29. *The Determination of the Melting Points of Organic Substances.*

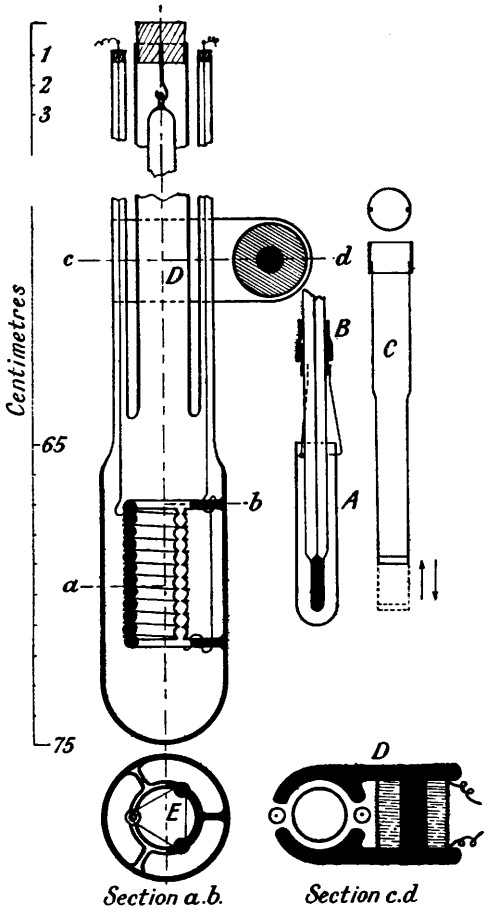
By FRANCIS FRANCIS and F. J. E. COLLINS.

IN investigations in organic chemistry, *melting points* are usually determined by the capillary-tube method, and *setting points* by means of a thermometer immersed in the melt. In our experience, a single observer can determine a melting point to within 0·1—0·2°, but the results of different observers, using the same apparatus and the same specimen, may differ by 0·2—0·3°. On the other hand, determinations of the setting point by different observers agree to within 0·02°. Although the melting point and the setting point should be identical for a pure substance, the former is invariably higher than the latter.

During our study of the *X*-ray crystal spacings of the higher *n*-fatty acids and their

derivatives, numerous very pure specimens of these compounds were prepared (Francis, Piper, and Malkin, *Proc. Roy. Soc.*, 1930, *A*, **128**, 214), and it has been found that, when melting or setting points of a homologous series of compounds are plotted against carbon content, graphs are obtained which are only slightly curved. It is therefore possible to check the accuracy of these constants, and a critical study was made of methods of determining melting and setting points. For this purpose we designed a melting-point apparatus by means of which different observers can obtain results which do not differ by more than 0·03°; in addition, it has proved of value in observing certain phenomena which occur in the neighbourhood of the melting point.

FIG. 1.



EXPERIMENTAL.

I. *Setting Points.*—(i) It is usual to take considerable amounts of material for the determination of setting points (*e.g.*, Landolt, *Z. physikal. Chem.*, 1889, **4**, 349, recommends 20 g.), but with a pure or nearly pure material, different observers can obtain results to within ± 0·02° by melting 2—3 g. of the material in a small test tube and stirring it, during solidification, with a thermometer on which 4·6 mm. of scale length is equivalent to 1°.

(ii) With mixtures such as palmitic and stearic acids, much larger quantities of material are necessary; *e.g.*, de Visser (*Rec. trav. chim.*, 1898, **17**, 182) used 50 g. With the apparatus shown in Fig. 1, however, only 2 g. are needed, and different observers can obtain results agreeing to within 0·01°.

