRT = constant.
Plotting p against pV gives a vertical line.

Option D: Incorrect
At constant V, $p = \frac{nR}{V}T$.
Plotting Vp against T gives a straight line graph passing through the origin with constant gradient $\frac{nR}{V}$.

6   D
Option A: Correct
Be in $BeCl_2$ is electron deficient, hence it can accept lone pair of electrons to achieve stable octet configuration.

Option B: Correct
Ba has a lower melting point than Sr. Less energy is required to overcome the weaker metallic bonds between the larger Ba^{2+} ions and electrons than the stronger metallic bonds between the smaller Sr^{2+} ions and electrons.

Option C: Correct
Ba has more electron shells than Ca. Its valence electrons are further away from the nucleus, hence less attracted to the nucleus, and so need less energy to be removed.

Option D: Incorrect
The charge density and hence polarising power of Mg^{2+} is higher than that of Ca^{2+} since Mg^{2+} is smaller than Ca^{2+}. Hence there is a greater distortion of the anionic charge cloud and so $MgCO_3$ is less stable to heat and decomposes at a *lower* temperature than $CaCO_3$.

7　C

Option A: Incorrect
N_2H_4 is the Bronsted–Lowry base in Reaction 1 as it accepts a proton to form $N_2H_5^+$.

Option B: Incorrect
$N_2H_5^+$ and N_2H_4, as well as NH_3 and NH_4^+, are conjugate acid–base pairs.
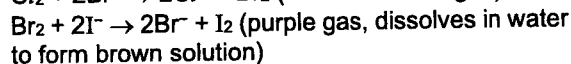
Option C: Correct
Since the POE lies to the right for both reactions, $HClO$ is a stronger acid than $N_2H_5^+$ from Reaction 1 as it prefers to donate a proton. Likewise for Reaction 2 where $N_2H_5^+$ is a stronger acid than NH_4^+.

Option D: Incorrect
N_2H_4 is a weaker base than NH_3 because in Reaction 2, the POE lies to the right.

8　A
Reactivity and oxidising power decreases down Group 17.
$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$ (reddish–brown gas)
$Br_2 + 2I^- \rightarrow 2Br^- + I_2$ (purple gas, dissolves in water to form brown solution)

9　C

	C_xH_y +	$(x+\frac{y}{4})O_2$	$\rightarrow$	xCO_2 +	$\frac{y}{2}H_2O$
Initial volume	10	90		0	
Change in volume	−10	$-10(x+\frac{y}{4})$		+30	
End volume	0	40		30	

$x = 3$
$90 - 10(x+\frac{y}{4}) = 40 \rightarrow y = 8$
Hence formula is C_3H_8.

10　D
Amount of $TeO_2 = \frac{1.01}{159.6} = 0.00633$ mol
Amount of $K_2Cr_2O_7 = 0.070 \times \frac{30}{1000} = 0.0021$ mol
Since solution changes from orange ($Cr_2O_7^{2-}$) to green (Cr^{3+}), $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$,
amount of electrons = $6 \times 0.0021 = 0.0126$ mol

$\frac{amount\ of\ e^-}{amount\ of\ TeO_2} = \frac{0.0126}{0.00633} = 2$
Oxidation state of Te in TeO_2 = +4
Since 1 mol of TeO_2 loses 2 mol of e^- in the reaction, oxidation state of Te in product = +6

11　B

$$Ca(s) + 2H_2O(l) \xrightarrow{\Delta H_r} Ca(OH)_2(s) + H_2(g);$$

$2\Delta H_f(H_2O)$ ↘　　↗ $\Delta H_f(Ca(OH)_2$

$$Ca(s) + 2H_2(g) + O_2(g)$$
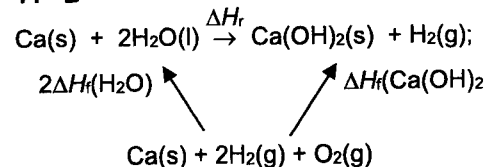
By Hess Law,
$\Delta H_f(Ca(OH)_2) = 2\Delta H_f(H_2O) + \Delta H_r$
$= 2\Delta H_c(H_2) + \Delta H_r$
Hence, other than ΔH_r, enthalpy change of combustion of hydrogen is needed.

12　C
Option A (Wrong)
$\Delta S > 0$ and $\Delta H > 0$
$\Delta G = \Delta H - T\Delta S < 0$ for large T only.
Option B (Wrong)
$\Delta S < 0$ and $\Delta H < 0$
$\Delta G = \Delta H - T\Delta S < 0$ for small T only.
Option C (Correct)
$\Delta S > 0$ and $\Delta H < 0$
$\Delta G = \Delta H - T\Delta S < 0$ for all T.
Option D (Wrong)
$\Delta S < 0$ and $\Delta H > 0$
$\Delta G = \Delta H - T\Delta S > 0$ for all T.

13　A
Rate law is determined by slow step in proposed mechanism, i.e. Rate = $k'[O_3][O]$.
This rate law cannot be compared directly with the experimental rate equation because it contains the concentration of an intermediate, O. Thus we need to express rate law in a way that removes the intermediate O.
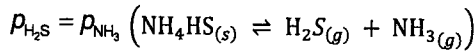From Step 1,
$K = [O_2][O]/[O_3] \Rightarrow [O] = K[O_3]/[O_2]$
Assuming that Step 1 equilibrium is established quickly before O is reacted with O_3 in Step 2,
Rate = $k'[O_3][O]$
$= k'K[O_3]^2/[O_2]$
$= k[O_3]^2/[O_2]$ where $k = k'K$

14   B

$$p_{H_2S} = p_{NH_3} \left(NH_4HS_{(s)} \rightleftharpoons H_2S_{(g)} + NH_{3(g)} \right)$$

Thus, $p_{H_2S} = p_{NH_3} = \frac{1}{2} \times 66.4 = 33.2$ kPa

1 $K_p = p_{H_2S} \times p_{NH_3} = (33.2)^2 \approx 1100 (kPa)^2$

2 Removal of H₂S will cause more NH₄HS to dissociate forming not only H₂S but also NH₃. Hence total pressure will increase.

3 Addition or removal of a solid has no effect on the position of equilibrium so long as there is still solid present.

15   B

A HA/A⁻ buffer with maximum buffer capacity will have its pH = pKₐ of HA.

So, pKₐ of HA = 6.38
=> pKᵦ of A⁻ = 14 – pKa = 7.62

Hence, H_2CO_3 / HCO_3^- can be used to prepare a buffer of pH 6.28 with maximum buffer capacity.
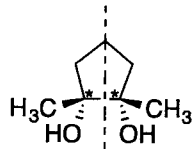
16   C

Stage **I** : oxidation of 2° alcohol to ketone
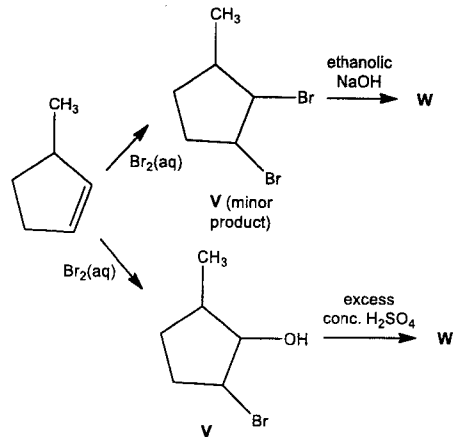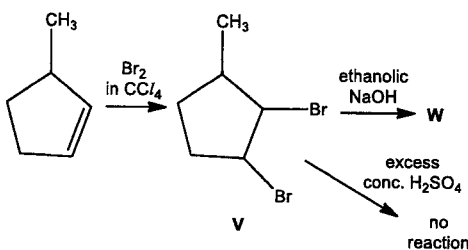Stage **II** : *nucleophilic* :OH⁻ *substitutes* for the –CI₃ group
Stage **III** : *basic* :CI₃⁻ abstracts a *proton* from the *acid* RCO₂H

17   C

While all 3 compounds have 2 chiral centres, the compound in option one has a plane of symmetry and is hence not optically active.
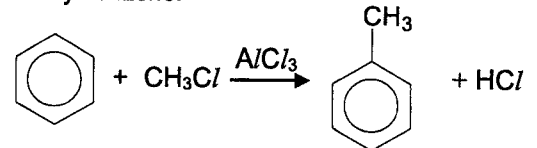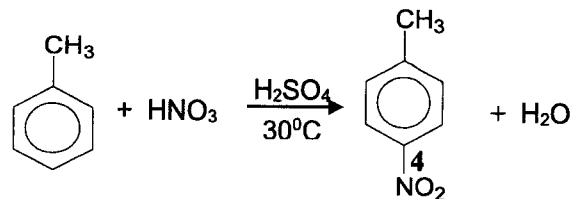

18   B

19   B

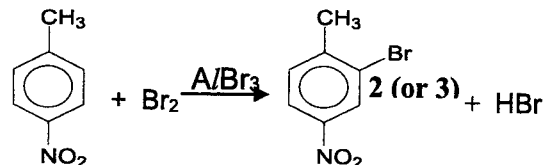Step 1: Alkylation of benzene to form methylbenzene:

Step 2: Nitration of methylbenzene to give 2–nitromethylbenzene and 4–nitromethylbenzene since –CH₃ group is 2,4–director.

For the formation of 4-nitroomethylbenzene:

Step 3: Bromination of 4–nitromethylbenzene to give 2–bromo–4–nitromethylbenzene since –CH₃ group is 2,4–director while –NO₂ group is 3–director.

20   D

Option A (incorrect)

C–Br bond in C₆H₅Br experiences partial double bond character, due to overlap of lone pair of electrons of Br with the pi electrons of the benzene ring. Hydrolysis does not take place hence no ppt is formed.

Option B (incorrect)

Silver iodide has a very low K_{sp}. The precipitate is insoluble in both aqueous and concentrated NH₃.

4

Option C (incorrect)

C–Cl bond in CH$_2$=CHCl experiences partial double bond character, due to overlap of lone pair of electrons of Cl with the pi electrons of the C=C. Hydrolysis does not take place hence no ppt is formed.

Option D (correct)

Only CH$_3$CH$_2$I and CH$_3$COCl undergo hydrolysis.
1 mole of organic compound will give 1 mole of AgX.
No. of moles of AgI = No. of moles of CH$_3$CH$_2$I
$$= 0.5 \div (12.0\times2+5.0+126.9)$$
$$= 3.21 \times 10^{-3} \text{ mol}$$
Mass of AgI = $3.21 \times 10^{-3} \times (107.9+126.9)$
$$= 0.754 \text{ g}$$
No. of moles of AgCl = No. of moles of CH$_3$COCl
$$= 0.5 \div (12.0\times2+3+16.0+35.5)$$
$$= 6.37 \times 10^{-3} \text{ mol}$$
Mass of AgCl = $6.37 \times 10^{-3} \times (107.9+35.5)$
$$= 0.914 \text{ g}$$

21   A

Among the alcohols formed, only 1° and 2° alcohols can be oxidised.

Butanone
Mr: 72

Butanoic acid
Mr: 88

2-methylpropanoic acid
Mr: 88
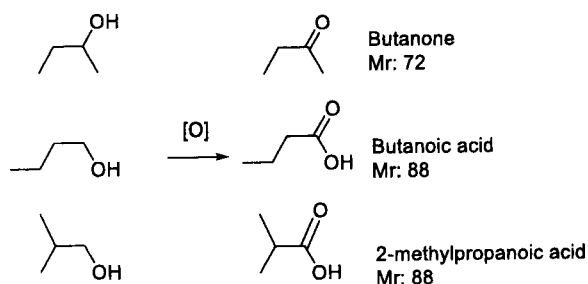
Mole of C$_4$H$_{10}$O that has reacted = $\frac{65}{74}$ = 0.878 mol
Since yield is 55%, moles of product formed will be $\frac{55}{100} \times 0.878$ = 0.483 mol
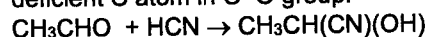Mass of butanone: 0.483×72 = 34.8 g
Mass of butanoic acid: 0.483×88 = 42.5 g
Mass of 2-methylpropanoic acid:
0.483×88 = 42.5

22   A

Ethanal undergoes nucleophilic addition with HCN whereby CN$^-$ acts as nucleophile which attacks e deficient C atom in C=O group:
CH$_3$CHO + HCN → CH$_3$CH(CN)(OH)
Similarly, $^-$CH$_2$COCH$_3$ from CH$_3$COCH$_3$ can also act as a nucleophile like CN$^-$ (from HCN) and attacks e$^-$ deficient C in C=O group of CH$_3$CHO to form CH$_3$CH(OH)(CH$_2$COCH$_3$)

23   C

Molecular formula of **X** suggests it is an alcohol. However as it can be oxidised to carboxylic acid **Y**, **X** has to be a primary alcohol.
Condensation reaction between carboxylic **Y** and butan-2-ol produces an ester **Z**.
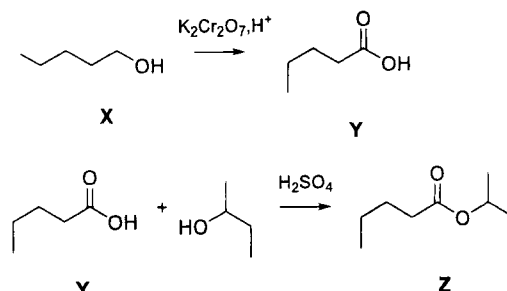
24   C

Option 1 is incorrect: As the alkyl chain of fatty acid has the formula R–C$_{15}$H$_{27}$, it would contain C=C bonds, hence it is unsaturated.

Option 2 is correct: condensation between alcohol and carboxylic acid to form ester.
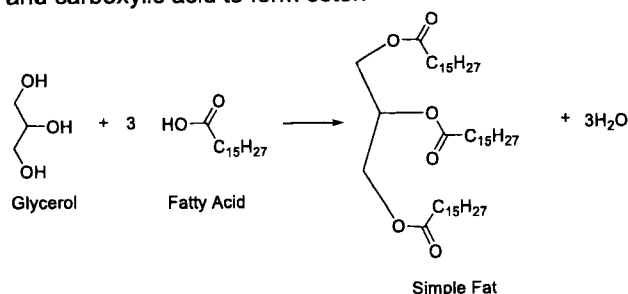
Option 3 is correct:

25 D

$C_{14}H_{20}NO_4Cl$

26 D

A is incorrect: Amide undergoes reduction with $LiAlH_4$ to give amine. The O in C=O will be replaced with 2 hydrogen atoms and hence W has 2 more H atoms than lidocaine.

B is incorrect: Lidocaine undergoes base hydrolysis with NaOH(aq) to form an amine and a carboxylate salt as the products present in Y.

