Coimisiún na Scrúduithe Stáit
State Examinations Commission

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LEAVING CERTIFICATE EXAMINATION, 2016

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CHEMISTRY – HIGHER LEVEL

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TUESDAY, 21 JUNE – AFTERNOON 2:00 to 5:00

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400 MARKS

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Answer **eight** questions in all.

These **must** include at least **two** questions from **Section A**.

All questions carry equal marks (50).

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The information below should be used in your calculations.

Relative atomic masses (rounded):   H = 1.0, C = 12, N = 14, O = 16, Na = 23, S = 32, K = 39

Avogadro constant = 6.0×10^{23} mol^{-1}

Molar volume at s.t.p. = 22.4 litres

Universal gas constant = 8.3 J K^{-1} mol^{-1}

The use of the *Formulae and Tables* booklet approved for use in the State Examinations is permitted. A copy may be obtained from the examination superintendent.

Section A
**Answer at least <u>two</u> questions from this section. See page 1 for full instructions.**

1. To determine the concentration of ethanoic acid in a sample of vinegar, 25.0 cm^3 of the vinegar were diluted to 250 cm^3 and then the diluted vinegar was titrated with a previously standardised solution which contained 1.20 g of sodium hydroxide in 500 cm^3 of solution. On average, 18.75 cm^3 of the diluted vinegar were required to neutralise 25.0 cm^3 of this sodium hydroxide solution.

   The equation for the titration reaction is:

   $$CH_3COOH \quad + \quad NaOH \quad \rightarrow \quad CH_3COONa \quad + \quad H_2O$$
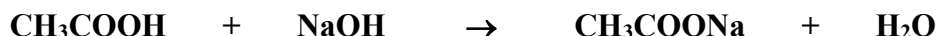
   (*a*) Describe in detail the procedures involved in measuring a 25.0 cm^3 sample of the vinegar and diluting it using deionised water to exactly 250 cm^3. (15)

   (*b*) Name a suitable indicator for this titration.

   What colour change is observed at the end point? (9)

   (*c*) Calculate

       (*i*) the number of moles of sodium hydroxide in each 25.0 cm^3 portion,

       (*ii*) the number of moles of ethanoic acid per cm^3 of *diluted* vinegar. (12)

   (*d*) Find the concentration of ethanoic acid in the *original* vinegar

       (*i*) in terms of moles per litre,

       (*ii*) as a percentage (w/v). (9)

   (*e*) Starting with a primary standard solution made from anhydrous sodium carbonate, what two titrations are required to standardise a sodium hydroxide solution? (5)

2. The two test-tubes on the left in the diagram contain pure samples of **A** and **B**, different gaseous hydrocarbons, one of which is unsaturated.

The pure liquids **C**, **D** and **E** in the other test-tubes are samples of ethanal, ethanoic acid and eugenol, but not necessarily in that order.

The crystalline solids **F** and **G** are two different benzoic acid samples.
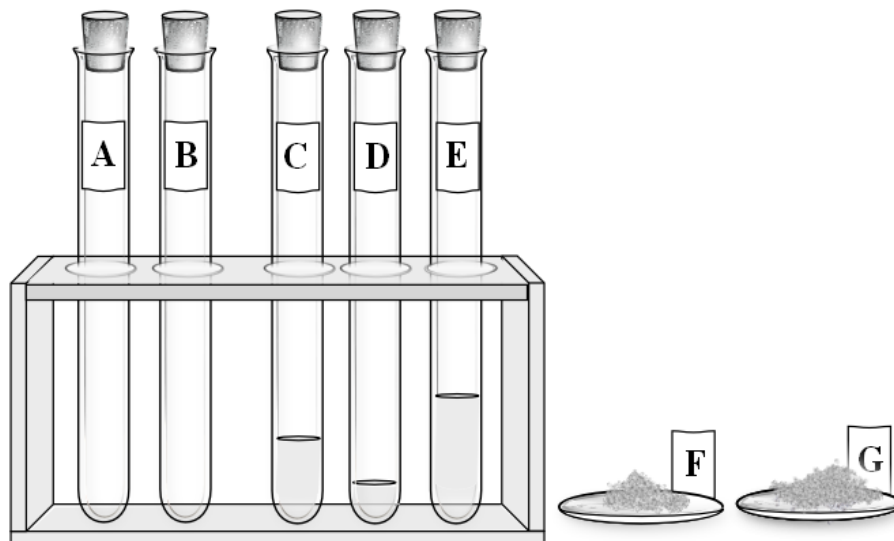
(*a*)   Describe how to chemically test sample **A** or **B** for unsaturation.   (9)

