2023. M34 2023L022A1EL

Coimisiún na Scrúduithe Stáit
State Examinations Commission

LEAVING CERTIFICATE EXAMINATION, 2023

CHEMISTRY – HIGHER LEVEL

TUESDAY, 20 JUNE – AFTERNOON, 2:00 to 5:00

400 MARKS

Answer any **eight** 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, S = 32, Ca = 40, Fe = 56

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

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.

Do not hand this up.

This document will not be returned to the State Examinations Commission.

Section A

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

1. (*a*) The reagent $\mathbf{(NH_4)_2SO_4{\cdot}FeSO_4{\cdot}6H_2O}$ (hydrated ammonium iron(II) sulfate) was used to prepare a standard solution.

State two properties of this substance that make it suitable for use as a primary standard. (8)

(*b*) (*i*) Describe how you would prepare exactly 250 cm^3 of a standard solution containing 9.31 g of $\mathbf{(NH_4)_2SO_4{\cdot}FeSO_4{\cdot}6H_2O}$ (hydrated ammonium iron(II) sulfate) that was supplied on a clock glass.

(*ii*) Why was dilute sulfuric acid added during the preparation of this standard solution? (15)

This standard solution of $\mathbf{Fe^{2+}}$ ions was used to determine by titration the concentration of a potassium manganate(VII) solution. The balanced equation for the titration reaction is:

$$\mathbf{MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O}$$

In each titration a little dilute sulfuric acid was added to a 25.0 cm^3 portion of the $\mathbf{Fe^{2+}}$ ion solution in a conical flask before adding the potassium manganate(VII) solution from a burette. On average, 22.6 cm^3 of the $\mathbf{KMnO_4}$ solution were required for complete reaction with 25.0 cm^3 of the solution of the $\mathbf{Fe^{2+}}$ ions in excess acid.

(*c*) (*i*) How was the end point of each titration detected?

(*ii*) If insufficient acid was present in the conical flask, what would have been observed as the $\mathbf{KMnO_4}$ solution was added from the burette to the $\mathbf{Fe^{2+}}$ ion solution? Explain. (9)

(*d*) Calculate

(*i*) the concentration of $\mathbf{(NH_4)_2SO_4{\cdot}FeSO_4{\cdot}6H_2O}$ in the standard solution in moles per litre,

(*ii*) the number of moles of $\mathbf{Fe^{2+}}$ ion in a 25.0 cm^3 portion of the standard solution,

(*iii*) the number of moles of potassium manganate(VII) reduced to $\mathbf{Mn^{2+}}$ by this quantity of $\mathbf{Fe^{2+}}$ ion,

(*iv*) the concentration of the potassium manganate(VII) solution in moles per litre.

(18)

2. (*a*) (*i*) Draw a labelled diagram to show a suitable arrangement of apparatus and chemicals for the preparation of ethyne from the reaction of calcium carbide with water and for the collection of the gas in test-tubes over water.

(*ii*) Why would you expect the first test-tube of gas collected to be less pure than the others? (14)

(*b*) (*i*) What was observed when a few drops of dilute bromine solution were added to one of the test-tubes of ethyne?

(*ii*) What was observed when a few drops of acidified, dilute potassium manganate(VII) solution were added to another one of the test-tubes of ethyne?

(*iii*) What information do the results of these tests give about ethyne? (12)

(*c*) (*i*) Describe how you would use one of the test-tubes of ethyne to confirm ethyne gas is flammable.

(*ii*) Describe the flame observed when ethyne is burned in air.

(*iii*) Write a balanced equation for the combustion of ethyne in excess oxygen.

(*iv*) How does the flame used in oxyacetylene welding, where ethyne is burned in pure oxygen, differ from the flame observed when ethyne was burned in air in a combustion test? (15)

(*d*) The balanced equation for the reaction between calcium carbide and water in the preparation of ethyne is:

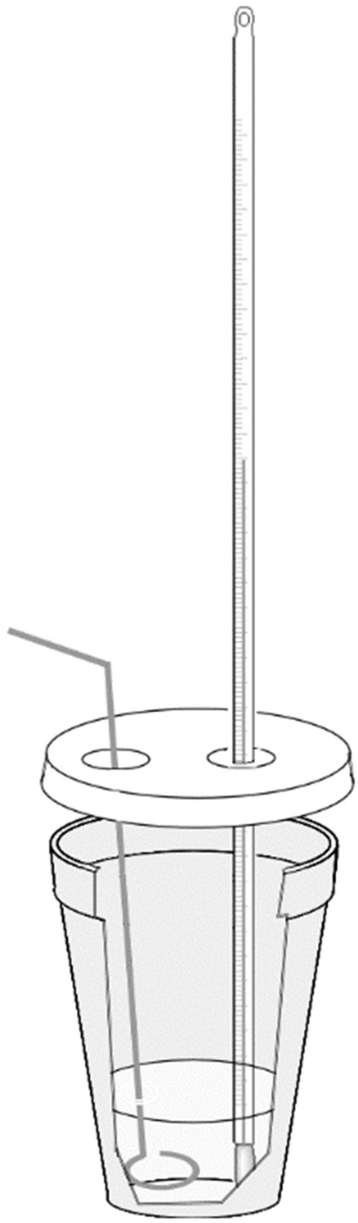
$$\mathbf{CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2}$$