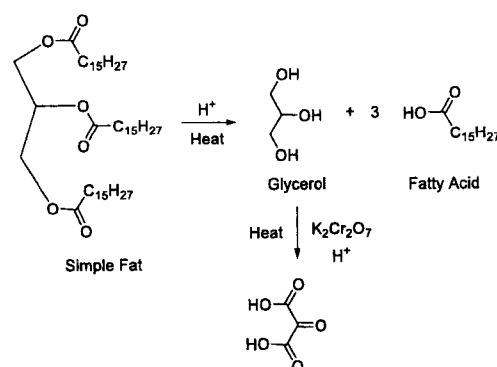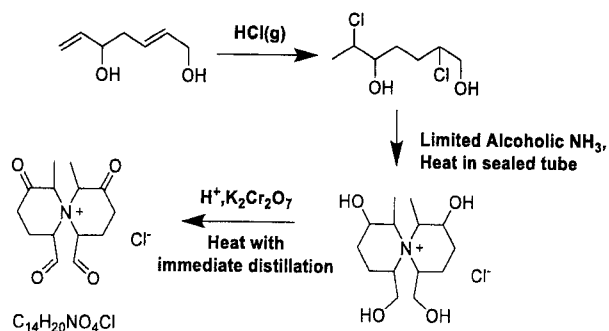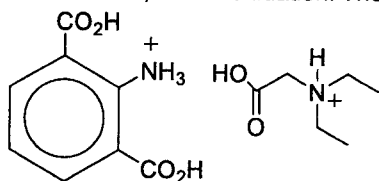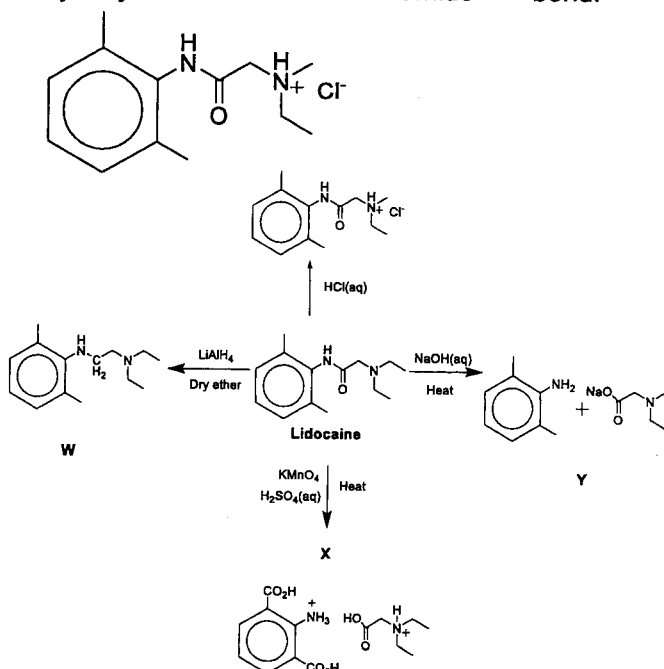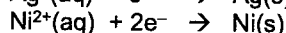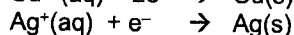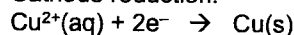**C is incorrect:** Reagents provided will result in acidic hydrolysis to occur first, before oxidation. The structure of X is

D is correct: No heating involved, therefore only an acid base reaction has occurred without hydrolysis of the amide bond.

27 D

Cathode reduction:
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
$Ag^+(aq) + e^- \rightarrow Ag(s)$
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$
Since the same current will flow through all the circuit.
Ratio of amount of Cu : Ag : Ni formed will be 1:2:1
Ratio of mass of Cu : Ag : Ni formed will be

Mass of Cu	Mass of Ag	Mass of Ni
1 (63.5)	2 (107.9)	1 (58.7)
63.5	215.8	58.7
1.08	3.68	1.00

28 C

From the E^o values for the half cells, H_2O_2 will be reduced while I^- will be oxidised.
Therefore the two half equations to be used will be:
$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$ +0.54V
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$ +1.77V
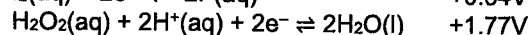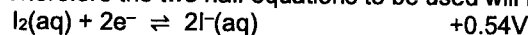
E^o cell $= E^o_{Red} - E^o_{Oxi} = +1.77 - (+0.54)$
$= + 1.23\,V > 0$
Overall equation for the reaction
$2I^- + H_2O_2(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$
            brown solution
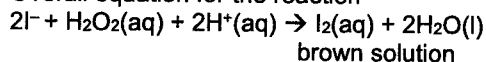
29 C

A is incorrect: Each of the three OH^- ions in $[Cr(H_2O)_3(OH)_3]$ each accepts a proton to form $[Cr(H_2O)_6]^{3+}$. $[Cr(H_2O)_3(OH)_3]$ acts as a Bronsted—Lowry base (proton acceptor) in reaction 1.

B is incorrect: For both reactions, no ligand exchange reactions are occurring. Reaction 1 involves the protonation of the OH^- ions, while reaction 2 involves the deprotonation of three water molecules to from three OH^- ions.

C is correct: For reaction 1, $[Cr(H_2O)_3(OH)_3]$ is behaving as a Bronsted—Lowry base by accepting protons. For reaction 2, $[Cr(H_2O)_3(OH)_3]$ is behaving as a Bronsted—Lowry acid by donating protons to form OH^- ions.

D is incorrect: For both reactions, no change in oxidation number of chromium (+3).

30 B

Since 2 mol of AgCl is formed from 1 mol of the compound, there are 2 mol of free Cl^- ions that are not ligands, and the complex ion has one chloride ligand.
So the compound is $[Co(H_2O)_5Cl]Cl_2.H_2O$

VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE
NAME ....

CT GROUP ....

CHEMISTRY

9729/02

Paper 2 Structured Questions

15 September 2022

Candidates answer on the Question Paper.

2 hours

Additional Materials: *Data Booklet*

READ THESE INSTRUCTIONS FIRST

Write your name and CT group in the space at the top of this page.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

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

A Data Booklet is provided.

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

For Examiner's Use	
1	/ 25
2	/ 13
3	/ 12
4	/ 19
5	/ 6
Total	/ 75

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1 (a) The most common oxidation states of iron are +2 and +3.

(i) Iron(II) and iron(III) both contain electrons in all five 3d orbitals.

Sketch and label the shape of the following two 3d orbitals:

- one 3d orbital from the lower energy level in an octahedral complex
- one 3d orbital from the higher energy level in an octahedral complex

Use the axes below.
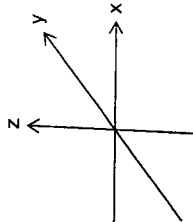
lower energy level
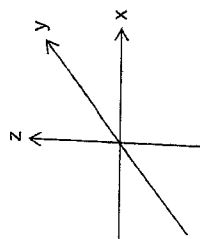
higher energy level

[2]

- **Lower energy level (in between axes)**

$3d_{xy}$ $3d_{xz}$ $3d_{yz}$
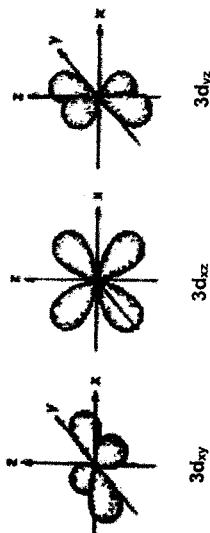
- **Higher energy level (on the axes)**

$3d_{x^2-y^2}$ $3d_{z^2}$
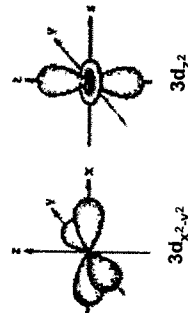
(ii) Explain why $Fe^{2+}(aq)$ ions are coloured, whereas $Zn^{2+}(aq)$ ions are colourless.

- The <u>degenerate</u> <u>3d orbitals</u> in Fe^{2+} octahedral complex is split into <u>2 different</u> <u>energy levels</u> due to the presence of water <u>ligands</u>.
- <u>d-d transition</u> took place whereby a 3d electron from the lower energy level is <u>promoted</u> to the upper energy level by <u>absorbing energy</u> from the <u>visible region</u> of the electromagnetic spectrum. The colour seen is the <u>complement of the colour</u> absorbed.
- Fe^{2+} has a partially-filled d subshell but Zn^{2+} has <u>completely filled 3d subshell and</u> so <u>d-d transition</u> whereby an electron is promoted from a lower energy level to a higher energy level is <u>impossible</u>.

[3]

3

(iii) Most naturally occurring samples of iron(II) oxide are found as the mineral wüstite. Wüstite has formula $Fe_{20}O_x$. It contains both Fe^{2+} and Fe^{3+} ions. 90% of the iron is present as Fe^{2+} and 10% is present as Fe^{3+}.

Deduce the value of x.

- $20 \times [0.9(+2) + 0.1(+3)] - 2x = 0$
- $x = 21$

[1]

When aqueous solutions of $S_2O_8^{2-}$ and tartrate ions, $C_4H_4O_6^{2-}$, are mixed, the reaction proceeds very slowly. However, this reaction proceeds quickly in the presence of an Fe^{3+}(aq) catalyst. The overall equation for this reaction is as shown.

$$C_4H_4O_6^{2-} + 3S_2O_8^{2-} + 2H_2O \rightarrow 2CO_2 + 2HCO_2^- + 6H^+ + 6SO_4^{2-}$$

(iv) State and explain the type of catalyst that Fe^{3+}(aq) functions in the above reaction.

- **Fe^{3+}(aq) is a <u>homogeneous</u> catalyst in this reaction <u>as it has the same physical state (OR phase) as the reactants.</u>**

[1]

(v) Write two equations to show how Fe^{3+}(aq) functions as a catalyst in this reaction.

- **$6Fe^{3+} + C_4H_4O_6^{2-} + 2H_2O \rightarrow 6Fe^{2+} + 2CO_2 + 2HCO_2^- + 6H^+$**
- **$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$**

[2]

(b) (i) Complete the 'dot-and-cross' diagram below, drawing the outer electrons only, to show the bonding in methanoic acid, HCO_2H. The two oxygen atoms in HCO_2H are labelled O^1 and O^2 respectively.

[2]

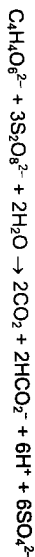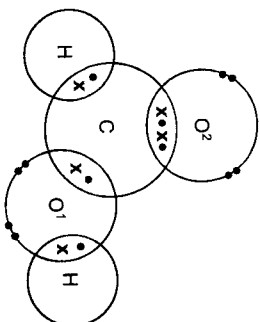(ii) The carbon atom in HCO_2H is sp² hybridised. Explain what is meant by sp² hybridisation with reference to the carbon atom in HCO_2H.

- **In sp² hybridisation, one 2s and two 2p orbitals of carbon are mixed to form three equivalent sp² hybrid orbitals that are arranged 120° apart.**

[1]

4

(iii) Similar to carbon, oxygen atom can also undergo hybridisation. By considering the number of electron densities around oxygen atom labelled O^1, suggest the type of hybridised orbitals for the oxygen atom labelled O^1.

- **sp³**

[1]

(iv) Sketch a diagram to show how two sp² hybridised orbitals can form a sigma bond.

OR
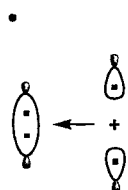
[1]

(c) Cyclohexane is immiscible with water. Iodine, I_2, can dissolve in both water and cyclohexane. The expression and numerical value for the partition coefficient, K_{pc}, of iodine between cyclohexane and water are given below.

$$K_{pc} = \frac{\text{concentration of } I_2 \text{ in cyclohexane}}{\text{concentration of } I_2 \text{ in water}} = 93.8$$

(i) 15.0 cm³ of C_6H_{12} is shaken with 20.0 cm³ of an aqueous solution containing I_2 until no further change is seen. It is found that 0.390 g of I_2 is extracted from water into the C_6H_{12}. Calculate the mass of I_2 that remains in the aqueous layer. Show your working.

Let mass of I_2 that remains in the aqueous layer be x g.

$$K_{pc} = \frac{\text{concentration of } I_2 \text{ in cyclohexane}}{\text{concentration of } I_2 \text{ in water}}$$

- $93.8 = (0.390/15) \div (x/20)$
- $x = 5.54 \times 10^{-3}$ g

[2]

(ii) Suggest how the value of K_{pc} of I_2 between hexan-2-one, $CH_3(CH_2)_3COCH_3$, and water would compare to the value given in (c). Explain your answer.

- **K_{pc} of I_2 between hexan-2-one and water would be <u>lower than 93.8.</u>**
- **Iodine being <u>non-polar</u> would be <u>less soluble</u> in hexa-2-one which is a <u>polar solvent</u>.**
- **Hence <u>concentration of I_2</u> in hexa-2-one would be <u>lesser than in cyclohexane</u> in the presence of water.**

[2]

(d) Some data relating to calcium and oxygen are listed in table 1.1.

Table 1.1

process	value / kJ mol⁻¹
first ionisation energy of oxygen	+1310
second ionisation energy of oxygen	+3390
first electron affinity of oxygen	−142
second electron affinity of oxygen	+844
enthalpy change for $\frac{1}{2}O_2(g) + 2e^- \rightarrow O^{2-}(g)$	+951
enthalpy change for $Ca(s) \rightarrow Ca^{2+}(g) + 2e^-$	+1933
lattice energy of CaO(s)	−3517

(i) Suggest why the first electron affinity of oxygen is negative.

• First electron affinity of oxygen is negative (or exothermic) due to energy released from the <u>attraction between the nucleus (or protons)</u> of the gaseous oxygen atom <u>and the incoming electron.</u>   [1]

(ii) Suggest why the second electron affinity of oxygen is positive.

• Second electron affinity of oxygen is positive (or endothermic) due to energy needed to overcome the <u>repulsion between the negatively charged O^- ion and the incoming electron.</u>   [1]

(iii) Oxygen exists as O_2 molecules. Use relevant data from table 1.1 to calculate the bond energy of the O=O bond. Show your working.

$$\frac{1}{2}O_2(g) + 2e^- \xrightarrow{+951} O^{2-}(g)$$
$$\frac{1}{2}BE(O=O) \qquad -142 + (+844)$$
$$O(g) + 2e^-$$
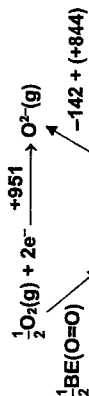
• $\frac{1}{2}BE(O=O) -142 + (+844)= +951$
• $\frac{1}{2}BE(O=O) = 249$
• $BE(O=O) = 498$ kJ mol⁻¹   [2]

(iv) Use relevant data from table 1.1 to calculate the enthalpy change of formation of calcium oxide, CaO(s). Show your working.

$$Ca(s) + \frac{1}{2}O_2(g) \xrightarrow{\Delta H_f} CaO(s)$$
$$+1933 + 951 \qquad\qquad -3517$$
$$Ca^{2+}(g) + O^{2-}(g)$$
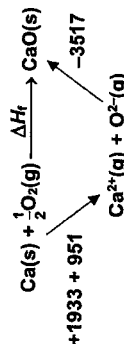
• $\Delta H_f = +1933 + 951 - 3517$
• $\Delta H_f = -633$ kJ mol⁻¹   [2]

(v) The lattice energy of lithium fluoride, LiF(s), is −1022 kJ mol⁻¹. Identify the factor that causes the lattice energy of calcium oxide to be more exothermic than that of lithium fluoride. Explain why this factor causes the difference in lattice energies.

• It is the <u>ionic charge</u> of the ions causes the lattice energy of CaO to be more exothermic than that of LiF.
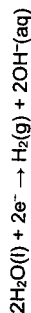
• $|LE| \propto \left|\dfrac{q_+q_-}{r_+ + r_-}\right|$

• Since the <u>charge</u> of each ion in CaO is <u>twice</u> of that in LiF, the lattice energy of CaO is more exothermic than LiF.   [2]
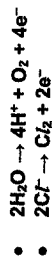
[Total: 25]

2 (a) Chlorine can be manufactured using the electrolysis of NaCl(aq). At the cathode, H₂(g) and OH⁻(aq) are produced. At the anode, the product mixture contains both $Cl_2(g)$ and $O_2(g)$. The mole ratio of each gas depends on the concentration of NaCl(aq).

(i) The half-equation for the cathode reaction is as shown.

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$

Starting from neutral NaCl(aq), write half-equations for the production of the following at the anode.

• $O_2(g)$,
• $Cl_2(g)$.

• $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$
• $2Cl^- \rightarrow Cl_2 + 2e^-$ [2]

(ii) Explain why the $Cl_2(g)$: $O_2(g)$ mole ratio increases as concentration of NaCl(aq) increases.

