Coimisiún na Scrúduithe Stáit
State Examinations Commission

———————————

LEAVING CERTIFICATE EXAMINATION, 2013

———————————

CHEMISTRY – HIGHER LEVEL

———————————

TUESDAY, 18 JUNE – AFTERNOON 2.00 TO 5.00

———————————

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, N = 14, O = 16, Al = 27, Fe = 56, Cu = 63.5

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

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

Avogadro constant = 6.0×10^{23} 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. In an experiment to measure the dissolved oxygen content of a river water sample, a small amount of a concentrated solution of compound **A**, followed by a small amount of a concentrated solution of alkaline potassium iodide (**KOH/KI**), were added to a bottle filled with the river water.

   These additions were made using the method shown in the diagram, avoiding the addition of bubbles of air. After both additions the stopper was replaced carefully and the bottle was inverted several times to ensure thorough mixing of the contents. A brown precipitate was observed at this stage.

   About 1 cm^3 of concentrated sulfuric acid (**H$_2$SO$_4$**) was then added, allowing the acid to run down the inside wall of the bottle. Again the bottle was stoppered and inverted several times to ensure thorough mixing.

   (*a*) Why was it important to avoid trapping air bubbles each time the stopper was inserted into the sample bottle and when using the dropper? (5)

   (*b*) Identify compound **A**. (3)

   (*c*) What was observed on addition of the concentrated sulfuric acid followed by the mixing of the contents of the bottle? (3)

   After the three additions, the thoroughly mixed contents of the sample bottle were titrated in 200 cm^3 portions with a 0.02 M solution of sodium thiosulfate (**Na$_2$S$_2$O$_3$**). The average titre was 9.4 cm^3.

   The balanced equation for the titration reaction is:

   $$2S_2O_3^{\ 2-} \quad + \quad I_2 \quad \rightarrow \quad S_4O_6^{\ 2-} \quad + \quad 2I^-$$
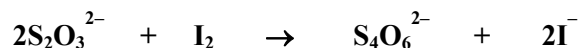
   (*d*) Describe how the burette was rinsed and filled for use in the titrations. (15)

   (*e*) Name the indicator used in the titrations. (3)

   (*f*) Calculate the concentration of iodine (**I$_2$**) in the sample bottle in moles per litre.

   For every **one** mole of dissolved oxygen (**O$_2$**) in the water sample, **two** moles of iodine (**I$_2$**) are liberated in this experiment. Calculate the concentration of dissolved oxygen in the river water sample
      (*i*)   in moles per litre,
      (*ii*) in grams per litre,
      (*iii*) in ppm. (15)

   (*g*) What conclusion should have been reached had a white precipitate been observed instead of the brown precipitate after the first two additions of reagents to the bottle filled with river water? (3)

   (*h*) Kits, designed for use in the field, allow the dissolved oxygen concentration to be measured immediately on collection of the sample. Why is the *immediate* determination of dissolved oxygen considered best practice? (3)

   ───────────────────────

2. In a practical examination, chemistry students were required to perform a number of tasks in a laboratory. They had access to all the necessary reagents and glassware and also to the required safety equipment and clothing.

(*a*) How could a student have carried out a simple chemical test to confirm that a colourless liquid sample was ethanoic acid and not ethanol? (5)

(*b*) A sample of ethene gas was supplied in a stoppered test tube. Describe fully how the gas could have been shown to be unsaturated. (12)

(*c*) Describe with the aid of a labelled diagram how a student could have used chromatography to separate a mixture of indicators. (12)

(*d*) One of the tasks in the practical examination was to measure the melting points of two benzoic acid samples (**A** and **B**) and to use the results to determine which was the purer sample. The melting points obtained by one of the students were as follows: sample **A** = 117 – 120 °C; sample **B** = 120 – 121 °C.

Which was the purer sample? Justify your answer. (6)

Arrows show direction of water flow.

The students were required to recrystallize the impure benzoic acid. What solvent should they have used for the recrystallization? Explain why this solvent is suitable. (9)

(*e*) The diagram shows a steam distillation apparatus assembled **incorrectly** by one of the students.