(*b*)   (*i*)   At room temperature (20 °C) it was observed that **D** evaporated more quickly than either **C** or **E**.
            Based on this observation deduce the identity of liquid **D**.
            Describe a chemical test to confirm that **D** can be very easily oxidised.   (12)

        (*ii*) Some water was added to liquids **C** and **E** and the test-tubes were stoppered and shaken vigorously. After the test-tubes were allowed to stand, a white emulsion was observed in the test-tube containing **C** and a colourless solution in the test-tube containing **E**. Identify **C** and **E**.

                A small volume of cyclohexane was then added to the test-tube containing **C**. The test-tube was stoppered and again shaken vigorously and the stopper loosened. What was observed after the test-tube was again allowed to stand?   (9)

        (*iii*) A piece of freshly-sanded magnesium ribbon was then added to the test-tube containing **E**. Write a balanced equation for the reaction that took place.   (6)

(*c*)   (*i*)   Describe with the aid of a labelled diagram a method used to measure the melting point of a sample of benzoic acid.

        (*ii*) The melting-point range of **F** is lower and broader than that of **G**.
                Which is the purer benzoic acid sample?

        (*iii*) Name a laboratory technique that could be used to purify impure benzoic acid.

                                                                                                  (14)

3. In an investigation into the decomposition of a hydrogen peroxide solution, using a manganese(IV) oxide catalyst, the volume of oxygen produced was monitored with time. Two runs were conducted under the same conditions of temperature and pressure, using the same initial volume of the same hydrogen peroxide solution, and the same mass of catalyst from two different suppliers, **A** and **B**. The volumes of oxygen collected at a set of times common to both runs are recorded in the table below.

	Time (minutes)	0.0	1.0	2.0	3.0	5.0	6.5	8.0	9.5	11.0	12.0
Run A	Volume (cm³)	0	25	41	54	72	78	81	82	82	82
Run B	Volume (cm³)	0	16	28	39	57	68	76	80	82	82

(*a*) Draw a labelled diagram of an apparatus that could have been used in either run of this investigation. (8)

(*b*) On the same sheet of graph paper, using a common set of axes, plot a graph of volume of oxygen produced *versus* time for each run. (18)

(*c*) Calculate the instantaneous rate of reaction (in cm³ O_2 per minute) for run **A** at 4.0 minutes. (6)

(*d*) Which run, **A** or **B**,

   (*i*) reached completion first,

   (*ii*) had the slower initial rate?

   What type of catalysis was involved in the reactions?

   Suggest how the catalyst used in run **A** may have differed from that used in run **B** to account for your answers to parts (*i*) and (*ii*). (12)

(*e*) The labels on the containers of the chemicals used in this investigation should carry appropriate warning symbols.

hydrogen peroxide		manganese(IV) oxide	
GHS*	Older**	GHS*	Older**

*New GHS (Globally Harmonised System) pictograms have red borders and black symbols on a white background.
**Older pictograms with black symbols on amber squares are to be phased out by June 2017.

What chemical hazard is indicated by the pictograms shown for

   (*i*) hydrogen peroxide,

   (*ii*) manganese(IV) oxide? (6)

Section B
See page 1 for instructions regarding the number of questions to be answered.

4.   Answer **eight** of the following (*a*), (*b*), (*c*), etc.   (50)

(*a*)   A dipositive ion, M^{2+}, has 25 electrons and 32 neutrons.
What is (*i*) the atomic number, (*ii*) the mass number, of **M**?

(*b*)   Describe the plum-pudding model of the atom proposed by Thomson around 1897.

