Coimisiún na Scrúduithe Stáit
State Examinations Commission

LEAVING CERTIFICATE EXAMINATION, 2022

CHEMISTRY – HIGHER LEVEL

TUESDAY, 21 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, O = 16, K = 39, Ca = 40

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}

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 total hardness values of a water supply before and after it had been passed through a laboratory deioniser were compared. This was done by adding a suitable indicator and a small volume of a buffer solution to 25.0 cm^3 samples of the water in a conical flask and titrating with a standard **edta** (ethylenediaminetetraacetic acid) salt solution.

The ions that cause hardness (represented by $\mathbf{M^{2+}}$) react with **edta** (represented by $\mathbf{H_2Y^{2-}}$) according to the following balanced equation.

$$\mathbf{M^{2+} + H_2Y^{2-} \rightarrow MY^{2-} + 2H^+}$$

(*a*) (*i*) Identify the two ions (represented by $\mathbf{M^{2+}}$) that most commonly cause hardness when dissolved in water.

(*ii*) Explain the term *total hardness*. (8)

(*b*) (*i*) Name a suitable indicator for this titration.

(*ii*) What colour change was observed in the conical flask at the end point? (9)

(*c*) (*i*) What pH does the buffer solution maintain in the mixture in the conical flask?

(*ii*) Why is it important to maintain this pH during the titration? (6)

(*d*) Describe the correct procedure for preparing a burette, that had been previously rinsed with deionised water and some 0.010 M **edta** solution, for this titration. (12)

On average, 9.2 cm^3 *less* of the 0.010 M **edta** solution was required to react completely with 25.0 cm^3 portions of the water that had been passed through the deioniser than with 25.0 cm^3 portions of the original hard water supply.

(*e*) Calculate

(*i*) the number of moles of **edta** in 9.2 cm^3 of a 0.010 M solution,

(*ii*) the number of moles of $\mathbf{M^{2+}}$ ion that reacted with this quantity of **edta**,

(*iii*) the number of moles of $\mathbf{M^{2+}}$ ion removed by the deioniser from a litre of the original supply of hard water,

(*iv*) the total hardness removed by the deioniser expressed in g l^{-1} of $\mathbf{CaCO_3}$ *and* in p.p.m. $\mathbf{CaCO_3}$. (15)

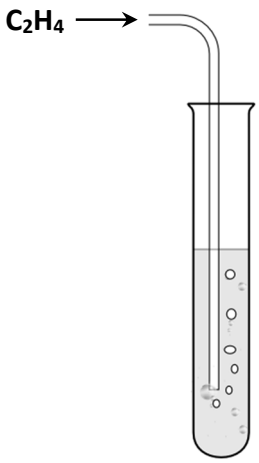
2. (*a*) Draw a labelled diagram of a suitable arrangement of apparatus and of chemicals for the preparation and collection over water of samples of pure ethene gas.

When carrying out this preparation, state one way of avoiding

(*i*) a suck-back of cold water into the reaction vessel,

(*ii*) a fire. (17)

(*b*) Some ethene was bubbled through a reagent as shown in the diagram on the right.



What colour change is observed when the reagent used is

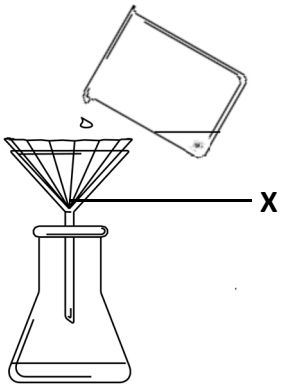
(*i*) dilute acidified **$KMnO_4$**,

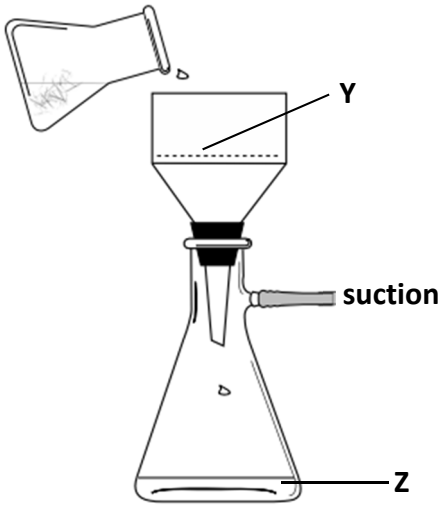
(*ii*) bromine water?

