1   **(a)**   **(i)**

(a)   (i)   Plot the experimental results on the grid below.

(ii) The order of reaction is the sum of all the powers of all the reactants' concentrations in the rate equation.

Or

If rate = $k[A]^m[B]^n$ where k is a rate constant and [A], [B] are concentrations of A and B respectively,
Order of reaction = m + n

(iii) From the graph,
time taken, t_1, for [product] to increase from 0 to $\frac{1}{2}C_o$ = 1.45 min
time taken, t_2, for [product] to increase from $\frac{1}{2}C_o$ to $\frac{3}{4}C_o$ = 1.35 min

If $t_1 \approx t_2 \approx 1.40$ min, then $t_{1/2}$ is constant.
Since $t_{1/2}$ is constant, the reaction is first-order with respect to the reactant.

Rate = $k[N_2O_5]$

(iv) $t_{1/2}$ = ln 2/ k
k = ln 2/ 1.40 mins = 0.495 min^{-1}

(b) **(i)** Pressure used is high as a high pressure favours the forward reaction.
By Le Chatelier's Principle, when pressure increases, the system will favour the side with fewer number of gaseous molecules.
Hence, position of equilibrium shifts to the right and this increases yield.

Since the forward reaction is exothermic, a lower temperature would result in a higher yield of ammonia.
However, the rate of production is too slow at low temperature.
On the other hand, a high temperature increases the rate of production but results in lower yield and higher production cost.
Thus, a compromise is needed and a moderately high temperature (of $450\,^{\circ}C$) is used to ensure a reasonable rate of production and yield.

(b) **(ii)** This reduces the surface area of the catalyst, hence reducing the activity of the catalyst.

(b) **(iii)** There is a general increasing trend in the ionisation energies, from left to right, as we remove one additional electron. This is because once the first electron is removed from the neutral atom, each successive electron is removed from an ion of increasing positive charge which attracts the electrons more strongly.

There is a significant difference between the third and the fourth ionisation energies because the fourth electron is removed from an inner principal quantum shell. Therefore there are 3 electrons in the outermost shell.

(iv) $1s^2\,2s^2\,2p^6$
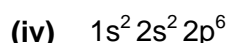
2 **(a)** In graphite, the carbons are arranged in six-membered hexagonal rings with 3 σ bonds for each carbon, the single electron not used for bonding forms delocalised pi bonds/electron cloud above and below the layers of graphite rings, allowing for the movement of electrons for electrical conductivity in a direction parallel to the layers.

In diamond, the carbons are arranged in a network of tetrahedral carbons with four σ bonds each, this network of σ bonds do not allow for electrical conductivity.

(b) **(i)**
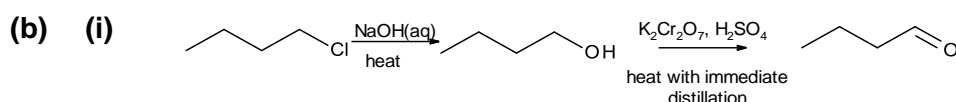
(ii) NaOH, I_2(aq), heat
or $KMnO_4$/$K_2Cr_2O_7$, H_2SO_4, heat or Tollen's/Fehling's, warm

(iii) Butanal will react faster than butanone as the H atom provides less steric hindrance than the methyl group on butanone.

(c) Chlorobutane will have a white precipitate upon addition of $AgNO_3$ while no change will be seen for chlorobenzene.

The p orbital on the chlorine atom on chlorobenzene is able to overlap with the pi electron cloud of the benzene ring, creating a partial double bond between the carbon and the chlorine. Hence there is no hydrolysis reaction with NaOH, resulting in no free Cl^- ion to form AgCl(s) when $AgNO_3$ is added.