$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $E^\circ(Cl_2|Cl^-) = +1.36$ V;
$E^\circ(O_2|H_2O) = +1.23$ V
• The higher concentration of chloride ions <u>will shift the equilibrium position to the left</u>, making the <u>oxidation of Cl^-(aq) to Cl_2(g) to be more favourable</u>.
• Hence, the <u>electrode potential</u> $E(Cl_2|Cl^-)$ will fall and more Cl^- will be oxidised to give Cl_2 thus the mole ratio of $Cl_2(g)$:$O_2(g)$ will increase.   [2]

7

(iii) Sodium chlorate(V) is prepared commercially by electrolysing NaCl(aq) in a cell that allows the electrolytes at cathode and anode to mix. The equation for the anode reaction is the same as that described in **(i)**. The cathode reaction is as shown.

$$Cl^-(aq) + 6OH^-(aq) \rightarrow ClO_3^-(aq) + 3H_2O(l) + 6e^-$$
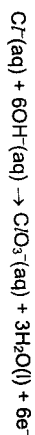
Calculate the mass of $NaClO_3$ that is produced when a current of 250 A is passed through the cell for 60 minutes.

• **Quantity of charge** $= 250 \times 60 \times 60 = 9.00 \times 10^5$ C
• **Amount of electrons transferred** $= \dfrac{9.00 \times 10^5}{96500} = 9.33$ mol
• **Amount of chlorate ions formed** $= \dfrac{9.33}{6} = 1.55$ mol
• **Mass of sodium chlorate formed** $= 1.55 \times 106.5 = 166$ g

[2]

(b) Trimethylphosphine can act as a ligand, which can be represented as PR₃. Chromium hexacarbonyl undergoes the following ligand exchange reaction with PR₃ as shown below.

$$Cr(CO)_6 + PR_3 \rightarrow Cr(CO)_5PR_3 + CO$$
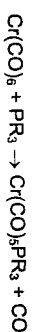
Two separate experiments were carried out to study the rate of this reaction.

In the first experiment, the ligand PR₃ was in a large excess and [Cr(CO)₆] was measured with time. The results are shown on the graph below whereby the y-axis represents the concentration of Cr(CO)₆.

8
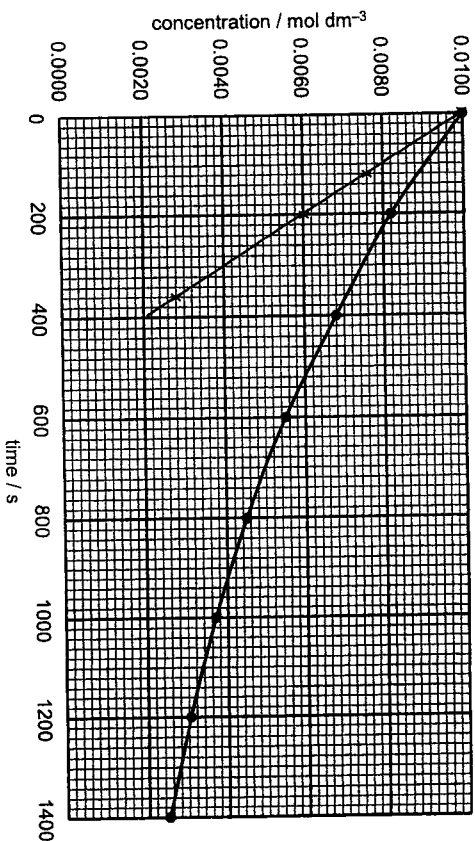
In the second experiment, Cr(CO)₆ was in a large excess, and [PR₃] was measured with time. Table 2.1 shows the results obtained.

Table 2.1

time / s	[PR₃] / mol dm⁻³
0	0.0100
120	0.0076
200	0.0060
360	0.0028

(i) Plot the data given in Table 2.1 on the graph above, using the same axis scales whereby the y-axis represents the concentration of PR₃. Draw the best-fit line through your points.

• **straight line from (0, 0.01) to point at (350, 0.0028) with all points on the line.** [1]

(ii) Use the graphs to determine the order of reaction with respect to Cr(CO)₆ and PR₃. Explain how you arrived at your answer.

• **Order w.r.t. Cr(CO)₆ is one**
• The graph for Cr(CO)₆ has a **constant half-life of 700**
• **Order w.r.t. PR₃ is zero.**
• The graph for PR₃ is a **straight line of constant gradient, hence rate of reaction is constant at any concentration of PR₃.** [2]

(iii) Define the term *rate equation*.

• **The rate equation relates the rate of reaction to the concentration of the reactants and is determined experimentally** [1]

(iv) Write the rate equation for the reaction and calculate the rate constant including its units.

• **rate = k[Cr(CO)₆] (ecf from (ii))**
• **k = $\dfrac{\ln 2}{t_{1/2}} = \dfrac{0.693}{700} = 9.90 \times 10^{-3}$ s⁻¹** [3]

[Total: 13]

3 (a) The chemistry of some period 3 elements and their compounds are discussed here.

(i) Explain why the first ionisation energy of aluminium is lower than that of magnesium.

- The 3p electron to be removed from Al is at a <u>higher energy level</u> than the 3s electron to be removed from Mg. Hence <u>less energy is required to remove the 3p electron in Al</u> than the 3s electron in Mg and so the first ionisation energy of Al is lower than that of Mg [1]

Table 3.1 shows some information regarding three oxides, **E**, **F** and **G**.

Table 3.1

oxide	melting point / °C	electrical conductivity when molten
E	1713	very poor
F	24	nil
G	2072	good

(ii) These three oxides, in no particular order, are Al_2O_3, SiO_2 and P_4O_6. Identify **E**, **F** and **G**.

- **E:** SiO_2 **F:** P_4O_6 **G:** Al_2O_3 [1]

(iii) With reference to structure and bonding, account for your answer in **(a)(ii)**.

- **E** is SiO_2 which has a <u>giant molecular structure with strong covalent bonds between its atoms</u> resulting in its high melting point. It conducts electricity poorly as there are <u>no charged particles in the molten state</u>.
- **F** is P_4O_6 which is a <u>simple covalent molecule with weak intermolecular forces of attraction</u> resulting in its low melting point. It does not conduct electricity as there are <u>no charged particles in the molten state</u>.
- **G** is Al_2O_3 which has <u>giant ionic lattice structure with strong electrostatic forces of attraction between its cations and anions</u> resulting in its high melting point. It conducts electricity in the molten state as its <u>ions become mobile</u>. [3]

(iv) Suggest the pH values of the mixture formed when **E**, **F** and **G** are added separately to water. Write balanced equations for each of these reactions, where appropriate.

- The pH values for solutions of E, F and G are 7, 2 – 3 and 7 respectively.
- $P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$ [2]

(v) Aluminium oxide is *amphoteric*. With the aid of equations, explain the meaning of the term *amphoteric*.

- <u>Aluminium oxide is amphoteric as it can react with both acids and bases.</u>
- $Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$
- $Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2[Al(OH)_4]^-$ [2]

(b) The nitrates of strontium and barium decompose on heating, forming the same gaseous products.

Explain whether strontium nitrate would decompose at a higher or lower temperature than barium nitrate.

- Although both ions have the <u>same charge</u> of +2, Sr^{2+} ions have <u>higher charge density than</u> Ba^{2+} ions due to its <u>smaller ionic radius.</u>
- Sr^{2+} is able to polarise and <u>distort the electron cloud of NO_3^- to a larger extent,</u> leading to <u>lower thermal stability.</u> $Sr(NO_3)_2$ will decompose at <u>a lower temperature.</u> [2]
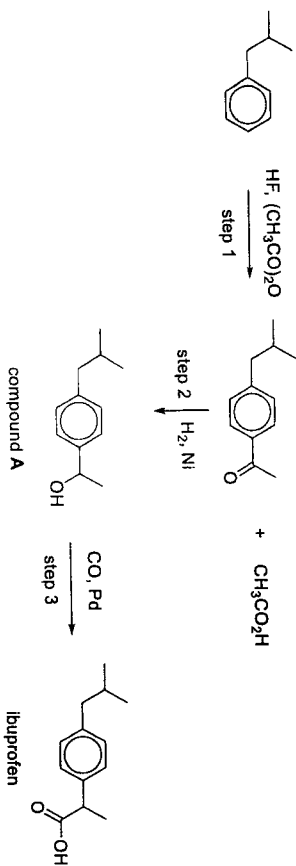
(c) Hydrogen chloride is stable to heat while hydrogen iodide decomposes to hydrogen and iodine when heated with a red-hot steel. Explain why this is so.

- The <u>bond energy of H–Cl is higher</u> than that of H-I due to its <u>smaller atomic radius</u> compared with that of iodine. Hence it is difficult for HCl to undergo thermal decomposition. [1]

[Total: 12]

4 Ibuprofen, $C_{13}H_{18}O_2$, a non-steroidal anti-inflammatory drug, is used for the treatment of pain, fever and inflammation.

(a) The industrial synthesis of ibuprofen developed by BHC Company in the 1980s is shown below. This synthetic route proved to be highly successful in terms of its environmental friendliness.

HF, $(CH_3CO)_2O$ step 1 →

step 2 H_2, Ni

compound **A** + CH_3CO_2H

step 3 CO, Pd → ibuprofen

The atom economy of a process can be calculated using the formula:

$$\text{atom economy} = \frac{\text{molar mass of desired product}}{\text{sum of molar mass of all products}}$$

(i) Calculate the atom economy of the BHC Company process in the synthesis of ibuprofen.

Molar mass of ibuprofen = $12.0 \times 13 + 1.0 \times 18 + 16.0 \times 2 = 206$ g mol^{-1}
Molar mass of ethanoic acid = 60.0 g mol^{-1}

Atom economy = $\frac{206}{206+60}$ = 0.774

An environmentally friendly chemical process is expected to have a high atom economy, indicating that a high proportion of the starting materials end up as part of the final product, hence reducing the amount of waste.

(ii) Suggest the type of reaction in step 1.

• **Electrophilic substitution** [1]

(iii) Outline a simple chemical test that could be carried out to distinguish compound **A** from ibuprofen.

• **Add NaCO₃(s) to both compounds.**
• **Only ibuprofen gives effervescence of CO₂ but compound A does not.**
OR
• **Heat both compounds with K₂Cr₂O₇, H₂SO₄(aq).**
• **Only compound A turns orange solution to green but ibuprofen does not.**
OR
• **Warm both compounds with I₂ in NaOH(aq).**
• **Only compound A forms pale yellow precipitate but ibuprofen does not.** [2]

[Turn over

(iv) Ethanoic anhydride, $(CH_3CO)_2O$, used in step 1 could be regenerated by dehydrating ethanoic acid. In this reaction, 2 mol of ethanoic acid form 1 mol of ethanoic anhydride and 1 mol of water.

Determine the new atom economy if ethanoic acid formed in step 1 is reused in this synthesis.

For every two moles of ibuprofen formed, there are two moles of ethanoic acid formed.
2 mol of CH₃CO₂H will produce 1 mol of water.

• **New atom economy would be $\frac{206 \times 2}{206 \times 2 + 18}$ = 0.958** [1]

(b) Instead of step 3 in **(a)**, compound **A** formed during the BHC Company process can react with PCl₅ to give compound **B** which then undergoes further reactions to yield ibuprofen.

compound **A** + PCl_5 → reaction I → compound **B** + Cl-P...+ HCl
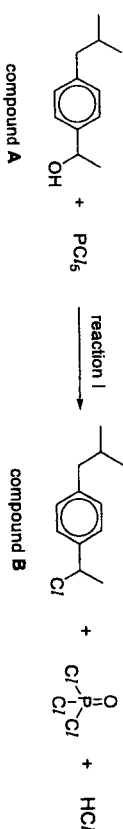
The mechanism of converting compound **A** into compound **B** is thought to involve the following three steps.

• The initial nucleophilic attack on P by the lone pair of electrons on the oxygen atom in compound **A** to form a P–O bond together with a loss of Cl⁻.
• This is followed by Cl⁻ acting as a base to abstract a proton.
• The third step involves a nucleophilic attack on a carbon atom by another Cl⁻ ion together with simultaneous P=O bond formation and P–Cl bond cleavage to form the products.

(i) Use the information given above to draw out the three-step full mechanism for the reaction of compound **A** with PCl₅. Show relevant lone pairs and dipoles and use curly arrows to indicate the movement of electron pairs.

You may use R to represent the

[3]

[Turn over

Tests	observations		
	HCHO	CH$_3$CHO	CH$_3$COCH$_3$
Add Tollens' reagent and heat	Silver Mirror formed	Silver Mirror formed	No silver Mirror formed
OR Add Fehling's reagent and heat	Brick-red ppt formed	Brick-red ppt formed	No brick-red ppt formed
OR Add K$_2$Cr$_2$O$_7$(aq), H$_2$SO$_4$(aq) and heat	Orange solution turns green	Orange solution turns green	Orange solution did not turn green
OR Add KMnO$_4$(aq), H$_2$SO$_4$(aq) and heat	Purple solution decolourised with effervescence of CO$_2$ which forms white ppt in limewater	Purple solution decolourised	Solution remains purple
Add I$_2$(aq), NaOH(aq) and heat	No pale yellow ppt. formed	Pale yellow ppt. formed	Pale yellow ppt. formed

[3]

[Total: 19]

(ii) Considering the bonds formed in the products, suggest a reason why reaction I goes to completion.

- The high bond energy / strength of P=O bond that is formed makes the reaction **highly exothermic.**
- Hence, ΔG of the reaction can be <u>very negative leading to a large K_c value so the reaction I goes to completion.</u>

[2]

(iii) Complete the reaction scheme to show how ibuprofen could be synthesised from compound **B** in two steps. Draw the structure of the intermediate and state the reagents and conditions for each step.

compound **B**

intermediate compound

reaction III → ibuprofen

reaction	reagents and conditions
II	Ethanolic KCN, heat
III	H$_2$SO$_4$(aq), heat
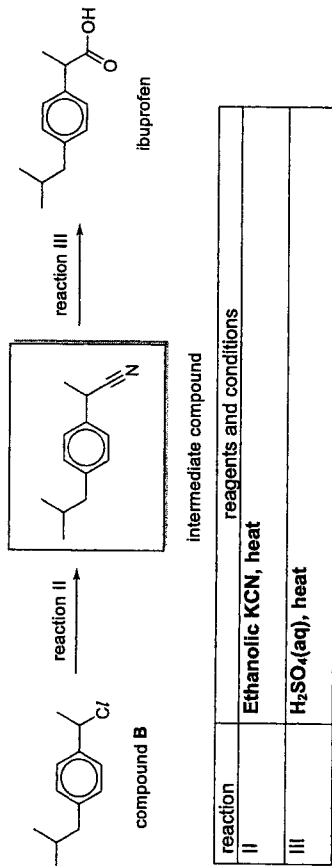
[3]

(c) When Group 2 salts of carboxylic acids are heated, it gives the metal carbonate and a carbonyl compound. For example, when calcium ethanoate is heated, it produces propanone.

$$(CH_3CO_2)_2Ca \rightarrow CaCO_3 + (CH_3)_2CO$$
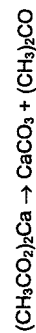
When this reaction is carried out by heating a 1:1 molar mixture of calcium ethanoate and calcium methanoate, (HCO$_2$)$_2$Ca, a mixture of three carbonyl compounds is formed, all having M_r < 60.

(i) Suggest the structures of the three carbonyl compounds and the ratio in which they might be produced.

Structure of carbonyl compound	HCHO	CH$_3$CHO	CH$_3$COCH$_3$
Ratio	1	2	1

[2]

(ii) Suggest **two** chemical tests that could be used to distinguish the three carbonyl compounds from each other. You should state what you would observe for each compound in each test.

[Turn over

[Turn over

5(a) Table 5.1 shows some information about the elements, calcium, iron and copper.

Table 5.1

	calcium	iron	copper
Relative atomic mass	40.1	55.8	63.5
Atomic radius (metallic) / nm	0.197	0.126	0.128
Ionic radius (2+) / nm	0.099	0.076	0.069
Melting point / K	1112	1808	1358
Density / g cm⁻³	1.54	7.86	8.93

(i) Describe the structure and bonding in calcium with the aid of a labelled diagram.
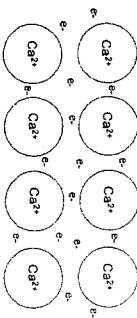
- Ca^{2+} cations are arranged in a <u>giant metallic structure held by strong electrostatic forces of attraction between the delocalised electrons and the cations</u>.

