

DETERMINATION OF PHYSICAL PROPERTIES

Determination of the melting point of a solid.

Fit up the apparatus shown in Fig. 1 and support the boiling-tube by means of a clamp and stand so that the bottom is about 8 in. above the bench. Into the boiling-tube pour a suitable liquid (see note 1) to the depth of about $1\frac{1}{2}$ in.

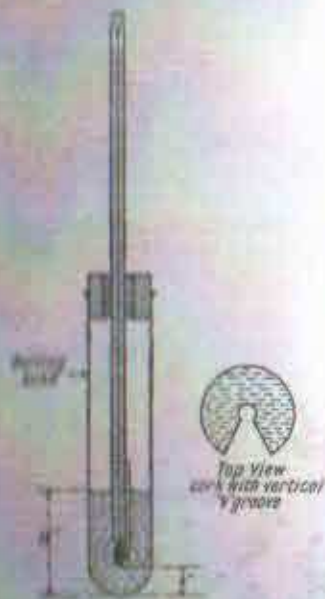


FIG. 1.

Place on a watch-glass a little of the well-dried substance (see note 2) the m.p. of which is to be determined, and powder it finely by pressing and rubbing it with the end of a suitable spatula.

Gently stab the open end of a capillary tube (prepared in the manner described on page 5) several times on to a little heap of the powder, in order to introduce into the tube an amount of substance, which, after tapping the closed end of the tube on the bench each time, finally forms a tightly packed layer, $\frac{1}{8}$ in. - $\frac{1}{4}$ in. deep, at the bottom. (If the substance is waxy in nature a somewhat wider capillary tube may have to be used.)

Proceed similarly with a second capillary tube.

Remove from the boiling-tube the cork and thermometer, and stroke the moistened end of the latter along

the lower portion of the capillary tube, then press the tube against the side of the thermometer so that the substance is opposite the middle of the bulb; the tube will adhere to the thermometer by capillary attraction.

Depress the cork and thermometer, gently heat the liquid with a small flame, and note the temperature at which the solid changes

to a transparent liquid (see note 3); an approximate value of the m.p. is thus obtained.

Carry out a more accurate determination at once, by repeating the procedure with the other capillary tube, raising, degree by degree, the temperature to which the liquid has fallen by periodically waving a small flame (about $\frac{1}{4}$ in. high) under the bottom of the boiling-tube until the m.p. of the solid is reached. With a little practice it is possible to reach, and not exceed or only slightly exceed, a particular temperature. (With this form of apparatus, where the liquid is not stirred, the flame should not be kept continuously under the boiling-tube, or the thermometer will register a temperature which is actually below that of the liquid.)

For each determination a freshly packed capillary tube should be used.

NOTES.

(1) For temperatures up to about 210° medicinal paraffin or glycerol are suitable and reasonably safe liquids to use.

For temperatures up to about 260° fresh concentrated sulphuric acid may be used, a crystal of KNO_3 being added to oxidise charred matter and prevent the acid from becoming discoloured. With this liquid, however, there is risk of serious injury should the tube break; safer liquids are esters of high b.p., e.g. butyl phthalate (b.p. 338°).

(2) It is essential that the substance be dry, since even a trace of moisture may lower the m.p. considerably.

For methods of drying substances see page 19.

(3) A pure compound usually has a sharp m.p., i.e. it melts completely within a range of about 1° . Any impurities present nearly always lower the m.p., and also render it indefinite, i.e. the change from solid to liquid extends over a number of degrees.

It may be necessary to recrystallise a substance one or more times before it melts sharply.

Some substances on heating undergo decomposition before the m.p. is reached, the decomposition products then acting as impurities and lowering the m.p. Even for these the method described (i.e. the introduction of the capillary tube into the liquid at a temperature only a little below the m.p. of the substance) enables a fairly accurate m.p. to be obtained, since the compound is exposed to the high temperature for only a short time before melting, and thus only slight decomposition occurs. If the substance and thermometer are placed in the cold liquid and the temperature raised slowly a much lower m.p. will be obtained.

(4) Since an ordinary thermometer may be inaccurate it should be standardised by using a range of pure substances of known m.p. (see note 2).

4. DETERMINATION OF THE MELTING POINT OF A SOLID AND BOILING POINT OF A LIQUID

We are now to identify the substance supplied. This involves two steps. The first step is to determine the melting point or boiling point as the case may be, of the substance supplied. As we have established the character of the characteristic group present in the substance supplied, we are only to compare the melting point of the relevant compounds to have a fair idea of the original substance.

The next step is the confirmation of the substance through formation of its derivatives.

