ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY **9729/01**
Higher 2

Paper 1 Multiple Choice

14 September 2021
1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

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

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

The use of an approved scientific calculator is expected, where appropriate.

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

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1 In an organic synthesis, a 62% yield of product is achieved.

Which conversions are consistent with the given information?

1 74 g of butan-2-ol (M_r = 74.0) → 44.64 g of butanone (M_r = 72.0)

2 72 g of butanal (M_r = 72.0) → 45.88 g of butan-1-ol (M_r = 74.0)

3 56 g of but-2-ene (M_r = 56.0) → 37.20 g of ethanoic acid (M_r = 60.0)

A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 1 only

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

Sodium percarbonate, $x(Na_2CO_3).y(H_2O_2)$ is a chemical that is used in cleaning powders. When dissolved in water, it releases hydrogen peroxide and sodium carbonate, both of which are useful cleaning agents.

A sample of 10.0 cm^3 of 0.100 mol dm^{-3} sodium percarbonate requires 20.0 cm^3 of 0.100 mol dm^{-3} of acidified KI before the end point of titration is reached.

Another identical sample releases 48.0 cm^3 of carbon dioxide at room conditions on reaction with excess acid.

What are the values of ***x*** and ***y*** respectively?

	x	***y***
A	2	1
B	3	2
C	2	3
D	3	1

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3 An ion X^{2+} contains 24 protons.

What is the electronic configuration of X^{3+}?

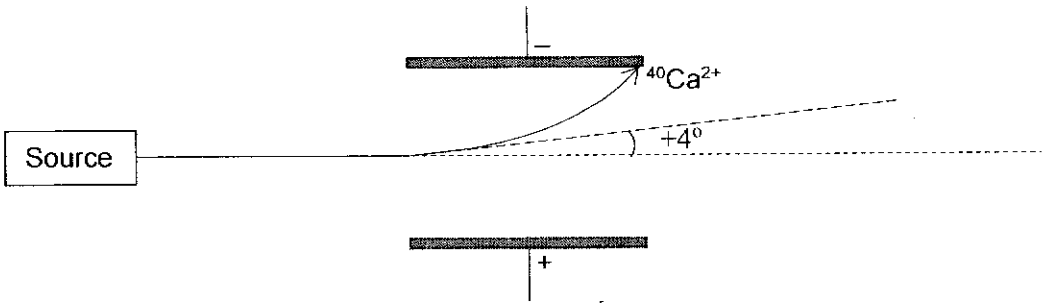
A $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$

B $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^4$

C $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$

D $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

4 A sample of the element calcium was vaporised, ionised and passed through an electric field. It was observed that a beam of $^{40}Ca^{2+}$ particles gave an angle of deflection of +4°.



Assuming an identical set of experimental conditions, by what angle would a beam of $^{19}F^-$ particles be deflected?

A +2° **B** – 2° **C** +4° **D** – 4°

5 *Use of Data Booklet is relevant to this question.*

X, **Y** and **Z** are isotopes of three different elements. An isotope of Argon has a mass number of 41 and the same number of neutrons in the nucleus as each of the isotopes **X**, **Y** and **Z**.

The species Ar, X^+, Y^{2+} and Z^{3+} all contain the same number of electrons.

What are the mass numbers of **X**, **Y** and **Z**?

	X	Y	Z
A	42	41	40
B	40	41	42
C	44	43	42
D	42	43	44

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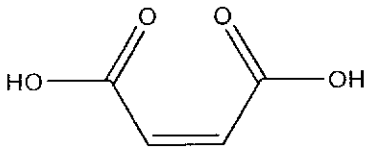
6 Equimolar amounts of the liquids, water and ethanol, are mixed together at 20 °C. The original intermolecular forces in the pure liquids are disrupted and weaker intermolecular forces between water and ethanol are made simultaneously.

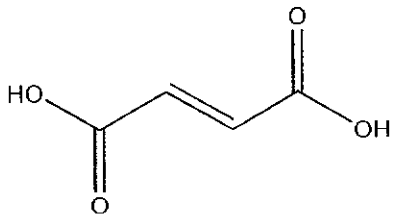
The boiling point of water is 100 °C. The boiling point of ethanol is 78 °C.

Which row is correct?

	initial temperature of **mixture**	boiling point of **mixture**
A	above 20 °C	above 78 °C
B	above 20 °C	below 78 °C
C	below 20 °C	above 100 °C
D	below 20 °C	below 100 °C

7 The pK_a and solubility values of maleic acid and fumaric acid are as follows:





	maleic acid	fumaric acid
pK_{a1}	1.94	3.03
pK_{a2}	6.22	4.54
solubility / g per 100g water	78.8	0.49

Which statements are correct?

1 The pK_{a1} value of maleic acid is less than the pK_{a1} value of fumaric acid because the conjugate base of maleic acid can form intramolecular hydrogen bond, while that of fumaric acid cannot form such intramolecular hydrogen bond.

2 The pK_{a1} value of maleic acid is less than the pK_{a1} value of fumaric acid because maleic acid is much more soluble in water than fumaric acid.

3 The pK_{a2} value of maleic acid is greater than the pK_{a2} value of fumaric acid because intramolecular hydrogen bond prevents the conjugate base of maleic acid from deprotonating the second hydrogen atom.

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

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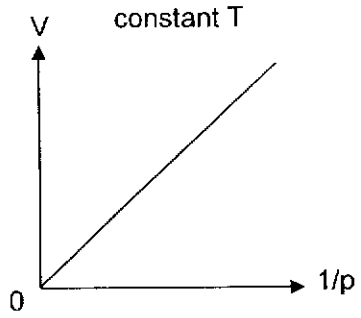
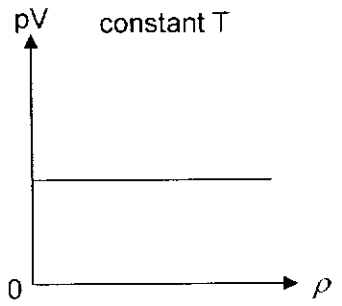
8 Which diagram **does not** describe the behaviour of a fixed mass of an ideal gas?
(ρ = density of the gas, T = temperature measured in K)

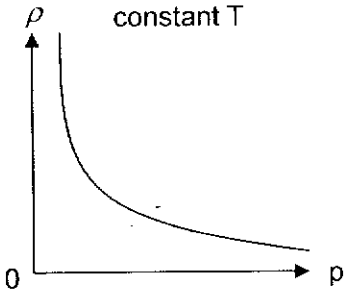
A



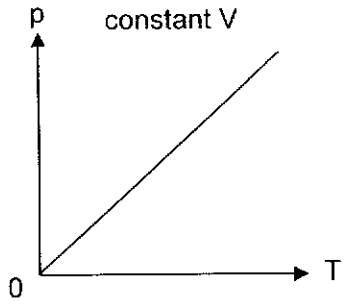
B



C



D



9 Which equation corresponds to the enthalpy change stated?

A	$H_2O(l) \rightarrow 2H(g) + O(g)$	ΔH = 2 × Bond Energy (O–H)
B	$\frac{1}{2} Cl_2(g) \rightarrow Cl^-(aq)$	$\Delta H_{formation}(Cl^-(aq))$
C	$CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g)$	$\Delta H_{combustion}(CO_2(g))$
D	$Na^+(g) \rightarrow Na^+(aq)$	$\Delta H_{solution}(Na^+(g))$

10 Given the following data in kJ mol^{-1}

enthalpy change of atomisation of Na(s)	+107
electron affinity of Cl atom	–349
enthalpy change of formation of NaCl(s)	–411
enthalpy change of atomisation of Cl(g)	+122
1st IE of Na atom	+494

What is the lattice energy of NaCl(s) in kJ mol^{-1}?

A –785 **B** –907 **C** –1269 **D** –1483

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11 Trouton's rule states that the entropy change of vaporisation is about +85 J K^{-1} mol^{-1} for various kinds of liquids.

Propan-1-ol boils at 371 K and its enthalpy change of vaporisation is +47 kJ mol^{-1}.

Which statement is correct?

A Entropy change of vaporisation of propan-1-ol cannot be calculated because there is no data on Gibbs free energy change of vaporisation of propan-1-ol.

B Entropy change of vaporisation of propan-1-ol is +85 J mol^{-1} K^{-1}.

C Entropy change of vaporisation of propan-1-ol is +127 J mol^{-1} K^{-1} which is more positive than +85 J mol^{-1} K^{-1} because of the strong hydrogen bonds between molecules.

D Entropy change of vaporisation of propan-1-ol is +127 J mol^{-1} K^{-1} which is more positive than +85 J mol^{-1} K^{-1} because of the weak instantaneous dipole induced dipole attraction between molecules.

12 Ethyl ethanoate undergoes a slow acid-catalysed hydrolysis in water.

$$CH_3CO_2CH_2CH_3 + H_2O \xrightarrow{H^+} CH_3CO_2H + CH_3CH_2OH$$

The rate equation is found to be

$$\text{rate} = k[CH_3CO_2CH_2CH_3][H^+]$$

When 0.1 mol dm^{-3} of HC*l* is reacted with 0.2 mol dm^{-3} of ethyl ethanoate, the half-life was found to be 62 min.

Another reaction was carried out with 0.2 mol dm^{-3} of HC*l* and 0.2 mol dm^{-3} of ethyl ethanoate.

How long does it take for the concentration of ethyl ethanoate to fall to 0.025 mol dm^{-3}?

A 31 min **B** 62 min **C** 93 min **D** 124 min

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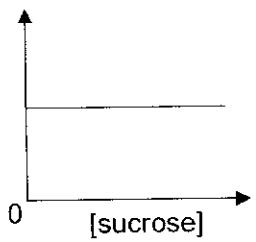
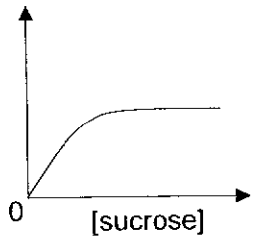
13 Sucrase is a digestive enzyme that catalyses the hydrolysis of sucrose to fructose and glucose. In an experiment, the amount of sucrase and the temperature of the reaction mixture is kept constant.

Which graph is correct?

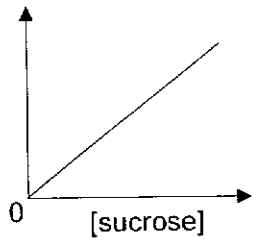
A



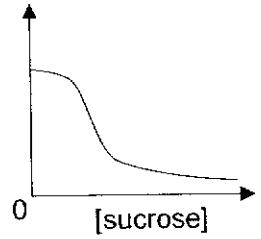
C



B



D



14 Highly toxic disulfur decafluoride, S_2F_{10}, decomposes by a free-radical process.

$$S_2F_{10}(g) \rightleftharpoons SF_4(g) + SF_6(g)$$

Some S_2F_{10} was placed in a 2.0 dm^3 flask and heated to 110 °C to reach equilibrium. The equilibrium concentration of S_2F_{10} was found to be 0.6 mol dm^{-3}. More S_2F_{10} was then added and the new equilibrium concentration of S_2F_{10} was 2.6 mol dm^{-3}.

What is the change in concentration of S_2F_{10} that occurred in terms of the equilibrium constant, K_c, of the decomposition reaction when more S_2F_{10} was added?

A $(0.6K_c)^{0.5} - (2.6K_c)^{0.5}$

B $(2.6K_c)^{0.5} - (0.6K_c)^{0.5}$

C $(2.4K_c)^{0.5} - (10.4K_c)^{0.5}$

D $(10.4K_c)^{0.5} - (2.4K_c)^{0.5}$

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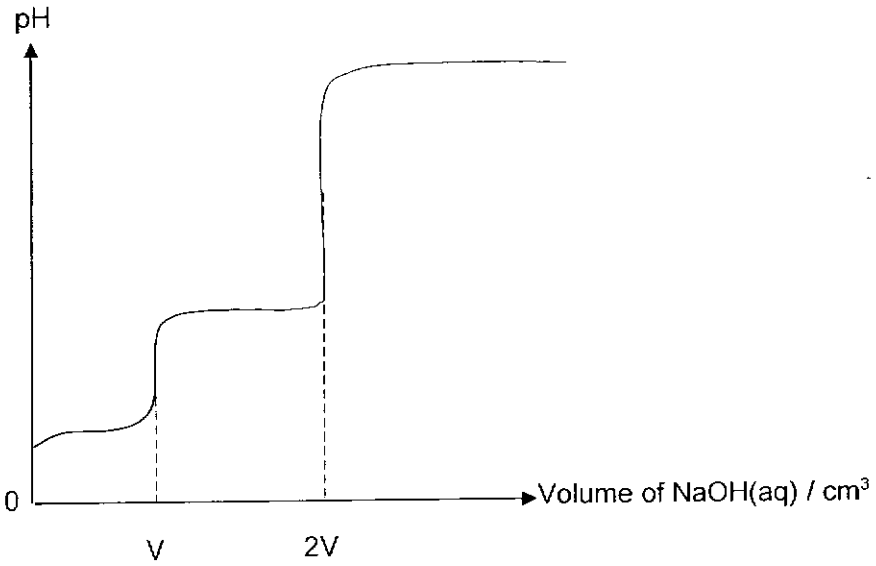
15 Ethanedioic acid has these pK_a values: pK_{a1} = 1.25 and pK_{a2} = 4.14.

