Section A

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

For Examiner's use

1 Under conditions of low pH, potassium manganate(VII) $KMnO_4$ would react with Fe^{2+} solutions according to the relevant half-equations given below.

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$

(a) **(i)** Use oxidation numbers to explain why this reaction is described as a redox reaction.

+7 O.N. in MnO_4^- is reduced to +2 in Mn^{2+}.

+2 O.N. in Fe^{2+} is oxidised to +3 in Fe^{3+}.

(ii) Use the half-equations given above to construct an ionic equation for the reaction between MnO_4^- ions and Fe^{2+} ions in acid solution. [3]

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

(b) A nail of mass 1.40 g was dissolved in an excess of dilute sulfuric acid to form 100 cm^3 of solution. A 10.0 cm^3 sample of this solutions required 4.0×10^{-4} mol of manganate(VII) ions for complete reaction.

By assuming that, in dissolving the nail in dilute sulfuric acid, the iron in the nail was converted entirely into Fe^{2+} (aq) ions,

(i) Calculate the number of moles of Fe^{2+} produced in 100 cm^3 of solution.

No mol of Fe^{2+} in 10 cm^3 sample
= $5 \times 4.0 \times 10^{-4}$ mol
= 2.00×10^{-3} mol

No mol of Fe^{2+} in 100 cm^3 of solution produced from the nail
= $10 \times 2.00 \times 10^{-3}$ mol
= 2.00×10^{-2} mol

(ii) Hence determine the percentage of iron in the nail. [3]

% of iron in the nail
$= 2.00 \times 10^{-2} \times 55.8/1.40 \times 100$
= 79.7 %

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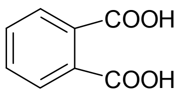
(c) **(i)** The percentage by mass of compound **X** is 57.8% C, 3.6% H and 38.6% O. Determine the empirical formula of **X**. [1]

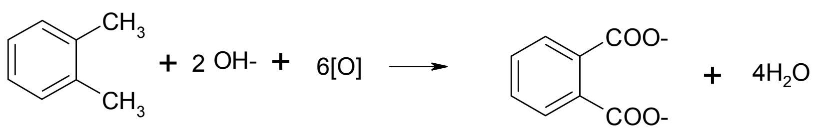
Element	**C**	**H**	**O**
% by mass	**57.8**	**3.6**	**38.6**
A_r	**12.0**	**1.0**	**16.0**
$\frac{\%\ by\ mass}{A_r}$	**4.817**	**3.6**	**2.415**
Simplest ratio	**2 = 4**	**3/2 =3**	**1 =2**

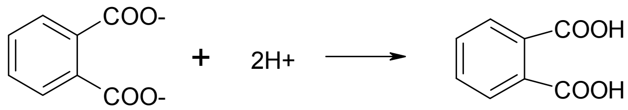
Empirical formula = $\underline{C_4H_3O_2}$

(ii) This organic compound **X** is formed by heating 1,2 dimethylbenzene under reflux with an alkaline solution of manganate(VII) ions, followed by acidification. Give the structure of **X** and balanced equations for the reactions. [3]



X





[Total: 10]

For Examiner's use

2 **(a)** A sample of vinegar contains 3 % by mass of ethanoic acid.

The K_a of ethanoic acid is 1.78×10^{-5} mol dm^{-3}.

(i) What do you understand by the term K_a *of ethanoic acid*?

For weak acid, CH_3COOH,

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

The acid dissociation constant, K_a, is given by

$$K_a = \frac{[H_3O^+(aq)][CHCOO^-(aq)]}{[CH_3COOH(aq)]} \quad \text{mol dm}^{-3},$$

and is a constant at a given temperature

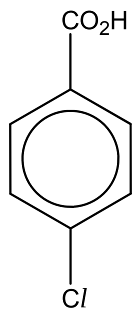
(ii) Assuming that the density of vinegar is 0.985 g cm^{-3}, calculate the concentration (in mol dm^{-3}) of ethanoic acid in vinegar.

