Coimisiún na Scrúduithe Stáit
State Examinations Commission

LEAVING CERTIFICATE EXAMINATION, 2019

CHEMISTRY – HIGHER LEVEL

TUESDAY, 18 JUNE – AFTERNOON 2:00 to 5:00

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400 MARKS

This examination will be marked on screen.

The superintendent will give you a special answerbook.

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 (rounded): H = 1.0, C = 12, N = 14, O = 16, Na = 23, S = 32, Hg = 201

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

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

Molar volume at room temperature and pressure = 24.0 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 superintendent.

Section A

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

1. A concentration of at least 5 p.p.m. of dissolved oxygen in a water system is required to support a large and varied fish population. The dissolved oxygen concentration of such a system was determined as described below.

A stoppered bottle, completely filled with a sample of the water, was shaken with a concentrated solution containing $\mathbf{Mn^{2+}}$ ions and then with a concentrated solution of alkaline potassium iodide (**KOH**/**KI**). The dissolved oxygen oxidised some of the $\mathbf{Mn^{2+}}$ ions to $\mathbf{Mn^{x+}}$ (***x*** = 3 or 4) ions. These $\mathbf{Mn^{x+}}$ compounds appeared as a brown precipitate. When a small volume of concentrated sulfuric acid was then added, all of the $\mathbf{Mn^{x+}}$ ions oxidised some of the $\mathbf{I^-}$ ions to free iodine ($\mathbf{I_2}$). The concentration of the free iodine was measured by titration with a standard solution of sodium thiosulfate using freshly prepared starch solution as an indicator.

The balanced equation for the titration reaction is:

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

Four moles of $\mathbf{S_2O_3^{2-}}$ were required for every **one** mole of dissolved $\mathbf{O_2}$ present originally.

(*a*) (*i*) Identify the compound usually added to the water to provide the $\mathbf{Mn^{2+}}$ ions.

(*ii*) Explain why a large excess of **KI** was required in this analysis.

(*iii*) What change was observed when the concentrated sulfuric acid was added and mixed thoroughly with the contents of the sample bottle? (12)

(*b*) (*i*) Describe how the conical flask was prepared for a titration and then used during the titration to help ensure that an accurate end point was reached.

(*ii*) Give one way of ensuring that the level of liquid in the burette was at eye level before taking a reading. (12)

(*c*) What colour changes were observed at the titration stage of the experiment

(*i*) up to the point when the indicator was added,

(*ii*) at the end point? (6)

(*d*) The sodium thiosulfate solution contained 3.1 g $\mathbf{Na_2S_2O_3.5H_2O}$ per litre. On average, 6.0 cm^3 of this solution were required for complete reaction with 200.0 cm^3 portions of the iodine solution.

Show by calculation that the dissolved oxygen levels were a threat to fish survival in this water system by finding

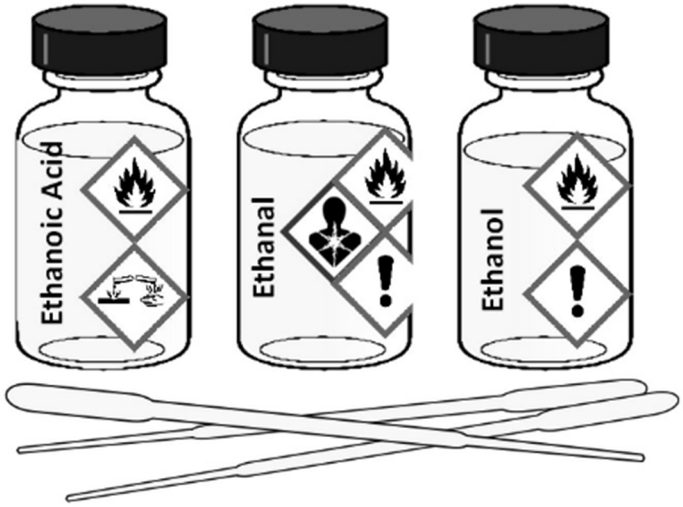
(*i*) the average number of moles of sodium thiosulfate used in a titration,

(*ii*) the number of moles of $\mathbf{O_2}$ that released the $\mathbf{I_2}$ detected in each titration,

(*iii*) the concentration of dissolved oxygen in the water in moles per litre,

(*iv*) the concentration of dissolved oxygen in the water in p.p.m. (mg l^{-1}). (20)

2. Ethanoic acid, ethanal and ethanol are three colourless organic substances, all liquids at 18 °C. A student was provided with small, pure samples of each of these substances in closed sample bottles.



