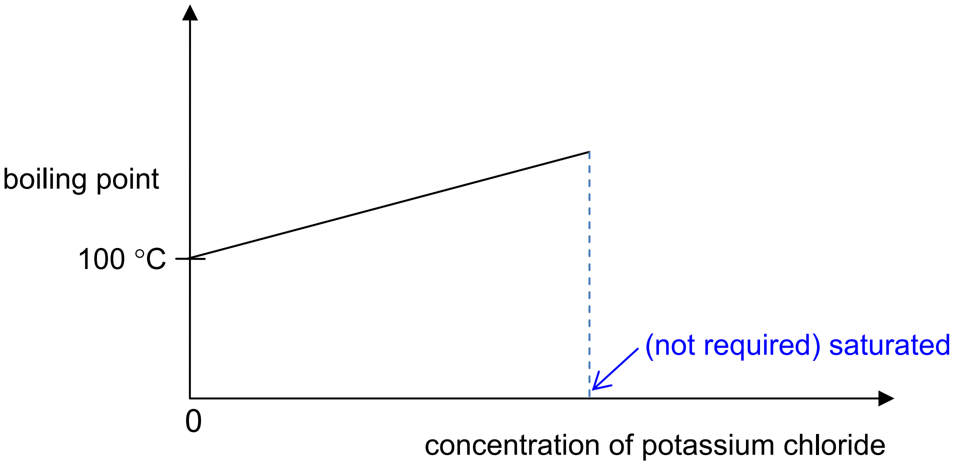
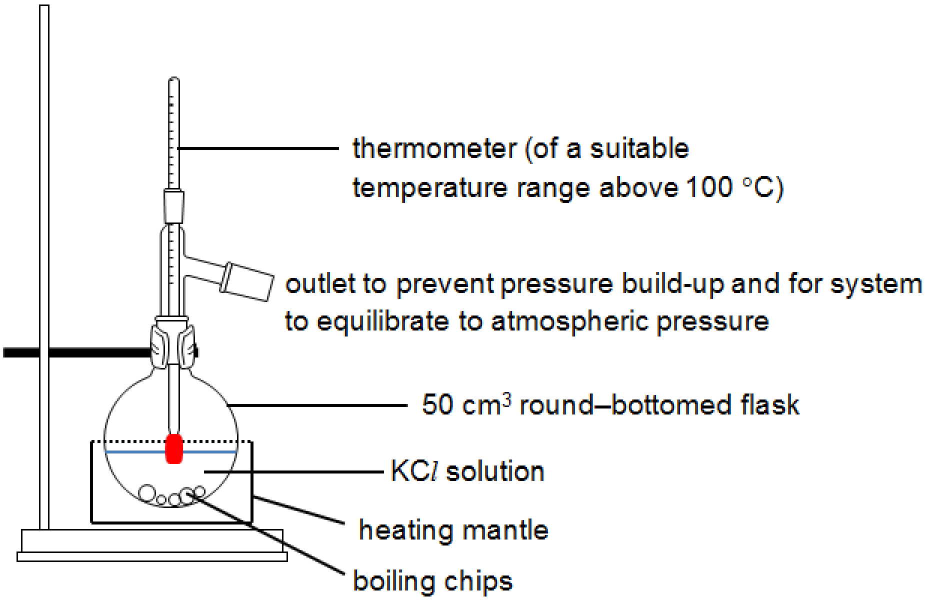
1 **(a)** **(i)** The boiling point increases with concentration because the temperature has to be raised in order to increase the lowered vapour pressure to that of the ambient value. [1]

(ii) [2]



- *[1m] straight–line or curve showing a gradual increase.*
- *[1m] line to begin on the y–axis with the value 100 ℃ (or 373 K) labelled with units. [there is no ecf here from (i) to (ii)]*

(b) [2]



- *[1m] for a diagram which shows some form of heating (not a water bath, but allow oil–bath or heating mantle) of an apparatus (50 cm^3 round–bottomed flask / boiling tube) containing the KCl solution.*
- *[1m] for showing the position of the thermometer bulb is half–immersed in the solution – the full line in the diagram indicates the water level (to allow accurate determination of the temperature of the equilibrium).*

(c) Experimental Procedure [6]

1. Weigh accurately about 2 g of solid KC*l* in a 50 cm^3 round–bottomed flask and record your reading.
2. Using a *50 cm^3 burette*, add 20 cm^3 of deionised water into the round–bottomed flask.
3. Stopper and shake the flask to dissolve the solid.
4. Add anti–bumping granules (boiling chips) to the solution.
5. Set up the apparatus as shown in **(b)**.
6. Using a heating mantle (or oil–bath), gently heat the flask containing KC*l* solution, until the temperature remains constant.
7. Record this temperature (i.e. the boiling point).
8. Repeat steps 1 to 7, using 3 g, 4 g, 5 g and 6 g KC*l*, respectively.

