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

# 1 Planning (P)

You are provided with solutions FA 1, FA 2 and FA 3.

**FA 1** and **FA 2** are either 1.0 mol dm<sup>-3</sup> nitric acid **or** 1.0 mol dm<sup>-3</sup> ethanoic acid

whereas **FA 3** is 2.0 mol dm<sup>-3</sup> sodium hydroxide.

You are to plan an experiment that will enable you to identify **FA 1** and **FA 2**, and hence, calculate the enthalpy change of neutralisation for the reaction between ethanoic acid and sodium hydroxide.

You are provided with the following apparatus:

a thermometer, a polystyrene cup, other common apparatus in the laboratory

(a) State the independent and dependent variables when determining the identity of each solution, FA 1 and FA 2. [1]

Independent variable – Strength of acid

**Dependent variable – Rise in temperature** 

(b) Plan an experiment to identify which of the two solutions, **FA 1** and **FA 2**, is 1.0 mol dm<sup>-3</sup> nitric acid and which is 1.0 mol dm<sup>-3</sup> ethanoic acid.

Your plan must identify the acids solely based on the change in temperature. Mathematical processing of the temperature change is thus **not** required.

Your plan should give a step by step description of the method including:

- the apparatus used for measurement
- appropriate volumes of reagents
- how you would measure the various variables

[3]

Step 1: Using a 100 cm<sup>3</sup> measuring cylinder, measure out 25 cm<sup>3</sup> of FA 3 into the polystyrene cup and record its initial temperature using a thermometer. Rinse the thermometer.

Step 2: Using ANOTHER 100 cm<sup>3</sup> measuring cylinder, measure 50 cm<sup>3</sup> of FA 1. Record its initial temperature.

Step 3: The initial temperature is given by the average of the initial temperature of FA 1 and FA 3.

Step 4: Carefully transfer the 50 cm<sup>3</sup> of FA 1 into the polystyrene cup containing FA 3, stir with the thermometer and record the highest temperature reached. Rinse the cup.

Step 5: Repeat steps 1 to 4, this time replacing FA1 with FA2.

(c) Either a burette with 0.1 cm<sup>3</sup> interval or a measuring cylinder with 1 cm<sup>3</sup> interval can be used to measure the volume of **FA 3** required.

It is known that the error (or uncertainty) that is associated with each reading when using a measuring cylinder with  $1 \text{ cm}^3$  interval is  $\pm 0.5 \text{ cm}^3$ , while that using a burette with 0.1 cm<sup>3</sup> interval is  $\pm 0.05 \text{ cm}^3$ .

Assuming that the volume of **FA 3** measured is  $V \text{ cm}^3$ , calculate the maximum total percentage error (or uncertainty) in the measurement of the volume of **FA 3**, in terms of *V*, when using:

- (i) a measuring cylinder with 1 cm<sup>3</sup> interval, Percentage error in measuring  $V \text{ cm}^3$ = ± (0.5/ V) x 100% = ± 50/V%
- (ii) a burette with 0.1 cm<sup>3</sup> interval. Percentage error in measuring  $V \text{ cm}^3$ = ± [(0.05/ V) x 100%] x 2 = ± 10/V %

[2]

(d) Explain clearly how you could determine the identity of the acids using the difference in temperature rise in the experiment proposed in (b). [2]

Ethanoic acid is a weak acid and nitric acid is a strong acid. The temperature rise will be lower when 1.0 mol dm<sup>-3</sup> ethanoic acid is used compared to 1.0 mol dm<sup>-3</sup> nitric acid for the same number of moles of water formed.

This is because some of the energy evolved from the neutralisation process is used to further dissociate the ethanoic acid completely.

(e) (i) Define the term standard enthalpy change of neutralisation.

The heat evolved when one mole of water is formed when an acid neutralises a base under standard conditions of 298K and 1 atm.

(ii) Show the mathematical expression for the enthalpy change of neutralisation for the reaction between ethanoic acid and sodium hydroxide, using the volumes proposed in (b).

The temperature change measured in (b) should be represented by  $\Delta T$ .

[You may assume that 4.2 J of heat energy raised the temperature of 1 cm<sup>3</sup> of any solution by 1°C.]

