H2

TAMPINES JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION

CHEMISTRY 9729/01

Paper 1 Multiple Choice

Tuesday, 18 September 2018

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

1 hour

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.
Write your name and Civics Group on the Answer Sheet in the spaces provided.

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.

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.

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

The ^{68}Ge isotope is medically useful because it undergoes a natural radioactive process to give an isotope of a different element, ^{68}X, which can be used to detect tumours. This transformation of ^{68}Ge occurs when an electron enters the nucleus and changes a proton into a neutron.

Which statement about the composition of an atom of ^{68}X is correct?

A It has 4 electrons in its outer p orbitals.

B It has 13 electrons in its valence shell.

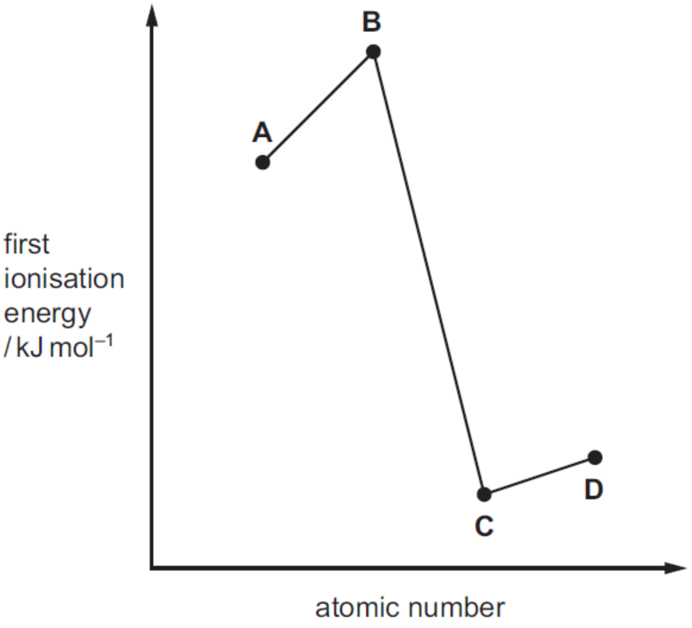
C It has 37 neutrons.

D Its proton number is 32.

2 The relative first ionisation energies of four elements with consecutive atomic numbers below 20 are shown on the graph.

One of the elements reacts with hydrogen to form a covalent compound with formula H**E**.

Which element could be **E**?



3 The airbags in cars contain sodium azide, NaN_3, and an excess of potassium nitrate, KNO_3.

In a car accident, the reactions shown occur, producing nitrogen. This causes the airbag to inflate rapidly.

$$2NaN_3 \rightarrow 2Na + 3N_2$$

$$10Na + 2KNO_3 \rightarrow K_2O + 5Na_2O + N_2$$

How many moles of nitrogen gas are produced **in total** when 1 mol of sodium azide, NaN_3, decomposes in an airbag?

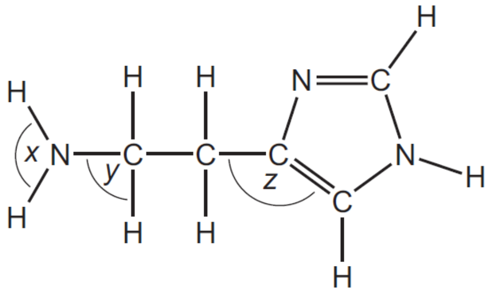
A 1.5 **B** 1.6 **C** 3.2 **D** 4.0

4 Which statements explain why nitrogen gas is unreactive?

1 Nitrogen atoms are highly electronegative.
2 Nitrogen molecules are non-polar.
3 The triple bond between nitrogen atoms is very strong.

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

5 Histamine is produced in the body to help fight infection. Its shape allows it to fit into receptors which expand blood vessels.



histamine

What are the bond angles x, y and z in histamine, from the largest to the smallest?

	largest bond angle	⟶	smallest bond angle
A	*x*	*y*	*z*
B	*x*	*z*	*y*
C	*z*	*x*	*y*
D	*z*	*y*	*x*

6 In an experiment, a sample of a pure gas is put into a gas syringe at a temperature of 300 K and pressure of 16 kPa. The gas is compressed until the volume occupied by the gas is halved.

After compression, the temperature of the gas in the syringe is 450 K and the pressure is 48 kPa.

Which statement is correct?

A Intermolecular forces between the gas molecules are significant.

B It is possible to calculate the number of moles of gas present using these data alone.

C The gas is behaving ideally.

D The pressures used are too high for ideal gas behaviour.

7 The following reaction takes place in a suitable solvent.

$$Na^+NH_2^- + NH_4^+Cl^- \rightarrow Na^+Cl^- + 2NH_3$$

Which statements explain why this reaction should be classified as a Brønsted-Lowry acid-base reaction?

1 NH_2^- is an electron pair acceptor.

2 Na^+Cl^- is a salt.

3 The ammonium ion acts as a proton donor.

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

8 Element **G** is one of the first five elements in Period 3 of the Periodic Table. The following four statements were made about the properties of element **G** or its compounds.

Three statements are correct descriptions and one is false.

Which statement does **not** fit with the other three?

A The oxide of **G** dissolves in excess dilute NaOH(aq).

B **G** exhibits only one possible oxidation number in its chloride, which is not a solid at room temperature.

C The oxide of **G** has a very high melting point.

D The chloride of **G** reacts with water to give an acidic solution with pH 1.

9 Which enthalpy change would best indicate the relative strengths of the intermolecular forces in liquid hydrogen halides?

A bond dissociation energy

B enthalpy change of formation

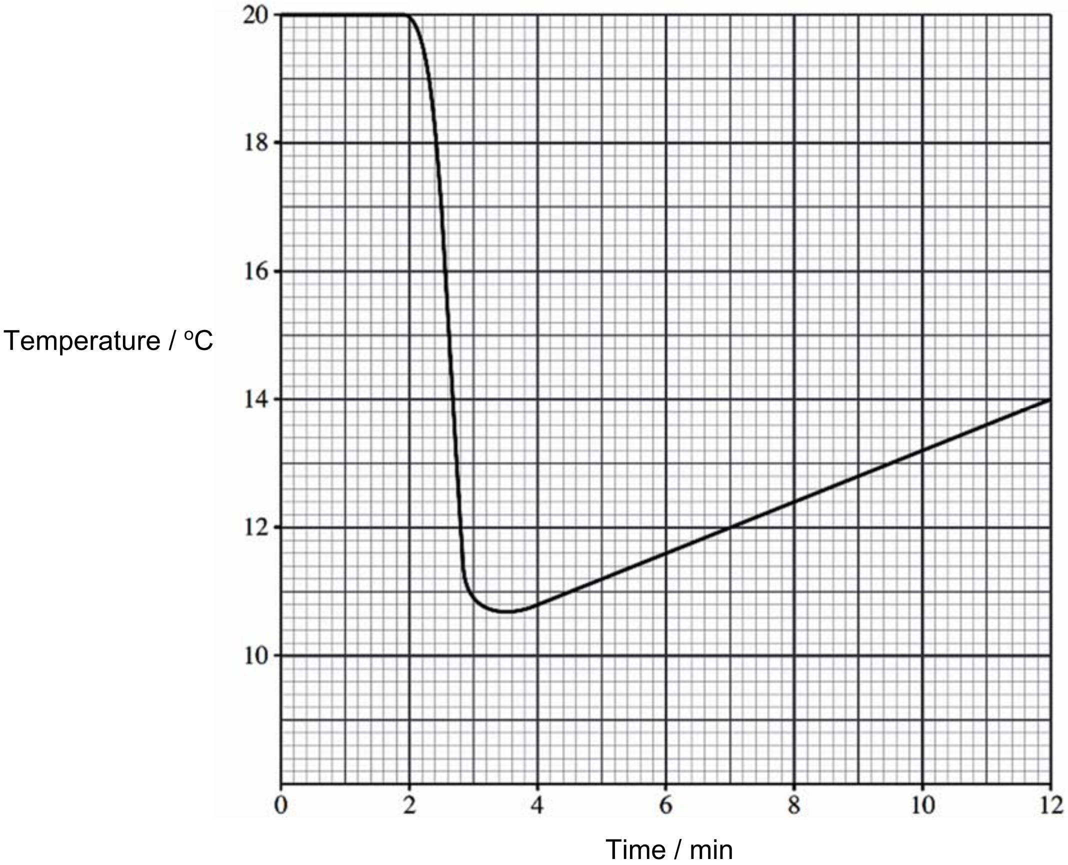
C enthalpy change of solution

D enthalpy change of vaporisation

10 Sodium carbonate reacts with ethanoic acid according to the equation below.

$$Na_2CO_3(s) + 2CH_3COOH(aq) \xrightarrow{\Delta H_r} 2CH_3COONa(aq) + H_2O(l) + CO_2(g)$$

In an experiment to determine the enthalpy change of reaction, ΔH_r, 6.8 g of solid sodium carbonate (M_r = 106) was added to 50 cm^3 of excess aqueous ethanoic acid at the second minute. The temperature of the resultant solution was monitored at various time intervals and the following graph was obtained.



With the use of the graph, what is the enthalpy change of reaction, ΔH_r?

The specific heat capacity of the solution is given to be 4.18 J cm^{-3} K^{-1}.

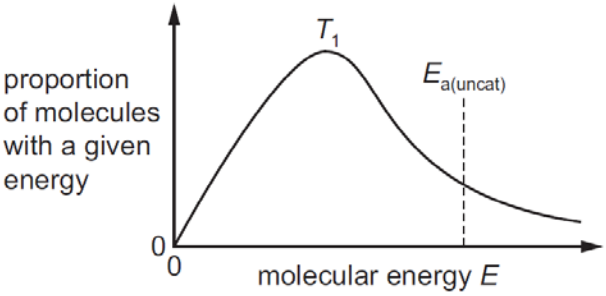
A +30.3 kJ mol^{-1}

B +32.6 kJ mol^{-1}

C +34.4 kJ mol^{-1}

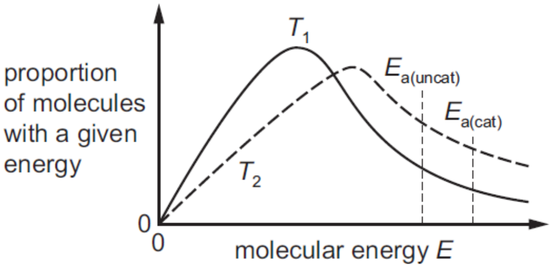
D +37.0 kJ mol^{-1}

11 The diagram shows the distribution of molecular energies in a sample of gas at a temperature T_1. The activation energy for an uncatalysed reaction of this gas, $E_{a(uncat)}$, is shown.

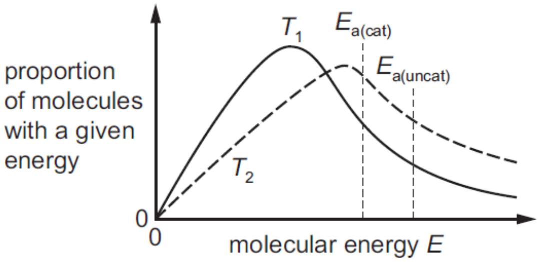


Which diagram correctly shows the new distribution and new activation energy, $E_{a(cat)}$, when the temperature is increased to T_2, and a catalyst is used that increases the rate of the reaction?

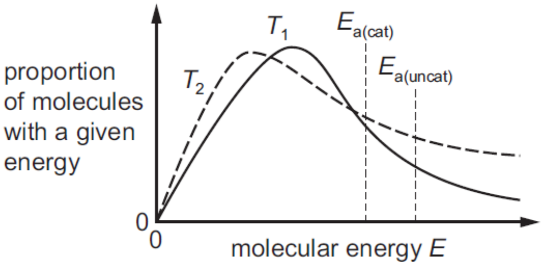
A



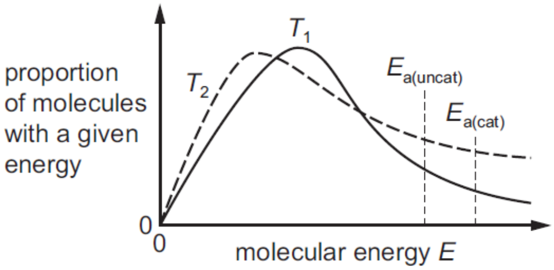
B



C



D



12 A radioactive element has two isotopes, **L** and **M**, with half–lives of 4 min and 6 min respectively.

An experiment starts with *n* times as many atoms of **L** as of **M**. After 12 min, the number of atoms of **L** and **M** are both equal.

Given that radioactive decay is a first order reaction, what is the value of *n*?

A 0.5 **B** 2 **C** 4 **D** 8

13 Hydrogen iodide dissociates into hydrogen and iodine.

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

In an experiment, *b* mol of hydrogen iodide were put into a sealed vessel at pressure *p*. At equilibrium, *x* mol of the hydrogen iodide had dissociated.

Which expression for K_p is correct?

A $\frac{x^2}{(b-x)^2}$ **B** $\frac{x^2p^2}{(b-x)^2}$ **C** $\frac{x^2p^2}{4b(b-x)}$ **D** $\frac{x^2}{4(b-x)^2}$

14 Nitrogen dioxide, NO_2, is a brown gas.
Dinitrogen tetroxide, N_2O_4, is a colourless gas.

An equilibrium is established between NO_2 and N_2O_4 in a closed vessel.

$$\underset{\text{brown}}{2NO_2(g)} \rightleftharpoons \underset{\text{colourless}}{N_2O_4(g)} \qquad \Delta H = -57\ \text{kJ mol}^{-1}$$

Which row describes the effects of changing conditions on the colour of an equilibrium mixture of NO_2 and N_2O_4?

	decreasing the pressure	decreasing the temperature
A	colour becomes darker	colour becomes darker
B	colour becomes darker	colour becomes lighter
C	colour becomes lighter	colour becomes darker
D	colour becomes lighter	colour becomes lighter

15 Which of the following mixtures will result in a significant pH change when a small amount of acid is added?

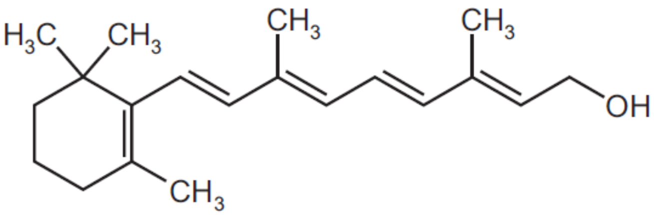
A 20 cm^3 of 1 mol dm^{-3} HCl and 20 cm^3 of 1 mol dm^{-3} $CH_3CH_2NH_2$

B 10 cm^3 of 1 mol dm^{-3} HCl and 20 cm^3 of 1 mol dm^{-3} $Ca(CH_3COO)_2$

C 20 cm^3 of 1 mol dm^{-3} H_2CO_3 and 20 cm^3 of 1 mol dm^{-3} $NaHCO_3$

D 10 cm^3 of 1 mol dm^{-3} KOH and 20 cm^3 of 1 mol dm^{-3} NH_4Cl

16 The diagram shows the structure of vitamin A.



vitamin A

Which bond is **not** present in the compounds above?

A a σ bond formed by $sp^3 - sp^3$ overlap

B a σ bond formed by $sp^3 - sp^2$ overlap

C a σ bond formed by $sp^2 - sp^2$ overlap

D a σ bond formed by $sp^2 - sp$ overlap

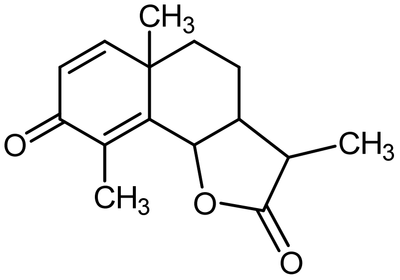
17 Modern cars are fitted with catalytic converters to reduce atmospheric pollution caused by unwanted reactions during the combustion of the fuel.

Which statements are correct?

1 Carbon monoxide is oxidised to carbon dioxide in a catalytic converter.
2 Catalytic converters have a very large surface area to mass ratio.
3 Nitrogen dioxide is reduced to nitrogen monoxide in a catalytic converter.

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

18 Santonin is a drug that was once widely used to expel parasitic worms from the body.

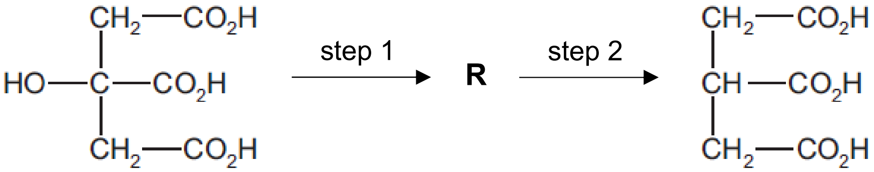


santonin

When santonin is treated with an excess of bromine dissolved in tetrachloromethane, an organic product **N** is obtained. How many chiral centres are present in one molecule of compound **N**?

A 4 **B** 6 **C** 8 **D** 10

19 Citric acid can be converted into tricarballylic acid in two stages. An intermediate, **R**, is formed.



Which reagents are needed for each step?

	step 1	step 2
A	concentrated H_2SO_4	H_2(g) and Ni
B	concentrated H_2SO_4	$LiAlH_4$
C	$LiAlH_4$	H_2SO_4(aq)
D	NaOH(aq)	H_2(g) and Ni

20 Which of the following compounds cannot be obtained from propene in a single reaction?

A $CH_3CH_2CH_3$

B $CH_3CH_2CH_2CN$

C $CH_2(OH)CH(OH)CH_3$

D CO_2

21 An enantiomer which rotates plane polarised light in a clockwise direction is known as the (+) form. The other enantiomer, which rotates plane polarised light in an anticlockwise direction, is known as the (–) form. For example, (–)-2-bromobutane rotates plane polarised light in an anticlockwise direction.

(+)-2-bromobutane undergoes two separate reactions as shown below.

Reaction 1: When (+)-2-bromobutane is warmed with aqueous NaOH, a racemic mixture of butan-2-ol is produced.

Reaction 2: When (+)-2-bromobutane is warmed with alcoholic KCN, (–)-2-cyanobutane is produced.

Which of the following statements are correct?

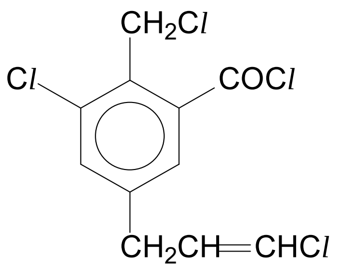
1 Reaction 1 proceeds via both S_N1 and S_N2 mechanisms.

2 Reaction 2 proceeds via a single-step reaction.

3 The rates of both reactions are dependent on the concentrations of the nucleophiles.

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

22 Compound **S** has the structure as shown below.

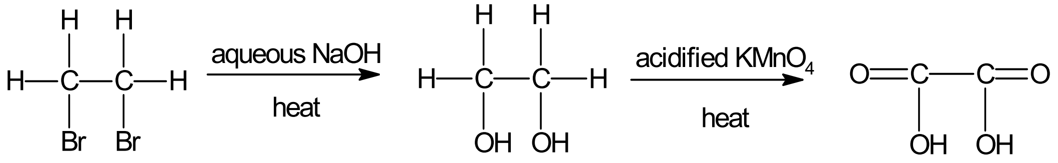


1 mol of compound **S** is warmed with excess ethanolic silver nitrate.
How many moles of silver chloride is precipitated out?