The titration curve below shows how the pH changes when 0.10 mol dm^{-3} aqueous sodium hydroxide is added to 25.0 cm^3 of 0.10 mol dm^{-3} ethanedioic acid.



Which statement is correct?

A The pH of ethanedioic acid is 1.03 before NaOH(aq) is added.

B The pH of solution mixture is 1.15 when 12.50 cm^3 of NaOH(aq) is added,.

C The pH of solution mixture is 3.54 when 30.00 cm^3 of NaOH(aq) is added.

D Methyl orange can be used as pH indicator for the second endpoint.

16 The numerical value of solubility product of silver chromate(VI), Ag_2CrO_4 is 2.5×10^{-22} at 25 °C.

Which statement is correct?

A The units of solubility product of silver chromate(VI) are $mol^2\ dm^{-6}$.

B The solubility of silver chromate(VI) is 3.97×10^{-8} mol dm^{-3}.

C Addition of aqueous sodium hydroxide will increase the solubility product of silver chromate(VI).

D Addition of aqueous sodium hydroxide will decrease the solubility of silver chromate(VI).

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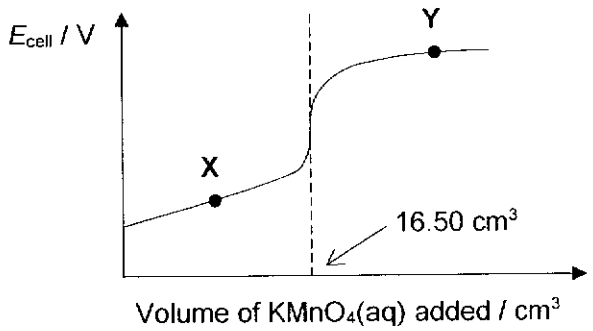
17 *Use of Data Booklet is relevant to this question.*

Iron(II) salts are often used as a dietary supplement to help cure anaemia. A pill was dissolved in 10 cm^3 of dilute sulfuric acid and titrated against 0.02 mol dm^{-3} $KMnO_4(aq)$.

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

The E_{cell} of the solution mixture was measured against a standard hydrogen electrode and the following graph was obtained.



Which statements are correct?

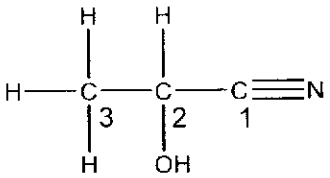
1 At point **X**, E_{cell} = +0.77 V.

2 At point **Y**, E_{cell} = +1.52 V.

3 The pill contains 1.65×10^{-3} mole of Fe^{2+}.

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

18 2-hydroxypropanenitrile has the following structure.



Which row correctly describes the bonding and hybridisation in the molecule?

	number of π bonds	hybridisation of C1 atom	hybridisation of N atom	hybridisation of O atom
A	2	sp	sp	sp^3
B	2	sp	sp^3	sp^2
C	4	sp^2	sp^2	sp^2
D	4	sp^2	sp^3	sp

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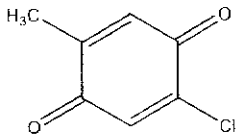
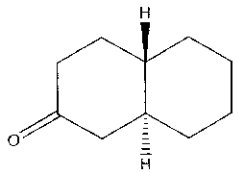
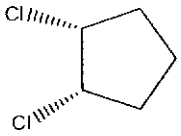
19 Which of the following molecules are meso compounds?

1 

2 

3 

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

20 CH_3F and CI_2 are mixed together in the presence of sunlight.

Which statements are correct?

1 F• free radicals are produced.
2 Hydrogen gas is produced.
3 The reaction involves homolytic fission and σ bond formation.

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

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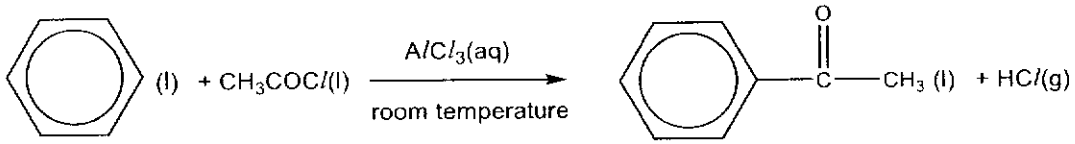
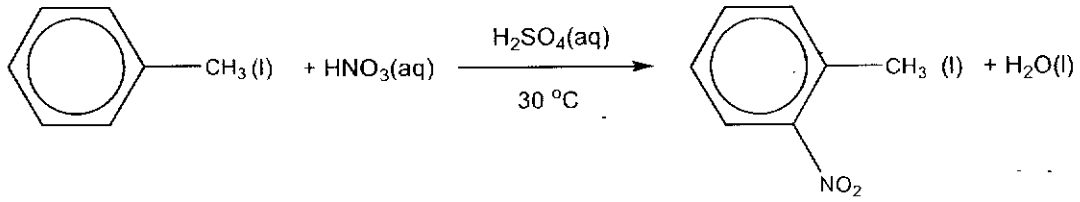
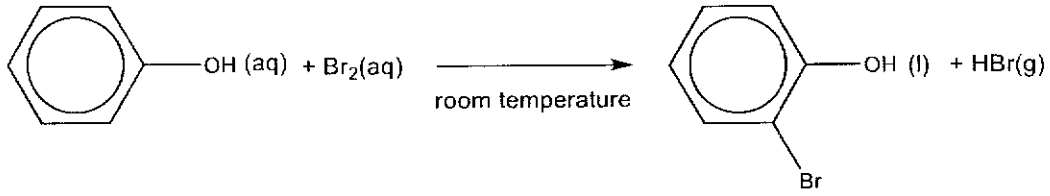
21 Which of the following transformation has a set of conditions that is **not** correct?

1 

2 

3 

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

22 A student added aqueous silver nitrate to bromoethane, bromoethene and bromobenzene.

Which statements are correct?

1 White precipitate forms for bromoethane.
2 Cream precipitate forms for bromoethene.
3 No precipitate forms for bromobenzene.

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

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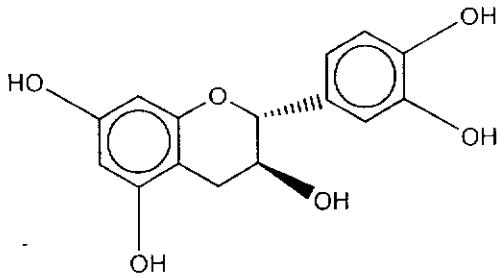
23 Catechin is an antioxidant found in green tea, chocolate and peaches.



Catechin

The C–O–C bond is inert.

Which statement is correct?

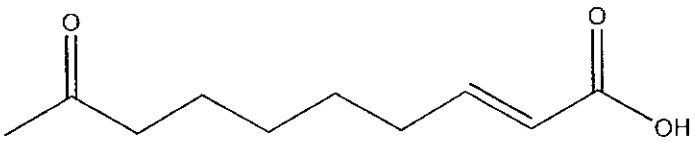
A 1 mol of catechin reacts with 5 mol of aqueous sodium hydroxide.

B 1 mol of catechin reacts with sodium to produce 5 mol of hydrogen gas.

C 1 mol of catechin reacts with 5 mol of aqueous bromine.

D A ketone functional group is produced when catechin is oxidised by hot acidified $KMnO_4(aq)$.

24 Queen honeybee secretes "queen substance" that is eaten by worker bees. This prevents them from producing rival queen bees in the same colony. The "queen substance" is 9-oxo-2-decenoic acid.



9-oxo-2-decenoic acid

What is the number of hydrogen atoms added per molecule of "queen substance" for the following reactions?

	reducing agent	number of hydrogen atoms added per molecule of queen substance
1	H_2, Pt	6
2	$LiAlH_4$ in dry ether	4
3	$NaBH_4$ in methanol	2

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

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25 Which of the following reagents and conditions are appropriate for making methanoic acid from methanol?

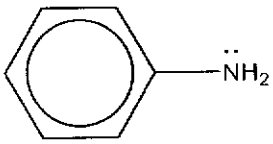
A $K_2Cr_2O_7(aq)$, dilute $H_2SO_4(aq)$, heat with distillation

B $K_2Cr_2O_7(aq)$, dilute $H_2SO_4(aq)$, heat under reflux

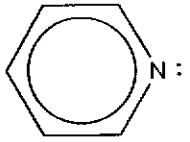
C $K_2Cr_2O_7(aq)$, dilute $HCl(aq)$, heat under reflux

D $KMnO_4(aq)$, dilute $H_2SO_4(aq)$, heat under reflux

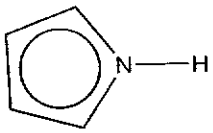
26 Consider the following compounds.



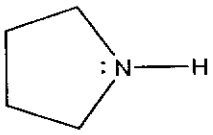
phenylamine



pyridine



pyrrole



pyrrolidine

Which of the following shows the correct order of decreasing pK_b value?

A pyrrole > phenylamine > pyridine > pyrrolidine

B pyrrolidine > pyridine > phenylamine > pyrrole

C pyrrole > phenylamine > pyrrolidine > pyridine

D phenylamine > pyridine > pyrrole > pyrrolidine

27 A particular section of keratin polypeptide was digested with two enzymes.

The first enzyme digests at the carboxyl end of leucine and yields the following peptides:

glu-ala
val-leu
glu-asp-thr-leu
ala-glu-leu

The second enzyme digests at the carboxyl end of glutamic acid and yields the following peptides:

ala
val-leu-glu
asp-thr-leu-ala-glu
leu-glu

What is the primary structure in this section of polypeptide chain?

A ala-glu-leu-glu-asp-thr-leu-val-leu-glu-ala

B val-leu-glu-asp-thr-leu-ala-glu-leu-glu-ala

C glu-asp-thr-leu-ala-glu-leu-val-leu-glu-ala

D glu-ala-ala-glu-leu-glu-asp-thr-leu-val-leu

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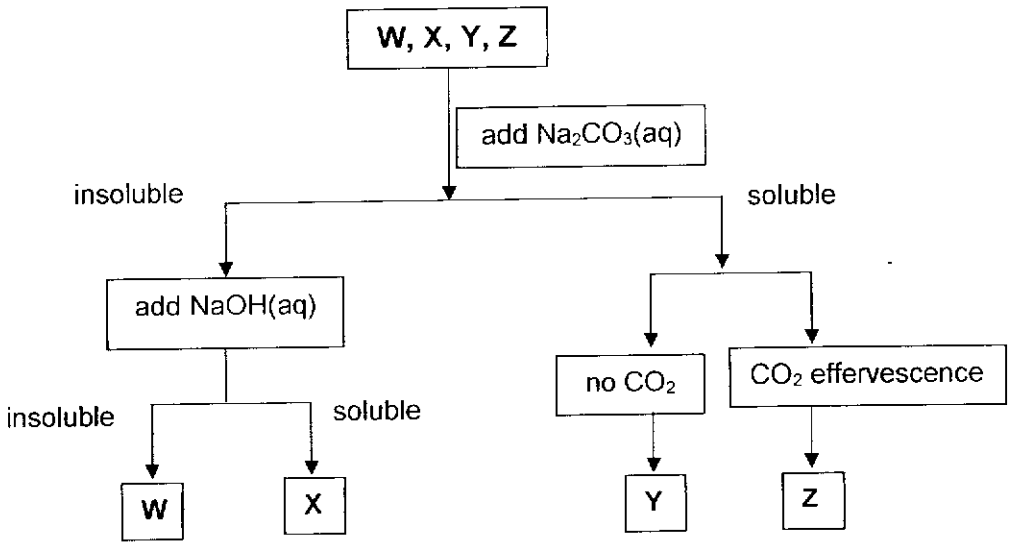
28 The labels of four containers containing NaCl, $AlCl_3$, Al_2O_3 and SiO_2 were detached from the containers. The compounds could be identified using the following flowchart.



What are **W**, **X**, **Y** and **Z**?

	W	X	Y	Z
A	SiO_2	Al_2O_3	NaCl	$AlCl_3$
B	Al_2O_3	SiO_2	NaCl	$AlCl_3$
C	NaCl	$AlCl_3$	SiO_2	Al_2O_3
D	SiO_2	Al_2O_3	$AlCl_3$	NaCl

29 Which of the following statements about Group 2 elements is **not** correct?

A The reactivity with cold water increases down the group.