- *[1m] for general outline of procedure with coherent sequence of steps leading to determination of boiling point (take reading when temperature remains constant).*
- *[2m] for a method, which gives details / a list of the masses / volumes of water to be used along with masses of solid KCl to produce a solution, provided that the total mass / volume of water does not exceed 100 g / 100 cm^3 AND*

  $\frac{\text{max. mass of solid KCl}}{\text{volume of water (same)}} < 0.357$ *or* $\frac{\text{mass of solid KCl (same)}}{\text{smallest volume of water}} < 0.357$
- *[1m] if at least five different concentrations of KCl are prepared.*

  (A method based on adding varying volumes of the water to one mass of solute is allowed, e.g. 10 cm^3, 15 cm^3, 20 cm^3, 25 cm^3, 30 cm^3)
- *[1m] for safety & reliability considerations: steps 3 and 4 (or in diagram)*

Calculation of Molality

Taking density of water to be 1 g cm^{-3}

$$\text{Molality} = \frac{\text{mass of solid KCl used}}{74.6} \times \frac{1000}{\text{volume of deionised water used} \times 1.00}$$

- *[1m] for correct general expression to calculate molality.*

(d) The experiment is limited by the solution becoming saturated. [1]

2 **(a)** Breath alcohol concentration = $\frac{1}{2100}$ x 80 mg / 100 cm^3 [1]

$= 0.03809$ mg / 100 cm^3

breath alcohol concentration (in mol cm^{-3}) = $\frac{0.03809}{10^3} \times \frac{1}{46.0} \times \frac{1}{100}$

$= \underline{8.28 \times 10^{-9}\ \text{mol cm}^{-3}}$ [1]

(b) **(i)** $E^\ominus(Cr_2O_7^{2-}/Cr^{3+}) = +1.33$ V

$E^\ominus_{cell} = +1.33 - 0.058 = \underline{+1.27\ \text{V}}$ [1]

$3C_2H_5OH + 2Cr_2O_7^{2-} + 16H^+ \longrightarrow 3CH_3CO_2H + 4Cr^{3+} + 11H_2O$ [1]

(ii) Q = It = 0.1 x 5 = 0.5 C
Q = nF $\Rightarrow$ n(e^-) = 0.5 / 96500 = 5.181×10^{-6} mol [1]

n(ethanol) = 5.181×10^{-6} x 1/4 = $\underline{1.30 \times 10^{-6}\ \text{mol}}$ [1]

(iii) n(ethanol) per cm^3 of exhaled air (breath) = 1.30×10^{-6} / 60.0
$= 2.166 \times 10^{-8}$ mol cm^{-3}

n(ethanol) per cm^3 of blood = $2.166 \times 10^{-8} \times 2100 = 4.548 \times 10^{-5}$ mol cm^{-3}
mass of ethanol per cm^3 of blood = $4.548 \times 10^{-5} \times 46.0$
$= \underline{2.09 \times 10^{-3}\ \text{g cm}^{-3}}$ [1]

Since 2.17×10^{-8} mol cm^{-3} >> 8.28×10^{-9} mol cm^{-3} (legal limit for breath alcohol concentration; answer to **(a)**), the driver is drink–driving. [1]

or

Legal limit to drive is 80 mg of ethanol per 100 cm^3 of blood
$\Rightarrow 80 \times 10^{-3} \times (1 / 100) = 8.00 \times 10^{-4}$ g cm^{-3} (mass of ethanol per cm^3 of blood)

Since 2.09×10^{-3} >> 8.00×10^{-4} g cm^{-3}, the driver is drink–driving.

(iv) By measuring the change in intensity of the colour change of orange $Cr_2O_7^{2-}$ to green Cr^{3+}. [1]

3 **(a)** The energy absorbed or evolved when one mole of a compound is formed from its constituent elements at standard states, under standard conditions of 298 K and 1 atm. [1]

(b) **(i)** $\Delta H_r^\ominus = \sum \Delta H_f^\ominus(\text{products}) - \sum \Delta H_f^\ominus(\text{reactants})$

$= 2(-393.5) + 4(-241.8) - [83.3 + 2(9.10)]$ [1]

$= \underline{-1855.7 \text{ kJ mol}^{-1}}$ [1]

[1m] for correct substitution
[1m] for final answer given to 1 d.p.