(*iii*) Name the organic reaction type that occurs in the case of the bromine reagent.

(*iv*) Identify an organic product of the reaction between ethene and the bromine solution. (12)

(*c*) A student practiced the technique of recrystallisation using benzoic acid containing small quantities of two solid impurities: water-soluble potassium chloride (**KCl**) and black, insoluble charcoal (**C**). The two filtration stages in the recrystallisation of the benzoic acid using water as the solvent are shown in the diagrams below in the order in which they are carried out.





(*i*) Identify the substance(s) collected at locations **X**, **Y** and **Z**.

What steps are carried out to maximise the yield of pure benzoic acid,

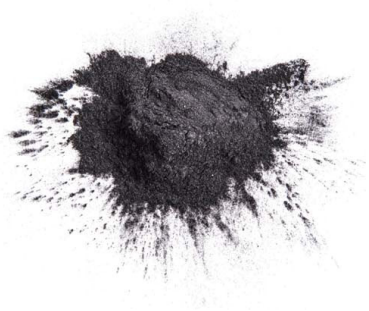
(*ii*) between the first and second filtrations,

(*iii*) after the second filtration?

(*iv*) How would you expect the melting point value of a recrystallised sample of benzoic acid to differ from that of an impure sample? (21)

3. The rate of decomposition of a hydrogen peroxide solution using manganese(IV) oxide as a catalyst was investigated.

A 25.0 cm^3 volume of a hydrogen peroxide solution of suitable concentration decomposed in the presence of 0.5 g manganese(IV) oxide, which was in the form of a fine black powder, as illustrated. The volume of oxygen produced was monitored over time.



(*a*) Write a balanced equation for the decomposition of hydrogen peroxide. (5)

(*b*) Give one risk associated with the use or storage of hydrogen peroxide. State how you could manage this risk. (6)

(*c*) The volumes of oxygen collected at room temperature and pressure over 16 minutes, when the initial temperature of the hydrogen peroxide solution was 24 °C and the mass of catalyst used was 0.5 g, are recorded in the table below.

Time (minutes)	0.0	1.0	3.0	5.0	8.0	10.0	12.0	14.0	16.0
Volume $\mathbf{O_2}$ (cm^3)	0	30	66	88	104	109	111	112	112

Use this data to plot a graph of volume *versus* time for the decomposition of the hydrogen peroxide solution under these conditions.

Use your graph to find

(*i*) the time taken for this reaction to be complete,

(*ii*) the average rate of the reaction over the first 4.0 minutes (in cm^3 $\mathbf{O_2}$ per minute at room temperature and pressure),

(*iii*) the instantaneous rate of the reaction at 4.0 minutes (in cm^3 $\mathbf{O_2}$ per minute at room temperature and pressure). (24)

(*d*) Sketch, and label clearly on your graph, an approximate volume *versus* time curve you would expect to plot for the decomposition of 25.0 cm^3 of a hydrogen peroxide solution, with an initial temperature 24 °C,

(*i*) of half the concentration used in (*c*) and in the presence of 0.5 g of catalyst,

(*ii*) of the same concentration used in (*c*) above but now in the presence of 0.6 g of the catalyst instead of 0.5 g.

Justify the shape of the curve you predicted in each case. (15)

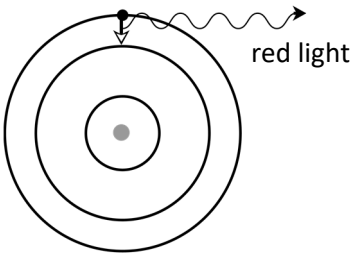
Section B

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*) The set of elements {**Li**, **Na**, **K**} is one of Dobereiner's triads. Refer to this example to explain Dobereiner's contribution to the development of the periodic table.

(*b*) The diagram shows the origin of one of the lines in the Balmer series of the hydrogen emission spectrum. Why is a photon emitted as the electron moves from one energy level to another as shown?



(*c*) Why is the second ionisation energy of lithium significantly larger than its first?

(*d*) What colour is observed in a flame test on a salt of
(*i*) lithium,
(*ii*) copper?

(*e*) State Avogadro's law.

(*f*) One of the largest diamonds ever mined was found in Botswana in June 2021. The diamond had a mass of 1098 carats and contained exactly 18.3 moles of carbon. Assuming this stone contained only carbon, calculate the mass of one carat expressed in grams.