3 **(a)** If the concentration of H^+ ions in the blood increases, the HCO_3^- present reacts with the additional H^+ ions and thus the pH remains virtually unchanged.
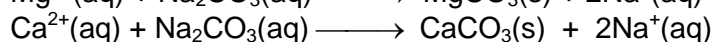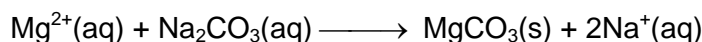
or

$$HCO_3^-(aq) + H^+(aq) \longrightarrow H_2CO_3(aq)$$
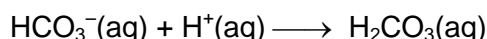
(b) In 100 cm^3 sample,
mass of Mg^{2+} = 127 mg = 0.127 g
mass of Ca^{2+} = 40 mg = 0.04000g

Amount of Mg^{2+} = 0.127 ÷ 24.3 = 0.005226 mol
Amount of Ca^{2+} = 0.04000 ÷ 40.1 = 0.0009975 mol

$$Mg^{2+}(aq) + Na_2CO_3(aq) \longrightarrow MgCO_3(s) + 2Na^+(aq)$$
$$Ca^{2+}(aq) + Na_2CO_3(aq) \longrightarrow CaCO_3(s) + 2Na^+(aq)$$

Amount of $MgCO_3$ = 0.005226 mol
Amount of $CaCO_3$ = 0.0009975 mol

Maximum combined mass of $CaCO_3$ and $MgCO_3$ precipitated
= (0.005226 × 84.3) + (0.0009975 × 100.1)
= 0.540 g

(c) Aqueous $BaCl_2$/ $Ba(NO_3)_2$. Accept aqueous Ba^{2+}.
White ppt.

(d) **(i)** $2Mn^{2+}(aq) + O_2(aq) + 4OH^-(aq) \longrightarrow 2\ MnO_2(s) + 2H_2O(l)$

(ii) Amount of $S_2O_3^{2-}$ reacted = $\frac{5.5}{1000}$ × 0.020 = 0.0001100 mol.

Amount of dissolved O_2 = Amount of $S_2O_3^{2-}$ reacted ÷ 4
= 0.0001100 ÷ 4
= 2.750×10^{-5} mol.

Mass of dissolved oxygen = (2.750×10^{-5}) × 32.0
= 8.800×10^{-4} g
= 8.800×10^{-1} mg
Concentration of dissolved oxygen = (8.800×10^{-1}) ÷ $(\frac{50}{1000})$
= 1.76×10 mg dm^{-3}

(e) Ice is a molecular solid in which the lattice forces are hydrogen bonds. The hydrogen bonds and covalent bonds are arranged tetrahedrally around each H_2O molecule.

This results in a very open structure/ empty spaces and prevents the molecules from getting too close to one another.

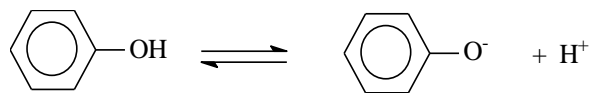As a result, there are more molecules per unit volume in liquid water than in ice.

(f) Sparingly soluble, reacts to form a weak base .

$$MgO(s) + H_2O(l) \rightleftharpoons Mg(OH)_2(aq)$$
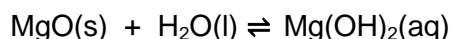
Section B (40 marks)

4 **(a)** **(i)** A – ketone
B – secondary alcohol

(ii) Phenol dissociates to give the phenoxide ion, $C_6H_5O^-$.

The p-orbital of O overlaps with the π-electron cloud of the benzene ring so that the negative charge on O delocalises into the benzene ring. The dispersal of negative charge stabilises the phenoxide ion so that it is more stable than the alkoxide ion.
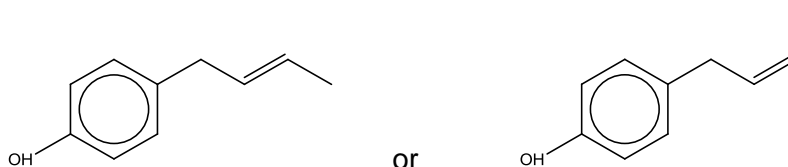
An alcohol dissociates to give the alkoxide ion, RO^-.
$$ROH \rightleftharpoons RO^- + H^+$$
The electron-donating alkyl group intensifies the negative charge on O atom. Charge on RO^- ion also remains localised on a single electronegative O.
The alkoxide ion is, therefore, the least stable and most likely to accept a proton.
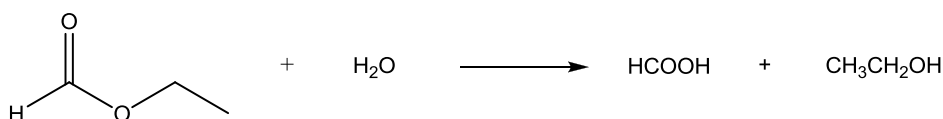
(iii) Concentrated H_2SO_4, 170°C