Heat evolved by neutralisation reaction =  $mc\Delta T$ = (vol. of FA1 or FA2 + vol of FA3) x c x  $\Delta T$ = (50 + 25) x 4.2 x  $\Delta T$ = 315 $\Delta T$  J  $\Delta H_{neutralisation} = -315\Delta T / amount of water formed$ =  $-315\Delta T / 0.050$ =  $-6300\Delta T$  J mol<sup>-1</sup> [3]

(f) A student suggests titrating FA 3 against FA 1 and FA 2 separately, using phenolphthalein as indicator, to identify the acids. Explain why this proposed method cannot work. [1]

Both FA 1 and FA 2 are of the same concentration and basicity (monobasic). Both acids would hence require the same amount of NaOH for a complete reaction, and hence same volume. The volume of FA 3 (NaOH) required at end point would hence be the same.

[Total: 12]

2 Nitrogen dioxide, NO<sub>2</sub> undergoes dimerisation to form dinitrogen tetraoxide, N<sub>2</sub>O<sub>4</sub>.

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

(a) (i) Draw the dot-and-cross diagram of NO<sub>2</sub>.



- (ii) State the shape and bond angle of the O–N–O bond in NO<sub>2</sub>.
  Shape of NO<sub>2</sub>: <u>Bent</u>
  Bond angle: accept any value where <u>110° < angle < 120°</u>
- (iii) Draw the dot-and-cross diagram of NO<sub>2</sub><sup>-</sup> ion. With reference to your answer in (a)(i) and (ii), suggest a bond angle of the O–N–O in NO<sub>2</sub><sup>-</sup> ion, as compared to NO<sub>2</sub>. Explain your answer.

Bond angle of  $NO_2^-$  ion: bond angle must be smaller than  $NO_2$ , but still within range of  $110^\circ$  < angle <  $120^\circ$ 

Lone pair of electrons present in  $NO_2^-$  ion occupies a larger volume of space than the single lone electron present in  $NO_2$  molecule. Hence, lone pair-bond pair repulsion in  $NO_2^-$  ion is greater than lone electron-bond pair repulsion in  $NO_2$ , causing  $NO_2^-$  ion to have a smaller bond angle than  $NO_2$ .

[5]

The general rate equation for the dimerisation of nitrogen dioxide can be represented as:

Rate = 
$$k(p_{NO_2})^n$$
,

where *n* represents the order of reaction with respect to nitrogen dioxide.

To determine the value of n, an experiment was carried out to collect experiment data on the partial pressure of nitrogen dioxide ( $p_{NO_2}$ ) measured at a constant temperature of 500 K. The results were given below.

Time/ s	p <sub>NO2</sub> / atm	Rate /atm s <sup>-1</sup>	ate /atm s <sup>-1</sup> (p <sub>NO2</sub> ) <sup>2</sup> / atm <sup>2</sup>		
0	0.917	9.48 x 10 <sup>-5</sup>	0.48 x 10 <sup>-5</sup> <b>0.841</b>		
1000	0.827	7.75 x 10⁻⁵	0.683		
2000	0.753	6.45 x 10 <sup>-5</sup>	0.567		
3000	0.691	5.45 x 10 <sup>-5</sup>	0.477		
4000	0.638	4.67 x 10 <sup>-5</sup>	0.407		
Table 1					

(b) (i) Given that *n* is 2, process the results in the Table 1 to produce data that would enable you to plot a **straight line graph**.

(ii) Hence, use the processed data to plot the graph on the grid below.



(iii) A student repeated the experiment at the temperature of 250 K. Sketch, on the same axes in (ii), the graph obtained by this student. Label this graph as **250 K**.

Straight line graph still obtained, with y-intercept = 0. Gradient (k) decreases.

[4]

[Total: 9]

**3** The following reaction scheme shows the chemistry of some chromium-containing species in aqueous solution.



(a) (i) Write the formulae of the following chromium-containing species.

A: [Cr(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> or Cr<sup>3+</sup> or Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> B: Cr(OH)<sub>3</sub> C: CrO<sub>4</sub><sup>2-</sup> or Na<sub>2</sub>CrO<sub>4</sub>

(ii) State the type of reaction that has occurred in VIII. Construct a balanced equation to represent the reaction.

Ligand exchange has taken place.

