Coimisiún na Scrúduithe Stáit
State Examinations Commission

LEAVING CERTIFICATE EXAMINATION

CHEMISTRY – HIGHER LEVEL

3 HOURS DURATION

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, 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}

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

The use of the *Formulae and Tables* booklet approved for use in the State Examinations is permitted. A copy may be obtained from the superintendent.

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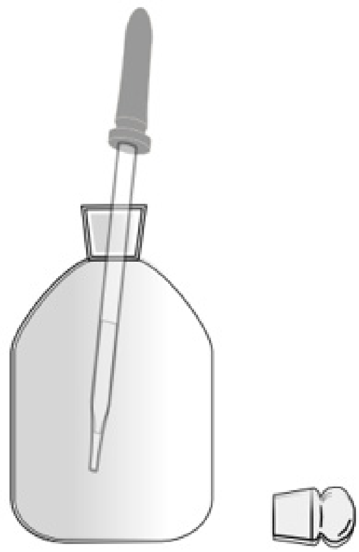
Section A

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

1. The dissolved oxygen concentration of lake water, supplied in a stoppered sample bottle completely filled with the water, was determined as summarised below. A small quantity of a concentrated solution of $\mathbf{Mn^{2+}}$ ions was added, using a dropper as shown in the diagram. The stopper was replaced carefully and the bottle was inverted several times. Then a small quantity of a concentrated solution of alkaline potassium iodide (**KOH**/**KI**) was added to the bottle. This addition was made in a similar way and the bottle was stoppered and inverted again. Some of the $\mathbf{Mn^{2+}}$ ions were oxidised by the dissolved oxygen present to $\mathbf{Mn^{x+}}$ ($\boldsymbol{x}$ = 3 or 4). The $\mathbf{Mn^{x+}}$ compounds appeared as a precipitate.



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

(*ii*) Explain why an excess of this compound was required in this analysis.

(*iii*) What colour is the precipitate of $\mathbf{Mn^{x+}}$ compounds? (9)

A small volume of concentrated sulfuric acid was then added to the water sample using a dropper so that it flowed down the inside of the neck of the bottle and once again the bottle was stoppered and inverted several times. Some of the $\mathbf{I^-}$ ions added earlier were now oxidised by the $\mathbf{Mn^{x+}}$ ions present to form a solution of free iodine ($\mathbf{I_2}$).
Then 150.0 cm^3 portions of the solution from the sample bottle, measured into a conical flask, were titrated with a standard solution of sodium thiosulfate to determine their average free iodine concentration. The balanced equation for the titration reaction is:

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

(*b*) (*i*) What is a standard solution?

(*ii*) Using a pipette, how could 150.0 cm^3 of iodine solution have been measured accurately and transferred into the conical flask?

(*iii*) Name the indicator used in the titrations.

(*iv*) What colour change was observed in the conical flask at the end point? (18)

For every **one** mole of dissolved oxygen ($\mathbf{O_2}$) in the lake water sample, **two** moles of free iodine ($\mathbf{I_2}$) were formed.

(*c*) The sodium thiosulfate solution used in the titrations contained 3.72 g $\mathbf{Na_2S_2O_3{\cdot}5H_2O}$ per litre. If, on average, 7.6 cm^3 of this solution were required for complete reaction with 150.0 cm^3 portions of the $\mathbf{I_2}$ solution titrated, find

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

(*ii*) the number of moles of $\mathbf{I_2}$ in 150.0 cm^3 of the solution titrated,

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

(*iv*) the concentration of dissolved oxygen in the lake water in p.p.m. (mg l^{-1}). (23)

2. (*a*) (*i*) When combustion tests were carried out separately on samples of pure ethene and pure ethyne, both gases burned in air with luminous yellow flames but one test produced a lot of black soot while only a little smoke was produced in the other. Which gas, ethene or ethyne, burned with the cleaner flame?

(*ii*) State what you would expect to observe on adding a few drops of dilute acidified **$KMnO_4$** to a sample of either of these gases in a stoppered test-tube. Justify your answer. (9)

(*b*) Pure samples of propanone, ethanal and ethanoic acid were provided in separate stoppered sample bottles.