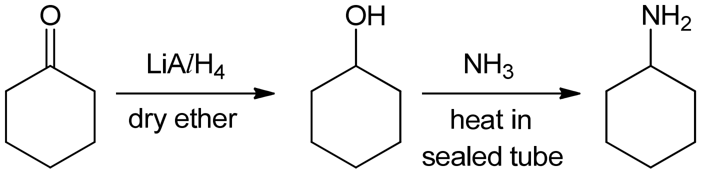
A 1 **B** 2 **C** 3 **D** 4

23 Which is the most feasible synthetic route?

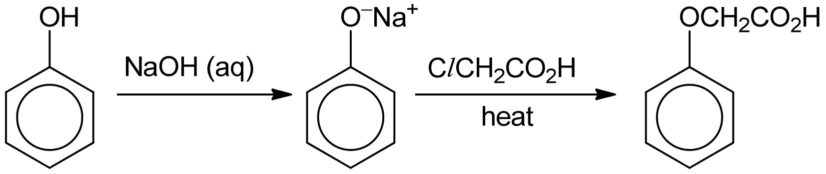
A



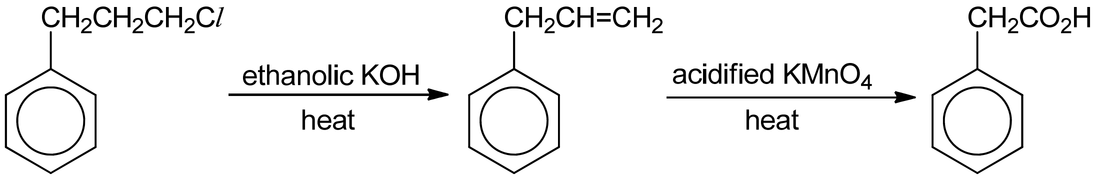
B



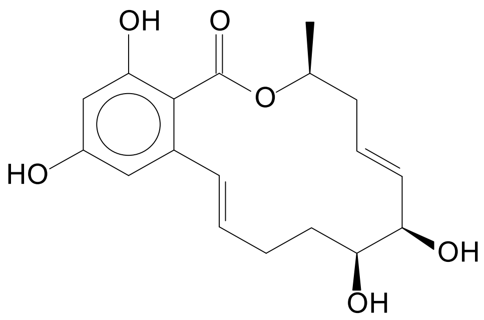
C



D



24 *Aigialomycin D*, a fungal metabolite, has the structure shown below.



Aigialomycin D

Which of the following statements about *Aigialomycin D* are correct?

1 It reacts with hot, acidified $K_2Cr_2O_7$ to give a diketone.
2 One mole of *Aigialomycin D* reacts with Na metal to produce 2 moles of hydrogen gas.
3 One mole of *Aigialomycin D* reacts with 4 moles of $SOCl_2$.

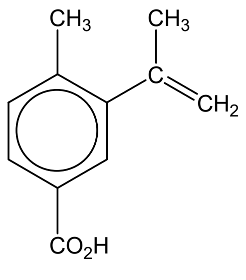
A 1, 2 and 3 **B** 1 and 2 only **C** 1 and 3 only **D** 2 only

25 Compound **T** has the following properties:

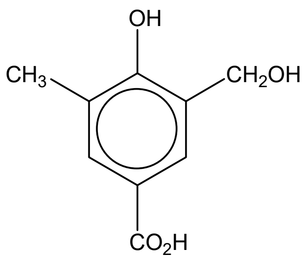
(i) it does not decolourise aqueous bromine,
(ii) it produces an effervescence when reacted with Na_2CO_3(aq), and
(iii) it decolourises hot acidified $KMnO_4$(aq).

Which of the following can be Compound **T**?

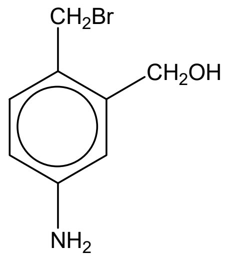
A



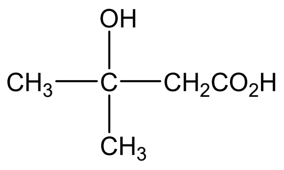
B



C



D



$$CH_3-\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{C}}-CH_2CO_2H$$

26 Which of the following shows the correct order of increasing pK_b in an aqueous solution of equal concentration?

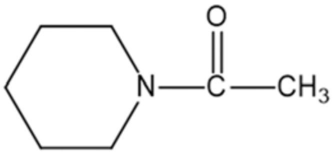
A $C_2H_5CONH_2 < C_6H_5NH_2 < C_2H_5NH_2 < C_2H_5NH(CH_3)$

B $C_2H_5CONH_2 < C_2H_5NH_2 < C_2H_5NH(CH_3) < C_6H_5NH_2$

C $C_2H_5NH(CH_3) < C_2H_5NH_2 < C_6H_5NH_2 < C_2H_5CONH_2$

D $C_2H_5NH_2 < C_2H_5NH(CH_3) < C_6H_5NH_2 < C_2H_5CONH_2$

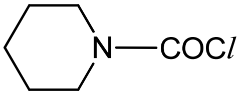
27 The structure of Compound **W** is shown below.



compound **W**

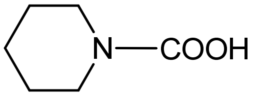
Which pair of compounds would produce compound **W** when reacted together?

A



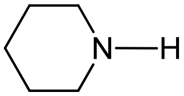
+ CH_3OH

B



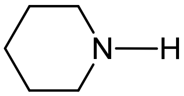
+ CH_3OH

C



+ CH_3COCl

D



+ CH_3COOH

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

The reaction between iodide and peroxodisulfate ($S_2O_8^{2-}$) is slow due to its high activation energy. Which of the following cannot function as a catalyst for the above-mentioned reaction?

A Cr^{2+} **B** Co^{3+} **C** Mn^{3+} **D** Fe^{2+}

29 During the anodising of aluminium, 1 mol dm^{-3} sulfuric acid is electrolysed between Al anode and graphite cathode, using a constant current for 90 s.

What affects the mass of oxide layer deposited on the Al anode?

1 changing the electrolyte to 1 mol dm^{-3} hydrochloric acid
2 increasing the time taken
3 increasing the concentration of the electrolyte solution

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

30 Which of the following is **not** a result of the small energy gap between 3d and 4s orbitals?

A Transition metals ions are usually coloured.
B Transition metals can exhibit variable oxidation states.
C Transition metals have higher melting point than calcium.
D Transition metals have higher electrical conductivity than aluminium.

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2018 TPJC Preliminary Examination
H2 Chemistry Paper 1 Answers

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

Worked Solutions

1 Answer: C

^{68}Ge has has 32 protons and 36 neutrons.
When 'a proton changes into a neutron', ^{68}X contains 31 protons and **37 neutrons**.
X is gallium (Ga) which is in Group 13, i.e. 3 valence electrons, only 1 of which is in outer p orbitals.

2 Answer: A

Since **E** forms covalent hydride with formula H**E**, it is a Group 17 element.
The steep drop in first I.E. between B and C suggests that C has one quantum shell more than B, i.e. B is in Group 18 while C is from Group 1. Hence, A is from Group 17, i.e. element **E**.

3 Answer: B

Nitrogen gas is produced in both reactions.
First eqn: Since $2NaN_3 \equiv 3N_2$, moles of N_2 produced = 3/2 x 1 = 1.5 mol, and
$NaN_3 \equiv Na$, moles of Na produced = 1 mol
Second eqn: $10Na \equiv N_2$, moles of N_2 produced = 0.1 mol

Total moles of N_2 produced = 1.6 mol

4 Answer: D (2 and 3 only)

Option 1: Highly electronegative elements have tendency to attract electrons and undergo reduction ⇒ does **not** account for unreactivity.
Option 2: Non-polar molecules do not attract electrophiles or nucleophiles ⇒ unreactive.
Option 3: A lot of energy required to break triple bond ⇒ unreactive.

5 Answer: D

Bond angles x, y and z are 107°, 109.5° and 120° respectively.

6 Answer: C

For ideal gas, $pV/T = nR =$ constant
Before compression, $pV/T = (16V)/300 = 0.0533\ V$
After compression, $pV/T = (48 \times 0.5\ V)/450 = 0.0533\ V$
Since pV/T is constant under different conditions, the gas is behaving ideally.

7 Answer: D (3 only)

Brønsted-Lowry acid is defined as a proton donor while Brønsted-Lowry base is a proton acceptor.
In this reaction, NH_4^+ is the proton donor while NH_2^- is the proton acceptor.

8 Answer: A

Options B, C and D apply to Si while Option A does not (SiO_2 does not dissolve in dilute acid).

9 Answer: D

Strength of the <u>intermolecular</u> forces in liquid hydrogen halides (simple molecular compound) will affect properties such as melting and boiling points (i.e. enthalpy change of vaporisation), as well as solubility in solvents.

Options A & B will involve breaking covalent bonds, and will be affected by bond energies.
Option D compares the relative strengths of ionic bonds in ionic compounds.

10 Answer: B

By extrapolation of curve to the 2nd minute to compensate for heat gain during the experiment, minimum temperature reached is 10.0°C. Hence temperature drop = 20 – 10 = 10°C

Heat absorbed = 50 (4.18) (10) = 2090 J
Moles of sodium carbonate reacted = 6.8 / 106 = 0.06415 mol

$\Delta H_r = +\ 2090 / 0.06415\ \text{J mol}^{-1} = +\ 32.6\ \text{kJ mol}^{-1}$

11 Answer: B

When temperature is increased, the peak of energy distribution curve should
- shift to the right (average energy increased) and
- height of peak should be lower (to maintain area under the curve, i.e. same number of particles)

The activation energy for catalysed reaction should be lower than uncatalyzed reaction.

12 Answer: B

Let the number of atoms of L after 12 min be *x*.

$$\textbf{L} \quad 8x \xrightarrow{t_{1/2} = 4\text{ min}} 4x \xrightarrow{t_{1/2} = 4\text{min}} 2x \xrightarrow{t_{1/2} = 4\text{ min}} x$$

$$\textbf{M} \quad 4x \xrightarrow{\qquad t_{1/2} = 6\text{ min} \qquad} 2x \xrightarrow{\qquad t_{1/2} = 6\text{ min} \qquad} x$$

Hence, at start of experiment, **L : M** = $8x : 4x$ = 2: 1

13 Answer: D

	$2HI(g)$	$\rightleftharpoons$	$H_2(g)$	+	$I_2(g)$
Initial moles	b		0		0
Δ in moles	–x		+0.5x		+0.5x
Eqm moles	b – x		+0.5x		+0.5x

Total moles of gas at eqm = b

$$p_{HI} = \frac{b - x}{b}\,p$$

$$p_{H_2} = p_{I_2} = \frac{0.5x}{b}\,p$$

$$K_p = \frac{(p_{H_2})(p_{I_2})}{(p_{HI})^2} = \frac{\left(\frac{0.5x}{b}\right)\left(\frac{0.5x}{b}\right)}{\left(\frac{b-x}{b}\right)^2} = \boldsymbol{\frac{x^2}{4(b-x)^2}}$$

14 Answer: B

Decreasing pressure favours the reaction that increases number of gaseous particles. Hence, reverse reaction is favoured and colour becomes darker.

Decreasing temperature favours the exothermic reaction, i.e. the forward reaction. Hence, the colour becomes lighter

15 Answer: A

Significant change in pH ⇒ **not** buffer

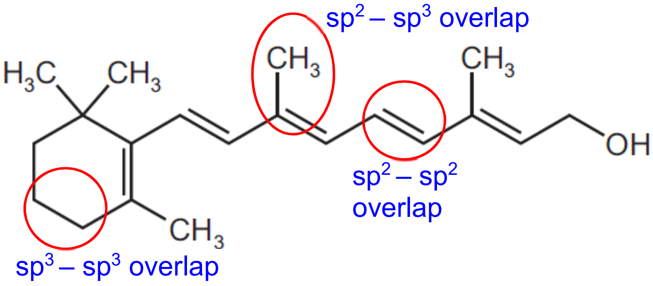
Option A: Resultant solution contains only $CH_3CH_2NH_3^+\ Cl^-$ (i.e. salt) present ⇒ **not** buffer, i.e. pH changes significantly when acid is added.

Option B: Resultant solution is mixture of CH_3COOH ($CH_3COO^- + H^+$) and CH_3COO^- present ⇒ buffer

Option C: Resultant solution is mixture of H_2CO_3 and HCO_3^- present ⇒ buffer

Option D: Resultant solution is mixture of NH_3 ($NH_4^+ + OH^-$)and NH_4^+ present ⇒ buffer

16 Example of σ bond formed from…

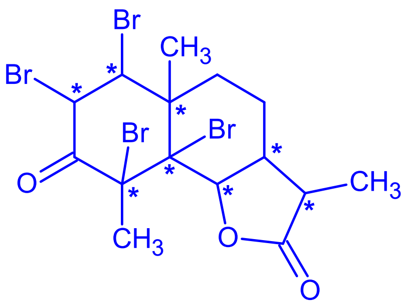


17 Answer: B (1 and 2 only)

Catalytic converters convert harmful gases to less harmful/ harmless ones.
Examples: CO to CO_2 *(Option 1)* and oxides of nitrogen to N_2.

Catalysts have a honeycomb structure to provide large surface area, i.e. more active sites for adsorption of reactant molecules. *(Option 2)*

18 Answer: C



19 Answer: A

Step 1: use of concentrated H_2SO_4 dehydrates 3° alcohol to form alkene (C=C)
Step 2: use of $H_2(g)$ and Ni reduction of alkene to alkane. Note that $LiAlH_4$ cannot be used as it will reduce the carboxylic acid group to 1° alcohol.

20 Answer: B

Option A: propene + H_2/Ni $\rightarrow$ $CH_3CH_2CH_3$
Option C: propene + cold alkaline $KMnO_4$ $\rightarrow$ $CH_2(OH)CH(OH)CH_3$
Option D: propene + O_2 $\rightarrow$ CO_2

21 Answer: C

Reaction 1: While only 1 enantiomer was used for reaction, a racemic mixture was obtained. This suggests that the reaction underwent an S_N1 mechanism which involves a trigonal planar carbocation intermediate that allows OH^- to attack from either side of plane with equal probability.
Rate equation is Rate = k [(+)-2-bromobutane], i.e. independent of [nucleophile].

Reaction 2: Since only one enantiomer was obtained, this suggests that the reaction underwent an S_N2 mechanism which involved an inversion of stereochemistry of the chiral centre. The S_N2 mechanism is a single-step reaction *(option 2)*. Rate equation is Rate = k [(+)-2-bromobutane][CN^-].

22 Answer: B

Only the acyl chloride (-COCl) and chloroalkane (-CH_2Cl) would have undergone nucleophilic substitution to produce total of 2 moles of Cl^- ions to precipitate to form 2 moles AgCl precipitate.

23 Answer: C

Option A: In Step 2, 1,2-ethanediol will undergo vigorous oxidation to give CO_2 and H_2O.
Option B: Primary amine (final product) should be formed from nucleophilic substitution between ammonia and halogenoalkane, **not** ammonia and alcohol.
Option C: Step 1 is acid-base reaction to form phenoxide which then acts as nucleophile in nucleophilic substitution reaction with chloroalkane in the second step.
Option D: In Step 2, the alkyl group on benzene ring should be oxidised to benzoic acid instead.

24 Answer: D (2 only)

Option 1: Total of **three ketone functional groups**. Other than the two secondary (2°) alcohols that oxidise to give ketone functional group, the ester group will first undergo hydrolysis to give acid and 2° alcohol. The 2° alcohol is then oxidised to ketone.

Option 2: Total of 2° alcohol and 2 phenol groups. Each reacts with Na to give 0.5 mol H_2 gas. Hence, **total of 2 moles of H_2 gas**.

Option 3: Only the 2° alcohol groups will undergo nucleophilic substitution with **2 moles of $SOCl_2$.**

26 Answer: B

(i) does not decolourise aqueous bromine
⇒ **not** alkene, phenol, phenylamine *(options A & C eliminated)*
Option B not eliminated as 2- and 4- positions wrt phenol are all substituted.
Hence, phenol group in B does not react with aqueous bromine.
(ii) produces an effervescence when reacted with Na_2CO_3 ⇒ not carboxylic acid *(option D eliminated)*
(iii) decolourises hot acidified $KMnO_4(aq)$ ⇒ contains group that can be oxidised

26 Answer: C

Increasing pK_b ⇒ from strongest to weakest base
Basicity: 2° amine > 1° amine > phenylamine > amide

27 Answer: C

Amide is formed from the reaction between amine and acylchloride (-COCl)

28 Answer: A

$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\ominus = +0.54V$

$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ $E^\ominus = +2.01V$

Catalyst chosen must have reduction potential in between that of $E^{\ominus}_{I_2/I^-}$ and $E^{\ominus}_{S_2O_8^{2-}/SO_4^{2-}}$.
This is so that the catalyst can oxidise I^- and reduce $S_2O_8^{2-}$, i.e. $E^{\ominus}_{cell} > 0V$ for each reaction.

From Data Booklet,
$E^{\ominus}_{Cr^{3+}/Cr^{2+}} = -0.41V$
$E^{\ominus}_{Co^{3+}/Co^{2+}} = +1.89V$
$E^{\ominus}_{Mn^{3+}/Mn^{2+}} = +1.54V$
$E^{\ominus}_{Fe^{3+}/Fe^{2+}} = +0.77V$

Hence, only reduction potential for Cr^{3+}/Cr^{2+} is not within range, and cannot function as a catalyst.

29 Answer: C (2 only)

Amount of product obtained for electrolytic cell is dependent on Charge, Q = (current x time) only.

30 Answer: A

Option A: Coloured metal ions are due to energy gap between **upper and lower energy 3d-orbitals**, and not gap between 3d and 4s orbitals.

H2

TAMPINES JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

CANDIDATE NAME	
CIVICS GROUP	1 7
TUTOR NAME	

CHEMISTRY

9729/02

Paper 2 Structured Questions

Monday, 27 June 2018

2 hours

Candidates answer on the Question Paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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.

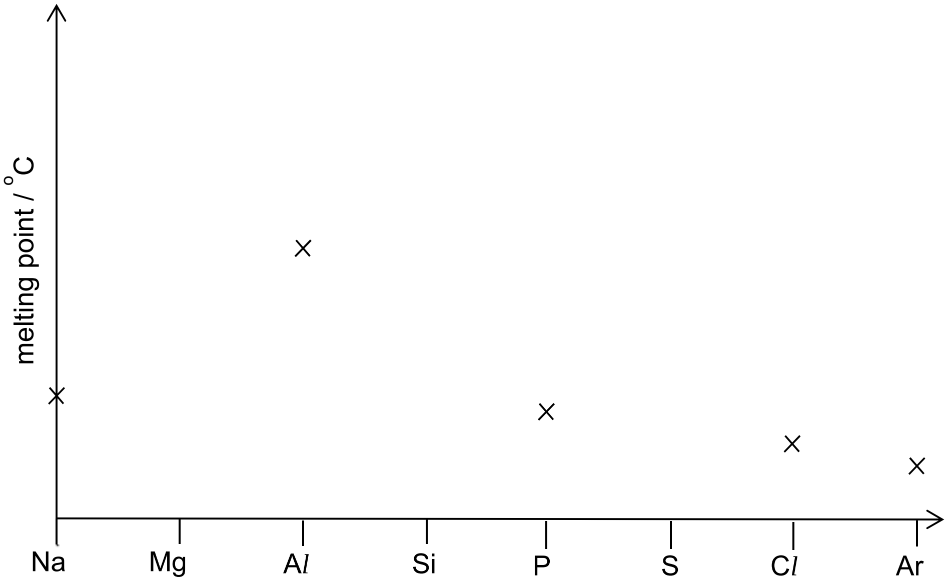
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

For Examiners' Use		
1	**9**	
2	**20**	
3	**15**	
4	**19**	
5	**12**	
Total	**75**	

Answer **all** the questions.

1 The graph below can be used to plot the melting point of the elements sodium to argon. Five of these elements have been plotted already.



(a) Use your knowledge of the variation in melting points of the elements of Period 3 to estimate and plot, on the graph in Figure 1.1, the melting points of the other three elements. [1]

(b) Justify your predictions in **(a)**, by explaining why the melting point of **each** element you have plotted is higher/lower/similar compared to the element to its left on the graph.

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………………………………………………………………………………………… [4]

(c) The use of the *Data Booklet* is required for this part of the question.
The first ionisation energies, in kJ mol^{-1} of Group 2 elements are given below.

element	1^{st} ionisation energies / kJ mol^{-1}
Be	900
Mg	736
Ca	590
Sr	548
Ba	502

(i) Explain why the first ionisation energies decrease in magnitude on descending the group.

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………………………………………………………………………………… [2]

(ii) Using your answer from **(c)(i)**, suggest how the reducing power of barium (Ba) compares to beryllium (Be).

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………………………………………………………………………………… [1]

(iii) Suggest why the first ionisation energy of indium (In) is greater than that of strontium (Sr).

