Coimisiún na Scrúduithe Stáit
State Examinations Commission

LEAVING CERTIFICATE EXAMINATION, 2018

CHEMISTRY – HIGHER LEVEL

TUESDAY, 19 JUNE – AFTERNOON 2:00 to 5:00

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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 (rounded): H = 1.0, C = 12, O = 16, P = 31, Ca = 40, Fe = 56

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

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

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

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

Section A

Answer at least <u>two</u> questions from this section. See page 1 for full instructions.

1. The total hardness in a water supply was estimated by titrating 50.0 cm^3 samples of the water with a standard solution of **edta** (ethylenediaminetetraacetic acid). The ions that cause hardness (represented by $\mathbf{M^{2+}}$) and the **edta** ions (represented by $\mathbf{H_2Y^{2-}}$) react according to the following balanced equation.

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

The average volume of 0.010 M **edta** solution required to react with 50.0 cm^3 of the water was 9.3 cm^3.

(*a*) Identify a compound of calcium that is one of the main causes of *permanent* hardness in water. (3)

(*b*) Describe the procedure used to measure out 50.0 cm^3 of the hard water from a beaker into a conical flask. (12)

(*c*) (*i*) Name the indicator added to the conical flask.
What colour was observed using this indicator
(*ii*) in the presence of $\mathbf{M^{2+}}$,
(*iii*) at the end point? (9)

(*d*) A small volume of another solution was added to the water samples before commencing the titrations.
(*i*) Identify this solution.
(*ii*) Why was this solution added? (6)

(*e*) Calculate
(*i*) the average number of moles of **edta** used in the titrations,
(*ii*) the number of moles of $\mathbf{M^{2+}}$ ion in 50.0 cm^3 of hard water,
(*iii*) the total hardness of the water expressed in grams per litre of $\mathbf{CaCO_3}$,
(*iv*) the total hardness of the water expressed as p.p.m. (mg l^{-1}) of $\mathbf{CaCO_3}$. (15)

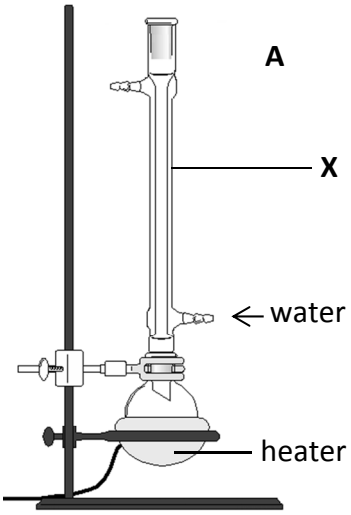
(*f*) Suggest a way to determine if this water supply contained temporary hardness. (5)

2. (*a*) Diagram **A** shows an arrangement used to reflux the reaction mixture in an experiment to prepare a sample of soap.

(*i*) Name the piece of glassware labelled **X**.

(*ii*) What is the purpose of refluxing a reaction mixture?

(*iii*) Identify the two reactants and the solvent initially present in the flask. (18)



(*b*) Diagram **B** shows a separating funnel in use in a liquid-liquid extraction of clove oil from the emulsion produced in a steam distillation of cloves.

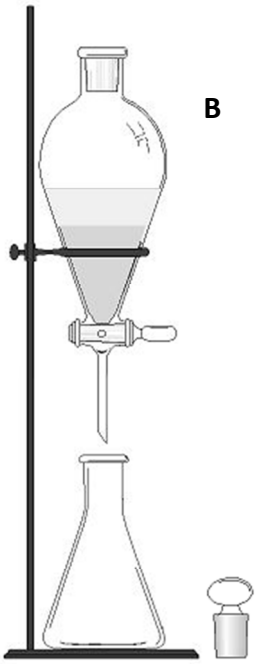
(*i*) What is an emulsion?

(*ii*) Name a suitable organic solvent for use in the liquid-liquid extraction of clove oil.

(*iii*) Other than wearing eye-protection, gloves and a laboratory coat, and tying back long hair, state one safety precaution that should be taken when using a separating funnel.

(*iv*) How is the clove oil isolated following the liquid-liquid extraction?