[2]

(ii) Suggest why the atomic radii of iron and copper are both smaller than that of calcium.

- The <u>nuclear charge</u> of both Fe and Cu are <u>higher than that of Ca</u> due to <u>greater number of protons.</u> Though Fe and Cu have greater number of inner electrons, <u>the shielding effect of d electrons in the penultimate subshells of Fe and Cu is not as effective.</u>
- Hence the <u>effective nuclear charge of Fe and Cu are higher</u>, leading to smaller atomic radii than that of Ca.

[2]

(iii) Use information from Table 5.1 to explain why the densities of iron and copper are significantly greater than that of calcium. [No calculations are required.]

- Both Fe and Cu have <u>smaller atomic radius</u> than Ca, hence Fe and Cu can be <u>packed more closely together</u> in a metallic lattice.
- Fe and Cu also have <u>higher relative atomic mass</u> than Ca. This leads to a high mass per unit volume ratio (density).

[2]

[Total: 6]

VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE
NAME   ....

CT GROUP   ....

CHEMISTRY   9729/03

Paper 3 Free Response   19 September 2022

                                             2 hours

Candidates answer on the Question Paper.
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.
Write in dark blue or black pen.
You may use a soft 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. If additional space is required, you should use the pages provided at the end of this booklet. The question number must be clearly shown.

Section A
Answer all questions.

Section B   [2]
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		
Section A	1	/ 18
	2	/ 22
	3	/ 20
Section B	4 OR 5	/ 20
	Total	/ 80

This document consists of **25 printed pages**.


Section A

Answer all the questions in this section.

1 (a) (i) Under what conditions of temperature and pressure would you expect the behaviour of a real gas to be most like that of an ideal gas?   [1]

* **High temperature and low pressure**

(ii) Barium ethanedioate, BaC_2O_4, decomposes on heating to produce a mixture of two different gases, **A** and **B**, and an oxide only.

Neither gas **A** nor gas **B** is an ideal gas. They have the following boiling points.

gas	boiling point / °C
A	−191.5
B	−78.5

The graph below shows the variation of $\dfrac{pV}{RT}$ with pressure, p, for 1 mol each of gas **A** and gas **B** at constant temperature. Identify the graph that corresponds to gas **A** and explain your choice.
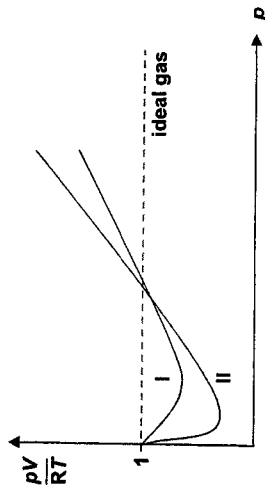
* **Graph I corresponds to gas A.**
* **Gas A has lower boiling point than B, hence, it has weaker intermolecular forces of attraction leading to less deviation from ideality.**

(iii) Free volume, V, refers to the volume of space between gas molecules. For an ideal gas, the free volume is essentially the same as the volume of the container. This can be calculated using the ideal gas equation, $pV = nRT$.

The pressure of a 72 g gaseous sample containing gas **A** and gas **B** in a container of volume 400 cm³ is measured to be 3.36×10^7 Pa at 527 °C.

Using the ideal gas equation, calculate the free volume of this gaseous sample in cm³. Assume the gaseous sample has an average $M_r = 36$.   [2]

* $n = 72 / 36 = 2.00 \text{ mol}$

* $pV = nRT$

  $V = \dfrac{2.00 \times 8.31 \times (527+273)}{3.36 \times 10^7}$

  $= \dfrac{3.36 \times 10^7}{}$
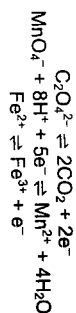
  $= 3.96 \times 10^{-4} \text{ m}^3$

  $= 396 \text{ cm}^3$

(iv) Explain why the volume you have calculated in (a)(iii) differs from that of the volume of the container. [1]

- The gaseous sample behaves non-ideally and the volume calculated in (a)(iii) is smaller than the volume of the container.

(v) Under high pressure, the volume of the gaseous molecules is <u>not negligible / significant</u>. Hence, the <u>actual free volume between the gas molecules is smaller</u>.

- An impure sample of barium ethanedioate, BaC_2O_4, of mass 0.500 g, is added to 50.0 cm³ of 0.0200 mol dm⁻³ acidified MnO_4^-(aq) and heated. A redox reaction takes place and all BaC_2O_4 are reacted. The resulting solution is titrated with Fe^{2+}(aq). The end-point is reached when 30.40 cm³ of 0.0500 mol dm⁻³ Fe^{2+}(aq) has been added.

$$C_2O_4^{2-} \rightleftharpoons 2CO_2 + 2e^-$$
$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$$
$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$$

Calculate the percentage by mass of BaC_2O_4 in the 0.500 g impure sample. Show your working. [M_r: BaC_2O_4, 225.3] [4]

- Initial total amount of MnO_4^- = 0.0200 × 50.0 × 10⁻³ = 1.00 × 10⁻³ mol
- Amount of Fe^{2+} used = 0.0500 × 30.40 × 10⁻³ = 1.52 × 10⁻³ mol

$$5Fe^{2+} \equiv MnO_4^-$$
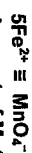
- Amount of MnO_4^- unreacted with $C_2O_4^{2-}$ = 1.52 × 10⁻³ / 5 = 3.04 × 10⁻⁴ mol
- Amount of MnO_4^- reacted with $C_2O_4^{2-}$ = 1.00 × 10⁻³ − 3.04 × 10⁻⁴ = 6.96 × 10⁻⁴ mol
- Amount of $C_2O_4^{2-}$ reacted = 6.96 × 10⁻⁴ × 5/2 = 1.74 × 10⁻³ mol
- Mass of BaC_2O_4 reacted = 1.74 × 10⁻³ × 225.3 = 0.392 g
Percentage by mass of BaC_2O_4 = $\frac{0.392}{0.500}$ × 100% = 78.4%

(b) The elements of Group 14 can form monoxides and dioxides. The monoxides are unstable and will disproportionate into their element and dioxide. The equations for the disproportionation reactions are given in **Table 1.1**, together with some thermodynamic data for the reactions.

Table 1.1

disproportionation equation	ΔS° / J mol⁻¹ K⁻¹	ΔH° / kJ mol⁻¹	ΔG° / kJ mol⁻¹
2CO(g) → C(s) + CO₂(g)	−176	−173	−120
2SiO(g) → Si(s) + SiO₂(s)	−363	−712	−603
2GeO(s) → Ge(s) + GeO₂(s)	−13.6	−127	−123
2SnO(s) → Sn(s) + SnO₂(s)	−9.20	−9.10	−6.36
2PbO(s) → Pb(s) + PbO₂(s)	−4.00	+157	+158

3

(i) Explain why the entropy change for the disproportionation of SiO(g) is much more negative than that for CO(g). [1]

- The disproportionation of SiO(g) leads to a <u>larger decrease in the amount of gas</u> than that for the disproportionation of CO(g). Thus, there are <u>less ways of arrangement</u>, leading to a <u>greater decrease in disorderliness</u> and hence a much more negative entropy change.

(ii) Explain why the entropy change for the disproportionation of PbO(s) is close to zero. [1]

- The disproportionation of PbO(s) only involves the <u>same amount of solid reactants and solid products</u>. Thus, there is <u>very little change in disorderliness</u> and hence a close to zero entropy change.

(iii) Use data from Table 1.1 to deduce the temperature above which the disproportionation of CO(g) becomes unfavourable. [1]

When disproportionation of CO(g) becomes unfavourable,
$\Delta G > 0$
$\Delta H - T\Delta S > 0$
$-173 - T(-176 \times 10^{-3}) > 0$
$T > 983$ K

- When T is greater than <u>983 K</u>, the disproportionation of CO(g) becomes unfavourable.

(iv) Explain why CO(g) does not spontaneously disproportionate at room temperature. [2]

- CO contains <u>strong C≡O bond (or triple bond)</u> which requires a lot of energy to be broken. The <u>activation energy is high</u> and the reaction is <u>kinetically not feasible at room temperature</u>.

(v) Carbon monoxide, CO, is a gas at room temperature and pressure. It contains a coordinate bond. Explain what is meant by a coordinate bond. [1]

- A coordinate bond is a <u>covalent bond in which both electrons come from only one of the atoms</u> in the bond.

(vi) Dicarbon monoxide, C₂O, is extremely reactive and is not encountered in everyday life. It is found in dust clouds in space and analysis has shown that the central atom is carbon with no unpaired electrons while the other carbon atom has a lone pair of electrons.

Draw the structure of dicarbon monoxide, stating its shape and bond angle. [2]

- C=C=O
- Shape: linear, bond angle: 180°

[Total: 18]

4

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6

(iv) Suggest the structure of the starting material needed to synthesise phenylalanine by the above general reaction. [1]
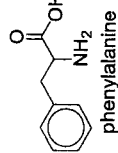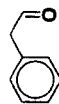
phenylalanine

(v) Phenylalanine can also be synthesised by reacting benzene and a halogen derivative, ClCH$_2$CH(NH$_2$)CO$_2$H, in the presence of aluminium chloride. Suggest the mechanism for this reaction. Show all charges and the movement of electron pairs using curly arrows. [3]
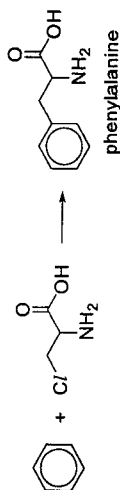
Mechanism: electrophilic substitution

Step 1: $ClCH_2CH(NH_2)CO_2H + AlCl_3 \longrightarrow {}^+CH_2CH(NH_2)CO_2H + AlCl_4^-$

Step 2:

Step 3:

$\longrightarrow$ phenylalanine $+ AlCl_3 + HCl$
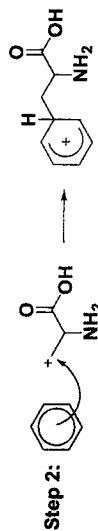
(vi) Compound **F** undergoes a reaction when heated in aqueous hydrochloric acid to produce two compounds, **G** and **H**.

F $\longrightarrow$ **G** (C$_6$H$_{12}$O$_2$NCl) + **H** (C$_5$H$_{10}$O$_4$NCl)
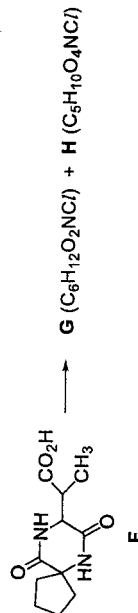
Suggest the type of reaction that has occurred. Draw the structures of compounds **G** and **H**. [3]

- Type of reaction: hydrolysis

5

2 (a) Alanine, CH$_3$CH(NH$_2$)CO$_2$H, is an amino acid that is used to make proteins. Its pK_a values are 2.34 and 9.87.

(i) Sketch a graph to show how the pH of the solution would change during the gradual addition of 25.0 cm^3 of 0.100 mol dm^{-3} NaOH to 10.0 cm^3 of 0.100 mol dm^{-3} fully protonated alanine. Label the pK_a values in your sketch. [2]
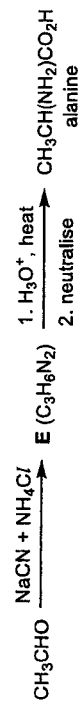

(ii) From the following list of indicators, suggest an indicator that could be used to detect the first end-point of the titration. Explain your answer.

indicator	pH at which colour changes
malachite green	0 – 1
thymol blue	1 – 2
bromophenol blue	3 – 4.6
thymolphthalein	9 – 10

- Indicator: bromophenol blue
- The working pH range of bromophenol blue lies within the rapid pH change at the first equivalence point. [2]

Alanine can be synthesised by a general reaction shown below.

$$CH_3CHO \xrightarrow{NaCN + NH_4Cl} E\ (C_3H_6N_2) \xrightarrow[\text{2. neutralise}]{\text{1. } H_3O^+,\ \text{heat}} CH_3CH(NH_2)CO_2H$$
alanine

(iii) Suggest the structure of compound **E**. [1]

- CH$_3$CH(NH$_2$)CN

[Turn over

G: (cyclopentane ring with CO_2H and NH_3Cl substituents)

H: HO_2C — NH_3Cl — CO_2H

(b) An electric cell was set up using a $Ag^+(aq)|Ag(s)$ half-cell and a $M^{2+}(aq)|M(s)$ half-cell where M is an unknown metal. The standard cell potential, E°_{cell}, was found to be +1.96 V. The silver electrode in this cell was the positive electrode.

(i) Draw the experimental set-up of the above cell, label clearly the species in each cell and the direction of the electron flow. [2]

high-resistance voltmeter

salt bridge

M(s) anode (−)

Ag(s) cathode (+)

$M^{2+}(aq)$, 1 mol dm⁻³

$Ag^+(aq)$, 1 mol dm⁻³
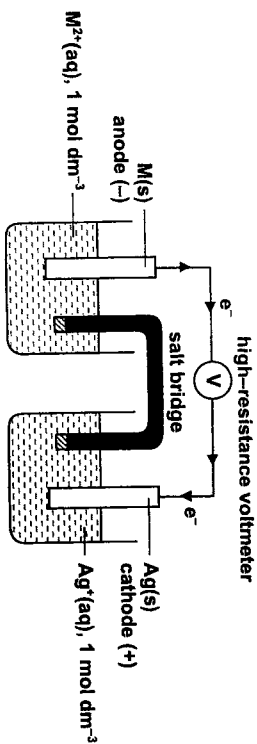
(ii) Use data from the *Data Booklet* to calculate the standard electrode potential of the $M^{2+}(aq)|M(s)$ half-cell. [1]

$E^\circ_{cell} = E^\circ_{red} - E^\circ_{ox}$

$+1.96 = E^\circ(Ag^+|Ag) - E^\circ(M^{2+}|M)$

$E^\circ(M^{2+}|M) = +0.80 - 1.96$

$= -1.16 \text{ V}$

(iii) State and explain how the E_{cell} value measured would change when 200 cm³ of water is added to the $Ag^+(aq)|Ag(s)$ half-cell. [2]

When water is added to the $Ag^+(aq)|Ag(s)$ half-cell, [Ag⁺] decreases. The equilibrium position of $Ag^+ + e^- \rightleftharpoons Ag$ shifts to the left to increase [Ag⁺]. Hence, $E(Ag^+|Ag)$ is less positive.

The E_{cell} value measured becomes less positive.

(c) Silver chloride, AgCl, is sparingly soluble in water. The numerical value of the solubility product, K_{sp}, for silver chloride is 1.80×10^{-10} mol² dm⁻⁶ at 25 °C.

(i) Solid AgCl is stirred at 25 °C with 5.00×10^{-3} mol dm⁻³ $AgNO_3$ until no more AgCl dissolves. Calculate the concentration of chloride ions in this solution. [1]

Let s be the solubility of AgCl in the given $AgNO_3$ solution.

$K_{sp} = [Ag^+][Cl^-] = 1.80 \times 10^{-10}$

$(s + 5.00 \times 10^{-3})(s) = 1.80 \times 10^{-10}$

Assuming $s \ll 5.00 \times 10^{-3}$,

$s = 3.60 \times 10^{-8}$ mol dm⁻³

Hence, $[Cl^-] = 3.60 \times 10^{-8}$ mol dm⁻³

(ii) Silver ions and thiosulfate ions react in a molar ratio 1:2 to form a soluble complex in aqueous solution. [2]

Explain, with the aid of two equations, how the solubility of silver chloride is affected when solid sodium thiosulfate is added to an aqueous solution of silver chloride at 25 °C.

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ (1)

$Ag^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq)$ (2)
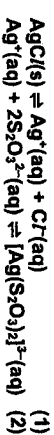
When solid sodium thiosulfate is added, soluble silver complex is formed. [Ag⁺] decreases in the solution, causing ionic product of AgCl to fall below its K_{sp}. By Le Chatelier's principle, equilibrium position of (1) shifts right, and so increases the solubility of AgCl.