Find the maximum theoretical volume of ethyne gas produced in the reaction above, in litres measured at **room** temperature and pressure, from 2.0 g of calcium carbide that is 80% pure. (9)

3. A student carried out an experiment to measure the heat of reaction (ΔH) for the neutralisation of hydrochloric acid by sodium hydroxide according to the following equation.

$$\mathbf{HCl}_{(aq)} \quad + \quad \mathbf{NaOH}_{(aq)} \quad \rightarrow \quad \mathbf{NaCl}_{(aq)} \quad + \quad \mathbf{H_2O}_{(l)}$$

In the experiment the student used an expanded foam polystyrene cup with a plastic lid through which a thermometer and a plastic stirrer were inserted, as shown on the right. The student first added 50 cm^3 of 1.0 M **HCl** solution at room temperature to the polystyrene cup and then quickly added 50 cm^3 of 1.0 M **NaOH** solution, also at room temperature, and having lowered the lid stirred the mixture while observing the thermometer. The temperature of the mixture rose rapidly by 6.8 K and then began to fall very slowly.



(*a*) Define heat of reaction. (5)

(*b*) State (*i*) one advantage, and (*ii*) one disadvantage of using a 50 cm^3 burette to measure out the base and to add it directly to the polystyrene cup. (6)

(*c*) (*i*) Why did the temperature rise when the solutions were mixed?

(*ii*) Suggest a reason why the temperature, having risen, then began to fall gradually.

(*iii*) Explain the advantage of using an expanded foam polystyrene cup in preference to a glass beaker as the reaction vessel for this experiment. (9)

(*d*) Calculate

(*i*) the number of moles of **HCl** neutralised in the polystyrene cup,

(*ii*) the heat in kJ produced in the reaction mixture by the neutralisation reaction, assuming the density of the resultant **NaCl** solution is 1.0 g cm^{-3} and the specific heat capacity of the solution is 4.2 kJ kg^{-1} K^{-1},

(*iii*) the value in kJ mol^{-1} of ΔH, the heat of reaction for the neutralisation reaction described by the equation above, using the data given. (18)

(*e*) (*i*) Explain why using 50 cm^3 volumes of moderately concentrated 1.0 M solutions instead of 50 cm^3 volumes of dilute 0.1 M solutions in this experiment gives a more accurate result.

(*ii*) Why would the same temperature rise of 6.8 K be expected if the experiment were repeated using 150 cm^3 of 1.0 M hydrochloric acid and 150 cm^3 of 1.0 M sodium hydroxide solution in the same polystyrene cup as before? (12)

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*) Define (*i*) atomic number, (*ii*) mass number.

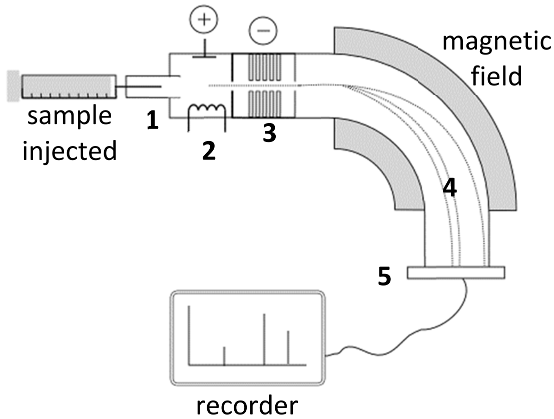
(*b*) Taking the valency of gallium (**Ga**) as 3, write the formula for the simplest compound formed from (*i*) gallium and nitrogen, (*ii*) gallium and oxygen.

(*c*) Predict the two possible shapes of a molecule $\mathbf{AB}_{\boldsymbol{n}}$ where $\boldsymbol{n} = 2$.

(*d*) Identify the energy change associated with the following balanced equation:
$\mathbf{X}^{+}{}_{(g)} \rightarrow \mathbf{X}^{2+}{}_{(g)} + \boldsymbol{e}^{-}$

(*e*) What is diffusion?

