Coimisiún na Scrúduithe Stáit
State Examinations Commission

LEAVING CERTIFICATE EXAMINATION, 2021

CHEMISTRY – HIGHER LEVEL

TUESDAY, 22 JUNE – AFTERNOON 2:00 to 5:00

300 MARKS

Answer any **six** questions.

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, Cl = 35.5, K = 39, Cu = 63.5, Br = 80, Ag = 108

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 superintendent.

Section A

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

1. To determine the concentration of hypochlorite ion (**ClO^-**) in a solution of bleach, 25.0 cm^3 of the bleach solution were first diluted to exactly 500 cm^3.

Then a 25.0 cm^3 portion of this diluted bleach solution in a conical flask was acidified with sulfuric acid and, when an excess of concentrated **KI** solution was added, the following reaction took place producing iodine.

$$ClO^- + 2I^- + 2H^+ \rightarrow Cl^- + I_2 + H_2O$$

This iodine solution was titrated with a 0.09 M solution of sodium thiosulfate. The procedure was repeated with a number of 25.0 cm^3 portions of diluted bleach. The balanced equation for the titration reaction is:

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

(*a*) Describe how the 25.0 cm^3 sample of the original bleach solution, provided in a beaker, was diluted to exactly 500 cm^3. (9)

(*b*) Why must *excess* **KI** be added to the diluted bleach? (6)

(*c*) State the colour change observed in the conical flask as a result of the first reaction. (6)

(*d*) (*i*) Identify a suitable indicator for use in the titration stage of the analysis.

(*ii*) Using this indicator, what final colour change was observed in the conical flask at the end point? (9)

(*e*) On average, 21.4 cm^3 of 0.09 M sodium thiosulfate solution were required to completely reduce the iodine generated in the conical flask by a 25.0 cm^3 portion of diluted bleach.

Find by calculation

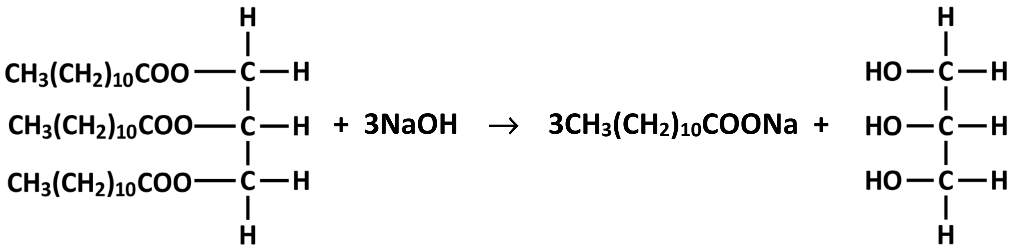
(*i*) the average number of moles of sodium thiosulfate used up in one of the titrations,

(*ii*) the number of moles of iodine reduced in each titration,

(*iii*) the molarity of the original bleach in terms of hypochlorite ion,

(*iv*) the concentration of **ClO^-** ion in the original bleach, to the nearest whole number, expressed as a % (*w*/*v*). (20)

2. Sodium cocoate soap is manufactured by the base hydrolysis of tri-ester molecules in coconut oil. The following is a balanced equation for the hydrolysis of a tri-ester molecule in coconut oil.



tri-ester   soap   co-product

To make sodium cocoate soap, a student mixed some coconut oil, an excess of solid **NaOH**, water and ethanol as solvents, and anti-bumping material in a round-bottomed flask and refluxed the mixture gently for about 20 minutes. The student then removed the ethanol by distillation and transferred the residue of the reaction mixture into a beaker containing brine. The student separated the soap that precipitated from the solution in the beaker and washed it with a small volume of ice-cold water. The product was tested by shaking a small sample of it with deionised water in a stoppered test-tube to confirm that a lather formed.

(*a*) (*i*) Why was the reaction mixture refluxed?

(*ii*) Suggest a suitable heating method for refluxing the reaction mixture and then distilling off the ethanol.

(*iii*) Justify the suitability of your suggested heating method.

(*iv*) Why is it desirable to remove all the ethanol? (14)

(*b*) (*i*) Name the co-product of the reaction.