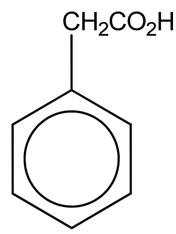
Mass of CH_3COOH in 1 cm^3 of vinegar = 0.03 x 0.985 =0.02955 g
Amt of CH_3COOH in 1 cm^3 of vinegar
= 0.02955 $\div$ 2(12.0)+2(16.0)+4(1.0)
= 4.925×10^{-4} mol
Concentration of CH_3COOH in vinegar = 4.925×10^{-4} mol cm^{-3}
= 0.4925 mol dm^{-3}
= 0.493 mol dm^{-3}

(iii) 10.0 cm^3 of the vinegar solution was titrated against 0.500 mol dm^{-3} of aqueous sodium hydroxide using a suitable indicator.
Calculate the volume of sodium hydroxide that is required to completely neutralise the ethanoic acid in the vinegar. [4]

Amt of NaOH required = Amt of CH_3COOH present
= 0.4925 x 0.01 = 4.925×10^{-3} mol
Volume of NaOH required = 4.925×10^{-3} $\div$ 0.500
= 9.85×10^{-3} dm^3 = 9.85 cm^3

(b) 4-chlorobenzoic acid and phenylethanoic acid are two compounds containing benzene rings. Both compounds are not particularly soluble in water under room temperature conditions. [2]





4-chlorobenzoic acid **phenylethanoic acid**

State and explain which of these two acids is more acidic.

4-Chlorobenzoic acid is more acidic.

Strength of acid depends on the relative stability of its conjugate base.

4-Chlorobenzoic acid forms the more stable conjugate base as there is an extra electron-withdrawing Cl on the benzene ring which helps to further disperse the negative charge on the conjugate base it forms, making it more stable.

OR

4-Chlorobenzoic acid contains an extra Cl substituent group attached to the 4^{th} position of the benzene ring which is electron-withdrawing, it better withdraws the electron cloud in
the O- H bond of the carboxyl group, making it more polarized.

As such, it undergoes dissociation more readily to form the H^+ ions, making it more acidic.

(c) Phenol is a monoprotic acid commonly used as an active ingredient in household disinfectants. A solution of phenol in water containing 2.50 mol dm^{-3} has a pH of 4.8.

(i) Explain, with the aid of appropriate calculations, whether phenol is a strong or weak acid.

pH = 4.8; $\therefore [H^+] = 10^{-4.8} = \underline{1.58 \times 10^{-5} \text{ mol dm}^{-3}}$