B The thermal stability of the carbonate increases down the group.

C The solubility of the hydroxide decreases down the group.

D The solubility of the sulfate decreases down the group.

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30 A mixture of two halogens was reacted with excess aqueous sodium thiosulfate. The resulting solution was colourless. When excess aqueous barium nitrate was added, precipitate **X** was formed.

Precipitate **X** was then filtered off and the filtrate was treated with excess aqueous silver nitrate. Some precipitates were formed and then filtered off. Excess dilute aqueous ammonia was added to wash this residue. The remaining residue was precipitate **Y** that dissolved in excess concentrated ammonia. The filtrate was treated with excess dilute nitric acid to give precipitate **Z**.

What are **X**, **Y** and **Z**?

	X	**Y**	**Z**
A	BaS_4O_6	AgI	AgBr
B	BaS_2O_3	AgBr	AgCl
C	$BaSO_4$	AgI	AgBr
D	$BaSO_4$	AgBr	AgCl

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ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY **9729/01**
Higher 2

Paper 1 Multiple Choice

14 September 2021
1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

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

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

The use of an approved scientific calculator is expected, where appropriate.

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

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1 In an organic synthesis, a 62% yield of product is achieved.

Which conversions are consistent with the given information?

1 74 g of butan-2-ol (M_r = 74.0) → 44.64 g of butanone (M_r = 72.0)

2 72 g of butanal (M_r = 72.0) → 45.88 g of butan-1-ol (M_r = 74.0)

3 56 g of but-2-ene (M_r = 56.0) → 37.20 g of ethanoic acid (M_r = 60.0)

A 1, 2 and 3

B* 1 and 2 only

C 2 and 3 only

D 1 only

Answer B

62% yield $\Rightarrow \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 = 62\%$

Option 1
$CH_3CH(OH)CH_2CH_3 \rightarrow CH_3COCH_2CH_3$ $\frac{74}{74} = 1$ mol $\quad\quad$ $\frac{44.64}{72} = 0.62$ mol
% yield = $\frac{0.62}{1} \times 100 = 62$ %
correct

Option 2
$CH_3CH_2CH_2CHO \rightarrow CH_3CH_2CH_2CH_2OH$ $\frac{72}{72} = 1$ mol $\quad\quad$ $\frac{45.88}{74} = 0.62$ mol
% yield = $\frac{0.62}{1} \times 100 = 62$ %
correct

Option 3
$CH_3CH{=}CHCH_3 \rightarrow 2CH_3COOH$ $\frac{56}{56} = 1$ mol $\quad\quad$ $\frac{37.2}{60} = 0.62$ mol
% yield = $\frac{0.62}{2} \times 100 = 31$ %
Incorrect

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

Sodium percarbonate, $x(Na_2CO_3).y(H_2O_2)$ is a chemical that is used in cleaning powders. When dissolved in water, it releases hydrogen peroxide and sodium carbonate, both of which are useful cleaning agents.

A sample of 10.0 cm^3 of 0.100 mol dm^{-3} sodium percarbonate requires 20.0 cm^3 of 0.100 mol dm^{-3} of acidified KI before the end point of titration is reached.

Another identical sample releases 48.0 cm^3 of carbon dioxide at room conditions on reaction with excess acid.

What are the values of ***x*** and ***y*** respectively?

	x	***y***
A*	2	1
B	3	2
C	2	3
D	3	1

Answer A

Amount of sodium percarbonate = 10/1000 x 0.10 = 0.001 mol
As 1 mole of sodium percarbonate will produce y mole of H_2O_2 and x mole of Na_2CO_3
Amount of H_2O_2 = 0.001y mol
Amount of Na_2CO_3 = 0.001x mol

$H_2O_2 + 2H^+ + 2I^- \rightarrow I_2 + 2H_2O$
Amount of KI reacted = 20/1000 x 0.100 = 0.002 mol
Since KI: H_2O_2 is 2:1,
Amount of H_2O_2 = 0.001 mol, thus y = 1

$Na_2CO_3 + 2H^+ \rightarrow H_2O + CO_2 + 2Na^+$
Amount of carbon dioxide released = 48.0/24000 = 0.002 mol
Since Na_2CO_3: CO_2 is 1:1

Amount of Na_2CO_3 = 0.002 mol, thus x =2

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3 An ion X^{2+} contains 24 protons.

What is the electronic configuration of X^{3+}?

A* $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$

B $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^4$

C $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$

D $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

Answer A

X contains 24 electrons.

Electronic configuration of X is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^4\ 4s^2$

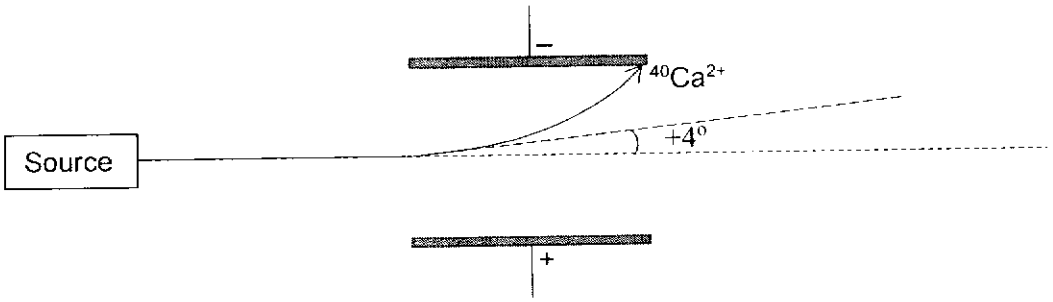
X^{2+} contains 22 electrons.

Electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^4$

Loss of 1 electron from X^{2+} leads to the formation of X^{3+}.

Hence, electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$

4 A sample of the element calcium was vaporised, ionised and passed through an electric field. It was observed that a beam of $^{40}Ca^{2+}$ particles gave an angle of deflection of +4°.



Assuming an identical set of experimental conditions, by what angle would a beam of $^{19}F^-$ particles be deflected?

A +2° **B** – 2° **C** +4° **D*** – 4°

Solution

Angle of Deflection $\propto \frac{Charge}{Mass}$

For $^{40}Ca^{2+}$, $+4^o \propto \frac{+2}{40}$

and therefore for $^{19}F^-$, $\frac{-1}{19} \propto -4^o$

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5 *Use of Data Booklet is relevant to this question.*

X, **Y** and **Z** are isotopes of three different elements. An isotope of Argon has a mass number of 41 and the same number of neutrons in the nucleus as each of the isotopes **X**, **Y** and **Z**.

The species Ar, $\mathbf{X}^{+}$, $\mathbf{Y}^{2+}$ and $\mathbf{Z}^{3+}$ all contain the same number of electrons.

What are the mass numbers of **X**, Y and **Z**?

	X	Y	Z
A	42	41	40
B	40	41	42
C	44	43	42
D*	42	43	44

Solution

	$^{41}_{18}Ar$	$^{42}_{19}K^{+}$	$^{43}_{20}Ca^{2+}$	$^{44}_{21}Sc^{3+}$
No. of electrons	18	18	18	18
No. of neutrons	23	23	23	23

6 Equimolar amounts of the liquids, water and ethanol, are mixed together at 20 °C. The original intermolecular forces in the pure liquids are disrupted and weaker intermolecular forces between water and ethanol are made simultaneously.

The boiling point of water is 100 °C. The boiling point of ethanol is 78 °C.

Which row is correct?

	initial temperature of **mixture**	boiling point of **mixture**
A	above 20 °C	above 78 °C
B	above 20 °C	below 78 °C
C	below 20 °C	above 100 °C
D*	below 20 °C	below 100 °C

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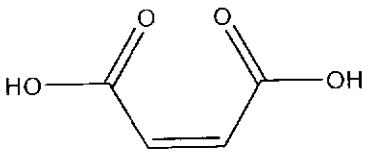
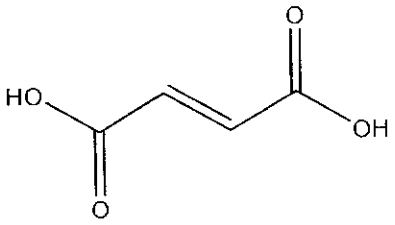
Solution
The reaction is endothermic because weaker intermolecular forces are made.
Therefore the initial temperature of mixture is below 20 °C.
Molecules will vaporise more easily since weaker intermolecular forces are made.
Therefore the boiling point of mixture is below 100 °C.

7 The pK_a and solubility values of maleic acid and fumaric acid are as follows:





	maleic acid	fumaric acid
pK_{a1}	1.94	3.03
pK_{a2}	6.22	4.54
solubility / g per 100g water	78.8	0.49

Which statements are correct?

1 The pK_{a1} value of maleic acid is less than the pK_{a1} value of fumaric acid because the conjugate base of maleic acid can form intramolecular hydrogen bond, while that of fumaric acid cannot form such intramolecular hydrogen bond.

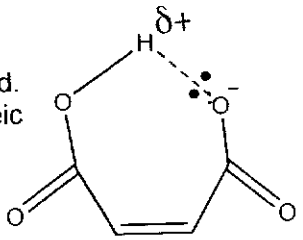
2 The pK_{a1} value of maleic acid is less than the pK_{a1} value of fumaric acid because maleic acid is much more soluble in water than fumaric acid.

3 The pK_{a2} value of maleic acid is greater than the pK_{a2} value of fumaric acid because intramolecular hydrogen bond prevents the conjugate base of maleic acid from deprotonating the second hydrogen atom.

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

Solution

Option 1 is correct:
Conjugate base of maleic acid can form intramolecular hydrogen bond. Therefore it is stable, and more readily formed than that of fumaric acid. Maleic acid is more acidic than fumaric acid.
Hence pKa_1 is lower.



Option 3 is correct:
Conjugate base of maleic acid can form intramolecular hydrogen bond. It is stable, and not likely to lose the second hydrogen atom as H^+. Maleic acid is less acidic than fumaric acid.
Hence pKa_2 is higher.

Option 2 is wrong:
Acid Strength does not depend on solubility.

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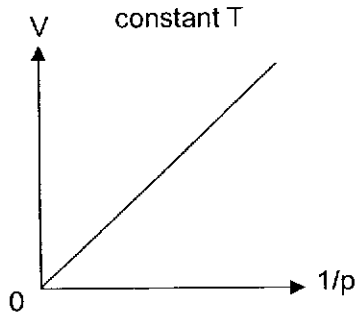
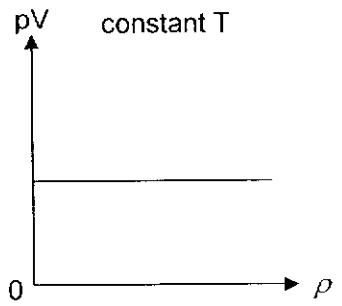
8 Which diagram **does not** describe the behaviour of a fixed mass of an ideal gas?
(ρ = density of the gas, T = temperature measured in K)

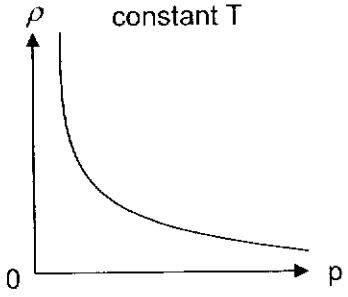
A



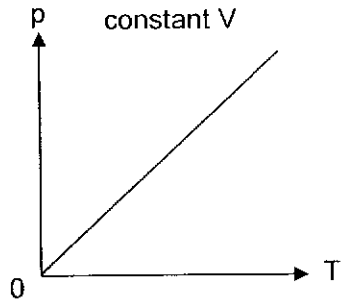
B



C*



D



Answer C

For a given mass of gas, the no. of moles of gas, n, will be constant since Mr unchanged.

pV = nRT

Option A: $V = nRT\left(\frac{1}{P}\right)$

V = constant x $\left(\frac{1}{p}\right)$, at constant T for a given mass of gas.

Hence, $V \propto \left(\frac{1}{p}\right)$

Option B: pV = nRT

pV = constant, at constant T for given mass of gas, regardless of changes in P, V or ρ

Option C: $pV = nRT = \frac{m}{M_r}RT$

$\rho = \frac{m}{V} = \frac{M_r}{RT}(P)$ = constant x (P), at constant T for a given mass of gas.

Hence, $\rho \propto P$ and it should be a Y = mX + C linear graph, passing through origin.

Option D:

$P = \frac{nR}{V}(T)$

P= constant x (T), at constant V for a given mass of gas.

Hence, $P \propto T$

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9 Which equation corresponds to the enthalpy change stated?