When a few drops of the liquid from one of these sample bottles were added to some damp solid sodium carbonate in a test-tube, effervescence was observed and the gas produced turned limewater milky.

(*i*) Identify this liquid.

(*ii*) Write a balanced equation for the reaction which took place between this liquid and the sodium carbonate.

When a few drops of the liquid from a second sample bottle were added to a little freshly prepared ammoniacal silver nitrate (Tollens' reagent) in a thoroughly clean test-tube, a silver mirror was formed when the test-tube was warmed gently.

(*iii*) Based on this observation, identify the liquid in the second sample bottle.

(*iv*) Describe another redox chemical test to confirm this identification. (21)

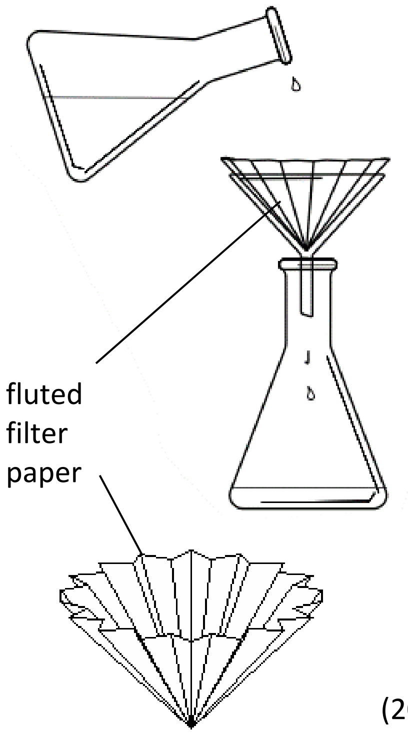
(*c*) Recrystallisation was used to purify a 2.32 g sample of benzoic acid that had a melting point range of 114 – 118 °C. A mass of 1.88 g of dry crystals was obtained from the recrystallisation process.

(*i*) Describe, with the aid of a labelled diagram, a method that could be used to measure the melting point range of a sample of benzoic acid.

(*ii*) How could it have been verified that the recrystallised benzoic acid crystals were purer than the original sample?

(*iii*) Calculate the percentage recovery of crystals from the recrystallisation procedure.

(*iv*) During the recrystallisation a hot solution of benzoic acid in water was filtered through a fluted filter paper as shown. State the specific purpose of this step of the recrystallisation process.



(20)

3. A student carried out an investigation into the rate of decomposition of a solution of hydrogen peroxide (H_2O_2) in the presence of an MnO_2 catalyst.
The balanced equation for the decomposition reaction is as follows:

$$H_2O_2 \xrightarrow{MnO_2} H_2O + \tfrac{1}{2}O_2$$

(*a*) Solutions of hydrogen peroxide are unstable and can decompose on storage. The warning symbol on the label of the hydrogen peroxide solution used in the experiment is shown on the right.

(*i*) What chemical hazard is indicated by this pictogram?

(*ii*) Give one safety precaution that should be taken when using or storing hydrogen peroxide solutions.

(*iii*) Describe the appearance of the MnO_2 catalyst. (11)

(*b*) A 10.0 cm^3 volume of a solution labelled 6.8% (w/w) hydrogen peroxide was decomposed in this investigation.

(*i*) Calculate the number of moles of hydrogen peroxide in 10.0 cm^3 of a 6.8% (w/w) H_2O_2 solution, taking its density as 1.0 g cm^{-3}.

(*ii*) Find the theoretical volume of oxygen gas, measured at room temperature and pressure, produced on decomposition of this number of moles of H_2O_2.

(*iii*) Suggest a suitable vessel to collect and measure the oxygen gas expected to be produced in the investigation, assuming no prior decomposition of the H_2O_2 has occurred.

(*iv*) Draw a labelled diagram of an arrangement of apparatus and chemicals used to carry out this investigation. (21)

(*c*) The volumes of oxygen collected at room temperature and pressure at intervals over 480 seconds are recorded in the table below.