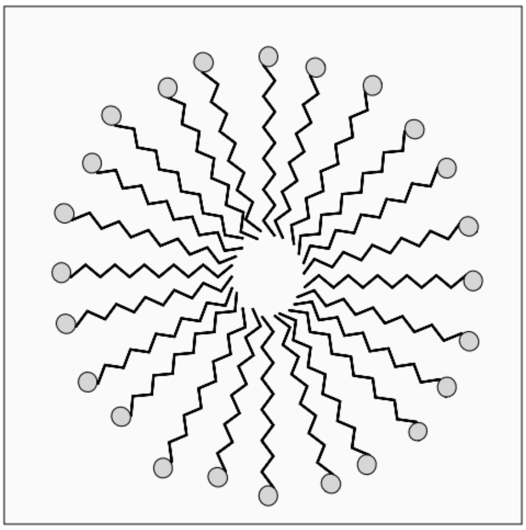
(*ii*) What is brine?

(*iii*) Explain the function of the brine in the procedure. (12)

(*c*) (*i*) Describe how the solid soap was separated from the solution in the beaker.

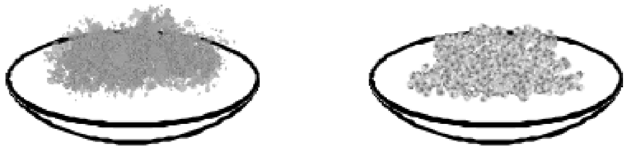
(*ii*) Where is the excess **NaOH** at this stage of the procedure? (9)

(*d*) The diagram represents the arrangement of a number of soap molecules in water. Explain why one end of a soap molecule is described as water loving (hydrophilic). (6)



(*e*) When 0.03 moles of the tri-ester shown in the equation above are hydrolysed, what is the theoretical yield, in grams, of $\mathbf{CH_3(CH_2)_{10}COONa}$? (9)

3. (*a*) Sodium sulfite and barium chloride are both white crystalline salts.



Describe how a student could have carried out flame tests to distinguish between unlabelled samples of these two salts provided on separate clock glasses. (15)

(*b*) A student investigated the oxidising properties of bromine using aqueous solutions (in suitable concentrations) of the substances listed in the table on the right.

Solution	Reagent
bromine water	$\mathbf{Br_2}$
sodium sulfite	$\mathbf{Na_2SO_3}$
barium chloride	$\mathbf{BaCl_2}$
hydrochloric acid	**HCl**

(*i*) Describe how the student could have first carried out a test on a sample of the sodium sulfite solution to verify that it contained **no** sulfate ions.

(*ii*) What was observed as bromine water was added dropwise to another sample of this sodium sulfite solution in a test-tube?

How could the student have verified that the sulfite ion in this sample was oxidised to sulfate ion by the bromine water? (18)

(*c*) When a student added a freshly sanded strip of magnesium ribbon to a solution of copper(II) sulfate, the blue colour disappeared from the solution. When the same mass of granulated zinc was added to the same volume of the same solution of copper(II) sulfate, the blue colour of the solution faded but did not completely disappear. In each case a brown precipitate was formed.

What information do these observations provide about the relative reducing abilities of

(*i*) magnesium metal and copper metal,

(*ii*) zinc metal and copper metal?

(*iii*) Write a balanced chemical equation for the reaction of either the magnesium or the zinc with the copper(II) sulfate solution.

(*iv*) Suggest a reason why the blue colour completely disappeared in the case of adding magnesium to the copper(II) sulfate solution but only faded in the case of adding the zinc. (17)

Section B

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

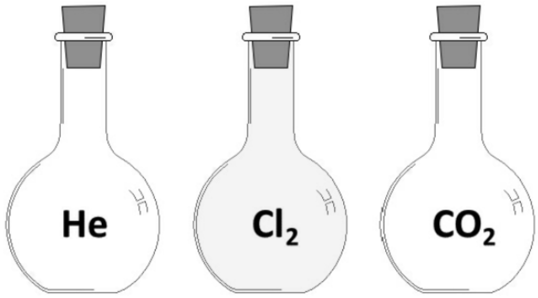
4. Answer **eight** of the following (*a*), (*b*), (*c*), etc. (50)

(*a*) How many (*i*) electrons, (*ii*) neutrons, does a $^{32}_{16}\mathbf{S}^{2-}$ ion have?

(*b*) Define an atomic orbital.