A	$H_2O(l) \rightarrow 2H(g) + O(g)$	ΔH = 2 × Bond Energy (O–H)
B*	$\frac{1}{2}\ Cl_2(g) \rightarrow Cl^-(aq)$	$\Delta H_{formation}(Cl^-(aq))$
C	$CO(g) + \frac{1}{2}\ O_2(g) \rightarrow CO_2(g)$	$\Delta H_{combustion}(CO_2(g))$
D	$Na^+(g) \rightarrow Na^+(aq)$	$\Delta H_{solution}(Na^+(g))$

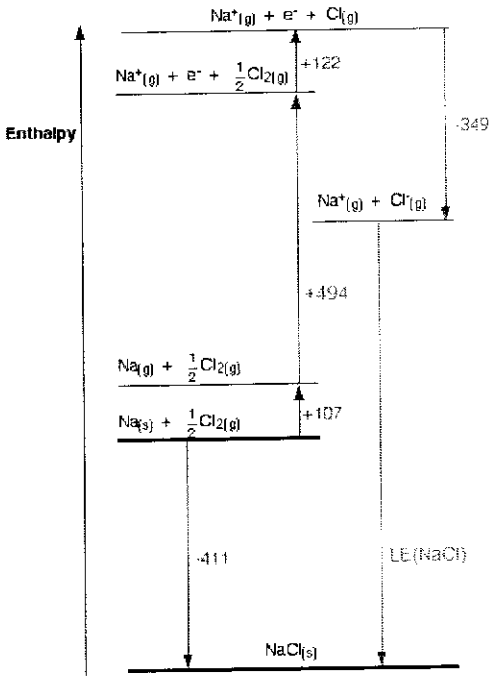
Solution
Option A is wrong:
It should be: $H_2O(g) \rightarrow 2H(g) + O(g)$
Option B is correct:
Enthalpy change when one mole of the substance is formed from its elements.
Option C is wrong:
It should be: $\Delta H_{combustion}(CO(g))$
Option D is wrong:
It should be: $\Delta H_{hydration}(Na^+(g))$

10 Given the following data in kJ mol^{-1}

enthalpy change of atomisation of Na(s)	+107
electron affinity of Cl atom	–349
enthalpy change of formation of NaCl(s)	–411
enthalpy change of atomisation of Cl(g)	+122
1st IE of Na atom	+494

What is the lattice energy of NaCl(s) in kJ mol^{-1}?

A* –785 **B** –907 **C** –1269 **D** –1483



By Hess' Law

LE(NaCl(s))

= –411 – [+107 + 494 + 122 + (–349)]

= –785 kJ mol^{-1}

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11 Trouton's rule states that the entropy change of vaporisation is about +85 J K^{-1} mol^{-1} for various kinds of liquids.

Propan-1-ol boils at 371 K and its enthalpy change of vaporisation is +47 kJ mol^{-1}.

Which statement is correct?

A Entropy change of vaporisation of propan-1-ol cannot be calculated because there is no data on Gibbs free energy change of vaporisation of propan-1-ol.

B Entropy change of vaporisation of propan-1-ol is +85 J mol^{-1} K^{-1}.

C* Entropy change of vaporisation of propan-1-ol is +127 J mol^{-1} K^{-1} which is more positive than +85 J mol^{-1} K^{-1} because of the strong hydrogen bonds between molecules.

D Entropy change of vaporisation of propan-1-ol is +127 J mol^{-1} K^{-1} which is more positive than +85 J mol^{-1} K^{-1} because of the weak instantaneous dipole induced dipole attraction between molecules.

Solution

Boiling is an equilibrium process between $H_2O(l)$ and $H_2O(g)$.

$\Delta G = 0$

$\Delta H - T\Delta S = 0$

$47{,}000 - 371 \times \Delta S = 0$

$\Delta S = +127$ J mol^{-1} K^{-1}

Option C is correct. Most gases have the same entropy values. Having a more positive ΔS value means that propan-1-ol has lower entropy value in the liquid state (or more orderly). This is due to the ability of propan-1-ol molecules being able to form hydrogen bonds between molecules.

12 Ethyl ethanoate undergoes a slow acid-catalysed hydrolysis in water.

$$CH_3CO_2CH_2CH_3 + H_2O \xrightarrow{H^+} CH_3CO_2H + CH_3CH_2OH$$

The rate equation is found to be

$$\text{rate} = k[CH_3CO_2CH_2CH_3][H^+]$$

When 0.1 mol dm^{-3} of HC*l* is reacted with 0.2 mol dm^{-3} of ethyl ethanoate, the half-life was found to be 62 min.

Another reaction was carried out with 0.2 mol dm^{-3} of HC*l* and 0.2 mol dm^{-3} of ethyl ethanoate.

How long does it take for the concentration of ethyl ethanoate to fall to 0.025 mol dm^{-3}?

A 31 min **B** 62 min **C*** 93 min **D** 124 min

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Answer C

When [HC*l*] = [H^+] = 0.1 mol dm^{-3},
$t_{½}$ = 62 min.

When [HC*l*] = [H^+] = 0.2 mol dm^{-3} (increased by two times),
$t_{½}$ = 31 min.

For [$CH_3CO_2CH_2CH_3$] to fall to 0.025 mol dm^{-3}, three $t_{½}$ are required.

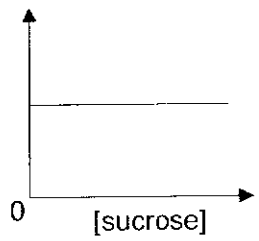
0.2 → 0.1 → 0.05 → 0.025

Time taken = 3 x 31 = 93 min

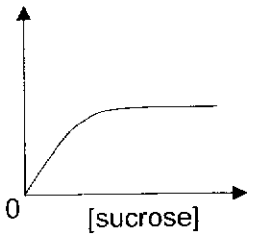
13 Sucrase is a digestive enzyme that catalyses the hydrolysis of sucrose to fructose and glucose. In an experiment, the amount of sucrase and the temperature of the reaction mixture is kept constant.

Which graph is correct?

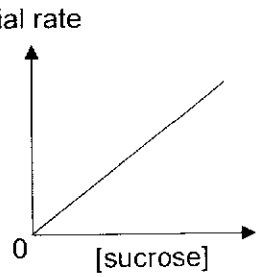
A



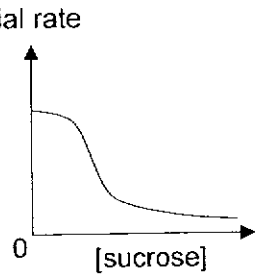
C*



B



D



Solution

Option C is correct.
At low [sucrose], the enzymes are not saturated with sucrose substrate molecules. Increasing [sucrose] will increase the rate. Reaction is first order at low [sucrose].
At high [sucrose], the enzymes are saturated with sucrose substrate molecules. Increasing [sucrose] further will not increase the rate. Reaction is zero order at high [sucrose].

Option A is wrong. It is a graph for zero-order reaction.
Option B is wrong. It is a graph for first-order reaction.
Option D is wrong. It is a graph for autocatalytic reaction.

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14 Highly toxic disulfur decafluoride, S_2F_{10}, decomposes by a free-radical process.

$$S_2F_{10}(g) \rightleftharpoons SF_4(g) + SF_6(g)$$

Some S_2F_{10} was placed in a 2.0 dm^3 flask and heated to 110 °C to reach equilibrium. The equilibrium concentration of S_2F_{10} was found to be 0.6 mol dm^{-3}. More S_2F_{10} was then added and the new equilibrium concentration of S_2F_{10} was 2.6 mol dm^{-3}.

What is the change in concentration of S_2F_{10} that occurred in terms of the equilibrium constant, K_c, of the decomposition reaction when more S_2F_{10} was added?

A $(0.6K_c)^{0.5} - (2.6K_c)^{0.5}$

B* $(2.6K_c)^{0.5} - (0.6K_c)^{0.5}$

C $(2.4K_c)^{0.5} - (10.4K_c)^{0.5}$

D $(10.4K_c)^{0.5} - (2.4K_c)^{0.5}$

Answer B

Calculating the equilibrium $[SF_4]$ and $[SF_6]$ when the equilibrium $[S_2F_{10}]$ = 0.6 mol dm^{-3}

Let the equilibrium $[SF_4]$ = a

Equilibrium $[SF_6]$ = equilibrium $[SF_4]$ = a

$$K_c = \frac{a^2}{0.6}$$

$a = (0.6\ K_c)^{0.5}$

Calculating the equilibrium $[SF_4]$ and $[SF_6]$ when more S_2F_{10} was added and the equilibrium $[S_2F_{10}]$ = 2.6 mol dm^{-3}

Let the equilibrium $[SF_4]$ = b

Equilibrium $[SF_6]$ = equilibrium $[SF_4]$ = b

$$K_c = \frac{b^2}{2.6}$$

$b = (2.6\ K_c)^{0.5}$
$[S_2F_{10}]$ reacted = additional $[SF_4]$ produced = $b - a = (2.6\ K_c)^{0.5} - (0.6\ K_c)^{0.5}$

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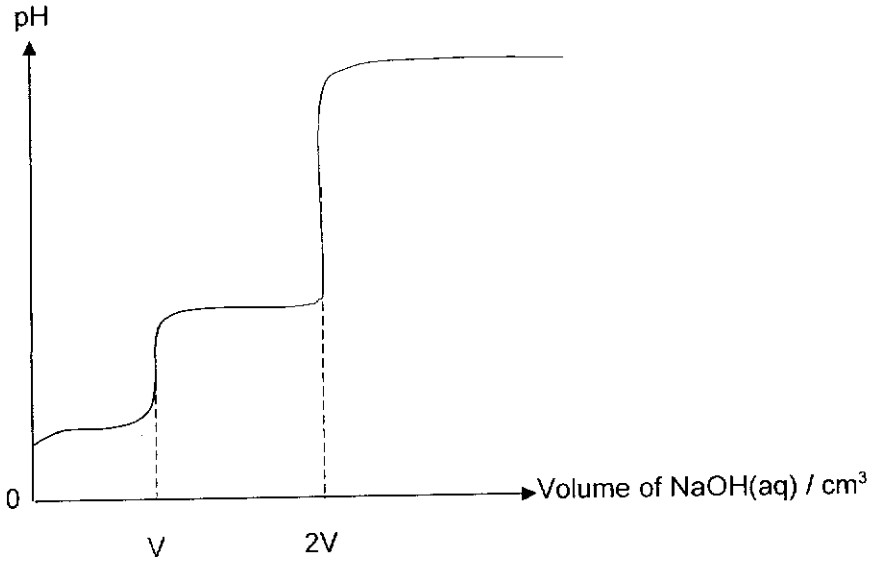
15 Ethanedioic acid has these pK_a values: pK_{a1} = 1.25 and pK_{a2} = 4.14.

The titration curve below shows how the pH changes when 0.10 mol dm^{-3} aqueous sodium hydroxide is added to 25.0 cm^3 of 0.10 mol dm^{-3} ethanedioic acid.



Which statement is correct?

A The pH of ethanedioic acid is 1.03 before NaOH(aq) is added.

B The pH of solution mixture is 1.15 when 12.50 cm^3 of NaOH(aq) is added,.

C* The pH of solution mixture is 3.54 when 30.00 cm^3 of NaOH(aq) is added.

D Methyl orange can be used as pH indicator for the second endpoint.

Solution

Option A is wrong.

	HOOC–COOH(aq)	⇌	HOOC–COO$^-$(aq)	+	H$^+$(aq)
Initial	0.10		0		0
Change	–x		+x		+x
Eqm	0.10 – x		x		x

$K_{a1} = x^2 / (0.10 - x)$
$x = 0.0750$
$[H^+] = 0.0750$
$pH = -\log [H^+] = 1.125$

Option B is wrong.
At Max Buffer Capacity, pH = pK_{a1} = 1.25

Option C is correct.
Amount of $^-$OOC–COO$^-$ produced = Amount of HOOC–COO$^-$ reacted
= (30.00 – 25.00) ÷ 1000 x 0.10 = 0.0005 mol
Remaining Amount of HOOC–COO$^-$ = 0.0025 – 0.0005 = 0.0020 mol
Acid Buffer: pH = pK_{a2} + log [salt] / [acid] = 4.14 + log (0.0005 / 0.055) / (0.0020 / 0.055) = 3.54

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Option D is wrong.
Sharp rise in pH from about 4.3 at second endpoint.
Working pH range of methyl orange: $3.1 < pH < 4.4$
pH range of methyl orange does not fall within the pH change at second endpoint.

16 The numerical value of solubility product of silver chromate(VI), Ag_2CrO_4 is 2.5×10^{-22} at 25 °C.

Which statement is correct?

A The units of solubility product of silver chromate(VI) are $mol^2\ dm^{-6}$.

