

*A revision of the international practical scale of temperatures is in the making, and some steps being taken in that direction are discussed in this account of the most recent meeting of the Advisory Committee on Thermometry of the International Committee on Weights and Measures. The author is dean of the College of Chemistry and Physics at Pennsylvania State University.*

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# International Practical Temperature Scale

ON September 25-27, 1962, the Advisory Committee on Thermometry of the International Committee on Weights and Measures met under the presidency of Professor J. de Boer of Amsterdam, in Sèvres (a suburb of Paris), in the Pavillon de Breteuil, the home of the International Bureau of Weights and Measures, and for three days discussed important matters relating to international standards of thermometry.<sup>1</sup> The Advisory Committee on Thermometry is one of the working groups of the International Committee on Weights and Measures, a committee established in 1875 by the "Convention du Mètre", an international treaty between the principal industrial and scientific nations for obtaining international agreement on physical standards of measurement for science, technology, and industry.

The most recent, previous meeting of the Advisory Committee on Thermometry was held in 1958 when the 1958 He<sup>4</sup> vapor-pressure scale of temperatures<sup>2</sup> was approved and recommended as the international standard for 0.5 to 5.2°K. At the 1962 meeting of the Advisory Committee, a He<sup>3</sup> vapor-pressure scale was approved and was recommended for the determination of temperatures from measurements of the vapor pressure of He<sup>3</sup> between 0.25 and the critical temperature, 3.324°K. The scale is defined by the equation:

$$\ln P = 2.24846 \ln T - 2.49174/T + 4.80386 - 0.286001T + 0.198608T^2 - 0.0502237T^3 + 0.00505486T^4$$

which relates the vapor pressure  $P$  of He<sup>3</sup> (mm Hg at 0°C) to the temperature  $T$  on the Kelvin scale. This He<sup>3</sup> vapor-pressure equation was developed by S. G. Sydoriak, T. R. Roberts, and R. H. Sherman of the Cryogenic Laboratory of the Los Alamos Scientific

Laboratory (LASL). It is based: (a) below 0.9°K, on the theoretical vapor-pressure equation of statistical mechanics, using the best available information on the thermodynamic properties of He<sup>3</sup> for the evaluation of the terms dependent on He<sup>3</sup>; (b) above 2.0°K, on the most recent (LASL) isothermal comparisons of the vapor pressures of He<sup>3</sup> and He<sup>4</sup>, and the 1958 He<sup>4</sup> temperature scale; and (c) between 0.9 and 2.0°K, on the procedures of both (a) and (b). It is believed that this 1962 He<sup>3</sup> scale is in agreement with the 1958 He<sup>4</sup> scale between 0.9 and 3.0°K to within some tenths of a millidegree. At 0.25°K, the 1962 scale may depart from the thermodynamic scale by as much as  $\pm 0.004$  degrees.

Below 2.17°K, the lambda-point of liquid He<sup>4</sup>, the He<sup>4</sup> vapor-pressure thermometer encounters two difficulties, because of the creeping liquid-helium-II film in the vapor-pressure tube, that are avoided with the use of the He<sup>3</sup> vapor-pressure thermometer. The evaporation of the helium-II film and the recondensation of the He<sup>4</sup> in the vapor-pressure bulb give rise to: (1) a flow of He<sup>4</sup> vapor and a pressure gradient in the vapor-pressure tube, and (2) a flow of heat of condensation through the walls of the vapor-pressure bulb, resulting in the rise of the temperature of the bulb and its liquid-He<sup>4</sup> charge appreciably above the temperature of its surroundings because of the Kapitza thermal resistance at the interface between the liquid He and the vapor-pressure-bulb wall.