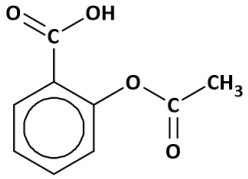
(*g*) What reagents are used to confirm the presence of nitrate ions in an aqueous solution?

(*h*) Identify a substance commonly added during drinking water treatment
(*i*) to cause flocculation in the water,
(*ii*) to fluoridate the water.

(*i*) What elements are the products of the electrolysis of an aqueous solution of potassium iodide (**KI**) using inert electrodes?

(*j*) Which one of the following four compounds would you expect to have the strongest carbon to carbon bonding: ethane, ethene, ethyne, benzene?

(*k*) The structure of aspirin is shown. Calculate the average daily dose (in mg) when a person took a total of 0.146 moles of 'low dose' aspirin over 365 days.



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

A Write balanced equations to show the dissociation of carbonic acid in water to form first hydrogencarbonate ions and then carbonate ions.

or

B Iodine ($\mathbf{I_2}$) is an example of a molecular crystal.
What distinguishes molecular crystals from other types of crystals?

5. Knowledge of atomic structure is fundamental to understanding the properties of the elements, chemical reactivity, and nuclear reactions.

(*a*) Around 1909 Rutherford and his researchers bombarded thin gold foil with positively charged alpha particles from a radioactive radon–222 source and observed their resultant pathways. Most alpha particles passed through the foil with no deflection or very slight deflections, a small number were deflected through large angles, and a very tiny number rebounded back along their original paths.

(*i*) Based on the model of the atom that Thomson had proposed after his discovery of the electron in 1898, which one of these three observations was the most unexpected?

(*ii*) What conclusion did Rutherford reach about the structure of the atom from all of the observations in the gold foil experiments taken together? (8)

(*b*) Define (*i*) isotopes, (*ii*) relative atomic mass. (12)

(*c*) Write the *s*, *p* electron configuration for an atom of calcium in its ground state.

In an atom of calcium in its ground state how many

(*i*) main energy levels (shells),

(*ii*) orbitals, are occupied by electrons?

Use the electron configuration of calcium to predict how a calcium atom is likely to behave in a chemical reaction. Explain your reasoning. (18)

(*d*) (*i*) Define radioactivity.

(*ii*) Copy and complete the following nuclear equation for the alpha decay of the radon–222 isotope.

$$^{222}_{86}\mathbf{Rn} \rightarrow \quad + \; ^{4}_{2}\mathbf{He}$$

(*iii*) Suggest a reason why it is *not* possible to change lead (**Pb**) atoms into gold (**Au**) atoms by a chemical reaction or a series of chemical reactions. (12)

6. While electric and hybrid electric cars grow in popularity, two-thirds of all new private cars licenced in Ireland between January and June 2021 were powered only by petrol or diesel. Petrol and diesel are mixtures of mostly hydrocarbons obtained from crude oil.

(*a*) Compare petrol (a mixture of light gasoline and naphtha) and diesel (gas oil) in terms of

(*i*) average molecular mass of the hydrocarbons present,

(*ii*) boiling point. (5)

(*b*) (*i*) Explain the term octane number of a fuel.

Give the systematic IUPAC name and draw the structure of a molecule of the alkane fuel

(*ii*) assigned an octane number of zero,

(*iii*) assigned an octane number of 100.

(*iv*) What structural feature of the molecules of the alkane fuel assigned octane number 100 accounts for its high octane number? (18)

Since July 2021, Dublin Bus has been testing hydrogen fuel-cell electric double-decker buses as part of Ireland's climate action strategy to reduce greenhouse gas emissions.
The overall fuel-cell reaction is that hydrogen combines with oxygen to form water and energy is released in the form of an electric current.
The balanced equation for the overall fuel-cell reaction is:

$$\mathbf{H_2}\,(g) + \mathbf{\tfrac{1}{2}O_2}\,(g) \rightarrow \mathbf{H_2O}\,(l)$$

Currently, steam reforming of natural gas is the source of most of the world's hydrogen.
The following is the balanced equation for the steam reforming of methane, an endothermic reaction:

$$\mathbf{CH_4}\,(g) + \mathbf{H_2O}\,(g) \rightarrow \mathbf{CO}\,(g) + \mathbf{3H_2}\,(g) \quad \boldsymbol{\Delta H = 206.2\ kJ}$$

(*c*) (*i*) Suggest a reason why elemental hydrogen (**H_2**) does *not* occur in nature on Earth as a fuel source.

