Changes to the Leaving Certificate Chemistry Syllabus with Regard to Experimental Work

Change 1

(i) the preparation of ethanal and **(ii) the preparation of ethanoic acid by the oxidation of ethanol using acidified sodium dichromate** will no longer be examined as experiments (the theory is still required). The reason for this is that sodium dichromate is considered no longer suitable for use in laboratory work as it has been deemed a substance of very high concern by the European Chemicals Agency.

A new experiment has been introduced to replace the above experiments and will be examined at Higher and Ordinary Level from 2015 onwards. This new experiment is outlined below.

New Mandatory Experiment: The oxidation of phenylmethanol (benzyl alcohol) to benzoic acid using the oxidising agent potassium manganate (VII) in alkaline conditions.

INTRODUCTION:

- Benzoic acid may be prepared by the oxidation of phenylmethanol using potassium manganate (VII) in the presence of sodium carbonate (alkaline conditions).
- The balanced equation for the reaction is as follows:

$$3C_6H_5CH_2OH + 4KMnO_4 \rightarrow 3C_6H_5COOH + 4MnO_2 + H_2O + 4KOH$$

N.B. this reaction will be given in the exams.

- During the reaction there is a structural change from the alcohol to the acid as shown in Fig. 1.

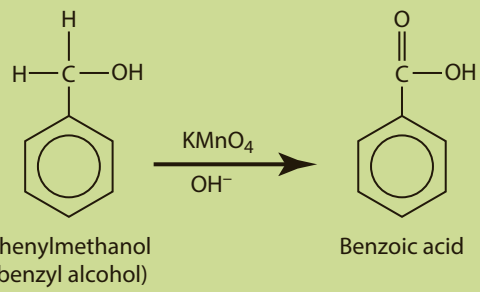

Fig. 1 Phenylmethanol (benzyl alcohol) is oxidised to benzoic acid by potassium manganate.