Time (seconds)	0	60	120	180	240	300	360	420	480
Volume O_2 (cm^3)	0	100	150	182	206	224	234	238	238

(*i*) Use the data in the table to plot a graph of volume *versus* time for the decomposition of the hydrogen peroxide solution.

(*ii*) Use your graph to determine the instantaneous rate at 240 seconds (in cm^3 O_2 per second at room temperature and pressure). (18)

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)

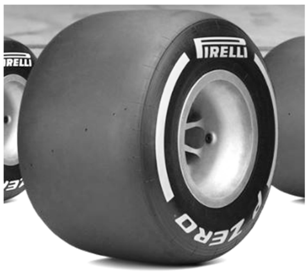
(*a*) Iridium has two naturally occurring stable isotopes, iridium–191 and iridium–193. What are isotopes?

(*b*) Identify the first two fundamental processes of mass spectrometry in the order in which they occur.

(*c*) Copy and complete the following equation for the alpha decay of polonium–208.

$$^{208}_{84}\mathbf{Po} \rightarrow \_\_\_ + {}^{4}_{2}\mathbf{He}$$

(*d*) As polar ice caps melt, environmentalists are concerned about the release into the atmosphere of the methane trapped in the ice as methane hydrate ($CH_4{\cdot}xH_2O$). Calculate the value of ***x*** correct to one decimal place if methane hydrate is on average 13.4% CH_4 by mass.

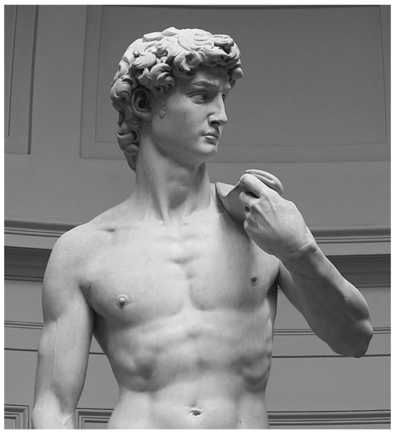


(*e*) State Avogadro's law.

(*f*) A racing car tyre like that shown contained 294 g of nitrogen gas occupying a volume of 0.168 m^3 at a temperature of 293 K. Calculate the pressure of the gas inside the tyre in Pa.

(*g*) Why is a $BeCl_2$ molecule linear in shape but a H_2O molecule is not?

(*h*) How would you confirm the presence of sulfite ions in an aqueous solution?



(*i*) The marble statue of *David* by Michelangelo is kept indoors in Florence in Italy to protect it from rain. Write a balanced equation for the reaction that could occur between the calcium carbonate in the marble and the carbonic acid (H_2CO_3) in rain water.

(*j*) What is the total number of sigma bonds in a benzene molecule?

(*k*) Draw the structure of a molecule of propane-1,2,3-triol (glycerol).

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

A Explain why nitrogen is chemically inert.

or

B Explain, with reference to its *d* sublevel, why zinc is *not* considered to be a transition metal.

5. Refer to pages 79 and 80 of the *Formulae and Tables* booklet when answering this question.

Between 1807 and 1808 Humphry Davy isolated the elements sodium, potassium, calcium, magnesium, strontium and barium using electrolysis. Sodium and potassium are in Group 1 of the modern periodic table and calcium, magnesium, strontium and barium are in Group 2. In 1829, before the periodic table had been devised, Dobereiner placed the elements calcium, strontium and barium in a *triad*.

(*a*) What was a triad of elements according to Dobereiner? (5)

(*b*) Describe how to carry out a flame test to confirm the presence of strontium in a salt. (12)

(*c*) (*i*) Write the *s*, *p* electron configuration for a potassium atom in its ground state.