Determination of melting point of a solid :

(i) A little of the original substance is finely powdered. If it is not already dry it is dried over porous plate or upon filter paper. The dried substance is then subjected to melting point determination.

A small quantity of the sample is forced into the open end of a thin walled glass capillary tube, sealed at one end and by gently tapping on a hard surface the powdered solid is forced down to the closed end. The fine capillary tube is then attached by moistening it with the liquid of the bath to a calibrated thermometer so that the enclosed sample is as near as possible to the middle of the thermometer bulb. The thermometer is now suspended in a bath of concentrated sulphuric acid, with the bulb a few millimetres below the surface (Fig 2.)

The bath is heated steadily and uniformly by a small flame and temperature at which the solid melts is noted. Repeat the experiment by heating the bath to ten degrees below the expected melting point and thereafter in such a way that the temperature rises about two degrees per minute. The temperature at which softening of the sample begins is not its melting point. Melting point of the sample is the temperature at which a clear melt is produced.

Notes (i) For low melting solids the sulphuric acid bath may be replaced by a liquid having lower boiling point.

(ii) Some substances on heating undergo decomposition before the melting point is reached, the decomposition products then act as impurities and lower the melting point of the sample. For these compounds the bath should be heated to a temperature slightly below the expected melting point, then the capillary tube contain-

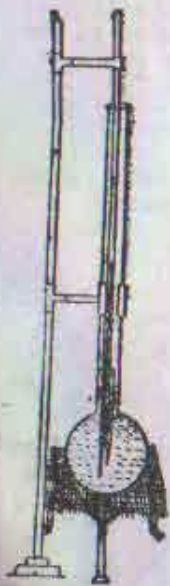


Fig. 2

ing the sample should be introduced. The sample, in that case, would be subjected to the high temperature only for a short time before melting and will give a fairly accurate reading of its M. P.

(iii) On prolong use, sulphuric acid in the bath becomes coloured owing to the presence of charred matter. To get clear bath, drop a few crystals of KNO_3 in it and gently warm.

*Determination of the boiling point of a liquid :

Fit up an apparatus as shown in fig. 3 and see that the bulb of the thermometer is just at the centre of the side tube of the distilling flask. Disconnect the distilling flask, remove the cork and the thermometer attached to it, pour in liquid to fill up about half of the distilling flask. Drop a few pieces of porous pot in the liquid.

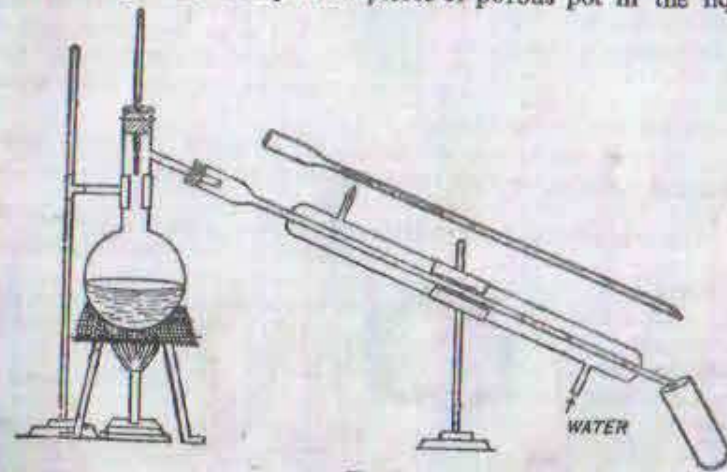


Fig. 3

Replace the cork and the thermometer. Care must be taken to see that the bulb of the thermometer does not touch the sides of the distilling flask. Connect the flask to the condenser, gently heat the liquid by a small flame for smooth distillation.

If the liquid is pure, and distils without decomposition, practically the whole of it will pass over at a constant temperature, which is the boiling point of the liquid. However, if during distillation the temperature continually rises, the liquid is not pure.

CLASSIFIED TESTS FOR QUALITATIVE
ORGANIC ANALYSIS

1. Physical Characteristics :

- (a) State (b) Colour
(c) Odour
(d) Solubility in water (hot and cold), alcohol, dil. acids, dil. alkalis.
(e) Litmus reaction
(f) Melting point.