(*a*) The student placed a short strip of freshly-sanded magnesium ribbon into a test tube containing a few drops of ethanoic acid in approximately 10 cm^3 of water and swirled the test tube.

(*i*) What was observed?

(*ii*) Write formulae for both products of the reaction that occurred. (11)

(*b*) Describe a chemical test to show that ethanal can be very easily oxidised. (9)

(*c*) The student was asked to prepare a small quantity of ethene from ethanol using the reaction shown by the balanced equation below. A suitable catalyst and a heat source were provided.

$$C_2H_5OH \rightarrow C_2H_4 + H_2O$$

(*i*) Draw a diagram of an arrangement of apparatus for the preparation and collection of ethene. Indicate clearly on your diagram the location of the ethanol, the catalyst, the heat source, and the ethene produced.

(*ii*) Identify the catalyst and describe its appearance at the beginning of the preparation.

(*iii*) Explain clearly why a risk of hot glassware shattering, due to rapid cooling, is associated with this preparation.
How can this risk be minimised?

(*iv*) A student prepared ethene, starting with 2.9 cm^3 of ethanol (density 0.8 g cm^{-3}). Calculate the volume of ethene gas produced in 26% yield when measured at room temperature and pressure. (30)

3. To determine the relative molecular mass (M_r) of compound **X**, a volatile liquid, a small volume of the pure liquid was vaporised in a suitable container. The atmospheric pressure at the location was obtained using a smart phone barometric sensor, as shown below.

(*a*) Draw a large, labelled diagram of an arrangement of apparatus you used to carry out this experiment.

Show in your diagram

(*i*) how **X** was vaporised,

(*ii*) how the temperature of the vapour was obtained. (11)

(*b*) With reference to your diagram, explain

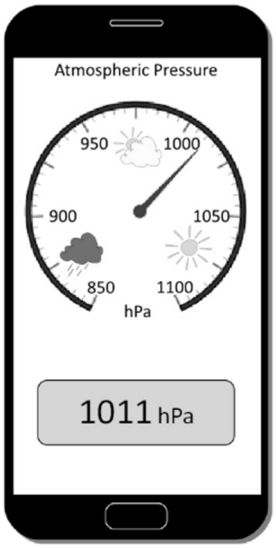
(*i*) why the pressure of the vapour at the end of the heating stage of the experiment was known to be equal to the atmospheric pressure at your location,

(*ii*) how the volume of the vapour was measured. (9)

(*c*) With reference to your diagram, describe how the mass of the vapour in the container at the end of the heating stage was found. (6)

(*d*) Calculate, correct to the nearest whole number, the relative molecular mass of **X**, given that 0.22 g of **X** occupied a volume of 76 cm^3 at a pressure of 1.011×10^5 Pa and a temperature of 99 °C. (15)

(*e*) Bromine (**Br_2**) (M_r = 160) has a significantly greater relative molecular mass than water (M_r = 18). Account for the volatility of bromine (boiling point 58.8 °C) compared to that of water (boiling point 100 °C). (9)



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*) What are cathode rays?

(*b*) Bananas contain small quantities of potassium-40, a radioactive isotope. What is the daughter nucleus when **K**-40 emits an electron in beta decay?

(*c*) State Avogadro's law.

(*d*) What is the oxidation number of sulfur in

(*i*) sulfur dioxide ($\mathbf{SO_2}$),

(*ii*) the sulfate ion ($\mathbf{SO_4^{2-}}$)?

(*e*) Give two differences between a sigma and a pi covalent bond.

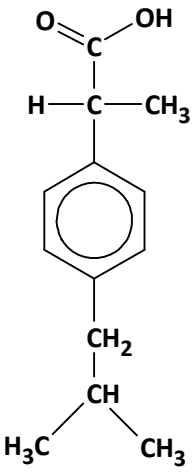
(*f*) In the electrolysis of aqueous **KI** with inert electrodes one half-equation is:

$$\mathbf{2I^-}_{(aq)} \rightarrow \mathbf{I_2}_{(aq)} + \mathbf{2}e^-$$

Write a balanced half-equation for the reaction that takes place at the negative electrode during this electrolysis.