(*ii*) How many energy sublevels are occupied by the electrons in a potassium atom in its ground state? (9)

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

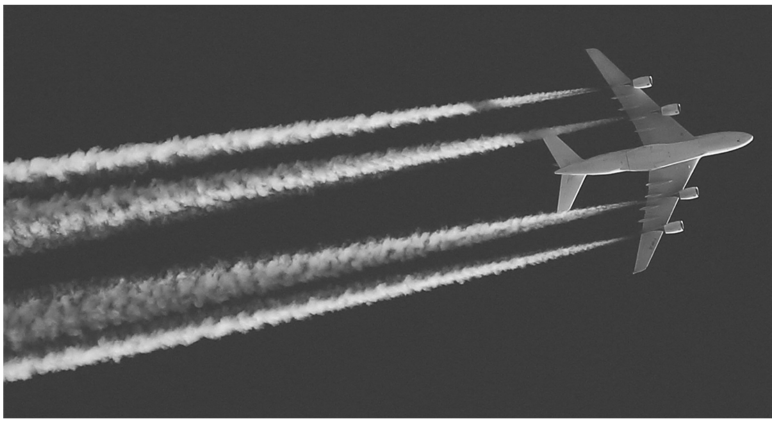
(*ii*) Write a balanced equation to represent the first ionisation of a potassium atom.

(*iii*) Account for the decreasing trend in first ionisation energy values down Group 1 of the periodic table.

(*iv*) Why is there a general increase in first ionisation energy values across the elements of the third period?

(*v*) Explain why magnesium has a *significantly* larger first ionisation energy value than sodium. (24)

6. Condensation trails (also known as 'contrails') are produced behind aircraft jet engines as they burn kerosene at high altitudes.



(*a*) (*i*) Describe with the aid of a labelled diagram how kerosene is obtained in an oil refinery by the fractional distillation of crude oil.

(*ii*) What property of kerosene allows it to be separated from the other constituents of crude oil?

(*iii*) Kerosene is a mixture of hydrocarbons and some of the compounds that occur in kerosene are <u>structural isomers</u>.
Explain the underlined term. (21)

(*b*) The balanced equation for the complete combustion of $\mathbf{C_{12}H_{26}}$ (a typical constituent of kerosene) is:

$$\mathbf{C_{12}H_{26}}\,_{(l)} + \mathbf{18\tfrac{1}{2}O_2}\,_{(g)} \rightarrow \mathbf{12CO_2}\,_{(g)} + \mathbf{13H_2O}\,_{(l)}$$

(*i*) Calculate the heat of combustion of $\mathbf{C_{12}H_{26}}$ given that the heats of formation of $\mathbf{C_{12}H_{26}}$, carbon dioxide and water are –349.3, –393.5 and –285.8 kJ mol^{-1}, respectively.

(*ii*) A particular aircraft fuel tank holds 235,000 moles of kerosene.
Taking the kerosene to be composed entirely of $\mathbf{C_{12}H_{26}}$ molecules,
find the number of $\mathbf{CO_2}$ molecules released into the atmosphere when all this fuel is burned. (18)

(*c*) Kerosene is a fossil fuel and its use poses environmental challenges. However, aircraft capable of running on hydrogen are currently being developed.

(*i*) How is hydrogen gas manufactured on an industrial scale?

(*ii*) Suggest a disadvantage of hydrogen as a fuel for aircraft. (11)

7. The reaction between sulfur dioxide and oxygen to produce sulfur trioxide is an important stage in the industrial manufacture of sulfuric acid. When $\mathbf{SO_2}$ and $\mathbf{O_2}$ were mixed the following <u>chemical equilibrium</u> with $\mathbf{SO_3}$ was established at 730 K and at atmospheric pressure using a solid $\mathbf{V_2O_5}$ catalyst.

$$\mathbf{2SO_2}\,_{(g)} + \mathbf{O_2}\,_{(g)} \rightleftharpoons \mathbf{2SO_3}\,_{(g)}$$

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

(*ii*) State Le Châtelier's principle. (9)

(*b*) (*i*) This equilibrium is established faster when the particle size of the $\mathbf{V_2O_5}$ catalyst is very small. Suggest an explanation for this result.

(*ii*) Platinum metal was originally used as the catalyst for this conversion. However, platinum is more easily poisoned than $\mathbf{V_2O_5}$ by arsenic impurities in the $\mathbf{SO_2}$.
Describe how a catalyst poison reduces the effectiveness of a solid catalyst. (6)

(*c*) A 6,000 litre reaction vessel was filled with 65.6 moles of $\mathbf{SO_2}$ and 65.6 moles of $\mathbf{O_2}$. It was found that 62.3 moles of $\mathbf{SO_3}$ had been formed in the reaction vessel when equilibrium was reached at 730 K.

