Rotating Blade Stirrer and Small Sample Technique in the Determination of Freezing Points

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Two new stirrers have been developed which markedly increase the usefulness and scope of the established cryoscopic technique for the determination of purity. A stirrer with a flat blade revolving coaxially about the thermometer has been designed for melting point determinations on organic sulfur compounds. The uniformity and shape of the time-temperature curves obtained using this stirrer indicate that thermal equilibrium is established with compounds which give very unsatisfactory results with the conventional reciprocating wire coil type. A second stirrer in the form of an internally threaded aluminum tube of 10-ml. capacity differs in principle from the first in that the tube containing the sample rotates and the stirring action is provided by the combined effect of the stationary thermometer and the rotating thread. This arrangement enables freezing points to be determined on samples as small as 8 ml. with an accuracy of ±0.01° C., and the corresponding freezing points for zero impurity to be calculated with an accuracy of ±0.1° C. These values are within the accepted limits of accuracy for freezing point determinations. The purity of a compound may be assessed satisfactorily with this form of freezing point apparatus on a much smaller sample, providing that the cryoscopic constant is known.

THE estimation of purity by cryoscopic methods requires a knowledge of the cryoscopic constant and an accurate determination of the time-temperature curve from which the freezing points of the sample and of the pure compound can be obtained. The procedure developed for the determination of freezing points by Rossini and coworkers (*12, 16, 17*) in connection with the American Petroleum Institute Research Project 6 and now generally accepted as a standard procedure, while satisfactory with hydrocarbons, is frequently unsatisfactory with compounds other than hydrocarbons. Organic sulfur compounds in particular, because of their rapid increase in viscosity at or near their freezing points and their tendency to melt unevenly, give very irregular time-temperature curves with the reciprocating wire helix stirrer recommended by Rossini. By replacing the latter with a blade on a rotating shaft, these difficulties can be overcome, while at the same time this type of stirrer not only gives more efficient stirring but also less frictional heat input to the sample.

This is shown with a somewhat similar stirrer which has been described by Kaye (*13*), who encountered difficulties of the same nature with certain hydrocarbons and some of the intermediates involved in the preparation of high purity fuels. The advantages of the rotating blade stirrer described in the present work, compared with Kaye's, are its much simpler construction, general applicability, and resistance to corrosion by sulfur compounds. Further, the screw stirrer designed by Kaye requires several sets of vanes of different pitch to deal with various crystal sizes. This has not been found necessary with the blade stirrer.

Both helix and blade stirrers suffer from the disadvantage that a relatively large sample is required to enable an accurate determination to be made. Even though the introduction of the rotating blade stirrer made possible a reduction in sample size from 50 to 35 ml., this amount of purified material is frequently not available, and a further appreciable reduction in volume was desirable. This has been accomplished by constructing a small aluminum tube to hold the sample. The tube can be screwed on to the rotating shaft in place of the blade and is threaded internally throughout its length so that when rotated the thread acts as a spiral fin causing mixing by vertical displacement of the sample. With this type of stirring it has been possible to reduce the volume of sample required to 6 to 8 ml. without appreciably affecting the accuracy of the method.

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APPARATUS

Rotating Blade Stirrer. This is used in conjunction with the freezing tube assembly described by Rossini and coworkers (*12, 16, 17*). Diagrams of the stirrer blade and shaft and their dimensions are given in Figures 1 and 2. The blade was constructed from a solid aluminum rod through which a central hole was drilled to take the platinum resistance thermometer. Slots were cut along the length of the rod to allow free access of the sample to the thermometer. Below the head (which was threaded internally for attachment to the shaft) the rod was cut away as shown to leave only two fins at opposite ends of one diameter.