2. Detection of Elements in Organic Compounds

Experiments	Observations	Inferences
1. Soda-lime test : Heat substance and soda-lime (1 : 2) in a test tube.	Smell of NH_3 (a) turns red litmus paper—blue. (b) turns mercurous nitrate paper—black.	Nitrogen present. [All nitrogenous compounds do not respond to this test.]
2. Lassaigne's test : Fuse a little of the subs. with a pea sized metallic sodium in a fusion tube, heat at first gently and then strongly, extract the melt with distilled water, filter : (i) To 5 ml of filtrate add 2-3 drops of NaOH , 1-2 bits of FeSO_4 and boil. Add 2-3 drops of FeCl_3 and acidify with conc. HCl . (ii) To a part of filtrate add fresh soln of Na-nitroprusside. (iii) Another part acidify with acetic acid and add Pb -acetate soln. (iv) (a) To 2 ml of filtrate add dil. HNO_3 to acidify, boil for a few minutes, cool, and add AgNO_3 soln.	Blue or green ppt. or colouration (Prussian blue) Violet colour Black ppt. (a) Curdy white ppt. (b) Curdy yellow ppt. (Pale or distinct.)	Nitrogen present. Sulphur present. Sulphur present. Chlorine present. Bromine & /or Iodine present.

Experiments	Observations	Inferences
(b) To 2 ml of filtrate add dil. H_2SO_4 to acidify, then a few drops of fresh chlorine water and 2 ml chloroform or CCl_4 or CS_2 . Shake well. If the organic solvent layer is violet, add more chlorine water and shake well until the violet colour is discharged.	(i) Organic solvent layer—violet. (ii) Organic solvent layer—yellowish brown. (c) Organic solvent layer—yellow.	Iodine present. Bromine present. Bromine in presence of Iodine present.
3. Alkali-Sugar test : Heat subs. with alkali-sugar mixture (1 : 0.1) in a bulb tube (see under nitrogen); break it under water, boil and filter. Examine filtrate for N, S, and Cl, Br and I by test (i), (ii), (iii), (iv), (a), (b) under Test 2.		
4. Alkali-Zinc test : Heat substance with alkali-zinc mixture (1 : 0.5) in a bulb tube (see under nitrogen). Break under water boil, filter : Examine filtrate for nitrogen by Test (2) (i) above.	A deep blue ppt. or a bluish green colouration.	Nitrogen present.
5. Ballstein's test : Heat a thick copper wire till it ceases to colour the flame. Cool the wire. Take a little of substance at its end and heat it in the lower outer edge of the flame.	A green colour.	Halogens present.

3. Detection of Functional Groups in Organic Compounds Containing C, H, O and N

Experiments	Observations	Inferences
<p>(a) <i>Test for —COOH group :</i></p> <p>1. Test a little of the sample soln. with blue litmus paper.</p> <p>2. Dissolve or suspend the sample in water, add solid or aq. soln. of NaHCO_3, small quantity at a time.</p> <p>3. Warm little of the sample with 1 ml of methyl alcohol in presence of few drops of conc. H_2SO_4 and then pour the reaction product into a large volume of water.</p>	<p>Blue litmus paper turns red</p> <p>Effervescence with evolution of CO_2.</p> <p>Sweet smell of ester.</p>	<p>—COOH gr. present.</p> <p>—COOH gr. present.</p> <p>—COOH gr. present.</p>
<p>(b) <i>Test for phenolic OH group:</i></p> <p>1. Test a little of the sample soln. with a blue litmus paper.</p> <p>2. Dissolve the substance in water or alcohol and add a drop of FeCl_3 solution. (Some phenols give reaction only in alcohol solution. It is therefore advisable to repeat the reaction in both the media. (Exceptions are α-naphthol and β-naphthol. They give transient green colour changing to white ppt. with FeCl_3.)</p> <p>3. <i>Back dye Test :</i> Dissolve a few drops of aniline in 5 ml of dil. HCl, cool the solution and add a few drops of NaNO_2 solution. Pour this diazotised soln. into a cold soln. of the compound in NaOH.</p> <p>Libermann's Test for phenols : Add a small fragment of solid NaNO_2 to 5 ml of conc. H_2SO_4. Warm until it dissolves then add a little of the phenol. Now pour the mixture in water then add NaOH solution.</p>	<p>Blue litmus paper turns red</p> <p>(a) Reddish colouration or ppt.</p> <p>(b) Green, blue or violet colouration.</p> <p>Rose red ppt. of an azo dye.</p> <p>Red colour in acid medium. It becomes green to blue in alkaline medium.</p>	<p>Phenolic —OH gr. present.</p> <p>(a) Simple carboxylic acids.</p> <p>(b) Phenolic —OH gr. present.</p> <p>Phenolic —OH gr. present.</p> <p>Phenolic —OH gr. present.</p>