(*f*) Five fundamental processes occur during mass spectrometry. These are numbered **1** to **5** on the outline diagram of a mass spectrometer on the right. Identify the fundamental processes corresponding to stages **2** and **4**.



(*g*) A laboratory technician diluted 25.0 cm^3 of a 0.12 M solution to 30.0 cm^3 by adding deionised water. Find the new concentration of the solution in moles per litre.

(*h*) What is an enzyme?

(*i*) Draw a structure of propane-1,2,3-triol (glycerol) to show all of its atoms and all of its bonds.

(*j*) Give the oxidation number of sulfur
(*i*) in $\mathbf{SO_4^{2-}}$,
(*ii*) in $\mathbf{Na_2S_4O_6}$.

(*k*) Real manuka honey from New Zealand, considered to have exceptional taste, is supplied with certification of authenticity. Correct to one significant figure, calculate the minimum number of molecules of 2-methoxybenzoic acid (M_r = 152) present in the jar containing 250 g of manuka honey shown on the right, certified to contain at least 1 × 10^{-3} g per kg of this substance.

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

A Write one or more balanced equations to explain how limestone can be used as a scrubber to remove sulfur dioxide from waste gases.

or

B Explain why metallic crystals are good conductors of electricity.

5. Refer to pages 79 and 81 of the *Formulae and Tables* booklet when answering this question.

(*a*) The electron was first identified as a negative subatomic particle by Thomson in 1897 as a result of his and others' research into cathode rays. The electron was the first of the subatomic particles to be identified. Rutherford stated, in 1911, that atoms are composed of a nucleus and an electron cloud and Bohr proposed, in 1913, that the electrons in atoms occupy energy levels.

(*i*) How did Thomson account for the fact that atoms are electrically neutral?

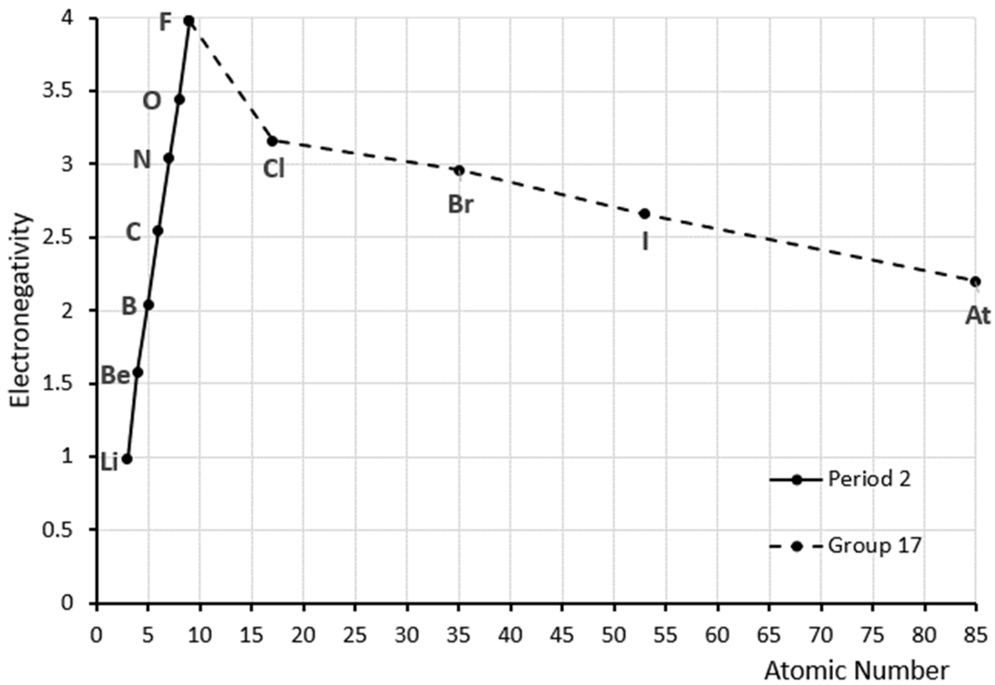
(*ii*) State one piece of evidence for the existence of energy levels in atoms.

(*iii*) State two limitations of Bohr's atomic theory that led to its modification.

(*iv*) Define an atomic orbital.

(*v*) Write the *s*, *p*, *d* electron configuration for an atom of bromine in its ground state. (24)

(*b*) In the graph below the trends in electronegativity values for the elements across the second period and down Group 17 of the periodic table are illustrated.



(*i*) Define electronegativity of an element.

(*ii*) Account for the increase in electronegativity values across the second period.

(*iii*) Explain why electronegativity values decrease down Group 17.