(ii) Entropy change is highly positive because there is a large increase in the number of moles of gaseous particles (from 0 to 9). Hence, there are more ways in which particles and energies of the particles can be distributed. [1]

(iii) $\Delta G = \Delta H - T\Delta S$

Decreasing the temperature decreases the magnitude of $T\Delta S$ ($-T\Delta S$ becomes less negative). ΔG becomes less negative and hence the reaction becomes less spontaneous. [1]

(c) **(i)** $2N_2H_4 + N_2O_4 \longrightarrow 4H_2O + 3N_2$ [1]

(ii)

$\Delta H_r^\ominus = \sum BE_{\text{reactants}} - \sum BE_{\text{products}}$

$= [8(BE_{N-H}) + 2(BE_{N-N}) + 2(BE_{N=O}) + 2(BE_{N-O}) + BE_{N-N}] - [8(BE_{O-H}) + 3(BE_{N\equiv N})]$

$= [8(390) + 2(160) + 2(607) + 2(201) + 160] - [8(460) + 3(994)]$

$= \underline{-1446 \text{ kJ mol}^{-1}}$ [1]

(iii) The bond energies in the *Data Booklet* are average values. [1]

or

In their standard states at 298 K, N_2H_4 and N_2O_4 are liquids whereas the $\Delta H_r^\ominus$ calculated in **(c)(ii)** is based on reactions in the gas phase.

(d) **(i)** M_r UDMH = 60.0; M_r N_2O_4 = 92.0

Since UDMH : N_2O_4 = 1 : 2,

Mass of UDMH $= \dfrac{60}{60 + 2(92.0)} \times 244 = \underline{60.0 \text{ kg}}$ [1]

(ii) Since UDMH : product gases = 1 : 9,

No. of moles of UDMH = $60 \times 10^3 / 60.0$ = 1000 mol
No. of moles of product gases = 1000 x 9 = 9000 mol [1]

(iii) $pV = nRT$
$V = nRT / p$
$= 9000 \times 8.31 \times (-10 + 273) / 600$
$= \underline{3.28 \times 10^4 \text{ m}^3}$ [1]

(e) **(i)** Gradient calculated from graph = $\frac{8.5 - 1.1}{0.0010 - 0.00152)}$ = –14230.7 [1]

Gradient = $-E_a / R$
$-14230.7 = -E_a / 8.31$
$E_a = 14230.7 \times 8.31 = 118257 = +118 \text{ kJ mol}^{-1}$ [1]

(ii) Yes, the mechanism is consistent with the given rate equation.

Two molecules / moles of NO_2 are involved in slow step / rate–determining step. [1]

The sum of the 2 steps gives the overall balanced equation of the reaction. [1]

(f) **(i)** Rate = $k\,(p_{NO})^a\,(p_{H2})^b$

Comparing Expt. 1 & 2, when p_{NO} decreases by 2 times (from 120 to 60 torr), the initial rate decreases by 4 times (from 8.66×10^{-2} to 2.17×10^{-2} torr s^{-1}). [1]

$\Rightarrow$ order of reaction w.r.t. p_{NO} = 2; i.e. a = 2

Comparing Expt. 2 & 3, when p_{H2} increases by 3 times (from 60 to 180 torr), the initial rate also increases by 3 times (from 2.17×10^{-2} to 6.62×10^{-2} torr s^{-1}). [1]

$\Rightarrow$ order of reaction w.r.t. p_{H2} = 1; i.e. b = 1

(Mathematical method is accepted here)

rate = $k\,(p_{NO})^2\,(p_{H2})$ [1]

Using results from Expt. 1,
$k = (8.66 \times 10^{-2}) / (120^2 \times 60) = 1.00 \times 10^{-7} \text{ torr}^{-2} \text{ s}^{-1}$ [2]

[1m] for final answer
[1m] for units

(ii) rate = $\Delta p_{N2O} / \Delta t = -½\,(\Delta p_{NO} / \Delta t)$

Initial rate of formation of $N_2O = 1.00 \times 10^{-7} \times 200^2 \times 100 = 0.400$ torr s^{-1} [1]
$= \Delta p_{N2O} / \Delta t$

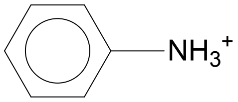
Initial rate of **disappearance** of NO = $\Delta p_{NO} / \Delta t = 2 \times 0.400 = 0.800$ torr s^{-1} [1]

(iii) rate = $k\,(p_{NO})^2\,(p_{H2})$

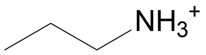
As $p_{NO} >> p_{H2}$,

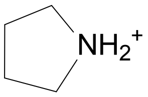
rate = $k'\,p_{H2}$ where $k' = k\,(p_{NO})^2$ [1]
$k' = 1.00 \times 10^{-7} \times (800)^2 = 0.064 \text{ s}^{-1}$
$t_{1/2} = \ln 2 / k' = \ln 2 / 0.064 = 10.8$ s [1]

