

Name _____ Class: 17S _____ Reg Number: _____



MERIDIAN JUNIOR COLLEGE
2017 JC1 Promotional Examination
Higher 2

Chemistry

9729

Section B and C

27 September 2017

2 h 20 min

Additional Materials: Data Booklet
 Writing Papers

READ THESE INSTRUCTIONS FIRST

Write your name, class and register number in the spaces at the top of this page.

This booklet contains Section B and Section C.

Section B: Pg 2 to 19

Answer all questions in Section B in the spaces provided on the question paper. You are advised to spend about 1 hour 30 minutes on Section B.

Section C: Pg 20 to 24

Answer all questions in Section C on the foolscap paper. You are advised to spend about 50 minutes on Section C.

Begin each question on a *fresh page* of writing paper.

Hand in Section C *separately* from Section B.

Fasten your answers for Section C using the Cover Page at the back of this booklet.

INFORMATION FOR CANDIDATES

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

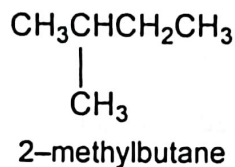
Examiner's Use		
Section A	MCQ	/ 20
Section B	Q1	/ 8
	Q2	/ 9
	Q3	/ 14
	Q4	/ 13
	Q5	/ 16
		/ 60
Section C	Q1	/ 15
	Q2	/ 15
		/ 30
Total		/ 110
Percentage		/ 100
Grade		

This document consists of **24** printed pages and one Cover Page.

Section B: Structured Questions (60 marks)

You are advised to spend **not more than 1 h 30 min** on this section.

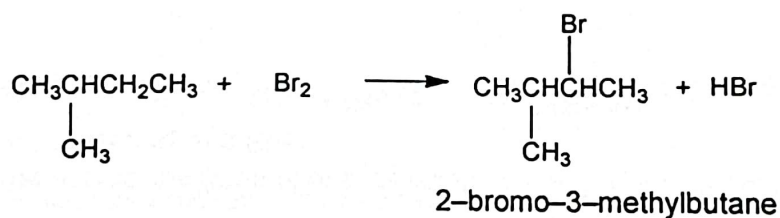
- 1 2-methylbutane is an extremely volatile and flammable liquid at room temperature. It is used in conjunction with liquid nitrogen in cryosectioning in histology.



- (a) Alkanes are generally unreactive. Suggest a possible reason why this is so.

[1]

- (b) 2-methylbutane reacts with bromine gas under ultraviolet light to form a mixture of products. One possible product is 2-bromo-3-methylbutane.



- (i) Name and outline the mechanism for the reaction of 2-methylbutane with bromine gas to form 2-bromo-3-methylbutane.

[3]

- (ii) Other possible isomeric products that could be formed from the reaction of 2-methylbutane and bromine gas are listed in the table below.

Predict the ratio in which these 3 isomeric products are formed.

[1]

	$\begin{array}{c} \text{Br} \\ \\ \text{CH}_2\text{CHCH}_2\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{Br} \\ \\ \text{CH}_3\text{CCH}_2\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{Br} \\ \\ \text{CH}_3\text{CHCH}_2\text{CH}_2 \\ \\ \text{CH}_3 \end{array}$
Ratio			

- (c) 2-methylbutane reacts with excess chlorine gas to give a mixture of various chlorinated products such as $\text{C}_5\text{H}_{11}\text{Cl}$, $\text{C}_5\text{H}_{10}\text{Cl}_2$ and $\text{C}_5\text{H}_9\text{Cl}_3$.

In one such reaction, a sample of this mixture of chlorinated products weighing 0.451 g was vaporised at 200 °C and 101 kPa, and found to occupy a volume of 127 cm³.

- (i) Calculate the apparent molar mass of the resultant gas mixture.

[2]

- (ii) Hence, deduce with reasoning which chlorinated product was present in highest abundance in the mixture.

[1]

[Total: 8]

2 This question is related to the atomic properties of gaseous diatomic molecules.

- (a) At low temperatures and pressures, the alkali metals can exist as gaseous diatomic molecules. Recent research has investigated the mixing of gaseous diatomic molecules of different alkali metals (reported in *Science* 2010). Spectroscopic techniques can be used to measure the bond energies of diatomic molecules. When measured in this way, the values of bond energies are given in wavenumbers, which has the unit cm^{-1} .