Experiments	Observations	Inferences
<p>5. <i>Phthalein test :</i> Heat the sample with phthalic anhydride (1:2 proportion) and few drops of conc. H_2SO_4 in a dry test tube. Cool and make it alkaline with NaOH solution. Dilute with excess of water.</p>	<p>Yellow, blue, green or red fluorescence.</p>	<p>Phenolic —OH gr. present.</p>
<p>(c) <i>Test for alcoholic OH group :</i></p> <p>1. Add to a dry sample few thin slices of metallic sodium in an inert solvent like dry benzene.</p> <p>2. Add small amount of PCl_5 to 2 ml of the dry substance.</p> <p>3. Add to a small quantity of sample about equal volume of freshly distilled acetyl chloride in cold condition.</p> <p>4. <i>Xanthate test :</i> Take a little of the sample and solid KOH (1:10) in a clean dry test tube and warm slightly. Cool, then add 1 ml of ether and 5 drops of CS_2. (i) Shake the mixture for 5 minutes. (ii) Then add few drops of 1% NH_4-molybdate soln. and then acidify with 2(N) H_2SO_4. Add about 2 ml CHCl_3 and shake.</p>	<p>Hydrogen gas evolves.</p> <p>Copious evolution of HCl gas.</p> <p>Copious evolution of HCl gas.</p> <p>(i) A yellow ppt. (ii) CHCl_3-layer turns violet or reddish blue.</p>	<p>Alco. —OH gr. present.</p> <p>Alco. —OH gr. present.</p> <p>Alco. —OH gr. present.</p> <p>Alco. —OH gr. present.</p> <p>Alco. —OH gr. present.</p>
<p>(e) <i>Test for ester group :</i></p> <p>1. Add two beads of NaOH to a little of the sample in min. vol. of water boil for few minutes, cool then acidify with dil. HCl.</p> <p>2. Place 0.5 ml hydroxylamine hydrochloride solution in methanol containing 0.02% thymolphthalein indicator, add little of the sample to it. Now add dropwise 2(N) KOH sol.</p>	<p>White solid [In case of ester of water insoluble acids].</p> <p>A red or bluish red colour.</p>	<p>—COOR gr. present.</p> <p>Ester group (—COOR) present.</p>

Experiments	Observations	Inferences
<p>in methanol until the mixture turns blue and then add 5 drops of KOH in methanol. Heat the mixture just to boiling. Cool and acidify with 2 (N) HCl until blue colour disappears and add a drop of 1% FeCl₃ solution.</p> <p><i>N.B.</i> Before performing this experiment, make sure that with FeCl₃ soln., the original sample soln. does not produce any colour. Hydroxamic acid in slightly acid soln. exhibits coloured complex with FeCl₃ soln.</p> <p><i>Test for carbonyl group :</i></p> <p>1. To a small portion of the alcoholic solution of the substance or to a small amount of the sample add minimum quantity of glacial acetic acid, warm till clear solution results, then add 2 ml of saturated solution of 2, 4-dinitrophenyl hydrazine in alcohol. Shake, gently heat to boiling for few minutes. Allow to cool, if no ppt. appear, add 2 drops of conc. H₂SO₄, warm for few minutes again, and scratch inside of the test tube, with a glass rod cool and allow to stand.</p> <p>2. Take equal amount of semi carbazide hydrochloride and sodium acetate in a test tube, add minimum quantity of water to dissolve it by heating. Now add a little of the sample and shake. If the mixture becomes turbid, add dropwise alcohol to make a clear solution. Warm on water bath for few minutes and then cool.</p>	<p>Orange or red ppt.</p> <p>White crystal-line ppt.</p>	<p>Carbonyl gr. present (>C=O or -CHO).</p> <p>Carbonyl gr. present (>C=O or -CHO).</p>