 or

(iv) Geometrical isomerism arises due to the restricted rotation in the presence of π bonds.

(v)

Reagent	Product	Observation
2,4-DNPH		Orange ppt
$K_2Cr_2O_7$/ H_2SO_4(aq), heat		Orange $K_2Cr_2O_7$ turned green, white ppt formed

(b) **(i)** Ethyl methanoate

(ii)
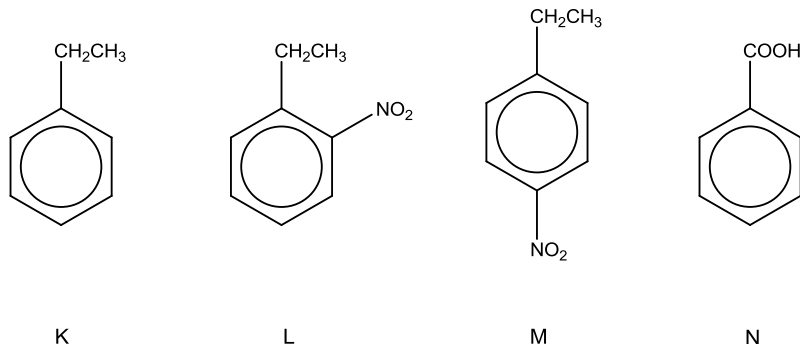
  + H_2O $\longrightarrow$ HCOOH + CH_3CH_2OH

5

(iii) A strong acid is fully dissociated whereas a weak acid is partially dissociated.

(iv) pH = -log (0.2)
     = 0.70

(c)

CH_2CH_3 CH_2CH_3 CH_2CH_3 COOH

(benzene ring) K   (benzene ring with NO_2) L   (benzene ring with NO_2) M   (benzene ring) N
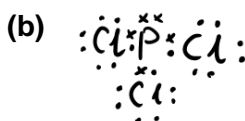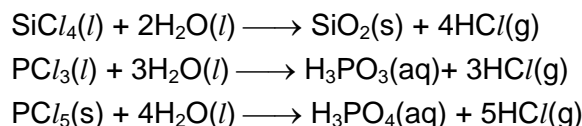
5 (a) (i) Atomic radius decreases from aluminium to silicon to phosphorus. Across a period, electrons are being added to the same outermost principal quantum shell thus shielding effect remains approximately constant and nuclear charge increases, leading to increasing effective nuclear charge.

(ii) $AlCl_3$, which have cations of very high charge density, dissolve in water to form acidic solutions. The small, highly polarising cation weakens the O–H bonds of the water molecules in its surrounding sphere of coordination and results in the release of hydrogen ions in solution.

$AlCl_3(s) + 6H_2O(l) \longrightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$
$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$
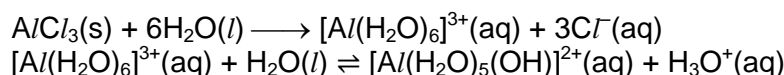
Acidic chlorides of silicon and phosphorus dissolve readily in water to form white fumes of hydrogen chloride. The resulting solution is strongly acidic due to the hydrogen chloride produced.

