the HELIUM VAPOR-PRESSURE SCALE of TEMPERATURES

A report on this NBS Conference was made at the Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, August 26–30, 1957. Dr. Brickwedde is consultant to the Director of the National Bureau of Standards and is also Dean of the College of Chemistry and Physics, The Pennsylvania State University.

By ***F. G. Brickwedde***

SINCE the Fourth International (Paris) Conference on Low-Temperature Physics in 1955, precision low-temperature research has been plagued by having *two* standard scales for temperature in the range 1 to 5.2°K. These are the helium vapor-pressure scales of J. R. Clement (the 55E Scale), and of H. van Dijk and M. Durieux (the L55 Scale). The differences between these scales (Fig. 1) are within the experimental uncertainties of the measurements on which the scales are based. A reliable decision as to which of these two scales is superior to the other calls for a study and reevaluation of all the data on which the scales are based. The original or *raw* experimental data from which published values for the vapor pressure, and calorimetric and state properties of helium were calculated should be recalculated using the present *best* values for physical constants and related properties of helium. The magnitude of this reevaluation may be better appreciated when it is realized that the temperature scales used by the original investigators are in error and have to be corrected for, but that these corrections cannot be determined until the ultimate objective, *the* standard scale, has been determined. This is a big, though possible, undertaking. There are real difficulties, however, because some investigators have not published sufficient data for a complete reevaluation of their work. Then the personal judgment of the reevaluator becomes important. Difficulties of this kind seemed to be blocking agreement of Clement and van Dijk on a single helium vapor-pressure scale of temperatures.

A conference was held at the National Bureau of Standards, July 30–August 1, 1957, for a discussion of these difficulties. Besides J. Reid Clement of the U. S. Naval Research Laboratory and H. van Dijk and D. deKlerk of the Kamerlingh Onnes Laboratory, Leiden, the Conference was attended and participated in by W. E. Keller of the Los Alamos Scientific Laboratory, J. A. Erickson of the Ohio State University, and members of the NBS staff (C. W. Beckett, G. Cataland, H. H. Plumb, H. F. Stimson, and F. G. Brickwedde).

The Conference was held in a spirit of cooperation and good will. Considerable progress was made in harmonizing different views and the Conference ended with an optimistic expectation that it would not be long before agreement on a single standard scale from 1 to 5.2°K would be complete—maybe within a year.

The task that Clement and van Dijk laid out for themselves is big, but the Conference agreed that it is desirable. It was decided *not* to derive a new scale from the L55 or 55E Scales because neither scale is satisfactory in all respects, and new data on the latent and specific heats of liquid helium are available now that were not available when the L55 and 55E Scales were developed. It was agreed to obtain the new scale by starting with the theoretical vapor-pressure equation from statistical thermodynamics:

$$\ln p = i - \frac{L_0}{RT} + \frac{5}{2}\ln T - \frac{1}{RT}\int_0^T S_l\,dT - \int_0^T V_l\left(\frac{dp}{dT}\right)_{\text{Sat}} dT - \phi(T) \quad (1)$$

where $i = \ln (2\pi m)^{3/2}k^{5/2}h^{-3}$ is the chemical constant; $\phi(T) = 2B/V + 3C/2V^2 - ln\ (pV/RT)$ is the virial correction where $(pV/RT) = 1 + B/V + C/V^2$; L_0 is the heat of vaporization at 0°K; and V_l and S_l are, respectively, the molecular volume and entropy of liquid helium. Equation (1) was the starting point of van Dijk and Durieux for the development of the L55 Scale. Agreement to proceed in this way in deriving the new scale was a concession on the part of Clement whose starting point for the 55E Scale was the measured vapor pressures of liquid helium.

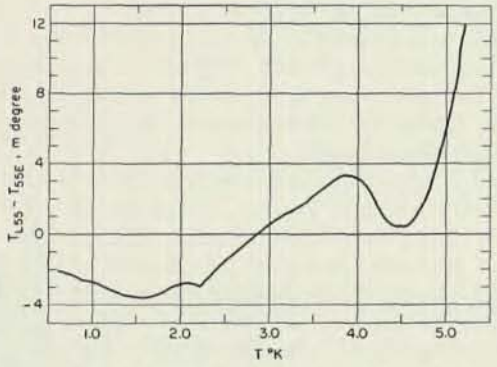

Fig. 1. A diagram of differences between the L55 and 55E Scales. A difference $(T_{L55} - T_{55E})$ corresponds to a given value of the vapor pressure of helium on the two Scales.