On the recommendation of the Advisory Committee, the International Committee on Weights and Measures has requested the United States and Russian governments to make pure He<sup>3</sup> available for precision thermometry to all countries. The Mound Laboratory at Miamisburg, Ohio, operated for the US Atomic Energy



Commission by the Monsanto Chemical Company, is prepared to furnish  $\text{He}^3$  containing less than  $10^{-4}$  parts of  $\text{He}^4$  and less than  $10^{-9}$  parts of tritium. The National Bureau of Standards was requested to prepare and distribute samples of  $\text{He}^3$  containing measured amounts of  $\text{He}^4$  for the calibration and for checks on the calibration of instruments (mass spectrographs) for the analysis of  $\text{He}^3$  for vapor-pressure thermometry. A  $\text{He}^4$  impurity of 0.1 percent in  $\text{He}^3$  causes an error of 0.0006 degrees at  $3^\circ\text{K}$ , if not corrected for, and 0.05 degrees at  $0.5^\circ\text{K}$ .

Plans are being laid for a thorough revision of the "International Practical Scale of Temperatures" in 1966. The international practical temperature scale (ITS), which extends from  $-182.97^\circ\text{C}$  to higher temperatures, was recommended by the International Committee on Weights and Measures and approved by the Seventh General Conference on Weights and Measures in 1927. This scale has had universal acceptance. Thermometers are calibrated on it at the NBS and in the national standardizing laboratories of all countries. In 1948, after instruments and procedures of higher precision had been developed, some changes were made in the ITS scale to improve the precision of measurement on it and to obtain closer agreement with the thermodynamic scale at high temperatures (above  $630^\circ\text{C}$ ). The changes made were within the limits of uncertainty of the scale in 1927. Within the precision of a temperature measurement, the ITS scale of today from  $-182.97^\circ$  to  $630.5^\circ\text{C}$  is the same scale adopted in 1927. One of the important features of the ITS scale has been its permanence.

After 35 years, however, difficulties have arisen with the ITS scale. The scientific temperature scale is the thermodynamic Kelvin scale and its use is required for the validity of the equations of thermodynamics. When the ITS was adopted in 1927, it was in a close agreement with the thermodynamic scale as the thermodynamic scale could then be established experimentally. As a result of improvements in accuracy since 1927 in the establishment of the thermodynamic scale, notably with improved gas thermometers, differences between the thermodynamic and ITS scales are now measurable. The differences are so large that, with improvements in the accuracy of the measurements of other properties, the difference between the scales has become a limitation on the accuracy obtainable from thermodynamic equations when used with recent data of the highest accuracy on properties of matter and with temperatures measured with thermometers calibrated on the ITS scale. Table 1 indicates the magnitude of the differences between the thermodynamic and practical scales.

There are other reasons for revising the practical scale. At present, the low-temperature end of the ITS is  $90^\circ\text{K}$ . An extension of the scale to lower temperatures is very desirable now, because of the practical use of these lower temperatures for industrial purposes and for engineering research and development. Joining a thermodynamic scale below  $90^\circ\text{K}$  to the ITS scale

Table 1. Differences between Temperatures on the Thermodynamic and ITS Scales

$\Delta t \equiv T_{\text{thermo}}^\circ\text{K} - 273.15^\circ - t^\circ\text{C (ITS)}$						
<i>Physikalisch-Technische Bundesanstalt Data (a)</i>						
$t^\circ\text{C (ITS)}$	1063.	960.	780.	630	444.6	419.5
$\Delta t$ deg.	1.5	1.1	0.8	0.17	0.07	0.07
<i>MIT Data (b)</i>						
$t^\circ\text{C (ITS)}$	444.6	250	100	50	0	
$\Delta t$ deg.	0.10	0.07	0.0	-0.013	0.00	
<i>Kamerlingh Onnes Laboratory (c) and Physikalisch-Technische Reichsanstalt Data (d)</i>						
$t^\circ\text{C (ITS)}$	$0^\circ\text{C}$	$-80^\circ\text{C}$				
$\Delta t$ deg.	0.0	+0.04				
<i>1962 Meeting of Advisory Committee on Thermometry, ICW and M</i>						
$t^\circ\text{C (ITS)}$	$-182.97$					
$\Delta t$ deg.	-0.01					