(*g*) Define bond energy.

(*h*) GC and HPLC are instrumental chromatographic techniques. What is the principle of the separation of the components in a mixture using any type of chromatography?



(*i*) The structure of ibuprofen is shown. Ibuprofen is the active ingredient in many fever and pain-relief suspensions given to children. A single 5 cm^3 dose, suitable for children aged 1 to 3 years, contains 4.86×10^{-4} moles of ibuprofen. How many milligrams of ibuprofen are in this single dose?

(*j*) Write a balanced equation for the reaction – between limestone and carbonic acid in rainwater – that gives rise to temporary hardness in the water.

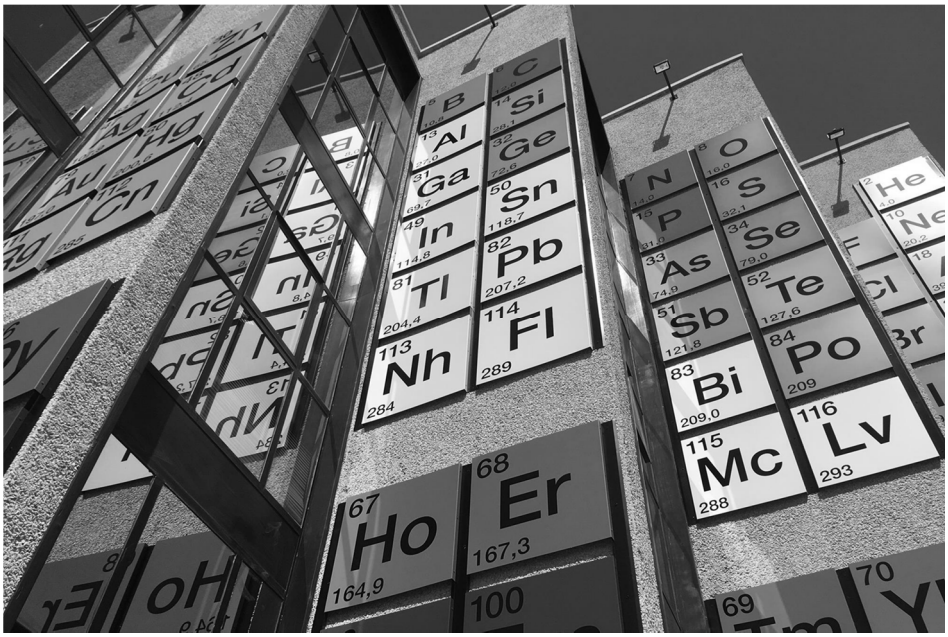
(*k*) Answer part **A** *or* part **B**.

A Why is nitrogen gas unreactive?

or

B Draw two repeating units of the polymer poly(propene).

5. To celebrate the 150th anniversary of the discovery of the periodic system, 2019 has been designated as the International Year of the Periodic Table of Chemical Elements by the United Nations (UN).



(*a*) (*i*) What is meant by the *periodic system* in the context of Mendeleev's 1869 periodic table of the elements?

(*ii*) Comment on the positioning of tellurium (**Te**) and iodine (**I**) in the 1869 table.

(*iii*) Why did the 1869 table not include any noble gases? (11)

(*b*) Modern periodic tables arrange the elements in order of <u>atomic number</u> and not in order of <u>relative atomic mass</u>.

(*i*) Define the underlined terms.

(*ii*) Give an advantage of arranging the elements in order of atomic number. (12)

(*c*) Explain

(*i*) why all the elements of Group 18 in the periodic table are chemically inert,

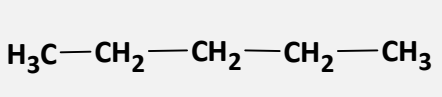
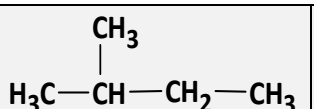
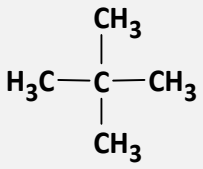
(*ii*) how *and* why the reactivity of the halogens changes down Group 17. (12)

(*d*) The element francium (**Fr**), atomic number 87, was discovered by Marguerite Perey in 1939 but its physical and chemical properties had already been predicted by the periodic system.