It was decided that values reported in the literature for the properties of helium should not be the ones substituted in Eq. (1) but that the original experimental data should be reevaluated. Consideration was given to the values for the fundamental constants and auxiliary properties of helium to be used consistently in all calculations including the reevaluation of reported properties in the literature. The liquid densities and boiling point of helium were agreed upon. The virial coefficients of helium were more of a problem and further investigation of them appeared desirable. It was decided to reevaluate the helium isotherm data in the literature using the calculated second virial coefficients, $B(T)$, of Kilpatrick, Keller, and Hammel [1] for a reevaluation of the third virial coefficients of helium, $C(T)$. It was agreed that third virial coefficients should be used not only in Eq. (1) but also in calculations of the heats of vaporization $L(T)$ of liquid helium from raw calorimetric data and in calculations of L_0, the heat of vaporization at 0°K, from the $L(T°\mathrm{K})$ data. Published data on the specific heat of liquid helium are to be reevaluated for the calculation of S_l and L_0 in Eq. (1). For this, temperature scale corrections must be applied to the obsolete temperature scales used by the original investigators, but these scale corrections can not be found until the new standard vapor-pressure scale itself has been determined. Hence a thorough reevaluation of data and a fully consistent calculation of the vapor pressures of helium can be realized only through repeated iteration of the calculations of vapor pressure with Eq. (1) and reevaluation of the published data, until further repetitions make no further changes in the calculated vapor pressures that are significant.

It was recommended by the Conference that low-temperature scientists continue to use the L55 and 55E Scales as they have already been issued until this new scale now being calculated by van Dijk and Clement is completed. It is feared that the introduction of other scales or modifications of the L55 and 55E Scales now would further confound the situation of multiple standards which already is bad enough. It is expected that Clement and van Dijk will complete their calculations as expeditiously as possible. Indeed, it is hoped that arrangements will be made for Clement to work with van Dijk and Durieux in the Kamerlingh Onnes Laboratory in Leiden for a time. This should materially expedite the work since most of the original laboratory records needed for reevaluation of the published data on helium are in Leiden.

The L55 (Leiden) Scale has been published by van Dijk and Durieux in Volume 2 (Chapter IV) of *Progress in Low-Temperature Physics* (1957). The 55E (NRL) Scale was presented by Clement at the Baton Rouge, Louisiana, National Science Foundation Low-Temperature Conference, December 1955. It has been issued as a report (*Liquid Helium Vapor-Pressure Temperature Scale*) by Clement and is available on request to Clement. Both scales are in use in the United States and elsewhere.

[1] J. E. Kilpatrick, W. E. Keller, and E. F. Hammel, Phys. Rev. **97**, 9 (1955).

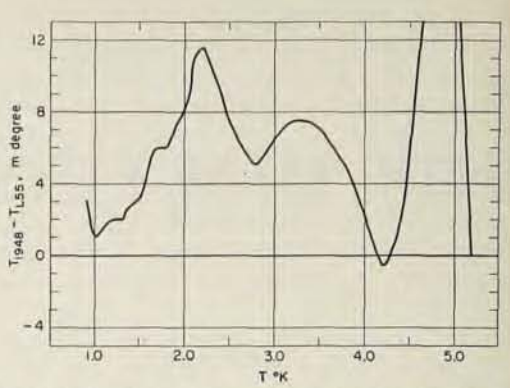

Fig. 2. A diagram of differences between the L55 and the "1948" Scales. This figure shows the improvement in the temperature scale already made by van Dijk and Durieux. The 55E Scale represents a similar improvement made by Clement.

Fig. 1 is a diagram of the differences between the L55 and 55E Scales. These differences do not exceed 3.6 millidegrees between 1 and 4.8°K. Clement and van Dijk think the program laid out by the Conference, including the reevaluation of published data, will result in a new scale correct probably to ± 2 millidegrees, except in the region of the critical temperature (5.2°K). The improvement of the helium vapor-pressure scale since 1948 may be seen in Fig. 2 which shows the differences between the L55 Scale and the "1948 Scale", the predecessor of the L55 and 55E Scales.