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

(*ii*) Calculate the number of moles of $\mathbf{SO_2}$ and $\mathbf{O_2}$ present at equilibrium, and hence, the value of K_c at 730 K. (18)

(*d*) If the pressure in the reaction vessel was increased by decreasing its volume and the temperature was kept at 730 K, how, if at all, would

(*i*) the equilibrium yield of $\mathbf{SO_3}$ change as a result,

(*ii*) the value of K_c change as a result?

(*iii*) State an industrial disadvantage of operating at a higher pressure than atmospheric pressure. (9)

(*e*) The value of K_c for this equilibrium decreases as temperature increases.

(*i*) Is the forward reaction exothermic or endothermic?
Explain your reasoning.

(*ii*) Suggest why a temperature lower than 730 K is *not* used for this stage of sulfuric acid manufacture. (8)

8. Consider the following four compounds:

A	**B**	**C**	**D**
C_2H_4	C_2H_6	$C_6H_5CH_3$	CH_3CH_2Cl

(*a*) (*i*) Give the systematic IUPAC names of **B** and **C**.

(*ii*) Which one of the four compounds has molecules that contain only carbon atoms that are in planar geometry? (9)

(*b*) Compound **B** undergoes free radical substitution to produce compound **D**.

(*i*) State the reagent and conditions required to bring about this conversion.

(*ii*) Describe the mechanism for this reaction.

(*iii*) How can the addition of a little tetraethyl lead to the reaction mixture provide evidence for the mechanism you have described? (24)

(*c*) Compound **D** can also be synthesised directly from compound **A**.

(*i*) State the reagent required to bring about this conversion.

(*ii*) What organic reaction type is involved in this conversion? (6)

(*d*) Compound **A** can undergo addition polymerisation.

(*i*) Name the polymer produced in this reaction.

(*ii*) Draw two repeating units of the polymer.

(*iii*) How does the geometry around the carbon atoms change during the polymerisation reaction? (11)

9. (*a*) What is an acid according to

(*i*) the Arrhenius theory,

(*ii*) the Brønsted-Lowry theory?

(*iii*) Identify the two species acting as Brønsted-Lowry acids in the equilibrium below.

$$\mathbf{NH_3 + HCO_3^- \rightleftharpoons NH_4^+ + CO_3^{2-}}$$

(*iv*) Why can ammonia (**NH_3**) *not* be classified as a base according to the Arrhenius theory? (20)

(*b*) (*i*) Define pH.

(*ii*) State one limitation of the pH scale.

(*iii*) Ammonium hydroxide (**NH_4OH**) is produced when gaseous ammonia is dissolved in water. Calculate the pH of a 0.20 M solution of ammonium hydroxide.
The base dissociation constant K_b for ammonium hydroxide is 1.8×10^{-5}. (18)

(*c*) A certain acid-base indicator is a weak acid and can be represented by **HIn**.
HIn dissociates in water as follows:

$$\mathbf{HIn + H_2O \rightleftharpoons H_3O^+ + In^-}$$

yellow blue

Undissociated **HIn** has a yellow colour and the dissociated form **In^-** is blue.

(*i*) Explain how **HIn** acts as an acid-base indicator.

(*ii*) The indicator **HIn** changes colour in the pH range of 3.8 to 5.4.
Would this indicator be suitable for use in a titration between a 0.20 M ammonium hydroxide solution and a hydrochloric acid solution of approximately 0.2 M concentration?
Justify your answer. (12)

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

(*a*) On being heated in air a 12.5 g mixture containing only **FeO** and $\mathbf{Fe_3O_4}$ was completely converted to $\mathbf{Fe_2O_3}$. The mixture originally contained 7.2% **FeO** by mass. The following are the balanced equations for the reactions involved:

$$\mathbf{2FeO}_{(s)} + \mathbf{½O_2}_{(g)} \rightarrow \mathbf{Fe_2O_3}_{(s)}$$

$$\mathbf{2Fe_3O_4}_{(s)} + \mathbf{½O_2}_{(g)} \rightarrow \mathbf{3Fe_2O_3}_{(s)}$$