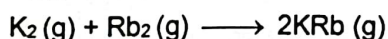
Some values are shown in the table.

diatomic molecule	Bond energy (BE) / cm^{-1}
K_2	4405
Rb_2	3966
KRb	4180

The enthalpy change, in cm^{-1} for a reaction, ΔH can be determined using the following mathematical expression:

$$\Delta H = \sum \text{BE}(\text{bonds broken in reactants}) - \sum \text{BE}(\text{bonds formed in products})$$

- (i) Using the expression given above, calculate the enthalpy change, in cm^{-1} , for the reaction between K_2 and Rb_2 .



[1]

- (ii) Complete the electronic configuration of a potassium atom.

[1]

$1s^2$ _____

- (iii) Explain why potassium has a higher first ionisation energy than rubidium.

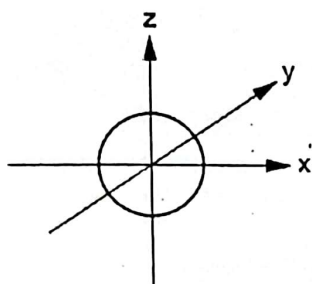
[2]

(b) Non-metallic diatomic molecules such as halogens Cl_2 and Br_2 are commonly used in halogen incandescent lamps.

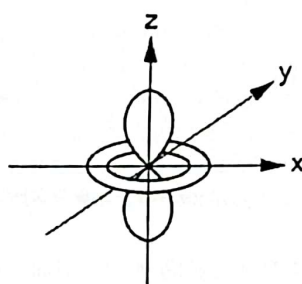
(i) Sketches of the shapes of *some* atomic orbitals from the principal quantum shells of $n=3$ and $n=4$ of the bromine atom are shown below in random order.

Suggest a possible label for each orbital.

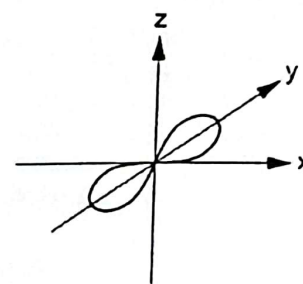
[2]



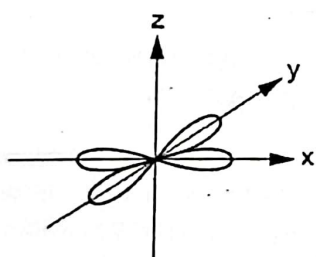
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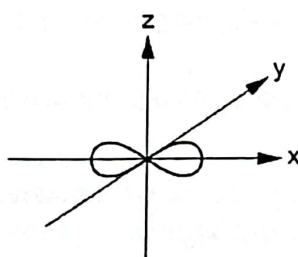
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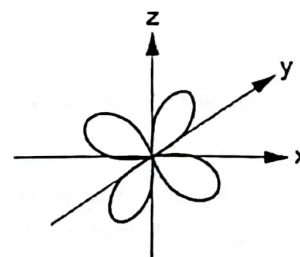
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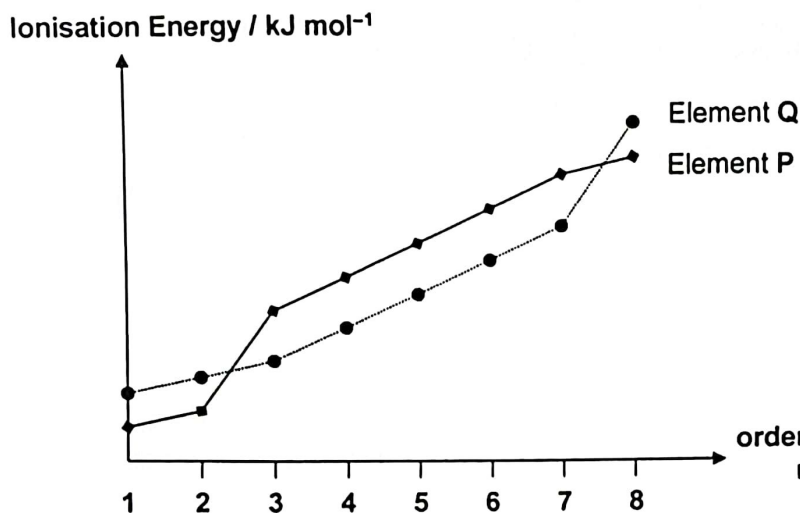


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(ii) The first ionisation energy of bromine is higher than that of selenium. Explain this observation.