B* The solubility of silver chromate(VI) is 3.97×10^{-8} mol dm^{-3}.

C Addition of aqueous sodium hydroxide will increase the solubility product of silver chromate(VI).

D Addition of aqueous sodium hydroxide will decrease the solubility of silver chromate(VI).

Solution

$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$

$K_{sp} = 2.5 \times 10^{-22}\ mol^3\ dm^{-9}$
$K_{sp} = [Ag^+(aq)]^2\ [CrO_4^{2-}(aq)]$
$(2x)^2(x) = 2.5 \times 10^{-22}$
$x = 3.97 \times 10^{-8}$ mol dm^{-3}
Option B is correct.

Option A is wrong.

Option C is wrong. Ksp only depends on Temperature (if $\Delta H \neq 0$)

Option D is wrong.
$Ag^+(aq) + OH^-(aq) \rightarrow AgOH(s)$
[Ag+] will decrease.
This causes the equilibrium to shift to the right: $Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$
Hence more $Ag_2CrO_4(s)$ dissolves.

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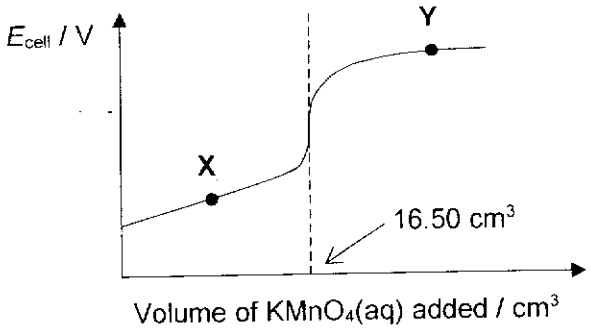
17 *Use of Data Booklet is relevant to this question.*

Iron(II) salts are often used as a dietary supplement to help cure anaemia. A pill was dissolved in 10 cm^3 of dilute sulfuric acid and titrated against 0.02 mol dm^{-3} $KMnO_4(aq)$.

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

The E_{cell} of the solution mixture was measured against a standard hydrogen electrode and the following graph was obtained.



Which statements are correct?

1 At point **X**, E_{cell} = +0.77 V.

2 At point **Y**, E_{cell} = +1.52 V.

3 The pill contains 1.65×10^{-3} mole of Fe^{2+}.

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

Solution

Option 1 is correct.
At point X, there are approximately equal concentrations of $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$.
They are at equilibrium.
$Fe^{3+}(aq) + e \rightleftharpoons Fe^{2+}(aq)$

Option 2 is correct.
At point Y, there are approximately equal concentrations of $Mn^{2+}(aq)$ and $MnO_4^-(aq)$.
They are at equilibrium.
$MnO_4^-(aq) + 8H^+(aq) + 5e \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$

Option 3 is correct.
Amount of MnO_4^- = (0.02)(16.50/1000) = 3.3×10^{-4} mol
Amount of Fe^{2+} = $5 \times 3.3 \times 10^{-4} = 1.65 \times 10^{-3}$ mol

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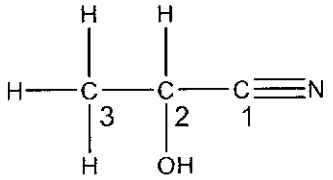
18 2-hydroxypropanenitrile has the following structure.

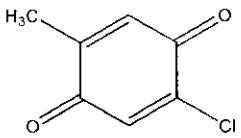


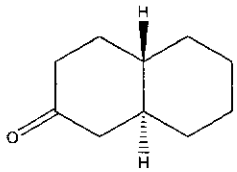
Which row correctly describes the bonding and hybridisation in the molecule?

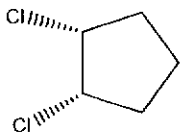
	number of π bonds	hybridisation of C1 atom	hybridisation of N atom	hybridisation of O atom
A*	2	sp	sp	sp^3
B	2	sp	sp^3	sp^2
C	4	sp^2	sp^2	sp^2
D	4	sp^2	sp^3	sp

Solution
Shape around C1 atom is LINEAR. Hence it is sp hybridised.
Shape around N atom is LINEAR (considering the lone pair on N as well). Hence it is sp hybridised.
Shape around O atom is TETRAHEDRAL (considering the two lone pairs of electrons on O as well). Hence it is sp^3 hybridised.

19 Which of the following molecules are meso compounds?

1 

2 

3 

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

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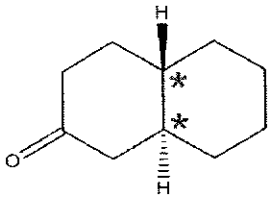
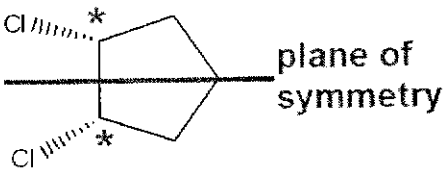
Solution

Option 1 does not have any chiral carbon.

Option 2 has two chiral carbons and no plane of symmetry.
Bulk sample is optically active.
It is not meso compound.

Option 3 has two chiral carbons and also plane of symmetry.
Bulk sample is not optically active.
It is a meso compound.





20 CH_3F and Cl_2 are mixed together in the presence of sunlight.

Which statements are correct?

1 F• free radicals are produced.

2 Hydrogen gas is produced.

3 The reaction involves homolytic fission and σ bond formation.

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

Solution

Option 1 is wrong.
C–F bond is strong and will not be broken by sunlight.

Option 2 is wrong.
H• radicals are not formed during propagation. Hence H_2 gas cannot be produced.

Option 3 is correct.

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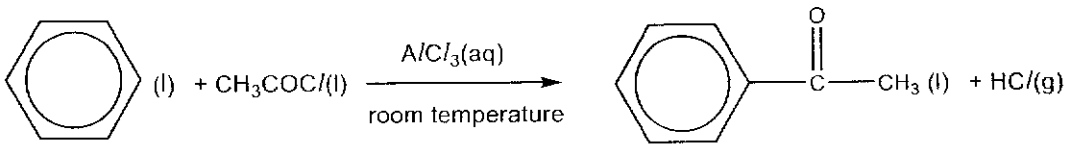
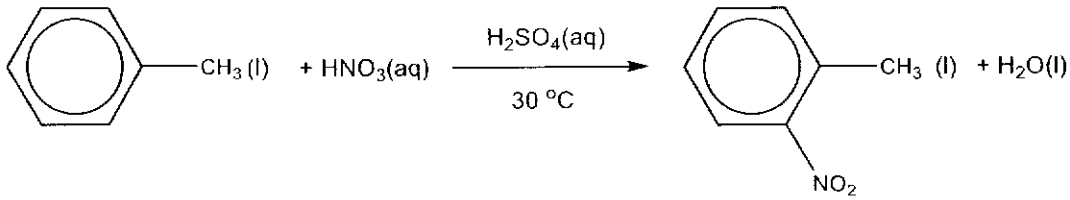
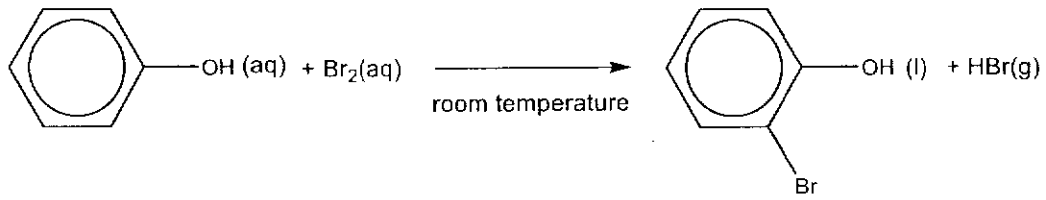
21 Which of the following transformation has a set of conditions that is **not** correct?

1 

2 

3 

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

Solution

Option 1 is wrong.
For this reaction to occur: $AlCl_3 + CH_3COCl \rightarrow CH_3CO^+ + AlCl_4^-$
Water must not be present.
If not, $AlCl_3$ will dissolve in water to give $Al^{3+}(aq)$ and $Cl^-(aq)$ ions.
There is no $AlCl_3$ halogen carrier anymore.

Option 2 is wrong.
For this reaction to occur: $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$
Water must not be present
If not $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$
$[NO_2^+]$ will be low.

Option 3 is wrong.
$Br_2(aq)$ leads to tri-substitution on phenol.
For mono-substitution on phenol, Br_2 (in CCl_4) should be used.

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22 A student added aqueous silver nitrate to bromoethane, bromoethene and bromobenzene.

Which statements are correct?

1 White precipitate forms for bromoethane.

2 Cream precipitate forms for bromoethene.

3 No precipitate forms for bromobenzene.

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

Solution

Option 1 is wrong.

$CH_3CH_2Br + H_2O \rightarrow CH_3CH_2OH + H^+ + Br^-$

$Ag^+ + Br^- \rightarrow AgBr$ (cream ppt)

Option 1 is wrong.

$CH_2=CHBr + H_2O \rightarrow$ No reaction

Partial double bond overlap for C–Br bond with C=C bond.

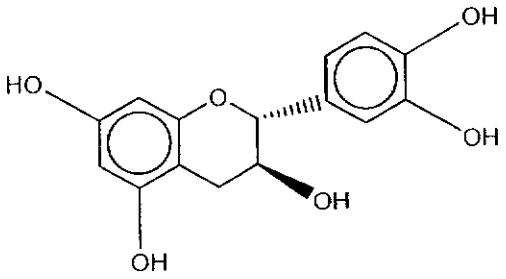
Stronger C–Br bond does not break. No ppt formed.

Option 1 is correct.

Partial double bond overlap for C–Br bond with π system of delocalised electrons in benzene ring.

Stronger C–Br bond does not break. No ppt formed.

23 Catechin is an antioxidant found in green tea, chocolate and peaches.



Catechin

The C–O–C bond is inert.

Which statement is correct?

A 1 mol of catechin reacts with 5 mol of aqueous sodium hydroxide.

B 1 mol of catechin reacts with sodium to produce 5 mol of hydrogen gas.

C* 1 mol of catechin reacts with 5 mol of aqueous bromine.

D A ketone functional group is produced when catechin is oxidised by hot acidified $KMnO_4(aq)$.

Solution

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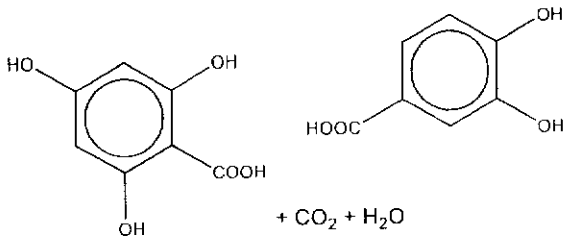
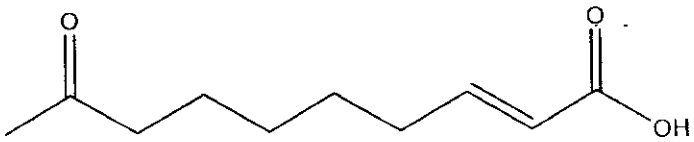
Option 1 is wrong.
4 moles of phenol react with 4 moles of NaOH(aq).
Alcohol does not react with NaOH(aq).
Option 2 is wrong.
4 moles of phenol and 1 mole of alcohol react with sodium to produce 2.5 moles of $H_2(g)$.
Option 3 is correct.
Option 4 is wrong.



24 Queen honeybee secretes "queen substance" that is eaten by worker bees. This prevents them from producing rival queen bees in the same colony. The "queen substance" is 9-oxo-2-decenoic acid.



9-oxo-2-decenoic acid

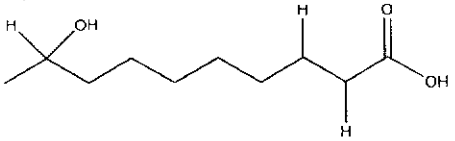
What is the number of hydrogen atoms added per molecule of "queen substance" for the following reactions?

	reducing agent	number of hydrogen atoms added per molecule of queen substance
1	H_2, Pt	6
2	$LiAlH_4$ in dry ether	4
3	$NaBH_4$ in methanol	2

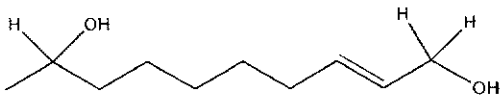
A 1, 2 and 3 **B*** 2 and 3 only **C** 2 only **D** 1 only

Solution

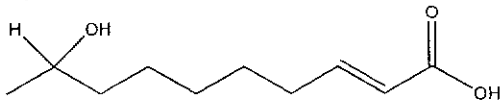
Option 1 is wrong.



Option 2 is correct.



Option 3 is correct.



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25 Which of the following reagents and conditions are appropriate for making methanoic acid from methanol?