(iii) 7.00×10^{-5} mol of solid silver chloride is added to 2.50 dm³ of aqueous sodium thiosulfate. 1.88×10^{-5} mol of silver chloride remained undissolved after equilibrium has been established.

Determine the concentration of silver ions that has been used to form the silver-thiosulfate complex in the solution. [2]

Amount of AgCl dissolved
= $(7.00 - 1.88) \times 10^{-5}$
= 5.12×10^{-5} mol

Amount of Ag⁺ ions in solution
= $[1.8 \times 10^{-10} / (5.12 \times 10^{-5}/2.5)] \times 2.5$
= 2.20×10^{-5} mol

Amount of Ag⁺ ions involved in forming the complex
= $5.12 \times 10^{-5} - 2.20 \times 10^{-5}$
= 2.92×10^{-5} mol

Concentration of Ag⁺ ions involved in forming the complex
= $2.92 \times 10^{-5} / 2.50$
= 1.17×10^{-5} mol dm⁻³

[Total: 22]

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(b) (i) When white anhydrous $CuSO_4$ is dissolved in liquid ammonia at -40 °C, a deep blue solution F is formed.

Solid NaOH is then added to solution F, and the ammonia solvent is allowed to evaporate leaving behind a solid residue. Heating the residue to 220 °C produces a mixture of two solids. When water is added to this mixture, one of the solids remains as a black solid G.

Solid G dissolves in HNO_3(aq) on warming without the evolution of gas to give a pale blue solution.

Suggest the chemical formulae of the compounds F and G. [2]

- F: $[Cu(NH_3)_4]SO_4$ or $[Cu(NH_3)_6]SO_4$
- G: CuO

(ii) When water is added to the white anhydrous $CuSO_4$, the solid dissolves to give a blue solution. The solution changes to a yellow-green colour when concentrated NH_4Cl is added to it. Concentrating the solution produces green crystals of an ammonium salt with the empirical formula $CuN_2H_8Cl_4$.

State the type of reaction occurring and give the chemical formula of the ammonium salt formed. Explain these observations with the aid of an equation. [3]

- **The reaction occurring is ligand exchange.**

- **The chemical formula of the ammonium salt is $[NH_4]_2CuCl_4$.**

- $[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$
  $CuSO_4$ dissolves in water to form a **blue $[Cu(H_2O)_6]^{2+}$. When concentrated NH_4Cl was added, ligand exchange takes place to form yellow $[CuCl_4]^{2-}$. Presence of a mixture of blue $[Cu(H_2O)_6]^{2+}$ and yellow $[CuCl_4]^{2-}$ causes the solution to appear yellow-green.**

(c) Figure 3.2 shows the octahedral geometry of a transition metal complex with six monodentate ligands, **L**.

Figure 3.2

With reference to an octahedral complex, the *cis-trans* configuration is defined as follows:

Cis configuration:
Same groups of atoms are on the same side of the central metal atom, i.e. 90° from each other.

Trans configuration:
Same groups of atoms are on directly opposite sides of the central metal atom i.e. 180° from each other.

$[Co(NH_3)_4Cl_2]^+$ is an octahedral complex. Similar to organic molecules, this complex can exist as a pair of *cis-trans* isomers.

Using the information above, draw the 3-dimensional structures of the *cis-trans* isomers of $[Co(NH_3)_4Cl_2]^+$ and label the configuration. [2]

---

3 (a) Compound A has a molecular formula of $C_{12}H_{16}O$.

Ozone can be used to convert a C=C bond into two C=O bonds. Under certain conditions, ketones and/or carboxylic acids are formed, as shown in **Figure 3.1**. Ozone has no reaction with benzene.
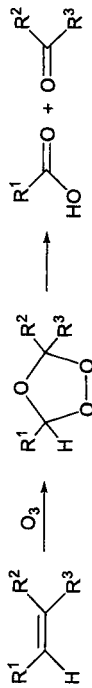

Figure 3.1

Compound A reacts with an excess of ozone under similar conditions to form two organic compounds, B, $C_9H_{10}O$, and C, $C_3H_6O_3$.

Compounds A, B and C form a yellow precipitate with alkaline aqueous iodine but only compound B forms an orange precipitate with 2,4-dinitrophenylhydrazine.

When compound B is reacted with concentrated HNO_3 and concentrated H_2SO_4, two possible mono-nitro compounds can be formed but only D is formed in practice.

Compound C has a chiral centre and effervesces with aqueous sodium carbonate. When warmed with concentrated H_2SO_4, C forms E, $C_6H_8O_4$.

(i) Explain what is meant by a *chiral centre*. [1]

- **A chiral centre is a carbon atom bonded to four different groups or atoms.**

(ii) Suggest possible structures of A, B, C, D and E. For each reaction, state the *type of reaction* described and explain what the information tells you about the functional groups present in each compound. [9]

A   B   C   D   E
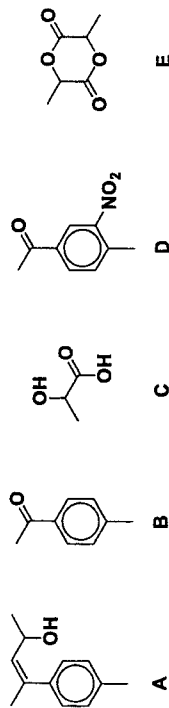
- A undergoes **oxidation** with ozone to form B and C. Thus, **A is an alkene.**
- A, B and C undergo **oxidative cleavage (or oxidation)** with alkaline aqueous iodine. They have either **CH₃CO– or CH₃CH(OH)–** structures.
- B undergoes **condensation** with 2,4-DNPH. B is a **ketone with CH₃CO–** structure since B has only one O atom.
- B undergoes **electrophilic substitution** with concentrated nitric acid and sulfuric acid, hence B is **aromatic or has a benzene ring.**
- B forms two possible mono-nitro compounds. **D is formed according to the orientating effect of groups already present on the benzene ring.** D is **1,4-disubstituted.**
- C undergoes **acid-base reaction** with Na_2CO_3(aq). Thus, C is a **carboxylic acid.**
- C undergoes **condensation reaction with itself when warmed with concentrated H_2SO_4, to form E, a diester.**
- **Thus, C has both alcohol and carboxylic acid functional groups.**

(d) Radium was discovered in the ore, pitchblende, by Marie Curie in 1898. The metal was first isolated in 1910.

The metal was obtained by first reacting the radium present in the pitchblende to form insoluble radium sulfate which was converted into aqueous radium bromide. This solution was then electrolysed using a mercury cathode and a carbon anode. The radium formed react vigorously with water to form an alkaline solution.

(i) Write an equation, with state symbols, for the reaction of radium with water. [1]

- $Ra(s) + 2H_2O(l) \rightarrow Ra(OH)_2(aq) + H_2(g)$

(ii) State and explain if the reaction will be more or less vigorous than the reaction of barium with water. [2]

- The reaction will be more <u>vigorous</u> as radium is a stronger reducing agent.

- Down the group, electrons are being added to a higher energy principal quantum shell which is further away from the nucleus. Since there is an <u>increase in distance between the nucleus and the valence electrons</u>, there is <u>weaker attraction between the nucleus and the valence electrons</u>, making it easier for electrons to be removed from radium.

[Total: 20]

Trans

Cis

[Turn over

Section B

Answer one question from this section.

4 **(a)** With reference to $E^o(X_2|X^-)$ values from the *Data Booklet*, describe the relative reactivity of the halogens Cl_2, Br_2 and I_2 as oxidising agents. [2]

- The $E^o(X_2|X^-)$ values become <u>less positive (OR decrease)</u> down the group.
- Thus, the halogens are <u>less reactive as oxidising agents</u> down the group.

(b) Lactic acid, $CH_3CH(OH)CO_2H$, was first isolated in sour milk. It is also formed in our body during anaerobic respiration.

(i) Lactic acid exhibits stereoisomerism. State the type of stereoisomerism and draw the pair of stereoisomers. [2]

- Enantiomerism

mirror
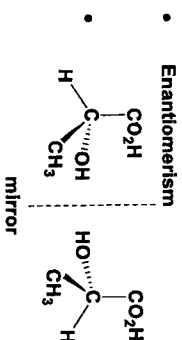
Lactic acid can be synthesised from ethanol as shown below.

$$CH_3CH_2OH \xrightarrow{\text{step 1}} CH_3CHO \xrightarrow{\text{step 2}} CH_3CH(OH)CN \xrightarrow{\text{step 3}} CH_3CH(OH)CO_2H$$
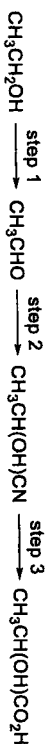
(ii) State the reagents and conditions for steps 1 and 2. [2]

- step 1: $K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$, heat with immediate distillation
- step 2: $HCN(aq)$ with $NaCN(aq)$ catalyst

(iii) Describe the reaction mechanism for step 2. Show all relevant charges, dipoles, lone pairs and electron movement using curly arrows. [2]

Mechanism: nucleophilic addition
CN^- is the nucleophile.
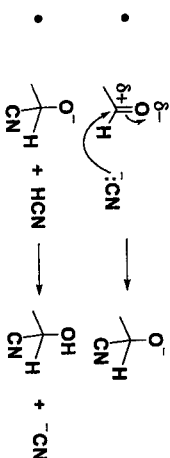
(iv) State and explain how K_a of lactic acid would compare to that of propanoic acid. [2]

- K_a of lactic acid is <u>larger</u> than that of propanoic acid.
- When lactic acid dissociates, $CH_3CH(OH)CO_2^-$ ion is formed which is <u>more stable</u> than $CH_3CH_2CO_2^-$ ion from the dissociation of propanoic acid. The <u>OH group</u> exerts an electron-withdrawing inductive effect to help <u>disperse the negative charge on oxygen. Hence, lactic acid is a stronger acid with a larger K_a.</u>

(c) Lactic acid undergoes dimerisation by forming two hydrogen bonds between two molecules.

$$2CH_3CH(OH)CO_2H(g) \rightleftharpoons (CH_3CH(OH)CO_2H)_2(g)$$
$$\text{dimer}$$

In a container, 6.65 bar of lactic acid undergoes dimerisation at 127 °C. The total pressure of the gas mixture at equilibrium is found to be 3.52 bar.

(i) Calculate the partial pressures of lactic acid and its dimer, in bar, at equilibrium. [2]

- Let x bar be the partial pressure of dimer formed at equilibrium. At equilibrium,

  partial pressure of lactic acid = 6.65 − 2x bar
  partial pressure of dimer = x bar
  total pressure of gas mixture = 6.65 − 2x + x = 6.65 − x = 3.52
  $x = 3.13$

- Hence, in the gas mixture,
  partial pressure of dimer = 3.13 bar
  partial pressure of lactic acid = 6.65 − 2(3.13) = 0.39 bar (ecf)

(ii) Write the K_p expression for this equilibrium and calculate its value in bar⁻¹. [2]

- $$K_p = \frac{P_{dimer}}{P^2_{lactic\ acid}}$$

- $$K_p = \frac{3.13}{(0.39)^2} = 20.6\ bar^{-1}\ (ecf)$$

The Gibbs free energy change for this reaction is related to K_p by the following equation.

$$\Delta G = -RTlnK_p$$

In the above equation, ΔG is in J mol⁻¹, T is in K and K_p is in bar⁻¹.

(iii) Calculate the Gibbs free energy change of the dimerisation. [1]

- $$\Delta G = -RTlnK_p$$
  $$= -(8.31)(127 + 273)\,(ln\ 20.6)$$
  $$= -10100\ J\ mol^{-1}$$

(iv) The entropy change for the dimerisation is −30.0 J K⁻¹ mol⁻¹. Calculate the enthalpy change of the dimerisation. Hence, estimate the strength of hydrogen bond in the dimer in kJ mol⁻¹. [2]

- $$\Delta G = \Delta H - T\Delta S$$
  $$-10100 = \Delta H - (127 + 273)(-30.0)$$
  $$\Delta H = -22100\ J\ mol^{-1} = -22.1\ kJ\ mol^{-1}$$

- Strength of hydrogen bond
  = 22.1 ÷ 2 = 11.05 = 11.1 kJ mol⁻¹

(d) The K_a value of lactic acid is 1.4×10^{-4} while the K_{a1} and K_{a2} values of carbonic acid, H_2CO_3, are 4.5×10^{-7} and 4.7×10^{-11}.

(i) Estimate the K_c value for the reaction between lactic acid and hydrogencarbonate ion. [2]

Let lactic acid be HA.
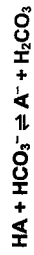
$$HA + HCO_3^- \rightleftharpoons A^- + H_2CO_3$$
$$K_c = \frac{[A^-][H_2CO_3]}{[HA][HCO_3^-]}$$
$$= \frac{[H^+][A^-]}{[HA]} \times \frac{[H_2CO_3]}{[H^+][HCO_3^-]}$$
$$= \frac{1.4 \times 10^{-4}}{4.5 \times 10^{-7}}$$
$$= 311$$

**(ii)** A student claims that the reaction between lactic acid and hydrogencarbonate ion is negligible as it is a reaction between a weak acid and a weak base. Do you agree with this claim? Explain your answer. [1]

- I disagree with this claim. Since K_c is a large number, the equilibrium position lies to the right.

[Total: 20]

5 (a) Piperazine, $C_4H_{10}N_2$ was used as an anti-parasites drug in the early 20th century. It can be synthesised from an organic compound K, C_2H_6NCl under suitable conditions. Piperazine can be used to prepare 1,4-dihydropyrazine via a two-step pathway as shown below.

piperazine   1,4-dihydropyrazine
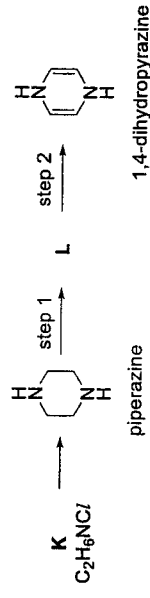
(i) Suggest and explain if 1,4-dihydropyrazine can exhibit *cis-trans* isomerism. [1]

- 1,4-dihydropyrazine **cannot** exhibit *cis-trans* isomerism. **Both C=C bonds are in the six-membered ring. Due to ring strain, the *trans* isomer cannot be formed.**

(ii) Suggest the structures of compounds **K** and **L**. [2]

- **K:** $NH_2CH_2CH_2Cl$

- **L:**

(iii) State the reagents and conditions for steps 1 and 2. [2]

- step 1: Br₂, UV light
- step 2: NaOH in ethanol, heat

(iv) The preparation of 1,4-dihydropyrazine from piperazine in the above pathway gives a very low yield. Suggest which step in the pathway contributed to this low yield. Explain your answer.

- **Step 1** results in a low yield as __any one of the four C atoms can be substituted by Br with equal probability__. Thus, a mixture of different substituted products can be obtained with the given condition. __Only two of them can give the desired product__ and hence, it results in a low yield. [1]

(v) State and explain how the K_b of piperazine would compare to that of diethylamine, $(CH_3CH_2)_2NH$.

- K_b of piperazine is __smaller than that of diethylamine.__
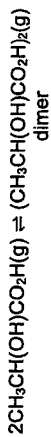- There is an additional electronegative N on piperazine and it exerts an __electron-withdrawing inductive effect__ which makes the __lone pair on N less available for donation__. Thus, piperazine is a __weaker base with a smaller K_b value.__ [2]

(vi) The two pK_b values of piperazine are 5.35 and 9.73 respectively.

A buffer solution is prepared by adding 11.2 g of piperazine into 100 cm³ of 1.00 mol dm⁻³ hydrochloric acid solution.

Calculate the pH of this buffer solution. [3]

Let piperazine be B. After protonation, BH^+ is formed initially.