(*iv*) Predict the type of bonding that occurs in the compound bromine monochloride (**BrCl**).

(*v*) Which of the two atoms in one of the **O**–**F** bonds in a molecule of the compound $\mathbf{OF_2}$ has a partial negative charge (δ^-)? Justify your answer. (26)

6. (*a*) The alkanes are saturated hydrocarbons.

(*i*) What is a hydrocarbon?

(*ii*) Why are alkanes described as *saturated* hydrocarbons? (12)

(*b*) Pentane and 2-methylbutane are structural isomers of $\mathbf{C_5H_{12}}$.
Give the systematic IUPAC name of the other structural isomer of $\mathbf{C_5H_{12}}$ *and* draw its molecular structure. (9)

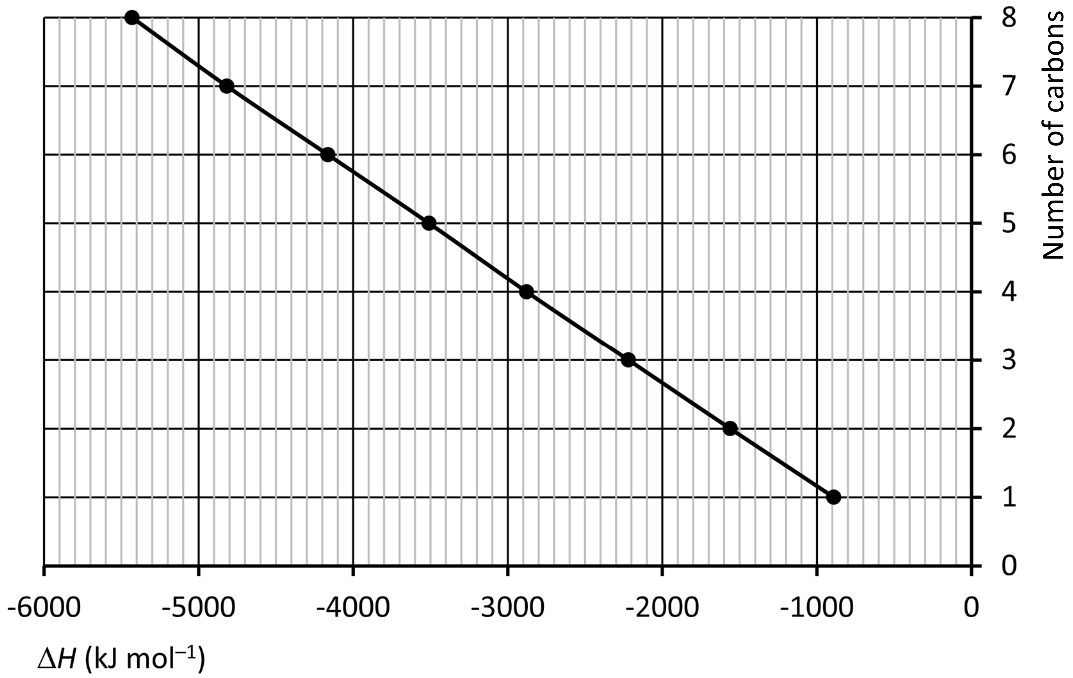
(*c*) The alkane $\mathbf{C_{15}H_{32}}$ occurs in the gas oil fraction obtained from crude oil refining.
A molecule of $\mathbf{C_{15}H_{32}}$ was converted into a molecule of 2-methylbutane, a molecule of but-1-ene and one other molecule during catalytic cracking.
What was the molecular formula of the third molecule formed? (6)

(*d*) The balanced equation for the complete combustion of the alkane $\mathbf{C_{15}H_{32}}$ in a plentiful supply of oxygen is as follows:

$$\mathbf{C_{15}H_{32}}_{\,(l)} + \mathbf{23O_2}_{\,(g)} \rightarrow \mathbf{15CO_2}_{\,(g)} + \mathbf{16H_2O}_{\,(l)}$$

Calculate a value for the heat of combustion of $\mathbf{C_{15}H_{32}}$ using the heats of formation of $\mathbf{C_{15}H_{32}}$, carbon dioxide and water which are –428.8, –393.5 and –285.8 kJ mol^{-1}, respectively. (12)

(*e*) The graph below shows the variation in heat of combustion for the first eight members of the alkane homologous series.



(*i*) What is the difference in the molecular formulae of two successive members of the alkane homologous series that can be used to account for the near linear trend shown in the graph?

(*ii*) Estimate from the graph the difference between the values of ΔH of combustion of two successive members of the alkane homologous series. (11)

7. (*a*) Sulfuric acid is a strong dibasic acid; chloric(I) acid (**HOCl**) is a weak monobasic acid.