[1]

- (c) P and Q are elements in the third period of the Periodic Table. The figure below shows the ionisation energies when the first eight outermost electrons are removed from each atom of elements P and Q.



- (i) State the Group of the Periodic Table that each element P and Q belongs to.

[1]

Element P belongs to Group _____ Element Q belongs to Group _____

- (ii) R is an element which is in the same Group as element P.

R and Q can form a corresponding compound that is a non-conductor of electricity in molten state.

Using the above information as well as that from (c)(i), draw the dot-and-cross diagram to illustrate the bonding in the compound formed between R and Q.

[1]

[Total: 9]

- 3 Lead(IV) oxide, PbO_2 is an odourless dark-brown crystalline powder. It is sparingly soluble in water and is a strong oxidising agent.

Under basic conditions, solid PbO_2 reacts with solid $\text{Cr}(\text{OH})_3$ to form CrO_4^{2-} and PbO_2^{2-} ions.

- (a) Write the balanced half-equations and hence construct an overall equation for the reaction between solid PbO_2 and solid $\text{Cr}(\text{OH})_3$ under basic conditions.

[2]

Oxidation: _____

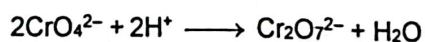
Reduction: _____

Overall: _____

The percentage by mass of PbO_2 in a sample can be determined by the following titrimetric method.

A 5.00 g of sample containing PbO_2 was reacted with excess solid $\text{Cr}(\text{OH})_3$ in an alkaline medium. The resultant solution containing CrO_4^{2-} was then diluted to 250 cm^3 in a volumetric flask.

A 25.0 cm^3 aliquot of this diluted solution was then acidified to give $\text{Cr}_2\text{O}_7^{2-}$ as shown in the following equation:



The 25.0 cm^3 aliquot was then titrated against $0.150 \text{ mol dm}^{-3}$ aqueous iron(II), Fe^{2+} using a suitable indicator.



The experimental results for the titration are shown in the data table below.

Titration number	1	2	3
Final burette reading / cm^3	25.55	33.75	40.90
Initial burette reading / cm^3	0.00	8.35	15.60
Volume of Fe^{2+} (aq) used / cm^3			

- (b) Complete the data table above. Using the experimental results, calculate the amount of Fe^{2+} ions required to react with $\text{Cr}_2\text{O}_7^{2-}$ ions in the 25.0 cm^3 aliquot.

[2]

- (c) The maximum uncertainty of any single burette reading is $\pm 0.05 \text{ cm}^3$. Calculate the maximum percentage uncertainty in the litre volume calculated in (b).

[1]

- (d) Calculate the percentage by mass of PbO_2 in the given sample.

[2]

Lead(II) iodide, PbI_2 and lead(II) sulfate, PbSO_4 are two commonly used lead-based reagents. PbI_2 exists as a yellow solid while PbSO_4 exists as a white solid. Their solubility products, K_{sp} at 20 °C are given in the table below:

Compound	Numerical value of K_{sp}
PbI_2	4.4×10^{-9}
PbSO_4	2.1×10^{-8}

- (e) Suggest using quantitative calculations, which of these two compounds is more soluble in water at 20 °C.

[2]

- (f) 50 cm³ of 0.00200 mol dm⁻³ NaI solution and 50 cm³ of 0.00500 mol dm⁻³ Na₂SO₄ solution are mixed at 20 °C. To the resultant solution, 100 cm³ of 0.0100 mol dm⁻³ Pb(NO₃)₂ was then added.

State and explain, with the aid of relevant calculations if precipitation will occur. Hence, state the expected observation when these solutions are mixed.

[3]

- (g) State and explain how the solubility of PbI_2 would be affected if PbI_2 is dissolved in an aqueous solution of KI .

[2]

[Total: 14]

- 4 Chlorous acid, HClO_2 is the main component present in 'KlorusKare®', a disinfectant for food products such as vegetables and seafood.

(a) Chlorous acid contains two central atoms.

