Section B

Answer **all** questions on foolscap paper.
Begin each question on a fresh page of writing paper.

1 **(a)** Many carboxylic acids are produced industrially on a large scale and are often involved in the production of polymers, pharmaceuticals, solvents and food additives.

The acidities of 2-chlorobutanoic acid and 2-fluorobutanoic acid are compared with butan-1-ol. Arrange the three compounds in order of increasing acidity. Explain your answer.

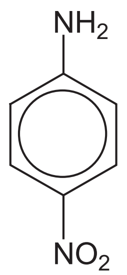
2-chlorobutanoic acid	2-fluorobutanoic acid	butan-1-ol
$CH_3CH_2CH(Cl)CO_2H$	$CH_3CH_2CH(F)CO_2H$	$CH_3CH_2CH_2CH_2OH$

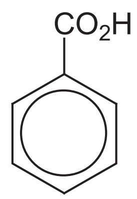
[5]

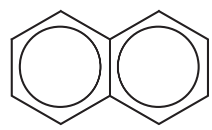
(b) Suggest a simple chemical test to distinguish butan-1-ol and 2-chlorobutanoic acid. State the reagent and condition for the test, and the observation you would expect to make.

[2]

(c) Solvent-solvent extraction is a widely employed method to obtain organic compounds from mixtures. A 0.2 g solid mixture containing 4-nitrophenylamine, benzoic acid and naphthalene was dissolved in 2 cm^3 of dichloromethane.


4-nitrophenylamine


benzoic acid


naphthalene

[4-nitrophenylamine is a base of low solubility in water.]

To extract one of the organic compounds from the dissolved mixture, 2 cm^3 of aqueous NaOH was subsequently added and the mixture was shaken vigorously. As dichloromethane and water are immiscible, the mixture separated into two layers.

Layer	Solvent	Formula	Density / g cm^{-3}	Boiling point / °C
Organic	Dichloromethane	CH_2Cl_2	1.33	39.6
Aqueous	Water	H_2O	1.00	100

(i) Explain which layer is on top.

(ii) State the type of reaction that occurred upon addition of aqueous NaOH. Write an equation for the reaction.

(iii) Suggest which of the three compounds was extracted by the aqueous layer. Explain.

The aqueous layer was removed from the organic layer and cooled in an ice bath. HCl was gradually added to the layer and the solid formed was isolated by filtration.

(iv) Suggest the role of ice bath.

(v) Explain the difference in boiling points between the two solvents, dichloromethane and water.

(vi) Suggest why dichloromethane is a suitable solvent in this experiment, apart from its ability to dissolve all three organic compounds.

[9]

(d) Volumetric analysis was conducted on a 2 g solid mixture of 4-nitrophenylamine, benzoic acid and naphthalene. 4-nitrophenylamine is a base of low solubility in water.

30 cm^3 of 0.5 mol dm^{-3} NaOH was added to the solid mixture. The reaction mixture was filtered and the filtrate diluted to 100 cm^3. 17.00 cm^3 of 0.1 mol dm^{-3} HCl was needed to react with the excess NaOH in a 25 cm^3 aliquot of diluted solution.

When excess acid was added to the residue from the previous step, 0.44 g of unreacted solid naphthalene was recovered.

(i) Calculate the amount of unreacted NaOH in 100 cm^3 of diluted filtrate.

(ii) Hence calculate the percentage of 4-nitrophenylamine in the mixture.

[M_r: benzoic acid, 122.0; 4-nitrophenylamine, 138.0; naphthalene, 128.0]

[4]

[Total: 20]

Answers to 2014 JC1 H1 Promotional Examination

Section B

Answer **all** questions on foolscap paper.
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1 **(a)** Many carboxylic acids are produced industrially on a large scale and are often involved in the production of polymers, pharmaceuticals, solvents and food additives.

The acidities of 2-chlorobutanoic acid and 2-fluorobutanoic acid are compared with butan-1-ol. Arrange the three compounds in order of increasing acidity. Explain your answer.

$CH_3CH_2CH(Cl)CO_2H$	$CH_3CH_2CH(F)CO_2H$	$CH_3CH_2CH_2CH_2OH$
2-chlorobutanoic acid	2-fluorobutanoic acid	butan-1-ol

[5]

- **Order of acidity:**
  butan-1-ol< 2-chlorobutanoic acid <2-fluorobutanoic acid
- **[General explanation] Acid strength is dependent on stability of anion, for more stable anions, protons leave the acid molecules more readily and the acids are stronger.**
- **The carboxylic acidsare stronger as there is <u>delocalisation of negative charge</u> (or electrons) <u>over the two oxygen atoms in the carboxylate ion. The negative charge is dispersed</u>, stabilizing the anion.**
- **The negative charge is confined on the oxygen atom of the butoxideand is <u>intensified by electron releasing alkyl group</u>, making the butoxide ion less stable. Thus butan-1-ol is the weakest acid.**
- **2-fluorobutanoic acid is a stronger acid than 2-chlorobutanoic acid as <u>F atom is a stronger electron withdrawing group</u> (or F is more electronegative). <u>The negative charge on the anion is more dispersed</u>, thereby stabilizing the ion.**

(b) Suggest a simple chemical test to distinguish butan-1-ol and 2-chlorobutanoic acid. State the reagent and condition for the test, and the observation you would expect to make.