(*i*) Define an acid according to the Brønsted-Lowry theory.

(*ii*) What is a strong acid?

(*iii*) Identify the conjugate base of **HOCl**.

(*iv*) Identify the conjugate acid of $\mathbf{HSO_4^-}$. (12)

(*b*) Calculate, correct to one decimal place, the pH of

(*i*) a 0.04 M solution of sulfuric acid,

(*ii*) a 0.04 M solution of chloric(I) acid ($\boldsymbol{K}_a = 3.0 \times 10^{-8}$). (12)

(*c*) (*i*) Identify two processes that help remove suspended solids in the treatment of a large water supply to make it suitable for drinking.

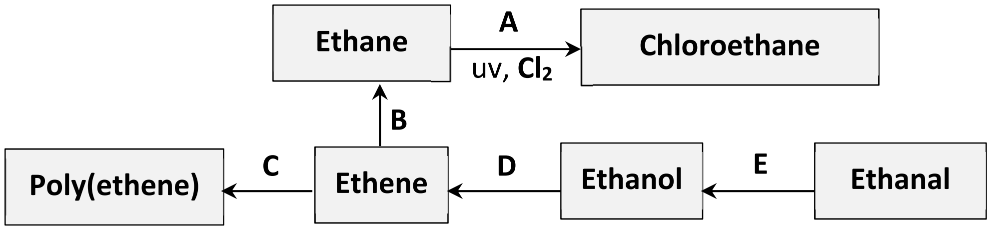
(*ii*) A mass of 1.24 g was collected by a piece of filter paper when 800 cm^3 of water was filtered through it.
Calculate the concentration of suspended solids in the water in p.p.m. (12)

(*d*) According to the Environmental Protection Agency, significant numbers of Irish rivers, lakes, and estuaries now contain too much nitrate and phosphate and the concentrations of these ions are increasing. Phosphate ion concentrations can be reduced during tertiary sewage treatment.

(*i*) Write a balanced equation for the reaction of aluminium sulfate with sodium phosphate ($\mathbf{Na_3PO_4}$) to form both insoluble aluminium phosphate ($\mathbf{AlPO_4}$) and soluble sodium sulfate.

(*ii*) Describe how you would test for the presence of the nitrate ion in a an aqueous solution, given a sample of about 2 cm^3 of the solution in a test-tube. (14)

8. Study the reaction scheme and answer the questions below.



(*a*) (*i*) What is an elimination reaction?

(*ii*) Identify the elimination reaction in the scheme. (8)

(*b*) The same reactant and metal catalyst can be used in conversions **B** and **E** above. Identify (*i*) the reactant, (*ii*) a suitable metal catalyst, for these conversions. (6)

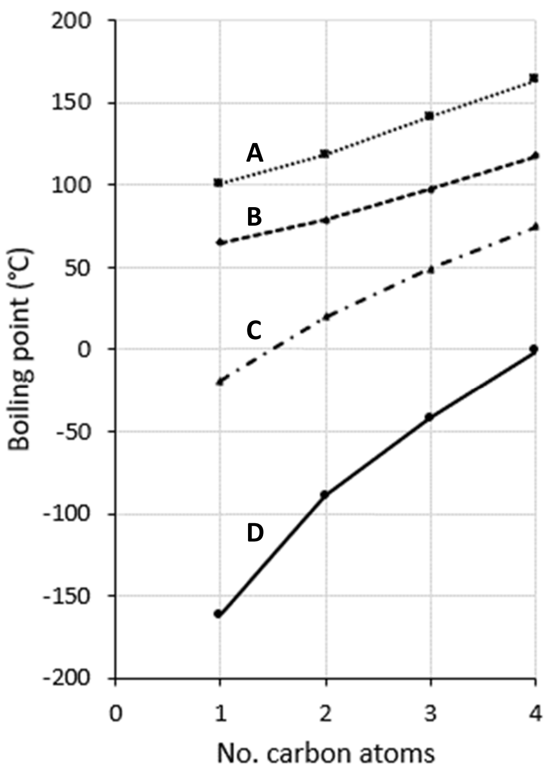
(*c*) (*i*) Draw two repeating units of the polymer poly(ethene).

(*ii*) How does the geometry around the carbon atoms change during conversion **C**? (12)

(*d*) (*i*) Identify the inorganic product of conversion **A**.

(*ii*) Traces of butane are formed during conversion **A**. What is the significance of this result? (6)

(*e*) Consider the following straight-chain homologous series: the alkanes, the primary alcohols, the aldehydes, and the carboxylic acids. Each of **A**, **B**, **C** and **D** shown on the right is a graph of the boiling points of the first four members of one of these homologous series.



