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THE CRITICAL TEMPERATURE OF MERCURY.

BY ALAN W. C. MENZIES.

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The results of some work in this field were presented orally by the writer at the Minneapolis meeting of the American Chemical Society, in December, 1910.[1] Publication in printed form was delayed until the completion of similar work on other substances. In view, however, of the appearance of an article with the above title by J. Königsberger,[2] who, using the same method as the present writer, reaches different conclusions, it may be well at this time to make a brief statement of the facts encountered. Königsberger and the writer both heated the mercury in capillary quartz tubes; Königsberger reports the critical temperature as near 1270°, whereas the writer found and reported that the critical temperature is not reached at 1275°.

Comparing experimenting details, one notes that, while the writer employed transparent quartz glass tubes of 0.2 mm. bore,[3] Königsberger employed similar tubes of 0.1–0.2 mm. bore.[4] The writer charged and sealed the tubes, which were about 7 cm. long, after exhausting to 0.03 mm. of air pressure, and supported them in the center of a very large D-muffle, heated by illuminating gas with compressed air blast, in a large muffle furnace. The front of the muffle was closed except for an oval sighting hole, 2 × 3 cm., for the observing telescope, and a hole of a few mm. diameter to lead in the thermocouple. That the heating was, in some experiments at least, remarkably uniform, was proved by the ob-

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[1] "A Lower Limit for the Critical Temperature of Mercury," presented before the Section of Inorganic and Physical Chemistry.

[2] *Chem. Ztg.*, **135**, 1321 (1912).

[3] These were procured from The Silica Syndicate, London.

[4] Procured from The Zirkonglas Gesellschaft, Frankfurt a/M.

servation that the capillary, after such experiments, was blown out and trebled in bore apparently perfectly *uniformly* throughout its entire length. The readings of the thermocouple used for the temperature measurements were verified by means of the eutectic point $Cu\text{-}Cu_2O$ taken as 1063°, and attained as recommended by Waidner and Burgess.[1] Königsberger heated his tubes in a vertical blast-lamp flame fed by a mixture of air and oxygen. He determined the temperature optically by observation of a spiral of platinum wire coiled round the tube. He states that the temperature measurement is preliminary and only approximate, and promises higher accuracy later.

The writer observed the liquid phase to disappear at 1275°. This was found to be due, however, not to attainment of the critical temperature, but to the blowing out of the quartz tube with consequent enlargement of its volume. In presenting his results, the writer pointed out that quartz glass is, after all, a supercooled liquid, and that, computed by the formula proposed by Smith and himself,[2] the vapor pressure of mercury at 1275° would be in the neighborhood of 675 atmospheres. In no case was the quartz tube ruptured. Königsberger's statement is "Die kritische Temperatur liegt bei etwa 1270°." He states further that his "tubes withstood the critical temperature only a few seconds, exploding with a sharp report, although they contained only about 5 mg. of mercury." It is this last statement, especially, that leads the writer, in view of his own findings, to doubt that Königsberger actually reached the critical temperature of mercury at 1270°.

It may be of interest to recall that Happel[3] computed the critical temperature of mercury to lie at 1097°. In order to do this, he employed the empirical equation of van der Waals:

$$-\log \frac{p}{p_c} = f\,\frac{T_c - T}{T}$$

where p and T stand for vapor pressure and absolute temperature, and p_c and T_c for critical values. Happel found that f is not constant but has different values for different groups of substances, and also that f is a function of the reduced temperature. He endeavors to show that mercury should be grouped with the monotomic gases of the atmosphere, and selects his values for f accordingly.

The use of the well-known equation between the same variables proposed by Nernst[4] has led the writer to results no more satisfactory. One may, however, go back to the experimental fact expressed by Mathias,[5]

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[1] *Bull. Bur. Standards*, **6**, 171 (1909).

[2] THIS JOURNAL, **32**, 1434 (1910).

[3] *Ann. Physik*, [4] **13**, 340 (1904).

[4] Cf. Bingham, THIS JOURNAL, **28**, 717 (1906).

[5] *J. de physique*, **3**, 11 (1893).

in his law of the rectilinear diameter. Combining this with Guldberg's finding[1] that the critical density is four times the density of a substance at absolute zero, Davies[2] has shown that

$$\alpha = \frac{1}{2T_c - T}$$

where α is the coefficient of cubic expansion of the liquid. This would lead to a critical temperature for mercury above 2600°.

One may also employ the equivalent but older relationship of Thorpe and Rücker[3]

$$T_c = \frac{T_2 s_1 - T_1 s_2}{A(s_1 - s_2)}$$

where s_1 and s_2 are densities of the liquid at the temperatures T_1 and T_2. Young gives a value 1.974 for the constant A, and states that for twenty-four substances for which the required data are accurately known, the discordances only in a few cases exceed 2%. This formula leads also to a critical temperature for mercury above 2600°.

The rule of Guldberg[4] connecting critical temperature and boiling point is clearly inapplicable here, as it rests ultimately on the assumption that the critical pressures of all substances are nearly identical.

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THE MECHANICAL STIMULUS TO CRYSTALLIZATION.[5]

BY S. W. YOUNG AND W. J. VAN SICKLEN.

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In two previous papers on this subject[6] it has been shown that crystallization in supercooled liquids may be forced at any temperature below their melting points. In other words, there is no so-called metastable field, in which crystallization can only be stimulated by the addition of a crystal of the new phase which is to appear. Since the publication of these papers there has appeared a most interesting paper by the Earl of Berkeley,[7] in which the matter of the metastable limit is taken up from the theoretical point of view in a very clear manner. Basing the theoretical necessity for the existence of a metastable limit on the van der Waals type of doubly flexed curve, which he shows is likewise applicable to solutions, he seeks for some explanation which will harmonize the theory

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[1] *Chem. Zentr.*, **1898**, p. 1042.

[2] *Phil. Mag.*, [6] **23**, 657 (1912).

[3] *J. Chem. Soc.*, **45**, 135 (1884).

[4] *Z. physik. Chem.*, **5**, 374 (1890).

[5] Abstracted from a Thesis for the Degree of Master of Arts, presented by Mr. W. J. Van Sicklen to the Faculty of Stanford University, December, 1912.

[6] THIS JOURNAL, **33**, 148, 1375.

[7] *Phil. Mag.*, Aug., 1912, 254.