(*ii*) Give a major source of hydrogen gas, other than steam reforming.

(*iii*) Define heat of reaction.

(*iv*) Explain why the same amount of energy is released when one mole of hydrogen is used up in a fuel-cell as when one mole of hydrogen is burned in excess oxygen.

(*v*) Use the heat of reaction for the steam reforming of methane above and the heats of formation of steam and carbon monoxide, –241.8 and –110.5 kJ mol^{-1}, respectively, to calculate the heat of formation of methane. (27)

7. Methanol is manufactured from carbon monoxide and hydrogen in the following equilibrium reaction.

$$\mathbf{CO}_{(g)} + \mathbf{2H_2}_{(g)} \rightleftharpoons \mathbf{CH_3OH}_{(g)} \qquad \Delta H = -94.4 \text{ kJ mol}^{-1}$$

A researcher mixed 5.0 moles of carbon monoxide and 10.0 moles of hydrogen in a 5.0 litre container and equilibrium was reached at a temperature of 250 °C in the presence of a catalyst.

(*a*) Explain chemical equilibrium in terms of

(*i*) rates of reaction,

(*ii*) the concentrations of the substances involved. (8)

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

(*ii*) Calculate the value of K_c under the conditions described above based on the researcher's report of a 25% conversion of carbon monoxide to methanol at equilibrium. (18)

(*c*) Starting with 5.0 moles of carbon monoxide and 10.0 moles of hydrogen in a 5.0 litre container at a temperature of 250 °C in the presence of either of two different catalysts the same equilibrium was reached.

What is an advantage of using a catalyst in an equilibrium reaction? (6)

(*d*) Equilibrium was re-established in the 5.0 litre container at 250 °C after the addition of some more carbon monoxide to the initial equilibrium mixture.

(*i*) State Le Châtelier's principle.

(*ii*) How was the yield of methanol affected when more carbon monoxide was added and equilibrium was allowed to re-establish?
Explain your answer.

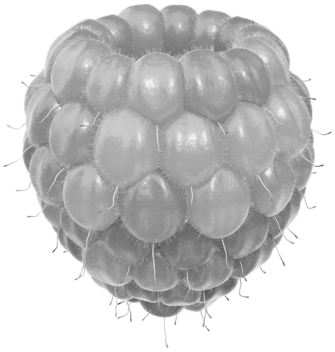
(*iii*) How was the value of K_c affected when more carbon monoxide was added and equilibrium was allowed to re-establish?
Explain your answer. (18)

8. (*a*) (*i*) Explain, with the aid of a diagram, the acidic nature of the carboxylic acid functional group.

(*ii*) Give an example of a reaction that demonstrates the acidic nature of ethanol.

(*iii*) Would you expect to observe a reaction when a drop of pure ethanol is added to damp solid sodium carbonate on a clock glass? Explain. (18)

(*b*) The pure ester **E** has a rum-like aroma and is partially responsible for the flavour of raspberries.



(*i*) Write a balanced chemical equation for the formation of **E** from methanoic acid and ethanol.

(*ii*) Give the systematic IUPAC name for **E**.

(*iii*) How many carbon atoms in a molecule of the ester **E** are in planar geometry?

(*iv*) Classify this esterification reaction as a redox reaction, an acid-base reaction or a substitution reaction.

(*v*) Another ester **F** has a glue-like smell and is a structural isomer of **E**. Identify **F**.

(*vi*) Identify the products of the base hydrolysis reaction between the ester methyl methanoate and an **NaOH** solution.

(*vii*) Explain why the boiling point of ethanoic acid (118 °C) is significantly higher than that of methyl methanoate (32 °C) although the two compounds have the same molecular formula $\mathbf{C_2H_4O_2}$. (32)

9. (*a*) Define pH.
Write an expression for K_w, the ionic product (the dissociation constant) of water. (8)