The substance under investigation was placed in the container, tube *A*, hanging from clips soldered to a ring which was attached to the thermometer by a piece of rubber tubing at *B*. The stirrer *C* was of platinum, soldered to a ring of soft iron, and operated by the electromagnet *D*. The assembled thermometer, stirrer, and containing tube were placed inside the apparatus shown on the left-hand side, and suspended from a hook at the top, so that the containing tube came within the heating coil, *E*. The whole apparatus was then placed inside a thermostat 70 cm. deep, and 20 × 20 cm. in cross-section, with plate-glass front and back and with a plate-glass vertical part in it, extending to within 5 cm. of the top and bottom to screen the effect in operating a helical stirrer. The temperature in the thermostat was maintained at 0·5° below the setting point of the substance in the containing tube *A*, as determined by the method given in section (i) above. The substance was then heated by means of the coil to 1—2° above its m. p., and readings taken every ½ minute as it cooled. The results were plotted against time, and at the setting point the graph became horizontal, remaining so in the case of a pure substance for 30 minutes or more. The thermometer (8 mm. of stem length = 1°) was calibrated for total immersion at the temperature of observation, and no stem correction was necessary.

In this apparatus, there is no difficulty in obtaining values which agree to ± 0·01°, and with the small amounts of the palmitic and stearic acid mixtures we employed, our results for a series of mixtures agree remarkably with those of de Visser (*loc. cit.*); these will be published later.

The setting point of pure naphthalene (made for calorimetric work) by the method of section (i) was 80·10° ± 0·02°, and by that just described 80·09° ± 0·01° (Landolt, *loc. cit.*, gives 80·028° ± 0·016°). Our own highly purified specimen of palmitic acid had s. p. 62·53° ± 0·01°, and stearic

acid, s. p. 69·35° ± 0·01°; these values are very close to those of de Visser and are the highest recorded for these acids.

II. *Determination of Melting Points by the Capillary-tube Method.*—Tseng (*J. Chinese Chem. Soc.*, **1933**, **1**, 143; *Sci. Quart., Nat. Univ. Peking*, **1934**, **4**, 237, 283) has studied the determination of m. p.'s by the capillary-tube method, and states that, when different types of apparatus are used, discrepancies ranging from a fraction of a degree up to more than 2° are observed. He points out, further, that in the same apparatus individual determinations agree closely and often coincide, although with different observers the divergence may reach 1°. We seldom differed from each other, however, by more than 0·2° in the determination of m. p.'s in the ordinary apparatus, with a bath of sulphuric acid, controlling the temperature by means of a Bunsen flame, and using a thermometer on which 1 mm. of scale length was equivalent to 1°. When

FIG. 2.

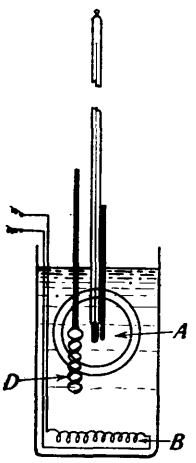
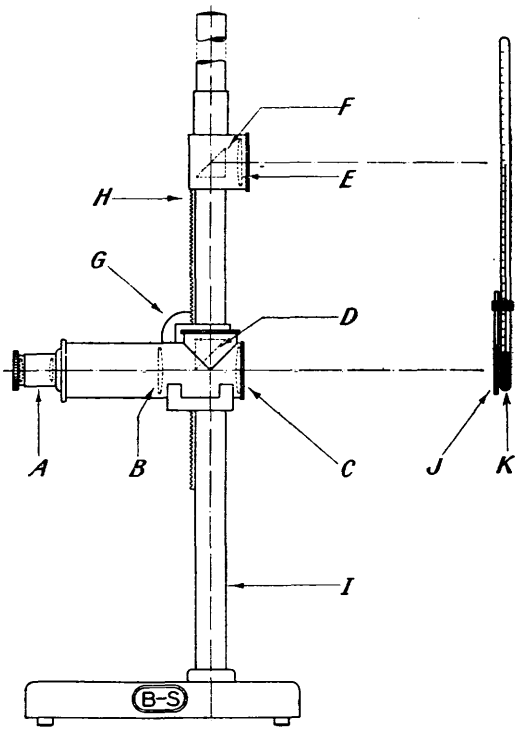


FIG. 3.



thermometers with more open scales are used, the temperature of the bath must be controlled much more accurately than is possible with a Bunsen flame, and efficient stirring becomes essential. Further, it is necessary for the observer to watch the material in the capillary tube and the thread of the thermometer through the same eyepiece, and thus to obviate the alternate observation of mercury column and capillary tube, which is necessary in all the ordinary forms of m. p. apparatus.