$SiCl_4(l) + 2H_2O(l) \longrightarrow SiO_2(s) + 4HCl(g)$
$PCl_3(l) + 3H_2O(l) \longrightarrow H_3PO_3(aq) + 3HCl(g)$
$PCl_5(s) + 4H_2O(l) \longrightarrow H_3PO_4(aq) + 5HCl(g)$

(b)

(Lewis structure of PCl_3: central P atom bonded to three Cl atoms with lone pairs)

There are 3 bonding pairs and 1 lone pair of electrons around the P atom. Since the lone pair – bonding pair repulsion is greater than the bonding pair – bonding pair repulsion, PCl_3 has a trigonal pyramidal shape. The bond angle is 100°.

(c) Lattice energy (L.E.) is the energy released when one mole of an ionic compound is formed from its gaseous ions.

$$|L.E.| \alpha \left| \frac{q^+ q^-}{r^+ + r^-} \right|$$

Since Mg^{2+} has double the charge of Na^+, and the ionic radius of Mg^{2+} is smaller than that of Na^+, the magnitude of the lattice energy of $MgCl_2$ is expected to be larger than that of $NaCl$.

**(d) (i)** $\Delta H_{rxn} = \frac{1}{2}(362 + 113 - 163) = +156$ kJ

(ii) Oxides of nitrogen contribute to the formation of acid rain as well as low level ozone. It also contributes to photochemical smog and damage to the ozone layer.

6 **(a)** **(i)** Initial concentration of CH_4 = 4.00 mol dm^{-3}
Initial concentration of H_2S = 8.00 mol dm^{-3}

concentration (mol dm^{-3})	$CH_4(g)$	+	$2H_2S(g)$	$\rightleftharpoons$	$CS_2(g)$	+	$4H_2(g)$
initial	4.00		8.00		4.00		8.00
change	+1.56		+3.12		-1.56		-6.24
at equilibrium	5.56		11.12		2.44		1.76

$$K_c = \frac{[CS_2][H_2]^4}{[CH_4][H_2S]^2} = \frac{(2.44)(1.76)^4}{(5.56)(11.12)^2} = 0.0341 \text{ mol}^2\text{dm}^{-6}$$

(ii) When a system in equilibrium is subjected to a change, the system responds in such a way as to counteract the effect of the change and re–establish the equilibrium state.

(iii) Equilibrium position will shift left, to reduce the increase in pressure as there are 3 moles of gaseous reagents compared to 5 moles of gaseous products.
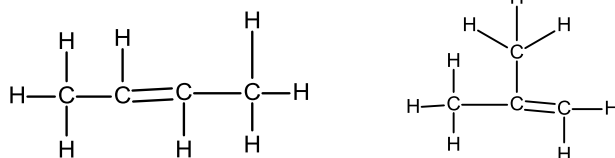
(b) **(i)** $CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$
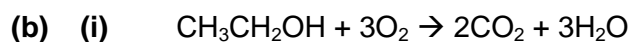
(ii) Heat released = (200)(4.2)(80-25) = 46200 J = 46.2 kJ
Moles of ethanol = 1.75 / 46.0 = 0.03804 mol
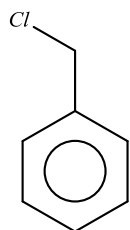Enthalpy change of combustion of ethanol = – 46.2 / 0.03804 = -1210 kJ mol^{-1}

(iii) Percentage efficiency = 100/1368 x1210 = 88.45 ≈ 88.5 %

Heat loss to surroundings during the combustion, not all energy from the burning of ethanol was used to heat the water.

(c)
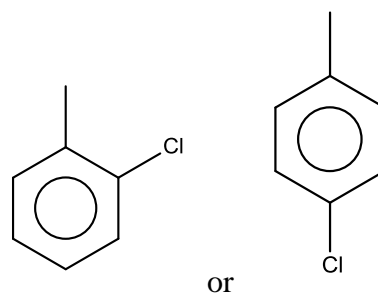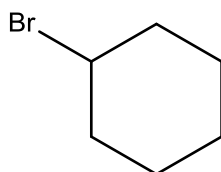

(d) **(i)** Reagents and conditions: Cl_2, UV   Reagents and conditions: Cl_2, FeCl_3

or

(ii)

With HBr

With cold acidified KMnO$_4$

(structure: cyclohexane-1,2-diol with two HO groups)