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[Cr(NH_3)_6]^{3+} + 3 H_2NCH_2CH_2NH_2 \Rightarrow [Cr(H_2NCH_2CH_2NH_2)_3]^{3+} + 6 NH_3
```

(iii) Hence, using your knowledge of Gibbs free energy, explain why the reaction in (a)(ii) occurs spontaneously.

 $[Cr(NH_3)_6]^{3+} + 3 \text{ en} \Rightarrow [Cr(en)_3]^{3+} + 6 \text{ NH}_3$ This ligand exchange proceeds with the breaking and formation of similar chemical bonds (N:**a** Cr dative bonds).  $\triangle H$  of reaction is hence approximately zero.

However, displacement of monodentate NH<sub>3</sub> ligands by bidentate en ligands causes an increase in number of molecules in the system, resulting in an increase in disorderliness and hence  $\Delta$ S is positive.

Since  $\Delta G = \Delta H - T\Delta S$ ,  $\Delta G$  is always negative, accounting for spontaneity of ligand exchange.

[7]

[3]

(b) Explain why carbon dioxide is evolved when Na<sub>2</sub>CO<sub>3</sub>(aq) is added to A in III.
 Include any relevant equations in your answer. [2]

 $Cr^{3+}$  ion has a high charge density and high polarising power. Hence  $[Cr(H_2O)_6]^{3+}$  can undergo hydrolysis in water, polarising and weakening the O-H bonds of surrounding H<sub>2</sub>O molecules, to release H<sup>+</sup> ions. H<sup>+</sup> ions react with carbonate ions via acid-base reaction to form CO<sub>2</sub>.

 $[Cr(H_2O)_6]^{3+}(aq) \neq [Cr(OH)(H_2O)_5]^{2+}(aq) + H^+(aq)$ 

 $2H^{+}(aq) + CO_{3}^{2-}(aq) \ge CO_{2} + H_{2}O$ 

(c) Explain why aqueous solutions of chromium ions are coloured.

In the presence of ligands, the partially filled, originally degenerate 3d orbitals of Cr split into two different sets of energy, separated by a small energy gap  $\Delta E$ . An electron from the lower energy d-orbital absorbs a specific wavelength of light from the visible light spectrum corresponding to  $\Delta E$  and is promoted to a higher energy d-orbital, undergoing d to d electron transition. The colour absorbed is complementary to colour observed.

(d) In a separate experiment, a chemist prepared two compounds with the general formula CrCl<sub>3</sub>.6H<sub>2</sub>O. Upon adding AgNO<sub>3</sub>(aq) to aqueous solutions of compounds E and F separately, he noted the following:

Solution containing	Amount of AgC <i>l</i> precipitated per mole of compound	
Compound E	1	
Compound F	2	

Based on these observations, deduce the formula of compounds **E** and **F** in the solutions. Explain your answer. [3]

Formula of E: [Cr(H<sub>2</sub>O)<sub>4</sub>Cl<sub>2</sub>]Cl.2H<sub>2</sub>O

Formula of F: [Cr(H<sub>2</sub>O)<sub>5</sub>Cl]Cl<sub>2</sub>.H<sub>2</sub>O

Only free chloride ions can be precipitated as AgC*l*. Chloride ions coordinated to Cr<sup>3+</sup> as ligands cannot be precipitated.

OR:

E contains 1 free  $Cl^-$  ion, which can be precipitated as AgCl by Ag<sup>+</sup>. F contains 2 free  $Cl^-$  ions, which can be precipitated as AgCl by Ag<sup>+</sup>.

[Total: 15]

4 In the vapour phase, ethanoic acid associates to form dimers and an equilibrium is established as shown.

 $2CH_3COOH(g) \rightleftharpoons (CH_3COOH)_2(g)$ 

At 177 °C and 1 atm, 0.084 g of the equilibrium mixture occupies 37.8 cm<sup>3</sup>.

(a) (i) Calculate the average relative molecular mass of the gaseous mixture, giving your answer to 1 decimal place.

 $(101000)(37.8 \times 10^{-6}) = \frac{0.084}{\text{average M}_r} (8.31)(177 + 273)$ Average M<sub>r</sub> = 82.3

(ii) Calculate the proportion of ethanoic acid and its dimer in the equilibrium mixture.

Let fraction of CH<sub>3</sub>COOH in mixture be x and that of  $(CH_3COOH)_2$  be (1 - x).

60x + 120(1 - x) = 82.3x = 0.628

Fraction of CH<sub>3</sub>COOH in mixture = 0.628Fraction of (CH<sub>3</sub>COOH)<sub>2</sub> in mixture = 0.372

(iii) Hence, calculate the value of  $K_p$  for the dimerisation of ethanoic acid at 177 °C, giving its units.

$$K_{\rm p} = \frac{{\sf P}_{({\sf CH}_3{\rm COOH})_2}}{{({\sf P}_{{\sf CH}_3{\rm COOH}})^2}}$$
$$= \frac{0.372 \,{}^{\prime}\,1}{{(0.628 \,{}^{\prime}\,1)^2}}$$
$$= 0.943 \,\,{\rm atm}^{-1}$$

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(c) State and explain the effect of an increase in temperature on the average  $M_r$  of the equilibrium mixture. [3]

The dimerisation of CH<sub>3</sub>COOH is an exothermic process as it involves the formation of two hydrogen bonds.

According to Le Chatelier's Principle, increasing the temperature favours an endothermic reaction. Thus, position of equilibrium shifts to the left. There will be a greater proportion of  $CH_3COOH$  in the reaction mixture, causing the average  $M_r$  of the reaction mixture to decrease.

[Total: 7]

**5** Cinnamaldehyde is an essential oil with the distinctive odour of cinnamon.



## cinnamaldehyde

(a) Sketch the shapes of the hybrid orbitals around one carbon atom in the cinnamaldehyde molecule, indicate clearly the hybridisation of the carbon atom.[1]



- (b) A yellow oil is suspected to be cinnamaldehyde.
  - (i) Assuming the oil is cinnamaldehyde, complete the table below, giving the reagent and conditions to confirm the presence of the two functional groups. Give the expected observation for each test.

Functional group	Reagent and conditions	Expected observation
alkene	Br₂(aq)	Orange/ reddish- brown Br₂(aq) decolourises.
aldehyde	Tollens' reagent and warm Or Fehling's solution and warm	Silver mirror observed. Or Brick red precipitate observed.

(ii) Write an equation for the reaction between cinnamaldehyde with the reagent you have chosen to test for presence of the aldehyde.

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\begin{array}{l} C_{6}H_{5}CH=CHCHO\ +\ 2Ag^{+}\ +\ 3OH^{-} \rightarrow C_{6}H_{5}CH=CHCOO^{-}\ +\ 2Ag\ +\ 2H_{2}O\\ Or\\ C_{6}H_{5}CH=CHCHO\ +\ 2Cu^{2+}\ +\ 5OH^{-} \rightarrow C_{6}H_{5}CH=CHCOO^{-}\ +\ Cu_{2}O\ +\ 3H_{2}O \end{array}
```

