Coimisiún na Scrúduithe Stáit
State Examinations Commission

LEAVING CERTIFICATE EXAMINATION, 2014

CHEMISTRY – HIGHER LEVEL

TUESDAY, 17 JUNE – AFTERNOON 2.00 TO 5.00

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400 MARKS

Answer **eight** questions in all.

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

All questions carry equal marks (50).

The information below should be used in your calculations.

Relative atomic masses: H = 1, C = 12, N = 14, O = 16, Na = 23, S = 32, K = 39, Cr = 52, I = 127

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

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

Ionic product of water, $K_w = 1.0 \times 10^{-14}$ mol^2 l^{-2} at 25 °C

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. A batch of washing soda crystals (hydrated sodium carbonate, $\mathbf{Na_2CO_3 . \mathit{x}H_2O}$) had lost some of its water of crystallisation by a process called efflorescence. A chemist was required to determine the percentage water of crystallisation in the crystals and the value of $\boldsymbol{x}$, the average number of water molecules in the formula.

A sample of the crystals was accurately weighed and found to have a mass of 2.50 g. The sample was dissolved in deionised water and made up to 250 cm^3 of solution. A number of 25.0 cm^3 portions of this solution were titrated with a previously <u>standardised</u> 0.10 M hydrochloric acid (**HCl**) solution. The mean volume of the hydrochloric acid solution required to reach the end point was 21.6 cm^3.

The balanced equation for the titration reaction is:

$$\mathbf{2HCl + Na_2CO_3 \rightarrow 2NaCl + H_2O + CO_2}$$

(*a*) Explain the underlined term. (5)

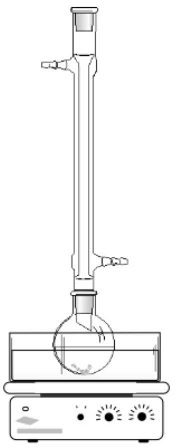
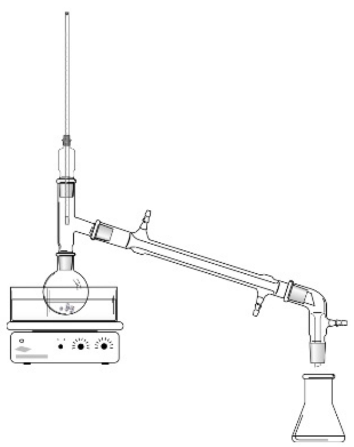
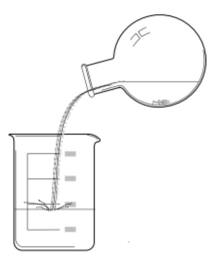
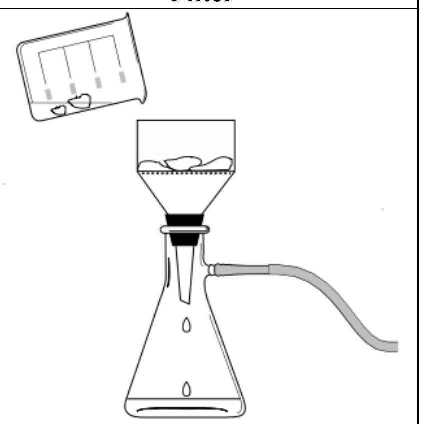
(*b*) Describe in detail how the chemist should have dissolved the weighed sample of washing soda crystals and made the solution up to exactly 250 cm^3. (12)

(*c*) State **one** precaution that should have been taken as the end point of the titration was approached. Explain how this precaution would have contributed to the accuracy of the titration result. (6)

(*d*) Name a suitable indicator for this titration. State the colour change in the titration flask at the end point. (9)

(*e*) From the mean volume of the hydrochloric acid solution, calculate the concentration of sodium carbonate ($\mathbf{Na_2CO_3}$) in the original solution in (*i*) moles per litre, (*ii*) grams per litre. (9)

(*f*) Calculate the percentage water of crystallisation in the crystals and the value of $\boldsymbol{x}$, the average number of water molecules in the formula $\mathbf{Na_2CO_3 . \mathit{x}H_2O}$. (9)