- (a) H. Moser, J. Otto, and W. Thomas. *Wiss. Abhandlungen der Phys. Techn. Bundesanstalt* 12, Part 1, p. 22 (1960).  
 (b) J. A. Beattie. *Temperature, Its Measurement and Control in Science and Industry* (Reinhold Publishing Corporation, New York), Vol. 2, p. 94 (1955). Beattie's experimental values of thermodynamic temperature were reduced to consistency with  $T(0^\circ\text{C}) = 273.150^\circ\text{K}$ . Beattie's values were determined on basis of  $T_0(0^\circ\text{C}) = 273.166^\circ\text{K}$ .  
 (c) W. H. Keesom and B. G. Dammers. *Physica* 4, 305 (1937); Leiden Comm. No. 230e.  
 (d) W. Heuse and J. Otto. *Ann. Physik* (5) 14, 181 (1932).

is made difficult by the departures of the ITS scale from the thermodynamic. The normal boiling point of  $\text{O}_2$  on the ITS scale departs from the thermodynamic value by 0.01 degree, and the temperature coefficients of resistance,  $d(R/R_{0^\circ\text{C}})/dT$ , of a platinum resistance thermometer at the oxygen point on the ITS and thermodynamic scales differ by about 0.2 percent. These differences between the scales make it impossible to extend the ITS scale to lower temperatures in a manner consistent with the thermodynamic scale.

The construction of platinum resistance thermometers for temperatures from  $630^\circ$  to  $1063^\circ\text{C}$ , for which range the Pt versus Pt-10%Rh thermocouple is now the standard thermometer of the ITS scale, has been so improved that it is likely that the platinum resistance thermometer will replace the standard thermocouple with a factor-of-ten increase in precision and reproducibility of measurement. Such a change of standard thermometer defining the ITS scale makes a change of the temperatures of the calibration points to more reliable thermodynamic values seem both timely and appropriate.

The Advisory Committee on Thermometry, at its 1962 meetings, appointed two working groups to gather information about the ITS and thermodynamic scales upon which a revision of the ITS can be based. One



working group<sup>3</sup> is to prepare a table or graph of the differences between the IPTS and thermodynamic scales that can be acceptable internationally. Also, this group will urge standardizing laboratories in different countries to determine the resistance ratio ( $R/R_{0^\circ\text{C}}$ ) for platinum from 630° to 1063°C. The other working group<sup>4</sup> is to derive the *best* values of ( $R/R_{0^\circ\text{C}}$ ) for platinum between 14° and 90°K as a function of the thermodynamic Kelvin temperature. These ( $R/R_{0^\circ\text{C}}$ ) values are to be obtained from the intercomparisons made within the last year at the National Physical Laboratory, Teddington, and at the Physico-Technical, Radio-Technical Measuring Institute, Moscow, of the thermometers furnished by each of four laboratories: namely, the National Bureau of Standards, the Pennsylvania State University, the National Physical Laboratory, and the Physico-Technical, Radio-Technical Measuring Institute. These thermometers have been calibrated on the scale between 14° and 90°K established independently in each of the four laboratories with a constant-volume He gas thermometer.

The Advisory Committee agreed on 90.17°K as the present most probable value for the thermodynamic temperature for the normal boiling point of oxygen. This value is 0.01 lower than the IPTS value (273.15°–182.97°). The Committee agreed also on 20.267°K and 20.384°K as the present most probable values of the thermodynamic temperatures of the normal boiling points of the 20.4°K-equilibrium mixture of the ortho and para varieties of  $\text{H}_2$ , and of the normal mixture, 75 percent ortho and 25 percent para, of hydrogen, respectively.