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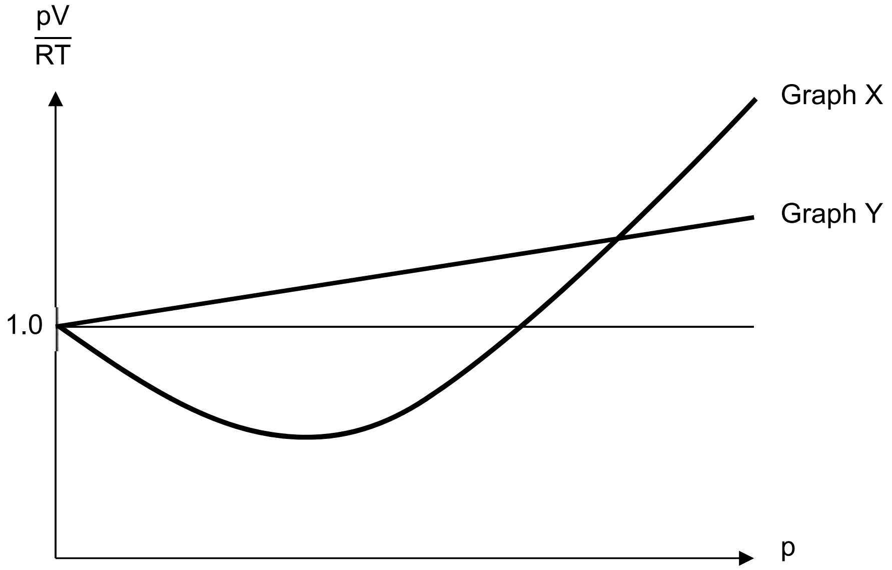
………………………………………………………………………………… [1]

[Total: 9]

2 At 700K, HI readily dissociates into H_2 and I_2.

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

(a) The graphs of $\frac{pV}{RT}$ against p for 1 mol each of H_2 and HI at room temperature are plotted below.



Deduce which of the graphs is the plot for HI.

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………………………………………………………………………………………… [2]

(b) 1.60 mol of gaseous HI was placed in a 2 dm^3 evacuated flask at 700K. After 30 minutes, equilibrium was established. The flask was then rapidly cooled and the HI is dissolved in 1000 cm^3 of water. 10 cm^3 of the solution obtained was titrated against 0.500 mol dm^{-3} NaOH(aq). 25.20 cm^3 of NaOH(aq) was required to reach end-point.

(i) Write the expression for K_p.

[1]

(ii) Calculate the partial pressures of HI, H_2 and I_2 at equilibrium.

[4]

(iii) Calculate the value of K_p at 700K.

[1]

(iv) The equilibrium constant for the dissociation of HBr at 700K is given below. Explain the difference in this value and your answer to **(b)(iii)**.

K_p (HBr) = 0.0172

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…………………………………………………………………………………….. [2]

HI readily reacts with alkenes.

(c) When HI was added to $CH_3CH{=}C(CH_3)_2$, products **A** and **B,** which are constitutional isomers of each other, were formed.

(i) **A** was formed in larger proportion than **B**.
Draw the possible structures of **A** and **B** in the boxes below. Explain your answer, by naming the mechanism for the reaction and by considering the stability of the intermediate formed.

A	**B**

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……………………………………………………………………………………….. [3]

(ii) One of the two isomers drawn in **(c)(i)** exhibits stereoisomerism. Name the type of stereoisomerism and draw diagrams to illustrate it.

type of stereoisomerism: ………………………………….

[2]

(iii) Suggest, with reason, how the rate of the reaction described in **(c)(i)** would differ if HC*l* had been used instead of HI.

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……………………………………………………………………………………….. [1]

(iv) When HI was added to another alkene with molecular formula of C_5H_8, only one product was formed. Suggest a structure for this alkene.

[1]

(v) State and explain, in terms of structure and bonding, how the boiling point of the products drawn in **(c)(i)** would differ if the halogen atom was chlorine instead of iodine.

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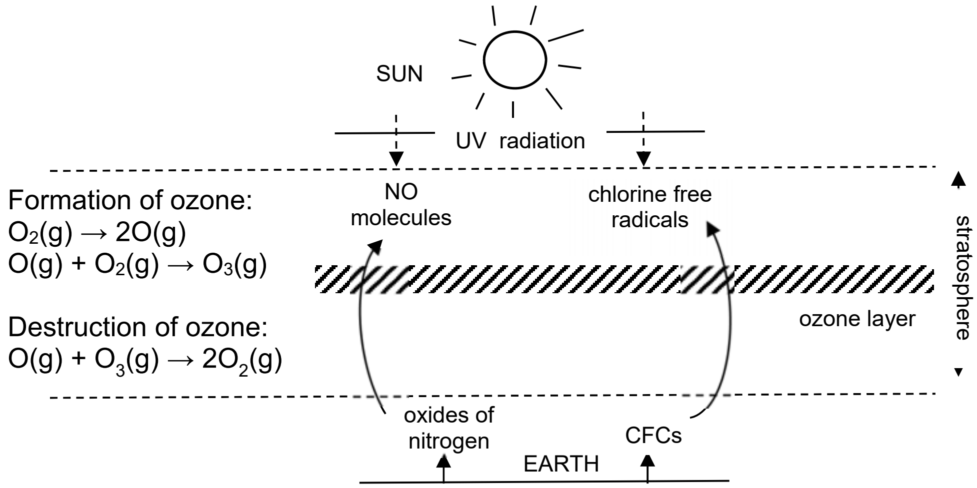
[Total: 20]

3 The stratospheric ozone has a vital role in protecting organisms on the Earth's surface from excessive exposure to high-energy radiation which can be very damaging. This protection arises because the natural reactions leading to the formation and destruction of ozone, as shown in the diagram below, absorb a significant amount of the incoming ultraviolet radiation.



Formation of ozone:
$O_2(g) \rightarrow 2O(g)$
$O(g) + O_2(g) \rightarrow O_3(g)$

Destruction of ozone:
$O(g) + O_3(g) \rightarrow 2O_2(g)$

However, the ozone layer is at risk due to human activities that produce nitrogen monoxide (NO) and chlorofluorocarbons (CFCs).

NO is formed during lightning discharges in a similar reaction to the combustion of nitrogen in car engines. NO catalyses the destruction of ozone in the stratosphere. Several experiments were carried out to understand the reaction and the following rate-concentration graphs were obtained for the reactants.

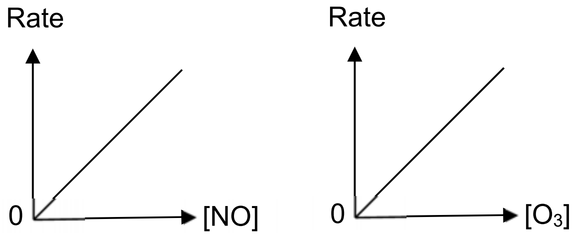


Figure 3.1

The use of CFCs poses an even more significant threat to the ozone layer. Their inertness has led to many useful daily applications but has also caused environmental issues. They diffuse upwards through the atmosphere unchanged until they reach the stratosphere where they dissociate photolytically in an initiation reaction to generate chlorine atoms. These chlorine free radicals subsequently undergo these reactions.

Propagation: $O_3(g) + Cl\bullet(g) \rightarrow O_2(g) + ClO\bullet(g)$
$O(g) + ClO\bullet(g) \rightarrow O_2(g) + Cl\bullet(g)$

Termination: $CH_4(g) + Cl\bullet(g) \rightarrow CH_3\bullet(g) + HCl(g)$
$NO_2(g) + ClO\bullet(g) \rightarrow ClONO_2(g)$

Figure 3.2

In stratospheric clouds of polar regions, the HC*l* and C*l*ONO2 can react together to form chlorine and nitric acid.

$$HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$$

(a) Explain, with the aid of an equation, why nitrogen monoxide is formed during lightning discharges.

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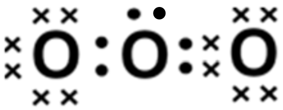
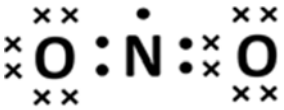
………………………………………………………………………………………………… [2]

(b) Draw dot-and-cross diagrams to show the bonding in O_3 and NO_2.

 O_3	 NO_2

[2]

(c) Based on your diagram in **(b)**, suggest if NO_2 undergoes reactions readily.

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………………………………………………………………………………………………… [1]

(d) Suggest a value for the bond angle in each of the above two molecules, giving reasons for your choice.

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………………………………………………………………………………………………… [2]

(e) With reference to Figure 3.1, deduce the orders of reaction with respect to each of the reactants involved in the production of nitrogen monoxide. Explain the significance of these orders in relation to the mechanism.

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………………………………………………………………………………………………… [3]

(f) Using your answer to **(e)**, suggest a possible mechanism for destruction of ozone by NO.

[2]

(g) With reference to the equations in Figure 3.2, explain why small amounts of CFCs are able to destroy large amounts of ozone.

………………………………………………………………………………………

……………………………………………………………………………………… [1]

(h) Would tetrafluoroethane, $C_2H_2F_4$, be able to destroy the ozone layer like CFCs? Explain your answer.

………………………………………………………………………………………

……………………………………………………………………………………… [1]

(i) The removal of chlorine-containing free radicals in the termination steps in Figure 3.2 help to limit the destruction of ozone. However, at polar regions when sunlight intensity increases during spring time, more severe depletion of the ozone layer occurs. Suggest a reason for this phenomenon.

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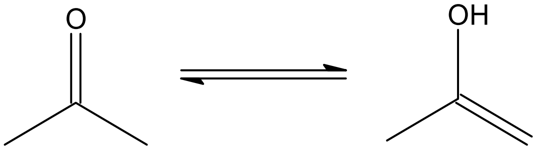
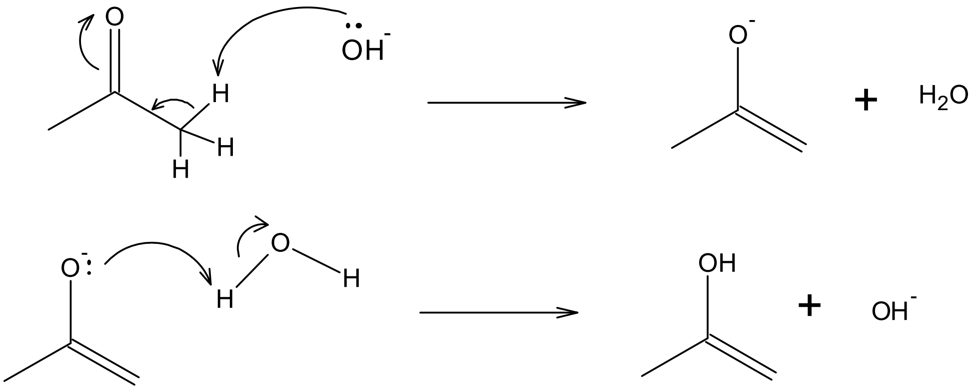
[Total: 15]

4 **(a)** In organic chemistry, keto–enol tautomerism refers to a chemical equilibrium between a keto form (a ketone or an aldehyde) and an enol (an alcohol). The enol and keto forms are said to be tautomers of each other.

Acetone, also known as propanone, can undergo tautomerisation with its corresponding alcohol according to the following equilibrium.



The interconversion can be base-catalysed. The mechanism is illustrated below.

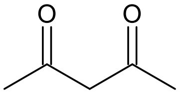
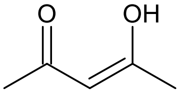


(i) In the above mechanism, acetone functions as a Brønsted−Lowry acid. Explain why this is so.

……………………………………………………………………………………….. [1]

(ii) Acetone can also function as a Lewis base. Using $AlCl_3$ as a Lewis acid, draw a structure to show how acetone functions as a Lewis base.

[1]

(iii) Another ketone, , pentane-2,4-dione, also exhibits keto–enol tautomerism with its enol form . The enol form is energetically more stable than the keto form.

Sketch a clearly labelled reaction pathway diagram for the keto–enol tautomerisation of pentane-2,4-dione.

[2]

(iv) Suggest a reason why the enol form of pentane-2,4-dione is more stable.

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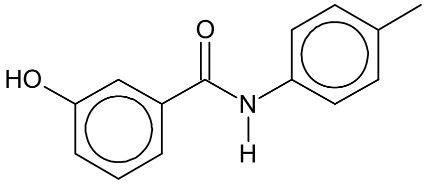
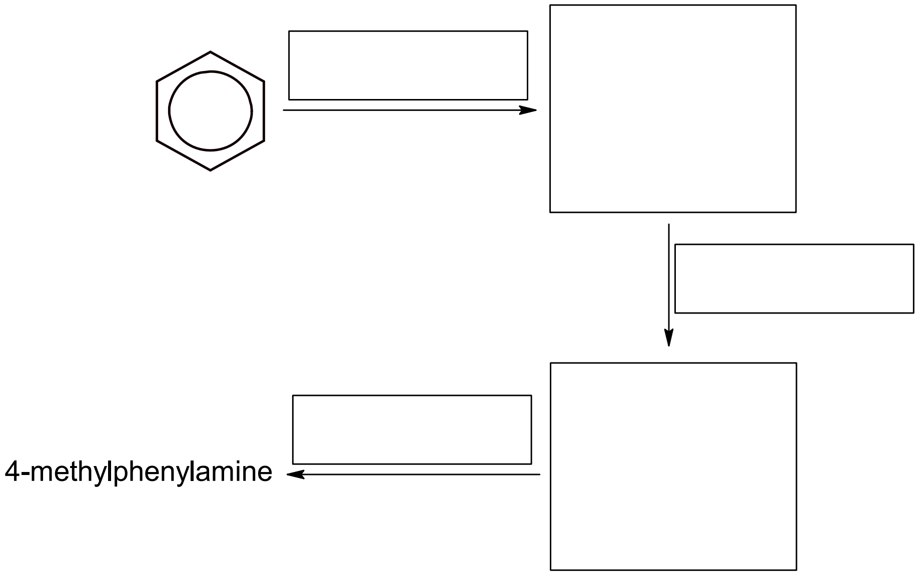
…………………………………………………………………………………….. [1]

(b) **(i)** Compound **P** is a component of a commercial dye.



Compound **P**

4-methylphenylamine is one of the starting materials needed to manufacture the above dye.
Devise a 3-step synthesis to convert benzene into 4-methylphenylamine. State the reagents and conditions needed for each of the steps and draw the structures of all intermediates in the spaces provided in Figure 4.1.



[5]

Figure 4.1

(ii) Explain the following observations fully.

P does not react with dilute HC*l* at room temperature.
However, when **P** reacts with LiA*l*H$_4$ in dry ether, the organic product, **Q**, reacts with dilute HC*l* at room temperature.
Include the structure of **Q** in your answer.

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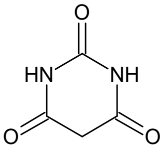
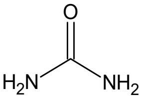
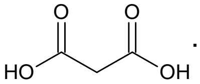
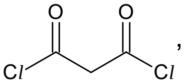
Q

[4]

(c) Barbituric acid is the parent compound of barbiturate drugs, a class of compounds that is used as anticonvulsants and general anaesthetics. It has the following structure.



Barbituric acid can be synthesised using urea,  and malonic acid, .

(i) In the first step of the synthesis, malonic acid has to be converted to , explain why this step is critical in the synthesis process.

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…………………………………………………………………………………….. [1]

(ii) The mechanism of the synthesis is essentially 2 condensation reactions taking place simultaneously. The following points are the description of the steps that took place during the condensation.

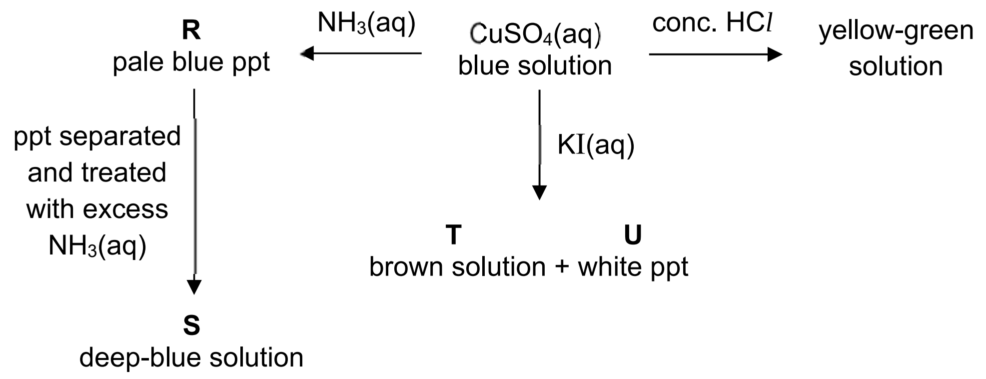
- The N atoms of urea attack the electron-deficient C atoms. The C=O bonds become saturated. There is a negative charge on each of the O atoms and a positive charge on each of the N atoms.
- The C=O double bonds are reformed and 2 Cl^- ions are released.
- The Cl^- ions remove the H^+ ions to give barbituric acid and 2 HCl molecules.

Using the points given, draw the mechanism for the formation of barbituric acid, including curly arrows showing the movement of electrons, and all charges.

[4]

[Total: 19]

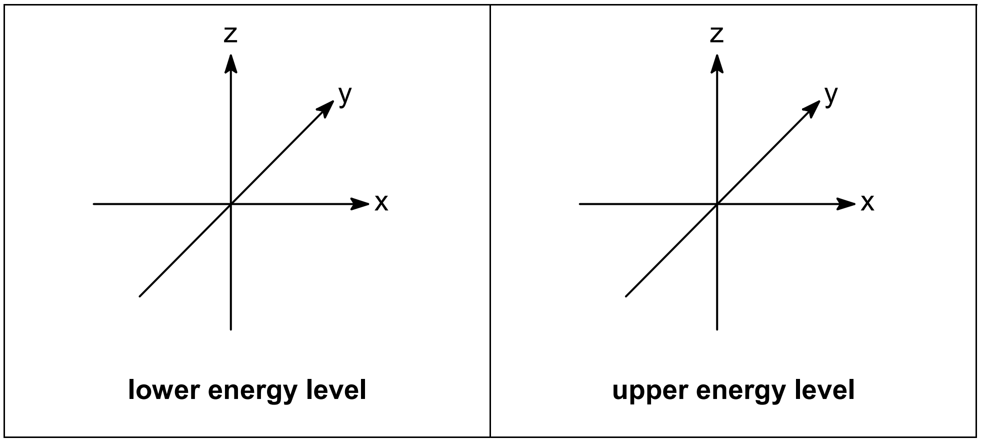
5 Aqueous copper(II) sulfate, $CuSO_4$, is a blue solution which gives the following reactions.



The $[Cu(H_2O)_6]^{2+}$ complex in $CuSO_4$ is octahedral. In an octahedral complex, the d subshell of a transition metal ion is split into two energy levels.

(a) Using the given Cartesian axes, draw fully-labelled diagrams of the following:

- one of the d orbitals at the lower energy level in an octahedral complex
- one of the d orbitals at the higher energy level in an octahedral complex



lower energy level **upper energy level**

[2]

(b) Explain why splitting of the d subshell occurs in an octahedral complex, using your d orbital diagrams in **(a)**.

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…………………………………………………………………………………………… [1]

(c) Explain why a solution of $CuSO_4(aq)$ is coloured whereas $Cu_2SO_4(aq)$ is colourless.

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…………………………………………………………………………………………… [3]

(c) Explain why the solution turns yellow-green when concentrated HC*l* was added to a solution containing $CuSO_4$.

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…………………………………………………………………………………………… [2]

(d) Write equations for the reactions forming **R** and **S** in the flowchart above.

……………………………………………………………………………………………

…………………………………………………………………………………………… [2]

(e) State the identities of **T** and **U**.

T : …………………………..

U : ………………………….. [2]

[Total: 12]

For Examiners' Use

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H2

TAMPINES JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

CANDIDATE NAME	ANSWERS

CIVICS GROUP	1	7				TUTOR NAME	

CHEMISTRY 9729/02

Paper 2 Structured Questions

Monday, 27 June 2018

2 hours

Candidates answer on the Question Paper.

Additional materials: Data Booklet

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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.
A Data Booklet is provided.

