Section A

Answer **all** questions in this section in the spaces provided.

1 **(a)** Write a complete equation to represent the first ionization energy of lithium.

[1]

(b) (i) Using the Data Booklet, list the first ionization energies of the alkali metals, lithium, sodium and potassium in the table below.

Element	First ionization energy / kJ mol^{-1}
Lithium	
Sodium	
Potassium	

(ii) Explain the trend observed.

[2]

(c) Sodium hydride, NaH, is a solid of high melting point ($800^{o}C$) whereas hydrogen fluoride, HF, is a gas at room temperature.

(i) State how these two hydrides differ in their bonding and suggest a reason for this difference.

(ii) Draw dot-and-cross diagrams to show the different electron arrangements in the two compounds.

[4]
[Total : 7]

2 Benzene and methylbenzene are added to petrol as anti-knocking additives in unleaded petrol. As they are carcinogenic, the amounts of these aromatic hydrocarbons in petrol are strictly regulated in Singapore.

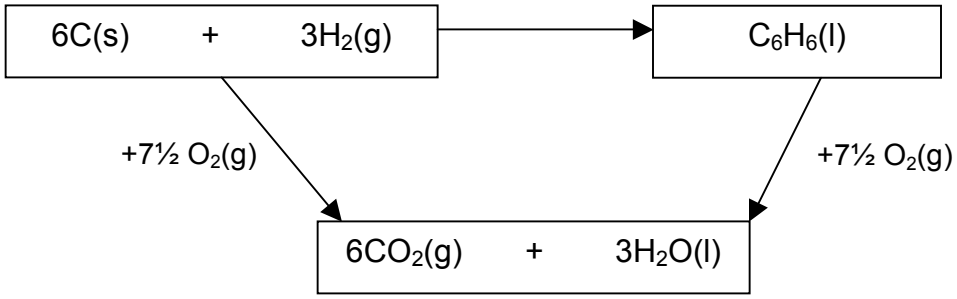
(a) (i) Both benzene and methylbenzene react with bromine in the dark at 60^{o}C. Give the name of this reaction and the condition required for it to occur.

(ii) Describe one simple test-tube reaction you could carry out to distinguish methylbenzene from benzene. State clearly what would be seen with each compound, and write balanced equations where appropriate.

[5]

(b) (i) When burnt in a limited supply of air, benzene forms a mixture of carbon, carbon monoxide and water. Write a balanced equation for the reaction.

(ii) Complete combustion of 1 mole of benzene under standard conditions evolves 3276 kJ of heat. The diagram below shows an energy cycle involving benzene.



Use the energy cycle and the thermochemical data below to calculate the standard enthalpy change of formation of benzene.

enthalpy change of formation of carbon dioxide = -393 kJ mol^{-1}
enthalpy change of combustion of hydrogen = -286 kJ mol^{-1}

2 (b) (ii)

(iii) The standard enthalpy change of formation of methylbenzene is +55.0 kJ mol^{-1}. With reference to your answer in b(ii), deduce the relative stabilities of benzene and methylbenzene.

[6]

(c) Through the use of unleaded petrol and installation of catalytic converters in car engines, the amount of lead and oxides of nitrogen released to the environment has been reduced. Unfortunately excessive use of petrol still pollutes the environment. Name two other gaseous pollutants arising from the use of petrol.

[1]
[Total: 12]

3 **(a)** The ionic product of water at 25°C is 1.0×10^{-14} mol^2 dm^{-6}.

(i) Calculate the pH of 2.0×10^{-2} mol dm^{-3} hydrochloric acid.

(ii) Why is the pH of 1.0×10^{-8} mol dm^{-3} hydrochloric acid not 8?

[3]

(b) For *each* of the following reactions **A** and **B**:

(i) identify the two acids present;

(ii) suggest, with reasons, which ion or molecule is the stronger acid.

A $H_2SO_4 + HNO_3 \rightleftharpoons HSO_4^- + H_2NO_3^+$ $\quad K_c = 1.6 \times 10^2$ mol dm $^{-3}$

two acids present:

stronger acid:

reason:

B $CH_3CONH_2 + NH_3 \rightleftharpoons CH_3CONH^- + NH_4^+$ $\quad K_c = 3.6 \times 10^{-9}$ mol dm^{-3}

two acids present:

stronger acid:

reason:

[3]

3 (c) The chlorides of the elements sodium to aluminium all dissolve in water to give solutions of different pH values.