(*c*) Write the *s*, *p*, *d* electron configuration for a nickel atom in the ground state.

(*d*) The diagram shows three containers, each filled with a different gas. Each container holds the same volume of gas at the same temperature and pressure.
Which contains the largest number of atoms? Explain.



(*e*) Define electronegativity.

(*f*) Take the average bond energies for the **C—C** single bond and the **C≡C** triple bond as 348 and 839 kJ mol^{-1} respectively.
Why is the average bond energy for the **C≡C** triple bond less than three times the average bond energy for the **C—C** single bond?

(*g*) Two volumes of an oxide of nitrogen decomposed in the presence of a heated catalyst to form two volumes of nitrogen gas and one volume of oxygen gas, all volumes measured at the same conditions of temperature and pressure.
Use this information to deduce the formula of the oxide of nitrogen that decomposed.

(*h*) The use of $\mathbf{KBrO}_x$ as a flour additive has been banned in the EU for many years but it is sometimes used to bleach flour and strengthen dough in some jurisdictions.
$\mathbf{KBrO}_x$ contains 47.9% bromine by mass.
Find the value of ***x***.

(*i*) Show by means of an equilibrium equation the self-ionisation of water that occurs even in 'deionised' water.

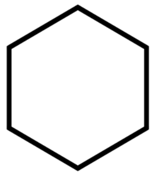
(*j*) Give a use that propanoic acid, benzoic acid and the salts of these acids have in common.

This question continues on the next page.

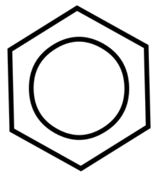
(*k*) What is the average number of electrons shared between any two adjacent carbon atoms in a molecule of

(*i*) cyclohexane,

(*ii*) benzene?



cyclohexane



benzene

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

A Give one advantage *and* one disadvantage of using a batch process in the chemical industry.

or

B What is the structural difference between LDPE or low-density poly(ethene) and HDPE or high-density poly(ethene)?

5. Consider the data given in the table about the elements chlorine, argon and potassium.

Element	Year discovered	First ionisation energy (kJ mol^{-1})	Second ionisation energy (kJ mol^{-1})
Cl	1774	1251	2298
Ar	1894	1521	2666
K	1807	419	3052

(*a*) Mendeleev did not include argon in his 1869 periodic table of the elements as it was undiscovered at the time. While Mendeleev did predict the future discovery and the properties of a number of other elements, e.g. gallium and germanium, also unknown in 1869, argon was not one of the elements whose existence he predicted.

(*i*) How did Mendeleev arrange the elements in his periodic table of 1869?

(*ii*) Suggest a reason why Mendeleev did not suspect the existence of argon.

(*iii*) How do we know that any new elements discovered in the future will be 'super-heavy', i.e. elements that have very large relative atomic masses? (11)

(*b*) (*i*) Why does an individual atom **not** have a definite boundary?

(*ii*) How is *atomic (covalent) radius* defined?

(*iii*) The bond length of the single **Cl**—**Cl** covalent bond is 0.199 nm.
Predict the value in nm for the atomic (covalent) radius of chlorine.

(*iv*) Account for the general decrease in atomic (covalent) radii of the elements across the third period of the periodic table from sodium to chlorine.

(*v*) Why is establishing an atomic (covalent) radius for argon problematic? (21)

(*c*) (*i*) Define first ionisation energy of a neutral gaseous atom in its ground state.

(*ii*) Why is the first ionisation energy of potassium lower than that of argon or chlorine?

(*iii*) Why is the second ionisation energy value for each element in the table bigger than its first ionisation energy value?

(*iv*) Why is the second ionisation energy of potassium very significantly bigger than its first? (18)

6. Bio-**LPG** is a co-product in the manufacture of bio-diesel from renewable crops and domestic and industrial waste. Hydrogen gas is a reagent in the production of these biofuels.

(*a*) (*i*) Give two commercial sources of hydrogen gas.

(*ii*) State two main advantages of using hydrogen gas itself as a fuel. (11)

(*b*) Crude oil is separated into different fractions in fractional distillation. Bio-**LPG** and bio-diesel can be used interchangeably with the **LPG** obtained from the *refinery gas* fraction of crude oil and the diesel obtained from the *gas oil* fraction, respectively.

(*i*) What are the two main hydrocarbon components of **LPG**?