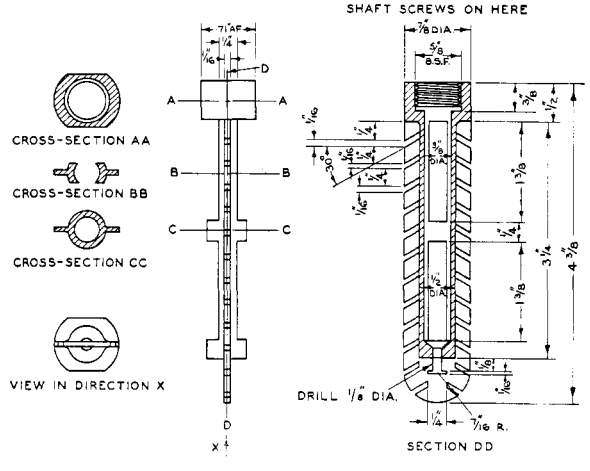

Figure 1. Blade stirrer constructed of aluminum

For clarity all hidden lines have been omitted

The stirrer shaft consists of a hollow Tufnol tube threaded at its lower end to secure the blade, which can be removed easily for cleaning. Tufnol, a laminated synthetic resinoid material, is used rather than metal to prevent heat being conducted to the sample down the stirrer shaft. The Tufnol tube is supported by a journal bearing and rotated by a belt drive from an electric motor at a speed of 300 r.p.m. The belt drive must be slack, or some other similar clutch device provided to prevent damage to the thermometer should the sample freeze completely. The platinum resistance thermometer is inserted through the hollow Tufnol shaft and clamped in position with the coil of the thermometer centrally placed inside the stirrer. The liquid level should be below the lower end of the Tufnol shaft but such that the thermometer coil is completely immersed.

Tube Stirrer for Small Samples. This consists of a small aluminum tube (Figure 3) machined from 7/8-inch aluminum rod, interchangeable with the blade of the rotary stirrer described above and rotated in the same manner. The tube is placed inside the normal glass freezing tube which provides the means of con-

trolling the cooling rate. The internal thread functions as an Archimedean screw and the direction of rotation is such that the material in contact with the wall of the tube is carried downward providing an efficient stirring action. The thread form is B.S.W. with a pitch of 10 turns per inch; any similar coarse thread may be used. [B.S.W. and B.S.F. refer to British Standard Whitworth and British Standard Fine thread scales, respectively (*15*)].

The tube is covered on the outside with a layer of sheet cork which reduces the annular space between the aluminum tube and the inner wall of the glass freezing tube to give the minimum running clearance. The cork is primarily to protect the glass tube from damage, but at the same time it serves to reduce the air space which would otherwise give rise to convection currents and erratic heat transfer.

PROCEDURE

Rotating Blade Stirrer. The experimental procedure is essentially the same as that described by Rossini and coworkers (*12, 16, 17*). In assembling the apparatus, care must be taken to ensure that the thermometer, stirrer, and freezing tube are correctly aligned to minimize the frictional heat and prevent damage to the platinum resistance thermometer.

Tube Stirrer for Small Samples. Using this stirrer, there is a greater time lag in the heat transfer from the sample to the cooling bath and the normal technique has therefore been altered. The sample (8 ml.) is pipetted into the aluminum tube which is then screwed on to the Tufnol shaft. The thermometer is inserted down the shaft and clamped in position. The glass freezing tube is fitted over the aluminum tube and connected to the vacuum system by a universal glass joint. By slowly rotating the stirrer assembly the alignment can be suitably adjusted, whereupon the glass tube is isolated by a tap from the rest of the system and the system evacuated. An external cooling bath is placed around the freezing tube and the sample cooled rapidly to approximately 25° C. above its freezing point. The glass freezing tube is then evacuated to a pressure of approximately 0.001 mm. of mercury. Readings are taken on the resistance bridge at 1-minute intervals until a constant rate of cooling is obtained. This can then be adjusted to the optimum value of 0.3° to 0.5° C. per minute, by either further evacuation of the jacket or raising the pressure. Owing to the small amount of sample employed, the time of freezing or melting is much shorter than with a 50-ml. sample using the accepted method. This necessitates a reduction in the time interval between readings in order that the curve may be as well defined as possible. Thus, when the temperature of the sample is approximately 6° C. above its freezing point, resistance readings are commenced at 0.5-minute intervals and continued until the completion of the determination.

If the sample tends to supercool, crystallization may be induced by switching off the motor and inserting down the gap between the thermometer and the inner wall of the Tufnol shaft, a length of thin Nichrome wire which has been cooled in liquid nitrogen.

RESULTS

Rotating Blade Stirrer. About 1000 determinations have been carried out using the rotating blade stirrer. Although the majority of these were on sulfur compounds, the stirrer has also been used successfully with ketones, alcohols, and paraffinic, naphthenic, and aromatic hydrocarbons. Some of the data on sulfur compounds compiled as a result of these determinations have already been reported (*8–11, 14, 18*).

Table I illustrates the agreement between values obtained using the rotary and reciprocating stirrers. On account of the poor performance of the latter with sulfur compounds, the examples are confined to hydrocarbons. API values (*1–7*) are included for comparison.

Melting curves for 3-methyl-2-thiabutane (Figure 4) show the difference in performance between the rotating blade stirrer and the conventional type. Although the variation is very marked in this instance, such behavior has been noted to the same or lesser degree in a large number of melting point determinations on sulfur compounds, many of which gave such irregular curves with a reciprocating stirrer that not even an approximation to the melting point could be obtained.