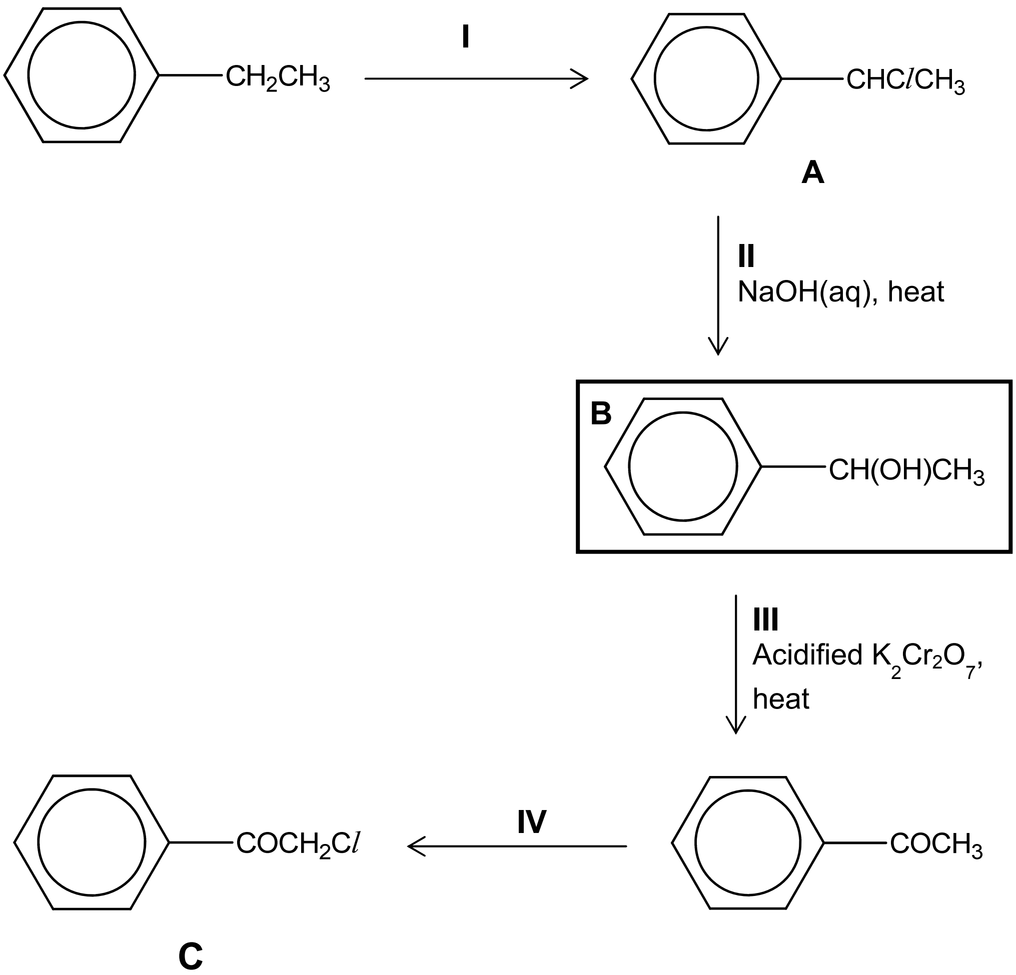
<u>Phenol is a weak acid</u> as <u>$[H^+]$ is much lower</u> than the concentration of the phenol solution (or) $[H^+] \neq$ [phenol].

(ii) Use the data given to calculate the value of K_a of phenol. [3]

$K_a = [H^+]^2 / [HA] = (1.58 \times 10^{-5})^2 / 2.50 = \underline{9.99 \times 10^{-11}} \text{ mol dm}^{-3}$

[Total: 9]

3 Chloroacetophenone (compound **C**, below) was formerly the most widely used tear gas, under the code name *CN*. It was used in warfare and in riot control. It can be synthesised from ethylbenzene, by the following sequence of reactions below.



(a) In the appropriate box draw the structure **B**. [1]

(b) For the reaction in the scheme shown above, state

The reagents and conditions for reaction **I**

C*l*$_2$, uv light

The type of reaction in reaction **I**

Free radical substitution

The type of reaction in reaction **II** [3]

Nucleophilic substitution

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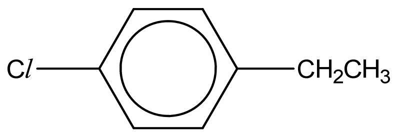
(c) **(i)** Suggest reagents and conditions for converting ethylbenzene into compound **D**, an isomer of **A**.



D

Cl_2, $AlCl_3$

(ii) Describe in terms of orbital overlap, the bonding of the two carbon atoms of the carbon-carbon bond in the benzene ring of ethylbenzene, with the aid of a clearly labelled diagram. [4]

(Drawings) of C-C p-orbitals side on overlap for ring and of C-C sp^2-orbitals head-on overlap

With drawing, labelling/mention of σ bond and π bond/orbital

(d) The efficiency of a tear gas is expressed by its 'Intolerable Concentration', I.C. The I.C. of the tear gas *CN* has been measured as 0.030 g m^{-3} of air. How many moles of chloroacetophenone need to be sprayed into a room of volume 60 m^3 in order to achieve this concentration? [2]

M_r of *CN* = (8 x 12.0) + 7x1.0 + 16.0 + 35.5 = 154.5

Mass of *CN* in 60 m^3 = 0.03x60 = 1.8 g

No of moles of *CN* = 1.8/154.5 = 0.01165 = 0.117

[Total: 10]

For Examiner's use

4 Hydrazine, N_2H_4, is a popular choice of fuel with NASA as CO_2 is not produced in the process. The stored hydrazine is passed over a suitable catalyst and decomposes to its elements. This rapid production of hot gaseous elements provides the thrust required. In the decomposition process, ammonia can also be formed as an intermediate.