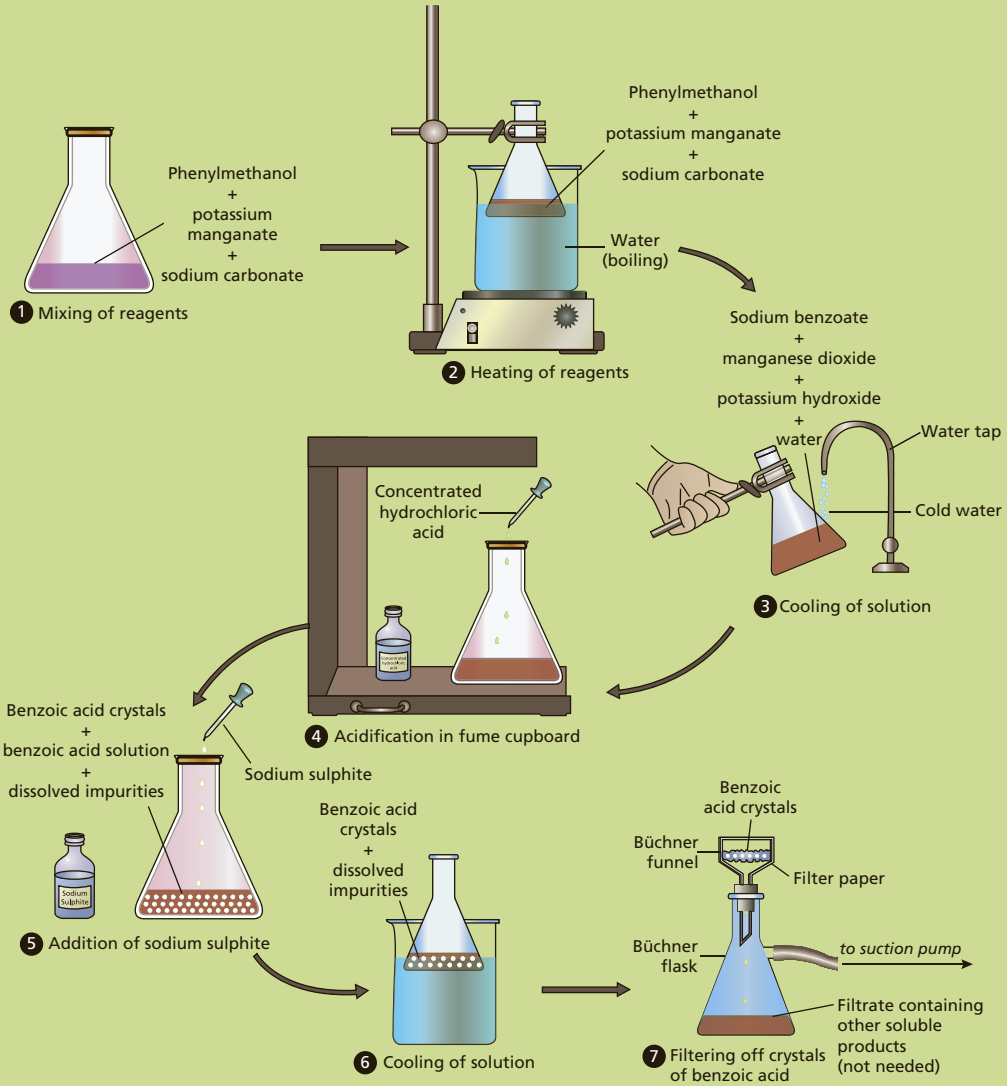

Fig. 2 Summary of steps involved in the oxidation of phenylmethanol (benzyl alcohol) to benzoic acid.

PROCEDURE:

- A solution containing a known mass of phenylmethanol, potassium manganate (VII) and sodium carbonate are heated in a water bath (see step 2 Fig. 2).
- The potassium manganate is present in excess to ensure all the phenylmethanol is oxidised to benzoic acid.
- The sodium carbonate ensures the solution is alkaline as oxidation is faster under alkaline conditions.

- As the reaction proceeds in the conical flask there is a colour change from purple to brown. The reason for this is that the manganese ion is reduced from an oxidation state of +7 in $KMnO_4$ where it is purple to an oxidation state of +4 in MnO_2 where it is brown.
- A brown precipitate of manganese dioxide is formed in the conical flask and this precipitate is not soluble in water.
- The contents of the conical flask are now cooled under a cold water tap (see step 3 Fig. 2).
- Following cooling concentrated hydrochloric acid is added dropwise to the conical flask. This should be carried out in a fume cupboard as hydrochloric acid gives off dangerous fumes. To ensure contents of the flask are acidic dip a glass rod into the solution and see does it turn blue litmus red (see step 4 Fig. 2).
- The addition of concentrated hydrochloric acid is added for three reasons:
  (i) to form benzoic acid from sodium benzoate which is an intermediate product in this reaction
  (ii) to neutralise any excess sodium carbonate and the basic product potassium hydroxide
  (iii) to ensure that the manganese ion is reduced from the brown +4 state to the colourless +2 state.
- Now, using a dropper, sodium sulphite is added until the brown precipitate reacts fully with it. The sodium sulphite is a reducing agent and fully reduces the insoluble solid specks of manganese dioxide that have formed from the +4 state to the colourless +2 state (see step 5 Fig. 2).
- The brown precipitate now disappears and white crystals of benzoic acid are now visible. The solution is now cooled by placing in ice and this further produces benzoic acid crystals as benzoic acid is only slightly soluble in cold water (see step 6 Fig. 2).
- The white crystals of benzoic acid are filtered by pouring the contents of the conical flask through a Büchner funnel (see step 7 Fig. 2).
- The conical flask should be rinsed with the filtrate in the Büchner flask and again passed through the Büchner funnel to ensure all crystals of benzoic have been removed from the conical flask.
- The crystals are washed with ice cold water. This removes any soluble impurities that may be present.
- The damp crystals are allowed to dry overnight and then placed in a dessicator to remove any water still clinging to them.
- The mass of the crystals can be measured and the percentage yield worked out.

Change 2

The properties of ethanal are limited to reactions with:

(i) acidified potassium manganate (VII) solution
(ii) Fehlings reagent
(iii) ammoniacal silver nitrate.