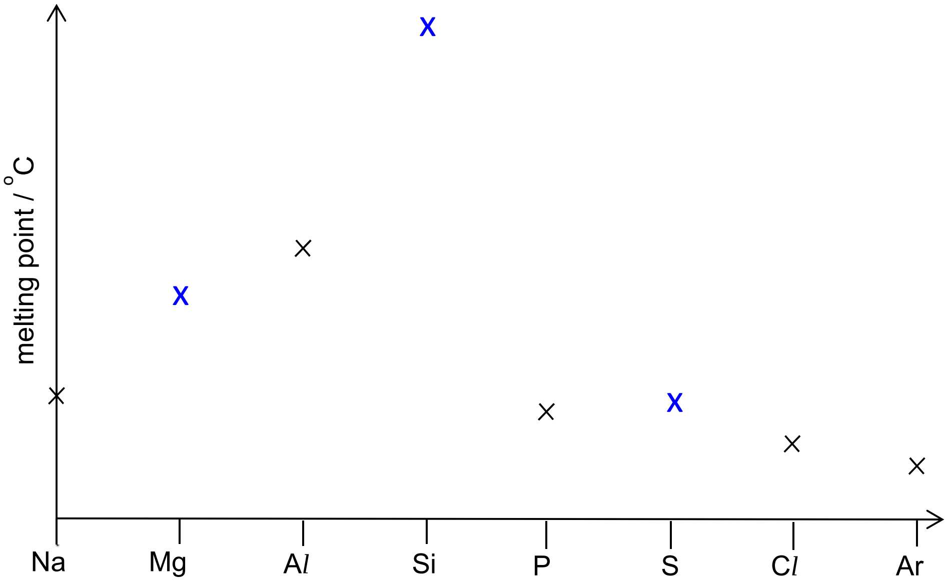
At the end of the examination, fasten all your work securely together.

For Examiners' Use		
1	**9**	
2	**20**	
3	**15**	
4	**19**	
5	**12**	
Total	**75**	

This document consists of **17** printed pages and **1** blank page.

Answer **all** the questions.

1 The graph below can be used to plot the melting point of the elements sodium to argon. Five of these elements have been plotted already.



(a) Use your knowledge of the variation in melting points of the elements of Period 3 to estimate and plot, on the graph in Figure 1.1, the melting points of the other three elements. [1]

(b) Justify your predictions in **(a)**, by explaining why the melting point of **each** element you have plotted is higher/lower/similar compared to the element to its left on the graph.

m.p. of : Mg > Na

Mg has more delocalised electrons per atom and smaller cationic radius leading to stronger metallic bonds which require more energy to break.

m.p. of : Si > Al

Si has a giant molecular structure comprising of Si atoms held together by numerous strong covalent bonds which require larger amounts of energy to overcome compared to Al which has giant metallic structure comprising cations and sea of delocalised electrons held by strong electrostatic forces of attraction.

m.p. of : S_8.> P_4

S_8 has greater no. of electrons and hence stronger instantaneous dipole-induced dipole attractions than P_4 which requires more energy to overcome.

[4]

(c) The use of the *Data Booklet* is required for this part of the question.
The first ionisation energies, in kJ mol^{-1} of Group 2 elements are given below.

element	1st ionisation energies / kJ mol^{-1}
Be	900
Mg	736
Ca	590
Sr	548
Ba	502

(i) Explain why the first ionisation energies decrease in magnitude on descending the group.

Down Group 2, the nuclear charge increases with increasing proton number and shielding effect increases with an increase in the number of inner electron shells. However, the increase in shielding effect outweighs the increase in nuclear charge. Hence, valence electrons are less strongly attracted to the nucleus, and less energy is required to remove a valence electron.

[2]

(ii) Using your answer from **(c)(i)**, suggest how the reducing power of barium (Ba) compares to beryllium (Be).

Since it is easier to remove the valence electron from Ba than Be, the reducing power of Ba will be stronger than Be.

[1]

(iii) Suggest why the first ionisation energy of indium (In) is greater than that of strontium (Sr).

The electronic configurations:
Sr : $1s^22s^22p^63s^23p^63d^{10}4s^24p^65s^2$.
In : $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^1$
The 4d electrons provides poor shielding to the 5p electron of In, so the 5p electron is more strongly attracted to the nucleus and thus needs more energy to be removed.

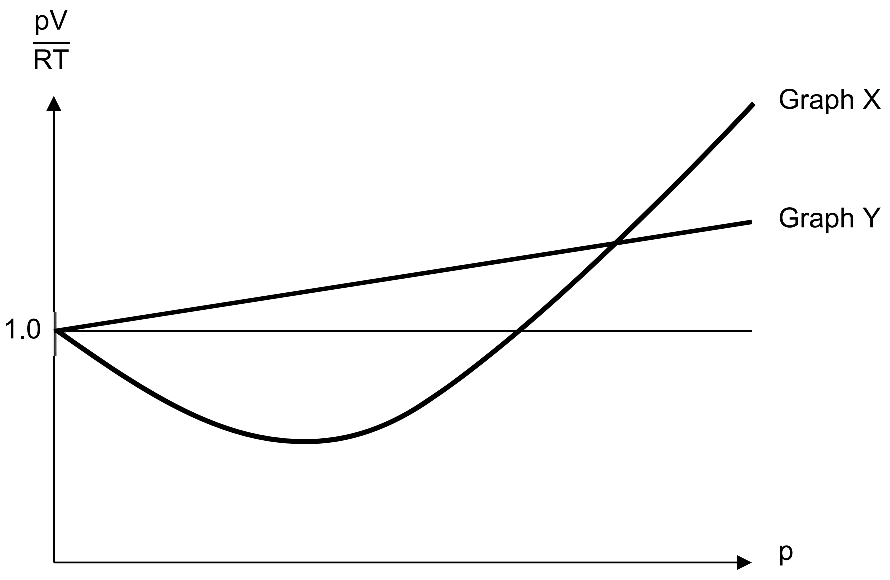
[1]

[Total: 9]

2 At 700K, HI readily dissociates into H_2 and I_2.

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

(a) The graphs of $\frac{pV}{RT}$ against p for 1 mol each of H_2 and HI at room temperature are plotted below.



Deduce which of the graphs is the plot for HI.

There are permanent dipole–permanent dipole interactions between HI molecules which are more significant than the instantaneous dipole-induced dipole interactions between H_2 molecules (OR HI has stronger instantaneous dipole-induced dipole attraction than H_2 due to greater number of electrons), hence HI deviates more from the ideal gas assumption that there is negligible intermolecular forces of attraction. Therefore Graph X is the plot for HI.

[2]

(b) 1.60 mol of gaseous HI was placed in a 2 dm^3 evacuated flask at 700K. After 30 minutes, equilibrium was established. The flask was then rapidly cooled and the HI is dissolved in 1000 cm^3 of water. 10 cm^3 of the solution obtained was titrated against 0.500 mol dm^{-3} NaOH(aq). 25.20 cm^3 of NaOH(aq) was required to reach end-point.

(i) Write the expression for K_p.

$$K_p = \frac{(p_{H_2})(p_{I_2})}{(p_{HI})^2}$$

[1]

(ii) Calculate the partial pressures of HI, H_2 and I_2 at equilibrium.

HI ≡ NaOH

Amount of NaOH = Amount of HI in 10 cm^3 = $25.20/1000 \times 0.5 = 0.0126$ mol

Amount of HI in 1000 cm^3 = $0.126 \times 1000 / 10 = 1.26$ mol

	2HI (g)	$\rightleftharpoons$	H_2 (g)	+	I_2 (g)
Initial amount/ mol	1.60		0		0
Change in amount/ mol	–0.34		+0.170		+0.170
Equilibrium amount/ mol	1.26		0.170		0.170

$$pV = nRT \Rightarrow p = \frac{nRT}{V}$$

$$p_{H_2} = p_{I_2} = \frac{0.170 \times 8.31 \times 700}{2 \times 10^{-3}} = 4.94 \times 10^5 \text{ Pa}$$

$$p_{HI} = \frac{1.26 \times 8.31 \times 700}{2 \times 10^{-3}} = 3.66 \times 10^6 \text{ Pa}$$

Alternative answer: ICE table can be worked in terms of partial pressures as total volume is kept constant.

Initial $p_{HI} = \frac{1.60 \times 8.31 \times 700}{2 \times 10^{-3}} = 4.654 \times 10^6$ Pa

Equilibrium $p_{HI} = \frac{1.26 \times 8.31 \times 700}{2 \times 10^{-3}} = 3.66 \times 10^6$ Pa [1]

	2HI (g)	$\rightleftharpoons$	H_2 (g)	+	I_2 (g)
Initial p/ atm	4.654×10^6		0		0
Change in p/ atm	-0.994×10^6		$+0.497 \times 10^6$		$+0.497 \times 10^6$
Equilibrium p/ atm	3.66×10^6		0.497×10^6		0.497×10^6

[4]

(iii) Calculate the value of K_p at 700K.

$$\boxed{K_p = \frac{(4.94 \times 10^5)(4.94 \times 10^5)}{(3.66 \times 10^6)^2} = 0.0182}$$

[1]

(iv) The equilibrium constant for the dissociation of HBr at 700K is given below. Explain the difference in this value and your answer to **(b)(iii)**.

K_p (HBr) = 0.0172

HI has a larger K_p value than HBr indicating that the extent of dissociation of HI is greater. This is due to H–I bond being weaker than H–Br and is hence easier to break.

[2]

HI readily reacts with alkenes.

(c) When HI was added to $CH_3CH=C(CH_3)_2$, products **A** and **B,** which are constitutional isomers of each other, were formed.

(i) **A** was formed in larger proportion than **B**.
Draw the possible structures of **A** and **B** in the boxes below. Explain your answer, by naming the mechanism for the reaction and by considering the stability of the intermediate formed.

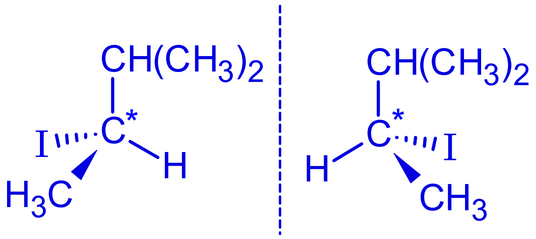
$CH_3CH(I)CH(CH_3)_2$	$CH_3CH_2C(CH_3)_2I$
A	**B**

Electrophilic addition occurred. **A** is the major product as the carbocation intermediate is more stable due to more electron-donating alkyl groups which disperse the positive charge.

[3]

(ii) One of the two isomers drawn in **(c)(i)** exhibits stereoisomerism. Name the type of stereoisomerism and draw diagrams to illustrate it.

type of stereoisomerism: enantiomerism



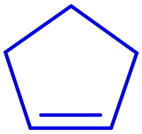
[2]

(iii) Suggest, with reason, how the rate of the reaction described in **(c)(i)** would differ if HC*l* had been used instead of HI.

The rate of reaction will be slower if HC*l* was used instead as the H–C*l* bond is stronger and the breaking of HC*l* bond occurs in the rate determining step.

[1]

(iv) When HI was added to another alkene with molecular formula of C_5H_8, only one product was formed. Suggest a structure for this alkene.



[1]

(v) State and explain, in terms of structure and bonding, how the boiling point of the products drawn in **(c)(i)** would differ if the halogen atom was chlorine instead of iodine.

Both product molecules have simple molecular structures with instantaneous dipole – induced dipole (id-id) (and permanent dipole –permanent dipole) interactions between the molecules.

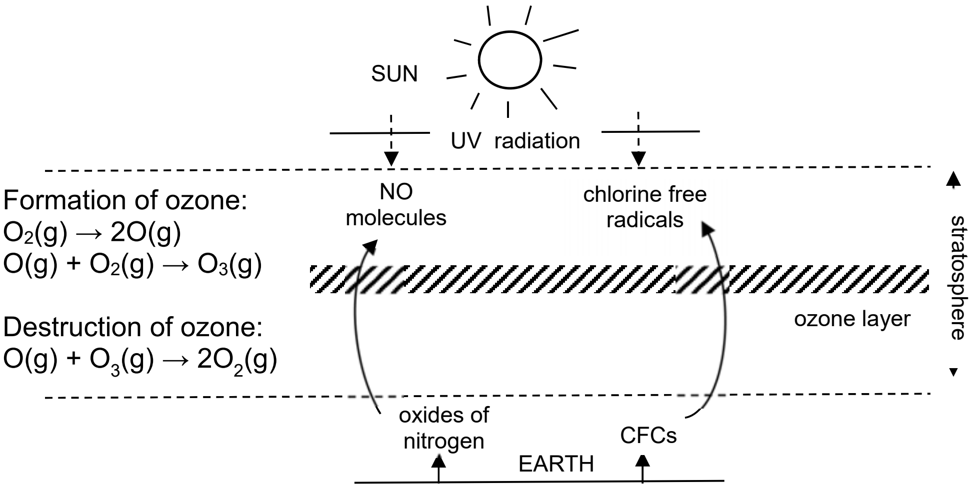
The iodoalkane has a greater electron cloud size (or greater number of electrons).

Thus, more energy is required to overcome the stronger id-id forces between iodoalkane molecules and hence iodoalkane will have a higher boiling point.

[3]

[Total: 20]

3 The stratospheric ozone has a vital role in protecting organisms on the Earth's surface from excessive exposure to high-energy radiation which can be very damaging. This protection arises because the natural reactions leading to the formation and destruction of ozone, as shown in the diagram below, absorb a significant amount of the incoming ultraviolet radiation.



Formation of ozone:
$O_2(g) \rightarrow 2O(g)$
$O(g) + O_2(g) \rightarrow O_3(g)$

Destruction of ozone:
$O(g) + O_3(g) \rightarrow 2O_2(g)$

However, the ozone layer is at risk due to human activities that produce nitrogen monoxide (NO) and chlorofluorocarbons (CFCs).

NO is formed during lightning discharges in a similar reaction to the combustion of nitrogen in car engines. NO catalyses the destruction of ozone in the stratosphere. Several experiments were carried out to understand the reaction and the following rate-concentration graphs were obtained for the reactants.

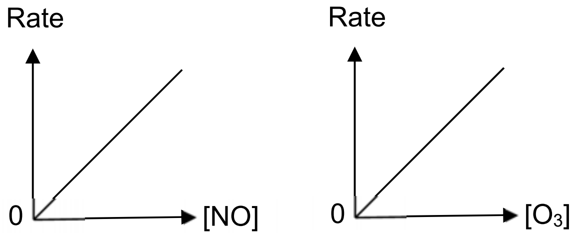


Figure 3.1

The use of CFCs poses an even more significant threat to the ozone layer. Their inertness has led to many useful daily applications but has also caused environmental issues. They diffuse upwards through the atmosphere unchanged until they reach the stratosphere where they dissociate photolytically in an initiation reaction to generate chlorine atoms. These chlorine free radicals subsequently undergo these reactions.

Propagation: $O_3(g) + Cl\bullet(g) \rightarrow O_2(g) + ClO\bullet(g)$
$O(g) + ClO\bullet(g) \rightarrow O_2(g) + Cl\bullet(g)$

Termination: $CH_4(g) + Cl\bullet(g) \rightarrow CH_3\bullet(g) + HCl(g)$
$NO_2(g) + ClO\bullet(g) \rightarrow ClONO_2(g)$

Figure 3.2

In stratospheric clouds of polar regions, the HC*l* and C*l*ONO$_2$ can react together to form chlorine and nitric acid.

$$HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$$

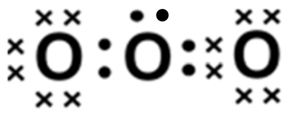
For
Examiners'
Use

(a) Explain, with the aid of an equation, why nitrogen monoxide is formed during lightning discharges.

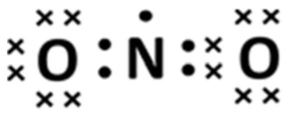
$N_2 + O_2 \rightarrow 2NO$
A great amount of energy is released during discharges which can break the strong N≡N bond.

[2]

(b) Draw dot-and-cross diagrams to show the bonding in O_3 and NO_2.



O_3



NO_2

[2]

(c) Based on your diagram in **(b)**, suggest if NO_2 undergoes reactions readily.

It is a radical/ contains an unpaired electron, making it highly reactive.

[1]

(d) Suggest a value for the bond angle in each of the above two molecules, giving reasons for your choice.

The central oxygen atom in O_3 is surrounded by two electron bond pairs and an electron pair. Since a lone electron pair or provides greater repulsion than a bond pair (or occupies a greater volume), the angle will be about 115° (value between 110° and 120° allowed).
For NO_2, the central nitrogen atom is surrounded by two electron bond pairs and a lone electron. The lone electron provides lesser repulsion than a (lone or bond) pair of electrons. Therefore, the bond angle for NO_2 should be greater than that for O_3 and should be about 130° (allow value between greater than O_3 and 170°).
[See 2010 P3 Q4(c) examiner report]

[2]

(e) With reference to Figure 3.1, deduce the orders of reaction with respect to each of the reactants involved in the production of nitrogen monoxide. Explain the significance of these orders in relation to the mechanism.

Each of the graphs is a straight line passing through the origin showing that rate is directly proportional to [NO] and [O_3] respectively.
The reaction is first order with respect to NO and to O_3.

This means that 1 molecule of NO and 1 molecule of O_3 is involved in the slow (rate-determining) step.

[3]

(f) Using your answer to **(e)**, suggest a possible mechanism for destruction of ozone by NO.

Step 1: $NO + O_3 \rightarrow NO_2 + O_2$ (slow)
Step 2: $NO_2 + O \rightarrow O_2 + NO$ (fast)

[2]

(g) With reference to the equations in Figure 3.2, explain why small amounts of CFCs are able to destroy large amounts of ozone.

Chlorine radicals are regenerated in the propagation reaction which can go on to decompose more molecules of ozone.

[1]

(h) Would tetrafluoroethane, $C_2H_2F_4$, be able to destroy the ozone layer like CFCs? Explain your answer.

No it cannot as the C–F bonds are too strong and cannot be broken so the radicals cannot be formed.

[1]

(i) The removal of chlorine-containing free radicals in the termination steps in Figure 3.2 help to limit the destruction of ozone. However, at polar regions when sunlight intensity increases during spring time, more severe depletion of the ozone layer occurs. Suggest a reason for this phenomenon.

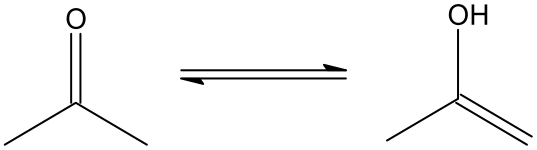
The chlorine molecules produced would undergo homolytic fission/ dissociate to form chlorine radicals which will continue to destroy the ozone layer.

[1]

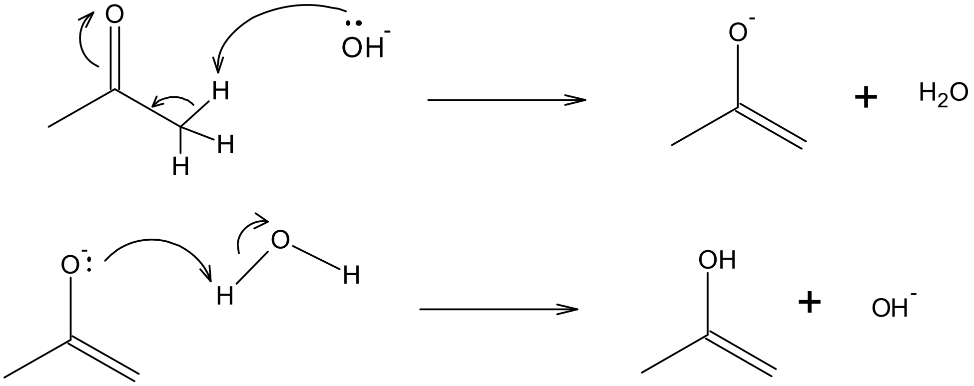
[Total: 15]

4 **(a)** In organic chemistry, keto–enol tautomerism refers to a chemical equilibrium between a keto form (a ketone or an aldehyde) and an enol (an alcohol). The enol and keto forms are said to be tautomers of each other.

Acetone, also known as propanone, can undergo tautomerisation with its corresponding alcohol according to the following equilibrium.



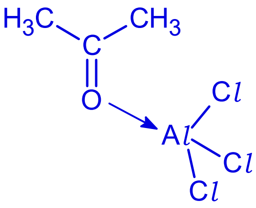
The interconversion can be base-catalysed. The mechanism is illustrated below.



(i) In the above mechanism, acetone functions as a Brønsted−Lowry acid. Explain why this is so.

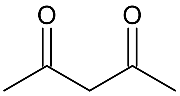
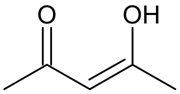
It donates a proton to OH^-. [1]

(ii) Acetone can also function as a Lewis base. Using $AlCl_3$ as a Lewis acid, draw a structure to show how acetone functions as a Lewis base.