(*ii*) With the aid of a labelled diagram explain how crude oil is fractionally distilled.

(*iii*) Show on your diagram where the refinery gas and gas oil fractions separate. (18)

(*c*) What is the purpose of adding mercaptans to natural gas or to **LPG**? (6)

(*d*) The heat of combustion of ethanethiol, a mercaptan, according to the following balanced equation, is –1867.5 kJ mol^{-1}.

$$\mathbf{C_2H_5SH}_{(l)} + \mathbf{4\tfrac{1}{2}O_2}_{(g)} \rightarrow \mathbf{2CO_2}_{(g)} + \mathbf{3H_2O}_{(l)} + \mathbf{SO_2}_{(g)}$$

Use this heat of reaction and the heats of formation of carbon dioxide, water and sulfur dioxide, –393.5, –285.8 and –296.8 kJ mol^{-1}, respectively, to calculate the heat of formation of ethanethiol. (15)

7. (*a*) Define an acid according to the theory of (*i*) Arrhenius, (*ii*) Brønsted and Lowry.

(*iii*) State one limitation of Arrhenius' acid-base theory.

(*iv*) What is a conjugate acid-base pair in Bronsted-Lowry theory? (17)

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

(*c*) Sulfuric acid is a strong dibasic acid. Write a balanced equation to show that the conjugate base of $\mathbf{H_2SO_4}$ acts as a Brønsted-Lowry acid in water. (6)

(*d*) (*i*) Write a balanced equation to show the dissociation into ions in water of a weak monobasic acid represented by **HA**.

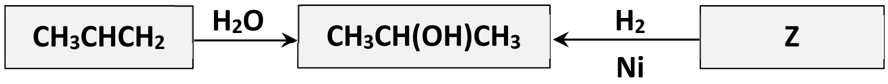
If **HA** is 1.5% dissociated in a 0.10 M solution,

(*ii*) find the concentrations of $\mathbf{H_3O^+}$ ion and $\mathbf{A^-}$ ion in moles per litre in the solution,

(*iii*) calculate the pH of the 0.10 M **HA** solution,

(*iv*) hence or otherwise, calculate the value of the acid dissociation constant K_a for **HA**, assuming ionisation does not alter the concentration of the non-ionised form, i.e. take [**HA**] = 0.10 M after dissociation. (21)

8. Study the reaction scheme below in which compound **Y** is produced by the reaction of compound **X** with water. **Y** is often called isopropyl alcohol and it is a component in many personal care products. **Y** can also be produced by the reduction of compound **Z**.



X **Y**

(*a*) (*i*) What is the systematic IUPAC name for **Y**?

(*ii*) Classify **Y** as a primary or a secondary alcohol. Justify your answer. (8)

(*b*) (*i*) Identify **Z**.

(*ii*) Draw an expanded molecular structure for **Y**, indicating clearly which of its bonds are formed when **Z** is reduced.

(*iii*) How does the geometry around the carbon atoms in **Z** change during this reduction reaction? (15)

(*c*) (*i*) What type of reaction is involved in the conversion of **X** to **Y**?

(*ii*) Identify another product of the reaction of **X** with water. (6)

(*d*) (*i*) Write a balanced equation for the reaction of **Y** with sodium.

(*ii*) What information does this reaction give about the –**OH** functional group in an alcohol? (9)

(*e*) Hand sanitizers with a high concentration of an alcohol are effective in destroying most bacteria and viruses on the skin. The ability of alcohols to form strong hydrogen bonds is involved in the mechanism of disrupting bacteria and virus protein.