The bath finally devised is made of cylindrical glass, 9 cm. deep by 5 cm. diameter, into the side of which is fused a small plate-glass window, *A*, through which the capillary tube and its contents can be seen (Fig. 2). The vessel contains heavy liquid paraffin and is heated by a spiral of resistance wire, *B*, immersed at the bottom. The current, and hence the temperature of the bath, is regulated by a rheostat with a lead-screw adjustment. The paraffin is stirred by a small metal stirrer, *D*, driven through a straight shaft coupled to a split-phase A.C. motor. It was essential that this stirrer should run at a constant speed in order to maintain a steady temperature. The thermometer was graduated in 0·1°, 4·6 mm. of scale length corresponding to 1°. It was calibrated by immersion to 2·5 cm., and is supported in the bath to this depth by a rigid iron rod, and a small clip at the side holds the capillary tube close to the bulb of the

thermometer. The temperature of the bath can be maintained to within about ± 0·02° for a period sufficiently long for the determination.

The capillary and its contents *J* (Fig. 3) are viewed by a telescope which incorporates a periscope device, *E*, *F*, so that in the same eyepiece *A* (magnification = 6) both capillary *J* and thermometer scale *K* can be seen together.* A rack-and-pinion adjustment *GH* brings under observation any desired portion of the thermometer scale. Small 12-volt lamps, suitably screened, illuminate both capillary and scale, and are so arranged that the contents of the tube can be viewed by either reflected or transmitted light, or by both simultaneously.

The approximate m. p. is first determined by raising the temperature rapidly, the material is then allowed to resolidify, and the accurate value obtained by raising the temperature to 1° below that point and then at the rate of about 0·1° in 4 minutes, until a clear liquid first appears on the surface of the solid. Under these conditions, different observers do not differ in their readings of the m. p. by more than ± 0·03°.

On slowly raising the temperature of a pure substance which has been previously melted in a capillary tube, a point is reached where a liquid appears over the surface of the solid, and if the temperature is maintained at this point, the whole contents of the tube ultimately liquefy. It is for this reason that the temperature at which the liquid first appears is taken as the m. p. With such substances, there is no " fusion range " or " fusion interval," often mentioned by many and inferentially by those who record a lower and an upper limit when recording m. p.'s. We consider that a " fusion range " is due to impurity of the specimen, or to the formation of metastable forms, or to the fact that the bath has not been maintained at a constant temperature for a sufficient period after the first appearance of the liquid phase. For instance, with mixtures of stearic and palmitic acids containing 47·5 mols. % of the former, the fusion range is 0·35°; this rises with increasing amounts of stearic acid, being 1·3° with 57·5 mols. %, and then falls until with 98·8 mols. % it is 0·1°.

III. *Size of Capillary Tube.*—The most suitable capillary-tube diameter is 1 mm., and all observations should be made on specimens of the material which have been previously melted in it. We have been unable to confirm Landolt's observation (*loc. cit.*) that the m. p. depends on the diameter of the capillary; he found that naphthalene had m. p.'s lying between 79·83° and 80·62° according to the diameter of the tube, but in capillaries of diameters 0·5—3 mm. we always obtained the same value, *viz.*, 80·3°, for the pure hydrocarbon.

IV. *Comparison of Melting Points in Different Forms of Apparatus.*—Melting points taken in the apparatus just described are generally lower than those determined in the usual form. The following comparison was made with nine aliphatic acids and alcohols. The four acids had been described in a previous communication (*loc. cit.*), and the present observations were made in the new form of apparatus and on the same specimens. Our synthetic specimens of the five alcohols were compared with the values given by Piper, Chibnall, and Williams (*Biochem. J.*, 1934, **28**, 2175) for their preparations. In several cases, these authors give a range between which the substances melted, and for the reason previously mentioned, the comparison was made taking the lower temperature as the correct m.p.

