Liquid Helium Vapor Pressure Equation

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An empirical equation for the vapor pressure of liquid helium has been developed. This equation is valid throughout the entire range of temperatures below the critical point, and is in accord with the latest available data on the vapor pressure to within about $\pm0.002°$K.

THE problem of representing the vapor pressure of liquid helium by analytic functions has been solved in the past by means of three empirical equations, one valid in the temperature range below the λ point (2.17°K), a second valid between the λ point and the normal boiling point (4.22°K), and still a third between the boiling point and the critical point (5.20°K).[1] In 1948 a table, prepared at the Kamerlingh Onnes Laboratory in Leiden, giving the vapor pressure as a function of temperature was adopted as the definition of an "agreed" scale which all cryogenic laboratories should use in reporting data.[2] The accuracy of the data in this table had already been questioned some two years prior to its adoption.[3,4] Extensive research during the past two years[5–10] has demonstrated beyond question that there exist small, but significant, differences between the 1948 scale and the true thermodynamic scale ($\sim$0.01° at 2.2°K and $\sim$0.02° at 4.9°K). A recent examination of the 1948 scale by the authors[11] further verified these major errors and, in addition, revealed point-to-point roughness in the scale itself. In particular, some rather large and abrupt changes in slope of the 1948 scale were found, the most notable of these occurring near the λ point, near 2.8°K and near 4.2°K.

During the course of the authors' investigation of the 1948 scale, the derivative of the logarithm of the vapor pressure with respect to reciprocal temperature ($d\ln P/dT^{-1}$) was calculated, directly from the 1948 scale at first and subsequently from thermodynamic data. These data were found to fit the following empirical function rather well over the entire temperature range below the critical point,

$$-d\ln P/dT^{-1} = A + BT + CT^3 - D\tan^{-1}(\alpha T - \beta), \quad (1)$$

where A, B, C, D, α, and β are adjustable constants. Integration of this equation yields

$$\ln P = I - \frac{A}{T} + B\ln T + \frac{C}{2}T^2$$
$$- D\left(\frac{\alpha\beta}{\beta^2+1} - \frac{1}{T}\right)\tan^{-1}(\alpha T - \beta)$$
$$- \frac{\alpha D}{2(\beta^2+1)}\ln\frac{T^2}{1+(\alpha T - \beta)^2}, \quad (2)$$

where I is the constant of integration. The constants in Eq. (2) were determined from the 1948 scale plus an average of all measured corrections with the following results: $I = 4.6202_5$, $A = 6.399$, $B = 2.541$, $C = 0.00612$, $D = 0.5197$, $\alpha = 7.00$, and $\beta = 14.14$. Pressure, P, is in mm Hg (20°C and standard gravity) and $-\pi/2 < \tan^{-1}(\alpha T - \beta) < \pi/2$ radians.

Figure 1 demonstrates graphically the results. The various experimental data points plotted in Fig. 1 are, with the exception of the thermodynamic calculation of Erickson[12] and the isotherms of Keller, an average of several individual measurements, all at temperatures within about 0.1°, or less, of the averaged temperature at which the point is plotted. The rather jagged curve drawn in the figure was obtained in the following manner. The pressure corresponding to each 0.01° temperature interval between 0.66°K and 5.20°K was calculated from Eq. (2).[13] At each of these calculated pressures, the corresponding value of T_{48} was found from the "agreed" scale. The difference between T_{48} and the temperature used in the calculation, T, was plotted at each value of T and the individual points were connected by straight lines.

Equation (2) appears to eliminate most of the difficulties previously encountered in consolidating measure-

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[5] R. A. Erickson and L. D. Roberts, Phys. Rev. **93**, 957 (1954).

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[10] Corak, Garfunkel, Satterthwaite, and Wexler, Westinghouse Research Report 60–94466–5–R1, December, 1954 (unpublished).

[11] Clement, Logan, and Gaffney, Naval Research Laboratory Report No. 4542, May, 1955 (unpublished).

[12] R. A. Erickson (private communication). A re-calculation of the helium vapor pressure scale from thermodynamic data as done by Erickson and Roberts in reference 5, using the virial coefficient data reported by Kilpatrick, Keller, and Hammel [Phys. Rev. **97**, 9 (1955)]. (The authors are indebted to Dr. Erickson for a tabulation of the numerical results of his calculations.)