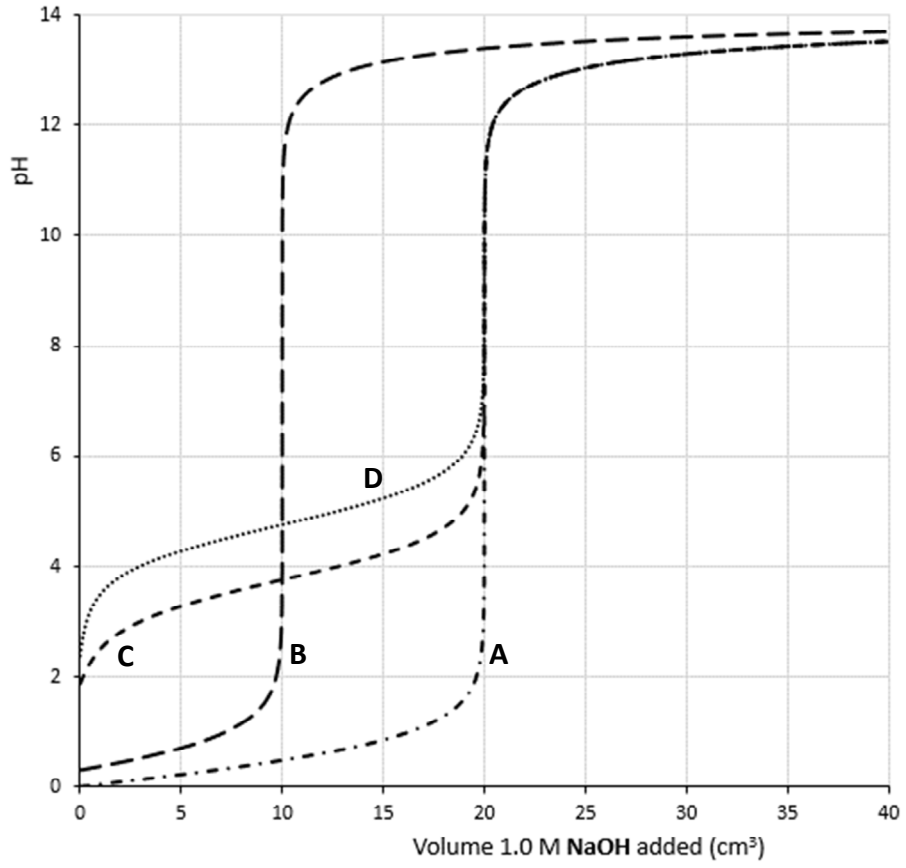
(*b*) The pH scale is most effective from 0 to 14.
State another limitation of the pH scale. (6)

(*c*) The pH of a certain mouthwash solution containing a weak acid is 5.65.
Calculate

(*i*) the molar concentration of a monobasic strong acid (**HX**) with the same pH,

(*ii*) the molar concentration of OH^- in the mouthwash. (12)

(*d*) In the graph below four curves are shown for the changes in pH values of four different 20 cm^3 solutions **A**, **B**, **C** and **D**, each containing one monobasic acidic substance, as 40 cm^3 of 1.0 M **NaOH** solution were slowly added.



(*i*) What volume of the **NaOH** solution neutralised solution **A**?

(*ii*) Deduce the molar concentrations of solutions **A**, **B**, **C** and **D**.

(*iii*) Which of the weak acids **C** and **D** has the greater acid dissociation constant (K_a) value? Justify your answer.

(*iv*) **D** is **CH_3COOH**. What is the conjugate base of **D**? (24)

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

(*a*) (*i*) What is meant by the term *ideal gas*?

(*ii*) State the conditions under which real gases come closest to being ideal.

(*iii*) Which one of the noble gases would you expect to behave most like an ideal gas? Justify your answer.

(*iv*) The volume occupied by 4.85 g of a gaseous compound was 60.0 litres at a pressure of 99 kPa and a temperature of 22 °C.

Calculate, correct to the nearest whole number, the relative molecular mass of the gas. (25)

(*b*) Define electronegativity.

Account for the decreasing trend in electronegativity values down Group 17 of the periodic table.

Predict the shape of a molecule of

(*i*) silicon tetrachloride (**$SiCl_4$**), a colourless liquid,

(*ii*) sulfur dichloride (**SCl_2**), a cherry-red liquid,

(*iii*) phosphorus trichloride (**PCl_3**), another colourless liquid.