A $K_2Cr_2O_7(aq)$, dilute $H_2SO_4(aq)$, heat with distillation

B* $K_2Cr_2O_7(aq)$, dilute $H_2SO_4(aq)$, heat under reflux

C $K_2Cr_2O_7(aq)$, dilute $HCl(aq)$, heat under reflux

D $KMnO_4(aq)$, dilute $H_2SO_4(aq)$, heat under reflux

Solution

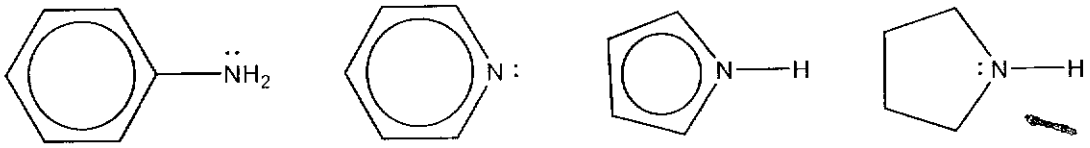
Option A is wrong.
$CH_3OH + [O] \rightarrow HCHO + H_2O$
Since HCHO has lower boiling point than CH_3OH, HCHO will be distilled over before further oxidation is possible.

Option B is correct.
$CH_3OH + [O] \rightarrow HCHO + H_2O$
$HCHO + [O] \rightarrow HCOOH$

Option C is wrong.
HCl should not be used because it will be oxidised to Cl_2 by hot $K_2Cr_2O_7(aq)$.

Option D is wrong.
$CH_3OH + [O] \rightarrow HCHO + H_2O$
$HCHO + [O] \rightarrow HCOOH$
HCOOH will be further oxidised by hot $KMnO_4(aq)$ to give CO_2 and H_2O.
$HCOOH + [O] \rightarrow H_2CO_3 \rightarrow CO_2 + H_2O$

26 Consider the following compounds.



phenylamine pyridine pyrrole pyrrolidine

Which of the following shows the correct order of decreasing pK_b value?

A* pyrrole > phenylamine > pyridine > pyrrolidine

B pyrrolidine > pyridine > phenylamine > pyrrole

C pyrrole > phenylamine > pyrrolidine > pyridine

D phenylamine > pyridine > pyrrole > pyrrolidine

Solution

HINT: Lone pair of electrons is indicated on N atom.

Huckel's rule says that (4n + 2) electrons should be in the ring, where n = 1, 2, 3 ...

Pyrrole is least basic. N atom already has 3 bonds. Its lone pair of electrons is delocalised into the ring. It is not available for protonation.

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Pyrrolidine is most basic. N atom has 3 bonds. Its lone pair of electrons is NOT delocalised into any ring. It is available for protonation. In addition, it is a secondary amine where two alkyl groups donate electrons to N atom, increasing the availability of lone pair for protonation.

Phenylamine is second least basic. The lone pair of electrons on N atom is partially delocalised into the benzene ring.

Pyridine is second most basic. N already has three bonds in the ring, with one electron delocalised into the ring. The lone pair of electrons on N atom is not part of the ring. It is available for protonation.

27 A particular section of keratin polypeptide was digested with two enzymes.

The first enzyme digests at the carboxyl end of leucine and yields the following peptides:

glu-ala
val-leu
glu-asp-thr-leu
ala-glu-leu

The second enzyme digests at the carboxyl end of glutamic acid and yields the following peptides:

ala
val-leu-glu
asp-thr-leu-ala-glu
leu-glu

What is the primary structure in this section of polypeptide chain?

A ala-glu-leu-glu-asp-thr-leu-val-leu-glu-ala

B* val-leu-glu-asp-thr-leu-ala-glu-leu-glu-ala

C glu-asp-thr-leu-ala-glu-leu-val-leu-glu-ala

D glu-ala-ala-glu-leu-glu-asp-thr-leu-val-leu

Solution

val-leu
val-leu-glu
glu-asp-thr-leu
asp-thr-leu-ala-glu
ala-glu-leu
leu-glu
glu-ala
ala
val-leu-glu-asp-thr-leu-ala-glu-leu-glu-ala

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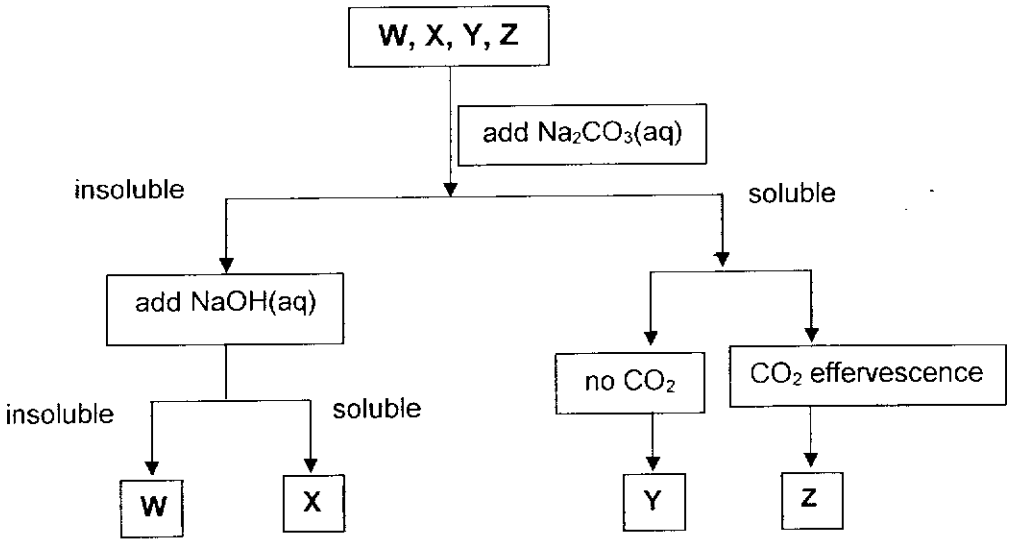
28 The labels of four containers containing NaCl, $AlCl_3$, Al_2O_3 and SiO_2 were detached from the containers. The compounds could be identified using the following flowchart.



What are **W**, **X**, **Y** and **Z**?

	W	X	Y	Z
A*	SiO_2	Al_2O_3	NaCl	$AlCl_3$
B	Al_2O_3	SiO_2	NaCl	$AlCl_3$
C	NaCl	$AlCl_3$	SiO_2	Al_2O_3
D	SiO_2	Al_2O_3	$AlCl_3$	NaCl

Solution

SiO_2 and Al_2O_3 does not dissolve in water. They do not react with Na_2CO_3(aq).

$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$
$Na^+(aq)$ is neutral. It is not acidic to react with Na_2CO_3(aq).

$AlCl_3(s) \rightarrow Al^{3+}(aq) + 3Cl^-(aq)$
$Al^{3+}(aq)$ is acidic with pH about 3.
$[Al(H_2O)_6]^{3+}(aq) \rightarrow [Al(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$
It is acidic enough to react with Na_2CO_3(aq).
$2H^+(aq) + CO_3^{2-}(aq) \rightarrow H_2CO_3(aq) \rightarrow H_2O(l) + CO_2(g)$

SiO_2 does not react with NaOH(aq). It reacts with fused NaOH.
With fused NaOH: $SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$

$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na^+(aq) + 2Al(OH)_4^-(aq)$
Note: $Al_2O_3(s)$ also reacts with HCl(aq). It is amphoteric oxide.

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29 Which of the following statements about Group 2 elements is **not** correct?

A The reactivity with cold water increases down the group.

B The thermal stability of the carbonate increases down the group.

C* The solubility of the hydroxide decreases down the group.

D The solubility of the sulfate decreases down the group.

Solution

Option A is correct.
The sea of delocalised electrons is further away from the nuclei of metal cations. There is weaker electrostatic attraction. Less energy is needed to remove these outermost electrons. Metals are more reducing down the group.

Option B is correct.
Polarising Power of Cation $\alpha \frac{Charge}{Size\ of\ Cation}$
Down the group, the cation becomes larger. Polarising power becomes weaker. It is harder to polarise and weaken the C–O bonds in CO_3^{2-} ion. The thermal stability of carbonate increases down the group.

Option C is wrong.
$\Delta H_{solution} = -LE + \Delta H_{hydration}$
Down the group, the change in LE magnitude is less than the change in $\Delta H_{hydration}$. Hence $\Delta H_{solution}$ is more negative down the group. The solubility of the hydroxide increases down the group
Note: This is the opposite of sulfates. The solubility of the sulfate decreases down the group.

Option D is correct.

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30 A mixture of two halogens was reacted with excess aqueous sodium thiosulfate. The resulting solution was colourless. When excess aqueous barium nitrate was added, precipitate **X** was formed.

Precipitate **X** was then filtered off and the filtrate was treated with excess aqueous silver nitrate. Some precipitates were formed and then filtered off. Excess dilute aqueous ammonia was added to wash this residue. The remaining residue was precipitate **Y** that dissolved in excess concentrated ammonia. The filtrate was treated with excess dilute nitric acid to give precipitate **Z**.

What are **X**, **Y** and **Z**?

	X	Y	Z
A	BaS_4O_6	AgI	AgBr
B	BaS_2O_3	AgBr	AgCl
C	$BaSO_4$	AgI	AgBr
D*	$BaSO_4$	AgBr	AgCl

Solution

When $S_2O_3^{2-}(aq)$ is added:

$4Br_2 + S_2O_3^{2-} + 5H_2O \rightarrow 8Br^- + 2SO_4^{2-} + 10H^+$

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

$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

white ppt **X**

When $AgNO_3(aq)$ is added:

$Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$

cream ppt

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

white ppt

When dilute $NH_3(aq)$ is added to wash these precipitates:

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

White ppt dissolves.

$Ag^+(aq) + 2NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq)$

Note: AgBr(s) does not dissolve in dilute $NH_3(aq)$. It dissolves in concentrated $NH_3(aq)$.

When dilute $HNO_3(aq)$ is added to the filtrate:

$H^+(aq) + NH_3(aq) \rightarrow NH_4^+(aq)$

$Ag(NH_3)_2^+(aq) \rightarrow Ag^+(aq) + 2NH_3(aq)$

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

white ppt

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

A	B	C	D
8	7	9	6

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Name	Index Number	Form Class	Tutorial Class	Subject Tutor

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY
Higher 2

9729/02

Paper 2 Structured Questions

25 August 2021
2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS CAREFULLY

Write your name, index number, form class, tutorial class and subject tutor's name on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

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.

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

For Examiner's Use	
Question no.	**Marks**
1	/ 15
2	/ 15
3	/ 12
4	/ 5
5	/ 19
6	/ 9
Presentation of answers	
TOTAL	/ 75

This document consists of **25** printed pages and **1** blank page.

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

1 Hydrobromic acid, HBr, is one of the strongest mineral acids known and is even stronger than hydrochloric acid. Both the industrial and laboratory syntheses of HBr are well documented due to the usefulness of HBr in many chemical reactions.

(a) The primary industrial preparation of HBr involves the platinum-catalysed reaction between hydrogen and bromine at temperatures between 450 K to 700 K.

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

The reaction was carried out in a 250 m^3 vessel at 334 °C.

(i) Calculate the amount of HBr present at equilibrium, given that the equilibrium partial pressure of HBr is 2 atm.

[1]

(ii) At 334 °C, the equilibrium constant, K_p, for the above reaction is 2.50.

Write the expression for the equilibrium constant, K_p, for the above reaction.

[1]

(iii) At equilibrium, the number of hydrogen molecules is ten times that of bromine molecules.

Calculate the amount of bromine present at equilibrium.

[2]

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(iv) Given that the equilibrium in **(a)** was established using hydrogen and bromine only, determine the mass of bromine (in kg) that was used.

[2]

(v) Predict, with explanation, the effect on the equilibrium position if the volume was decreased at constant temperature.

.....

.....

.....

.....[1]

(b) The preparation of the acid, HBr, in the laboratory can be carried out by the reaction between bromine, sulfur dioxide and water **only**. The only by-product formed is also a strong acid.

(i) Write the equation for the above laboratory preparation of HBr.

.....[1]

(ii) When concentrated solutions of the two products formed in the above preparation react with each other, Br_2 is regenerated.

State and explain the type of reaction that HBr undergoes.

.....

.....[2]

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(c) Inter and intramolecular bondings respectively can explain the trends in the volatility and thermal stability of the hydrogen halides.

(i) State and explain the trend in the volatility of hydrogen halides from HF to HI.

.....

.....

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.....

.....[3]

(ii) State and explain the trend in the relative thermal stabilities of hydrogen halides from HF to HI.

.....

.....

.....

.....

.....

.....

.....[2]

[Total: 15]

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2 This question is about nitrogen and its oxides.

(a) **(i)** N^{3-} is *isoelectronic* with F^- and Na^+.