When both reactions were complete, calculate

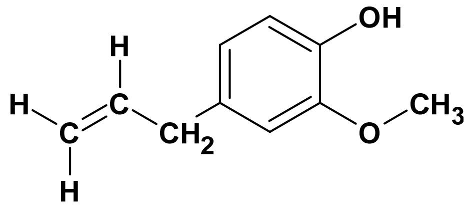
(*i*) the mass of oxygen that had reacted with the **FeO** in the sample,

(*ii*) the total mass of oxygen that had reacted with the whole sample,

(*iii*) the total number of moles of $\mathbf{Fe_2O_3}$ produced.

(*iv*) What are the oxidation numbers of iron in **FeO**, $\mathbf{Fe_3O_4}$ and $\mathbf{Fe_2O_3}$, respectively? (25)

(*b*) Gas chromatography analysis showed that a sample of clove oil was composed of a mixture of compounds with one main component **X**. This main component **X** was isolated from the clove oil and its infrared spectrum was recorded. Infrared indicated the presence of an **–OH** group and a benzene ring in the molecular structure of **X**. Using a database of infrared spectra, **X** was identified as the compound eugenol. The structure of eugenol is shown.



(*i*) Name a technique suitable for the extraction of clove oil from cloves.

(*ii*) What is the principle of the separation of the components in a mixture using any type of chromatography?

(*iii*) Why is infrared spectrometry described as a 'fingerprinting' technique?

(*iv*) What is the relative molecular mass (M_r) of eugenol?

(*v*) Calculate the elemental percentage composition by mass of eugenol.

(*vi*) Would you expect eugenol to decolourise a solution of bromine? Justify your answer. (25)

(*c*) Chemicals are added at various stages of the treatment of a water supply to make it suitable for drinking. Addition of excess of any of these chemicals is problematic.

(*i*) Identify a chemical used to cause flocculation in water treatment.

(*ii*) What is the result of adding the flocculant?

(*iii*) What is the purpose of adding chlorine to a drinking water supply?

(*iv*) Why is it important not to add too much chlorine?

(*v*) Identify a chemical used to fluoridate drinking water.

(*vi*) Why is it important not to add too much of this fluorine-containing compound?

(*vii*) Give an example of a problem that could arise if the pH of a public water supply were too low. (25)

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

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

Consider the compounds of hydrogen listed below.

$\mathbf{CH_4}$ $\mathbf{H_2O_2}$ $\mathbf{NH_3}$ **HF** **HCl**

(*ii*) In which of the compounds listed does hydrogen bonding occur?

(*iii*) Identify a compound from the list in which hydrogen bonding does *not* occur but which is very soluble in water.

Identify the main type of intermolecular force that occurs in this compound.

Describe, using a diagram, how these intermolecular forces arise.

Account for the fact that this compound is very soluble in water.

(*iv*) Explain how the weak intermolecular forces that occur in hydrogen gas ($\mathbf{H_2}$) arise. (25)

(*b*) (*i*) Define the rate of a chemical reaction.

(*ii*) What is meant by the activation energy for a reaction?

Consider reactions that can be represented by the equation

$$\mathbf{A}_{(aq)} + \mathbf{B}_{(aq)} \rightarrow \mathbf{C}_{(aq)} + \mathbf{D}_{(aq)}$$

and account for each of the following observations.

(*iii*) The rates of many of these reactions increase when the concentration of one of the reactants is increased.

(*iv*) The rates of these reactions generally increase with temperature.