Amount of HCl added $= 1.00 \times 100 \times 10^{-3} = 0.100$ mol
Amount of B added $= 11.2 \div (12.0 \times 4 + 1.0 \times 10 + 14.0 \times 2) = 0.130$ mol (excess)

HCl will react with B to give BH^+.
Amount of $BH^+ = 0.100$ mol
Amount of B left $= 0.130 - 0.100 = 0.030$ mol

$$K_{b1} = \frac{[BH^+][OH^-]}{[B]}$$
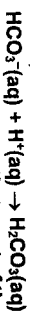
$$[OH^-] = \frac{(10^{-5.35})(0.030)}{0.100} = 1.34 \times 10^{-6}$$

$$pOH = -lg\,[OH^-] = 5.87$$

$$pH = 14 - 5.87 = 8.13$$

(b) In order to function properly, the human body needs to maintain a blood pH between 7.35 and 7.45. Large deviations from this pH range are extremely dangerous. pH values greater than 7.8 or less than 6.8 often result in death. Blood contains large amounts of carbonic acid and hydrogencarbonate which help to maintain the blood pH. Describe, with the aid of equations, how the pH of blood is controlled by carbonic acid and hydrogencarbonate. [2]

- As the blood becomes too acidic, HCO_3^- ions will react with the H^+ ions.
$$HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq)$$
__Large reservoir of HCO_3^- ions__ help to ensure that most of the added H^+ ions are removed. Hence, pH of blood remains __almost constant.__

- As the blood becomes too alkaline, H_2CO_3 molecules will react with the OH^- ions.
$$H_2CO_3^-(aq) + OH^-(aq) \rightarrow HCO_3^-(aq) + H_2O(l)$$
__Large reservoir of undissociated H_2CO_3 molecules__ help to ensure that most of the added OH^- ions are removed. Hence, pH of blood remains __almost constant.__
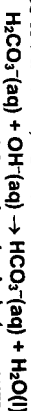
(c) The reaction between NO_2 and SO_2 is a key stage in the formation of acid rain.

$$NO_2(g) + SO_2(g) \rightarrow NO(g) + SO_3(g)$$

The initial rate of this reaction was measured for different concentrations of reactants and the rate equation was obtained as shown.

$$rate = k[NO_2][SO_2]^2$$

(i) Explain if the reaction between NO_2 and SO_2 is an elementary step reaction. [1]

- If this is an elementary step reaction, from the given equation of the reaction, there will be one molecule of NO_2 colliding with one molecule of SO_2. In the rate determining step. Hence, both NO_2 and SO_2 should have __first order of reaction.__ However, this is __not consistent with the experimentally determined rate equation.__ Thus, it is __not an elementary step.__

(ii) NO_2 is produced in the car engine when the temperature of the engine is very high. Write an equation to show how NO_2 is removed by the catalytic convertor. [1]

- CO is another pollutant produced in the car engine. In the presence of the catalytic convertor,
$$2NO_2 + 4CO \rightarrow N_2 + 4CO_2$$

(iii) The catalyst in the catalytic convertor functions as a heterogeneous catalyst. Outline the mode of action of the heterogeneous catalyst. [2]

- __Adsorption of reactant molecules on the catalyst's surface increases rate of reaction__ as adsorption weakens the covalent bonds within the reactant molecules, thereby __reducing the activation energy for the reaction.__
- __Adsorption also increases the concentration of reactant molecules at the catalyst surface__ allowing reactant molecules to come into close contact with __proper orientation__ for reaction. In the final stage, products formed __desorb__ from the catalyst surface.

(iv) Explain, with the aid of a labelled Boltzmann distribution diagram, the effect of catalyst on the rate constant of a reaction. [3]
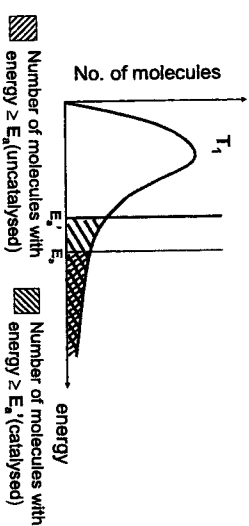
- Catalyst __increases__ the value of rate constant.
- At the same temperature T_1, a catalyst provides an __alternative reaction pathway__ with a __lower activation energy E_a'.__ Thus, there is a __larger number of molecules with energy $\geq E_a'$__ leading to a __larger rate constant.__

[Total: 20]

VICTORIA JUNIOR COLLEGE
PRELIMINARY EXAMINATION
Higher 2

CANDIDATE
NAME ....

CT GROUP ....

CHEMISTRY **9729/04**

Paper 4 Practical **29 Aug 2022**

Candidates answer on the Question Paper. **2 hours 30 minutes**

Additional Materials: As listed in the instructions below

READ THESE INSTRUCTIONS FIRST

Write your name and CT group 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 a 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 13 and 14.

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	/ 9
2	/ 12
3	/ 11
4	/ 15
5	/ 8
Total	**/ 55**

This document consists of **14** printed pages.

[Turn over

Answer all the questions in the spaces provided.

1 In acidic solutions, iron(III) ions are reduced by iodide ions to form iron(II) ions. The iodide ions are oxidised to iodine.

$$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$$

The rate of this reaction can be investigated by using starch indicator, which turns blue-black in the presence of iodine. Sodium thiosulfate is added to the reaction mixture to react with iodine as it is formed. The blue-black colour is seen when all the thiosulfate has reacted.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$
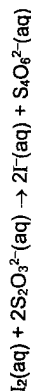
You will investigate how the rate of reaction is affected by changing the concentration of the iodide ions.

FA 1 is 0.050 mol dm^{-3} potassium iodide, KI.
FA 2 is 0.050 mol dm^{-3} acidified iron(III) chloride, FeCl$_3$.
FA 3 is 0.0050 mol dm^{-3} sodium thiosulfate, Na$_2$S$_2$O$_3$.
FA 4 is starch indicator.

(a) Experiment 1
1. Use the burette **labelled FA 1** to transfer 10.00 cm^3 of **FA 1** into a 250 cm^3 conical flask.
2. Use a 25 cm^3 measuring cylinder to transfer 10.0 cm^3 of deionised water into the conical flask.
3. Use the burette **labelled FA 3** to transfer 20.00 cm^3 of **FA 3** and a 50 cm^3 measuring cylinder to transfer 10 cm^3 of **FA 4** to the same conical flask.
4. Use a 10 cm^3 measuring cylinder to measure 10 cm^3 of **FA 2**.
5. Add this **FA 2** into the same conical flask and start timing immediately.
6. Swirl the mixture once and place the conical flask on the white tile.
7. Stop timing as soon as the solution turns **intense** blue-black.
8. Record the time taken, t, to the nearest second.
9. Wash out the conical flask and stand it upside down in a beaker to drain for use again.

Experiment 2
10. Repeat Experiment 1 but use 20.00 cm^3 of **FA 1** instead of 10.00 cm^3 of **FA 1** and use 0.0 cm^3 of deionised water instead of 10.0 cm^3 in step 2.

Experiments 3 to 5
11. Carry out **three** further experiments to investigate how the reaction time changes with different volumes of potassium iodide, **FA 1**.
The combined volume of **FA 1** and deionised water must always be 20 cm^3.
Do not use a volume of **FA 1** that is less than 6 cm^3.

In the space on the next page, prepare a table to record the following for each of the five experiments.

- V, Volume of **FA 1** used,
- Volume of water used,
- t, Reaction time, to the nearest second,
- Vt,
- V^2t.

Keep solutions **FA 1**, **FA 3** and **FA 4** for use in Question 2.

3

Results

Experiment	V, Volume of FA 1 / cm³	Volume of water / cm³	t, Reaction time / s	Vt	V²t
1	10.00	10.0	120	1200	12000
2	20.00	0.0	30	600	12000
3	7.00	13.0	226	1600	11000
4	13.00	7.0	59	770	10000
5	16.00	4.0	45	720	12000

(b) V is the volume of **FA 1** used in cm³ and t is the time taken in seconds. On your table above, compute the values of Vt and V^2t for each experiment, to 2 significant figures. [4]

(c) The rate of the reaction in this investigation can be calculated using the following formula:

rate = 1 / reaction time. Explain why this is so. [1]

• Rate of reaction is equal to the <u>change in concentration of iodine with time</u>. Since the <u>same amount of thiosulfate is used in all experiments</u>, the change in concentration of iodine is <u>constant</u>. So rate = 1 / reaction time.

(d) Deduce the order of reaction with respect to iodide ions. Explain your answer by referring to your calculated values of Vt and V^2t. [1]

• The reaction is second order with respect to iodide ions since <u>V^2t is constant.</u>

• $V \propto$ [FA 1] since total volume is constant
  Rate = 1/t
  Since V^2t = constant
  1/$t \propto V^2$
  Hence, **rate $\propto$ [FA1]²**

(e) Another student investigated the effect of concentration of iron(III) ions on the rate of this reaction. The student carried out another experiment, **Experiment 6**, and the rate is compared to that of **Experiment 1**. Suggest the volumes the student could use for **Experiment 6**. [1]
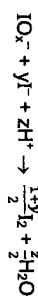
reagent	volume / cm³
FA 1	10
FA 2	20
FA 3	20
FA 4	10
deionised water	0

[Total: 9]

4

2 In this experiment you will determine the formula of the ion, IO_x^-. To do this, you will first react IO_x^- ions with an excess of iodide ions, I^- to form iodine, I_2.

The equation for this reaction is:

$$IO_x^- + yI^- + zH^+ \rightarrow \frac{1+y}{2}I_2 + \frac{z}{2}H_2O$$

where x, y and z are all integers.

The amount of iodine produced will then be determined by titration with thiosulfate ions.

In addition to FA 1, FA 3 and FA 4 used in question 1, you are also provided with the following.

FA 5 is a solution containing 0.00600 mol dm⁻³ IO_x^- ions.
FA 6 is 1.0 mol dm⁻³ sulfuric acid, H_2SO_4.

(a) <u>Dilution of FA 5</u>

1. Pipette 25.0 cm³ of **FA 5** into the 250 cm³ volumetric flask.
2. Make the solution up to the mark using deionised water.
3. Shake the flask thoroughly.
4. Label this diluted solution of IO_x^- as **FA 7**.

<u>Titration</u>

1. Pipette 25.0 cm³ of **FA 7** into a conical flask.
2. Using the burette **labelled FA 1**, transfer 10.00 cm³ of **FA 1** into the same conical flask.
3. Using a measuring cylinder, transfer 10 cm³ of **FA 6** into the same conical flask.
4. Titrate the mixture in the conical flask against **FA 3** in the burette **labelled FA 3** until the solution turns yellow.
5. Add 10 drops of **FA 4** into the conical flask.
6. Continue the titration until the blue-black colour just disappears.
7. Carry out as many titrations as you deem necessary to obtain consistent results.
8. In the space provided, prepare a table to record all your burette readings and the volume of **FA 3** used in each titration.

(b) (i)

Final burette reading / cm³	18.00	36.00
Initial burette reading / cm³	0.00	18.00
Volume of FA 3 added / cm³	18.00	18.00

• From your titration results, obtain a suitable volume of **FA 3** to be used in your calculations. Show clearly how you obtained this volume. [5]

• **Volume of FA 3 used** = (18.00 + 18.00) ÷ 2 = 18.00 cm³

(ii) Calculate the amount of iodine formed when 25.0 cm³ of **FA 7** reacts with 10.00 cm³ of **FA 1**. Show your working. [1]

• **Amount of thiosulfate** = 0.0050 × 0.0180 = 9.00 × 10⁻⁵ mol dm⁻³
• **Amount of iodine formed** = 9.00 × 10⁻⁵ ÷ 2 = 4.50 × 10⁻⁵ mol dm⁻³

(iii) Calculate the amount of IO_x^- in 25.0 cm³ of **FA 7**. Show your working. [1]

• **Concentration of IO_x^- in FA 1** = 0.00600 × 25 ÷ 250 = 0.000600 mol dm⁻³
• **Amount of IO_x^- in 25.0 cm³ of FA 7** = 0.000600 × 25 ÷ 1000 = 1.50 × 10⁻⁵ mol dm⁻³

[1]

3 **FA 8** is a solid of Group 1 metal hydrogencarbonate, $LHCO_3$. When it is heated, carbon dioxide and stream are produced.

In this experiment you will determine the relative atomic mass of the metal **L** in **FA 8** using gravimetric analysis.

(a) Gravimetric Analysis

1. Weigh and record the mass of a dry boiling tube.
2. Transfer all the **FA 8** from the container into the boiling tube.
3. Reweigh and record the total mass of the boiling tube and **FA 8**.
4. Heat the boiling tube gently for approximately one minute and then strongly for another four minutes.
5. Leave the boiling tube to cool on a wire gauze for at least five minutes.
6. After cooling, reweigh the boiling tube and its contents.
7. Repeat the heating, cooling and weighing process until you are satisfied that the decomposition is complete. The residue is **FA 9**, keep the residue for use in **3(b)**.
8. Record your results in an appropriate form in the space below.

Results

Mass of empty boiling tube / g	30.215
Mass of boiling tube and FA 8 / g	32.227
Mass of FA 8 used / g	2.012
Mass of boiling tube and residue after first heating / g	31.484
Mass of boiling tube and residue after second heating / g	31.484
Mass of residue / g	1.269

[4]

(b) (i) Pour 1 cm depth of dilute hydrochloric acid into a test-tube. Add a spatula measure of the residue, **FA 9** to the acid.

Record all your observations and identify any gas formed.

• Effervescence of CO_2 gas which forms white precipitate in limewater. [1]

(ii) Use your observation in **(b)(i)** to identify the anion in **FA 9**. Assume that all the $LHCO_3$ has decomposed.

Anion in **FA 9** is • CO_3^{2-} [1]

(iii) Hence, write a balanced equation for the thermal decomposition of $LHCO_3$. Include state symbols.

• $2LHCO_3(s) \rightarrow L_2CO_3(s) + CO_2(g) + H_2O(g)$ [1]

(iv) Using your answer in **(b)(ii)** and **(b)(iii)**, determine the value of y. Show your working.

Amount of IO_x^- : Amount of I_2 = 1.50 × 10^{-5} : 4.50 × 10^{-5} = 1 : 3

• 1 : (1+y)/2 = 1 : 3
  y = 5
[1]

(v) Using your answer in **(b)(iv)**, determine the value of x.

• By balancing the charges on both sides of equation,
  $-1 - 5 + z = 0$
  $z = 6$

• By balancing the number of O atom, $x = 6/2 = 3$.
[1]

(c) (i) The maximum error in the volume dispensed by the pipette is ±0.06 cm^3. Calculate the maximum percentage error in measuring the volume of **FA 5** used.

• Percentage error = ± 0.06 / 25.0 × 100% = ± 0.24%
[1]

(ii) A student suggested that a more accurate value of x can be determined if a 10.0 cm^3 pipette is used to measure the volume of **FA 6** rather than the measuring cylinder.

State whether you agree with this student. Explain your answer.

• I do not agree with this student. **FA 6** is used in excess, the exact volume of **FA 6** will have no impact on the value of x.
[1]
[Total: 12]

7

(iv) Calculate the amount of carbon dioxide given off in your experiment. Show your working.

• Amount of $CO_2 = \frac{2.012 - 1.269}{44.0 + 18.0} = 0.0120$ mol

[1]

(v) Hence, determine the relative atomic mass of metal **L**. Show your working.

Amount of LHCO$_3$ = 2 × 0.0120 = 0.0240 mol

Mr of LHCO$_3$ = $\frac{2.012}{0.0240}$ = 83.8

Ar of **L** = 83.8 − (1.0 + 12.0 + 16.0 × 3) = 22.8

[1]

(c) (i) In another experiment, a student used a crucible with lid instead of a boiling tube for the heating and it was found that the results obtained were more accurate. Suggest why the crucible with lid can give a better result.

• The residue may <u>absorb water vapour from the surrounding during the cooling process, this lead to a higher than the expected mass reading.</u>

[1]

(ii) Another student conducted a different experiment to determine the A$_r$ of **L** by measuring the volume of carbon dioxide formed in the following reaction.

LHCO$_3$ + HCl → LCl + CO$_2$ + H$_2$O

Suggest which method would give a more accurate determination of the A$_r$ of **L**.