(i) Write down the formula of each of these chlorides and suggest the pH values of the resulting solutions.

chlorides of	**formula**	**pH values of the solution**
sodium		
aluminium		
silicon		

(ii) Explain the behaviour of these chlorides with water. Give balanced equations where appropriate.

[5]

[Total: 11]

4 The **Fischer-Tropsch process** is a catalyzed chemical reaction in which a mixture of carbon monoxide and hydrogen is converted into liquid hydrocarbons of various forms.

$$n\ CO\ (g) + (2n+1)\ H_2\ (g) \rightarrow C_nH_{(2n+2)}\ (l) + n\ H_2O\ (g) \quad \text{where n is a positive integer}$$

The Fischer-Tropsch process is invented by German researchers Franz Fischer and Hans Tropsch. The most common catalysts are based on iron and cobalt, although nickel and ruthenium have also been used. The principal purpose of this process is to produce a synthetic petroleum substitute, typically from coal, for use as synthetic lubrication oil or as synthetic fuel. This synthetic fuel runs trucks, cars, and some aircraft engines.

The reactant mixture for the Fischer-Tropsch process (i.e. CO and H_2) is called *synthesis gas*. It can be produced by passing steam over coal at a temperature of 800 ^oC. This reaction is called *gasification* of coal.

$$C\ (s) + H_2O\ (g) \rightleftharpoons H_2\ (g) + CO\ (g)$$

At 800 ^oC, the equilibrium constant, K_c, for this reaction is 14.1. The energy requirement for the gasification of coal is usually provided by combustion of coal with oxygen.

$$C\ (s) + O_2\ (g) \rightarrow CO_2\ (g)$$

It was a concept pioneered during the 1920s in petroleum-poor-coal-rich Germany to extract oil from coal and became central to Nazi Germany's war efforts when imports of petroleum were restricted due to war. It was known as *Ersatz* oil, and accounted for nearly half the total oil used in World War II by Germany. Currently, only a handful of companies have commercialised their Fischer-Tropsch technology. Shell in Bintulu, Malaysia and Sasol in South Africa uses this technology to produce petrol and diesel fuel.

On average, these coal-based Fischer-Tropsch process plants can produce as much as 7 tonnes of CO_2 per tonne of liquid hydrocarbon products.

(a) (i) Write a balanced equation showing the production of octane from the Fischer-Tropsch process.

[1]

(ii) Given that the bond energy is CO is 1074 kJ mol^{-1}, use the *Data Booklet* to calculate the enthalpy change of the reaction in **a(i)**.

[1]

(b) **(i)** Suggest an expression for K_c for the gasification of coal and state its units.

[1]

(ii) The value of K_c for the gasification of coal is 1.7×10^{-21} at 25 ^{o}C, predict and explain whether the reaction is endothermic or exothermic.

[2]

(iii) To maximize the yield of synthesis gas, should the pressure of the system be increased or decreased? Explain.

[2]

(c) The synthesis gas derived from coal, typically have a H_2:CO ratio of about 0.7. However the ideal H_2:CO ratio for the Fischer-Tropsch process is about 2.

An important reaction called the water gas shift reaction is used to change the H_2:CO ratio of the synthesis gas as close as possible to 2. The water gas shift reaction involves steam reacting with carbon monoxide gas to produce hydrogen and carbon dioxide gas as shown below:

$$H_2O\ (g) + CO\ (g) \rightarrow H_2\ (g) + CO_2\ (g)$$

Briefly explain how do you think the water gas shift reaction can change the H_2:CO ratio of the synthesis gas.

[1]

(d) Suggest one environmental impact of using the Fischer-Tropsch process to produce liquid hydrocarbons.

[1]

(e) Suggest a reason why despite the high operation and maintenance costs as well as environmental concerns, the Fischer-Tropsch process still remains as an attractive alternative of producing liquid hydrocarbons.

[1]
[Total : 10]

Section B

Answer **two** of the three questions in this section on separate paper.

5 **(a)** The oxides of sodium, silicon and phosphorus differ in their bonding and their reactions with water.
Describe their reactions, relating them to the structure and bonding in each oxide. Write equations where appropriate.