(*v*) Steam distillation and liquid-liquid extraction were used to isolate 0.15 cm^3 of clove oil (density 1.05 g cm^{-3}) from 5.0 g of cloves. What was the percentage yield, by mass, of clove oil? (18)

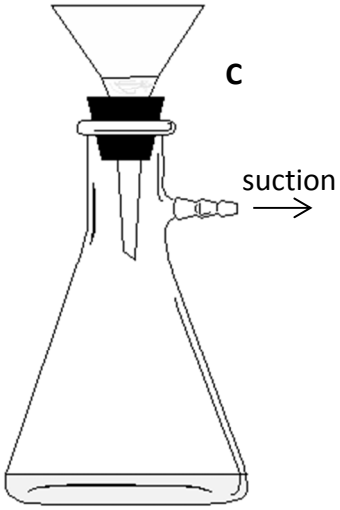


(*c*) A sample of benzoic acid, containing a small quantity of sodium chloride as the only impurity, was purified by recrystallisation. The impure crystals were dissolved in the minimum amount of boiling water. This solution was cooled thoroughly and the crystals that formed were separated by suction filtration as shown in diagram **C**. The crystals were then dried.

(*i*) Why was there no need, in this recrystallisation, to carry out a filtration of the hot solution?

(*ii*) State one advantage of suction filtration over gravity filtration.

(*iii*) Explain how you could verify that the recrystallised benzoic acid was purer than the original sample. (14)



3. The cardboard cup with plastic lid in the diagram contained 150 cm^3 of 1.0 M hydrochloric acid solution at room temperature. A volume of 160 cm^3 of 1.0 M sodium hydroxide solution – also at room temperature – was added quickly and the mixture was stirred. The temperature of the mixture rose rapidly by 6.4 K and then began to fall gradually.

The equation for the neutralisation reaction that took place is:

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

(*a*) Is this reaction exothermic or endothermic?
Justify your answer. (5)

(*b*) (*i*) Why should the mixture be stirred before taking temperature readings?

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

(*iii*) The thermometer used was accurate to 0.1 K.
What temperature rise would have been recorded if the thermometer used was accurate to 1 K? (9)

(*c*) (*i*) Why is it advantageous to use moderately concentrated solutions instead of dilute solutions in this experiment?

(*ii*) Draw *or* describe the hazard warning pictogram that should be displayed on a container used to store 1.0 M **NaOH**. (12)

(*d*) Calculate

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

(*ii*) the heat produced by the reaction mixture that had a total mass of 310 g, taking the specific heat capacity of the mixture as that of water, 4.2 kJ kg^{-1} K^{-1},

(*iii*) to one decimal place, the heat of reaction (ΔH) for the neutralisation of hydrochloric acid by sodium hydroxide according to the equation above. (18)

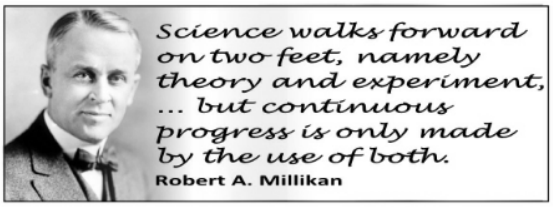
(*e*) The result obtained in this experiment was about 3% below the expected value. State and explain a modification to the method described that would give a more accurate result. (6)

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*) What was the purpose of Millikan's 'oil drop' experiments of 1908 to 1913?



(*b*) State and give the reason for the trend in atomic radii across the second period of the periodic table.

(*c*) Write the electron configuration (*s*, *p*, etc) for an iron atom.

(*d*) Give two reasons why real gases deviate from ideal behaviour at high pressures and low temperatures.

(*e*) Identify in the following reaction the Brønsted-Lowry acid and its conjugate base.

$$PO_4^{3-} + HNO_3 \rightarrow NO_3^- + HPO_4^{2-}$$

(*f*) During the Olympics in Rio de Janeiro in 2016 the water in some swimming and diving pools turned green. Sodium hypochlorite in the pools had reacted with hydrogen peroxide, added in error, and this allowed the rapid growth of green algae. The reaction that occurred was:

$$NaOCl + H_2O_2 \rightarrow NaCl + H_2O + O_2$$

Use oxidation numbers to show whether chlorine was oxidised or reduced.

(*g*) Write a balanced equation, or give the half equations, for the displacement reaction that occurs between chlorine gas and an aqueous solution of sodium bromide.