[13] Values of vapor pressure as given by Eq. (2) have been calculated by the Naval Research Laboratory electronic digital computer (NAREC) at each 0.005° temperature interval between 0.6° and 5.3°K, thanks to the kind assistance and cooperation of Dr. B. Lepson of this laboratory. Copies of these calculations may be had by writing to the authors.
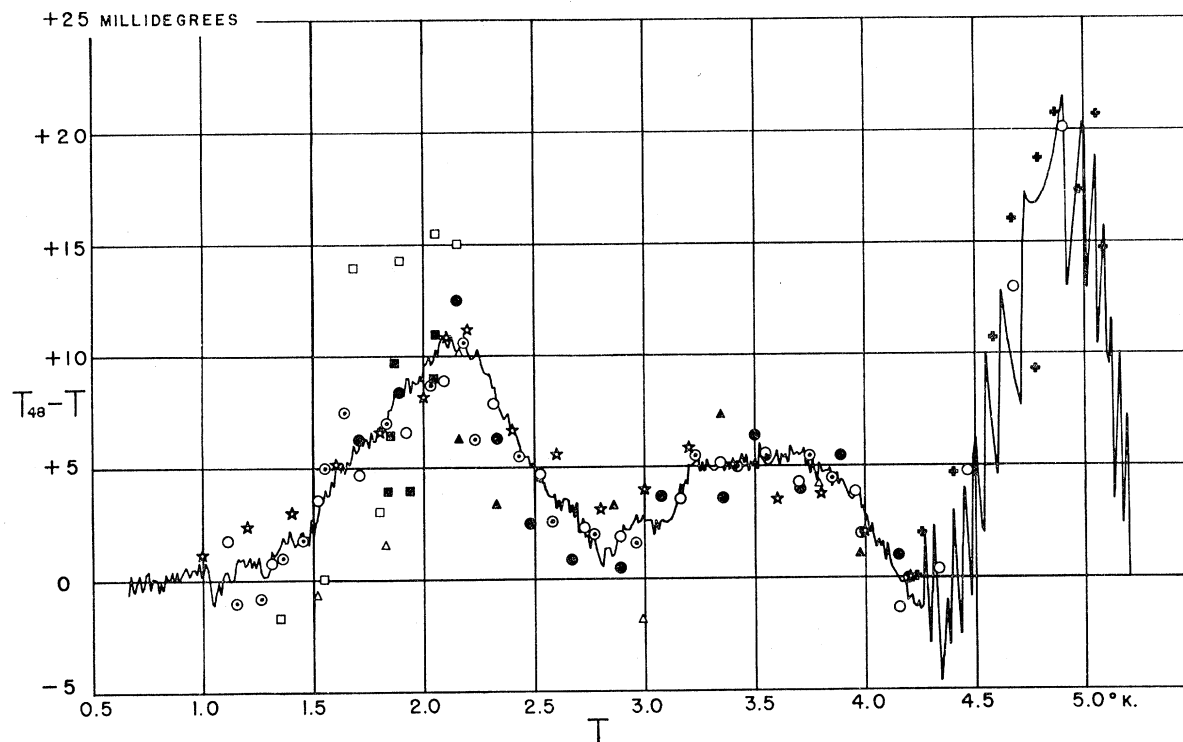
FIG. 1. Summary of data on errors in the 1948 liquid helium vapor pressure scale. The jagged curve is the difference between temperature as defined by the 1948 scale and by Eq. (2) of this report. Plotted points are measurements of ■ Kistemaker and Keesom,[3] □ Kistemaker,[4] ⊙ Erickson and Roberts (magnetic thermometer data of reference 5), + Berman and Swenson,[7] ▲ Keller,[8] △ Keller[9], ○ Corak, et al.,[10] ● Clement, et al.,[11] and ★ Erickson.[12]

ments of the vapor pressure of liquid helium. First, it is a single equation valid over the entire temperature range below the critical point. Second, it can be calculated to any precision desired, eliminating entirely the possibility of any point-to-point roughness or abrupt change in slope as found in the 1948 scale. Third, it seems to represent the relationship between the vapor pressure and the true thermodynamic temperature within ±0.002° or less, a deviation comparable in magnitude to the uncertainty in our present knowledge of this relationship.

Note added in proof.—Since the preparation of this report, a number of new results have appeared which lead to some modification of the conclusions stated above. First, Keller has made some corrections in the analysis of his He[4] isotherm data (reference 8).

Second, the data of Berman and Swenson (reference 7) have been re-examined in light of a redetermination of the boiling point of normal hydrogen reported by Moessen, Aston, and Ascah [J. Chem. Phys. 22, 2096 (1954)]. Third, new magnetic measurements (reported at the International Conference on Low Temperature Physics, Paris, September 2–8, 1955) have been made by Ambler and Hudson at the National Bureau of Standards. These new and corrected data show systematic deviations from Eq. (2), the maximum deviation being about 5 millidegrees. The carbon thermometer calibration data of Corak et al. [reference 10, an abridged version of which appeared in Phys. Rev. 98, 1699 (1955)] are consistent with these deviations.

During the recent Conference on Low Temperature Physics in Paris the vapor pressure-temperature relationship for He[4] was discussed and replacement of the 1948 scale was recommended. Part of the recommendation was that the conversion of vapor pressure to temperature, when the vapor pressure is measured in a bulb, be based on the experimental results mentioned in this note. A vapor pressure-temperature table which may be used for this purpose is being prepared and copies will be available shortly.