4 **(a)**



(lowest pK_a)





(highest pK_a)

[1]

(b) pK_a of BH^+ = 8.1 ⇒ $K_a = 10^{-8.1}$

$$K_a = \frac{[B][H^+]}{[BH^+]}$$

$$\frac{[B]}{[BH^+]} \text{ at pH 7.4} = 10^{-8.1}/10^{-7.4} = 0.200 \text{ or } 1/5$$ [1]

% Bupivacaine, B = 1/6 x 100 = 16.7 % [1]

(c) **(i)** Non–polar benzene ring and alkyl side chains of B enable it to attract to non–polar lipid molecules (through van der Waals' forces). [1]

(ii) As opposed to the uncharged (unionised) Bupivacaine, the positively charged conjugate acid can form strong ion–dipole interactions with polar water molecules. [1]

(d) B forms van der Waals' interactions with the lipid layer of the cell membrane and thus allowing it to pass through the cell membrane. [1]

As B passes through the membrane into the cell, its concentration outside the cell decreases, thus the position of equilibrium shifts right, more BH^+ converts to B and allowing more B to enter the cell. [1]

Within the cell, the position of equilibrium shifts left as [B] increases thus forming more BH^+ which can then interact with its target site. [1]

(e) As the $[H^+]$ increases in the infected tissues, position of equilibrium (1) shifts left, decreasing [B]. Hence, less drug molecules can pass through the cell membrane to exert effect. [1]

or

At pH lower than 7.4, position of equilibrium of (1) lies to the left, hence less B is available to pass through the cell membrane and it takes a longer time for the drug to take effect.

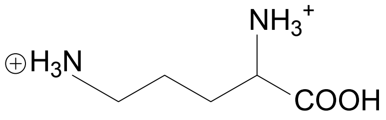
(f) Lone pair of electrons on N atom of amide group in Bupivacaine is more readily delocalised into the C=O group than the lone pair on O atom of ester group in Amethocaine, as N is less electronegative than O. [1]

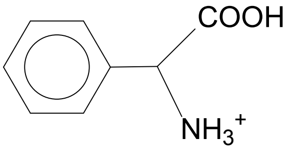
Hence, C–N bond in amide is stronger than C–O bond in ester. [1]
or C in amide is less electron deficient .

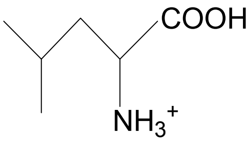
(g) **(i)** 5 different amino acids [1]

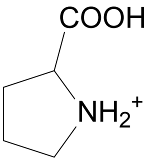
(ii) dilute HC*l* or H_2SO_4 or aq. NaOH [1]
AND heat for several hours or prolonged period

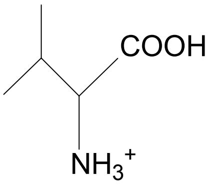
(iii) [2]











Any two; [1m] each
(Products formed from base–catalysed hydrolysis are accepted)

5 **(a)** **(i)** **D** and **E** [1]

(ii) **D** and **E** [1]

(iii) **B**, **C** and **D** [1]

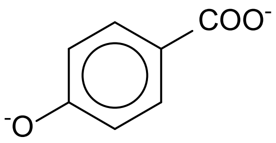
(iv) Identity of **F**: **D** [1]

Chemical test: Add **aqueous iodine** and **aqueous NaOH** to the compound and **warm**. [1]

Expected observation: A **yellow precipitate** is formed.

[1m] for chemical test & expected observation

CHI_3



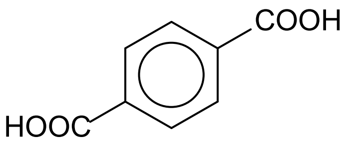
[1]

[1m] for both structural formulae of organic products

(v) 3230–3550 cm^{-1} [1]

(b) **(i)** nucleophilic substitution [1]

(ii) [1]



(iii) Add **Mg or Na** to both compounds separately. [1]
Effervescence of H_2 observed for **C** but **no effervescence** for **G**. [1]

or

Add **Na_2CO_3 or $NaHCO_3$** to both compounds separately.
Effervescence of CO_2 observed for **C** but **no effervescence** for **G**.

or

Add anhydrous **PCl_5** to both compounds separately.
Steamy fumes of HCl observed for **C** but not for **G**.

(iv) $Ag^+ + 2S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_2]^{3-}$ [1]

or

$AgI + 2S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_2]^{3-} + I^-$