Diagrams for Question 2			
Stage 1 Reflux	Stage 2 Distil	Stage 3 Decant	Stage 4 Filter
			

2. A student prepared a sample of soap in the school laboratory. The experiment was carried out in the four stages illustrated on the previous page. At Stage 1, using a water bath, the student refluxed for approximately 20 minutes 4.45 g of glyceryl tristearate (an animal fat) together with an excess of sodium hydroxide pellets, anti-bumping material and about 30 cm^3 of ethanol. The reaction shown in the following balanced equation took place.

$$\begin{array}{l} \mathbf{C_{17}H_{35}COOCH_2} \\ \quad\quad\quad\quad\quad | \\ \mathbf{C_{17}H_{35}COOCH} \\ \quad\quad\quad\quad\quad | \\ \mathbf{C_{17}H_{35}COOCH_2} \end{array} \quad + \quad \mathbf{3NaOH} \quad \rightarrow \quad \mathbf{3C_{17}H_{35}COONa} \quad + \quad \textbf{co-product}$$

glyceryl tristearate

soap (sodium stearate)

The apparatus was then allowed to cool and rearranged for Stage 2, distillation, again using a water bath. After distillation, the contents of the distillation flask were decanted or washed into a beaker containing brine – Stage 3. Filtration was used in Stage 4 to isolate the soap which was then thoroughly washed.

(*a*) What is the purpose of refluxing in Stage 1 of the preparation?
Name the type of reaction that occurred during this stage. (8)

(*b*) What substance was removed by distillation in Stage 2? (3)

(*c*) Explain the function of the brine in Stage 3. (6)

(*d*) Why was it necessary to wash the soap thoroughly in Stage 4?
How should the student have washed the soap? (6)

(*e*) Draw the structure *or* give the name of the co-product of the reaction.
Where was the co-product located at the end of the process? (9)

(*f*) Given that the sodium hydroxide was in excess, calculate the maximum yield in grams of soap that could have been obtained in this preparation. (12)

(*g*) Suggest, with reference to its structure, how a soap like sodium stearate can dissolve both the non-polar oils *and* the ionic salts in sweat from the skin. (6)

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3. An experiment to investigate the effect of temperature on the rate of the reaction between 0.05 M sodium thiosulfate solution and an excess of 3 M hydrochloric acid solution was carried out as follows. A timer was started as 5 cm^3 of the acid were added to 100 cm^3 of the sodium thiosulfate solution in a conical flask and a value was obtained for the time taken for the reaction to progress to a certain observable stage. The reciprocal of this time (1/time) was taken as an approximate measure of the initial rate of the reaction. This procedure was repeated at a number of different temperatures. The temperatures and their corresponding reaction times and rates are shown in the table below.

(*a*) Explain the term *rate of reaction*. (5)

(*b*) (*i*) Describe *and* explain the change observed in the conical flask during the reaction.

(*ii*) Describe how this observed change was used to obtain the reaction times. (12)

(*c*) Plot a graph of reaction rate (1/time) *versus* temperature. (12)

(*d*) Describe *and* explain the relationship shown in your graph between rate of reaction and temperature. (9)

(*e*) Use your graph to find the value for the reaction time at 35 ºC. Give your answer correct to the nearest second. (6)

temperature (ºC)	time (s)	1/time (s^{-1})
0	976	0.001
12	485	0.002
23	182	0.005
30	99	0.010
39	53	0.019
47	33	0.030
57	20	0.050

(*f*) What would be the effect on the reaction times if the experiment were repeated using 0.025 M sodium thiosulfate solution? Justify your answer. (6)

Section B

[See page 1 for instructions regarding the number of questions to be answered.]

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

(*a*) What colour is observed in a flame test on a salt of (*i*) barium, (*ii*) lithium?

(*b*) Describe the structure of Thomson's 'plum pudding' model of the atom.

(*c*) Write a balanced nuclear equation for the beta-particle decay of the $^{223}_{87}\mathbf{Fr}$ nucleus.