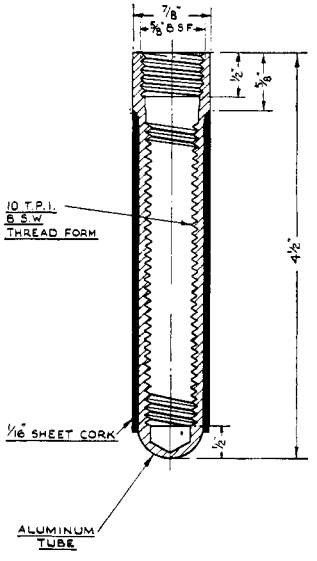

Figure 3. Tube stirrer for small samples

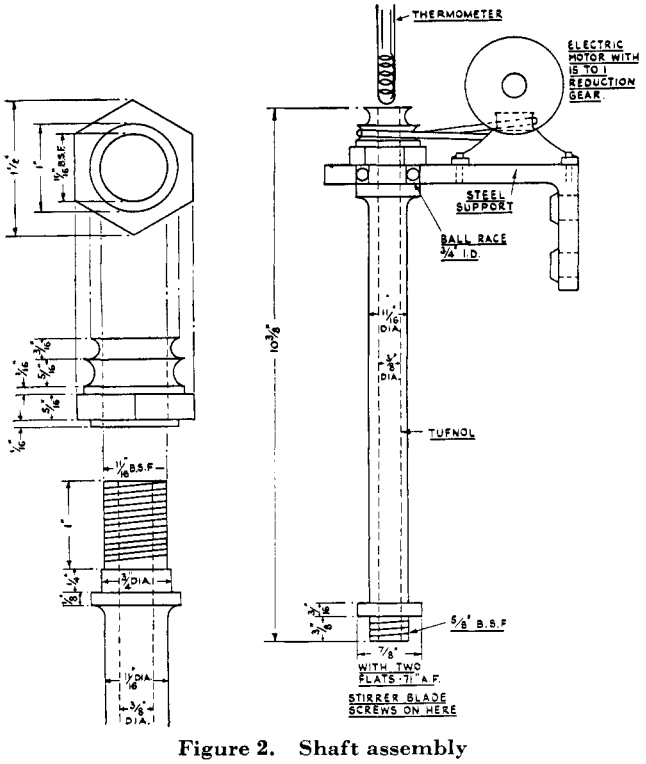

Figure 2. Shaft assembly

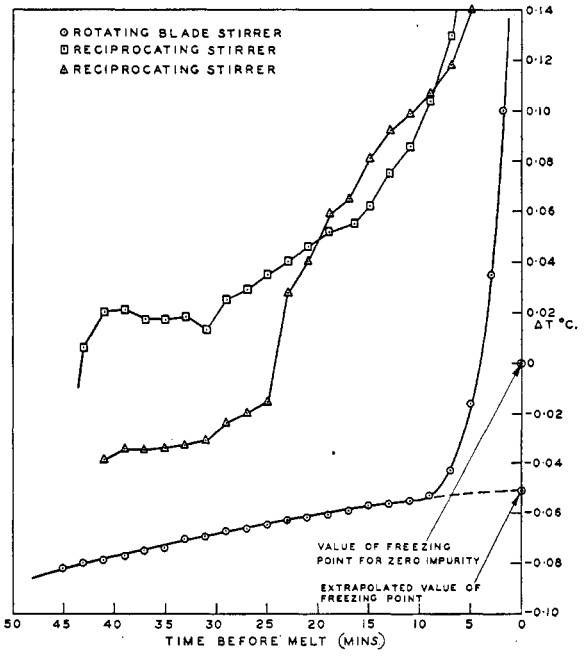

Figure 4. Comparison of rotating blade and reciprocating stirrers on 3-methyl-2-thiabutane

ΔT = ° C. above or below freezing point for zero impurity

Table I. Comparison of Rotating Blade and Reciprocating Stirrers

Compound	M.P./F.P., ° C. Rotating blade stirrer	M.P./F.P., ° C. Reciprocating stirrer	M.P. or F.P.	Calculated M.P./F.P. for Zero Impurity, ° C. Rotating blade stirrer	Calculated M.P./F.P. for Zero Impurity, ° C. Reciprocating stirrer	Calculated M.P./F.P. for Zero Impurity, ° C. API value	Ref.
n-Octane	−56.800 −56.798	−56.801	F.p.	−56.798 −56.796	−56.800	−56.795	(4)
n-Dodecane	−9.712	−9.710	F.p.	−9.615	−9.70	−9.587	(4)
n-Tetradecane	5.831	5.835	F.p.	5.84	5.85	5.863	(4)
2,2,4-Trimethylpentane							
First sample	−107.414 −107.416	−107.417	F.p.	−107.411 −107.415	−107.413		
Second sample	−107.376			−107.375		−107.380	(1)
1,2-Dimethylbenzene	−25.200 −25.198	−25.200	F.p.	−25.182	...	−25.182	(2)
1,4-Diethylbenzene	−43.133	−43.136	M.p.	−42.84	−43.09	−42.850	(3)
Methylcyclopentane	−142.449	−142.450	F.p.	−142.449	−142.450	−142.455	(5)
Methylcyclohexane	−126.596	−126.594 −126.594 −126.598	M.p.	−126.584	−126.55 −126.54 −126.585	−126.593	(6)