Deduce which of **A**, **B**, **C** or **D** is a graph of the boiling points

(*i*) of the first four alkanes,

(*ii*) of the first four aldehydes.

(*iii*) Why does boiling point increase with the number of carbon atoms in each of these graphs?

Account for the significant difference in the boiling points

(*iv*) of ethanal compared to propane (both have M_r = 44),

(*v*) of ethanoic acid compared to propanol (both have M_r = 60). (18)

9. Consider the formation of gaseous PCl_5 by the reversible reaction of PCl_3 gas with Cl_2 gas in a container of fixed volume kept at a certain temperature *T*.

$$PCl_{3\,(g)} + Cl_{2\,(g)} \rightleftharpoons PCl_{5\,(g)} \qquad \Delta H = -87.9 \text{ kJ mol}^{-1}$$

(*a*) (*i*) Explain why a state of equilibrium is reached sometime after mixing the PCl_3 and the Cl_2 in the container.

(*ii*) Would you expect the pressure in the container when equilibrium is reached to be greater than, less than, or equal to the pressure when the PCl_3 and the Cl_2 are initially mixed?

Explain your answer. (14)

(*b*) The value of the equilibrium constant K_c for this reaction is 2.5 at temperature *T*.

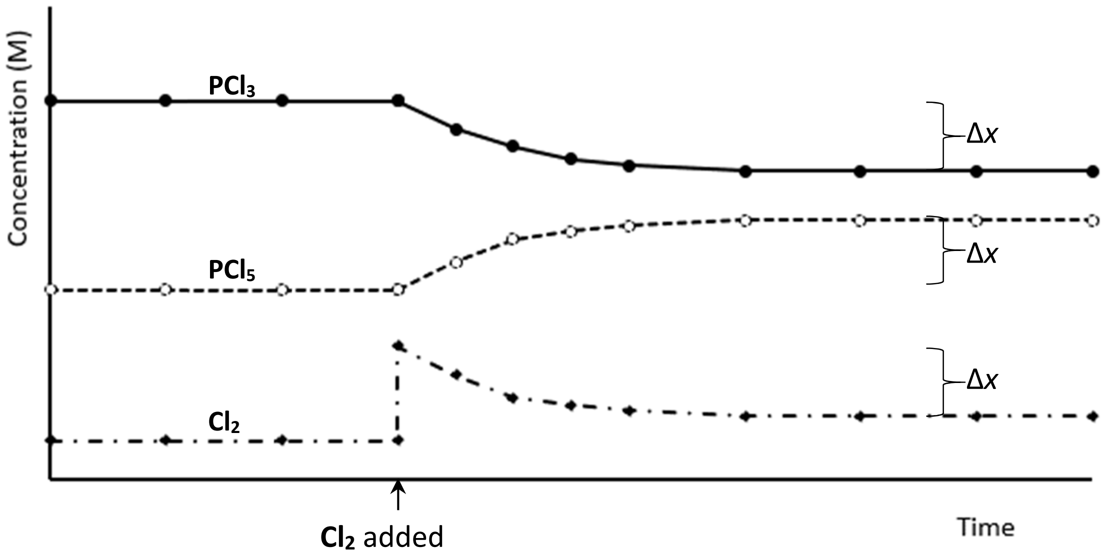
(*i*) Write an expression for K_c for this reaction.

(*ii*) Calculate the equilibrium concentration of each substance under these conditions if the initial concentrations of PCl_3 and Cl_2 were 3.00 mol l^{-1} and 1.20 mol l^{-1}, respectively and there was no PCl_5 present initially. (18)

(*c*) What would be the effect, if any, on the value of K_c for this equilibrium of increasing the temperature above *T*?

Explain your answer. (6)

(*d*) The graph below represents what happens when additional Cl_2 was added to the fixed volume container holding the equilibrium mixture, referred to in (*b*) (*ii*) above, and keeping the temperature of the gas mixture constant at *T*.



(*i*) Explain how the change in concentration of PCl_5 (Δx), when equilibrium is re-established after adding the Cl_2 to the original equilibrium mixture, is consistent with Le Châtelier's principle.

(*ii*) Why is the value of K_c for the new equilibrium 2.5, the same as before? (12)

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

(*a*) Petrol contains small quantities of the aromatic compound benzene (**C_6H_6**).

(*i*) Suggest a reason why the volume of benzene in petrol is limited to about 1% despite the fact that it improves petrol's octane number.

(*ii*) Name the oil refining process in which hexane is converted into benzene.