(*i*) How would you expect a small sample of francium to react in water? Justify your answer.

(*ii*) Predict the products of this reaction. (15)

6. (*a*) (*i*) What term is used to describe compounds like **A**, **B** and **C** below that have the same molecular formula but different structural formulae?

 **A**	 **B**	 **C**

(*ii*) Why do **A**, **B** and **C** separate in the same fraction in the distillation of crude oil?

(*iii*) Explain which of **A**, **B** and **C** is most likely to auto-ignite in a petrol engine.

(*iv*) Give the systematic IUPAC names for **A**, **B** and **C**. (18)

(*b*) (*i*) Name the oil refining process in which one molecule of alkane **W** was converted into one molecule of octane and two propene molecules.

(*ii*) Deduce the formula of **W**. (9)

(*c*) Tetraethyllead is a petrol additive, now used only in some aeroplane engines.

(*i*) What is the advantage of adding tetraethyllead to petrol?

(*ii*) Why was its use in car engines discontinued?

(*iii*) Tetraethyllead burns completely according to the equation:

$$\mathbf{2(C_2H_5)_4Pb}\ (l) + \mathbf{27O_2}\ (g) \rightarrow \mathbf{16CO_2}\ (g) + \mathbf{20H_2O}\ (l) + \mathbf{2PbO}\ (s)$$

The heats of formation of tetraethyllead, carbon dioxide, water and lead(II) oxide are 52.7, –393.5, –285.8 and –219.0 kJ mol^{-1} respectively.
Calculate the heat of reaction for the combustion of one mole of tetraethyllead. (23)

7. (*a*) Use equations to show that, when dissolved in water,

(*i*) **HCl** acts as a Brønsted-Lowry acid,

(*ii*) **NH_3** acts as a Brønsted-Lowry base.

Explain why

(*iii*) **HCl** has a weak conjugate base,

(*iv*) **NH_3** has a strong conjugate acid. (12)

(*b*) Pure water self-ionises as follows:

$$\mathbf{2H_2O}\ (l) \rightleftharpoons \mathbf{H_3O^+}\ (aq) + \mathbf{OH^-}\ (aq)$$

The ionic product of water (K_w) measures the extent of this self-ionisation. A table of K_w values for pure water at different temperatures is given.

Temperature (°C)	K_w
0	0.1×10^{-14}
10	0.3×10^{-14}
20	0.7×10^{-14}
30	1.4×10^{-14}
40	2.9×10^{-14}
50	5.3×10^{-14}
60	9.3×10^{-14}

(*i*) Write the self-ionisation constant (K_w) expression for water.

(*ii*) Are the data in the table consistent with the self-ionisation of water being an exothermic or an endothermic process? Justify your answer. (12)

(*iii*) Plot a graph of K_w *versus* temperature (°C).

(*iv*) Use your graph to predict the value of K_w at body temperature, 37 °C.

(*v*) Use this value to calculate the **H_3O^+** ion concentration of pure water at 37 °C.

(*vi*) The pH of pure water is close to 6.77 at one of the temperatures in the table. Find, by calculation, this temperature. (26)

8. The table shows the boiling points of four primary alcohols and two secondary alcohols.

Alcohol	Boiling point (°C)
methanol	64.7
ethanol	78.4
propan-1-ol	97.2
propan-2-ol	82.4
butan-1-ol	117.5
butan-2-ol	99.1

(*a*) (*i*) What is a secondary alcohol?

(*ii*) On the same sheet of graph paper and using the same pair of axes, plot the boiling points of these alcohols against the number of carbon atoms present.

(*iii*) State and explain the trend in the boiling points of the four primary alcohols shown as their relative molecular masses increase.

(*iv*) Predict the approximate boiling point of the next alcohol in the same series as propan-2-ol and butan-2-ol. (23)

(*b*) Consider the oxidation of alcohols in which *no* carbon-carbon bonds are broken.

(*i*) Give the systematic IUPAC names for the two possible organic products of such an oxidation of butan-1-ol.