The differences between the L55 and 55E Scales below the λ-point (Fig. 1) are in the main explainable on the basis of a difference in the experimental vapor-pressure data used by van Dijk and Clement as the bases for their scales between 1 and 2.2°K. Clement did not use the Kistemaker (Leiden) vapor-pressure data,[2] which were not only used by van Dijk and Durieux but were weighted heavily by them. The Kistemaker data were not used by Clement because Kistemaker's papers do not contain enough of the original raw data for the kind of a reevaluation that would put them on a basis consistent with other investigators.

The differences between the L55 and 55E Scales in Fig. 1, between the λ and boiling points of helium (2.2 to 4.2°K), would have been significantly smaller if the recent liquid helium specific heat data of Hill and Lounasmaa [3] had been available earlier for the calculation of the entropy S_l of liquid helium. Also, in this range, 2.2–4.2°K, there is considerable uncertainty in the ϕ-term of Eq. (1) arising from rather large uncertainties in the third virial coefficient of helium. Van Dijk and Durieux did not use the third virial coefficient in the calculation of the L55 Scale. Clement, however, did make use of them.

From 4.2 to 5.2°K, the L55 and 55E Scales were based on the Berman-Swenson [4] vapor-pressure data.

[2] J. Kistemaker and W. H. Keesom, Physica **12**, 227 (1946), or Leiden Comm. 269b; and J. Kistemaker, Physica **12**, 272 (1946), or Leiden Comm. 269c.
[3] R. W. Hill and O. V. Lounasmaa, Phil. Mag. **2**, 143 (1957).
[4] R. Berman and C. Swenson, Phys. Rev. **95**, 311 (1954).

Table 1. Some Constants Adopted for the Calculation of the Vapor Pressure of Helium

(a) Normal boiling point of normal H_2: 20.377°K.
(b) Normal boiling point of He: 4.215_5°K with a tolerance of $\pm 0.001_5$ degree as a criterion for the acceptability of the scale at a vapor pressure of 760 mm Hg(0°C).
(c) The λ-point pressure of He: 37.80 mm Hg(0°C).
(d) The critical point pressure of He: 1718 mm Hg(0°C).

However, Clement made use, also, of NRL helium vapor-pressure data taken with calibrated carbon resistor thermometers which data van Dijk and Durieux did not use. Clement used the carbon-resistor data for interpolation and the Berman-Swenson vapor-pressure data, which had been taken with a gas thermometer, to raise or lower and orient the 55E Scale between 4.2 and 5.2°K.

An important point of difference in the development of the L55 and 55E Scales between 1 and 4.2°K, also, is the use made of helium vapor-pressure data obtained with secondary thermometers (magnetic and carbon-resistor). Van Dijk and Durieux used magnetic thermometer data only as a check on the L55 Scale and made no use of carbon-resistor thermometer data. Clement, however, gave considerable weight to both, relying heavily on these data obtained with secondary thermometers for "smooth" short-range interpolation between vapor-pressure data obtained with gas thermometers.

The NBS Conference recommended that the helium vapor-pressure data obtained with magnetic and carbon-resistor thermometers be used for checking the smoothness and regularity of variation of the calculated vapor pressures with thermodynamic temperature and for making local adjustments of the scale if necessary to smooth it.

Values for some properties and physical constants were agreed upon (see Table 1) for the calculation of the scale. In some cases digits were carried that are not really significant, the boiling point of hydrogen being one of these. Agreement on the boiling point of hydrogen to better than 0.01 degree is needed, however, since the boiling point of helium calculated from helium vapor-pressure data obtained with a helium gas thermometer standardized at the boiling point of hydrogen varies by 2 millidegrees for a change of 0.01 degree in the boiling point of hydrogen.

The new helium vapor-pressure scale which Clement and van Dijk will provide may be expected to be in closer agreement with the thermodynamic scale than either the L55 or the E55 Scale. The double standard that exists now is unfortunate, but it is fortunate that we can look forward to a significant improvement of the scale as a reward for patience. Low-temperature science will be indebted to Clement and to van Dijk and Durieux for a long time for their perseverance and insistence on providing us with the best possible temperature scale.