- (i) Complete the dot-and-cross diagram of chlorous acid, HClO_2 in the sketch of the molecule given below.

[1]



- (ii) Using the *Valence Shell Electron Pair Repulsion* theory, state and explain the shape with respect to the chlorine atom.

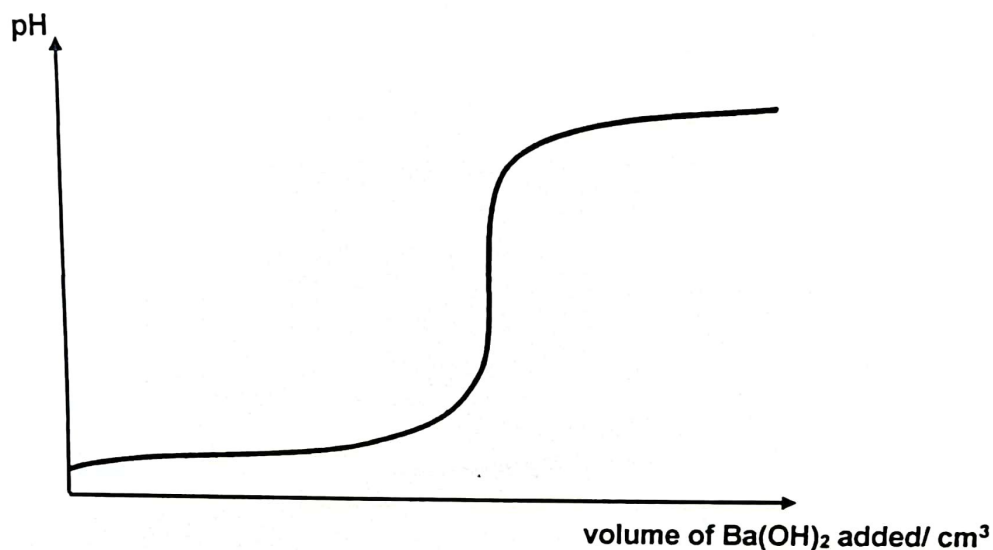
[2]

- (iii) Draw a labelled diagram to illustrate the solubility of chlorous acid in water.

[1]

Chlorous acid acts as a weak monobasic acid when dissolved in water. The acid dissociation constant, K_a of chlorous acid is $1.10 \times 10^{-2} \text{ mol dm}^{-3}$.

- (b) The following sketch of titration curve was obtained when $0.10 \text{ mol dm}^{-3} \text{ Ba(OH)}_2$ was gradually added to a 25.0 cm^3 aqueous solution of $0.160 \text{ mol dm}^{-3} \text{ HC/O}_2$ at 25°C .



- (i) Calculate the pH of $0.160 \text{ mol dm}^{-3}$ chlorous acid.

[1]

- (ii) Determine the equivalence volume of Ba(OH)_2 for the titration.

[1]

- (iii) Indicate clearly on the titration curve the region within which the solution is acting as a buffer.

[1]

- (iv) Calculate the pH of the resultant solution formed when only 12.0 cm^3 of $\text{Ba}(\text{OH})_2$ was added.

[2]

- (v) The pH at the equivalence point of the titration is greater than 7. Suggest an equation to account for the nature of this equivalence point.

[1]

The table shows a list of indicators.

Indicator	pH at which colour changes
bromocresol green	3.8 – 5.4
cresol red	7.2 – 8.8
indigo carmine	11.4 – 13.0

- (vi) Select the most suitable indicator for the titration, giving a reason for your choice.

[1]

Chloric(I) acid, HClO is an oxidising agent and the chlorate(I) ion, ClO^- , is used as an effective disinfectant in swimming pools.

- (c) A solution containing HClO (aq) and ClO^- (aq) can act as a buffer solution.

With the aid of an equation, explain how the pH of the buffer solution is maintained on addition of small amounts of base.

[2]

[Total: 13]

- 5 This question is about the kinetics of the reaction between peroxydisulfate, $\text{S}_2\text{O}_8^{2-}$ and iodide.

- (a) $\text{S}_2\text{O}_8^{2-}$ and I^- react in an acidified medium to produce I_2 as follows:



The kinetics of this reaction was studied.