Which one of these three compounds

(*iv*) is non-polar,

(*v*) has bonds that have the least degree of polarity? (25)

(*c*) A molecule of pharmaceutical **X** contains atoms of carbon, hydrogen, nitrogen, oxygen and sulfur, only. When **X** is burned in excess oxygen the only products are water, carbon dioxide, **SO_2** and **NO_2**.
When a sample of **X** was completely burned, the 0.018 moles of water formed was absorbed by anhydrous calcium chloride.
Then the carbon dioxide produced in the combustion of **X** was absorbed by potassium hydroxide. It was found that 3.584 g of potassium hydroxide reacted with this carbon dioxide according to the following balanced equation.

$$\mathbf{CO_2 + 2KOH \rightarrow K_2CO_3 + H_2O}$$

It was also found that 44.8 cm^3 of **SO_2**, measured at s.t.p., and 2.4×10^{21} molecules of **NO_2** were obtained in the combustion of **X**.

In the sample of **X** that was burned, calculate the number of moles of

(*i*) hydrogen (**H**),

(*ii*) carbon (**C**),

(*iii*) sulfur (**S**),

(*iv*) nitrogen (**N**).

If there were also 0.008 moles of oxygen (**O**) in the sample that was burned, what is the empirical formula of **X**, listing the elements in alphabetical order? (25)

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

(*a*) Define reduction in terms of

(*i*) electron transfer,

(*ii*) change in oxidation number.

(*iii*) The oxidation number of hydrogen in most of its compounds is +1.
Explain why the oxidation number of hydrogen in the metal hydrides is –1.

(*iv*) The oxidation number of oxygen in most of its compounds is –2.
What is the oxidation number of oxygen in $\mathbf{OF_2}$?

(*v*) The following unbalanced equation describes a reaction that occurs in aqueous solution.

$$\mathbf{Mn^{2+} + BiO_3^- + H^+ \rightarrow MnO_4^- + Bi^{3+} + H_2O}$$

Assign oxidation numbers and, hence or otherwise, balance this equation.

(*vi*) Identify the reducing agent in the reaction above. (25)

(*b*) A few drops of oxidising reagent were added to a 0.5 cm^3 sample of ethanal ($\mathbf{CH_3CHO}$) in a test-tube.

What was observed when the oxidising reagent used was

(*i*) warm dilute acidified $\mathbf{KMnO_4}$,

(*ii*) Fehling's reagent, pre-heated to about 40 °C?

(*iii*) Identify the organic product of the oxidation of ethanal using these reagents.

(*iv*) Fehling's reagent is quite difficult to reduce.
Is ethanal very easy or very difficult to oxidise?

(*v*) Write a balanced half-equation to show the reduction of the $\mathbf{Cu^{2+}}$ ions of the Fehling's reagent in the test.

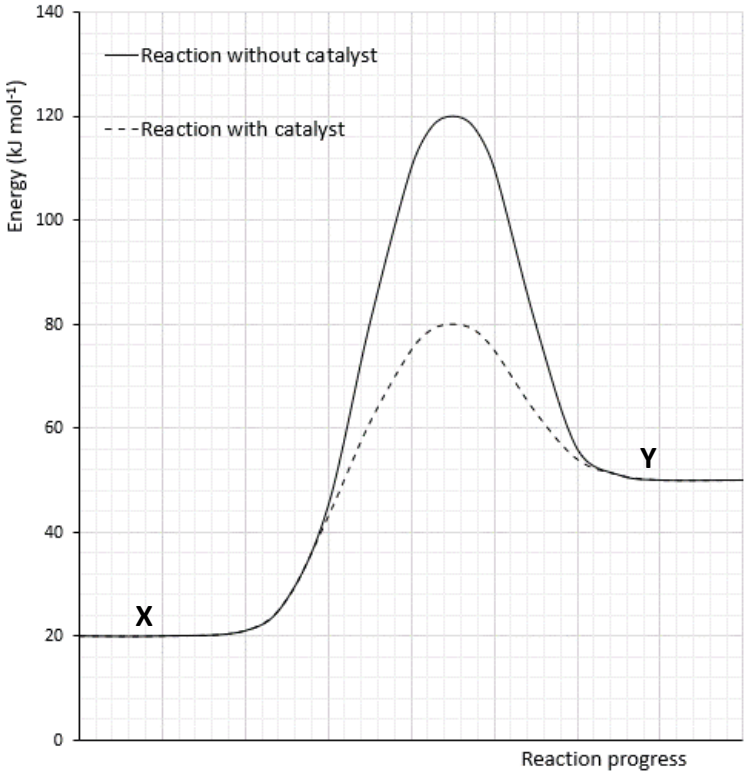
Ethanal is completely miscible with both of the aqueous oxidising reagents mentioned above.