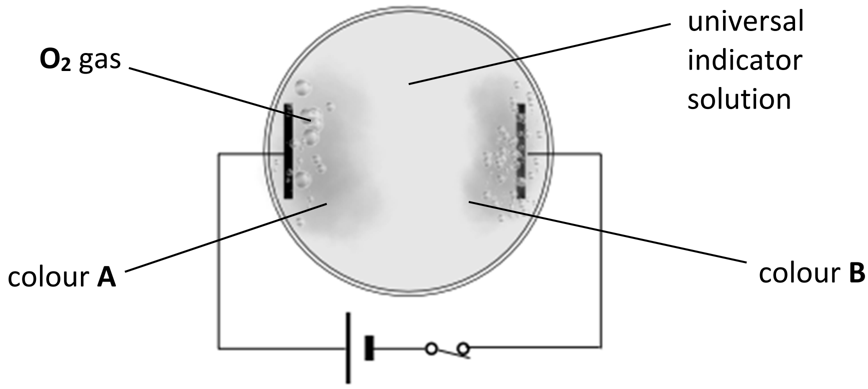
(*v*) These reactions are fast at room temperature when **A** and **B** are both ionic compounds.

(*vi*) These reactions are often slow at room temperature when the reactants **A** and **B** have some covalent bonding.

Some dry mixtures of solid substances can be stored without a reaction occurring, even though the compounds in the mixture react together quickly when added to water.

(*vii*) Suggest a reason why chemical reactions are generally slow when the reactants are kept together in the solid state. (25)

(*c*) The electrolysis of aqueous sodium sulfate (**Na_2SO_4**) using inert platinum electrodes was demonstrated using the arrangement shown in the diagram. The petri dish contained **Na_2SO_4** solution to which a little universal indicator had been added; the colour of the solution was green at the start. Bubbles of gas formed at each electrode during the electrolysis and the colour of the solution near each electrode changed from green to a different colour. Oxygen gas was produced at the positive electrode by the oxidation of water. A different gas was produced at the negative electrode by reduction.



(*i*) Define reduction in terms of electron transfer.

(*ii*) Why are the platinum electrodes used described as inert?

(*iii*) Identify the gas produced at the negative electrode during the electrolysis.

(*iv*) Write a balanced half-equation for the reduction reaction that occurred at the negative electrode.

(*v*) What colours **A** and **B** are observed at the electrodes as the electrolysis proceeds?

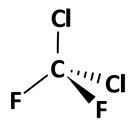
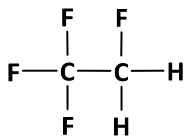
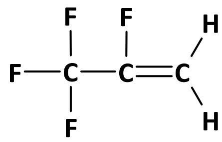
(*vi*) Explain why the sodium ions in solution are not reduced to sodium metal at the negative electrode, although they are attracted to this electrode during the electrolysis. (25)

This question continues on the next page.

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

A

The four compounds shown in the table below have all been used as refrigerants in the air conditioning systems of vehicles.

Compound	A	B	C	D
Structure				**O=C=O**
Period of use	Prior to 1994	1992 - 2011	2011 to present	2015 to present

(*i*) What is ozone?

(*ii*) Identify the type of electromagnetic radiation absorbed by the ozone layer of the Earth's stratosphere.

(*iii*) **A** is a CFC compound. What is a CFC compound?

(*iv*) Write a balanced equation for the breakdown of a molecule of **A** in the stratosphere giving a chlorine free radical.

(*v*) Write balanced equations to show how chlorine free radicals take part in a chain reaction in the stratosphere that damages the ozone layer.

All four compounds **A**, **B**, **C** and **D** are <u>greenhouse gases</u> and **D** is an acidic oxide.

(*vi*) Explain the underlined term.

(*vii*) How could you demonstrate that $\mathbf{CO_2}$ is an acidic oxide? (25)

or

B

Sodium metal is extracted electrochemically from molten sodium chloride in a Downs cell. The electrodes in the Downs cell are made of two different materials.

(*i*) What is the second product of the Downs cell?

(*ii*) Why do the two products have to be kept separate?
How is this achieved in the Downs cell?

(*iii*) Explain why the temperature of the molten electrolyte in the Downs cell is only about 600 °C although the melting point of **NaCl** is 801 °C.

(*iv*) What material is used for the positive electrode in a Downs cell?
Explain this choice of material.

(*v*) Write a balanced half-equation for the reaction that takes place at the positive electrode during the electrolysis of molten sodium chloride.

(*vi*) Why is it usually only electropositive metals that are extracted from their ores by electrochemical methods? (25)

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Leaving Certificate – Higher Level

Chemistry

3 Hours