A fixed volume of starch solution and a small measured volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution were added to an acidified $\text{K}_2\text{S}_2\text{O}_8$ solution. KI solution was then added, and the time taken for the mixture to turn blue-black was measured.

The reaction was repeated using different volumes of KI, with the same volumes of starch, $\text{K}_2\text{S}_2\text{O}_8$ and $\text{Na}_2\text{S}_2\text{O}_3$. Varying amounts of water was also added.

The following results were obtained.

Expt	Volume				Time, t / s	$\frac{1}{t}$ / s^{-1}
	$\text{S}_2\text{O}_8^{2-}$ / cm^3	I^- / cm^3	H^+ / cm^3	water / cm^3		
1	10.00	20.00	10.00	5.0	15.4	0.0649
2	10.00	15.00	10.00	10.0	20.5	0.0488
3	10.00	10.00	10.00	15.0	30.8	0.0325

- (i) Explain why water was added to the reaction mixture in each of the experiments.

[1]

- (ii) Deduce the order of reaction with respect to I^- ions.

[2]

- (iii) Predict what would happen if the reaction was carried out without the addition of $\text{Na}_2\text{S}_2\text{O}_3$ in the reaction mixture.

[1]

- (iv) Suggest a reason why the reaction between $\text{S}_2\text{O}_8^{2-}$ and I^- ions is unlikely to proceed as an elementary reaction.

[1]

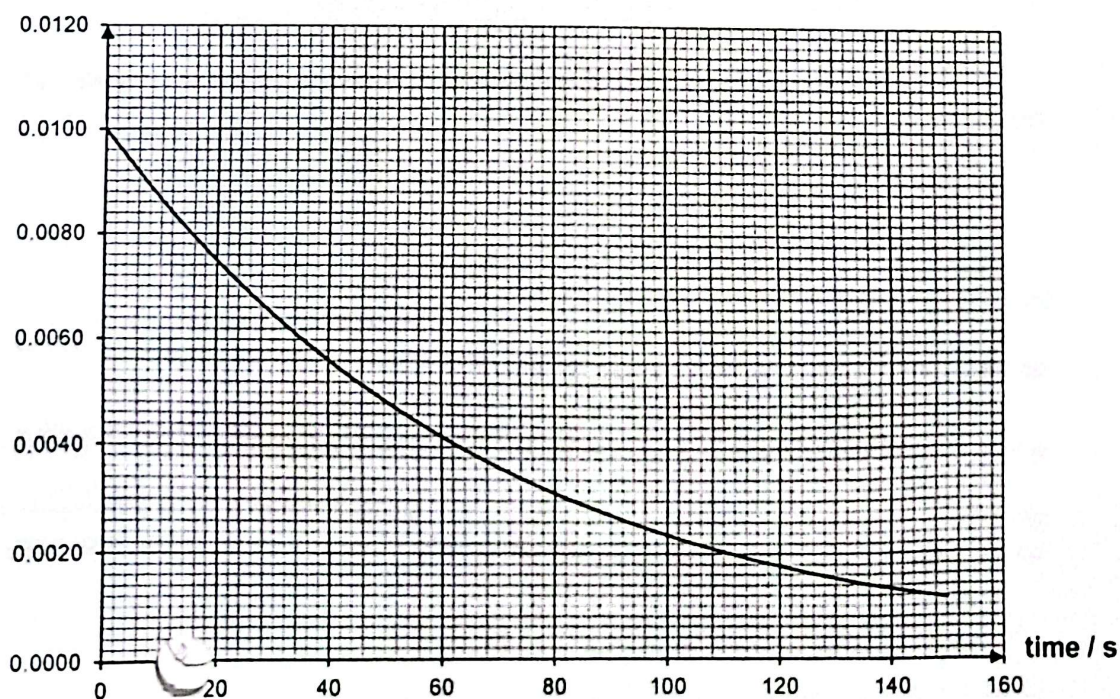
- (b) In another investigation, a 50 cm^3 solution of $\text{S}_2\text{O}_8^{2-}$ was reacted with 50 cm^3 solution of acidified I^- , which is in large excess.

10 cm^3 portions of the reaction mixture were drawn at various time intervals and transferred into aqueous solution of sodium hydrogen carbonate, NaHCO_3 to quench the reaction.