• **Gravimetric method is more accurate** as the volume of gas collected will vary with **temperature and pressure.**

OR

Gas collection is more accurate as the FA 8 may not be completely decomposed on heating.

[1]

[Total: 11]

8

4 Qualitative Analysis

(a) **FA 10** is a solid of a metal dioxide, MO$_2$.

Solution **S** is an acidic solution of sodium ethanedioate, Na$_2$C$_2$O$_4$.

You will perform tests to identify the element **M** in **FA 10**.

Perform the tests (i) and (ii) described in **Table 4.1** and record your observations in the table. The volume given below are approximate and should be estimated rather than measured.

Test and identify any gases evolved.

Table 4.1

Tests	observations
(i) Transfer all the solution **S** into a boiling tube and add one spatula of **FA 10** to the boiling tube.	• Effervescence of CO$_2$ gas which gives white ppt with limewater.
Warm the boiling tube cautiously.	
Leave the boiling tube to cool for about one minute and then filter the mixture into a test-tube.	• Colourless filtrate obtained with black residue.
(ii) To a 1 cm depth of the filtrate from (a)(i) in a test-tube, add NaOH(aq).	• Off-white ppt. insoluble in excess.
Leave to stand.	• Ppt. darkens on standing / turns brown / darker brown.
(iii) Aqueous hydrogen peroxide is added to an equal volume of H$_2$SO$_4$(aq) in a test-tube, followed by addition of one spatula of **FA 10**.	Vigorous effervescence of O$_2$ which rekindles a glowing splint.
The mixture is filtered into another test-tube.	A black/brown residue and a colourless filtrate obtained.
Leave the filtrate to stand.	The filtrate remains colourless.

[4]

(b) (i) Consider your observations in (a)(ii), give the name of the element **M** in **FA 10**. Explain your answer.

• **M is manganese**
• An **off-white precipitate**, Mn(OH)$_2$ is formed with NaOH(aq) which is insoluble in excess and darkens/turned darker brown on standing.

[2]

(ii) In (a)(i), the reaction between **FA 10** and ethanedioate occurs under acidic conditions. Write a balanced equation for this reaction.

• MnO$_2$ + 4H$^+$ + C$_2$O$_4{}^{2-}$ → Mn^{2+} + 2H$_2$O + 2CO$_2$

(iii) The filtrate obtained in (a)(i) turned pale yellow on standing.

[1]

5 Planning

Self-heating food packaging is an active packaging with the ability to heat food contents without external heat sources or power. Packets typically use an exothermic chemical reaction. These packages are useful for military operations, during natural disasters or whenever conventional cooking is not available. These packages are often used to prepare main courses such as meat dishes, which are more palatable when hot.

The source of the heat is initiated by pressing on the heat pack. The heat pack is manufactured with the heating agent (anhydrous calcium chloride) separated from water by a thin breakable membrane. When pressure is applied on the packaging, a rod pierces the membrane, allowing the water and anhydrous calcium chloride to mix. The resulting reaction releases energy and thus warms the food surrounding it. The enthalpy change of solution for this dissolution process is approximately −83.0 kJ mol⁻¹.

$$CaCl_2(s) \rightarrow Ca^{2+}(aq) + 2Cl^-(aq)$$
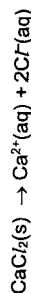
(a) Plan an investigation to determine the enthalpy change of solution when anhydrous calcium chloride is dissolved in deionised water using a non-graphical method.

You may assume that you are provided with:

- approximately 120 cm³ of deionised water
- approximately 10 g of anhydrous calcium chloride
- a thermometer
- Styrofoam cup
- common apparatus in the laboratory

In your plan, you should include brief details of:

- calculation of a suitable mass of calcium hydroxide you would use for a temperature rise of about 12 °C to 14 °C;
- the apparatus you would use;
- the quantities of reagents you would use;
- the procedure you would follow and the measurements you would make (you may find it useful to label measurements in your plan as **M1, T1** etc);
- how you would ensure that a **reliable** value of the enthalpy change of solution is obtained

Assume that 4.18 J of heat energy raises the temperature of 1.0 cm³ of the mixture by 1.0 °C.

Assume 50 cm³ of water is used for each experiment and the temperature change is 13 °C.

Heat evolved = $mc\Delta T = 50 \times 4.18 \times 13 = 2717$ J = 2.72 kJ

Amount of $CaCl_2$ dissolved = 2.72 ÷ 83 = 0.0328 mol

Mass of $CaCl_2$ = 0.0328 × (40.1 + 35.5 × 2) = 3.64 g

Procedure

1. Add about 3.64 g of solid $CaCl_2$ into a weighing bottle.
2. Weigh and record the total mass of the $CaCl_2$ and the weighing bottle in g (M1).
3. Using a measuring cylinder, transfer 50 cm³ of deionised water into a clean dry Styrofoam cup supported by a beaker.
4. Using a thermometer, measure and record the initial temperature of water (T1) in the Styrofoam cup in °C.
5. Add the $CaCl_2$ into the Styrofoam cup.
6. Stir the solution with the thermometer and record highest temperature reached (T2) in °C.

Compare the role of FA 10 in (a)(i) and (a)(iii). Explain your answer with reference to your observations in both tests.

- In (a)(i), FA 10 is an <u>oxidising agent</u> because $C_2O_4^{2-}$ was oxidised to CO_2 that gives **white precipitate in limewater while MnO₂ solid is reduced to colourless (or pale pink) Mn²⁺ ions.**

- In (a)(iii), FA 10 is a <u>catalyst</u> as O₂ is formed since **evolution of oxygen gas was vigorous or MnO₂ remained chemically unchanged as the filtrate remains colourless on standing (or the appearance of the residue is similar to original FA10).** [2]

(c) **FA 11, FA 12 and FA 13** are organic compounds with the molecular formulae C_7H_6O, C_3H_6O and C_2H_6O (not necessarily in any order).

Each compound has only one of the functional groups: alcohol, aldehyde and ketone.

(i) Perform the tests described in **Table 4.2** and record your observations in the table. If there is no observable change, write **no observable change**.

Prepare of Tollens'reagent using the following procedure.
Place a 2–3 cm depth of silver nitrate in a test-tube, add aqueous sodium hydroxide drop by drop until a small amount of brown precipitate is formed and then add aqueous ammonia drop by drop with shaking until the precipitate just dissolves. This is Tollens' reagent.

Table 4.2

test	Observations		
	FA 11	FA 12	FA 13
Add 1 cm depth of Tollens' reagent to test-tube containing 1 cm depth of each sample and place each test-tube in a hot water bath.	No observable change	Silver mirror formed	No observable change

[1]

(ii) Using only the bench reagents provided, suggest **one additional** chemical test that can help you identify the functional group present in each compound. Describe the test in the space provided in **Table 4.3**. Perform the test and record the observations in **Table 4.3**.

Table 4.3

test	observations		
	FA 11	FA 12	FA 13
To test-tube containing 1 cm depth of each sample, add 1 cm depth of dilute H₂SO₄ and then add about 10 drops of KMnO₄(aq). Place each test-tube in a hot water bath.	Purple KMnO₄ decolourised	Purple KMnO₄ decolourised	No observable change

[2]

(iii) Based on your observations in (c)(i) and (c)(iii), suggest the structures of the organic compounds present in **FA 11, FA 12 and FA 13**.
FA 11 is CH₃CH₂OH   FA 12 is C₆H₅CHO   FA 13 is CH₃COCH₃

[3]

[Total: 15]

7. Weigh and record the mass of the emptied weighing bottle in g (M2).

8. Repeat step 1 and 7 to get another set of results so as to obtain more reliable value for ΔH of solution.

(b) Describe how you would use the measurements in your plan in **(a)** to calculate a value for the enthalpy of solution of anhydrous calcium chloride.
[A_r: Ca = 40.1; Cl = 35.5]

[6]

M_r of $CaCl_2$ = 40.1 + 35.5x 2 = 111.1

ΔT_{max} = (T2 – T1) °C

Mass of $CaCl_2$ used = (M1 – M2) g

Amount of $CaCl_2$ = $\frac{M1-M2}{111.1}$ mol

Heat evolved = $mc\Delta T$ = 50 x 4.18 x (T2 – T1) = 209(T2 – T1) J

ΔH_{sol} = $\frac{209(T2-T1)}{(M1-M2)/111.1}$ J mol^{-1}

[2]

[Total:8]

[Turn over

Qualitative Analysis Notes
[ppt. = precipitate]

(a)   Reactions of aqueous cations

cation	reaction with	
	NaOH(aq)	NH₃(aq)
aluminium, Al³⁺(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH₄⁺(aq)	ammonia produced on heating	–
barium, Ba²⁺(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca²⁺(aq)	white. ppt. with high [Ca²⁺(aq)]	no ppt.
chromium(III), Cr³⁺(aq)	grey–green ppt. soluble in excess giving dark green solution	grey–green ppt. insoluble in excess
copper(II), Cu²⁺(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe²⁺(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), Fe³⁺(aq)	red–brown ppt. insoluble in excess	red–brown ppt. insoluble in excess
magnesium, Mg²⁺(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn²⁺(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, Zn²⁺(aq)	white ppt. soluble in excess	white ppt. soluble in excess

14

Chemical List

Label	Per candidate	Identity
FA 1	220 cm³	$0.0500 \text{ moldm}^{-3}$ potassium iodide, KI
FA 2	75 cm³	$0.0350 \text{ moldm}^{-3}$ acidified iron(III) chloride, $FeCl_3$
FA 3	220 cm³	$0.00500 \text{ moldm}^{-3}$ sodium thiosulfate, $Na_2S_2O_3$
FA 4	100 cm³	Starch indicator
FA 5	50 cm³	$0.0060 \text{ mol dm}^{-3}$ potassium iodate(V), KIO_3
FA 6	75 cm³	1.00 mol dm^{-3} sulfuric acid, H_2SO_4
FA 8	2.0 g	sodium hydrogencarbonate
FA 10	6 g	Manganese(IV) oxide, MnO_2
FA 11	10 cm³	0.1 mol dm^{-3} ethanol, CH_3CH_2OH
FA 12	10 cm³	0.1 mol dm^{-3} benzaldehyde
FA 13	10 cm³	Diluted propanone, CH_3COCH_3
S	10 cm³	Sodium ethanoedioate

Apparatus list

1	Two burettes – one labelled FA 1 and another labelled FA 3.
2	One 25.0 cm³ pipette
3	One 10 cm³ measuring cylinder
4	One 25 cm³ measuring cylinder
5	One 50 cm³ measuring cylinder
6	One 250 cm³ volumetric flask
7	Three 250 cm³ conical flasks
8	One 100 cm³ beaker
9	One 200 cm³ beaker
10	One pipette filler
11	One white tile
12	One stop watch
13	Two filter funnel
14	One Retort stand with burette clamp
15	One wash bottle with deionised water
16	One heatproof mat/wire gauze
17	One boiling tube
18	One test-tube rack
19	One test-tube holder
20	One Bunsen burner
21	One Delivery tube
22	One glass rod
23	One lighter
24	One small brush
25	One large brush
26	One Marker pen
27	One safety goggles
28	ACCESS to hot water
29	ACCESS to weighing balance
30	One spatula
31	Six teat/dropping pipette
32	Eight Test-tube
33	Two boiling tube
34	Three red litmus paper
35	Three blue litmus paper
36	Two paper towel
37	Two filter paper
38	Two wooden splinter

13

(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) Colour 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

YISHUN INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE
NAME

CG [   ] INDEX NO [   ]

CHEMISTRY

9729/01

Paper 1 Multiple Choice

14 September 2022

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid/tape.
Write your name and class on the Answer Sheet in the spaces provided unless this has been done for you.

There are **thirty** questions on 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 Answer Sheet very carefully.

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.

This document consists of **16** printed pages.

©YIJC

[Turn over

2

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

The table shows the fifth, sixth, seventh, eighth and ninth ionisation energies of an element in the third period.

	5th	6th	7th	8th	9th
ionisation energy / kJ mol^{-1}	6270	21270	25430	29870	35920

Which element has these ionisation energy values?

A P **B** S **C** Cl **D** Ar

2 Two elements X and Y have the following properties:

- X and Y form ionic compounds Na_2X and Na_2Y respectively.
- Element Y forms YF_6 molecule whereas X is not able to do so.

Which pair of electronic configurations for X and Y is correct?

	X	Y
A	[He] $2s^2 2p^4$	[He] $2s^2 2p^2$
B	[He] $2s^2 2p^2$	[He] $2s^2 2p^6 3s^2 3p^3$
C	[He] $2s^2 2p^2$	[He] $2s^2 2p^6 3s^2 3p^2$
D	[He] $2s^2 2p^4$	[He] $2s^2 2p^6 3s^2 3p^4$

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[Turn over

Use of the Data Booklet is relevant to this question.

An element **G** forms an ionic nitrate with formula **G**(NO₃)₂.

In a sample of this compound, the ion **G** contains 80 electrons and 126 neutrons.

Which row describes:

- the Group where **G** is found,
- the nucleon number of **G** in this sample?

	Group	nucleon number
A	2	204
B	2	208
C	14	204
D	14	208

4 The table identifies the shape and polarity of four molecules.

Which rows are correct?

	molecule	molecular shape	polarity
1	beryllium chloride	bent	non-polar
2	nitrogen dioxide	bent	polar
3	sulfur trioxide	trigonal planar	non-polar
4	chlorine trifluoride	trigonal planar	polar

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

4

5 Hydrazine, N₂H₄, and hydrogen peroxide, H₂O₂, are both used as rocket propellants because they can produce large volumes of hot gases from a small volume of liquid.

Which statements about these two compounds are correct?

1 The bond angle in N₂H₄ is larger than that in H₂O₂.

2 The N-H bond is shorter than the O-H bond.

3 N₂H₄ forms stronger intermolecular hydrogen bonds than H₂O₂.

4 There are σ bonds formed by sp³–s orbital overlap in both molecules.

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

6 In an experiment, 0.100 g of a volatile liquid Q formed 0.0250 dm³ of vapour at 100 °C at 1 bar.
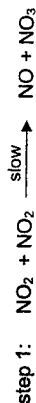
What is the relative molecular mass of Q?

A $\dfrac{0.100 \times 373}{0.0250 \times 22.7}$

B $\dfrac{0.0250 \times 273 \times 22.7}{0.100 \times 373}$

C $\dfrac{0.100 \times 273 \times 22.7}{0.0250 \times 373}$

D $\dfrac{0.100 \times 373 \times 22.7}{0.0250 \times 273}$

7 For the elements in Group 17, which trends down the Group are correct?

	volatility	oxidising power
A	decreases	decreases
B	decreases	increases
C	increases	decreases
D	increases	increases

5

8 Which statement about relative molecular mass is correct?

A It is the sum of the relative atomic masses of all the atoms within the molecule.

B It is the ratio of the average mass of a molecule to the mass of a ^{12}C atom.

C It is the ratio of the mass of 1 mol of molecules to the mass of 1 mol of ^{1}H atoms

D It is the average mass of all the atoms within the molecule.

9 The enthalpy change of reaction 1 is –114 kJ mol⁻¹.

$$2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l) \qquad \text{reaction 1}$$
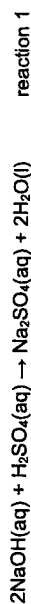
By using this information, what is the most likely value for the enthalpy change of reaction 2?

$$NaOH(aq) + CH_3COOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l) \qquad \text{reaction 2}$$

A –50 kJ mol⁻¹   B –57 kJ mol⁻¹   C –114 kJ mol⁻¹   D –228 kJ mol⁻¹

10 Which equations represent standard enthalpy changes at 298 K?

1 $H_2(g) + F_2(g) \rightarrow 2HF(g)$

2 $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

3 $\frac{1}{2}F_2(g) \rightarrow F(g)$

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

11 Melphalan is a drug used to treat infections.

The breakdown of melphalan in the blood is a first-order reaction. An original concentration of melphalan of 15.00 mg dm⁻³ decreases to 1.875 mg dm⁻³ after 270 minutes.

