Density of water as a function of temperature

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It was shown by the author long ago¹ that a plot of the densities of many liquids vs. temperature gives a curve that is not smooth: but exhibits inflection points, or kinks at some intervals. This can be shown to be true for any liquid for which there exists accurate experimental data. But water seemed an exception; for the temperature — density curve is perfectly smooth according to figures given in tables used at the present time.

It is observed that most people prefer not to believe in these kinks. One reason is that they are not predictable on the basis of the current theories.

Fig. 1. Density of water vs. temperature.

Another is that the previous experimentalists were not aware of these things, and have performed the measurements of densities at regular intervals of temperature. But the kinks, or places of deviation from the smooth path frequently fall in between the observed points, and thus remain unnoticed. Some may attribute these effects to conditions which cause experimental errors of more or less systematic character. This view, in the light of the present data, seems absurd.

It would not be easy to repeat the work of Ramsey and Sidney Young², for this requires complicated apparatus and takes much time. However, there is an easy method of demonstrating these phenomena at moderate temperatures³. The author took propylalcohol, which was purified by the procedure of Sidney Young, and determined its density in a pycnometer at various temperatures between 20° and 80°C. The curve so obtained showed a kink in the same place as it had appeared in the data of Sidney Young. Other liquids also show kinks in this region of temperature: benzene has a kink at 45°C, etc. The temperature was carefully regulated during these experiments, and by weighing a 25-cc. pycnometer the density may be determined to five decimal places. But such is not needed, for the third decimal is sufficient to demonstrate the kinks. And if the curve is plotted on graph paper in such a way that a fraction of a millimeter represents the fourth deci-

mal place, the experimental errors are not seen at all. Any deviations from the smooth path must be due to intrinsic causes.

But of all substances known to the author, water seemed an exception in that it alone seemed free of these discontinuities. However, experiments performed recently by the co-author show that this is not true, and that kinks are easily noticed in the density-temperature curve for ordinary distilled water. A 25-cc. pycnometer was used in these measurements, and densities determined for the range of temperatures from 47° to 53°C, in a thermostat regulated to 0.02°C. Between 47 and 50 there is a smooth stretch of the curve, and another between 50° and 53°. These intersect just a little above 50°C, giving a well defined kink (see Fig. 1). Below 47 another smooth stretch of the curve begins, which is not shown on the drawing. A figure drawn from the data given in the Smithsonian Tables may be seen to be perfectly smooth with only a slight curvature.

There can be no doubt that the experimental results were smoothed by applying the generally accepted rules for drawing a representative curve amidst erratic points due to experimental errors. In this case it is not legitimate to do so because, as explained above, the effect is well above the limits of experimental errors, and on a drawing of the scale indicated the errors do not appear.

This is not the only case where the figures given in tables show themselves adulterated, and especially in the study of liquids there are some cases where the entire experimental work ought to be done afresh.

¹ G. Antonoff, Philos. Mag. J. Sci. 1, 256 [1925].

² Sidney Young, Proc. Roy. Soc. Dublin 12, 374 [1910].

³ G. Antonoff, J. physic. Chem. 48, 80 [1944].

Über das dielektrische Verhalten des Diphenyläthers in Mischungen mit unpolaren Flüssigkeiten

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Die Molpolarisation des Diäthyläthers in Mischungen dieses Stoffes mit unpolaren Flüssigkeiten ist von der Konzentration nahezu unabhängig¹. Diäthyläther läßt sich also weder in die Gruppe der Stoffe, die in Lösung stöchiometrisch definierte Assoziate bilden, noch in die der Dipolschwarmbildner eindeutig einordnen². Dieser Sachverhalt hat uns veranlaßt, das dielektrische Verhalten des Diphenyläthers in Mischungen mit unpolaren Flüssigkeiten zu untersuchen, um vielleicht auf diesem Weg Einblick in die Gründe für das merkwürdige dielektrische Verhalten des Diäthyläthers zu gewinnen.

¹ P. Debye, Polare Molekeln, Leipzig 1929, S. 48.

² H. Hartmann, Z. Elektrochem. angew. physik. Chem. 47, 856 [1941]; Z. physik. Chem., Abt. B 51, 309 [1942], 53, 37, 49, 54 [1942].