[3]

(c) Cinnamaldehyde undergoes electrophilic addition with hydrogen bromide according to the equation as shown.



Draw the mechanism of the reaction and explain why the product obtained does **not** rotate the plane of polarised light. [4]



The reaction takes place with the formation of a carbocation. The C atom bearing the positive charge has a trigonal planar arrangement. There is equal likelihood of the Br<sup>-</sup> attacking from above and below the plane. Thus, resulting in the formation of a racemic mixture (equimolar quantities of the two enantiomers) in which the optical activity cancels out.

[Total: 8]

6 (a) Tyrosine, one of the 20  $\alpha$ -amino acids commonly found in proteins, was discovered in 1846 by German chemist Justus von Liebig in the protein casein from cheese. It has the following structure.



The Hell-Volhard-Zelinskii reaction is the one of oldest methods of  $\alpha$ -amino acids synthesis. It involves  $\alpha$  bromination of a carboxylic acid by treatment with Br<sub>2</sub> and PBr<sub>3</sub>, followed by the conversion of the  $\alpha$ -bromo acid to the  $\alpha$ -amino acid.

 $R-CH_2CO_2H \xrightarrow{I. Br_2, PBr_3} R-CHBrCO_2H \xrightarrow{II} R-CH(NH_2)CO_2H$ 

(i) Give the structure of the carboxylic acid that could be converted to tyrosine by the above reaction scheme.

(ii) Suggest reagent and condition for step II.

#### Excess NH<sub>3</sub> in ethanol, heat in sealed tube

The yield of the amino acid obtained in step **II** of the above reaction scheme tends to be low. A better method is to carry out the Gabriel amine synthesis, which involves the use of phthalimide as shown.



(iii) State the role of KOH in step A.

### KOH acts as a base to deprotonate the phthalimide.

(iv) What is the type of reaction in step **B**?

### **Nucleophilic substitution**

(v) Suggest a reason for the low yield of the amino acid obtained in step II of Hell-Volhard-Zelinskii the reaction. Hence, explain how the use of phthalimide in Gabriel amine synthesis would give a higher yield.