(*h*) State and explain the effect of adding a little tetraethyllead to an equimolar mixture of methane and chlorine exposed to weak sunlight.

(*i*) Epoxyethane is used to manufacture car antifreeze. It is composed of 54.5% carbon, 9.1% hydrogen and 36.4% oxygen by mass.
Find the empirical formula of epoxyethane.

(*j*) Explain the term *biochemical oxygen demand*.

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

A Which of the following gases makes the greatest contribution to the greenhouse effect?

carbon dioxide **water vapour** **methane**

Give the reason for your choice.

or

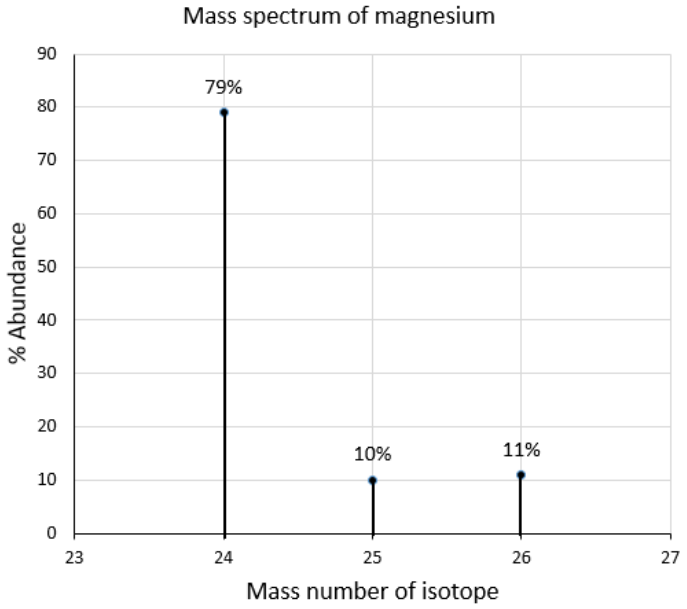
B Give an example of (*i*) a molecular crystal, (*ii*) a covalent macromolecular crystal.

5. (*a*) Define (*i*) mass number of an atom, (*ii*) relative atomic mass of an element. (8)

(*b*) A sample of magnesium metal was introduced into a mass spectrometer and vaporised.

What were the next three fundamental processes that occurred in the mass spectrometer? (9)

(*c*) The mass spectrum of the sample, given below, shows that magnesium has three naturally occurring isotopes.



Use the data given to calculate the relative atomic mass of magnesium correct to two decimal places. (6)

(*d*) The radioisotope carbon–14 emits beta particles and has a half-life of 5730 years.

(*i*) Define radioactivity.

(*ii*) What change takes place in the structure of the nucleus of an atom when beta decay occurs?

(*iii*) Write a balanced equation for the beta decay of a carbon–14 nucleus.

(*iv*) A piece of fossilised yew, from a tree that was alive about 6000 years ago, was excavated from Boora Bog, Co. Offaly. When a tiny fragment of it was analysed, it was found to contain 1.5×10^{12} carbon–14 atoms.

Explain why the fragment of yew must have contained 3.0×10^{12} carbon–14 atoms 5730 years before the analysis.

What mass of carbon–14 did the fragment contain 5730 years before the analysis? (27)

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6. Refinery gas, naphtha, kerosene and gas oil are products of the fractionation of crude oil.

(*a*) Explain the underlined term. (5)

(*b*) (*i*) Name the two major components of liquid petroleum gas (LPG), a fuel obtained from refinery gas.

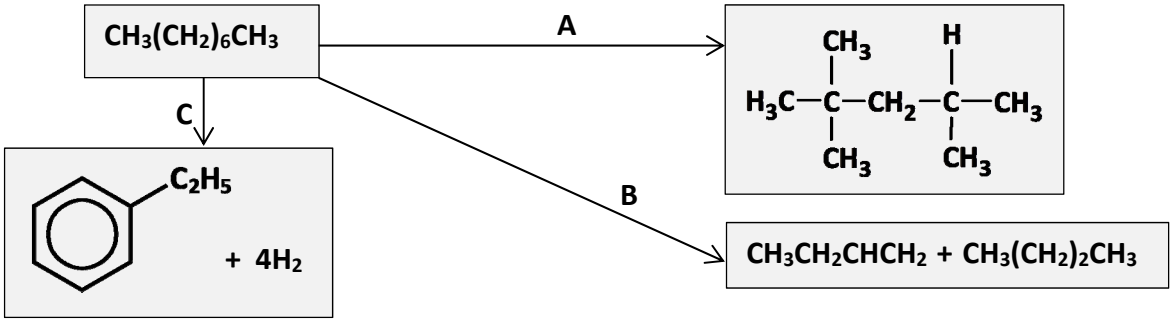
(*ii*) Why is methanethiol (**CH_3SH**), a mercaptan, added to natural gas and to LPG?