Identify the flaw in the assembly and state how it should have been rectified. (6)

_____
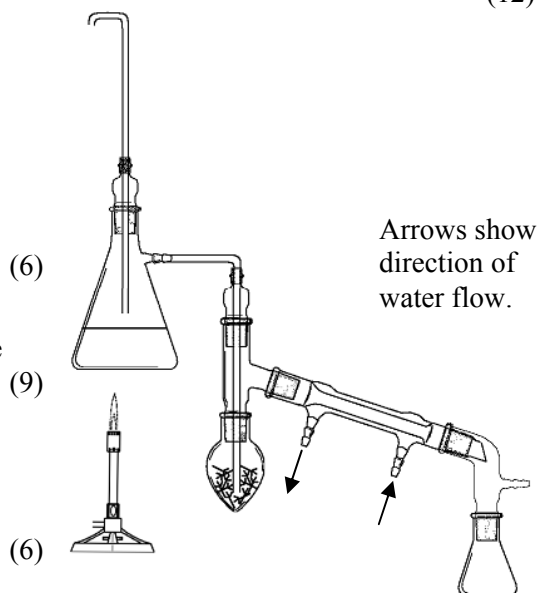
3. A reaction vessel of negligible heat capacity held 75 cm^3 of 1.0 M **HCl** solution at a temperature of 13.0 °C. A thermometer was placed in the liquid in the reaction vessel. A graduated cylinder was used to measure out and add 75 cm^3 of 1.0 M **NaOH** solution at a temperature of 15.0 °C to the reaction vessel. The highest temperature of the reaction mixture was recorded as 20.9 °C.

This information was used to calculate the heat of reaction of hydrochloric acid with sodium hydroxide. The equation for the reaction is:

$$\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$$
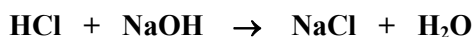
(*a*) Define *heat of reaction*. (5)

(*b*) Suggest a suitable material for the reaction vessel to avoid heat loss to the surroundings. (3)

(*c*) State (*i*) one advantage, (*ii*) one disadvantage, of the use of a burette instead of a graduated cylinder for measuring out the base and adding it to the reaction vessel. (6)

(*d*) State **two** ways of ensuring that the rise in temperature was measured as accurately as possible. (6)

(*e*) How many moles of **HCl** were neutralised in the reaction with **NaOH**?

Calculate the heat produced in the reaction vessel as a result of the reaction of the **HCl** with the **NaOH**. Take the density and the specific heat capacity of the reaction mixture – assumed equal to those of water – as 1.0 g cm^{-3} and 4.2 kJ kg^{-1} K^{-1} respectively.

Hence calculate the heat of reaction for the neutralisation reaction between hydrochloric acid and sodium hydroxide. (18)

(*f*) The solutions used in this experiment were moderately concentrated.

Identify the hazard associated with the use of these solutions.

Describe *or* draw the warning symbol that should have been used to label the two solutions.

What experimental problem would have been encountered if 0.1 M **NaOH** and 0.1 M **HCl** solutions had been used instead of 1.0 M solutions? (12)

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*) Write the electron configuration (*s*, *p*, *etc*.) of a zinc atom in its ground state.

(*b*) Define *relative atomic mass*.

(*c*) How many neutrons are there in 0.14 g of carbon–14?

(*d*) Give the shape and the corresponding bond angle for a molecule of formula **QX$_4$** where **Q** is an element from Group 4 of the periodic table.

(*e*) When hydrogen gas was passed over 1.59 g of copper oxide, 1.27 g of metallic copper were produced. Find by calculation the empirical formula of the copper oxide.

(*f*) Complete and balance the equation for the chemical reaction that occurs when a piece of sodium is added to ethanol: **C_2H_5OH + Na →**

(*g*) What reagents are needed to test a solution for the nitrate ion?

(*h*) State *Charles' law*.

(*i*) What happens during secondary sewage treatment?

(*j*) What is meant by *heterogeneous* catalysis?

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

A Write a balanced equation for the formation of calcium silicate (a component of slag) from calcium oxide in steelmaking.

or

B Write a balanced equation for the formation of ozone in the stratosphere.

———————————————

5. (*a*) The 350th anniversary of Robert Boyle's discovery of the relationship between the pressure and the volume of a fixed mass of gas at constant temperature is commemorated in this Irish stamp issued in 2012.

Boyle also contributed to the development of the use of the term *element* in Chemistry.