(*c*)   Explain why the first ionisation energy of oxygen is lower than that of nitrogen despite the general increase in values across the second period of the periodic table.

(*d*)   Distinguish between sigma and pi covalent bonding.

(*e*)   Write (*i*) the conjugate acid, (*ii*) the conjugate base, of $H_2PO_4^{-}$.

(*f*)   What was Gay-Lussac's observation about reactions involving gaseous reactants and products?

(*g*)   The structure of the cinnamaldehyde molecule is shown.
How many moles of cinnamaldehyde are there in 1.65 g of the pure compound?
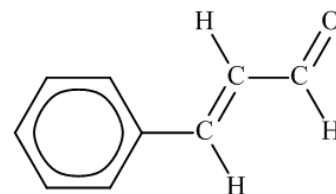
(*h*)   How would you confirm the presence of the sulfite ion in aqueous solution?

(*i*)   What is meant by the activation energy of a reaction?

(*j*)   By referring to the diagram of the infrared spectrum of aspirin, or otherwise, give a simple explanation of the *principle* of infrared spectrometry.
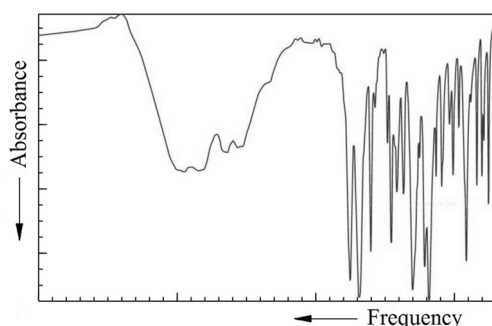
(*k*)   Answer part **A** *or* part **B**.

    A   Describe a chemical method for removing acidic gases from industrial chimney waste.

<p align="center">***or***</p>

    B   Name the analytical technique that was the basis of the work for which Dorothy Hodgkin was awarded the 1964 Nobel Prize for Chemistry.

5. (*a*) The diagram shows the relationship between the visible lines in the hydrogen spectrum and the corresponding energy levels in a hydrogen atom.
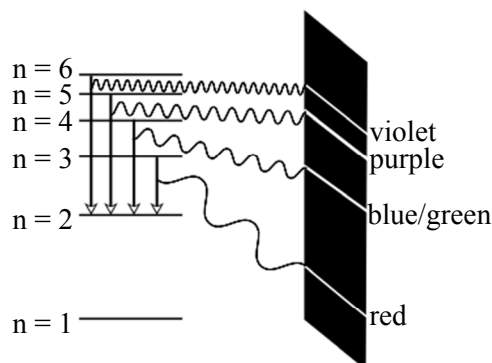
(*i*) Distinguish between the *ground state* and the *excited states* of the electron in a hydrogen atom.

(*ii*) How can the electron in a hydrogen atom become excited?

(*iii*) Explain the origin of the series of visible lines in the emission spectrum of hydrogen.

What name is given to this series?

(*iv*) Explain why there is no yellow line in the hydrogen emission spectrum. (24)

(*b*) Describe how to carry out a flame test to confirm the presence of lithium in a salt sample. (9)

(*c*) Atomic energy levels first described by Bohr are now known to contain energy sublevels and orbitals.

Define an atomic orbital.

Distinguish between a 2*p* orbital and a 2*p* sublevel.

Write the *s, p* electron configuration for a calcium atom.

Explain in terms of energy sublevels why the arrangement of electrons in the main energy levels in a calcium atom is 2, 8, 8, 2 and not 2, 8, 10. (17)

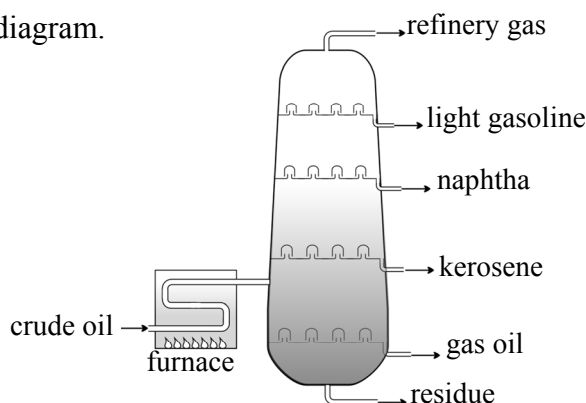**6.** (*a*) Name the oil refining process shown in the diagram.

