The Density of Solid Phenol

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APPARENTLY NO DATA exist for the density of phenol in the solid state. Published values, for temperatures below the melting point, appear to be extrapolations from data on the liquid at 40° C. or higher; they would therefore apply only to the undercooled liquid.

EXPERIMENTAL

All tests were carried out on synthetic phenol produced by the sulfonation process (Plastic and Coal Chemicals Division, Allied Chemical Corp.). The solidification point was 40.8° C.

Preliminary exploratory work showed the formation of bubbles during crystallization of the melted material. As the true density could not be obtained with bubbles present, an attempt was made to remove this air from the molten material by boiling. No improvement was obtained, however, either at atmospheric pressure or under reduced pressure. The only method which gave results was based on crystallization and remelting of the phenol several times under reduced pressure. By this treatment all bubbles were eliminated. However, a short exposure of the molten material to air brought it back to the original condition.

The density was determined by using a pycnometer, a cylindrical glass container having a capacity of about 45 ml. The bottom was connected to a 2-mm. straight stopcock. The top was connected by means of a small bore tube (2-mm. inside diameter) to a small chamber which in turn was connected to an upper reservoir by means of a capillary tube (2-mm. inside diameter) 100 ml. long.

Molten phenol was poured into the upper reservoir, and the apparatus alternately heated with a gas flame and then cooled until it was filled right up into the upper reservoir.

Reduced pressure (2-mm. of mercury) was then applied at the upper reservoir, and the phenol allowed to crystallize, care being taken to control the crystallization so that it occurred progressively from the bottom up. Considerable air was removed by this procedure. The phenol was then melted slowly from the top down, by means of the flame, thereby removing the greater portion of the remaining air. This entire operation was carried out two more times. At this point maximum air removal appeared to have been attained, although a few small bubbles always appeared during solidification. To reduce to a minimum the error introduced by this residual air, the final crystallization was carried out under atmospheric pressure. By so doing, any volume of residual air became 380 times smaller than under 2 mm. of mercury pressure. The purpose of the capillary tube was to prevent the air which dissolved in the phenol in the upper reservoir, when the vacuum was released, from penetrating into the body of the pycnometer. Nevertheless, in spite of this precaution, when the crystallization reached the upper portion of the pycnometer, bubbles began to form among the crystals. It was then necessary to reapply vacuum and remove the air by remelting the phenol at this particular portion.

When the contents were completely solid, the tube was cut a little above the body of the pycnometer, and the total weight of pycnometer and phenol was determined. The contents were then melted and removed by opening the stopcock on the lower portion. The weight of the pycnometer was then determined and also that of boiled distilled water it would contain at 40° C. From these data the density of phenol at 40°/4° was calculated, all weighing being corrected to vacuo.

The same apparatus was used to determine the density of phenol without removal of air.

RESULTS

A first determination gave a value for the density at 40°/4° of 1.125. Another determination, using greater precautions in air removal, gave a density value at 40°/4° of 1.132. The correct value is probably slightly higher, because traces of air spaces were still observable in spite of the greatest care in operation.

A determination without removal of air gave a density at 40°/4° of 1.075.

The appearance of solid phenol from which all air is removed is distinctly different from that of ordinary phenol. It is translucent, whereas ordinary phenol has a white, opaque appearance.

The color stability of phenol, on aging, is distinctly better when all air is removed.

DISCUSSION

The value of the density at 40°/4° of 1.132 is substantially higher than those reported in the literature, of which the following are typical:

Temperature, ° C.	Density	Reference
21	1.0598	(1)
25/4	1.0710	(2)
25/4	1.0710	(3)
25/4	1.0708	(4)
25/4	1.072	(5)

The increase in density from 1.075 for ordinary phenol, to 1.132 for air-free phenol, corresponds to a solubility of air in phenol of about 5% by volume at 40° C. as measured at atmospheric pressure.

Crystallization forces the air out and it remains occluded among the crystals, giving the mass a white, opaque appearance.

Since this work was completed, a similar effect has been observed qualitatively with *o*-cresol and phthalic anhydride. Small bubbles are expelled as solidification proceeds. No other compounds have been examined, but it is logical to assume that many, if not all, show this effect. It would be interesting to determine the relative proportions of oxygen and nitrogen contained in the expelled air. The solubility of other nonreactive gases would also be of interest.

LITERATURE CITED

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