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.

.....

.....

(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]

(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.

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

[3]

For Examiner's use

(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]

(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]

[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*?

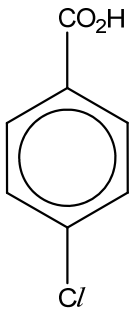
(ii) Assuming that the density of vinegar is 0.985 g cm^{-3}, calculate the concentration (in mol dm^{-3}) of ethanoic acid in vinegar.

(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.

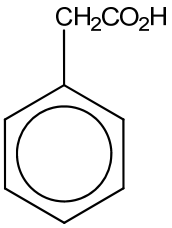
[4]

For Examiner's use

(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.



4-chlorobenzoic acid



phenylethanoic acid

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

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.....

.....

.....

..... [2]

(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.

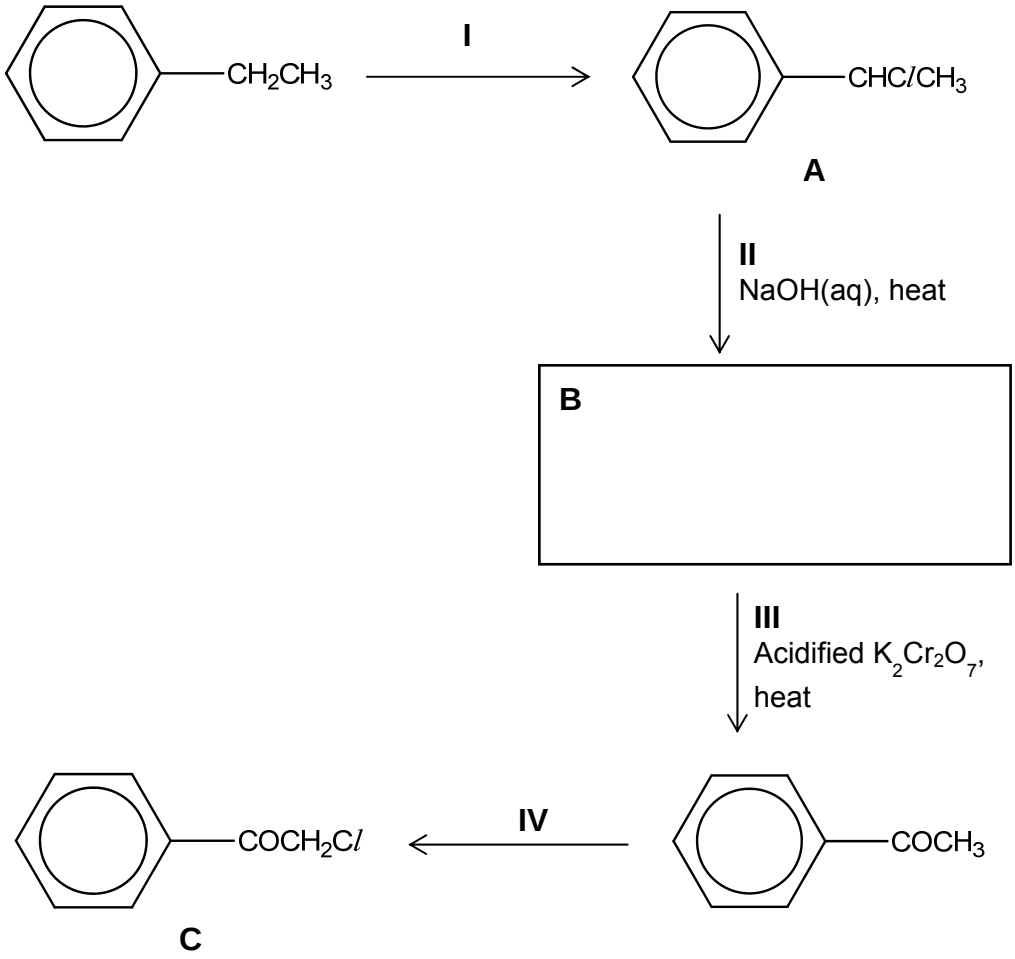
(ii) Use the data given to calculate the value of K_a of phenol.

[3]

[Total: 9]

For Examiner's use

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 shown 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**

.....

The type of reaction in reaction **I**

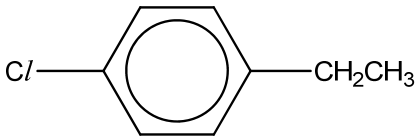
.....

The type of reaction in reaction **II**

..... [3]

For Examiner's use

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



D

.....

(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]

(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]

[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]

(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.

	$\Delta H_f^{\ominus}$ / 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

[2]

For Examiner's use

(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.

	N_2H_4	H_2O_2	N_2	H_2O
Oxidation state of N				
Oxidation state of O				

(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.

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

[5]

(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.

……..

(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]

[Total: 11]