The I_2 produced for each portion was then quantified by titrating the I_2 produced against $\text{Na}_2\text{S}_2\text{O}_3$. The volume of $\text{S}_2\text{O}_3^{2-}$ required was recorded at various time intervals. The amount of $\text{S}_2\text{O}_3^{2-}$ used corresponds to the amount of I_2 produced. Correspondingly, the amount of $\text{S}_2\text{O}_8^{2-}$ that has reacted can be determined.

The progress of the reaction can thus be monitored as a function of concentration of $\text{S}_2\text{O}_8^{2-}$ remaining against time. The following results were obtained.

$[\text{S}_2\text{O}_8^{2-}] / \text{mol dm}^{-3}$



- (i) Deduce the order of reaction with respect to $\text{S}_2\text{O}_8^{2-}$ ions. Show your working clearly on the graph.

[2]

- (ii) Calculate the rate constant of the reaction between $\text{S}_2\text{O}_8^{2-}$ and I^- , given that $[\text{I}^-]$ is in large excess of $0.500 \text{ mol dm}^{-3}$.

[1]

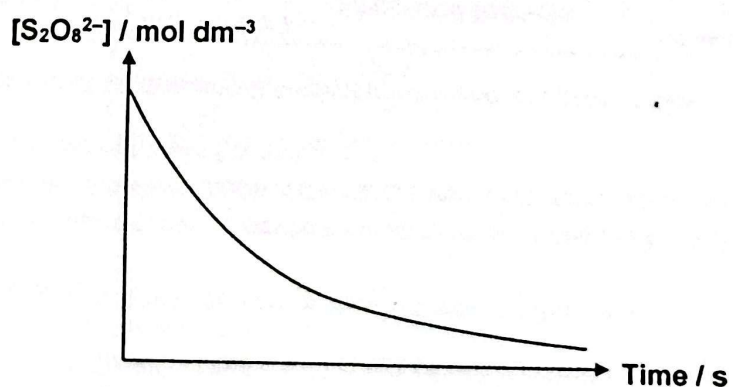
(c) The rate of the reaction between $\text{S}_2\text{O}_8^{2-}$ and I^- increases when a small amount of a transition metal ion such as Fe^{2+} is added.

- (i) With the aid of a Maxwell–Boltzmann distribution curve, explain how the presence of such ions increase the rate of reaction.

[3]

- (ii) On the diagram below, sketch the profile of the graph to be expected for the reaction involving Fe^{2+} ions.

[1]



- (iii) By means of clear steps, briefly outline the experimental procedure (including any appropriate apparatus) whereby the experiment in (b) can be modified to investigate the effect of adding aqueous Fe^{2+} .

[You do not need to describe the titration procedure of the quenched iodine portions.]

You may assume that you are provided with the following:

- 0.0100 mol dm⁻³ potassium peroxydisulfate, K₂S₂O₈ solution
- 0.500 mol dm⁻³ acidified potassium iodide, KI solution
- 1.00 mol dm⁻³ sodium hydrogen carbonate, NaHCO₃ solution
- 0.100 mol dm⁻³ iron(II) nitrate, Fe(NO₃)₂ solution
- stopwatch
- apparatus normally found in a college laboratory

[4]

[illegible]

[Total: 16]

End of Section B

Section C: Free Response Questions (30 marks)

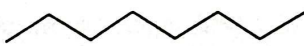
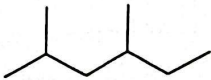
Answer **ALL** questions in this paper on foolscap paper.

Begin each question on a **fresh page** of writing paper.

You are advised to spend **not more than 50 min** on this section.

- 1 Crude oil, commonly known as petroleum, comprises mainly of hydrocarbons. Pentadecane, octane, 2,4-dimethylhexane and benzene are four examples of hydrocarbons that can be obtained from crude oil.

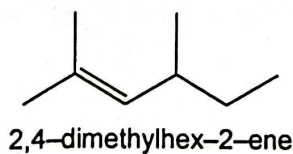
- (a) (i) The boiling points of octane and 2,4-dimethylhexane are given below.

compound	molecular formula	structural formula	boiling point / °C
octane	C_8H_{18}		125
2,4-dimethylhexane	C_8H_{18}		108

Briefly explain why octane has a higher boiling point than 2,4-dimethylhexane.