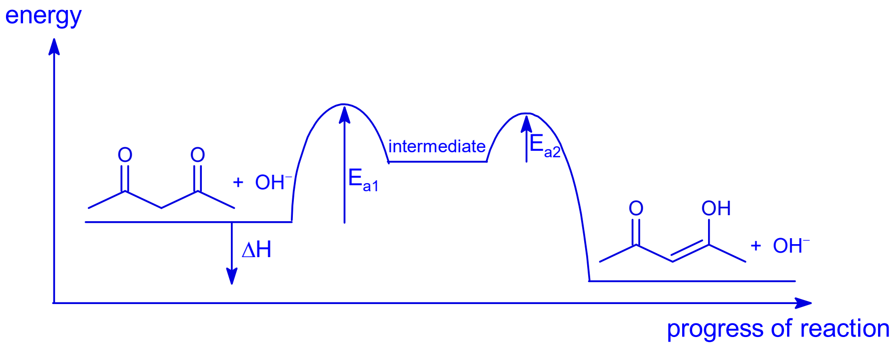


[Note: A Lewis base is a lone pair donor.]

[1]

(iii) Another ketone, , pentane-2,4-dione, also exhibits keto–enol tautomerism with its enol form . The enol form is energetically more stable than the keto form.

Sketch a clearly labelled reaction pathway diagram for the keto–enol tautomerisation of pentane-2,4-dione.



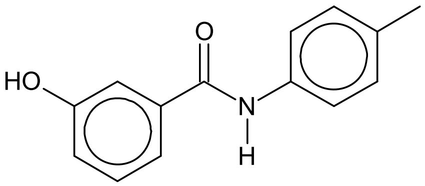
[2]

(iv) Suggest a reason why the enol form of pentane-2,4-dione is more stable.

The O atom of the carbonyl group can form hydrogen bonding with the neighbouring H atom of the OH group.
OR
The structure is resonance stabilised (due to delocalisation of lone pair of electrons on O atom onto the C=C and C=O / p orbital of O atom overlaps with π electron cloud of C=C and C=O).

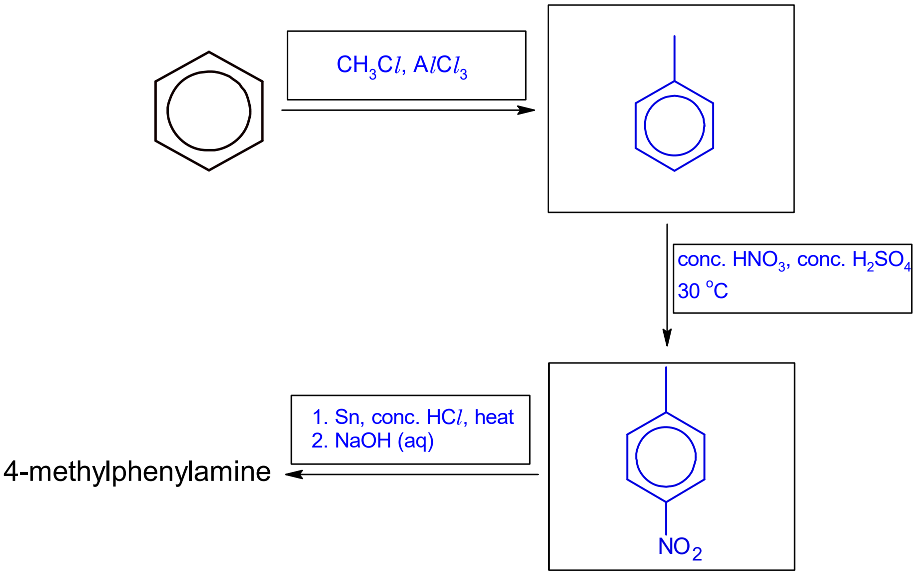
[1]

(b) **(i)** Compound **P** is a component of a commercial dye.



Compound **P**

4-methylphenylamine is one of the starting materials needed to manufacture the above dye.
Devise a 3-step synthesis to convert benzene into 4-methylphenylamine. State the reagents and conditions needed for each of the steps and draw the structures of all intermediates in the spaces provided in Figure 4.1.



[5]

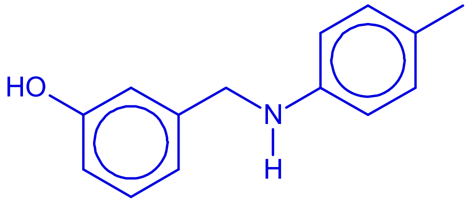
Figure 4.1

(ii) Explain the following observations fully.

P does not react with dilute HC*l* at room temperature.
However, when **P** reacts with LiA*l*H_4 in dry ether, the organic product, **Q**, reacts with dilute HC*l* at room temperature.
Include the structure of **Q** in your answer.

P is neutral/not basic as the p orbital of N overlaps with the π electron cloud of C=O (or lone pair of electrons on N delocalises into the neighbouring C=O) and is not available to accept H^+.

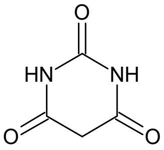
P undergoes reduction with LiA*l*H_4 to form an amine which undergoes acid-base reaction with HC*l* as the lone pair on N is available for dative bonding to H^+.

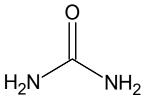
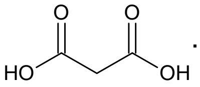


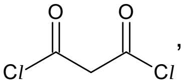
Q

[4]

(c) Barbituric acid is the parent compound of barbiturate drugs, a class of compounds that is used as anticonvulsants and general anaesthetics. It has the following structure.



Barbituric acid can be synthesised using urea,  and malonic acid, .

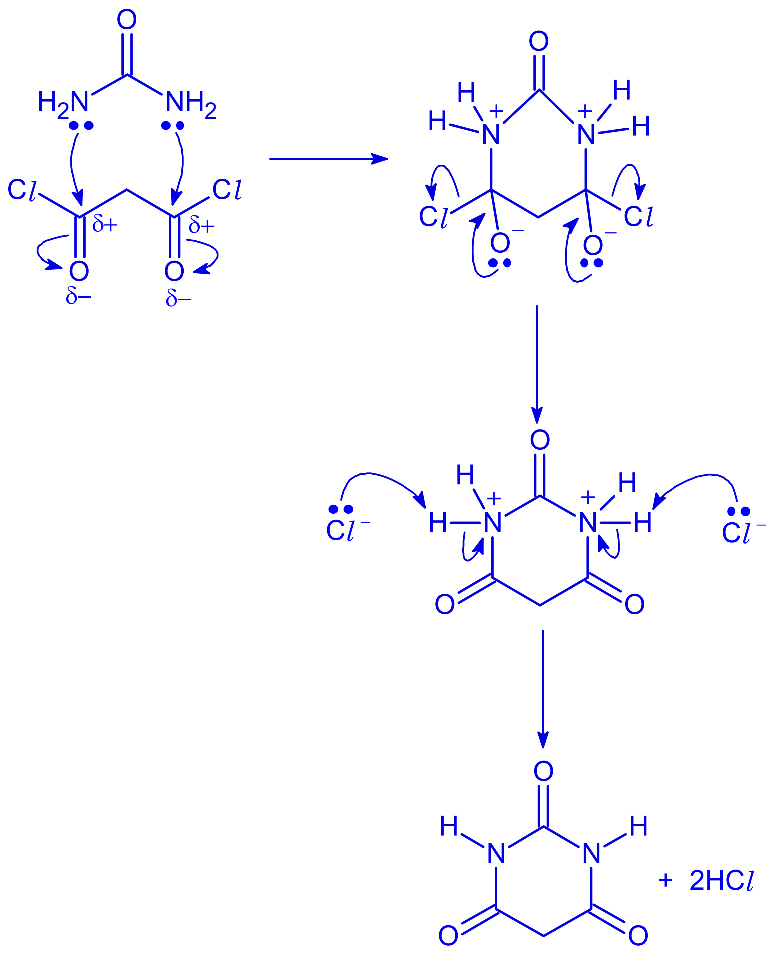
(i) In the first step of the synthesis, malonic acid has to be converted to , explain why this step is critical in the synthesis process.

It is to prevent acid-base reaction between the carboxylic acid and the amine of the 2 reactants instead of the intended condensation reaction that would result in the formation of babituric acid. [1]

(ii) The mechanism of the synthesis is essentially 2 condensation reactions taking place simultaneously. The following points are the description of the steps that took place during the condensation.

- The N atoms of urea attack the electron-deficient C atoms. The C=O bonds become saturated. There is a negative charge on each of the O atoms and a positive charge on each of the N atoms.
- The C=O double bonds are reformed and 2 Cl^- ions are released.
- The Cl^- ions remove the H^+ ions to give barbituric acid and 2 HCl molecules.

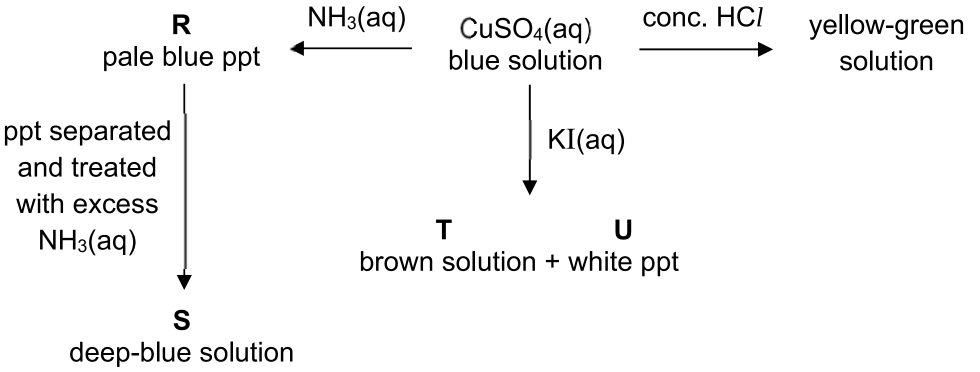
Using the points given, draw the mechanism for the formation of barbituric acid, including curly arrows showing the movement of electrons, and all charges.



[4]

[Total: 19]

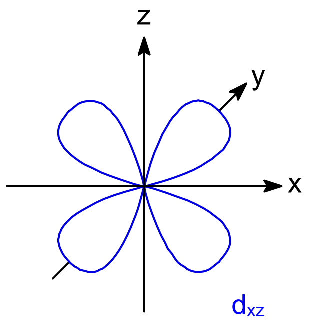
5 Aqueous copper(II) sulfate, $CuSO_4$, is a blue solution which gives the following reactions.



The $[Cu(H_2O)_6]^{2+}$ complex in $CuSO_4$ is octahedral. In an octahedral complex, the d subshell of a transition metal ion is split into two energy levels.

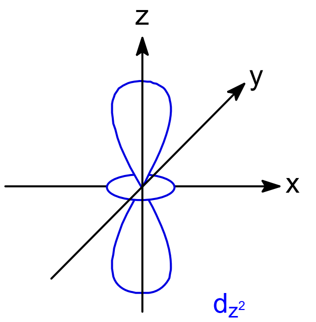
(a) Using the given Cartesian axes, draw fully-labelled diagrams of the following:

- one of the d orbitals at the lower energy level in an octahedral complex
- one of the d orbitals at the higher energy level in an octahedral complex



(d_{xy} or d_{yz} also accepted)

lower energy level



($d_{x^2-y^2}$ also accepted)

upper energy level

[2]

(b) Explain why splitting of the d subshell occurs in an octahedral complex, using your d orbital diagrams in **(a)**.

The electron pairs in the upper energy level d orbitals are pointing towards the lone pairs of the ligands, so will be repelled by them.

[1]

(c) Explain why a solution of $CuSO_4(aq)$ is coloured whereas $Cu_2SO_4(aq)$ is colourless.

Electrons in a lower energy d-orbital can be promoted to a higher energy level by absorbing light energy. This process is known as d →d electronic transition.
For $Cu^{2+}(aq)$, the energy corresponding to (orange) visible light is absorbed, and thus the complementary colour (blue) is observed.
For $Cu^{+}(aq)$, it has the electronic configuration of $[Ar]3d^{10}$ (or filled d subshell). Hence, even after the splitting, there is no vacant d orbital for d →d electron transition. Thus no colour is observed.

[3]

(c) Explain why the solution turns yellow-green when concentrated HC*l* was added to a solution containing $CuSO_4$.

Ligand exchange reaction takes place (or water ligands in $[Cu(H_2O)_6]^{2+}$ are replaced by Cl^- ligands) to form yellow $[CuCl_4]^{2-}$.

[2]

(d) Write equations for the reactions forming **R** and **S** in the flowchart above.

$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$

$Cu(OH)_2(s) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 2OH^-(aq)$

[2]

(e) State the identities of **T** and **U**.

T : I_2

U : CuI

[2]

[Total: 12]

H2

TAMPINES JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION

CHEMISTRY

9729/03

Paper 3 Free Response

Thursday, 13 September 2018

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions

Section B
Answer **one** question.

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

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.

Section A

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

1 Fuels are materials which can react with other substances to release energy. The most common fuels for machines are hydrocarbons and coal while common fuels for organisms are fats and carbohydrates contained in food sources.

(a) The energy provided by food sources is often measured in terms of the energy released during their combustion to form liquid water. A bomb calorimeter is commonly used to determine this energy, which is quoted in kilojoules (kJ) or kilocalorie (kcal), where 1 kcal = 4.184 kJ.

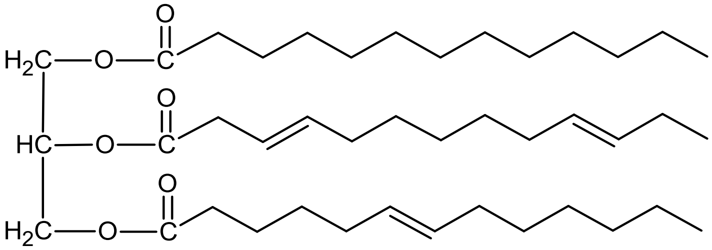
(i) A manufacturer claims that its new dessert has "fewer than 10 kcal per serving".

In order to test the claim, a chemist places one serving of the dessert in a bomb calorimeter and combusts it. The heat energy released raises the temperature of the calorimeter by 4.93 °C.

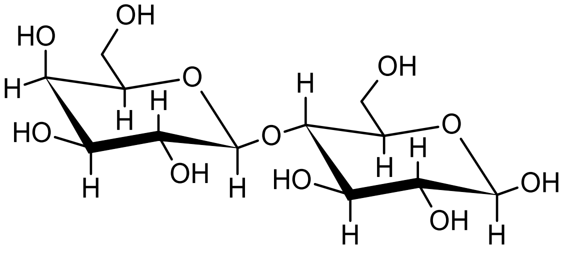
Given that the heat capacity of the calorimeter is 8.15 kJ K^{-1}, determine if the manufacturer's claim is correct. [2]

(ii) The structures of an example of a fat and carbohydrate are shown below:

fat



carbohydrate



Both fats and carbohydrates are metabolised in the body to CO_2 and H_2O. Suggest an explanation for why fats are often described as having "more kcal per gram" than carbohydrates. [2]

(b) In fuel cells, chemical energy from fuel is converted into electrical energy by reaction with an oxidising agent.

Methane is one of the hydrocarbons employed in hydrocarbon fuel cells, where it is oxidised at the anode to carbon dioxide. The electrolyte is usually an aqueous acid.

The cathode in this fuel cell is the oxygen electrode.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

(i) Construct an equation for the anode reaction. [1]

(ii) Hence construct the equation for the overall equation, showing your working. [1]

(iii) During discharge, the cell generates an electromotive force (e.m.f.) of 1.06 V. By using suitable data from the *Data Booklet*, suggest a value for the $E^\ominus$ of the CO_2/CH_4 electrode reaction. [2]

(iv) Draw a fully labelled diagram of the electrochemical cell you could use to measure the standard electrode potential of the CO_2/CH_4 half-cell. [3]

(v) Methanol is the first alcohol to be successfully used in a fuel cell. This cell produces an e.m.f. of 1.18 V and the overall reaction is:

$$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$$

Determine the standard Gibbs free energy change, $\Delta G^\ominus$, of this reaction. [2]

(vi) How many moles of methanol will be consumed when a methanol fuel cell delivers 254 A of current for 1 minute? [2]

(vii) Suggest a possible advantage of using a methanol fuel cell over the methane fuel cell. [1]

(c) Reactions in which a substance decomposes by losing CO_2 are called *decarboxylation* reactions. Methane can be obtained in the *decarboxylation* reaction of ethanoic acid.

$$CH_3COOH(l) \rightarrow CH_4(g) + CO_2(g) \qquad \Delta H_r^\ominus$$

(i) Use the following standard enthalpy changes to calculate the value of the standard enthalpy change of the *decarboxylation* reaction of ethanoic acid, $\Delta H_r^\ominus$.

	$\Delta H^\ominus$ / kJ mol^{-1}
standard enthalpy change of formation of $CH_3COOH(l)$	–487.0
standard enthalpy change of formation of $CH_4(g)$	–74.8
standard enthalpy change of combustion of C(s)	–393.5

[1]

(ii) The standard molar enthalpy, $S^\ominus$, of substances can be used determine the standard entropy change, $\Delta S^\ominus$, of a chemical reaction:

$$\Delta S^\ominus = \sum nS^\ominus(\text{products}) - \sum mS^\ominus(\text{reactants})$$

where *m* and *n* are the coefficients in the chemical equation.

Use the following standard molar entropies, $S^\ominus$, to calculate the standard entropy change, $\Delta S^\ominus$, of the *decarboxylation* reaction of ethanoic acid.

	$S^\ominus$ (J mol^{-1} K^{-1})
$CH_3COOH(l)$	159.8
$CH_4(g)$	186.3
$CO_2(g)$	213.6

[1]

(iii) Use your answers to **(c)(i)** and **(c)(ii)** to calculate the minimum temperature at which the *decarboxylation* of ethanoic acid will be spontaneous.
State an assumption that you have made. [3]

(iv) Both ethanoic acid and methane can be chlorinated to form ethanoyl chloride, CH_3COCl, and chloromethane respectively.

Ethanoyl chloride and chloromethane are both colourless liquids and can be distinguished by their reaction with water.

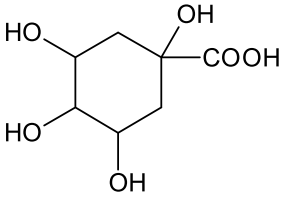
State what you might expect to observe when each reacts with water and explain why the two compounds react differently with water. [4]

[Total: 25]

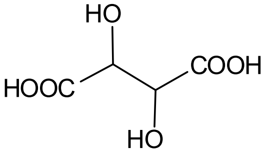
2 Buffer solutions are widely used in a wide variety of chemical applications commercially and in nature. Animals and plants are protected against extreme conditions by the presence of buffers.

(a) Define the term *buffers*. [1]

(b) Most foodstuff contain buffering systems are made from organic acids extracted from plants. Two such acids are shown below.



quinic acid



tartaric acid

Table 2.1 compares the pK_a values of quinic acid, tartaric acid and benzoic acid.

Table 2.1

acid	formula	pK_1	pK_2
quinic	$C_6H_{11}O_4CO_2H$	3.40	-
tartaric	$C_2H_4O_2(CO_2H)_2$	2.89	4.40
benzoic	$C_6H_5CO_2H$	4.20	-

(i) Suggest a reason why the pK_1 value of quinic acid is lower than that of benzoic acid. [2]

(ii) Suggest a reason why the pK_2 of tartaric acid is higher than its pK_1. [2]

(iii) A flask contains 200 cm^3 of 0.020 mol dm^{-3} solution of benzoic acid. Calculate the pH of this solution. [2]

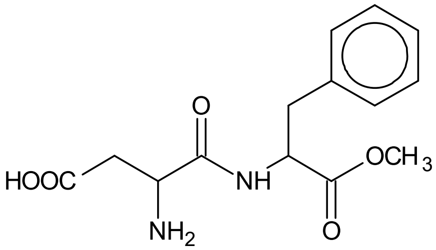
(iv) A buffer solution with a pH of 4.10 is made by adding 100 cm^3 of x mol dm^{-3} solution of sodium benzoate, to 200 cm^3 of 0.020 mol dm^{-3} solution of benzoic acid.

Calculate the value of x. [2]

(c) Buffers are also important in humans. If the pH of the body falls below 7.35, a condition known as acidosis results which can become very serious. One of the buffers present in blood is that of the H_3PO_4(aq) / $H_2PO_4^-$(aq) system.