[6]

(b) The melting points of GeO_2 and SeO_2 are 1115°C and 315°C respectively.
[germanium is $_{32}Ge$; selenium is $_{34}Se$]

(i) Suggest the likely structure and bonding of each of these oxides.

(ii) By means of balanced equaitons, indicate whether or not each oxide reacts with
1. NaOH(aq)
2. HCl(aq) [6]

(c) With suitable reagents, sulphur dioxide produces two oxochlorides with the formulae $SOCl_2$ and SO_2Cl_2. When 0.10 g of one of these oxochlorides was completely hydrolysed in water, all its chlorine was converted into chloride ions, and produced 0.240 g of silver chloride precipitate when an excess of aqueous silver nitrate was added.

(i) Deduce the identity of the oxochloride.

(ii) Give the formulae of the other hydrolysis product tor the oxochloride you have identified.

[4]

(d) Both oxochlorides are colourless fuming liquids and can be used for chlorinating organic compounds.
Give the structural formulae of **two** organic compounds from different homologous series that can be chlorinated by $SOCl_2$.

[2]

(e) Industrially, dichloroethane, $C_2H_4Cl_2$, is used to make chloroethene, C_2H_3Cl, which is the building block of the polymer PVC.

$$C_2H_4Cl_2 \xrightarrow{I} C_2H_3Cl \longrightarrow PVC$$

Name the type of reaction that occurs in step I, and suggest a reagent that could be used to carry out the reaction in the laboratory.

[2]

[Total: 20]

6 (a) Hydrogen peroxide decomposes according to the equation below:

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g) \qquad \Delta H^o = -98 \text{ kJ mol}^{-1}$$

The change in concentration of hydrogen peroxide in the presence of a catalyst during an experiment under room conditions was measured and the following results were obtained:

time / min	0	5	10	15	20	25	30
$[H_2O_2]$ / mol dm^{-3}	0.750	0.585	0.458	0.355	0.278	0.218	0.170

(i) Plot a graph of $[H_2O_2]$ against time for the experiment.

(ii) Use your graph to determine the order of reaction with respect to H_2O_2 , showing your working clearly. Hence give the rate equation for the reaction.

(iii) Determine the initial rate of the reaction, and use it, together with your rate equation in (ii) to calculate a value for the rate constant, including units.

(iv) Name a suitable catalyst for the decomposition of hydrogen peroxide.

[7]

(b) The uncatalysed reaction for the decomposition of hydrogen peroxide has an activation energy of +79 kJ mol^{-1} .

(i) Sketch and label a reaction pathway diagram for the uncatalysed reaction, showing all relevant energy changes.

(ii) What effect will the presence of a catalyst have on the rate constant for this reaction? Explain your answer.

[4]

(c) Explain briefly in molecular terms why the initial reaction rate would be expected to increase by increasing each of the following:

(i) concentration of H_2O_2 (ii) temperature.
[Note: a different explanation is required for each of these factors.]

[3]

(d) Hydrogen peroxide can be oxidised to oxygen by potassium manganate(VII).

(i) What volume of acidified potassium manganate(VII) of concentration 0.0200 mol dm^{-3} is decolourised by 50 cm^3 of hydrogen peroxide of concentration 0.0100 mol dm^{-3}?

(ii) What volume of oxygen is evolved at room temperature and pressure in this titration?

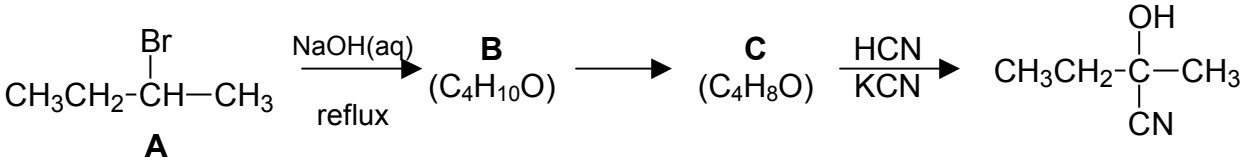
[4]

(e) Write the structural formulae of the carbon containing products formed when 2-methylpropene reacts with hot concentrated potassium manganate(VII).