(*iii*) Calculate the heat of combustion of methanethiol according to the equation:

$$CH_3SH\ (g) + 3O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (l) + SO_2\ (g)$$

The heats of formation of methanethiol, carbon dioxide, water, and sulfur dioxide are –22.8, –393.5, –285.8 and –296.8 kJ mol^{-1} respectively. (21)

(*c*) Octane is one of the compounds found in naphtha. In an oil refinery it is converted to various other substances by processes **A**, **B** and **C**.



(*i*) Give the IUPAC names for the four hydrocarbon *products* shown above.

(*ii*) Identify the processes **B** and **C**.

(*iii*) Why are processes **A**, **B** and **C** carried out? (21)

(*d*) Typically, petrol contains hydrocarbons with 5 to 10 carbon atoms per molecule and diesel contains hydrocarbons with 14 to 19 carbon atoms per molecule.
How would you expect the boiling points of petrol and diesel to compare? (3)

7. (*a*) (*i*) Define rate of a reaction.

(*ii*) What is meant by the activation energy of a reaction? (11)

The decomposition of nitrogen dioxide, described by the equation below, was carried out in a closed vessel at 300 °C. The table shows the molar concentrations of nitrogen dioxide and oxygen at a set of common times during the reaction.

$$2NO_2\ (g) \rightarrow 2NO\ (g) + O_2\ (g) \qquad \Delta H = 114.4\ \text{kJ}$$

Time (s)	0	50	100	150	200	250	300
Concentration **NO_2** (M)	0.0100	0.0079	0.0065	0.0055	0.0048	0.0043	0.0038
Concentration **O_2** (M)	0	0.0011	0.0018	0.0023	0.0026	0.0029	0.0031

(*b*) On the same sheet of graph paper, and using the same axes, draw graphs to show how the concentrations of **NO_2** and **O_2** vary with time. (18)

(*c*) Find the instantaneous rate of the decomposition (in M s^{-1}) of **NO_2** at 100 seconds. (9)

(*d*) (*i*) Suggest a reason why **NO** is *not* formed in every collision between a pair of **NO_2** molecules.

(*ii*) State one way of increasing the frequency of collisions.

(*iii*) Sketch a clearly labelled reaction profile diagram for this reaction. (12)

8. Consider compounds **A**, **B**, **C** and **D**, all of which have molecules of similar size and mass.

A	**B**	**C**	**D**
butane	**propan-1-ol**	**propanal**	**ethanoic acid**
M_r = 58	M_r = 60	M_r = 58	M_r = 60
b.p. = –1 to 1 °C	b.p. = 97 to 98 °C	b.p. = 46 to 50 °C	b.p. = 118 to 119 °C

(*a*) (*i*) Draw structures to show all the bonds in molecules of **B** and **C**.

(*ii*) Which one of the four compounds contains only one tetrahedrally bonded carbon atom in its molecules? (9)

(*b*) Propan-2-ol and **B** are structural isomers. **B** is a primary alcohol.

(*i*) Explain the underlined terms.

(*ii*) **C** and another compound **E** are structural isomers. Draw a structure for **E**.