Of the nine substances, eight gave m. p.'s in our apparatus which were 0·2—0·6° lower than the values with which they were compared, and only one was higher (by 0·2°). One of the most interesting of the former group is hexacosanoic acid, the same specimen of which had m. p.'s 88·2° and 87·7° in the old and the new apparatus respectively, thus confirming our opinion that the old value was too high. Francis, Piper, and Malkin (*loc. cit.*, p. 217) had given the m. p.'s of palmitic and stearic acids as 63·1° and 70·1° respectively; we now find with the same specimens the values 62·85° and 69·9°.

V. *Resolidification Temperature.*—After the m. p. of a substance has been taken, provided no metastable phase be formed, and whilst there is still some unmelted solid in the capillary, if the temperature is allowed to *fall very slowly*, the " resolidification point " can be determined as accurately as the m. p. itself; this point lies closer to the setting point, *i.e.*, the true m. p. of the substance, than does the m. p. determined in a capillary tube. From the table it will be seen that the resolidification temperature is lower than the m. p.—in two cases out of twelve by 0·6°, and in the others by about 0·4° or less. In our experience, a greater difference than 0·6° is an indication of the presence of impurities. Thus the difference between the m. p. of pure palmitic acid and the resolidification point of this acid containing 1% of stearic acid is 0·8°; and in the case of pure stearic acid and the acid containing 1% of palmitic acid, the difference is 1·2°.

* This apparatus was made for us by Messrs. Bellingham and Stanley, 71 Hornsey Rise, N. 19.

The resolidification temperature never differs from the setting point by more than ± 0·2° (see table, col. 6).

Substance.		S. p.	Capillary tube. M. p.	Capillary tube. R. p.	Differences. M. p.—S. p.	Differences. S. p.—R. p.
n-Fatty acids; C content	16	62·53°	62·85°	62·4°	0·32°	− 0·1°
	18	69·35	69·9	69·3	0·55	0·0
	24	83·9	84·15	83·8	0·25	− 0·1
	26	87·4	87·7	87·2	0·3	− 0·2
Ethyl esters of *n*-fatty acids; C content of acid	26*.....	59·6	59·95	59·5	0·35	− 0·1
	28	64·2	64·6	64·3	0·4	0·1
	30	68·3	68·45	68·3	0·15	0·0
	34	75·29	75·4	75·3	0·1	0·0
	36	78·3	78·6	78·3	0·3	0·0
Diphenyl †		68·8	69·3	68·7	0·5	− 0·1
Naphthalene †		80·1	80·3	79·9	0·2	− 0·2
Phenyl salicylate †		41·2	41·7	41·3	0·5	0·1

* Metastable modification. † Commercial preparations.

VI. *Effects of Small Amounts of Impurities on the Melting Point.*—Addition of 1% of palmitic or stearic acid to the other acid resulted in definite depressions of m. p.—for palmitic acid from 62·85° to 62·6°, and for stearic acid from 69·9° to 69·3°—but at about 0·1° below these temperatures, the material in the capillary tubes softened. There is also in both cases a small fusion interval of *ca.* 0·1°. These phenomena cover a range of temperature that could only be observed with difficulty in the ordinary form of m. p. apparatus. For reasons which will be discussed in a later communication, it should be stated that both acids were free from traces of oleic acid, which is only removed with difficulty.

VII. *Comparison of Melting Points (Capillary-tube) with Setting Points.*—It is generally recognised that m. p.'s determined by the capillary-tube method are higher than the setting point, but apart from papers by Landolt (*loc. cit.*) and Reissert (*Ber.*, 1890, **23**, 2239), there appear to be no data available as to these differences.