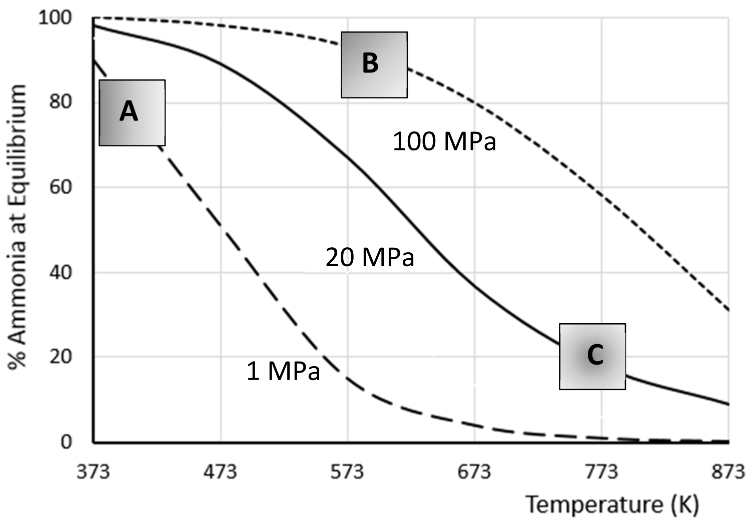
(*i*) A hand sanitizer labelled 70% (*v*/*v*) isopropyl alcohol contains only water and **Y**. Express its concentration in terms of moles per litre of isopropyl alcohol. Take the density of isopropyl alcohol as 0.8 g cm^{-3}.

(*ii*) What is the most influential type of intermolecular force that occurs in **Z**? (12)

9. In the Haber process the following chemical equilibrium is established using an iron catalyst.

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$$

The graph shows how, starting with N_2 and H_2 in a 1:3 molar ratio, the percentage NH_3 by volume at equilibrium varies with temperature for three different pressures.



(*a*) Select the area of the graph (box **A**, **B** *or* **C**) corresponding to the conditions most closely associated with

(*i*) good yields and slower rates of reaction,

(*ii*) higher yields but more costly and less safe ammonia production? (6)

(*b*) Use the information in the graph to deduce whether the production of ammonia in the Haber process is exothermic or endothermic and justify your answer. (9)

(*c*) When 9.0 moles nitrogen and 27.0 moles hydrogen were placed in a 10.0 litre container, there were 6.0 moles ammonia present when equilibrium was reached at temperature ***T***.

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

(*ii*) Calculate the value of K_c under these conditions.

(*iii*) Find the percentage by volume of NH_3 in the container at equilibrium. (21)

(*d*) State and explain the effect, if any, on the yield of ammonia, of

(*i*) increasing the pressure at temperature ***T*** (by compressing the gases),

(*ii*) using a more efficient catalyst. (14)

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

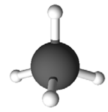
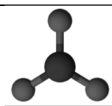
(*a*) Electron pair repulsion theory explains the specific shapes of the molecules of methane, boron trifluoride and ammonia and of molecules with general formula $\mathbf{QX_2}$.

(*i*) Draw a dot and cross diagram to show the arrangement of the valence electrons in an $\mathbf{NH_3}$ molecule.

(*ii*) Why are $\mathbf{NH_3}$ molecules *not* trigonal planar like $\mathbf{BF_3}$ molecules?

(*iii*) What are the two possible shapes of a molecule with general formula $\mathbf{QX_2}$?

(*iv*) Explain why both $\mathbf{CH_4}$ and $\mathbf{BF_3}$ are non-polar molecules.

Formula	Boiling point (°C)	Bond angle (°)	Shape
$\mathbf{CH_4}$	–161.5	109.5	
$\mathbf{BF_3}$	–100.3	120	
$\mathbf{NH_3}$	–33.3	107.0	
$\mathbf{QX_2}$	–	–	??

(*v*) What evidence is there in the table to support the claim that bond-pair bond-pair (bp bp) repulsions are weaker than lone-pair bond-pair (lp bp) repulsions? (25)

(*b*) Chloroethane decomposes when heated according to the balanced equation:

$$\mathbf{C_2H_5Cl}\ (g) \rightarrow \mathbf{C_2H_4}\ (g) + \mathbf{HCl}\ (g)$$

The following data were obtained at a certain temperature ***T*** for the decomposition of the chloroethane and the formation of the hydrogen chloride during this reaction.

Time (s)	0	80	160	320
Concentration $\mathbf{C_2H_5Cl}$ (M)	2.00	1.02	0.52	0.13
Concentration **HCl** (M)	0	0.98	1.48	1.87

(*i*) Define rate of a reaction.

(*ii*) Use the data given to plot, on the same sheet of graph paper and using the same set of axes, curves to compare the changes in concentration of the chloroethane and the hydrogen chloride with time.