(*iii*) Give the IUPAC name for **E**. (18)

(*c*) Explain clearly why

(*i*) the boiling point (b.p.) of propanal is much higher than that of butane,

(*ii*) the boiling point (b.p.) of ethanoic acid is higher than that of propan-1-ol. (12)

(*d*) What is the organic product of the reaction of **C** with acidified dilute **$KMnO_4$**? (6)

(*e*) Write a balanced equation for the reaction that occurs between sodium and **B**. (5)

9. Phosgene (**$COCl_2$**) is a toxic gas that was used as a chemical weapon in World War 1. It is now used in chemical synthesis. It is formed from carbon monoxide and chlorine using a charcoal catalyst in a reversible reaction given by:

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$$\underset{\text{colourless}}{CO\,(g)} + \underset{\text{green}}{Cl_2\,(g)} \leftrightharpoons \underset{\text{colourless}}{COCl_2\,(g)} \qquad \Delta H = -109.6 \text{ kJ mol}^{-1}$$

(*a*) What is meant by a *chemical equilibrium*? (5)

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

(*c*) Under certain conditions in a closed container this equilibrium mixture is green. State and explain the effect, if any,

(*i*) on the colour of the equilibrium mixture if the pressure is increased by reducing the container size,

(*ii*) on the equilibrium yield of phosgene of using a higher temperature,

(*iii*) on the value of the equilibrium constant (K_c) of using the charcoal catalyst. (18)

(*d*) A 12.0 litre container was filled with 0.200 moles of chlorine and 0.200 moles of carbon monoxide and heated to a certain temperature, *T*.
Calculate the value of the equilibrium constant for the reaction at this temperature if 85.0% of the chlorine gas had reacted when equilibrium was reached. (15)

(*e*) Le Châtelier's principle predicts best yields in a certain equilibrium process at low temperatures and high pressures.
Suggest reasons why these conditions might *not* be used industrially. (6)

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

(*a*) Describe how you could demonstrate that ethene readily undergoes an addition reaction with bromine water.

Would you expect benzene to readily undergo an addition reaction with bromine water? Explain your reasoning. (12)

Some of the electrons in a benzene molecule are <u>delocalised</u>.
Explain the underlined term.

How many electrons in a benzene molecule are

(*i*) delocalised,

(*ii*) involved in sigma bonds between carbon atoms?

What health hazard is associated with benzene? (13)

(*b*) Bohr said that the electron in a hydrogen atom could only occupy certain orbits $n = 1, 2, 3$, etc, with corresponding energy levels E_1, E_2, E_3, etc.

(*i*) What term is used to refer to the condition of the hydrogen atom when its electron occupies the E_1 level?

(*ii*) What term is used for the condition of the hydrogen atom when its electron occupies any of the levels E_2, E_3, etc?

(*iii*) What causes the electron to leave the E_1 level?

(*iv*) Why does the electron not remain in any of the levels E_2, E_3, etc?

(*v*) The visible lines in the atomic emission spectrum of a sample of hydrogen are produced when electrons fall to a particular energy level.

Identify this energy level.

Bohr's theory considered electrons as tiny particles restricted to orbits.

How does modern atomic theory describe the behaviour of electrons?

What are orbitals? (25)

(*c*) When a rusty object was coated with phosphoric acid, all of the rust (taken as $\mathbf{Fe_2O_3}$) on its surface was converted to iron phosphate according to the following balanced equation. The iron phosphate formed was found to have a mass of 4.53 g.

$$\mathbf{Fe_2O_3}\ (s) + \mathbf{2H_3PO_4}\ (aq) \rightarrow \mathbf{2FePO_4}\ (s) + \mathbf{3H_2O}\ (l)$$

(*i*) How many moles of iron were removed from the object in the rust treatment process?

(*ii*) What mass of rust was adhering to the object before the treatment?

(*iii*) What was the minimum volume in cm^3 of a 6.0 M solution of phosphoric acid needed to remove all of the rust?

(*iv*) What volume of liquid water (density 1.0 g cm^{-3}) was produced in the reaction? (25)

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

(*a*) Both carbon disulfide (**CS_2**) and tetrachloromethane (**CCl_4**) are colourless liquids at room temperature.

(*i*) Define electronegativity. (6)

(*ii*) Predict the type of bond formed between carbon and chlorine atoms in a **CCl_4** molecule. (3)

(*iii*) What is the valency of carbon in tetrachloromethane? (3)

(*iv*) State and account for the shape of a tetrachloromethane molecule. (6)

(*v*) Draw a dot and cross diagram to show the arrangement of all the valence shell electrons in a **CS_2** molecule. (7)

(*b*) What is the Arrhenius definition of a base?