In August 2012, the Mars Curiosity rover landed on Mars with the use of variable thrust mono-propellant hydrazine rocket thrusters.

The use of hydrazine as a fuel has been extended for use in aircraft as well. The first ever rocket-powered fighter plane, the Messerschmitt Me 163 *Komet*, was capable of performance unrivaled during that time. It reached a top speed of 1130 km/h in early July 1944 which was not broken until November 1947. The *Komet* was powered by the reaction between a hydrazine-methanol mixture and hydrogen peroxide.

Hydrazine is commonly combined with dinitrogen tetraoxide, N_2O_4, in rocket fuels. These reactants form a hypergolic mixture, which ignites spontaneously upon contact. NASA has used N_2H_4/N_2O_4 in many space vehicles and is likely to extend its usage to next-generation vehicles.

(a) Write a balanced equation for hydrazine decomposing to form ammonia and nitrogen gas. [1]

$3N_2H_4 \rightarrow N_2 + 4NH_3$

(b) Hydrazine may be obtained from the reaction between ammonia and hydrogen peroxide.

$2NH_3(g) + H_2O_2(l) \rightarrow N_2H_4(l) + 2H_2O(l)$

Given the following standard enthalpy changes, calculate the standard enthalpy change of the above reaction. [2]

	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
NH_3 (g)	- 46.1
H_2O_2 (l)	-187.8
N_2H_4 (l)	+50.6
H_2O (l)	-285.8

$\Delta H_r^{\ominus} = \sum\Delta H_f^{\ominus}$ (products) - $\sum\Delta H_f^{\ominus}$ (reactants)
$=[+50.6+ 2(-285.8)] – [2(-46.1) + (-187.8)]$
$=-241$ kJmol^{-1}

(c) In the *Komet*, the hydrogen peroxide and hydrazine-methanol mixture react to propel the plane.

Hydrogen peroxide reacts with hydrazine as shown in the equation.

$$N_2H_4(l) + 2H_2O_2(l) \rightarrow N_2(g) + 4H_2O(l)$$

(i) State the oxidation number of nitrogen and oxygen in the reactants and products.

For

	N_2H_4	H_2O_2	N_2	H_2O
Oxidation state of N	**-2**		**0**	
Oxidation state of O		**-1**		**-2**

Examiner's use

(ii) A fully filled fighter plane carries 225 litres of hydrazine and 862 litres of methanol. Using the data below, calculate the total heat evolved under standard conditions for combustion of this quantity of rocket fuel. Assume that all the hydrazine and methanol are fully combusted. [5]

	$\Delta H_c^\ominus$ / kJ mol^{-1}	Density/ g cm^{-3}
$N_2H_4\,(l)$	-622.2	1.02
$CH_3OH(l)$	-726.0	0.792

Amount of hydrazine = 225000 x 1.02/32.0 = <u>7171.875 mol</u>

Amount of methanol = 862000 x 0.792/32.0 = <u>21334.5 mol</u>

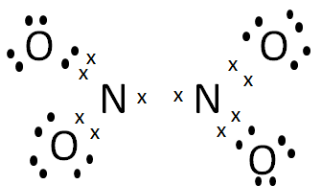
Total heat evolved = 7171.875 x 622.2 + 21334.5 x 726.0
= <u>19.9 x 10^6</u> kJ

(d) Products of reactions used in rocketry need to be chemically stable (making the reaction exothermic) and gaseous (to provide thrust).

(i) Suggest the reaction products that are formed in the reaction between N_2H_4 and N_2O_4 in the hypergolic mixture found in rockets.

N_2 and **H_2O**

(ii) Upon warming, pure N_2O_4 does not break down into its elements but produces a brown gas. Draw the 'dot and cross' structure of N_2O_4 and hence suggest the identity of the brown gas. [3]



Brown gas is NO_2.

[Total: 11]