(*iii*) Find the instantaneous rate of **HCl** formation (in M s^{-1}) at 120 s. (25)

(*c*) An alloy is an intimate mixture of elements, usually metals. When 76.20 g of an alloy composed only of silver and copper were added to an excess of concentrated nitric acid the following reactions took place. Brown fumes of nitrogen(IV) oxide gas were released and 22.50 g of copper(II) nitrate were formed.

$$\mathbf{Ag}\ (s) + \mathbf{2HNO_3}\ (aq) \rightarrow \mathbf{AgNO_3}\ (aq) + \mathbf{NO_2}\ (g) + \mathbf{H_2O}\ (l)$$

$$\mathbf{Cu}\ (s) + \mathbf{4HNO_3}\ (aq) \rightarrow \mathbf{Cu(NO_3)_2}\ (aq) + \mathbf{2NO_2}\ (g) + \mathbf{2H_2O}\ (l)$$

(*i*) Find the mass of silver in the alloy.

What was the ratio by mass of silver to copper in the alloy?

(*ii*) What total volume of nitrogen(IV) oxide gas, measured at s.t.p., was released in these reactions? (25)

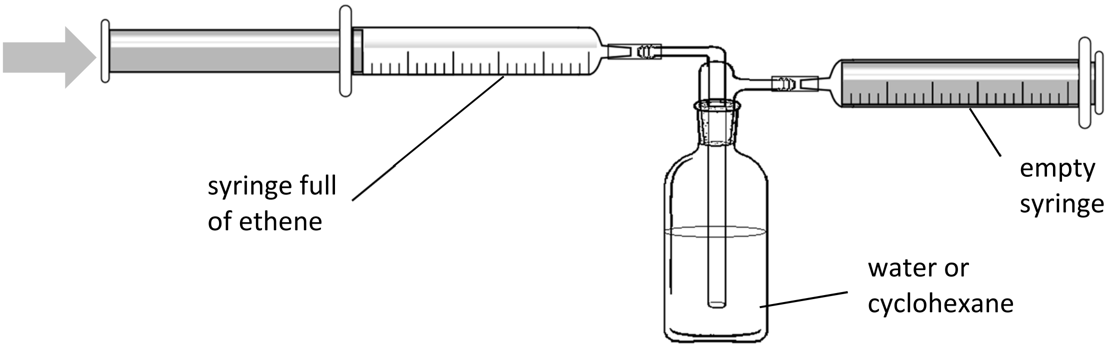
11. Answer any **two** of the parts (*a*), (*b*), (*c*) and (*d*). (2 × 25)

(*a*) More ethene is produced industrially than any other manufactured organic chemical.

(*i*) Give one major use for ethene.

(*ii*) Draw a labelled diagram of an arrangement of apparatus used to prepare and collect a small quantity of ethene in the school laboratory to examine its properties.

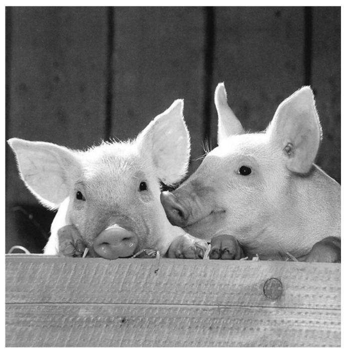
(*iii*) Draw the structure of an organic product of the reaction of ethene in a solution of bromine.



(*iv*) The diagram above shows an arrangement of apparatus used to compare the solubilities of ethene in water and in cyclohexane.

Explain how and why the solubility of ethene in water differs from its solubility in cyclohexane. (25)

(*b*) Pig slurry has a very high biochemical oxygen demand (BOD) and therefore effluent from pig farming must be very carefully managed. Spreading it on the ground as a fertilizer is one option for disposing of pig slurry and transfer to a treatment works is another.



(*i*) Explain the underlined term.

(*ii*) Why is the run-off from pig slurry fertilizer, or the addition of any other solution with a high BOD, into waterways undesirable?

(*iii*) How could a process like the secondary stage of sewage treatment reduce the quantities of organic matter in pig slurry effluent?

A 50.0 cm^3 raw pig slurry sample was diluted to 5.0 litres with well-aerated pure water and 50.0 cm^3 of the diluted pig slurry was diluted again in the same way to 5.0 litres. Some of this diluted, well-aerated slurry was analysed immediately and some was suitably stored and analysed later as part of a BOD test. The difference in the dissolved oxygen concentrations between the two analyses was 2.7 p.p.m.