(*ii*) Draw the structure of the organic product when butan-2-ol is oxidised in this way.

(*iii*) Identify clearly which bonds in butan-2-ol are broken in this oxidation. (15)

(*c*) The ester formed from methanol and propanoic acid is found in many fruits.

(*i*) Draw the structure of this ester.

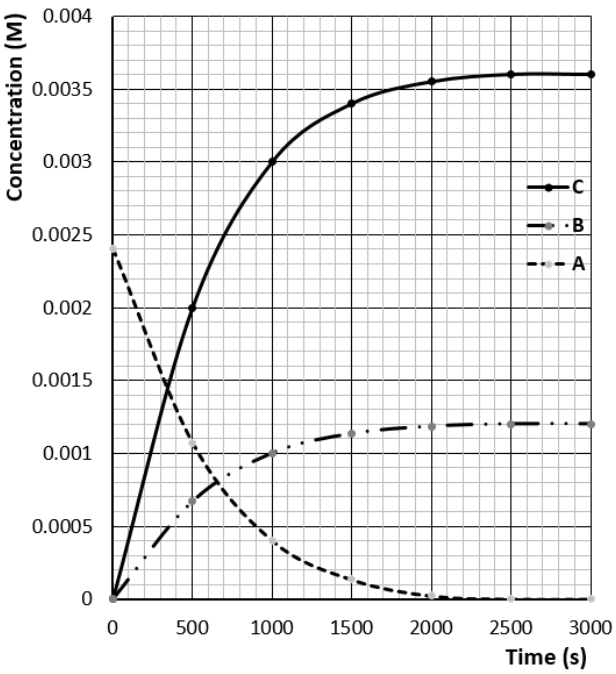
(*ii*) How many carbon atoms in a molecule of this ester are tetrahedrally bonded?

(*iii*) What are the products of the hydrolysis of this ester by **NaOH**? (12)

9. **A** reacts, heterogeneously catalysed by **X**, to form **B** and **C** at temperature ***T*** according to the following balanced equation:

$$\mathbf{2A}_{(g)} \xrightarrow{\mathbf{X}} \mathbf{B}_{(g)} + \mathbf{3C}_{(g)}$$

The graph shows that 0.0024 moles per litre of **A** decomposes to produce 0.0036 moles per litre of **C** over 3000 seconds.



(*a*) Define rate of reaction. (6)

(*b*) Use the graph to find the average rate of formation of **C**, in M s^{-1}, over the first 500 s.

How does the instantaneous rate at 500 s compare with this average rate? (6)

(*c*) Explain the term heterogeneous catalysis.

Describe the surface adsorption theory of catalysis.

Explain why pellets of **X** would be expected to be less effective as the catalyst in this reaction than the same mass of powdered **X**. (15)

(*d*) Without **X** this reaction has a large activation energy. Explain the underlined term.

State and explain two ways of increasing the rate of this reaction, other than by using a catalyst. (18)

(*e*) Is this an equilibrium reaction? Explain your reasoning. (5)

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

(*a*) The mechanism for the substitution reaction between methane and chlorine in ultraviolet light involves free radicals.

(*i*) Explain the underlined term.

(*ii*) How are chlorine free radicals formed at the initiation stage of this reaction?

(*iii*) What name is given to the stage of the mechanism where a chain reaction is occurring?

Write balanced equations, using dots to label the free radicals, for the two reactions that repeat in the chain reaction to give chloromethane and hydrogen chloride.

(*iv*) Identify a hydrocarbon formed in the process.

Explain why only a trace quantity of this product is formed. (25)

(*b*) (*i*) What is meant by an atomic energy level?

(*ii*) Give two differences between an atomic orbit, as described by Bohr, and an atomic orbital.

(*iii*) Use diagrams to distinguish between a *p* orbital and a *p* sub-level (*p* subshell).

(*iv*) Write the electron configuration for a nickel atom in its ground state.

(*v*) State one piece of evidence that supports the existence of atomic energy levels. (25)

(*c*) When 3.17 g of mercury thiocyanate [$\mathbf{Hg(SCN)_2}$] is heated in a well-ventilated fume cupboard it decomposes completely according to the following balanced equation.

$$\mathbf{2Hg(SCN)_2}\ (s) \rightarrow \mathbf{2HgS}\ (s) + \mathbf{CS_2}\ (l) + \mathbf{C_3N_4}\ (s)$$

(*i*) What mass of $\mathbf{C_3N_4}$ is produced in this reaction?