Table II. Test Determinations—Tube Stirrer for Small Samples

Compound	M.P./F.P., ° C. Tube stirrer	M.P./F.P., ° C. Blade stirrer	M.P. or F.P.	Calculated M.P./F.P. for Zero Impurity, ° C. Tube stirrer	Calculated M.P./F.P. for Zero Impurity, ° C. Blade stirrer	Calculated M.P./F.P. for Zero Impurity, ° C. API value	Ref.
n-Dodecane	−9.687	−9.687	F.p.	−9.616	−9.615	−9.587	(4)
1-Thiatetralin	−15.572	−15.565	M.p.	−14.90	−14.91	...	
3,4-Dithiahexane	−101.558	−101.555	M.p.	...	−101.46	...	
Isobutylbenzene	−51.562	−51.569	M.p.	...	−51.452	−51.48	(3)
Ethylcyclopentane	−139.232	−139.234	M.p.	...	...	−138.446	(5)
Thiophene	−38.309 −38.294	−38.307 −38.305	F.p.	−38.193 −38.215	−38.237	−38.21	(7)

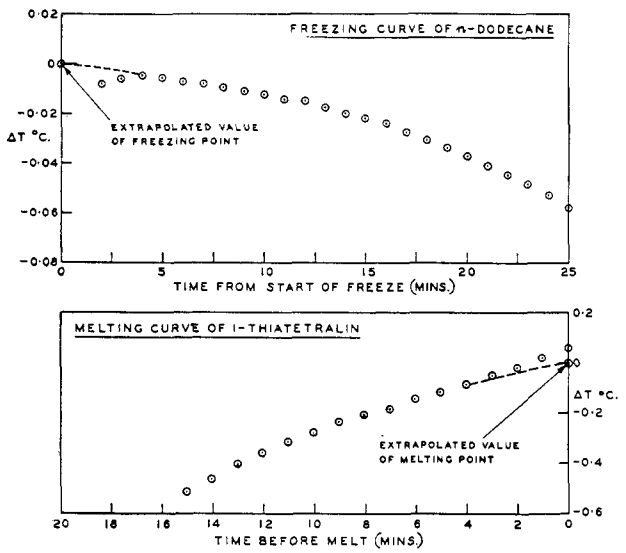

Figure 5. Specimen curves obtained with tube stirrer

ΔT = ° C. above or below extrapolated value of freezing point or melting point

Tube Stirrer for Small Samples. To assess the accuracy and characteristics of the rotating tube stirrer, a number of compounds were examined typical of those being investigated in these laboratories. In each instance the freezing point or melting point was checked on a 35-ml. sample, using the rotating blade stirrer, immediately prior to the determination using the rotating tube. The results are given in Table II together with the API values of the freezing points for zero impurity where available. As with the blade stirrer, the stirring efficiency was judged from the nature of the curves obtained and examples of these are given in Figure 5.

The combination of the rotating thread and the stationary thermometer appears to give a satisfactory equilibrium state, the rate of attainment of which is assisted by the high thermal conductivity of the aluminum tube. The accuracy of the method has not suffered appreciably as a result of the reduction in sample volume and a freezing point or melting point accurate to 0.01° C. is obtained which is within the limits of accuracy previously reported for the conventional method (*12*, *16*, *17*).

In freezing point determinations, thermodynamic equilibrium appeared to be maintained until slightly more than half of the material had crystallized. When this stage was reached, a sharp increase in the gradient of the curve took place, indicating loss of equilibrium, although the tube continued to rotate until the sample had almost completely frozen. This effect is not shown in Figure 5, which illustrates only those portions of the curves suitable for extrapolation. It was found that an estimation of the freezing point for zero impurity correct to 0.1° C. could be obtained using standard geometrical or analytical methods (*12*, *17*). In melting point experiments however, it seemed that equilibrium was only attained for the last few points of the curve following a sharp rise in temperature from the nonequilibrium state. Sufficient points were usually obtained to enable the melting point for zero impurity to be calculated, but for a number of the compounds examined only the melting point of the sample could be measured with any degree of accuracy.

In conclusion, the rotating blade stirrer is recommended for use with those samples which do not respond well to the reciprocating stirrer. The small sample tube allows satisfactory determinations to be made on samples too small for conventional apparatus.

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