[2]

- (ii) 2,4-dimethylhex-2-ene can be reduced to form 2,4-dimethylhexane.



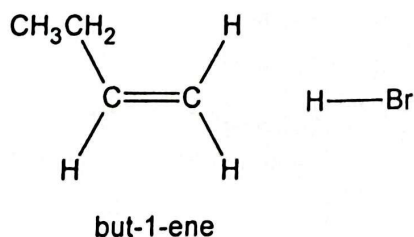
State the type of isomerism exhibited by 2,4-dimethylhex-2-ene. Draw the structures of the isomers.

[2]

- (b) Pentadecane, $C_{15}H_{32}$ can undergo cracking to produce propene, but-1-ene and octane.

- (i) Name and outline the mechanism of the reaction between but-1-ene and hydrogen bromide to obtain 2-bromobutane. The mechanism should show curly arrows, charges, dipoles and any relevant lone pairs.

[3]



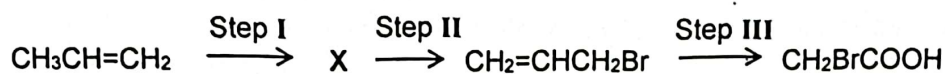
- (ii) Explain why this reaction produces an equimolar mixture of two isomers of 2-bromobutane.

[1]

- (iii) Describe one simple test-tube reaction you could carry out to distinguish propene from octane.

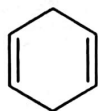
[2]

- (iv) Suggest the reagents and conditions required in steps I, II and III to carry out the following transformation. Identify the intermediate compound, X.



[2]

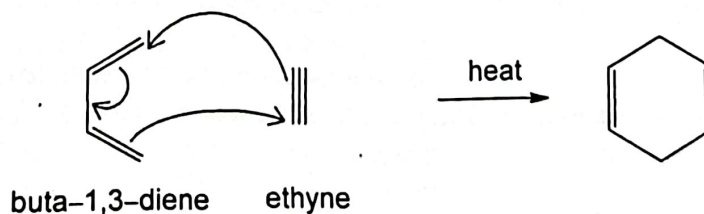
- (c) Benzene undergoes reduction to form cyclohexa-1,4-diene.



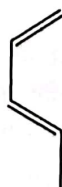
cyclohexa-1,4-diene

Cyclohexa-1,4-diene can also be formed by heating buta-1,3-diene with ethyne.

The diagram below shows the movement of electron pairs, represented by curly arrows, needed to generate cyclohexa-1,4-diene in a single step.



In a similar type of reaction, penta-1,3-diene reacts with propene to form two products that are constitutional isomers.



penta-1,3-diene

Deduce the structures of these two isomers.

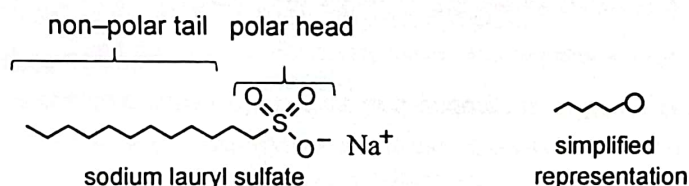
[1]

- (d) Occasionally, seabirds can become contaminated with hydrocarbons from oil spills. The contaminated birds can be cleaned by rubbing vegetable oil into their feathers before their feathers are then lathered with diluted shampoo. The birds are then rinsed thoroughly with water to remove the shampoo and oil.

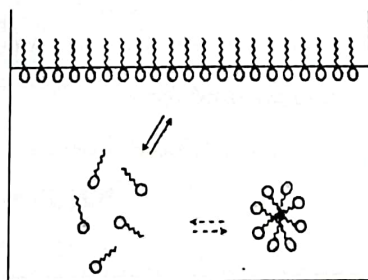


Photograph of a seabird affected by oil spills
Source: Bird Education Network Bulletin, Issue #32,
<http://www.birdeeducation.org/BENBulletin32.htm>
Last accessed 27 Aug 2017

The primary ingredient of a shampoo is a surfactant. A surfactant contains both a discrete polar head and a well-defined non-polar tail. A common surfactant used in shampoos is sodium lauryl sulfate.



When a surfactant is added to water, the molecules orientate themselves on the surface of water as shown in the diagram below. When even more surfactants are added, the surfactant molecules will group together in three-dimensional spherical clusters, with the non-polar tails filling the interior of the cluster and the polar heads composing the outer surface. These molecular clusters are known as *micelles*.