Naphtha is a mixture of hydrocarbons of similar relative molecular masses.

Identify the physical property that is the basis for these hydrocarbons being isolated as naphtha in this process. (11)

(*b*) Give a major use for
(*i*) kerosene,
(*ii*) residue. (6)

(*c*) Name the oil refining process that converts octane into 2,2,4-trimethylpentane.

Name the oil refining process that converts octane into ethylbenzene according to the following balanced equation.

$$C_8H_{18\ (l)} \quad \rightarrow \quad C_8H_{10\ (l)} \ + \ 4H_{2\ (g)}$$

Explain why these conversions are desirable.

Calculate the heat of reaction for the conversion of octane to ethylbenzene above, given that the heats of formation of octane and ethylbenzene are –250.1 and –12.5 kJ mol^{-1} respectively. (18)

(*d*) On undergoing catalytic cracking a gas oil molecule $C_{18}H_{38}$ is broken into three smaller molecules, each of which is a hydrocarbon. Two of these hydrocarbons are octane and propene. Deduce the molecular formula of the third molecule formed. (6)

(*e*) Draw the molecular structure of (*i*) octane, (*ii*) 2,2,4-trimethylpentane, (*iii*) ethylbenzene. (9)

7. In the Contact process for the manufacture of sulfuric acid, the key stage is the reaction of sulfur dioxide and oxygen, in contact with a vanadium(V) oxide (V_2O_5) catalyst, to form sulfur trioxide. Chemical equilibrium is established according to the following balanced equation.

$$2SO_{2\ (g)} \ + \ O_{2\ (g)} \ \leftrightharpoons \ 2SO_{3\ (g)} \qquad \Delta H = -196 \text{ kJ}$$

(*a*) State Le Châtelier's principle.

Use Le Châtelier's principle to predict and explain the conditions (i.e. high or low) of (*i*) *temperature*, (*ii*) *pressure*, that would maximise the yield of sulfur trioxide.

Explain why the temperature conditions predicted are *not* used industrially. (20)

(*b*) State and explain the effect, if any, of the presence of the catalyst on the equilibrium yield of sulfur trioxide. (6)

(*c*) A mixture of 96 g of sulfur dioxide and 24 g of oxygen was placed in a 50 litre container and reached equilibrium with sulfur trioxide at a certain temperature according to the balanced equation above. At equilibrium, 112 g of sulfur trioxide were present.

Write the equilibrium constant (K_c) expression for this reaction.

Calculate the value of K_c under these conditions. (24)

8. Consider the reaction scheme on the right.

(*a*) Name **A** and polymer **B**. (6)

(*b*) Identify substance **X** used in the conversion of **A** to ethene.

What organic reaction type is involved in this conversion?

How does the geometry around the carbon atoms change in this conversion? (9)

(*c*) What organic reaction type is involved in the conversion of ethane to chloroethane?

Describe in detail the mechanism for the reaction between ethane and chlorine in ultraviolet light to produce chloroethane.
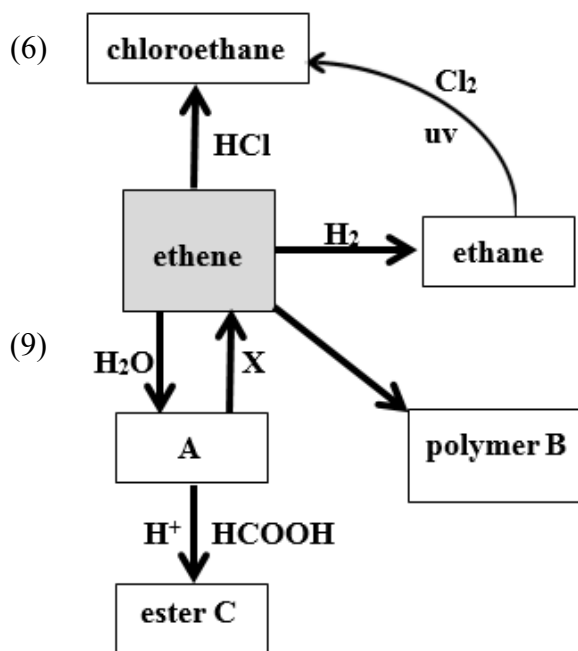
Explain the effect of the presence of a little tetraethyllead, **Pb(C₂H₅)₄**, on this conversion. (21)