[2]

[Total: 20]

7 In the reaction scheme below, the four-carbon bromoalkane, **A**, is converted into the five-carbon cyanohydrin, **D**.

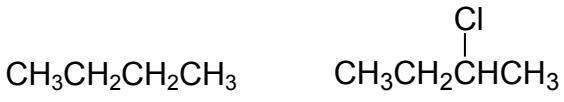


A **D**

(a) (i) Name compound **A**.
(ii) Draw the structural formulae of all other possible isomers of the compound having the same molecular formula as **A**. **[3]**

(b) (i) By comparing the molecular formulae of **B** and **C** suggest what type of reaction transforms **B** to **C**.
(ii) Draw the structural formula of compound **C**.
(iii) Describe what you might observe when compound **C** is added to alkaline aqueous iodine. Give the structural formula of the carbon-containing product(s). **[4]**

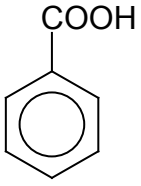
(c) (i) Arrange compound **A** and the following two compounds, **E** and **F**, in the order of increasing boiling point and explain your answer.



E **F**

(ii) Chlorofluorocarbons (CFCs) are commonly used as refrigerants and aerosol propellants. What kind of hazard does CFCs pose to our environment? **[4]**

(d) Benzoic acid and its salts are often used as a food preservative. It is also a constituent of Whitfield's ointment used to treat fungal skin diseases.



Benzoic acid

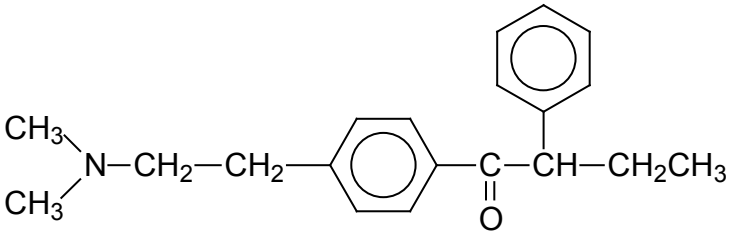
Write balanced equations for the reaction of benzoic acid with
(i) ethanol,
(ii) aqueous sodium carbonate and
(iii) $LiAlH_4$ in dry ether (you may use the symbol [H] in your equation). **[3]**

(e) The structural formula and pK_a of two acids are given in the table below.

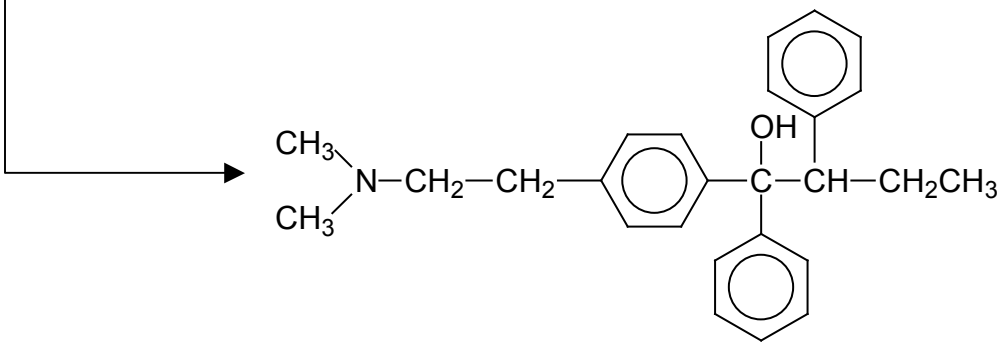
Acid	Butanoic acid	2,2-dichlorobutanoic acid
Structural formula	$CH_3CH_2CH_2COOH$	$CH_3CH_2C(Cl)_2COOH$
pK_a	4.8	3.9

Explain the difference in their pK_a values as fully as you can. **[2]**

(f) *Tamoxifen* is a drug that is used in the treatment of early and advanced stages of breast cancer and is currently one of the world's best selling drug. The drug was first discovered by ICI Pharmaceuticals in 1962. Tamoxifen is produced from compound **S** as shown below.



Compound **S**



Tamoxifen

(i) Describe a simple chemical test that can be used to distinguish compound **S** from *Tamoxifen*. **[2]**

(ii) Calculate the percentage by mass of carbon in *Tamoxifen*. **[2]**

[Total: 20]