Write equation(s) to show how H_3PO_4(aq) / $H_2PO_4^-$(aq) buffer system helps to maintain the pH of blood. [2]

(d) Aspartame, a dipeptide, is a high intensity artificial sweetener used in soft drinks. Buffers are usually added together with aspartame as pH affects the stability of aspartame.



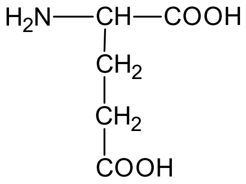
aspartame

(i) Draw the structural formula of the organic products formed when aspartame is treated with

- cold HC*l*(aq)
- hot HC*l*(aq)

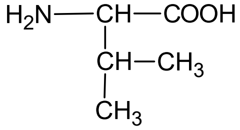
[3]

(ii) A *dipeptide* is formed when two amino acids combine.
Draw the structure of the dipeptide formed when the amino acids, glutamic acid and valine combine.



$H_2N-CH(CH_2CH_2COOH)-COOH$

glutamic acid



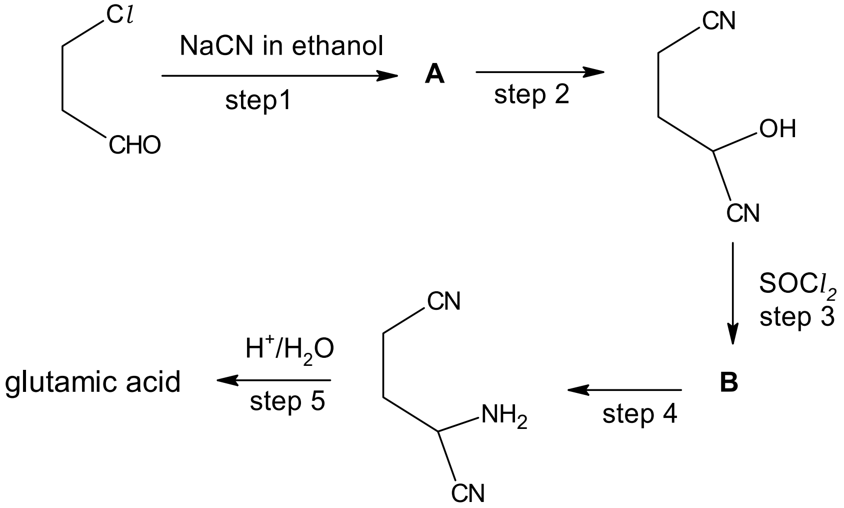
$H_2N-CH(CH(CH_3)CH_3)-COOH$

valine

[1]

(iii) Glutamic acid has pK_a values of 2.10, 4.07 and 9.47.
Draw the structural formula of the glutamic acid in its most stable state at pH 3. [1]

(e) Glutamic acid can be synthesised from 3-chloropropanal by the following route.



(i) Suggest structures for the intermediates **A** and **B**. [2]

(ii) Suggest reagents and conditions for step 2 and for step 4. [2]

[Total: 20]

3 Transition metals and their compounds are known for their catalytic activity in industry.

The reaction between peroxodisulfate ions, $S_2O_8^{2-}$, and potassium iodide is an example of a reaction that is catalysed by transition metal ions.

(a) The initial rate of the slow reaction between $S_2O_8^{2-}$ and potassium iodide solution can be studied by the "clock" method, using sodium thiosulfate. The equations for the reactions are as follows.

$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$ (slow) reaction **I**

$I_2(aq) + 2Na_2S_2O_3(aq) \rightarrow 2NaI(aq) + Na_2S_4O_6(aq)$ (fast) reaction **II**

When a small but constant amount of sodium thiosulfate is added to a reaction mixture, the iodine being slowly produced in reaction **I** will immediately be consumed in reaction **II** until all the sodium thiosulfate has been used up. At that point, free iodine will be present in the solution. The free iodine present reacts with starch to form a deep blue complex.

A series of experiments was carried out using different volumes of the five reagents, each solution being made up to the same volume with water.
The following results were obtained.

experiment number	volume of 0.10 mol dm^{-3} $S_2O_8^{2-}$ /cm^3	volume of 0.20 mol dm^{-3} KI /cm^3	volume of 0.010 mol dm^{-3} $Na_2S_2O_3$ /cm^3	volume of water /cm^3	volume of starch solution /cm^3	time taken for the appearance of deep blue colour /s
1	5.0	5.0	2.0	35.0	3.0	42
2	5.0	4.0	2.0	36.0	3.0	53
3	10.0	3.0	2.0	32.0	3.0	35
4	15.0	2.0	2.0	28.0	3.0	35

(i) What is the simple relationship between the time taken for the appearance of the blue colour and the initial rate of reaction **I**? [1]

(ii) Calculate the initial rate for each of these four experiments and use the results to deduce the order of reaction with respect to each of the two reactants in reaction **I**. Explain your reasoning. [3]

(iii) Hence write an overall rate equation for reaction **I**. [1]

(b) The above reaction between iodide and peroxodisulfate ions can be catalysed by a transition metal ion, such as, cobalt(II) ions, Co^{2+}.

(i) Suggest a reason why the reaction between iodide and peroxodisulfate ions requires a catalyst. [1]

(ii) Describe how Co^{2+} ions are able to catalyse the reaction between iodide and peroxodisulfate. Write equations where appropriate. [2]

(c) Another characteristic feature of the chemistry of transition elements is their tendency to form complexes.

When aqueous cobalt(III) chloride reacts with ammonia under various conditions, compounds containing different cobalt complexes can be formed.

Two of such compounds containing the cobalt complexes, **C** and **D**, have the same formula $CoCl_3(NH_3)_4$. A third compound, **E**, has the formula $CoCl_3(NH_3)_5$.

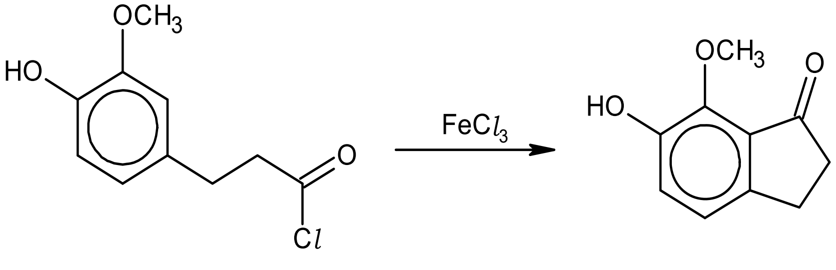
- When treated with aqueous silver nitrate, both **C** and **D** each form 1 mole of a white precipitate per mole of the compound whereas **E** forms 2 moles of the white precipitate.
- Although the cobalt complex ion in **C** and **D** have the same formula, the complex ion in **C** does not have a dipole moment whereas the ion in **D** has a dipole moment.

(i) Suggest the formulae of the cobalt complex ions in **C** and in **E**. [2]

(ii) Suggest a structure for the cobalt complex ion in **C** and in **D** which may be used to explain the presence or absence of a dipole moment. [2]

(d) Transition metals, such as manganese, iron and chromium have also been widely used in organic chemistry for various synthesis.

$FeCl_3$ can be used as a catalyst for the following reaction.



Given that the above reaction proceeds via electrophilic substitution mechanism, describe the mechanism, including curly arrows showing the movement of electrons, and all charges. [3]

[Total: 15]

Section B

Answer **one** question from this section.

4 **(a)** **(i)** Describe and explain the reactions of aluminium chloride with excess water, writing equations where appropriate. [2]

(ii) Molten sulfur and chlorine can react to form disulfur dichloride, S_2Cl_2.

$$S_8(l) + 4Cl_2(g) \rightarrow 4S_2Cl_2(l)$$

	melting point / °C	boiling point / °C
sulfur	115	444
chlorine	–102	–34
disulfur dichloride	–80	137

Describe how a sample of S_2Cl_2 can be made from solid sulfur and chlorine gas, and how it can be purified. Include relevant data from the table. [2]

(b) **(i)** Calculate the average bond energy of Si-C*l* bond using the data from the following table.

standard enthalpy change of formation of $SiCl_4(l)$	–610 kJ mol^{-1}
standard enthalpy change of vaporisation of $SiCl_4(l)$	+28.7 kJ mol^{-1}
standard enthalpy changes of atomisation of silicon	+338 kJ mol^{-1}
standard enthalpy changes of atomisation of chlorine	+122 kJ mol^{-1}

[2]

(ii) $SiCl_4$ readily hydrolyses in water according to the following equation to give an acidic resultant solution.

$$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(g)$$

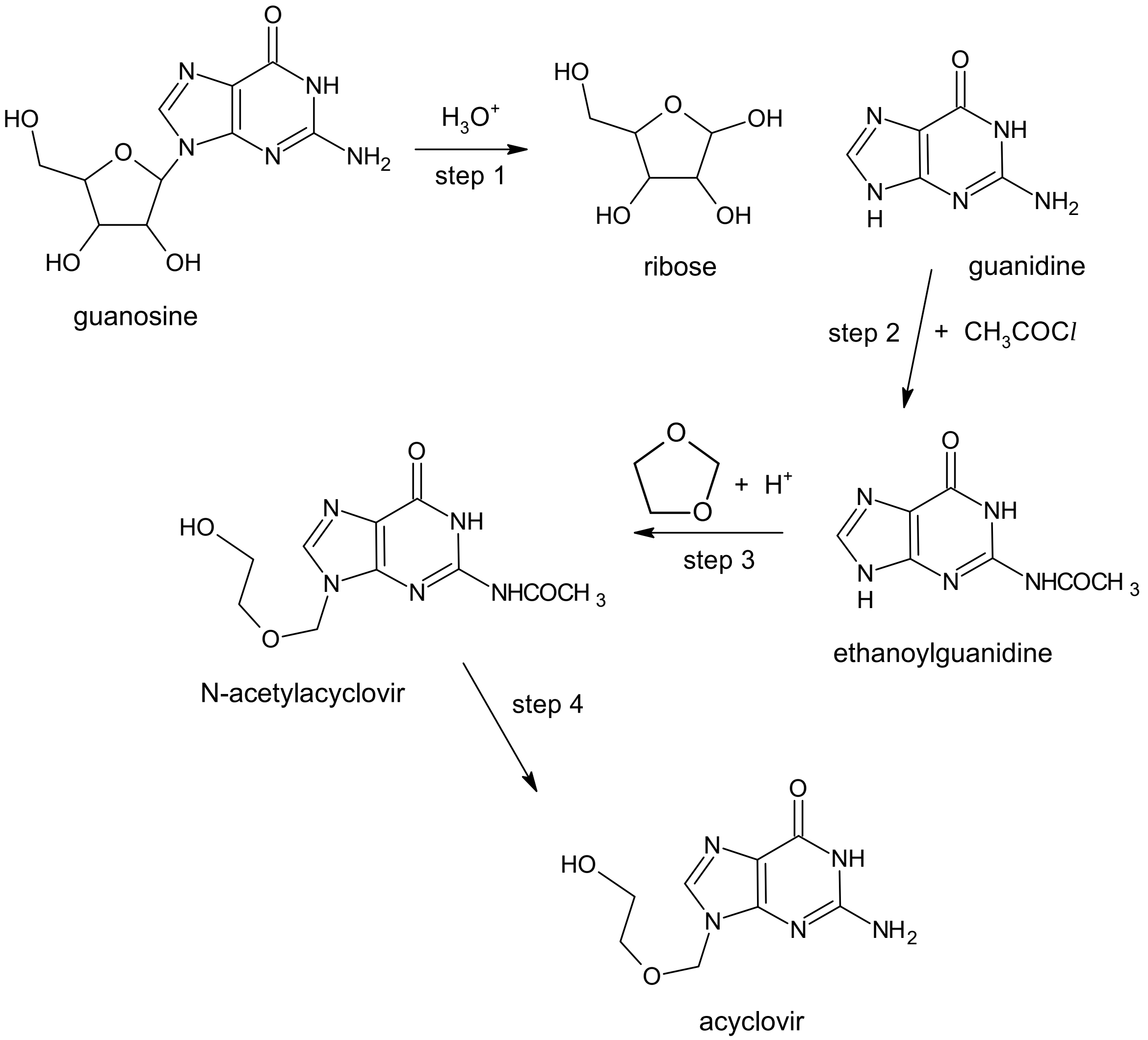
Describe and explain how the entropy of this reaction will change during the hydrolysis reaction. [2]

Drugs can be both inorganic or organic in nature. Magnesium hydroxide is an inorganic drug which can be used as an antacid to relieve heartburn and indigestion. Acyclovir is an organic drug which can be used to treat cold sores and shingles.

(c) **(i)** Given that the solubility product for magnesium hydroxide in water at 25 ºC is 1.10×10^{-11} mol^3 dm^{-9}, calculate the mass of solid magnesium chloride to be added to 30 cm^3 of sodium hydroxide solution of pH 9.0 to form a saturated solution of magnesium hydroxide. [3]

(ii) Explain how the solubility of magnesium hydroxide in aqueous sodium hydroxide would differ from that in water, including equation(s) where relevant. [2]

(d) Acyclovir can be made from guanosine as shown below.



(i) State the functional groups that are present in guanidine. Ignore imine (C=N) functional group. [2]

(ii) State the types of reaction that occur in each of the steps 1 & 2. [2]

(iii) A student proposed that step 4 can be carried out by heating with aqueous NaOH. Explain why the proposed method will not yield acyclovir. [1]

(iv) Describe a simple chemical test that you could use to distinguish between ethanoylguanidine and N-acetylacyclovir. You are to include reagents and conditions and observations in your answers. [2]

[Total: 20]

5 **(a)** A typical firework mixture consists of fuel, an oxidiser to provide the oxygen for burning, and the colour-producing metal compounds. The colours of most modern fireworks involve metal chlorides and nitrates.

(i) Strontium nitrate can be used as a red colouring agent in pyrotechnics. Upon strong heating, strontium nitrate decomposes to give a solid residue and 2 gases. One of the gases is a brown vapour and the other relights a glowing splint.
Write an equation for the reaction that occurs when strontium nitrate is heated. [1]

(ii) Explain why the ease of thermal decomposition of Group 2 nitrates decreases down the group. [2]

(b) Strontium chloride, $SrCl_2$, can also be used to produce a red colour in fireworks.

(i) Construct an energy level diagram for the formation of strontium chloride from its elements using relevant data from Table 5.1 and other appropriate values in the *Data Booklet*. Hence calculate the lattice energy of strontium chloride.

Table 5.1

	Energy/ kJ mol^{-1}
electron affinity per mole of chlorine atoms	– 349
standard enthalpy change of atomisation of Sr(s)	+ 164
standard enthalpy change of formation of $SrCl_2$(s)	– 830

[3]

(ii) The numerical values of lattice energy for the Group 2 chlorides decrease from $CaCl_2$ to $BaCl_2$. By quoting appropriate data from the *Data Booklet*, explain this trend. [2]

$SOCl_2$ and $NOCl$ are compounds of chlorine which are used in organic synthesis.

(c) Compound **F** has a molecular formula $C_{13}H_{16}O$. **F** decolourises aqueous bromine and produces white fumes with $SOCl_2$. It reacts with acidified potassium manganate(VII) under controlled conditions to produce **G** (C_8H_8O), **H** ($C_3H_2O_5$) and ethanoic acid. **G** does not react with Fehling's solution but reacts with aqueous alkaline iodine to give a yellow precipitate. **H** gives effervescence with solid sodium carbonate. **H** gives an orange precipitate with 2,4-dinitrophenylhydrazine.

Deduce the structures of **F**, **G** and **H**. [7]

(d) Nitrosyl chloride, $NOCl$, is a toxic yellow gas which can convert some cyclic amines to alkenes.

At 400 °C, $NOCl$ readily dissociates into NO and Cl_2.

$$2NOCl\ (g) \rightleftharpoons 2NO\ (g) + Cl_2\ (g)\ \square$$

(i) Write an expression for the equilibrium constant, K_c. [1]

(ii) In an experiment, 1.00 mol of $NOCl$, 2.00 mol of NO and 1.00 mol of Cl_2 are mixed in a 250 cm^3 vessel at 400 °C. The number of moles of $NOCl$ is found to be 1.40 mol when the system reaches equilibrium.
Calculate the value of K_c at 400 °C. [2]

(iii) Given that the value of K_c increases with temperature, deduce whether the forward reaction is an endothermic or exothermic reaction. [2]

[Total: 20]

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TAMPINES JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION

CHEMISTRY

9729/03

Paper 3 Free Response

Thursday, 13 September 2018

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions

Section B
Answer **one** question.

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

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.

This document consists of **11** printed pages.

Section A

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

[Tota
18

1 Fuels are materials which can react with other substances to release energy. The most common fuels for machines are hydrocarbons and coal while common fuels for organisms are fats and carbohydrates contained in food sources.

(a) The energy provided by food sources is often measured in terms of the energy released during their combustion to form liquid water. A bomb calorimeter is commonly used to determine this energy, which is quoted in kilojoules (kJ) or kilocalorie (kcal), where 1 kcal = 4.184 kJ.

(i) A manufacturer claims that its new dessert has "fewer than 10 kcal per serving".

In order to test the claim, a chemist places one serving of the dessert in a bomb calorimeter and combusts it. The heat energy released raises the temperature of the calorimeter by 4.93 °C.

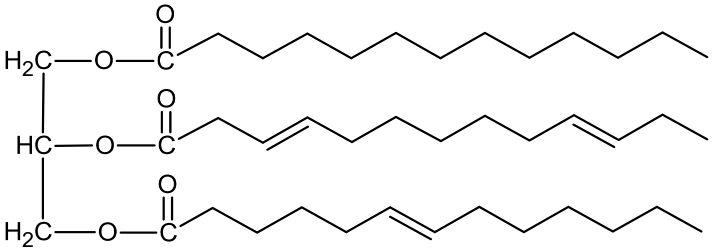
Given that the heat capacity of the calorimeter is 8.15 kJ K^{-1}, determine if the manufacturer's claim is correct. [2]

Heat gained by calorimeter = $4.93 \times 8.15 = 40.18$ kJ

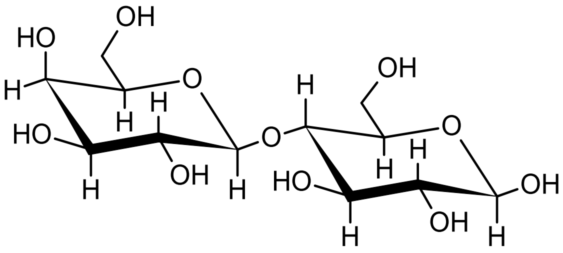
Heat released by food = $40.18 \div 4.184 = 9.60$ kcal
Therefore the manufacturer's claim is correct as 9.60 kcal is less than 10 kcal.

(ii) The structures of an example of a fat and carbohydrate are shown below:

fat



carbohydrate



Both fats and carbohydrates are metabolised in the body to CO_2 and H_2O. Suggest an explanation for why fats are often described as having "more kcal per gram" than carbohydrates. [2]

Either reason:

- For fat, there are **more** C=O and/or O–H bonds that needs to be formed, thus more energy is released/reaction is more exothermic.

OR

- In fat, there are less carbon and hydrogen atoms already bonded to oxygen, so more oxygen is required for conversion to CO_2 and H_2O/more energy is released.

OR any other chemically sound reason.

(b) In fuel cells, chemical energy from fuel is converted into electrical energy by reaction with an oxidising agent.

Methane is one of the hydrocarbons employed in hydrocarbon fuel cells, where it is oxidised at the anode to carbon dioxide. The electrolyte is usually an aqueous acid.