All the products of the reaction above are unstable and, if heating in air is continued, these products burn or decompose according to the following balanced equations.

$$\mathbf{HgS}\ (s) + \mathbf{O_2}\ (g) \rightarrow \mathbf{Hg}\ (l) + \mathbf{SO_2}\ (g)$$

$$\mathbf{CS_2}\ (l) + \mathbf{3O_2}\ (g) \rightarrow \mathbf{CO_2}\ (g) + \mathbf{2SO_2}\ (g)$$

$$\mathbf{2C_3N_4}\ (s) \rightarrow \mathbf{3(CN)_2}\ (g) + \mathbf{N_2}\ (g)$$

If all the reactions go to completion,

(*ii*) how many litres of oxygen gas, measured at s.t.p., are required for the complete combustion of the $\mathbf{CS_2}$,

(*iii*) what is the number of mercury atoms produced,

(*iv*) what is the total number of moles of gas formed? (25)

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

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

(*ii*) Account for the increase in electronegativity values across the second period of the periodic table. (6)

(*iii*) Use electronegativity values to predict the type of bonding in oxygen difluoride (**OF_2**). (3)

(*iv*) State and account for the shape of the **OF_2** molecule. (6)

(*v*) **180.0°** **109.5°** **120.0°** **103.0°**

Select, giving your reasons, which of these angles is the most probable value for the bond angle in oxygen difluoride. (4)

(*b*) Consider the equilibrium represented by the following balanced equation.

$$\mathbf{2BrCl}_{(g)} \rightleftharpoons \mathbf{Br_2}_{(g)} + \mathbf{Cl_2}_{(g)}$$

yellow **red-brown** **green**

(*i*) Write the equilibrium constant (K_c) expression for this reaction. (6)

(*ii*) Calculate the percentage decomposition into bromine and chlorine of 0.200 moles of **BrCl**, placed initially in a 5 litre closed container, and allowed to reach equilibrium at 1200 °C according to the equation above.

Take the value of K_c at this temperature as 0.220.

Give your answer correct to the nearest whole number. (12)

(*iii*) Increasing the pressure on this equilibrium mixture at 1200 °C, intensifies the colour of the mixture but does not change the percentage dissociation of **BrCl**.

Explain. (7)

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

A

The greenhouse effect is a natural phenomenon, enhanced by human activities.
The enhanced greenhouse effect is a cause of concern.

(*i*) What is the greenhouse effect? (3)

(*ii*) Why is the greenhouse effect essential for life on Earth? (3)

(*iii*) Give two human activities that have enhanced the natural greenhouse effect, particularly in recent times. (6)

(*iv*) Give two reasons why different atmospheric gases have different impacts on the greenhouse effect. (6)

(*v*) Compare the contributions of carbon dioxide and water vapour to the natural greenhouse effect.
Account for the difference. (7)

or

B

(*i*) What is a crystal? (4)

(*ii*) Crystals may be classified as ionic, molecular, metallic, and covalent macromolecular.
To which of these categories does crystalline iodine (**I_2**) belong?
Justify your answer. (6)

(*iii*) What technique was used by Dorothy Hodgkin to determine the molecular structure of vitamin B_{12}? (3)

(*iv*) Explain, in terms of its structure and bonding, why graphite can be used as a lubricant. (6)

(*v*) Explain, with reference to the structure of metallic crystals, why silver (**Ag**) is an excellent electrical conductor. (6)

Leaving Certificate – Higher Level

Chemistry

Tuesday, 18 June
Afternoon, 2:00 – 5:00

Image Q4(*b*) on page 5: Juan Zelaya from pixabay.com/en
File: banana-minimum-fruit-tropical-2449019.jpg, accessed 21 November 2018, CCO

Image Q5 on page 6: from the University of Murcia
File:131314_fachada_2_hero2.jpg, accessed 12 November 2018

Image Q11(*c*) A on page 11: Rebecca Humann from pixabay.com/en
File: smoke-stacks-power-plant-power-862929.jpg, accessed 20 October 2018, CCO