Multiple substitution (alkylation) may occur, giving a mixture of 2° amine, 3° amine and possibly an quaternary ammonium salt, instead of the desired 1° amine. By having N bonded to two CO groups, multiple alkylation cannot take place, hence a higher yield is obtained.

(vi) The protons of amide (-CONH<sub>2</sub>) are not known to be acidic ( $pK_a > 500$ ). Explain why the proton of phthalimide is acidic ( $pK_a = 8.3$ ).

The presence of the two electron withdrawing CO group helps to disperse the negative charge on the anion / the negative charge of the anion formed from deprotonation can be delocalised with the pi electron system of the two CO groups. This stabilises the anion, making it acidic.

(vii) Give the structure of the other organic product obtained when alkaline hydrolysis is carried out in step **C** of the Gabriel amine synthesis.



[9]

(b) The three  $pK_a$  values associated with tyrosine are 2.20, 9.11 and 10.13.

Make use of these  $pK_a$  values to suggest the major species present in solutions of tyrosine with the following pH values.

pH 1



pH 6



pH 11



[3]

[Total: 12]

**7** Benzoic acid can be prepared by the oxidation of benzaldehyde using alkaline potassium manganate(VII) as described below.

Data about the benzaldehyde and benzoic acid are given below.

compound	density / g cm <sup>-3</sup>	melting point / °C	boiling point / °C
benzaldehyde	1.05	-26	179
benzoic acid	1.27	122	229

## Preparation of impure benzoic acid

- 1 Place 2.00 g of solid potassium manganate(VII), 30 cm<sup>3</sup> of 1 mol dm<sup>-3</sup> sodium hydroxide and 1.5 cm<sup>3</sup> of benzaldehyde in a round-bottomed flask. Swirl the flask carefully to mix the contents thoroughly.
- 2 Fit a reflux condenser onto the round-bottomed flask and boil the mixture gently for 10 minutes.
- 3 Filter off the brown precipitate of manganese(IV) oxide formed, collect the filtrate in a 100 cm<sup>3</sup> beaker and allow the filtrate to cool.
- 4 Carefully add concentrated hydrochloric acid, with constant swirling, to the filtrate till the mixture is acidic enough to precipitate the benzoic acid.
- (a) By means of two ion-electron half-equations, write an equation for the oxidation of benzaldehyde by alkaline potassium manganate(VII). [2]

 $C_6H_5CHO + 3OH^- \rightarrow C_6H_5CO_2^- + 2H_2O + 2e$ 

 $MnO_4^{\text{-}} + 3e + 2H_2O \rightarrow MnO_2 + 4OH^{\text{-}}$ 

 $3C_6H_5CHO + OH^- + 2MnO_4^- \rightarrow 3C_6H_5CO_2^- + 2MnO_2 + 2H_2O$ 

(b) Show by calculation, which reagent, benzaldehyde or potassium manganate(VII), is in excess. [2]

Amount of benzaldehyde used = (1.5 x 1.05) / 106 = 0.0149 mol

Amount of KMnO<sub>4</sub> used = 2.00 / 158 = 0.0127 mol

2 mol of KMnO<sub>4</sub>  $\equiv$  3 mol C<sub>6</sub>H<sub>5</sub>CHO

0.0127 mol of KMnO<sub>4</sub> ≡ 0.01905 mol of C<sub>6</sub>H<sub>5</sub>CHO

Potassium manganate(VII) is in excess.

(c) Draw a diagram of the assembled apparatus for heating under reflux. Indicate clearly how water enters and leaves the condenser. [2]



## Purification of impure benzoic acid

- 5 Filter the benzoic acid that has been precipitated and wash it once with cold water.
- 6 The crude benzoic acid product is purified by recrystallisation from water.
- 7 Filter the recrystallised solid, wash with water and dry the solid by pressing it under several layers of filter paper.
- 8 Weigh the solid obtained.

(d) Give a description of the procedure you would use to purify the crude benzoic acid.

Dissolve the crude benzoic acid in a minimum volume of hot water. Cool the hot saturated solution to obtain the crystallised product.

(e) Explain how you would check for purity of the benzoic acid.

Purity of benzoic acid can be checked by melting point determination. Pure benzoic acid should melt very sharply at 122°C.

(f) Given that 1.40 g of benzoic acid is obtained from the preparation, calculate the percentage yield of the reaction.

Theoretical yield = 0.0149 x 122 = 1.818 g

Percentage yield = (1.40 / 1.818) x 100 = 77.0%

[Total: 9]

**END OF PAPER**