Using your knowledge of chemical bonding and the above information on surfactant and *micelles* formation, comment on the actions taken to treat the affected birds.

- Rubbing vegetable oil into the birds' feathers
- Lathering the feathers with shampoo
- Rinsing the feathers with water

[2]

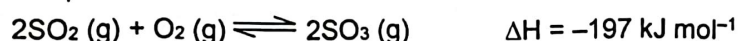
[Total: 15]

- 2 Sulfur dioxide, SO_2 is a gas with a pungent smell. While there are many useful applications of sulfur dioxide, SO_2 is also a toxic atmospheric pollutant and is a key component in the formation of acid rain.
- (a) SO_2 was previously used as a refrigerant as it has a relatively high heat of vapourisation. At 293 K, a 24 dm^3 refrigerant canister containing 1 mol of sulfur dioxide was found to exert an internal pressure of 0.992 atm instead of the theoretically expected 1.00 atm.

Using an assumption of kinetic theory, account for this discrepancy.

[2]

- (b) Sulfur dioxide is an important feedstock in the *Contact Process* to manufacture sulfuric acid industrially. One of the reactions in the *Contact Process* involves the reversible reaction between sulfur dioxide and oxygen.



In an experiment, a 3:1 ratio of SO_2 and O_2 was mixed at a total initial pressure of 3 atm and was passed over vanadium(V) oxide catalyst at 400°C in a fixed volume vessel. At equilibrium, the percentage of SO_3 present in the mixture of gases is found to be 60 %.

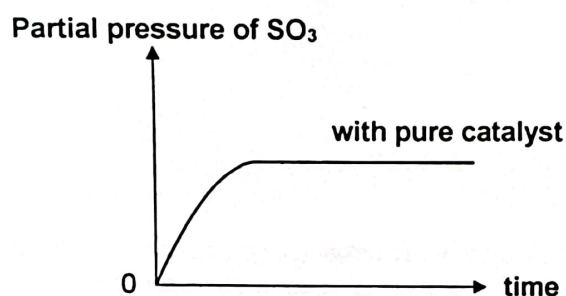
- (i) Write an expression for the equilibrium constant, K_p , for this reaction. [1]
- (ii) Calculate the value of K_p at 400°C , stating its units, clearly. [3]
- (iii) How would the percentage conversion of SO_2 into SO_3 be affected when the pressure is increased? Explain your answer. [2]
- (iv) Explain why a moderately high temperature of 400°C was used as one of the operating conditions for this reaction. [2]

- (v) In industrial processes such as the *Contact Process*, catalysts are often deactivated in the presence of impurities and loses its efficiency to catalyse the reactions.

The following graph shows how the partial pressure of SO_3 present varies with time at 400°C when pure vanadium(V) oxide catalyst was used.

Transfer the graph below onto the writing paper. Using the same axes, sketch another graph for this experiment to show the variation of partial pressure of SO_3 with time at 400°C , if the vanadium(V) oxide catalyst was **tainted with impurities**.

[1]

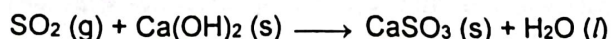


- (c) SO_2 and NO_2 are common atmospheric pollutants that are responsible for the formation of acid rain. While SO_2 can be oxidised atmospherically to form SO_3 , there has been no reported formation of NO_3 . Suggest an explanation for this observation.

[1]

- (d) SO_2 is a reactive chemical species and undergoes different reactions with various compounds.

- (i) SO_2 can be removed from exhaust flue gases generated in fossil-fuel power plants by passing the flue gases through a slurry of calcium hydroxide, $\text{Ca}(\text{OH})_2$. The reaction between SO_2 and $\text{Ca}(\text{OH})_2$ is shown in the following equation.



This reaction can be viewed as an oxide ion transfer from $\text{Ca}(\text{OH})_2$ to SO_2 . State the role of SO_2 in this reaction.

[1]

- (ii) Draw the structure of the adduct formed from the reaction of SO_2 and BF_3 , showing clearly the type of bonding, shape and bond angles around the central boron and sulfur atoms.

[2]

[Total: 15]

End of Section C