Experiments	Observations	Inferences
<p>8. Schiff's test : To 2 ml of the cold solution of the substance in a test tube add 3 ml of colourless Schiff's reagent, shake well and allow to stand for 2 minutes.</p> <p><i>N.B.</i> Do not heat the mixture.</p>	<p>Pink, or red colouration. (The appearance of a pink tint after the expiration of the time-limit of 2 mins. to be discarded.)</p>	<p>—CHO group present.</p>
<p>4. To a small portion of the substance add 5 ml Fehling's soln. and then warm on water bath for few minutes.</p> <p><i>Preparation of Fehling's soln :</i> To 2 ml of Fehling's A soln. add Fehling's B soln. a little at a time till the bluish white ppt. dissolves and a clear deep blue soln. results.</p>	<p>Red ppt. of cuprous oxide.</p>	<p>—CHO group present.</p>
<p>5. To 5 ml of Tollen's reagent add a small amount of the subs. & place the test tube in hot water bath.</p> <p><i>Preparation of Tollen's reagent :</i> Tollen reagent is prepared by adding dil NaOH to 5 ml AgNO₃ soln. shake and stand for few minutes, decant the clear soln. and dissolve the ppt. in minimum volume of conc. NH₃ soln.</p> <p>(f) <i>Test for ethylenic unsaturation :</i></p>	<p>Silver mirror appears on the sides of the test tube.</p>	<p>—CHO group present.</p>
<p>1. To a little soln. of the sample add a few drops of dilute KMnO₄ soln.</p> <p>2. Take a few drops of liquid Bromine in 2-3 ml of acetic acid in a test tube. Add a few drops of this Br₂-soln. to the soln. of the sample and warm gently.</p>	<p>Pink colour of the KMnO₄ soln. disappears.</p> <p>Brown colour of the Br₂ soln. disappears. No copious evolution of HBr gas.</p>	<p>Ethylenic saturation may be present.</p> <p>Ethylenic unsaturation is present.</p>

Experiments	Observations	Inferences
[If in the original comp. N, S or phenolic OH group be present do not perform tests for ethylenic unsaturation.]		
XXX Test for primary amine :		
* Carbylamine test : Warm a little of the sample with few drops of alcoholic KOH solution and a drop of CHCl_3 .	A characteristic obnoxious odour of carbylamine.	$-\text{NH}_2$ group present.
XXX Diazo reaction : Add a pinch of NaNO_2 to a well-cooled HCl solution of the sample. Then pour a little this diazotised solution into excess of cold alkaline solution of β -naphthol.	Immediate brilliant scarlet or red ppt.	$-\text{NH}_2$ group present.
(h) Test for secondary amine :		
1. Dissolve a little of the sample in 5 ml dil. HCl and add a few drops of NaNO_2 solution to the above cold solution. Then add a drop of it. Reaction product (nitroso compound) to a small amount of phenol dissolved in little conc. H_2SO_4 .	A blue colour which on warming and dilution with water changes to red and again blue in a alkaline medium.	$=\text{NH}$ group present.
2. Simen's test : Add one drop of the aq. soln. of the sample to 2 ml of aq. Na-nitroprusside soln. then add 1 ml of freshly prepared soln. of acetaldehyde. [Prepared by oxidation of $\text{C}_2\text{H}_5\text{OH}$ by red hot Cu-wire.]	Deep blue colour.	$>\text{NH}$ group present.
(i) Test for tertiary amines :		
1. To few ml of HCl-solution of the sample add few drops of potassium ferrocyanide.	White ppt.	$=\text{N}$ present.

Experiments	Observations	Inferences
2. To 2 ml of the HCl solution of the sample add few drops of Mayer's reagent. Preparation of Mayer's reagent : Mayer's reagent is prepared by dissolving 13.5 gm of HgCl_2 and 50 gm of KI in 940 ml of water	Pale yellow ppt. Dissolves on heating but reappears on cooling.	$=\text{N}$ group present.
(j) Test for amide group : Heat 0.5 gm of the sample with 2 ml 50% NaOH solution	Smell of NH_3 which turns $\text{Hg}_2(\text{NO}_3)_2$ paper black.	$-\text{CONH}_2$ gr. present.
2. Treat a little of the aq. soln. of the sample with a few drops of cold solution of HNO_3 (HCl and NaNO_2).	N_2 gas evolves.	$-\text{CONH}_2$ gr. present.
(k) Test for substituted amide (anilide) group : Hydrolyse 50 mg of the sample by boiling with 5 ml conc. HCl or 50% H_2SO_4 for a few minutes, cool, dilute with water, then perform diazo reaction.	Immediate brilliant scarlet or ppt.	Substituted amide gr. present (R = $\text{CONH}-\text{Ar}$)
(l) Test for Nitro group : Warm gently a little of the sample with a few pieces of metallic tin and 5 ml conc. HCl till the reaction is complete. Cool, filter if required, dilute, then perform diazo reaction [perform this test when $-\text{NH}_2$ gr. & or $\text{R}-\text{CONH}-\text{Ar}$ groups are absent.]	Immediate brilliant scarlet or red ppt.	$-\text{NO}_2$ group present.
Mulliken and Barker's test : Dissolve a little of the sample in 5 ml 50% alcohol then add a little solid NH_4Cl or 10% CaCl_2 solution and a pinch of Zn dust. Boil for few minutes, cool, stand for five minutes and then filter the above reaction product into 5 ml of Tollen's reagent (Ammo. AgNO_3 soln.) and warm on water bath.	A black or grey ppt	NO_2 group present.