A single benzene molecule has 42 electrons. How many of these electrons

(*iii*) are involved in carbon to hydrogen bonding,

(*iv*) are involved in carbon to carbon sigma bonding,

(*v*) are involved in delocalised pi bonding,

(*vi*) are involved in carbon to carbon bonding,

(*vii*) are *not* involved in bonding? (25)

(*b*) Succinic acid and its salts are food additives. The formula of a molecule of succinic acid is **$(CH_2)_n(COOH)_2$** where $n > 1$. Succinic acid reacts with sodium hydroxide according to the following balanced equation:

$$(CH_2)_n(COOH)_2 \;+\; 2NaOH \;\rightarrow\; (CH_2)_n(COONa)_2 \;+\; 2H_2O$$

When 1.77 g of succinic acid react completely with sodium hydroxide 2.43 g of **$(CH_2)_n(COONa)_2$** (disodium succinate) are formed.

(*i*) Write expressions in terms of ***n*** for the molar masses of **$(CH_2)_n(COOH)_2$** and **$(CH_2)_n(COONa)_2$**.

(*ii*) Write expressions in terms of ***n*** for the number of moles of succinic acid in 1.77 g of the acid and the number of moles of disodium succinate in 2.43 g of the salt.

(*iii*) Find the value of ***n*** and the mass of one mole of succinic acid.

(*iv*) What volume of a 0.12 M **NaOH** solution is required for complete reaction with an aqueous solution containing 1.77 g succinic acid? (25)

(*c*) People at risk from radiation exposure following a nuclear power plant accident or other nuclear fission incident can take potassium iodide (**KI**) pills to protect their thyroid glands. These pills contain stable iodine–127 and help the thyroid gland to becomes saturated with this isotope and therefore less likely to absorb the iodine–131 radioisotope, a product of nuclear fission, that could cause thyroid cancer.

(*i*) What are isotopes?

(*ii*) What is radioactivity?

When an iodine–131 nucleus decays to form a xenon–131 nucleus, a beta particle is released.

(*iii*) Copy and complete the following nuclear equation for this decay reaction.

$${}^{131}_{53}\mathrm{I} \rightarrow \qquad + \; {}^{\;0}_{-1}e$$

(*iv*) Explain the origin of the electron released as a beta particle in this reaction.

(*v*) Alpha particles can be stopped by a sheet of paper.
Are beta particles more or less penetrating than alpha particles? (25)

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

(*a*) (*i*) State Charles's law.

(*ii*) Explain why Charles's law is consistent with $pV = nRT$, the equation of state for an ideal gas.

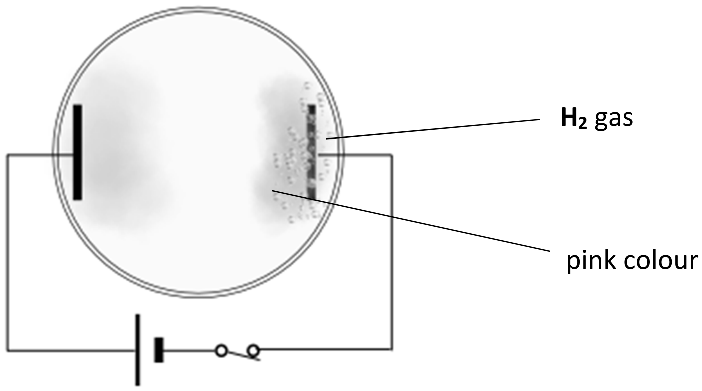
The equation $pV = nRT$ provides a good approximation for the behaviour of real gases under many conditions, but it has limitations.

(*iii*) Under what conditions of temperature and pressure does the equation $pV = nRT$ most accurately describe real gas behaviour?

(*iv*) Use the equation $pV = nRT$ to calculate the approximate volume occupied by one mole of ammonia gas at a pressure of 1×10^4 Pa and a temperature of 373 K.

(*v*) Give two reasons why ammonia gas deviates from ideal gas behaviour. (25)

(*b*) The electrolysis of aqueous potassium iodide (**KI**) using inert electrodes was demonstrated using the arrangement shown in the diagram. The petri dish contained **KI** solution to which a few drops of phenolphthalein indicator had been added; the solution was initially colourless. Iodine ($\mathbf{I_2}$) was formed at one electrode and hydrogen gas at the other.



(*i*) Identify a suitable material for the inert electrodes.

(*ii*) Define oxidation in terms of electron transfer.

(*iii*) Write a balanced half-equation for the oxidation reaction that occurs during this electrolysis.

(*iv*) Was the iodine formed at the positive electrode or at the negative electrode during the electrolysis?

(*v*) Explain why the pink colour of phenolphthalein appeared near the electrode at which hydrogen gas was produced.