Why is **NH_3** considered to be a base according to Brønsted-Lowry theory? (6)

Calculate the pH value of

(*i*) a 0.50 M solution of hydrochloric acid,

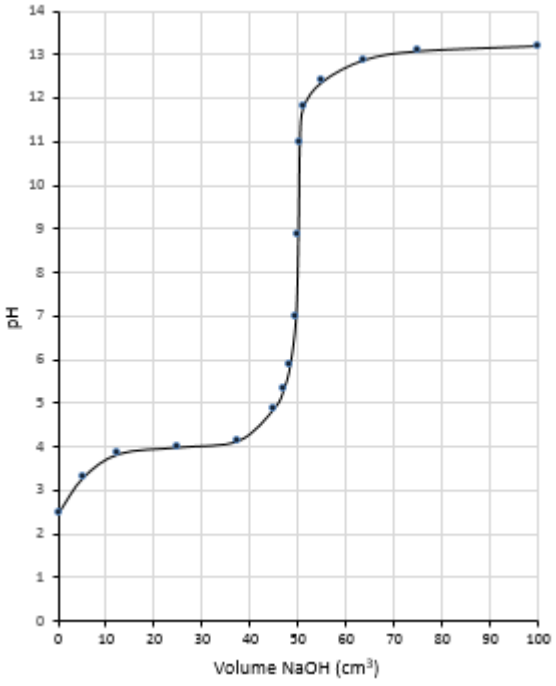
(*ii*) a 0.50 M solution of ethanoic acid. The acid dissociation constant (K_a) for ethanoic acid is 1.8×10^{-5}. (9)

The pH curve shown was obtained when 100 cm^3 of 0.50 M sodium hydroxide solution were gradually added to 50 cm^3 of one of the two acid solutions mentioned above.

Which of the two acid solutions was neutralised?

State two pieces of evidence from the pH curve in support of your answer.

What is the essential property of an indicator used to detect the end point in a titration between this acid and **NaOH**? (10)



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

A Answer (*i*), (*ii*) *or* (*iii*) based on an industrial chemistry case study.

(*i*) Premier Periclase in Drogheda, Ireland, and Ube Materials, Yamaguchi, Japan, are examples of industrial facilities that produce magnesium oxide from the magnesium chloride in seawater. In the first stages of the process a slurry of $\mathbf{Ca(OH)_2}$ is obtained from limestone.

Write balanced equations to describe the last two stages of the process. (12)

What is the major industrial use of the magnesium oxide produced?

Identify the substance whose concentration is higher in the seawater effluent than it is in the seawater feedstock.

State one measure taken by these companies to avoid ecological damage to their surroundings. (13)

or

(*ii*) The first stage in the conversion of ammonia to nitric acid is given by:

$$\mathbf{4NH_3}\,(g) + \mathbf{5O_2}\,(g) \rightarrow \mathbf{4NO}\,(g) + \mathbf{6H_2O}\,(g) \qquad \boldsymbol{\Delta H = -905.2\ kJ}$$

Identify the catalyst used in this reaction.

What is the economic significance of the ΔH value for this reaction? (9)

Write balanced equations for the next two stages of the process. (12)

Nitric acid production has the potential to impact very negatively on the local environment. Explain. (4)

or

(*iii*) Nitrogen and hydrogen gases are converted to ammonia in the Haber process, described by the following balanced equation.

$$\mathbf{N_2}\,(g) + \mathbf{3H_2}\,(g) \leftrightharpoons \mathbf{2NH_3}\,(g) \qquad \boldsymbol{\Delta H = -92\ kJ}$$

State the (approximate) optimal industrial conditions of temperature and pressure for the Haber process.

What catalyst is used? (9)

Write a balanced equation to show how the hydrogen feedstock is obtained.

Explain how the nitrogen feedstock is obtained. (10)

Write a balanced equation to describe the formation of urea from ammonia. (6)

or

B

Pure alumina is obtained from bauxite. The first of three chemical reactions in this process is the reaction between the alumina in the bauxite and sodium hydroxide to produce soluble sodium aluminate ($\mathbf{NaAlO_2}$).

(*i*) Write balanced equations to describe the last two stages of this process. (12)

(*ii*) How is the pure alumina then converted into aluminium metal? (9)

(*iii*) How does the aluminium industry produce aluminium from alumina economically while addressing climate change concerns? (4)

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