(*d*) Ester **C** is formed when **A** is heated with methanoic acid and a few drops of sulfuric acid acting as a catalyst.

Name **C** and draw its structure.

In your drawing, circle the carbonyl group of the ester.

What name is given to the type of reaction that occurs between sodium hydroxide and **C**? (14)

9. (*a*) To determine the biochemical oxygen demand (BOD) of the water in a lake, two samples were taken and one was tested immediately.

(*i*) Under what conditions was the second sample stored?

(*ii*) After what time interval was it tested? (9)

The result of the BOD test suggested that eutrophication had occurred in the lake.

(*iii*) Define *eutrophication* and state one of its harmful effects.

(*iv*) Suggest a possible cause of eutrophication. (9)

(*b*) Why is there concern about lead in drinking water?

Name an instrumental method used to analyse water for heavy metals.

How can lead be removed from a contaminated water supply? (12)

(*c*) How does temporary hardness arise in rainwater flowing over limestone? (6)

(*i*) Write a balanced equation to describe the formation of limescale when this water is boiled.

(*ii*) Explain in words or by balanced equations how this water with temporary hardness is deionised using a cation-exchange resin (**RH**) and an anion-exchange resin (**R*OH**). (14)

10. Answer any **two** of the parts (*a*), (*b*) and (*c*). (2 × 25)

(*a*) (*i*) Distinguish between a strong acid and a weak acid. (6)

(*ii*) Calculate the molarity of a sulfuric acid solution that has a pH of 2.0.

The acid dissociation constant (K_a) for a weak monobasic acid is 1.8×10^{-4}.
Calculate the molarity of a solution of this acid that also has a pH of 2.0. (12)

(*iii*) Define K_w (the ionic product of water). (6)

The value for K_w at 59 °C is 9.0×10^{-14}.
What is the hydrogen ion concentration in pure water at this temperature? (7)

(*b*) Define reduction in terms of (*i*) electron transfer, (*ii*) change in oxidation number. (6)

$$ClO^- + S_2O_3^{2-} + OH^- \rightarrow Cl^- + SO_4^{2-} + H^+$$

$$ClO_3^- + Br^- + H^+ \rightarrow Cl^- + Br_2 + H_2O$$
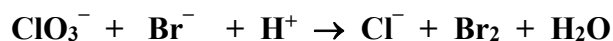
Assign oxidation numbers in the first equation above to identify
(*iii*) the reducing reagent, (*iv*) the oxidising reagent. (9)
Using oxidation numbers, or otherwise, balance *either* equation. (10)

(*c*) (*i*) What are isotopes?
What is a *radioisotope*?
Define the half-life of a radioisotope. (13)

(*ii*) John Joly was an Irish scientist who
in 1914 pioneered the treatment of cancer
using a radium compound containing
radium–226.

Complete the following nuclear equation to show the alpha decay of radium–226.

$$^{226}_{88}\text{Ra} \rightarrow \underline{\hspace{2cm}} + \underline{\hspace{2cm}}$$ (6)
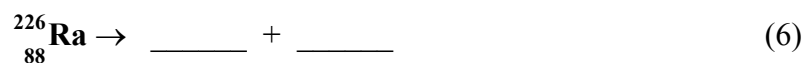
(*iii*) Radium–223 undergoes alpha decay and is also used in radiotherapy.
Starting with a sample containing 1.0×10^{-4} moles of radium–223, how many
of these atoms remain when 87.5% of the sample has decayed? (6)

11. Answer any **two** of the parts (*a*), (*b*) and (*c*).   (2 × 25)

(*a*)   A mixture of potassium nitrate and sulfur reacts according to the following balanced equation.

$$4KNO_{3\ (s)} + 5S_{(s)} \rightarrow 2K_2O_{(s)} + 2N_{2\ (g)} + 5SO_{2\ (g)}$$

One of the two reactants is in stoichiometric excess when 20.2 g of potassium nitrate is mixed with 24.0 g of sulfur.