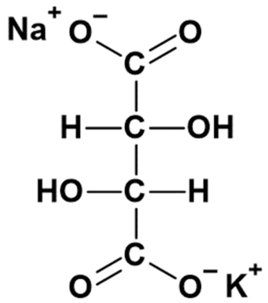
(*vi*) What colour appeared in the solution near the other electrode? (25)

(*c*) (*i*) Explain the term activation energy of a reaction.

(*ii*) How does decreasing its activation energy affect the rate of a reaction?

(*iii*) How can the activation energy of a reaction be changed?

The reaction between sodium potassium tartrate and hydrogen peroxide in solution is quite slow at room temperature. Both reactants contain covalent bonds.
Take the following as the balanced equation for the reaction that takes place:



+ $3H_2O_2 \rightarrow$ HCOONa + HCOOK + $4H_2O$ + $2CO_2$

(*iv*) Why are reactions in solution at room temperature, that involve compounds with covalent bonding, generally slower than reactions in solution at room temperature involving substances that only have ionic bonding?

(*v*) Suggest three practical ways that the rate of the reaction of sodium potassium tartrate solution with hydrogen peroxide solution, according to the equation given above, could be increased. (25)

This question continues on the next page.

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

A In Ireland atmospheric $\mathbf{NO_2}$ concentrations peak daily at about 10 a.m. and again at about 7 p.m. and total monthly emissions in the summer months are lower than in the winter months.

(*i*) Write balanced equations for the natural fixation by lightning of atmospheric nitrogen converting it first to **NO** and then to $\mathbf{NO_2}$.

(*ii*) Why is nitrogen gas unreactive?

(*iii*) The World Health Organisation (WHO) 2021 daily guideline for the maximum permissible $\mathbf{NO_2}$ concentration in air is 0.025 mg per m^3 averaged over any 24 hour period.

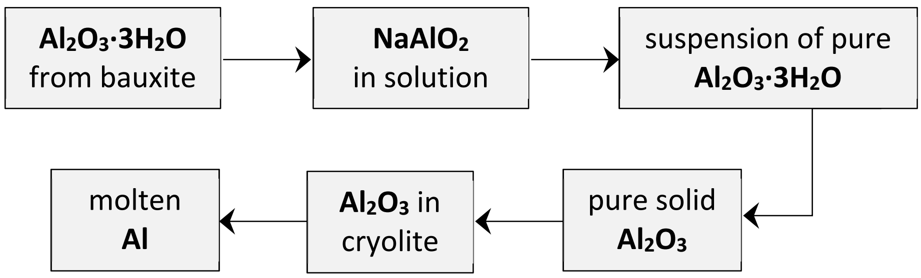
Show by calculation whether this guideline was exceeded in a 5,000 m^3 enclosed volume of air when 3.2×10^{-3} moles of $\mathbf{NO_2}$ were present on average over a particular 24 hour period.

(*iv*) Identify an industrial activity that causes emission of an oxide of nitrogen into the environment.

(*v*) Neither **NO** nor $\mathbf{NO_2}$ is a significant <u>greenhouse gas</u> although $\mathbf{N_2O}$ is.
Explain the underlined term. (25)

or

B Pure alumina ($\mathbf{Al_2O_3}$) is obtained from the ore bauxite which yields about 50% alumina by mass. Aluminium metal is then extracted electrochemically from alumina.



(*i*) Write a balanced equation for the conversion of $\mathbf{Al_2O_3{\cdot}3H_2O}$ to $\mathbf{NaAlO_2}$.

(*ii*) Identify a possible negative impact on the environment adjacent to a plant where the $\mathbf{Al_2O_3}$ is separated from the other materials present in the bauxite.

(*iii*) What is the main economic consideration when locating the plant where the electrolysis of the molten $\mathbf{Al_2O_3}$ is to take place?

(*iv*) Why must the $\mathbf{Al_2O_3}$ be molten or dissolved for the electrolysis stage?

(*v*) Write a balanced half-equation for the reaction that takes places at the negative electrode during the electrolysis of molten $\mathbf{Al_2O_3}$.

(*vi*) The melting point of $\mathbf{Al_2O_3}$ is 2,072 °C but the temperature of the electrolyte is only about 1,000 °C. Explain. (25)

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Image Q4 (*k*) on page 5 from New Zealand Honey Co.,
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Image Q7 (*d*) on page 8 Swans on Lough Derravaragh, County Westmeath by Comhar
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Image Q10 (*c*) on page 11 from BTG International Ltd.,
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Leaving Certificate – Higher Level

Chemistry

Tuesday, 20 June

Afternoon, 2:00 – 5:00