Define the term *isoelectronic*.

.....[1]

(ii) Sketch a graph of the successive ionisation energies of all the electrons of a nitrogen atom.

[2]

(iii) State and explain how the ionic radius of N^{3-} compares to that of P^{3-}.

.....

.....

.....

.....

.....[2]

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(b) N_2O_3 is a pale blue solid at very low temperatures. As the temperature is raised, N_2O_3 dissociates to form colourless nitrogen monoxide gas, NO and brown nitrogen dioxide gas, NO_2. The interesting feature of this reaction is that both products are molecular radicals, each with an unpaired electron on the nitrogen atom.

$$N_2O_3(s) \rightleftharpoons NO(g) + NO_2(g)$$

Draw the dot-and-cross diagram for N_2O_3, stating the shapes and bond angles about each N atom.

[3]

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(c) NO is an air pollutant produced by cigarette smoke, automobile engines and power plants. It reacts with oxygen to form $NO_2(g)$.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

The kinetics of the reaction was studied and the following results were obtained.

experiment	initial concentrations / mol dm^{-3}		initial rate of formation of NO_2 / mol dm^{-3} s^{-1}
	[NO]	$[O_2]$	
1	0.001	0.001	7.0×10^{-6}
2	0.001	0.002	1.4×10^{-5}
3	0.002	0.003	8.4×10^{-5}

Use this data to deduce the order of reaction with respect to each of the reactants. Hence, write the rate equation for the reaction and calculate a value for the rate constant.

[4]

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(d) In Singapore, all petrol-driven vehicles are fitted with three-way catalytic converters which convert harmful emissions of NO and NO_2 to less harmful products. A mixture of transition metals palladium, platinum and rhodium are used as catalysts.

Explain, with the aid of a Maxwell-Boltzman distribution curve, why a catalysed reaction has a higher rate of reaction than an uncatalysed reaction.

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.....[3]

[Total: 15]

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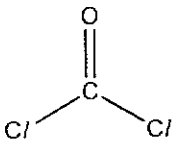
3 Phosgene with the formula $COCl_2$ is an important building block for many organic products. However it is a very poisonous gas and was used as a chemical weapon during the First World War.



Phosgene

(a) Phosgene is rapidly hydrolysed by water.

Complete the figure below to suggest a likely mechanism for this hydrolysis, showing the following:

- **Displayed structures** of the intermediates in steps 1, 2 and 3.
- All relevant charges.
- Relevant lone pairs and movement of electron pairs using curly arrows.

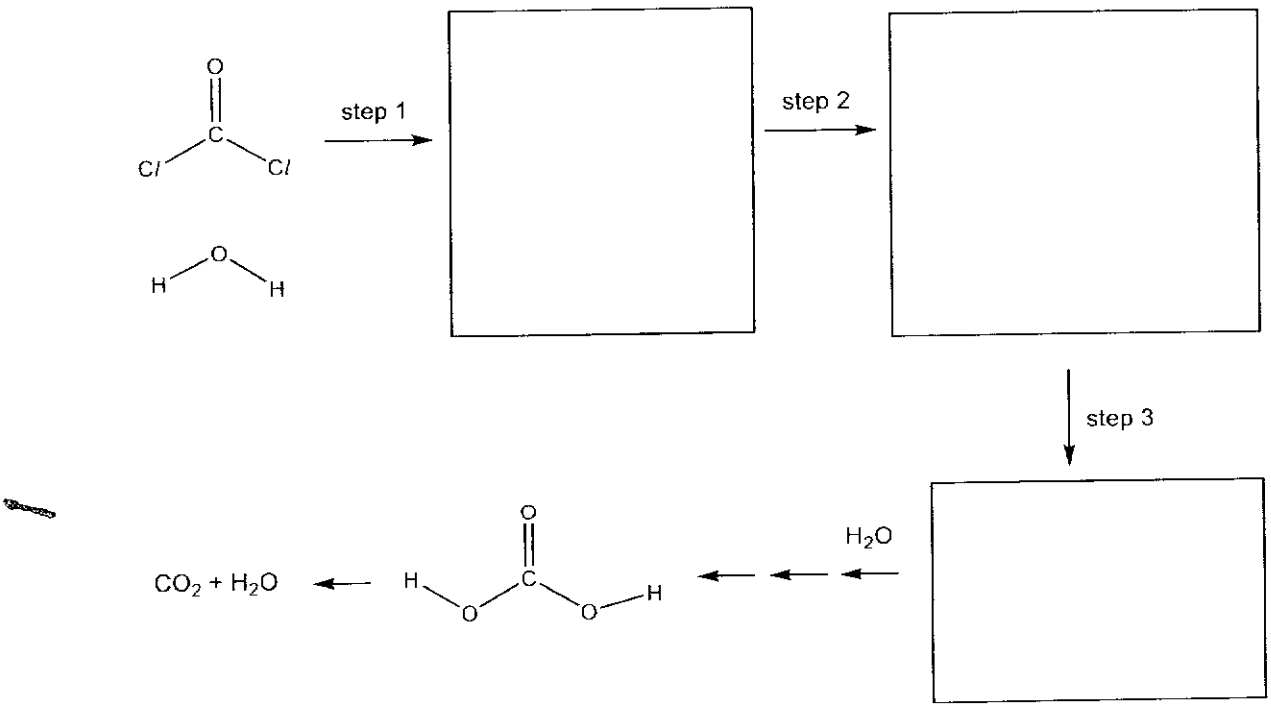


Figure 1

[4]

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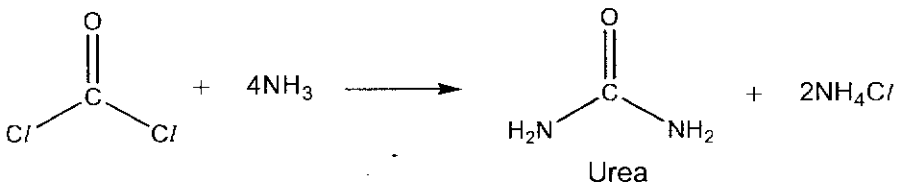
(b) Urea with the formula $CO(NH_2)_2$ is mainly used as a nitrogen-releasing fertilizer. It is also used to make skin care products that promote rehydration of the skin.

Urea can be made in the lab by reacting phosgene with excess ammonia.



Urea

(i) State the type of reaction between phosgene and ammonia.

.....[1]

(ii) Explain why urea is neutral in water, but it forms a salt with nitric acid.

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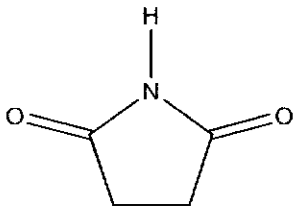
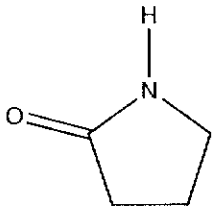
.....[1]

(c) Explain why succinimide is able to form a salt with aqueous sodium hydroxide, but butyrolactam does not.



succinimide



butyrolactam

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.....[2]

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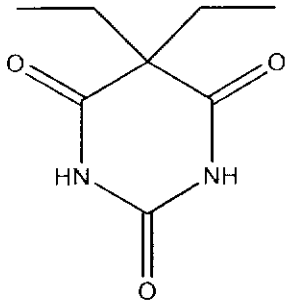
(d) Veronal is a sleep-inducing drug.

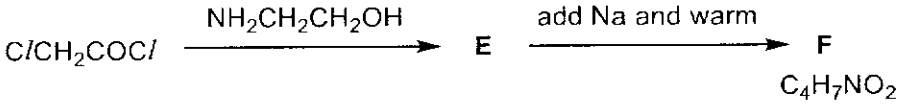


Veronal

Predict all products of hydrolysis of Veronal by aqueous sodium hydroxide.

[2]

(e) Draw the structures of intermediate **E** and product **F** for the following transformation.



E **F**

[2]

[Total: 12]

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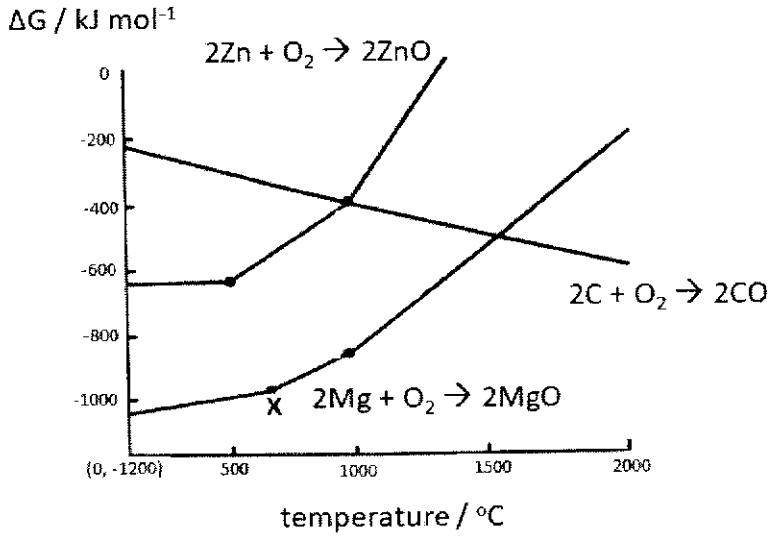
4 The Ellingham diagram is commonly used to show the variation in the Gibbs free energy change, ΔG, of a reaction with temperature. Since enthalpy change and entropy change are essentially constant with temperature unless a phase change occurs, the free energy versus temperature plot can be drawn as a series of straight lines. The graph showing the relationship between the Gibbs free energy change and the temperature of some oxides, as well as the melting points of some elements, are provided below.



element	melting point / °C
zinc	420
magnesium	650

Table 1

(a) Explain why the gradient for the reaction of $2C + O_2 \rightarrow 2CO$ is negative.

.....

.....

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.....[2]

(b) By considering the significance of point **X**, explain why the gradient for the reaction of $2Mg + O_2 \rightarrow 2MgO$ becomes more positive at point **X** as temperature increases.

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.....[1]

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(c) Explain how it can be deduced from the Ellingham diagram that below 1000 °C, the following reaction is spontaneous.

$$Zn + CO \rightarrow C + ZnO$$

.....

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.....[1]

(d) Estimate the range of temperatures for which the following reaction is spontaneous.

$$MgO + C \rightarrow Mg + CO$$

.....[1]

[Total: 5]

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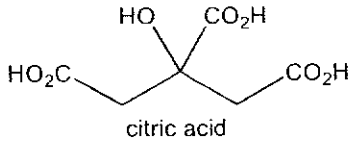
5 Citric acid (molecular formula $C_6H_8O_7$) is an important compound that occurs naturally in citrus fruits like lemons and oranges. It plays a central role in the Krebs cycle, which is a series of chemical reactions in all aerobic organisms to release stored energy. It is a solid at standard conditions.



citric acid

(a) Calculate the standard enthalpy change of formation of citric acid using the following data.

	$\Delta H^{\ominus}$ / kJ mol^{-1}
Standard enthalpy change of combustion of citric acid	−1960
Standard enthalpy change of combustion of hydrogen	−286
Standard enthalpy change of formation of carbon dioxide	−394

For simplicity, you may choose to use the molecular formula of citric acid to represent citric acid.

[3]

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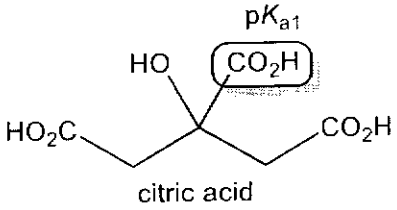
(b) As citric acid is a tricarboxylic acid, it has three pK_a values, denoted by pK_{a1}, pK_{a2} and pK_{a3}, arranged in increasing order.



citric acid

Explain why the boxed carboxylic acid group has the lowest pK_a value out of the three carboxylic acids in citric acid.

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.....