(*i*)   Which reactant is in excess?
What mass of this reactant is unused at the end of the reaction?   (13)

(*ii*)   Calculate the total volume (in litres) of gaseous products, measured at s.t.p., formed in the reaction.   (6)

(*iii*)   What mass of solid is produced?   (6)

(*b*)   Consider the three gaseous hydrides **NH₃**, **PH₃** and **AsH₃**.

Molecular formula	Common name	IUPAC name	Boiling point (°C)
NH₃	ammonia	azane	− 33.3
PH₃	phosphine	phosphane	− 87.7
AsH₃	arsine	arsane	− 62.5

Using data in the *Formulae and Tables* booklet determine the type of bonding arsine is expected to have.

Draw a dot and cross diagram (valence electrons are sufficient) to show the bonding in arsine.
Predict the shape of the arsine molecule.   (13)

Which, if any, of the three hydrides would you expect to have intermolecular hydrogen bonding?
Justify your answer.

Suggest a reason why
(*i*)   ammonia has the highest boiling point of the three hydrides,
(*ii*)   phosphine's boiling point is lower than that of arsine.   (12)

(*c*)   Answer part **A** *or* part **B**.

A

Environmental scientists continue to be concerned about the slow recovery of ozone concentrations in the stratosphere despite the successes of the 1987 Montreal Protocol, an international treaty designed to control substances that deplete ozone.

(*i*)   What is the beneficial effect of the ozone layer?   (4)

(*ii*)   How is ozone formed in the stratosphere?   (9)

(*iii*) CFCs release chlorine radicals when they photodissociate in the stratosphere. Describe using balanced equations why chlorine radicals are so damaging to the ozone layer.   (9)

(*iv*)   Why are HCFCs significantly less damaging to the ozone layer than CFCs?   (3)

or

B

The diagram shows a Downs cell used to electrolyse molten sodium chloride.
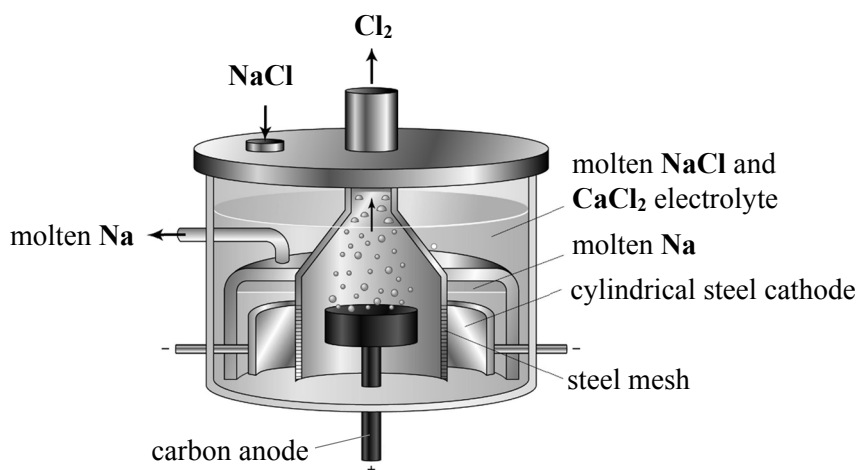
(*i*)   Give one everyday application for each product of this electrolysis.   (6)

(*ii*)   Why must the electrolyte be molten?
        How does using some calcium chloride as part of the electrolyte make the electrolysis more cost effective?   (6)

(*iii*) What is the function of the steel mesh?   (3)

(*iv*)   Write a balanced equation for the cell reaction.   (6)

(*v*)   Why is electrolysis the method of choice for the extraction of aluminium from its ores?   (4)

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