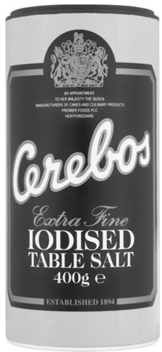
(*d*) The scientist pictured on the right is Werner Heisenberg.
State the famous principle, published in 1927, which bears his name.

(*e*) How many (*i*) sigma bonds, (*ii*) pi bonds, result from sharing of the valence electrons between the atoms in a molecule of nitrogen?

(*f*) What is meant by *one mole* of a substance?

(*g*) Find the empirical formula of a compound containing 40% sulfur and 60% oxygen, by mass.

(*h*) Potassium iodide (**KI**) is sometimes added to table salt to supplement diets low in iodide ion (**I⁻**). Calculate the daily mass of potassium iodide needed to supply 0.15 mg of iodide ion, the Recommended Daily Amount (RDA) for normal human thyroid function.



(*i*) Give **two** structural features of hydrocarbons with high octane numbers.

(*j*) State **two** processes that are carried out during the primary treatment of sewage.

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

A Give **two** uses for the oxygen gas produced by the fractionation of liquid air.

or

B State **two** advantages of anodising aluminium.

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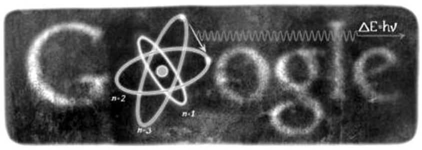
5. (*a*) Name the scientist whose work on energy levels in the hydrogen atom is depicted in the Google doodle reproduced on the right.



Distinguish between the terms *energy level* and *atomic orbital*. (14)

Write the electron configuration (*s*, *p*) of an atom of silicon showing the distribution of electrons in atomic orbitals in the ground state. (6)

Hence, state how many (*i*) main energy levels, (*ii*) atomic orbitals, are occupied in the silicon atom in its ground state. (6)

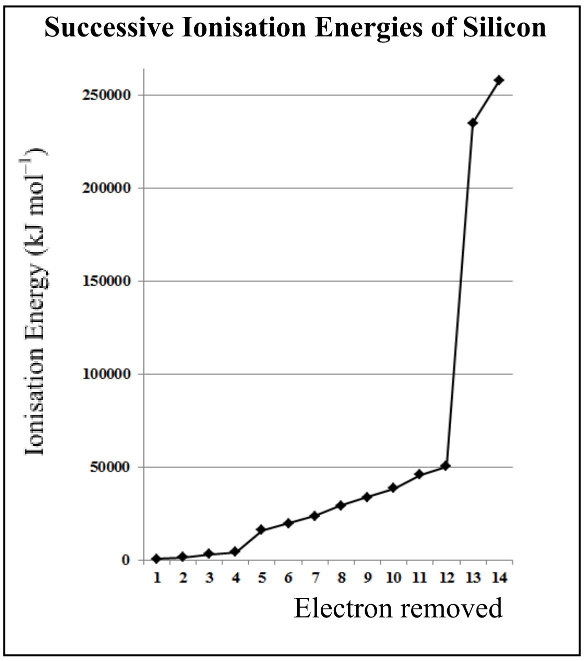
(*b*) Define *first ionisation energy*. (6)

Explain why the first ionisation energy value of silicon is

(*i*) greater than that of aluminium,

(*ii*) less than that of carbon. (9)

(*c*) The successive ionisation energies of silicon are shown in the graph on the right.



Explain how the graph provides evidence for energy levels in the silicon atom. (6)

What other experimental evidence do we have for the existence of energy levels in atoms? (3)

6. The fuel in camping gas cylinders, like the one pictured on the right, is a liquefied mixture of propane, butane, and another compound which is a structural isomer of butane.

(*a*) Name the homologous series to which propane and butane belong.
Draw the structural formula of propane. (8)

(*b*) Propane and butane have boiling points of –42.1 ºC and –0.5 ºC, respectively.
Explain why propane has a lower boiling point than butane. (6)

(*c*) (*i*) What is meant by saying that compounds are *structural isomers*?
(*ii*) Draw the structural formula of the isomer of butane. (12)

(*d*) Define *heat of combustion*.
Write the balanced equation for the complete combustion of butane in an adequate supply of oxygen.
Calculate the heat of combustion of butane, given that the heats of formation of carbon dioxide, water and butane are –393.5, –285.8 and –125.7 kJ mol^{-1}, respectively. (24)

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7. Nitrous acid (**HNO_2**) is a weak acid that is readily oxidised to the strong acid, nitric acid (**HNO_3**).