What was his understanding of this term? (5)

(*b*) Use Bohr's atomic theory of 1913 to account for the emission spectrum of the hydrogen atom. (15)

Explain, in terms of atomic structure, why different flame colours are observed in flame tests using salts of different metals. (6)

What colour is observed in a flame test on lithium chloride?

Describe the testing procedure. (9)

(*c*) Further research and scientific discoveries, including Heisenberg's <u>uncertainty principle</u> (1927), led to significant modification of Bohr's original atomic structure theory of 1913.

Explain the underlined term.

Give **one** other factor that also contributed to the need for modification of Bohr's 1913 theory.

These modifications included the introduction of the idea of atomic orbitals.

What is an *atomic orbital*? (15)

6. (a) Define the *octane number* of a fuel. (5)

(b) Compound **A** is obtained from the fractional distillation of crude oil and is converted to compound **B** by isomerisation.
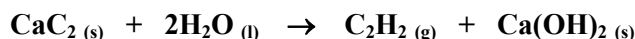
(i) Give the systematic (IUPAC) names for **A** and **B**.

(ii) Explain the term *isomerisation*.

Draw the structural formula of another isomer of **A** and **B**.

(iii) Predict whether **A** or **B** has the higher octane number. Justify your answer. (21)

(c) Ethyne is produced from calcium carbide and water according to the following balanced equation:
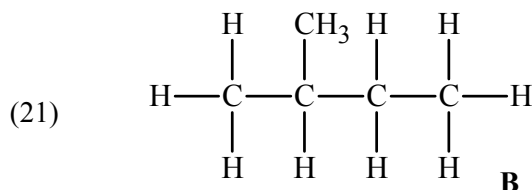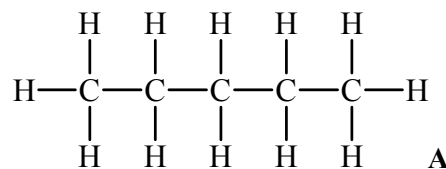
$$CaC_{2\,(s)} + 2H_2O_{\,(l)} \rightarrow C_2H_{2\,(g)} + Ca(OH)_{2\,(s)}$$

Calculate the heat change for this reaction given that the heats of formation of calcium carbide, water, ethyne and calcium hydroxide are -59.8, -285.8, 227.4 and -985.2 kJ mol^{-1} respectively. (15)

(d) Describe the structure of benzene in terms of

(i) the bonding between the carbon atoms and the hydrogen atoms,

(ii) the bonding between the carbon atoms. (9)

_____

7. (a) Define the *rate of a chemical reaction*. (5)

(b) Explain clearly why there is an almost instantaneous reaction between aqueous solutions of sodium chloride and silver nitrate. (6)

(c) When hydrogen gas and nitrogen gas are mixed in a ratio of 3 : 1 by volume at room temperature in a sealed container, the formation of ammonia (**NH$_3$**) is very slow.

Suggest **two** ways to increase the rate of this reaction.

Explain how each of the ways you suggest speeds up the reaction. (12)

(d) Describe how you would measure the reaction time when 10 cm^3 of 1.0 M hydrochloric acid solution and 50 cm^3 of 0.20 M sodium thiosulfate solution react according to the following balanced equation:

$$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + SO_2 + S + H_2O$$

If you were given additional sodium thiosulfate solutions of the following concentrations: 0.04 M, 0.08 M, 0.12 M and 0.16 M, describe how you would show that the rate of this reaction is directly proportional to the concentration of the sodium thiosulfate solution. (18)

(e) Draw a reaction profile diagram for an exothermic reaction indicating clearly on your diagram (i) the activation energy (E_A) for the reaction, (ii) the heat of reaction (ΔH). (9)

_____

8. Study the reaction scheme and answer the questions that follow.

(a) Ethane and ethene belong to the <u>homologous series</u> of alkanes and alkenes, respectively.

Explain the underlined term.
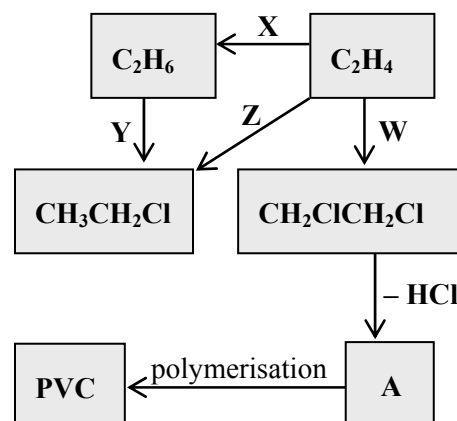
What type of reaction was involved in conversion **X**?