In making the comparisons between "melting," "resolidification," and "setting" points (m. p., r. p., and s. p., respectively) given in the table, we used the same thermometer for each class of determination. Setting points were determined by the method described in Section I, (i), which is sufficiently accurate for this purpose. It will be seen (col. 5) that in every case the difference between the m. p. and the s. p. lies between 0·1° and 0·55°. This may be compared with the corresponding data for the aliphatic acids (Francis, Piper, and Malkin, *loc. cit.*, p. 217) for which the m. p.'s were determined in the usual form of apparatus; in four cases the difference was 0·3° or less, whereas in the other seven it lay between 0·8° and 1·2°. It is clear that in the new form of apparatus the divergence between the m. p.'s taken by the two methods is reduced, but it is nevertheless real. The differences between the resolidification temperature and the setting point, however, are considerably less: in the 12 values given in col. 6, four are identical, six differ by 0·1°, and two by 0·2°.

Reissert (*loc. cit.*), in a series of comparisons with substances of m. p. $< 115°$, found that the differences between m. p. and s. p. were occasionally negative and varied from $-0·3°$ to $+0·75°$, but it is clear that in some cases his materials were not pure. We have had little experience with substances melting much above 100°. There is, however, no doubt that the divergence at high temperatures would be larger than those given above; *e.g.*, Landolt found that it was 1·8° in the case of mannitol (s. p. 165·64°), and about the same in anthracene (s. p. 200·61°).

The apparatus described above has been of great assistance in observing transition temperatures, particularly in cases such as that of hentriacontane where one is situated 0·2° below the m. p., or in determining the m. p.'s of the α- and the β-modification of ethyl behenate, which differ by 0·45°, or of the two ethyl tetracosanoates which differ by 0·42°. For instance, a specimen of ethyl behenate which has remained for some hours at room temperature in the capillary shows m. p. 48·7°; if the specimen is completely melted, the second α-form separates in the solid phase on cooling, and if a redetermination of the m. p. is made immediately, this form is found to fuse at 48·25°. In the ordinary m. p. apparatus, this phenomenon may be easily overlooked; *e. g.*, Francis, Piper, and Malkin (*loc. cit.*) gave the m. p. as 48·0°, and Levene and Taylor (*J. Biol. Chem.*, 1924, **59**, 905) gave it as 48·5—49·5°.

With some long-chain carbon compounds, a marked alteration takes place in the appearance of the solid in the capillary about 0·3° before the m. p. is reached. Substances may lose their crystalline appearance and pass into semi-translucent solids—possibly liquid crystals—or into an apparently amorphous opaque mass (cf. Malkin, J., 1931, 2800).

On the other hand, in the series of the higher aliphatic alcohols synthesised during the course of our work, and in no other derivatives, we noticed in the molten specimens of all those having a carbon content of more than 26 a marked opalescence, which disappeared when the temperature was raised about 0·3° above their m. p.'s. This was also observed in specimens sent to us by Professor Chibnall, and again we consider that this may be due, not to the presence of impurities, but to the formation of liquid crystals. These phenomena can be easily observed, and the temperatures recorded at which they take place, but they have not been further investigated. They may be correlated with transition temperatures, and with the changes observed in the heats of crystallisation and in the dipole moments, which occur at temperatures near the m. p.

SUMMARY.

The *setting point* is the only accurate experimental value for the transition temperature from solid to liquid. When a melting point is determined by the capillary-tube method, higher values are invariably obtained.

The divergence usually observed between the setting point and the melting point is reduced when the latter is determined in the apparatus described in this communication.

The setting point, however, lies nearer to the temperature at which the molten material, allowed to cool very slowly, commences to solidify in the capillary tube. Hence this temperature affords a better value for the true melting point of a substance than the criterion used at present.

The apparatus renders it possible to keep the substance under close observation at temperatures near the melting point. Under these conditions, the existence of metastable forms fusing within 1° of each other can be detected, transition temperatures recorded, and a judgment reached on the purity of the specimen.

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