[2]

- **Add aqueous sodium carbonate, room temperature, to the compounds separately**
- **Effervescence of CO_2 will be observed for 2-chlorobutanoic acid only**

Or

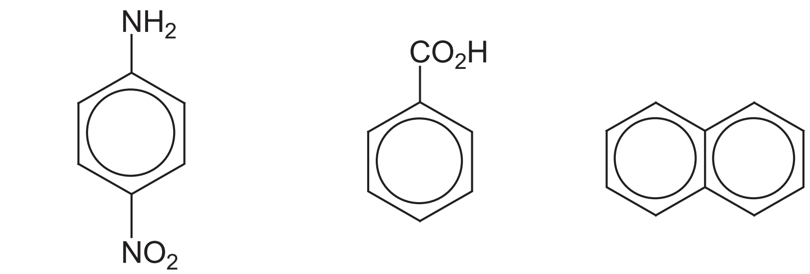
- **Add acidified $KMnO_4$, with heating, to the compounds separately**
- **Decolorisation of purple $KMnO_4$observed for butan-1-ol**

Or

- **Add acidified $K_2Cr_2O_7$, with heating, to the compounds separately**
- **$K_2Cr_2O_7$ changes from orange to green for butan-1-ol**

Note: Accept also tests on chloroalkanes for 2-chlorobutanoic acid

(c) Solvent-solvent extraction is a widely employed method to obtain organic compounds from mixtures. A 0.2 g solid mixture containing 4-nitrophenylamine, benzoic acid and naphthalene was dissolved in 2 cm^3 of dichloromethane.



4-nitrophenylamine   benzoic acid   naphthalene

[4-nitrophenylamine is a base of low solubility in water.]

To extract one of the organic compounds from the dissolved mixture, 2 cm^3 of aqueous NaOH was subsequently added and the mixture was shaken vigorously. As dichloromethane and water are immiscible, the mixture separated into two layers.

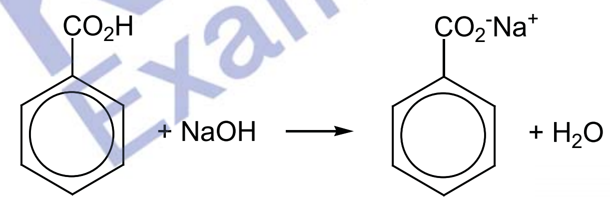
Layer	Solvent	Formula	Density / g cm^{-3}	Boiling point / °C
Organic	Dichloromethane	CH_2Cl_2	1.33	39.6
Aqueous	Water	H_2O	1.00	100

(i) Explain which layer is on top.

- **<u>Aqueous</u> layer, since water has a <u>lower density</u>.**

(ii) State the type of reaction that occurred upon addition of aqueous NaOH. Write an equation for the reaction.

- **<u>Neutralisation</u> took place between NaOH and benzoic acid, forming the salt, sodium benzoate, and water.**



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(iii) Suggest which of the three compounds was extracted by the aqueous layer. Explain.

- **Benzoic acid**
- **Sodium benzoate (formed from reaction with NaOH) formed <u>ion-dipole interactions</u> with water which released sufficient energy to overcome the strong ionic bonds in sodium benzoate and hydrogen bonds in water, making it <u>soluble in the aqueous</u> medium.**

Note: The salt sodium benzoate is charged and has a decreased solubility in dichloromethane. This facilitates the extraction of the salt into the aqueous medium.

The aqueous layer was removed from the organic layer and cooled in an ice bath. HC*l* was gradually added to the layer and the solid formed was isolated by filtration.

(iv) Suggest the role of ice bath.

- **To decrease the solubility of benzoic acid solid formed through lowering the temperature so as to obtain a higher yield.**

(v) Explain the difference in boiling points between the two solvents, dichloromethane and water.

•• [1 mark for structure and bonding, 1 mark for explanation]

Both compounds have simple molecular structure. A larger amount of energy is required to overcome the stronger hydrogen bonds between water molecules, compared to the weak van der Waals forces between dichloromethane molecules. Thus water has a much higher boiling point.

(vi) Suggest why dichloromethane is a suitable solvent in this experiment, apart from its ability to dissolve all three organic compounds.

[9]

- **It can be easily removed/heated off to obtain the pure compounds due to its low boiling point.**

(d) Volumetric analysis was conducted on a 2 g solid mixture of 4-nitrophenylamine, benzoic acid and naphthalene. 4-nitrophenylamine is a base of low solubility in water.

30 cm^3 of 0.5 $mol dm^{-3}$ NaOH was added to the solid mixture. The reaction mixture was filtered and the filtrate diluted to 100 cm^3. 17.00 cm^3 of 0.1 $mol dm^{-3}$ HC*l* was needed to react with the excess NaOH in a 25 cm^3 aliquot of diluted solution.

When excess acid was added to the residue from the previous step, 0.44 g of unreacted solid naphthalene was recovered.

(i) Calculate the amount of unreacted NaOH in 100 cm^3 of diluted filtrate.

- **No. of moles of unreacted NaOH in 25 cm^3**
  = No. of moles of HC*l*
  $= \frac{17}{1000} \times 0.1 = 1.70 \times 10^{-3}$ mol

- **No. of moles of unreacted NaOH in 100 cm^3**
  $= 1.70 \times 10^{-3} \times 4 = 6.80 \times 10^{-3}$ mol

(ii) Hence calculate the percentage of 4-nitrophenylamine in the mixture.

[M_r: benzoic acid, 122.0; 4-nitrophenylamine, 138.0; naphthalene, 128.0]

[4]

- **No. of moles of benzoic acid**
  = No. of moles of reacted NaOH
  $= \frac{30}{1000} \times 0.5 - 6.80 \times 10^{-3}$
  $= 8.20 \times 10^{-3}$ mol

Mass of benzoic acid
$= 8.20 \times 10^{-3} \times 122.0$
$= 1.00$ g

- % mass of 4-nitrophenylamine
  $= \frac{2-1-0.44}{2} \times 100$
  $= 28.0\%$

[Total: 20]