The properties of ethanoic acid are limited to reactions with sodium carbonate and magnesium and ethanol.

Change 3

Two of the three simple experiments to illustrate Le Chatelier's Principle are no longer required. The experiment

$$Fe^{3(+)} + CNS^{-} \quad \leftrightarrow \quad Fe(CNS)^{2(+)}$$

remains to demonstrate the effect of both concentration and temperature changes.

Change 4

The mandatory experiment the steam distillation of crude oil is being extended to include the liquid–liquid extraction of eugenol from the emulsion product using cyclohexane. The structure of eugenol is required at higher level only.

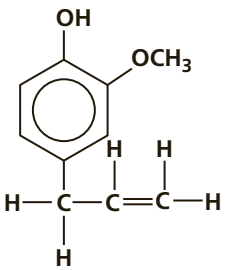

Fig. 3 Eugenol is the main constituent of oil of cloves.

The extra detail in the liquid–liquid extraction is described below.

Experiment: to separate clove oil from an emulsion of clove oil and water by liquid–liquid extraction using cyclohexane.

Theory

- Liquid–liquid extraction (also called solvent extraction) is a method whereby two immiscible liquids e.g. clove oil and water are separated using a solvent e.g. cyclohexane in which one of the liquids in the mixture is more soluble.
- In this extraction the two immiscible liquids are clove oil and water and the solvent is cyclohexane. Clove oil is very soluble in cyclohexane as both are non-polar. Water however is not soluble in cyclohexane as water is polar.

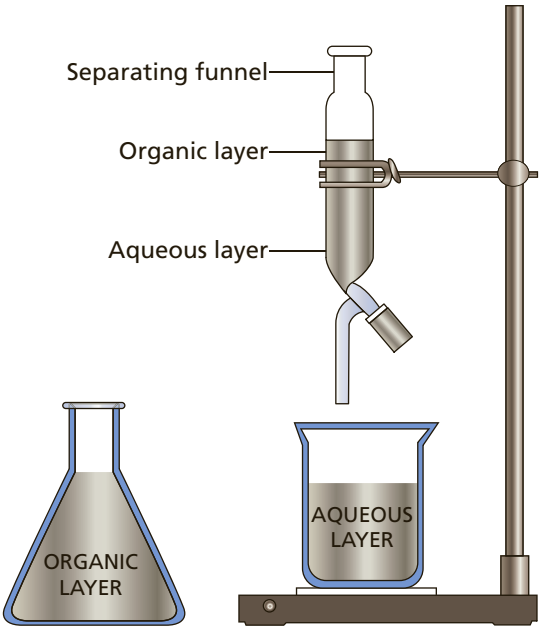

Fig. 4 When cyclohexane is added to the clove oil emulsion, the organic layer floats on the aqueous layer.

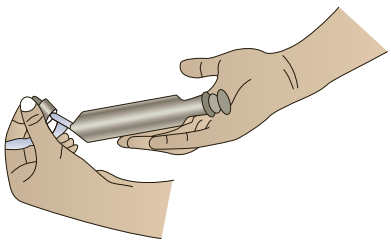

Fig. 5 The separating funnel must be held firmly when in use and the tap opened after shaking to release the pressure of vaporised liquid.

Procedure

- The oil from the emulsion will be extracted three times during the experiment using 10 cm^3 portions of cyclohexane.
- Set up a separating funnel containing about 50 cm^3 of clove oil emulsion. Add 10 cm^3 of cyclohexane to the funnel.
- Two layers are now visible i.e. cyclohexane floats on the water as it is not soluble in water and it is less dense than water.
- Now the two layers are thoroughly mixed. This is achieved by placing a stopper on the funnel, then inverting the funnel and shaking the funnel. It is important to open the tap of the funnel while shaking it to release pressure of vapourised liquid.
- Now place the separating funnel in a retort stand again. Open the tap and release the lower aqueous layer as it contains no clove oil.
- Now add 10 cm^3 of cyclohexane and repeat the mixing and separating procedure. Again release the aqueous layer.
- Repeat mixing and separating for a third addition of 10 cm^3 cyclohexane.