Some interesting problems relating to the temperature scale were discussed at the meeting of the Advisory Committee. The high-temperature (300° to 1063°K) expansivity of fused quartz (or silica glass)

was discussed because the differences between the values used for quartz gas-thermometer bulbs are so large that the temperatures calculated from gas-thermometer data are changed by as much as 0.7 degree at 1063°C by the use of the different coefficients. The replacement of boiling points by melting, or triple, points as thermometric fixed points in the definition of the IPTS scale looks attractive for an improvement in the precision of the calibration of thermometers. In 1958, the melting point of zinc, 419.505°C, was made alternative to the use of the boiling point of sulfur, 444.60°C, as a calibration fixed point. Recent measurements of ratios of Kelvin temperatures of fixed points at high temperatures using optical pyrometer techniques and Planck's law with infrared radiation and electrical photodetectors, by J. A. Hall at the National Physical Laboratory, Teddington, and by W. A. Heusinkveld and K. Schurer at the University of Utrecht, are yielding interesting results. When the value used for the radiation constant  $c_2$  is 1.4389 cm degrees, the latest value derived from atomic constants, the ratios are in better agreement with the gas-thermometer data of the Physikalisch-Technische Bundesanstalt (in Table 1) than when the IPTS value of 1.4380 is used. Of unusual interest were reports of encouraging progress in the development of ultrasonic electro-acoustic resonators at the National Bureau of Standards and at the D. I. Mendelev Institute of Metrology for the measurement of low temperatures (2 to 90°K) on the Kelvin thermodynamic scale. With these acoustical resonators, the velocity of sound in gaseous He is measured, and from the velocity, the temperature is derived. With some further improvement, the ultrasonic electro-acoustic resonator could become competitive in accuracy with the gas thermometer at low temperatures for the determination of thermodynamic temperatures.

## References

1. In attendance at the 1962 meeting of the Advisory Committee: J. de Boer, professor, University of Amsterdam, member of the International Committee on Weights and Measures, and president of the Advisory Committee; for the Physikalisch-Technische Bundesanstalt, Braunschweig, H. Moser and W. Thomas; for the National Physical Laboratory, Teddington, J. A. Hall and C. R. Barber; for the National Bureau of Standards, Washington, H. J. Kostkowski, H. H. Plumb, and J. L. Riddle; for the National Research Laboratory of Metrology, Tokyo, S. Takata; for the National Research Council, Ottawa, H. Preston-Thomas; for the D. I. Mendelev Institute of Metrology, Leningrad, B. Olejnik; for the Physico-Technical, Radio-Technical Measuring Institute, Moscow, M. P. Orlova; for the National Standard Laboratory, Chippendale, N.S.W., Australia, A. F. A. Harper; for the Kamerlingh Onnes Laboratory, Leiden, H. van Dijk and M. Durieux; for the Laboratoire National d'Essais, Paris, M. Debure; for the Bureau International des Poids et Mesures, Sèvres, J. Terrien and A. Bonhoure; G. Bozza, Director of the Institute for Applied Physics, Ecole Polytechnique, Milan; J. Timmermans, Boitsfort-les-Bruxelles; T. R. Roberts, Los Alamos Scientific Laboratory, Los Alamos, N. Mex.; B. Abraham, Argonne National Laboratory, Argonne, Ill.; G. R. Grove, Mound Laboratory, Monsanto Research Corporation, Miamisburg, Ohio; and F. G. Brickwedde, dean, College of Chemistry and Physics, The Pennsylvania State University, University Park, Pa.
2. *L'Echelle de Température à Tension de Vapeur dans le Domaine de L'Hélium Liquide*, Procès-Verbaux des Séances du Comité International des Poids et Mesures, 2<sup>e</sup> Série, 26-A, Annexe 22, pp. T 189–193 (1958). Also, F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement and J. K. Logan, J. Research Natl. Bur. Standards **64A**, 1 (1960).
3. Members: C. R. Barber, National Physical Laboratory; H. van Dijk, Kamerlingh Onnes Laboratory; H. Moser, Physikalisch-Technische Bundesanstalt; B. Olejnik, D. I. Mendelev Institute of Metrology; J. L. Riddle, National Bureau of Standards; and F. G. Brickwedde (Chairman), Pennsylvania State University.
4. Members: C. R. Barber, National Physical Laboratory; H. van Dijk, Kamerlingh Onnes Laboratory; M. P. Orlova, Physico-Technical, Radio-Technical Measuring Institute; J. L. Riddle, National Bureau of Standards; and F. G. Brickwedde (Chairman), Pennsylvania State University.