The cathode in this fuel cell is the oxygen electrode.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

(i) Construct an equation for the anode reaction. [1]

$CH_4 + 2H_2O \rightarrow CO_2 + 8H^+ + 8e^-$

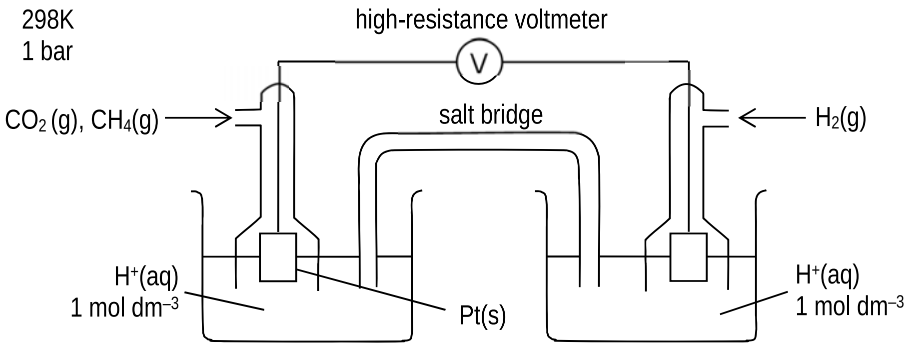
(ii) Hence construct the equation for the overall equation, showing your working. [1]

Combining the 2 half-equations:
$CH_4 + 2H_2O + 2O_2 + 8H^+ \rightarrow CO_2 + 8H^+ + 4H_2O$
which simplifies to:
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

(iii) During discharge, the cell generates an electromotive force (e.m.f.) of 1.06 V. By using suitable data from the *Data Booklet*, suggest a value for the $E^\ominus$ of the CO_2/CH_4 electrode reaction. [2]

From Data Booklet: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $E^\ominus = +1.23$ V
$1.06 = 1.23 - E^\ominus_{CO_2/CH_4}$
$E^\ominus_{CO_2/CH_4} = +0.17$ V

(iv) Draw a fully labelled diagram of the electrochemical cell you could use to measure the standard electrode potential of the CO_2/CH_4 half-cell. [3]



(v) Methanol is the first alcohol to be successfully used in a fuel cell. This cell produces an e.m.f. of 1.18 V and the overall reaction is:

$$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$$

Determine the standard Gibbs free energy change, $\Delta G^\ominus$, of this reaction. [2]

$\Delta G^\ominus = -nFE^\ominus$

From part (a) (or since O.S. of oxygen decreased from 0 to –2),
1 mol O_2 gains 4 mol e^-, $\Rightarrow$ n = 6
$\Delta G^\ominus = -6 \times (9.65 \times 10^4) \times 1.18$
$= -683\,220 \text{ J mol}^{-1} \approx -683 \text{ kJ mol}^{-1}$

(vi) How many moles of methanol will be consumed when a methanol fuel cell delivers 254 A of current for 1 minute? [2]

Quantity of charge, Q = 254 × 60 = 15 240 C
Amount of electrons transferred = 15240 ÷ 96500 = 0.158 mol
Amount of methanol required = 0.158 ÷ 6 = 0.0263 mol
ecf from n value in (v)

(vii) Suggest a possible advantage of using a methanol fuel cell over the methane fuel cell. [1]

Any one of the following:

- Liquid methanol is much easier to store / package / transport than gaseous methane.
- Methanol fuel cell generates higher e.m.f.
- Methanol fuel cell requires/consumes less oxygen per mole of fuel.

(c) Reactions in which a substance decomposes by losing CO_2 are called *decarboxylation* reactions. Methane can be obtained in the *decarboxylation* reaction of ethanoic acid.

$$CH_3COOH(l) \rightarrow CH_4(g) + CO_2(g) \qquad \Delta H_r^\ominus$$

(i) Use the following standard enthalpy changes to calculate the value of the standard enthalpy change of the *decarboxylation* reaction of ethanoic acid, $\Delta H_r^\ominus$. [1]

	$\Delta H^\ominus$ / kJ mol^{-1}
standard enthalpy change of formation of $CH_3COOH(l)$	–487.0
standard enthalpy change of formation of $CH_4(g)$	–74.8
standard enthalpy change of combustion of C(s)	–393.5

$\Delta H^\ominus = (-74.8) + (-393.5) - (-487.0) = +18.7 \text{ kJ mol}^{-1}$

(ii) The standard molar enthalpy, $S^\ominus$, of substances can be used determine the standard entropy change, $\Delta S^\ominus$, of a chemical reaction:

$$\Delta S^\ominus = \sum nS^\ominus(\text{products}) - \sum mS^\ominus(\text{reactants})$$

where *m* and *n* are the coefficients in the chemical equation.

Use the following standard molar entropies, $S^\ominus$, to calculate the standard entropy change, $\Delta S^\ominus$, of the *decarboxylation* reaction of ethanoic acid.

	$S^\ominus$ (J mol^{-1} K^{-1})
$CH_3COOH(l)$	159.8
$CH_4(g)$	186.3
$CO_2(g)$	213.6

[1]

$\Delta S^\ominus = 186.3 + 213.6 - 159.8 = 240$ J mol^{-1} K^{-1} (to 3 s.f.)

(iii) Use your answers to **(c)(i)** and **(c)(ii)** to calculate the minimum temperature at which the *decarboxylation* of ethanoic acid will be spontaneous.
State an assumption that you have made. [3]

$\Delta G = \Delta H - T\Delta S$

For a reaction to be spontaneous, $\Delta G < 0$

$$18.7 - T(240 \times 10^{-3}) < 0$$

$$T > 77.9 \text{ K}$$

(also accept 78.0)
ecf from (i) and (ii)

Assumed that (any one of the following):

- pressure was/remained at 1 bar.
- ΔH and ΔS do not vary with temperature.

(iv) Both ethanoic acid and methane can be chlorinated to form ethanoyl chloride, CH_3COCl, and chloromethane respectively.

Ethanoyl chloride and chloromethane are both colourless liquids and can be distinguished by their reaction with water.

State what you might expect to observe when each reacts with water and explain why the two compounds react differently with water. [4]

Ethanoyl chloride reacts with water to give white fumes.
No visible observation for chloromethane.

Ethanoyl chloride undergoes hydrolysis with water (OR eqn) but chloromethane does not.

The carbon atom of –COCl group (acyl chloride carbon) is bonded to 2 very electronegative atoms, making it more electron-deficient (δ+) than carbon of chloromethane. Thus the acyl chloride carbon is more susceptible to attack by nucleophiles/water.

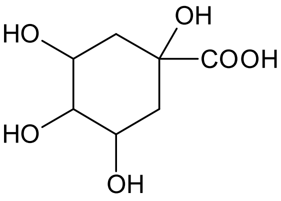
[Total: 25]

2 Buffer solutions are widely used in a wide variety of chemical applications commercially and in nature. Animals and plants are protected against extreme conditions by the presence of buffers.

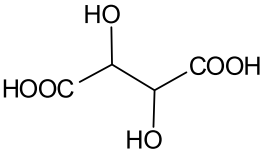
(a) Define the term *buffers*. [1]

Buffers are solutions which resists changes in pH when a small amount of acid or base is added to it.

(b) Most foodstuff contain buffering systems are made from organic acids extracted from plants. Two such acids are shown below.



quinic acid



tartaric acid

Table 2.1 compares the pK_a values of quinic acid, tartaric acid and benzoic acid.

Table 2.1

acid	formula	pK_1	pK_2
quinic	$C_6H_{11}O_4CO_2H$	3.40	-
tartaric	$C_2H_4O_2(CO_2H)_2$	2.89	4.40
benzoic	$C_6H_5CO_2H$	4.20	-

(i) Suggest a reason why the pK_1 value of quinic acid is lower than that of benzoic acid. [2]

The conjugate base of quinic acid ($C_6H_{11}O_4COO^-$) is more stable than the benzoate anion ($C_6H_5COO^-$). The presence of (many) electron withdrawing –OH group enhances the dispersal of the negative charge on the $C_6H_{11}O_4COO^-$.

Thus quinic acid dissociates to a greater extent and is a stronger acid and therefore has a lower pK_1.

(ii) Suggest a reason why the pK_2 of tartaric acid is higher than its pK_1. [2]

The $C_4H_4O_2(CO_2H)CO_2^-$ ion (or monoanion) carries a negative charge, while $C_4H_4O_2(CO_2H)_2$ (or tartaric acid) is neutral.

It is more difficult to remove a second proton from the already negatively charged monoanion than to remove a proton from the neutral tartaric acid molecule.

Hence, the monoanion is less likely to undergo dissociation than the tartaric acid molecule, and tartaric acid has a higher pK_2 value than pK_1 value.

(iii) A flask contains 200 cm^3 of 0.020 mol dm^{-3} solution of benzoic acid. Calculate the pH of this solution. [2]

$$K_a = \frac{[H^+][\text{benzoate}]}{[\text{benzoic acid}]}$$

Assume negligible dissociation of benzoic acid, and $[H^+]$ = [benzoate].

$\Rightarrow$ $10^{-4.20} = [H^+]^2 / 0.020$

$\Rightarrow$ $[H^+] = 1.12 \times 10^{-3}$ mol dm^{-3}

$\Rightarrow$ pH = $-\log_{10} (1.12 \times 10^{-3}) = 2.95$

Hence, pH of benzoic acid is 2.95.

(iv) A buffer solution with a pH of 4.10 is made by adding 100 cm^3 of x mol dm^{-3} solution of sodium benzoate, to 200 cm^3 of 0.020 mol dm^{-3} solution of benzoic acid.

Calculate the value of x. [2]

Resultant [benzoic acid]= $0.0200 \times (200/300)$

Resultant [sodium benzoate]= x (100/300)

Using formula, pH = pK_a + lg [$(100\,x/300) \div 0.0133$]

$4.10 = 4.20 + \lg [\,(100\,x/300) \div 0.0133]$

$x = 0.0317$ mol dm^{-3}

(c) Buffers are also important in humans. If the pH of the body falls below 7.35, a condition known as acidosis results which can become very serious. One of the buffers present in blood is that of the H_3PO_4(aq) / $H_2PO_4^-$(aq) system.

Write equation(s) to show how H_3PO_4(aq) / $H_2PO_4^-$(aq) buffer system helps to maintain the pH of blood. [2]

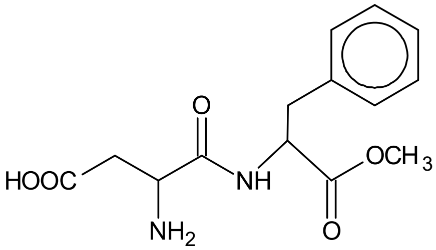
When a small amount of base is added, H_3PO_4 reacts with it,

$H_3PO_4 + OH^- \rightarrow H_2PO_4^- + H_2O$

When a small amount of acid is added, $H_2PO_4^-$ reacts with it,

$H_2PO_4^- + H^+ \rightarrow H_3PO_4$

(d) Aspartame, a dipeptide, is a high intensity artificial sweetener used in soft drinks. Buffers are usually added together with aspartame as pH affects the stability of aspartame.



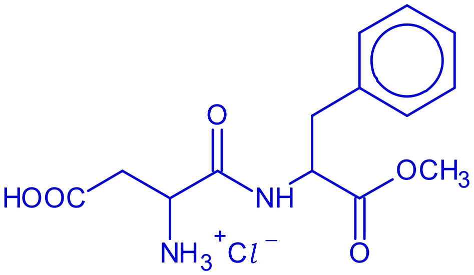
aspartame

(i) Draw the structural formula of the organic products formed when aspartame is treated with

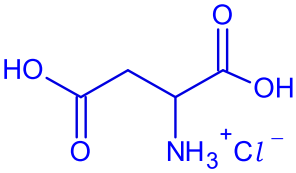
- cold HC*l*(aq)
- hot HC*l*(aq)

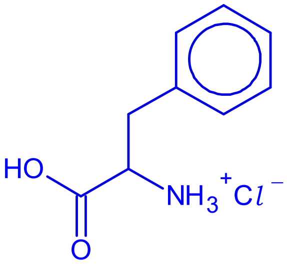
[3]

- cold HC*l*(aq)



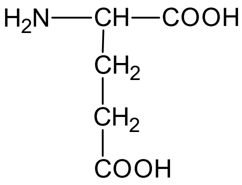
- hot HC*l*(aq)





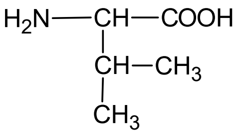
CH_3OH

(ii) A *dipeptide* is formed when two amino acids combine.
Draw the structure of the dipeptide formed when the amino acids, glutamic acid and valine combine.



$H_2N-CH(CH_2CH_2COOH)-COOH$

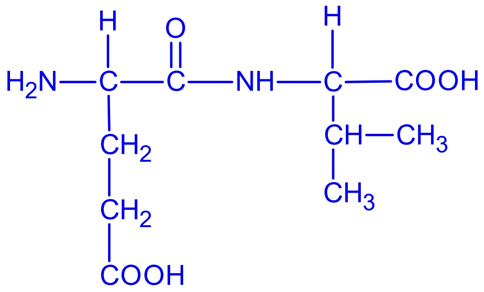
glutamic acid



$H_2N-CH(CH(CH_3)CH_3)-COOH$

valine

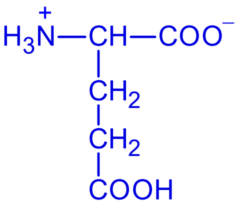
[1]



$H_2N-CH(CH_2CH_2COOH)-CO-NH-CH(CH(CH_3)CH_3)-COOH$

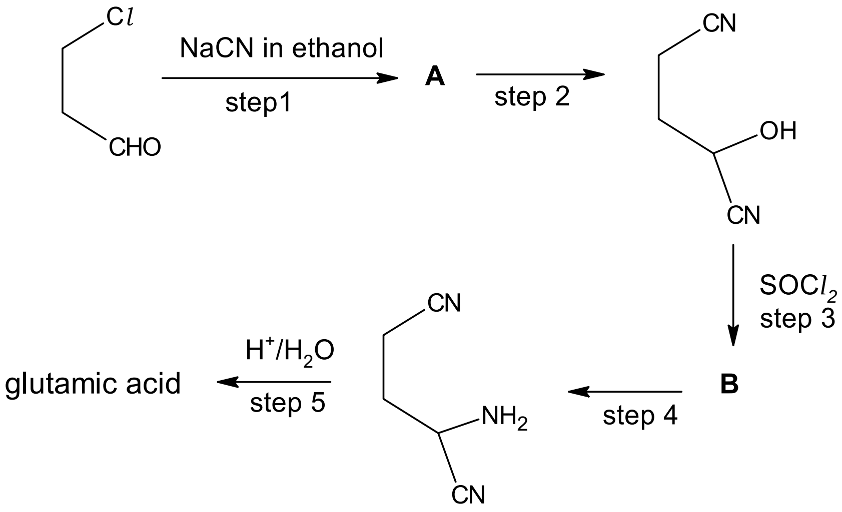
accept glu-val & val-glu

(iii) Glutamic acid has pK_a values of 2.10, 4.07 and 9.47.
Draw the structural formula of the glutamic acid in its most stable state at pH 3. [1]

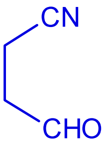


$H_3\overset{+}{N}-CH(CH_2CH_2COOH)-COO^-$

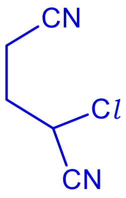
(e) Glutamic acid can be synthesised from 3-chloropropanal by the following route.



(i) Suggest structures for the intermediates **A** and **B**. [2]



A



B

(ii) Suggest reagents and conditions for step 2 and for step 4. [2]

Step 2: HCN, with trace NaCN (or NaOH), (cold)
Step 4: excess conc NH_3 heat in a sealed tube

[Total: 20]

3 Transition metals and their compounds are known for their catalytic activity in industry.

The reaction between peroxodisulfate ions, $S_2O_8^{2-}$, and potassium iodide is an example of a reaction that is catalysed by transition metal ions.

(a) The initial rate of the slow reaction between $S_2O_8^{2-}$ and potassium iodide solution can be studied by the "clock" method, using sodium thiosulfate. The equations for the reactions are as follows.

$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$ (slow) reaction **I**

$I_2(aq) + 2Na_2S_2O_3(aq) \rightarrow 2NaI(aq) + Na_2S_4O_6(aq)$ (fast) reaction **II**

When a small but constant amount of sodium thiosulfate is added to a reaction mixture, the iodine being slowly produced in reaction **I** will immediately be consumed in reaction **II** until all the sodium thiosulfate has been used up. At that point, free iodine will be present in the solution. The free iodine present reacts with starch to form a deep blue complex.

A series of experiments was carried out using different volumes of the five reagents, each solution being made up to the same volume with water.
The following results were obtained.

experiment number	volume of 0.10 mol dm^{-3} $S_2O_8^{2-}$ /cm^3	volume of 0.20 mol dm^{-3} KI /cm^3	volume of 0.010 mol dm^{-3} $Na_2S_2O_3$ /cm^3	volume of water /cm^3	volume of starch solution /cm^3	time taken for the appearance of deep blue colour /s
1	5.0	5.0	2.0	35.0	3.0	42
2	5.0	4.0	2.0	36.0	3.0	53
3	10.0	3.0	2.0	32.0	3.0	35
4	15.0	2.0	2.0	28.0	3.0	35

(i) What is the simple relationship between the time taken for the appearance of the blue colour and the initial rate of reaction **I**? [1]

rate $\propto \frac{1}{t}$ or rate is inversely proportional to time

(ii) Calculate the initial rate for each of these four experiments and use the results to deduce the order of reaction with respect to each of the two reactants in reaction **I**. Explain your reasoning. [3]

Experiment	Initial rate
1	1/42 = 0.0238 s^{-1}
2	1/53 = 0.0189 s^{-1}
3	1/35 = 0.0286 s^{-1}
4	1/35 = 0.0286 s^{-1}

[1] for all calculated initial rates

Using experiment 1 and 2, when the [$S_2O_8^{2-}$] remains constant and volume of reactant α [reactant] since total volume is constant,
the [I^-] × 1.25, the rate × 1.25.
Hence the order of reaction with respect to [I^-] is one.

Let the order of reaction for $S_2O_8^{2-}$ be n.
Using experiment 2 and 3,

$$\frac{rate_2}{rate_3}=\frac{k[S_2O_8^{2-}]^n[I^-]^1}{k[S_2O_8^{2-}]^n[I^-]^1}$$

$$\frac{0.0189}{0.0286}=\frac{k[5]^n[4]^1}{k[10]^n[3]^1}$$

$$\frac{0.0189}{0.0286}=(\frac{1}{2})^n \times \frac{4}{3}$$

$$0.495=(\frac{1}{2})^n$$

$$n = 1$$

therefore, order of reaction with respect to $S_2O_8^{2-}$ is one.

(iii) Hence write an overall rate equation for reaction **I**. [1]

rate = k [I^-] [$S_2O_8^{2-}$]

(b) The above reaction between iodide and peroxodisulfate ions can be catalysed by a transition metal ion, such as, cobalt(II) ions, Co^{2+}.

(i) Suggest a reason why the reaction between iodide and peroxodisulfate ions requires a catalyst. [1]

As both iodide and peroxodisulfate ions are anions, repulsion between the anions will cause the activation energy to be high, leading to a slow reaction rate. [1]

(ii) Describe how Co^{2+} ions are able to catalyse the reaction between iodide and peroxodisulfate. Write equations where appropriate. [2]

Co^{2+} first reduces $S_2O_8^{2-}$ while itself is oxidised to Co^{3+}:
$2Co^{2+} + S_2O_8^{2-} \rightarrow 2Co^{3+} + 2SO_4^{2-}$

Co^{3+} then oxidises I^- and is itself reduced to give Co^{2+}:
$2Co^{3+} + 2I^- \rightarrow 2Co^{2+} + I_2$

(c) Another characteristic feature of the chemistry of transition elements is their tendency to form complexes.

When aqueous cobalt(III) chloride reacts with ammonia under various conditions, compounds containing different cobalt complexes can be formed.

Two of such compounds containing the cobalt complexes, **C** and **D**, have the same formula $CoCl_3(NH_3)_4$. A third compound, **E**, has the formula $CoCl_3(NH_3)_5$.

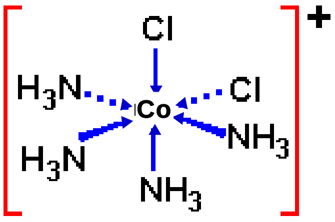
- When treated with aqueous silver nitrate, both **C** and **D** each form 1 mole of a white precipitate per mole of the compound whereas **E** forms 2 moles of the white precipitate.

- Although the cobalt complex ion in **C** and **D** have the same formula, the complex ion in **C** does not have a dipole moment whereas the ion in **D** has a dipole moment.