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.....[2]

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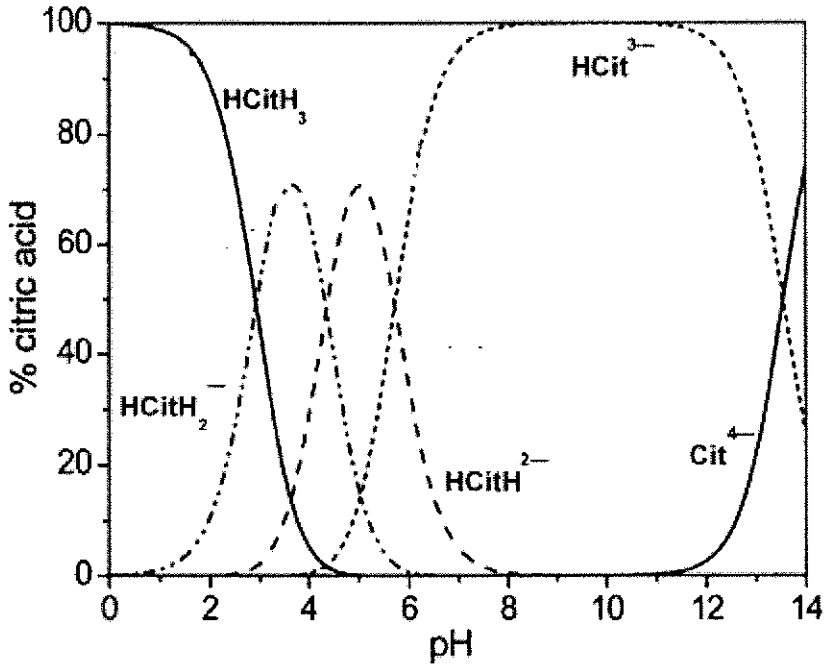
(c) A graph showing the correlation between the composition of the different ionic forms of citric acid (y-axis) and the pH of the solution (x-axis) is shown below.



The fully protonated form of citric acid is denoted as "$HCitH_3$", with the first H denoting the alcoholic hydrogen atom. Similarly, the tricarboxylate anion of citric acid is denoted as "$HCit^{3-}$".

(i) Given that pK_{a1} of citric acid is approximately 3.0, estimate the values of pK_{a2} and pK_{a3} from the above graph. You are to show your working clearly on the graph.

pK_{a2} .....

pK_{a3} ..... [2]

(ii) Assuming that citric acid is a weak monobasic acid, calculate the pH of a 0.120 mol dm^{-3} solution of citric acid.

[1]

Citric acid and its salts are used to make buffers of varying pH values.

(iii) Representing citric acid as "$HCitH_3$" and monosodium citrate as "$NaHCitH_2$", write an equation to illustrate how a solution containing both species maintains fairly constant pH when small amounts of NaOH is added to it.

.....[1]

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(iv) A solution was prepared by dissolving 3.84 g of solid citric acid in 1 dm^3 of water.

Calculate the volume of 0.500 mol dm^{-3} NaOH(aq) that needs to be added to the above solution to prepare a buffer of pH 2.7.

[3]

(d) Citric acid is used as the starting material for various other organic compounds, whether through metabolism or chemical synthesis.

(i) Isocitric acid is a constitutional isomer of citric acid. It exists in more than two stereoisomeric forms.

Equal volumes of carbon dioxide gas are obtained when excess sodium hydrogencarbonate is added to the same amount of each acid. Isocitric acid can be made by reacting a suitable aldehyde with HCN, followed by heating the product in aqueous sulfuric acid.

Give the structural formula of isocitric acid.

[1]

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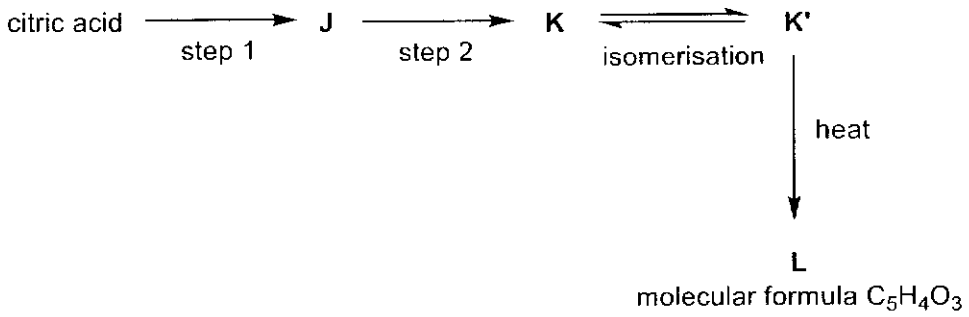
J, **K**, **K'** and **L** can be synthesised from citric acid through the synthetic route shown below.



(ii) Compound **J** has relative molecular mass of 174.0. The **mass ratio** of carbon to hydrogen to oxygen is 12:1:16 in **J**.

Find the molecular formula of **J**.

.....[1]

(iii) Both compounds **J** and **K** can be reacted with hot acidified $KMnO_4$ to give 2-oxobutanedioic acid, $HO_2CCOCH_2CO_2H$.

Deduce the structural formula of **J**. State the reagents and conditions used in step 1.

J

step 1 .....

[2]

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(iv) Compounds **K'** and **K** are a pair of positional isomers. They have a molecular formula of $C_5H_6O_4$. While **K'** can exhibit cis-trans isomerism, **K** does not show any form of stereoisomerism. Only the *cis*- form of **K'** forms **L**, which is a neutral compound.

Find the structural formulae of **K**, **K'** and **L**.

K

K'

L

[3]

[Total: 19]

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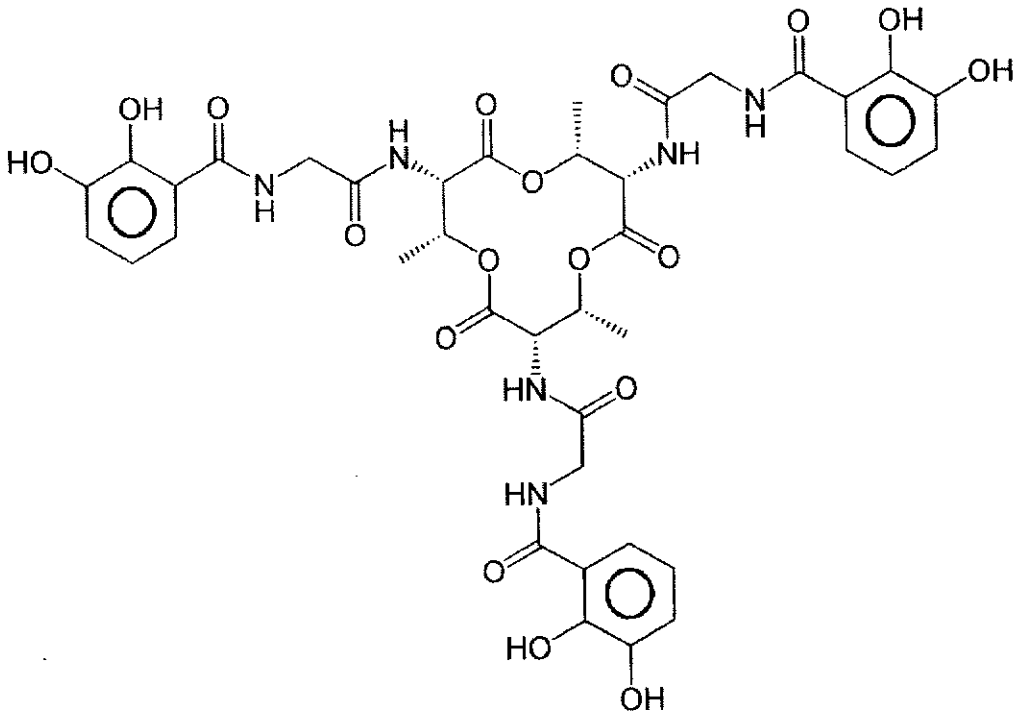
6 Microorganisms synthesise and secrete organic molecules called siderophores to increase the total concentration of available iron in the surrounding medium.

(a) Bacillibactin is a siderophore produced by bacteria.



Bacillibactin

(i) Bacillibactin binds to iron(III) ions via its oxygen atoms. This process facilitates the transportation of iron(III) ions into the interior of a cell.

Suggest what bonds are formed during this process and why iron(III) does not bind to nitrogen atoms in bacillibactin compounds.

.....

.....

.....

.....[2]

(ii) Draw the structures of the two α-amino acids formed when bacillibactin is hydrolysed.

[2]

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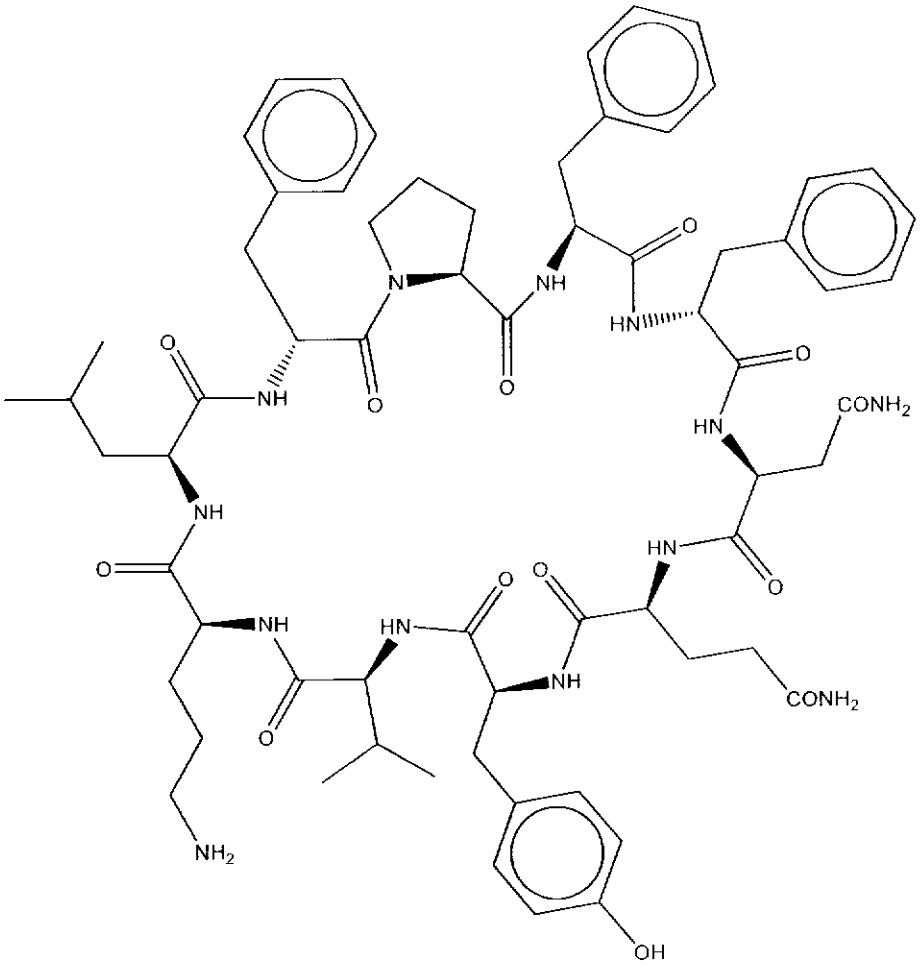
(b) Tyrocidine was the first commercially available antibiotic. Like bacillibactin, tyrocidine is also produced by bacteria. Tyrocidine has been found to be toxic towards human blood and reproductive cells.



Tyrocidine

(i) Amongst the many amino acids that make up tyrocidine, there is one pair of amino acids where the side chains have the same functional group.

Draw one amino acid from the pair in which the side chain is polar.

[1]

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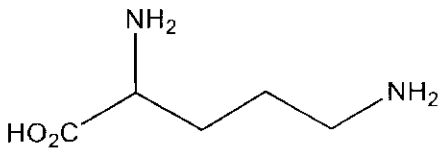
Ornithine is one of the α-amino acids found in tyrocidine.



Ornithine

The three pK_a values of ornithine are 2.17 (the carboxylic acid), 9.04 (the α-amino group) and 12.48.

(ii) Draw the zwitterionic form of ornithine.

[1]

(iii) Calculate the pH at which ornithine exists solely in its zwitterionic form.

[1]

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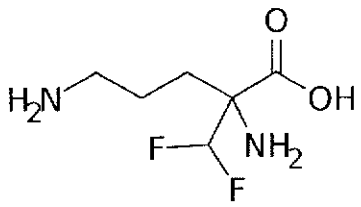
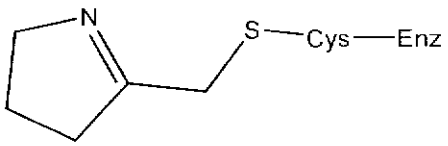
(iv) Eflornithine is a drug that is structurally similar to ornithine, as its name implies. It is used to treat sleeping sickness and excessive hair growth on the face in women.



Eflornithine

Extensive studies have been done on the metabolic products of eflornithine. It has been suspected that **Z** is the main metabolic product of eflornithine.



Z

To confirm that **Z** is indeed formed from the metabolism of eflornithine, chemists conducted two tests on it and studied the products, **Z'** and **Z''**.

For the two tests, you may assume that the $-CH_2-S-Cys-Enz$ is inert.

Z' is obtained by reacting **Z** with $NaBH_4$.The relative molecular mass of **Z'** is 2 units larger than that of **Z**. The relative molecular mass of **Z''** is 4 units smaller than that of **Z'**.

Suggest the structural formulae of **Z'** and **Z''**.

Z'	**Z''**

[2]

[Total: 9]

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Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.

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