(*iv*) Why was the raw slurry diluted and aerated before analysis?

(*v*) Calculate the BOD of the raw pig slurry. (25)

This question continues on the next page.

(*c*) According to the scientific method an existing theory is replaced when another theory can better account for certain experimental observations.

John Dalton's atomic theory of 1808 was replaced around 1898 by the plum-pudding model of the atom after the discovery of radioactivity and work on cathode rays. This model of the atom was in turn replaced around 1909 when Ernest Rutherford's experiments provided evidence for the existence of the nucleus and the electron cloud.

(*i*) The photograph shows wooden balls used by John Dalton to represent atoms.

What was Dalton's atomic theory?

(*ii*) Name the scientist whose work on cathode rays led him to identify the electron as a subatomic particle.

(*iii*) What happens in a radioactive nucleus during beta decay?

The measurement of the relative abundances of the isotopes of an element was first demonstrated by Aston in 1919 using a mass spectrograph. His results indicated that 90.0% of neon atoms had mass number 20 and the remainder had mass number 22. It was suggested at the time that a neon–20 atom had 20 protons and 10 electrons in its nucleus and another 10 electrons in its electron cloud while a neon–22 atom had 22 protons and 22 electrons with 12 of these electrons located in the nucleus. This explanation was changed in 1932 when Chadwick discovered the neutron.

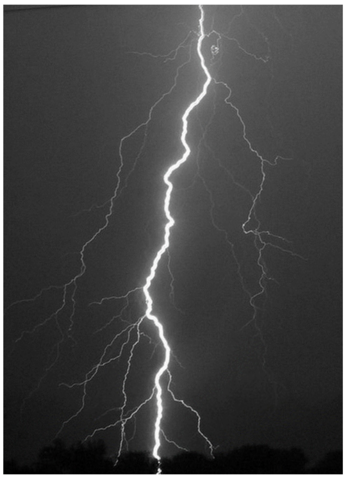
(*iv*) What is now the accepted composition of a neon–20 atom and a neon–22 atom in terms of subatomic particles?

(*v*) Calculate the relative atomic mass of neon using Aston's results above. (25)

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

A

The nitrogen cycle on Earth is a biogeochemical cycle of events that continuously removes unreactive nitrogen gas from the atmosphere and converts it into more reactive chemicals in soil that are used by plants. Some of this plant nitrogen is transferred to animals through food chains. Nitrogen in soil, in plants and in animals is continuously being restored to the atmosphere as nitrogen gas.



(*i*) Why is nitrogen gas unreactive?

(*ii*) Describe, using equations or otherwise, how lightning generates the gases **NO** and $\mathbf{NO_2}$ in the atmosphere.

(*iii*) Atmospheric $\mathbf{NO_2}$ lowers the pH of rainwater.
Write a balanced equation for the reaction of $\mathbf{NO_2}$ with water forming acid rain.

(*iv*) This rainwater forms nitrate compounds in soil that are absorbed by some plants through their root systems.
What use do plants make of these nitrate compounds?

(*v*) Describe one pathway by which nitrogen in animals is restored to the atmosphere completing the nitrogen cycle. (25)

or

B

Strongly electropositive metals, e.g. aluminium and sodium, are extracted from their ores by <u>electrolysis</u>. Chemical methods can be used to extract other metals, e.g. iron and zinc from their ores. Occasionally nuggets of metallic elements are found free in nature.
The photograph shows a large piece of elemental copper found in Michigan, U.S.A. It was torn away from a vein of copper by a moving glacier during the ice age.

(*i*) Explain the underlined term.

(*ii*) Aluminium is extracted from molten aluminium oxide by electrolysis.
Why must the aluminium oxide be molten?

(*iii*) Write balanced equations for the reactions that occur at the graphite electrodes, and for the overall reaction, during the electrolysis of aluminium oxide.

(*iv*) Identify the chemical method used to extract iron from iron ore.

(*v*) Suggest a reason why strongly electropositive metals were **not** isolated before 1800.

(*vi*) Refer to the electrochemical series to explain why only some metals are found free in nature. (25)

There is no examination material on this page.

Leaving Certificate – Higher Level

Chemistry

Tuesday, 22 June

Afternoon, 2:00 – 5:00