(*a*) Distinguish between a *strong acid* and a *weak acid* according to the Brønsted-Lowry theory. (8)

(*b*) Nitrous acid dissociates in water as follows:

$$\mathbf{HNO_2 \quad + \quad H_2O \quad \leftrightharpoons \quad H_3O^+ \quad + \quad NO_2^-}$$

Identify the two substances acting as bases in this equilibrium. (6)

(*c*) Define pH.
The pH of a 0.2 M solution of nitrous acid is 2.0 at a temperature of 25 °C.
Calculate the concentration of **H_3O^+** ion in this solution in moles per litre.
Explain clearly how this **H_3O^+** ion concentration confirms that nitrous acid is a *weak* acid.
What concentration of nitric acid would have the same **H_3O^+** ion concentration?
Calculate the **OH^-** ion concentration in both of these acidic solutions. (18)

(*d*) Nitric acid and its salts contain the nitrate ion (**NO_3^-**).
Describe in detail how you could test for the presence of the nitrate anion in aqueous solution. (12)

(*e*) Explain how high nitrate levels can result in a reduction in the dissolved oxygen content of lakes and rivers. (6)

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8. Answer the questions that follow with reference to hydrocarbons **A**, **B** and **C** below.

C_2H_2	**C_2H_4**	**C_2H_6**
A	**B**	**C**

(*a*) Give the IUPAC name and draw the structural formula of compound **B**. (5)

(*b*) Draw a labelled diagram to show how a sample of compound **A** can be prepared and collected in the school laboratory. (12)

(*c*) Describe a chemical test to distinguish between samples of compounds **B** and **C**. (9)

(*d*) Hydrocarbon **C** reacts with chlorine gas (**Cl_2**) in the presence of ultraviolet light.
(*i*) Name the type of mechanism by which this reaction takes place.
(*ii*) Give a detailed description of the mechanism of this reaction.
(*iii*) Explain clearly how the occurrence of another hydrocarbon in the product mixture provides evidence for the mechanism. (24)

9. Consider the following reversible reaction

$$2NO_{(g)} \leftrightharpoons N_{2\,(g)} + O_{2\,(g)} \qquad \Delta H = -183 \text{ kJ}$$

that has an equilibrium constant ($\boldsymbol{K}_c$) value of 20.25 at a certain high temperature T.

(*a*) Write the equilibrium constant expression for the reaction. (5)

(*b*) Calculate the number of moles of nitrogen gas (N_2) in the reaction mixture at equilibrium when a 2 mole sample of nitrogen monoxide decomposes to nitrogen gas and oxygen gas in a closed container at temperature T. (12)

(*c*) State *Le Châtelier's principle.* (6)

What effect, if any, would an increase in (*i*) the temperature, (*ii*) the pressure, have on the value of $\boldsymbol{K}_c$ for this reaction?

Justify your answer in each case. (12)

(*d*) This reaction is one of several that occur in the catalytic converters fitted to car exhausts. Since the exhaust gases are in the catalytic converter of the car for a very short time (0.1 – 0.4 seconds), the rate of reaction must be very high.

Name two of the metals used as catalysts in catalytic converters.

What type of catalysis occurs?

Give **one** way that the catalysts increase the rate of reaction.

Name a substance that could 'poison' the catalysts of the catalytic converter. (15)

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

(*a*) Study the reaction scheme below and answer the questions that follow with reference to the compounds **X**, **Y** and **Z**, each of which has two carbon atoms in its molecules.