What is the time taken, in minutes, for the concentration of melphalan to decrease from 10.0 mg dm⁻³ to 2.00 mg dm⁻³ in the blood?

A 105   B 180   C 209   D 360

6

12 The reaction between NO₂ and CO to produce NO and CO₂ is thought to occur in two steps:

step 1: $NO_2 + NO_2 \xrightarrow{\text{slow}} NO + NO_3$

step 2: $NO_3 + CO \longrightarrow CO_2 + NO_2$

Which statements are correct?

1 The rate constant has units of mol⁻² dm⁶ s⁻¹.

2 NO₂ is a catalyst.

3 The rate of reaction is independent on the concentration of CO.

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

13 Each of the following equilibria is subjected to two changes which are carried out separately:

• the pressure is reduced at constant temperature;
• the temperature is increased at constant pressure.

Which equilibrium will both changes result in an increase in the proportion of products?

A $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $\Delta H = +53$ kJ mol⁻¹

B $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$ $\Delta H = -950$ kJ mol⁻¹

C $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -92$ kJ mol⁻¹

D $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H = +57$ kJ mol⁻¹

14 At 25 °C, $K_w = 1.00 \times 10^{-14}$ mol² dm⁻⁶.

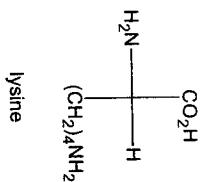At 62 °C, $K_w = 1.00 \times 10^{-13}$ mol² dm⁻⁶.

Which row is correct?

	the ionisation of water is	at 62 °C, water with a pH of 7.0 is
A	endothermic	alkaline
B	endothermic	neutral
C	exothermic	alkaline
D	exothermic	neutral

7

15 Lysine is an essential amino acid found in the body. It has three pK_a values associated with it.

H_2N — CO_2H
$(CH_2)_4NH_2$ — H

lysine

The pH curve below is obtained when one mole of the protonated lysine is titrated with hydroxide, OH^-, ions.
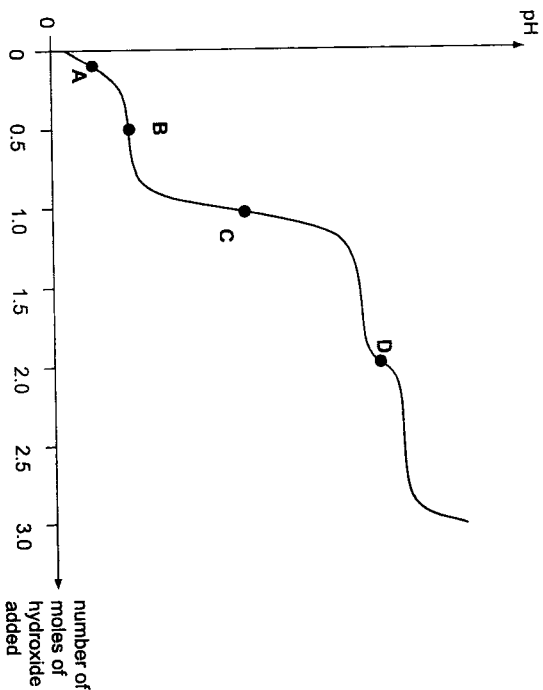
At which point on the graph does pH = pK_{a1} where K_{a1} is the first acid dissociation constant of lysine?

8

16 Vehicles produce exhaust emissions when the engine is running. These emissions can include harmful pollutants such as carbon monoxide, oxides of nitrogen and unburnt hydrocarbons.

A catalytic converter is used to change the gases emitted through chemical reactions.

Which reactions between the stated compounds occur in the catalytic converter?

1 hydrocarbons + oxides of nitrogen → carbon dioxide + water + nitrogen

2 carbon monoxide + oxides of nitrogen → carbon dioxide + nitrogen

3 carbon monoxide + hydrocarbons → carbon dioxide + water

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

17 The Gabriel synthesis is a useful method of preparing primary amines.
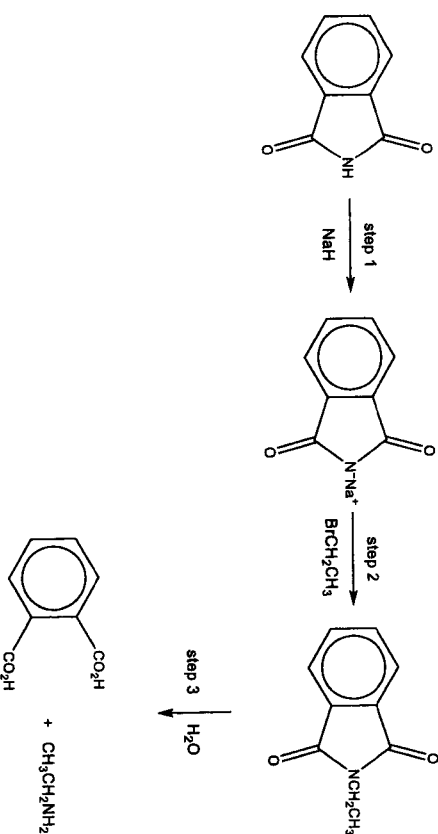
What are the types of reactions occurring in each of the steps?

	step 1	step 2	step 3
A	acid-base	electrophilic substitution	hydrolysis
B	acid-base	nucleophilic substitution	hydrolysis
C	oxidation	electrophilic substitution	oxidation
D	oxidation	nucleophilic substitution	oxidation

9

18 Benzene reacts with chloroethane to form ethylbenzene.

$$\text{benzene} + CH_3CH_2Cl \xrightarrow{AlCl_3} \text{ethylbenzene} + HCl$$
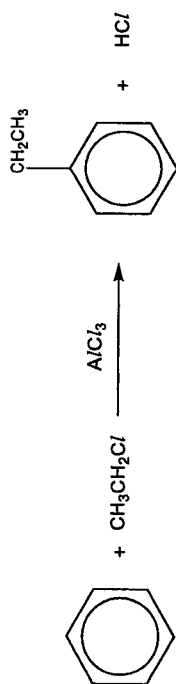
The reaction proceeds via several stages with two successive intermediates.

What could be the intermediates for this reaction?

A $[CH_3CH_2]^+$ and [structure: cyclohexadienyl cation with H and CH_2CH_3]

B $[CH_3CH_2]^-$ and [structure: cyclohexadienyl cation with H and CH_2CH_3]

C $[CH_3CH_2]^+$ and [structure: cyclohexadienyl cation with H and CH_2CH_3]

D $[CH_3CH_2]^-$ and [structure: cyclohexadienyl cation with H and CH_2CH_3]

10

19 Caffeic acid is found at relatively high levels in spearmint and star anise. It shows antioxidant and anti-inflammatory activities.
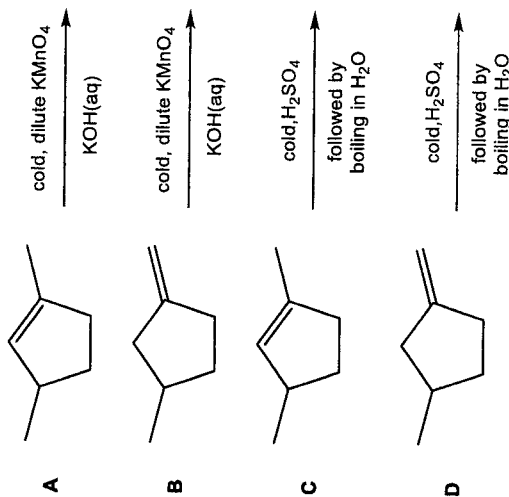
[structure of caffeic acid]
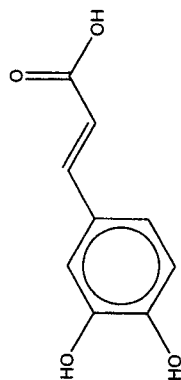
caffeic acid

When treated with aqueous bromine, what is the maximum number of bromine atoms that can be incorporated into a molecule of caffeic acid?

A 2   B 3   C 4   D 5

20 Which reaction forms a product which can be further oxidised to form a carboxylic acid?

A [structure] $\xrightarrow[KOH(aq)]{\text{cold, dilute } KMnO_4}$

B [structure] $\xrightarrow[KOH(aq)]{\text{cold, dilute } KMnO_4}$

C [structure] $\xrightarrow[\substack{\text{followed by} \\ \text{boiling in } H_2O}]{\text{cold, } H_2SO_4}$

D [structure] $\xrightarrow[\substack{\text{followed by} \\ \text{boiling in } H_2O}]{\text{cold, } H_2SO_4}$

21 Cholecalciferol is a type of vitamin D that is made by the skin when exposed to sunlight. It can also be found in the flesh of fatty fish and fish liver oils.
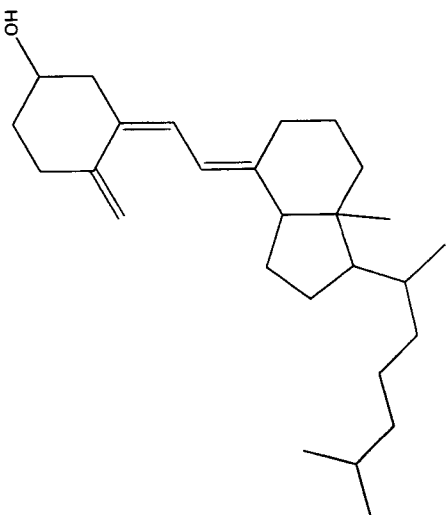
cholecalciferol

Which statements about cholecalciferol are correct?

1   There is a maximum of 128 stereoisomers.

2   Cholecalciferol can react with ethanoyl chloride to form a sweet-smelling product.

3   1 mole of cholecalciferol produces 3 moles of carbon dioxide when heated with acidified $KMnO_4$.

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

22 A comparison is made of the rate of hydrolysis of four halogenocompounds by hot aqueous NaOH.

$CH_3CH_2CH_2Cl$	CH_3CH_2COCl	$C_6H_5CH_2Br$	C_6H_5Cl
E	F	G	H

How will the rates of hydrolysis compare?

	fastest	⟶		slowest
A	E	G	H	F
B	G	H	E	F
C	F	G	E	H
D	F	E	G	H

23 Which pairs of compounds can be distinguished using the stated reagents and conditions?

|	compounds	reagents and conditions
1	$CH_3CH_2CO_2H$ and $CH_3CH_2CH_2OH$	Na, room temperature
2	$CH_3CO_2CH_2CH_3$ and $CH_3CONHCH_2CH_3$	NaOH(aq), I_2(aq), heat
3	$CH_3CON(CH_3)_2$ and $(CH_3)_2CHCONH_2$	NaOH(aq), heat

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

24 There is a range of reactions of the aldehyde group which have the pattern
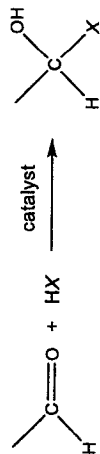
of which the formation of a cyanohydrin (where X = CN) is one.

Which compounds could be obtained by such an addition to an aldehyde group, followed by a dehydration?

1

2

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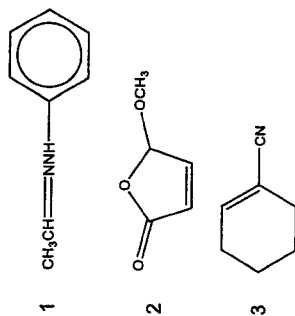
A 1, 2 and 3   B 1 and 2   C 2 and 3   D 3 only

25 The compound $C_3H_7CO_2C_6H_5$ is an ester.

Which statement about this ester is correct?

A Its name is phenyl propanoate.

B When heated with NaOH(aq), phenol is one of the products formed.

C When heated with H_2SO_4(aq), butanoic acid is one of the products formed.

D It can be formed using butanoic acid and phenol.

**26** A nonapeptide was hydrolysed partially using an enzyme to yield the following tripeptide fragments:

thr – ser –asn
pro – gly – his
asn – val – pro
pro –val –thr
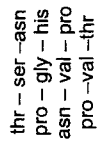
What is the correct amino acid sequence in the nonapeptide?

A asn – val – pro – gly – his – thr – ser – asn – val

B thr – ser – asn – val – pro – gly – his – val – pro

C pro – val – thr – ser – asn – val – pro – gly – his

D his – gly – pro – val – asn – ser – thr – val – pro

27 Which diagram correctly shows the arrangement of the six coordinate bonds in a regular octahedral complex of copper?

A   B   C   D
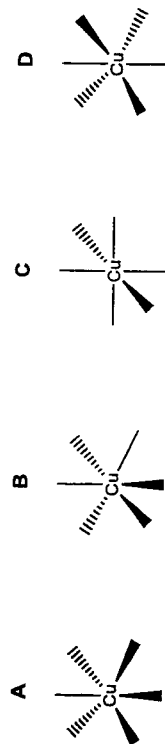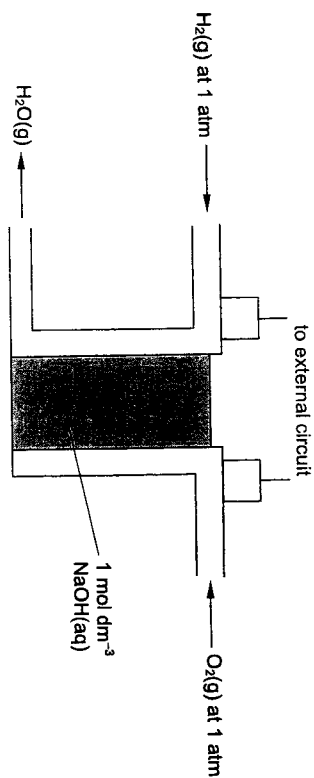
28 The standard redox potential for the half-cell reaction

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \text{ is } +0.77 \text{ V.}$$
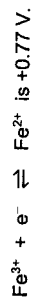
Which cell would be used to determine this standard value?

A Fe electrode in 1 mol dm^{-3} Fe^{3+} against Fe electrode in 1 mol dm^{-3} Fe^{2+}

B Pt electrode in 1 mol dm^{-3} Fe^{3+} against Pt electrode in 1 mol dm^{-3} Fe^{2+}

C Fe electrode in a solution containing 1 mol dm^{-3} Fe^{3+} and 1 mol dm^{-3} Fe^{2+} against a standard hydrogen electrode

D Pt electrode in a solution containing 1 mol dm^{-3} Fe^{3+} and 1 mol dm^{-3} Fe^{2+} against a standard hydrogen electrode

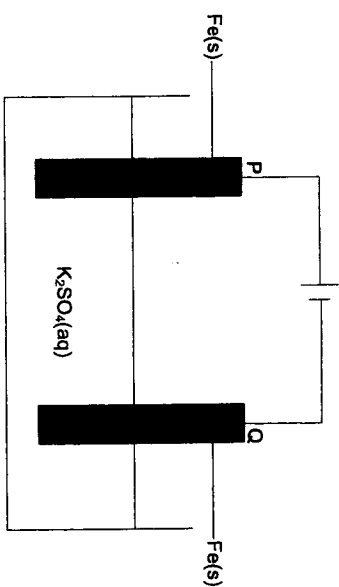**15**

Use of the Data Booklet is relevant to this question.

A hydrogen-oxygen fuel cell is shown.

H₂(g) at 1 atm

H₂O(g) →

to external circuit

O₂(g) at 1 atm

1 mol dm⁻³
NaOH(aq)

Which E° value should be used for the cathode?

A   −0.08 V

B   +0.40 V

C   +0.68 V

D   +1.23 V

16

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

An experiment is set up as shown to study the corrosion of iron.

Fe(s)

P

K₂SO₄(aq)

Q

Fe(s)

What will occur at electrodes P and Q?

	electrode P	electrode Q
A	no change in mass	decrease in mass and H₂ evolved
B	no change in mass	decrease in mass and SO₂ evolved
C	decrease in mass	no change in mass and SO₂ evolved
D	decrease in mass	no change in mass and H₂ evolved