How does the geometry around the carbon atoms change as a result of conversion **X**? (15)

(b) Identify the reagent required to bring about (i) conversion **Y**, (ii) conversion **Z**, (iii) conversion **W**. (9)

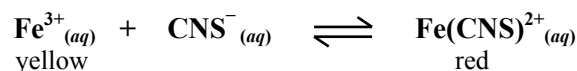(c) Describe the mechanism of reaction **W**. (12)

(d) Draw the structure of **A** and give its name. (9)

(e) Draw the structure of two repeating units of PVC. (5)

9. (*a*) What is meant by *chemical equilibrium*? Why is a chemical equilibrium described as *dynamic*? (8)

State *Le Châtelier's principle*. (6)

(*b*) When a yellow solution of iron(III) chloride (**FeCl₃**) and a colourless solution of potassium thiocyanate (**KCNS**) were mixed in a test tube, a red colour appeared and the following equilibrium was established:

$$Fe^{3+}_{(aq)} \quad + \quad CNS^{-}_{(aq)} \quad \rightleftharpoons \quad Fe(CNS)^{2+}_{(aq)}$$
$$\text{yellow} \qquad\qquad\qquad\qquad\qquad\qquad \text{red}$$

Explain
(*i*) the effect on the **Fe³⁺** ion concentration of adding **KCNS** to the equilibrium mixture,

(*ii*) why changing the pressure has no effect on this equilibrium. (9)

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

A mixture of 1.0×10^{-3} moles each of iron(III) chloride and potassium thiocyanate was allowed to come to equilibrium in 1 litre of solution at room temperature according to the equation above. It was found that 1.1×10^{-4} moles **Fe(CNS)²⁺** were present in the solution at equilibrium.

Calculate the value of the equilibrium constant (**K_c**) for the reaction. (12)

(*d*) The red colour faded when the test tube containing the equilibrium mixture was placed in an ice-water bath.

State whether the value of **K_c** for this reaction is bigger or smaller at the lower temperature.

Is the forward reaction exothermic *or* endothermic? Justify your answer. (9)

———————————

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

(*a*) Distinguish between *intramolecular* bonding and *intermolecular* forces. (7)

Explain each of the following in terms of intramolecular bonding *or* intermolecular forces *or* both.
(*i*) The boiling point of hydrogen (20 K) is significantly lower than that of oxygen (90.2 K).

(*ii*) Iodine has a very low solubility in water.

(*iii*) When a charged rod is held close to a thin stream of water flowing from a burette, the stream of water is deflected. (18)

(*b*) The following redox reaction is highly exothermic and is used to produce molten iron for welding pieces of steel together, e.g. sections of railway track:

$$8Al \quad + \quad 3Fe_3O_4 \quad \rightarrow \quad 4Al_2O_3 \quad + \quad 9Fe$$
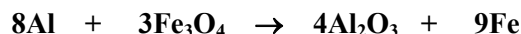
(*i*) Define *oxidation* in terms of change in oxidation number.

Show using oxidation numbers that this is a redox reaction.

Identify the reducing agent. (12)

(*ii*) What mass of aluminium powder is required to produce 1008 g of molten iron for a single railway track weld?

What mass of aluminium oxide is produced as waste in the process? (13)

(*c*) Caesium–137 is a radioactive isotope of the alkali metal caesium. Caesium–137 was released into the atmosphere when Japanese nuclear reactors were damaged by a tsunami in 2011. Caesium–137 decays by beta-particle emission with a half-life of 30 days.