(*i*) Give a major use for compound **Z**. (4)

(*ii*) Draw the structure of aldehyde **Y** showing the bonding between the atoms. (6)

(*iii*) Draw the structural formula of the ester formed from compounds **X** and **Z**.
Identify any carbon atom in this ester that is in planar geometry. (9)

(*iv*) How could aldehyde **Y** be reduced to alcohol **X**? (6)

(*b*) Define (*i*) mass number, (*ii*) relative atomic mass. (9)

Three of the five fundamental processes that occur in mass spectrometry are *detection*, *acceleration* and *vaporisation of substance*.

What are the two other fundamental processes that occur in mass spectrometry? (6)

List all five processes in the order in which they occur. (3)

A sample of the element gallium is composed of 60.1% gallium–69 and 39.9% gallium–71.

Calculate the relative atomic mass of gallium from this information. (7)

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

Use oxidation numbers to identify (*iii*) the oxidising agent, (*iv*) the reducing agent, in the following reaction.

$$Cd + H^+ + NO_3^- \rightarrow Cd^{2+} + NO + H_2O \qquad (12)$$

Hence, or otherwise, balance the equation. (7)

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

(*a*) Define *electronegativity*. (6)

Ammonia ($\mathbf{NH_3}$) and silane ($\mathbf{SiH_4}$) are small molecules, each of which has four electron pairs in the valence shell of the central atom.

Account for the difference in bond angle between the two molecules, 107.3° in ammonia and 109.5° in silane. (6)

Use electronegativity values to determine which bond, the N–H bond in ammonia or the Si–H bond in silane, is the more polar. (3)

Which of the two substances has hydrogen bonding between its molecules? Justify your answer. (6)

Give the reason why a molecule with polar bonds can be non-polar. (4)

(*b*) When crystals of ammonium dichromate [$\mathbf{(NH_4)_2Cr_2O_7}$] are heated strongly, they decompose fully according to the following balanced equation.

$$\mathbf{(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4H_2O}$$

When 12.6 g of these crystals were heated strongly, calculate

(*i*) how many moles of ammonium dichromate reacted, (6)

(*ii*) the mass of chromium(III) oxide ($\mathbf{Cr_2O_3}$) formed, (6)

(*iii*) the volume at s.t.p. of nitrogen gas evolved, (6)

(*iv*) the number of molecules of water produced.
How many atoms did this quantity of water contain? (7)

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

A

The Earth's human population is now estimated at 7 billion (7×10^9) and is expected to increase to between 8.3 and 10.9 billion by 2050. Rising levels of air pollution are a direct consequence of an increasing global human population. One manifestation of air pollution is the phenomenon of 'acid rain'.

The EPA (Environmental Protection Agency) reported in 2012 that '*Air quality in Ireland is of a high standard across the country and is among the best in Europe*'.

(*i*) Why is rainwater *always* acidic, even when there is no air pollution? (4)

(*ii*) Outline two damaging effects of 'acid rain' on the environment. (6)

(*iii*) Show, by means of equations, how sulfur dioxide pollution in the atmosphere results in 'acid rain'. (9)

(*iv*) How does human activity contribute to increasing sulfur dioxide levels in the atmosphere? (3)

(*v*) Suggest a reason why Ireland's air quality is of a high standard. (3)

or

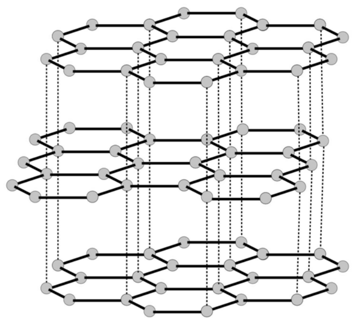
B

Many solid materials are classified as ionic, molecular, covalent or metallic <u>crystals</u>. Their properties can often be explained in terms of their crystal structures.

(*i*) Explain the underlined term. (7)

(*ii*) The 'lead' in pencils is actually graphite (mixed with clay). Graphite is a crystalline form of the element carbon. Part of the structure of graphite is shown.

Describe how the bonding in graphite enables it to be used for writing or as a lubricant. (6)



(*iii*) Diamond, another crystalline form of elemental carbon, is the hardest naturally-occurring substance.

Refer to its crystal structure to account for the hardness of diamond. (6)

(*iv*) Explain why metals are often excellent electrical conductors. (6)

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