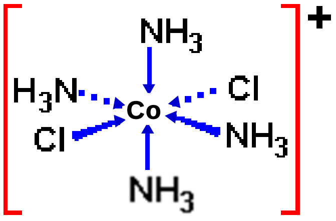
(i) Suggest the formulae of the cobalt complex ions in **C** and in **E**. [2]

C : $[Co(NH_3)_4(Cl)_2]^+$ **E** : $[Co(NH_3)_5(Cl)]^{2+}$

(ii) Suggest a structure for the cobalt complex ion in **C** and in **D** which may be used to explain the presence or absence of a dipole moment. [2]



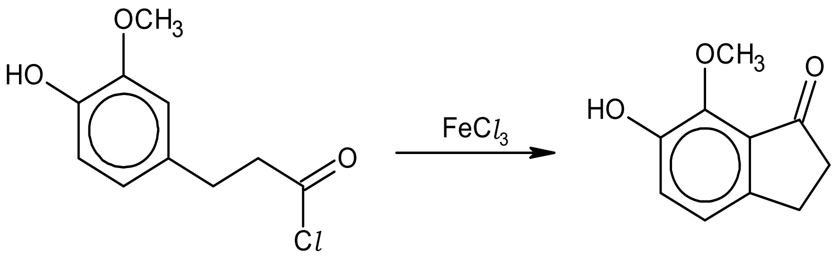
D



C

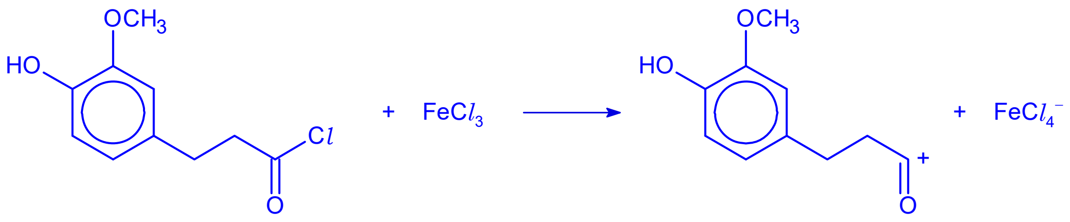
(d) Transition metals, such as manganese, iron and chromium have also been widely used in organic chemistry for various synthesis.

$FeCl_3$ can be used as a catalyst for the following reaction.

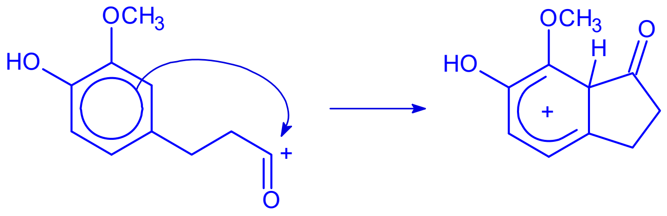


Given that the above reaction proceeds via electrophilic substitution mechanism, describe the mechanism, including curly arrows showing the movement of electrons, and all charges. [3]

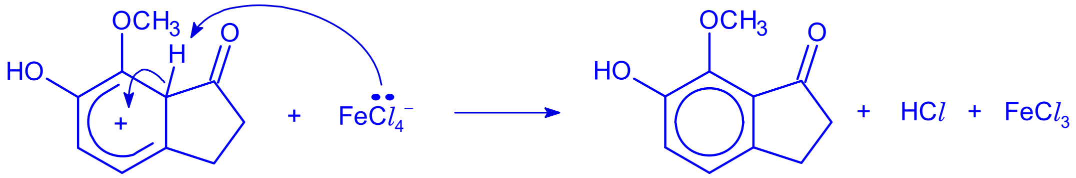
Step 1:



Step 2:



Step 3:



[Total: 15]

Section B

Answer **one** question from this section.

4 **(a)** **(i)** Describe and explain the reactions of aluminium chloride with excess water, writing equations where appropriate. [2]

- $AlCl_3$ dissolves in water. (or use of state symbol)
  $AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^{-}$
- Hydrolysis also occurs due to the high charge density of Al^{3+} ions. It further polarises the water molecule and weakens the O-H bond of water making it easier for an H^{+} ion to leave the water molecule.
  $[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(H_2O)_5OH]^{2+} + H^{+}$

(ii) Molten sulfur and chlorine can react to form disulfur dichloride, S_2Cl_2.

$$S_8(l) + 4Cl_2(g) \rightarrow 4S_2Cl_2(l)$$

[2]

	melting point / °C	boiling point / °C
sulfur	115	444
chlorine	–102	–34
disulfur dichloride	–80	137

Describe how a sample of S_2Cl_2 can be made from solid sulfur and chlorine gas, and how it can be purified. Include relevant data from the table.

Heat a mixture of S_8 and Cl_2 above 115°C (value suggested and must be within 115°C to 444°C) .
The product can be purified by distillation, collecting it at 137°C.

(b) **(i)** Calculate the average bond energy of Si-Cl bond using the data from the following table.

standard enthalpy change of formation of $SiCl_4(l)$	-610 kJ mol^{-1}
standard enthalpy change of vaporisation of $SiCl_4(l)$	$+28.7$ kJ mol^{-1}
standard enthalpy changes of atomisation of silicon	$+338$ kJ mol^{-1}
standard enthalpy changes of atomisation of chlorine	$+122$ kJ mol^{-1}

[2]

$$\begin{tikzcd}
Si(s) + 2Cl_2(g) \arrow[r, "\Delta H_f = -610"] \arrow[d, "\Delta H_{at}(Si) + 4\Delta H_{at}(Cl) = +338 + 4(122)"'] & SiCl_4(l) \arrow[d, "\Delta H_{vap} = +28.7"] \\
Si(g) + 4Cl(g) & SiCl_4(g) \arrow[l, "4\ BE(Si\text{–}Cl)"']
\end{tikzcd}$$

Bond Energy (Si-Cl) = $[-(-610) - (+28.7) + (+338 + 4(122))]/4$ [1]-method
$= +351.8$ kJ mol^{-1}
$\approx +352$ kJ mol^{-1} (3 s.f.) [1]-value, units

(ii) $SiCl_4$ readily hydrolyses in water according to the following equation to give an acidic resultant solution.

$$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(g)$$

Describe and explain how the entropy of this reaction will change during the hydrolysis reaction. [2]

ΔS is positive as there is an increase in the number of gaseous molecules which results in more ways of arranging the particles. The system becomes more disorderly, and the entropy of the system increases.

Drugs can be both inorganic or organic in nature. Magnesium hydroxide is an inorganic drug which can be used as an antacid to relieve heartburn and indigestion. Acyclovir is an organic drug which can be used to treat cold sores and shingles.

(c) **(i)** Given that the solubility product for magnesium hydroxide in water at 25 ºC is 1.10×10^{-11} mol^3 dm^{-9}, calculate the mass of solid magnesium chloride to be added to 30 cm^3 of sodium hydroxide solution of pH 9.0 to form a saturated solution of magnesium hydroxide. [3]

pOH = 14 – 9.0 = 5.0
$[OH^-] = 10^{-5.0} = 1.0 \times 10^{-5}$ mol dm^{-3}

At saturation, ionic product = K_{sp}
$[Mg^{2+}][OH^-]^2 = 1.10 \times 10^{-11}$
$[Mg^{2+}] = 1.10 \times 10^{-11} / (1.0 \times 10^{-5})^2$
$= 0.110$ mol dm^{-3}

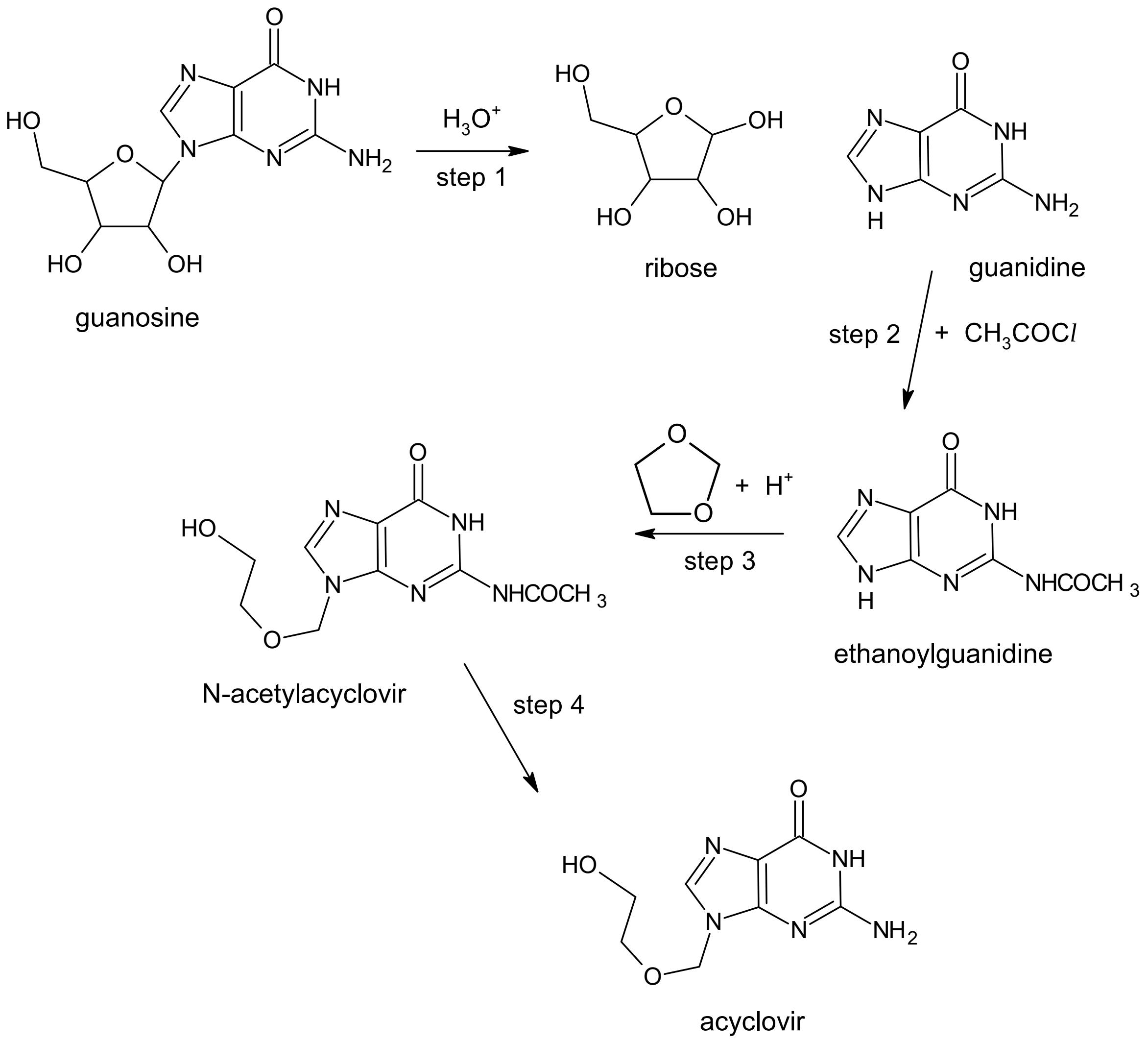
Mass of $MgCl_2 = 0.110 \times 0.0300 \times 95.3$
$= 0.314$ g

(ii) Explain how the solubility of magnesium hydroxide in aqueous sodium hydroxide would differ from that in water, including equation(s) where relevant. [2]

$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$ ------ (1)
$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$

NaOH(aq) dissociates to give OH^- ions which increases $[OH^-]$. According to LCP, position of equilibrium (1) shifts to the left. Hence, solubility in aqueous sodium hydroxide is lower than that in water.

(d) Acyclovir can be made from guanosine as shown below.



(i) State the functional groups that are present in guanidine. Ignore imine (C=N) functional group. [2]

amide, primary amine, secondary amine, alkene

(ii) State the types of reaction that occur in each of the steps 1 & 2. [2]

Step 1: Hydrolysis

Step 2: Nucleophilic (acyl) substitution

(iii) A student proposed that step 4 can be carried out by heating with aqueous NaOH. Explain why the proposed method will not yield acyclovir. [1]

Both amide groups of N-acetylacyclovir will be hydrolysed.

(iv) Describe a simple chemical test that you could use to distinguish between ethanoylguanidine and N-acetylacyclovir. You are to include reagents and conditions and observations in your answers. [2]

Reagents and Conditions (any one of the following)	N-acetylacyclovir	ethanoylguanidine

Acidified potassium dichromate, heat	Orange $K_2Cr_2O_7$ turns green.	Orange $K_2Cr_2O_7$ remains orange.
Na metal	Hydrogen gas evolved	No visible observation
PCl_5 room temperature	White fumes of HCl observed	No visible observation

[Total: 20]

5 **(a)** A typical firework mixture consists of fuel, an oxidiser to provide the oxygen for burning, and the colour-producing metal compounds. The colours of most modern fireworks involve metal chlorides and nitrates.

(i) Strontium nitrate can be used as a red colouring agent in pyrotechnics. Upon strong heating, strontium nitrate decomposes to give a solid residue and 2 gases. One of the gases is a brown vapour and the other relights a glowing splint. Write an equation for the reaction that occurs when strontium nitrate is heated. [1]

$2Sr(NO_3)_2(s) \rightarrow 2SrO(s) + 4NO_2(g) + O_2(g)$

(ii) Explain why the ease of thermal decomposition of Group 2 nitrates decreases down the group. [2]

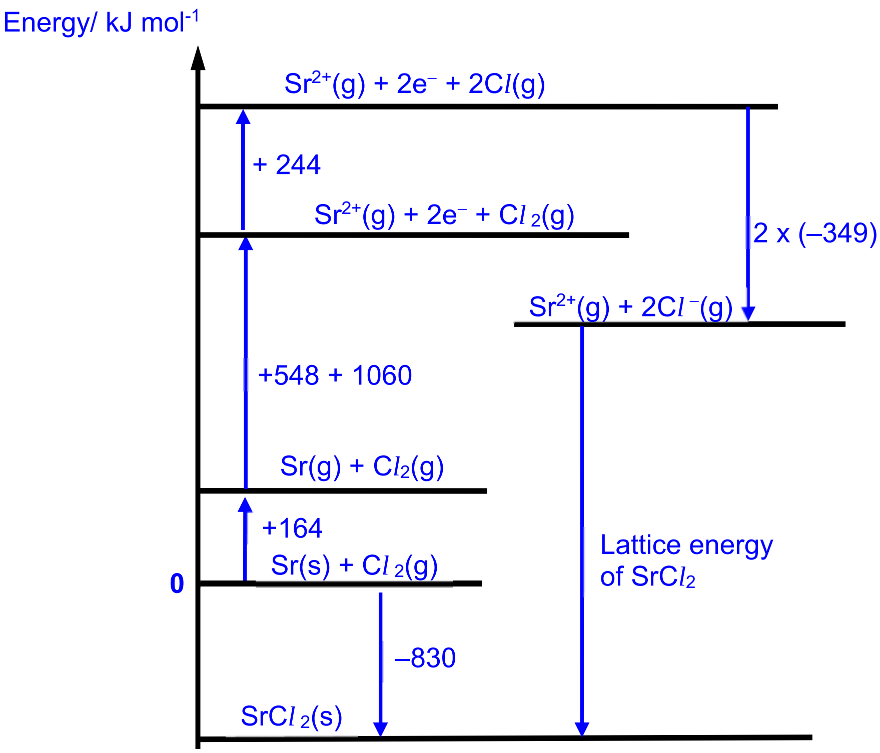
Down the Group, the charge density of the M^{2+} cation decreases as ionic charge remains the same while size of cation increases. The cations have less polarising power, and distort / polarise the electron cloud of the nitrate anion to a smaller extent. The covalent bonds in the anion are weakened to a smaller extent, and more energy is required to decompose the nitrate.

(b) Strontium chloride, $SrCl_2$, can also be used to produce a red colour in fireworks.

(i) Construct an energy level diagram for the formation of strontium chloride from its elements using relevant data from Table 5.1 and other appropriate values in the *Data Booklet*. Hence calculate the lattice energy of strontium chloride. [3]

Table 5.1

	Energy/ kJ mol^{-1}
electron affinity per mole of chlorine atoms	– 349
standard enthalpy change of atomisation of Sr(s)	+ 164
standard enthalpy change of formation of $SrCl_2$(s)	– 830



Using Hess' Law,
– 830 = + 164 + (548 + 1060) + 244 + 2 (–349) + Lattice energy
Lattice energy = – 2148 kJ mol^{-1} or – 2150 kJ mol^{-1} (3 s.f.)

(ii) The numerical values of lattice energy for the Group 2 chlorides decrease from $CaCl_2$ to $BaCl_2$. By quoting appropriate data from the *Data Booklet*, explain this trend. [2]

From the data booklet, the ionic radii of Ca^{2+} is 0.099 nm, Sr^{2+} is 0.113 nm, Ba^{2+} is 0.135 nm.
Lattice energy $\propto \frac{q^+ \times q^-}{r^+ + r^-}$, where q represents the ionic charge and r represents the ionic radius of the ions. Going from $CaCl_2$ to $BaCl_2$, q^+, q^- and r^- remains the same whilst r^+ is increasing down the group . Thus lattice energy decreases down Group 2.

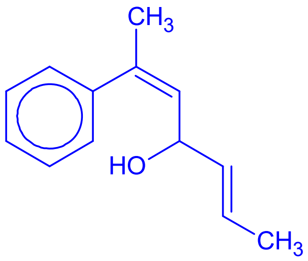
$SOCl_2$ and $NOCl$ are compounds of chlorine which are used in organic synthesis.

(c) Compound **F** has a molecular formula $C_{13}H_{16}O$. **F** decolourises aqueous bromine and produces white fumes with $SOCl_2$. It reacts with acidified potassium manganate(VII) under controlled conditions to produce **G** (C_8H_8O), **H** ($C_3H_2O_5$) and ethanoic acid. **G** does not react with Fehling's solution but reacts with aqueous alkaline iodine to give a yellow precipitate. **H** gives effervescence with solid sodium carbonate. **H** gives an orange precipitate with 2,4-dinitrophenylhydrazine.

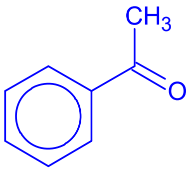
Deduce the structures of **F**, **G** and **H**. [7]

Observation	Deduction
F decolourises aqueous bromine.	electrophilic addition across the alkene (C=C) functional group
F produces white fumes with $SOCl_2$	(nucleophilic) substitution reaction of the (secondary) alcohol functional group to form white fume of HCl
F produced 3 compounds, **G**, **H** and ethanoic acid with hot acidified potassium manganate (VII)	vigorous/strong oxidation of the (two) alkene functional groups present
G does not react with Fehling's solution	**G** does not undergo mild oxidation with Fehling's reagent as it is not an aldehyde.
G reacts with aqueous alkaline iodine to give a yellow precipitate.	**G** gives a yellow ppt (of CHI_3) with aq alkaline iodine due to the (mild) oxidation. **G** contains R-$COCH_3$ or R-$CH(OH)CH_3$ structure.
H gives effervescence with solid sodium carbonate.	**H** gives an effervescence (of CO_2) with Na_2CO_3(s) due to a neutralisation reaction of the carboxylic acid functional group.
H gives an orange precipitate with 2,4-DNPH	Condensation with the ketone functional group in **H**.

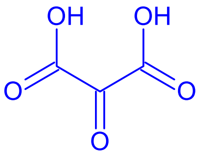
F:



G:



H:



(d) Nitrosyl chloride, NOC*l*, is a toxic yellow gas which can convert some cyclic amines to alkenes.

At 400 °C, NOC*l* readily dissociates into NO and C*l*$_2$.

$$2NOCl\,(g) \rightleftharpoons 2NO\,(g) + Cl_2\,(g)$$ □

(i) Write an expression for the equilibrium constant, K_c. [1]

$K_c = \frac{[Cl_2][NO]^2}{[NOCl]^2}$

(ii) In an experiment, 1.00 mol of NOC*l*, 2.00 mol of NO and 1.00 mol of C*l*$_2$ are mixed in a 250 cm^3 vessel at 400 °C. The number of moles of NOC*l* is found to be 1.40 mol when the system reaches equilibrium.
Calculate the value of K_c at 400 °C. [2]

	$2NOCl(g)$	$\rightleftharpoons$	$2NO(g)$	+	$Cl_2(g)$
Initial amount / mol	1.00		2.00		1.00
Change in amount / mol	+0.40		–0.40		–0.20
Equilibrium amount / mol	1.40		1.60		0.80
Equilibrium conc / mol dm^{-3}	5.60		6.40		3.20

$K_c = 3.20 \times 6.40^2 / (5.60)^2 = 4.18$ mol dm^{-3}

(iii) Given that the value of K_c increases with temperature, deduce whether the forward reaction is an endothermic or exothermic reaction. [2]

Since K_c increases with temperature, forward reaction is favoured (or eqm position shifts right). By Le Chatelier's Principle, increase in temperature will favour endothermic reaction. Hence, the forward reaction is endothermic.

[Total: 20]