(*i*) Define *radioactivity*. (6)

(*ii*) Give **two** differences between chemical reactions and nuclear reactions. (6)

(*iii*) Give **two** properties of beta-particles. (6)

(*iv*) A certain mass of caesium–137 leaked on a particular day. What fraction of this mass remained as caesium–137 after 90 days? (7)
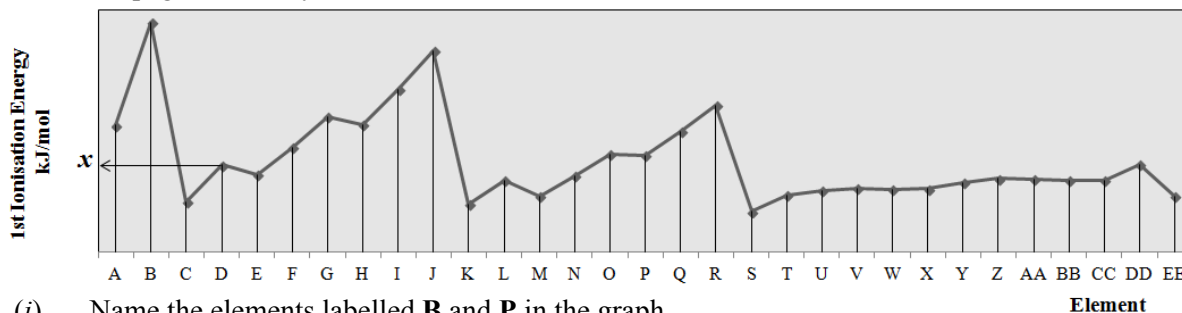
11. Answer any **two** of the parts (*a*), (*b*) and (*c*). (2 × 25)

(*a*) Define *first ionisation energy*. (7)

The graph shows the first ionisation energy values, displayed in order of increasing atomic number, for the first 31 elements of the periodic table. Refer to the table of first ionisation energy values on page 80 of the *formulae and tables booklet*.

(*i*) Name the elements labelled **B** and **P** in the graph.

What is the numerical value of *x*? (9)

(*ii*) What is the principal reason for the large decrease in first ionisation energy between the elements labelled **R** and **S**? (3)

(*iii*) Explain why the first ionisation energy value of the element labelled **H** is lower than that of the element labelled **G**. (6)

(*b*) Define a base according to (*i*) the Arrhenius theory, (*ii*) the Brønsted-Lowry theory. (7)

Give (*i*) the conjugate acid, (*ii*) the conjugate base, of HPO_4^{2-}. (6)

Ammonium hydroxide (NH_4OH) is produced by dissolving gaseous ammonia in water.

Calculate the pH of an ammonium hydroxide solution that contains 7.0 g NH_4OH per litre. The value of the base dissociation constant (K_b) for ammonium hydroxide is 1.8×10^{-5}. (12)

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

A

An arrangement to demonstrate the electrolysis of molten lead bromide ($PbBr_2$) using inert electrodes is shown in the diagram. The demonstration is carried out in a fume cupboard.

(*i*) What is meant by *electrolysis*? (4)

(*ii*) Why must the lead bromide be molten? (3)

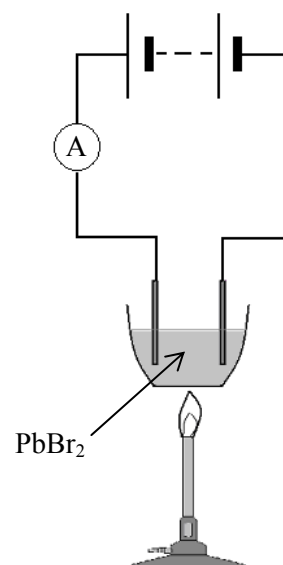(*iii*) Suggest a suitable material for the electrodes. (3)

(*iv*) Write balanced half equations for the reactions that occur at the electrodes during the electrolysis. (9)

(*v*) Name a metal, other than lead, that is extracted from one of its compounds by electrolysis.

Name the compound that is electrolysed to produce this metal. (6)

or

B

Answer the following questions with respect to the chemical industry.

(*i*) Distinguish between the terms *feedstock* and *raw materials* in the chemical industry. (6)

(*ii*) Explain whether labour costs are a fixed cost *or* a variable cost. (6)

(*iii*) Why are glass and steel widely used as the materials for the reaction vessels in the chemical industry? (3)

(*iv*) Give one advantage of a batch process and one advantage of a continuous process. (6)

Select one of the following Irish manufacturing industries:

ammonia manufacture	nitric acid manufacture	periclase manufacture
Cobh (now closed)	Arklow (now closed)	Drogheda

Give a reason why the process you chose was located at the site mentioned. (4)

Blank Page