(*vi*) Describe the polarity across the carbonyl group in ethanal.

(*vii*) Refer to the polarity across the carbonyl group to explain why ethanal is *very* soluble in water. (25)

(*c*) (*i*) Explain the term activation energy (E_a).

The reaction profile diagram for the reaction **X** $\rightarrow$ **Y**, with and without catalyst **C**, is shown below.



(*ii*) What is the value of E_a for the reaction **X** $\rightarrow$ **Y** without the catalyst?

(*iii*) By how much does catalyst **C** lower the value of E_a for the reaction?

(*iv*) What is the value of ΔH for the reverse reaction **Y** $\rightarrow$ **X**?

The reaction between pure hydrogen and oxygen gases, mixed in the ratio 2:1 by volume and forming water, is very slow at room temperature but is violently rapid when a little powdered platinum catalyst is added. This is an example of heterogeneous catalysis.

(*v*) Explain the underlined term.

(*vi*) Describe the mechanism by which the catalyst increases the rate of this reaction. (25)

This question continues on the next page

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

A

Ozone is formed and broken down by photodissociation in the stratosphere. Chlorofluorocarbons (CFCs) in the atmosphere were identified as a major contributor to damage to the ozone layer and their phasing out was agreed internationally in the Montreal Protocol (1987).

(*i*) Explain the underlined term.

(*ii*) Write a balanced equation for the photodissociation of ozone in the stratosphere.

(*iii*) State one major use for CFCs before the Montreal Protocol.

(*iv*) Show by means of balanced equations the photodissociation of a molecule of **CCl_3F** giving a chlorine free radical and how chlorine free radicals break down ozone in a chain reaction.

(*v*) Explain using a balanced equation how the presence of methane in the atmosphere can help absorb chlorine free radicals. (25)

or

B

Electrochemical reactions are involved in the corrosion of metals, corrosion prevention and in the extraction of metals from their salts.

Galvanising is a method of protecting everyday iron and steel objects from rusting by coating them with a thin layer of zinc.

(*i*) Explain how galvanising protects an iron object from corrosion even when the zinc coat is scratched.

Sacrificial anodes are used to help protect underground and underwater iron and steel objects from corrosion.

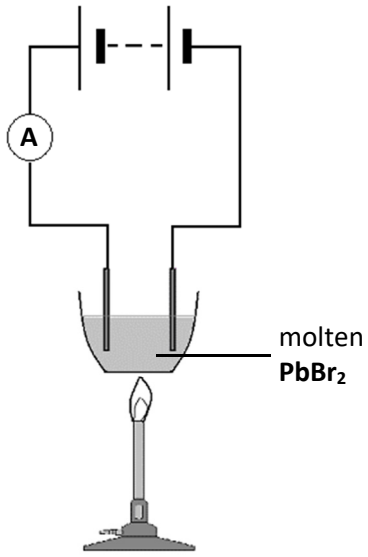
(*ii*) Identify a metal often used to make sacrificial anodes.

(*iii*) How does a sacrificial anode help protect the steel hull of a ship from rusting?

Anodised aluminium is more resistant to corrosion than ordinary aluminium.

(*iv*) What is anodised aluminium?

The diagram shows an arrangement for carrying out the electrolysis of molten lead(II) bromide using inert electrodes in a fume-cupboard.



(*v*) Write balanced half-equations for the reactions that occur at the two electrodes.

(*vi*) How is charge transmitted through the molten **$PbBr_2$** electrolyte? (25)

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Image Q3 on page 4: from sibelco.com
File: wp-content/uploads/manganese-dioxide.jpg, accessed 14 July 2021

Image Q4(*f*) on page 5: static.euronews.com
File: articles/stories/05/77/35/82/1024x576_cmsv2_a179b301-99a7-5b91-8601-f9ed9ab27d6b-5773582.jpg?1623932893, accessed 05 September 2021

Image Q6 on page 7: from www.fleetbusandcoach.ie
File: wp-content/uploads/d1596936-aae2-4bb5-9a98-6487b664812f-768x1024.jpg, accessed 05 September 2021

Image Q8(*b*) on page 9: from MasterTux at Pixabay
File: https://pixabay.com/photos/raspberry-fruit-berry-close-up-2636394, accessed 26 August 2021

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Leaving Certificate – Higher Level

Chemistry

Tuesday, 21 June
Afternoon, 2:00 – 5:00