

DEVIATION OF T_{58} FROM THERMODYNAMIC TEMPERATURES*

T. C. Cetas and C. A. Swenson

Institute for Atomic Research and Department of Physics, Iowa State University, Ames, Iowa 50010

(Received 4 June 1970)

Chromic methylammonium alum and manganous ammonium sulfate have been used in complementary experiments to establish a paramagnetic salt temperature scale (T_M) from 0.9 to 18 K which is based on the N.B.S.-1955 platinum resistance thermometer scale. The liquid-helium vapor-pressure scales differ from T_M almost linearly in temperature up to 4 K with a maximum deviation $T_M - T_{58} = 6.7$ mK at 4.2 K. Satisfactory agreement is found between T_M and an earlier constant-volume gas thermometer scale. T_M and the N.B.S. acoustic scale differ systematically by 0.03% from 2.2 to 19 K with a maximum deviation of 5 mK from a linear relation.

The bases for the establishment of the presently accepted liquid He⁴ vapor pressure scale T_{58} have been discussed at length in the original publication,¹ a subsequent paper by van Dijk,² and in the series of papers which establish the He³ vapor pressure scale T_{62} .³⁻⁶ Several recent measurements have suggested that the T_{58} value for the boiling point of liquid helium, 4.215 K, may be too low by as much as 10 mK. These data, which are summarized in Fig. 1, include sound-velocity measurements in He^{4,7,8} and He^{3,8} gas as well as a constant-volume gas thermometer (CVGT) scale⁹ which will be referred to as RTAS in the following. Each point in Fig. 1 has associated with it roughly the same uncertainty of 2 or 3 mK, and there is agreement within these limits. The acoustic data⁷ and the CVGT data above 4 K can be made to agree better if a slight adjustment (+6 mK) is made to the value of the calibration temperatures of the CVGT experiment near 20 K.⁹ The lack of precision of the CVGT data is due to a deliberate choice of a small sensitivity to minimize errors due to uncertainties in the virial coefficient of helium gas. It is difficult to establish the major sources of uncertainties in the acoustic measurements.¹⁰

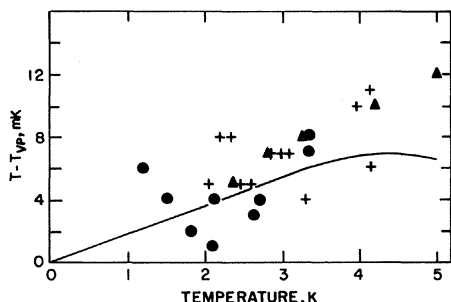


FIG. 1. The differences between recent thermometry and the liquid helium vapor-pressure scales. Triangles, Cataland and Plumb (Ref. 7); circles, Grimsrud and Werntz, Ref. 8; crosses, RTAS (Ref. 9). The solid line is a smooth representation of the present results.

Helium gas is used in thermometry investigations because its equation of state closely resembles the theoretical ideal gas equation of state. Dilute paramagnetic salt systems can be represented by susceptibility versus temperature relations which are relatively simple and which also contain the thermodynamic temperature. T_{58} and T_{62} , for instance, were derived in part using the results of paramagnetic salt thermometry. Durieux and his collaborators^{11,12} have used paramagnetic salt thermometry based on assumed temperatures near 2, 4, and 20 K to investigate the helium and hydrogen vapor-pressure relations. The recently defined International Practical Temperature Scale of 1968 (IPTS-68)¹³ below 20 K is based in part on their investigations.

The work which we describe below is similar to that of Durieux *et al.*,^{11,12} except that we calibrated our paramagnetic salt thermometer from 20 to 30 K using the N.B.S.-1955 platinum resistance thermometer scale and then extrapolated this calibration into the liquid-helium region. This procedure can be carried out with high precision and is completely independent of the systematic errors which enter into the CVGT or acoustic measurements. The major disadvantage is that four independent parameters enter into the analysis of the experimental data.

The ac susceptibility of a paramagnetic salt can be determined through the use of a mutual inductance bridge with the salt located at the center of a set of mutual inductance coils. The bridge readings X then are given by

$$X = A + \frac{B}{T + \Delta + \delta/T + \dots},$$

with A and B dependent both on the coil geometry and the salt used, Δ dependent on the type of salt and its shape, and δ presumably dependent only on the type of salt. The behavior of the Cr⁺⁺⁺ ion in chromic methylammonium alum (CMA)

[Cr(CH₃NH₂)(SO₄)₂·12H₂O] has been studied in some detail both experimentally and theoretically, and a value of $\delta = 2.8 \times 10^{-3} \text{ K}^2$ has been suggested.^{11,12} The behavior of the other paramagnetic salt which we used, manganous ammonium sulfate (MAS) [Mn(NH₄)(SO₄)₂·6H₂O], is much more complex and both Δ and δ must be determined experimentally.^{11,12}

The procedure for determining these parameters from experimental data and for establishing that only four parameters are necessary is based on two assumptions:

(1) The N.B.S.-1955 platinum resistance thermometer scale represents thermodynamic temperatures between 18 and 30 K.

(2) The liquid helium vapor-pressure scales T_{58}^1 and T_{62}^6 are proportional to the thermodynamic scale from 0.9 to 2.6 K or higher. This appears to be reasonable since thermodynamic arguments and relations played a large role in the establishment of these scales. We also have compared both T_{62} and T_{58} with the susceptibility of a powdered cerium magnesium nitrate sample (for which both Δ and δ are zero) and have verified this proportionality to within ± 0.3 mK between 0.9 and 2.6 K. Our measurements on this salt showed large deviations from Curie's law above 2.6 K; presumably if we had used single-crystal samples we could have verified the linearity of the vapor-pressure scales up to the temperature of 3.6 K, which is suggested by the work with the other salts.

The constants A and B must be determined using the high-temperature susceptibility data, and their precise value is dependent slightly on the values of Δ and δ which are assumed. The extrapolation to low temperature is very sensitive to these latter parameters, however, and it is for this reason that the linearity of the helium vapor-pressure scales is assumed. Once a value of A has been determined using the high-temperature data, precise values of Δ and δ can be calculated from the susceptibility data taken below 3 K. The interdependence of A and B and these parameters necessitates a self-consistent approach to obtain final values.

We will not describe the apparatus in detail. The mutual inductance bridge (33 Hz) is of the highly stable type which we have developed for low-temperature thermal expansion work¹⁴ and is similar to that described by Maxwell.¹⁵ If $X = 1.000\,000\,0$ represents the maximum bridge reading, the stability of the bridge and its reproducibility were of the order of 10^{-7} . The pow-

dered paramagnetic salt was packed in silicone oil in a nylon container and was connected to a 2-kg copper thermometer block by fine copper wires 25 cm long. This thermometer block contained a heater, a chamber into which liquid helium or liquid hydrogen could be condensed for operating below bath temperature, three vapor-pressure bulbs, an N.B.S.-calibrated platinum resistance thermometer, and four germanium resistance thermometers. The paramagnetic salt was surrounded by a "coil-foil" shield which was attached to the block at a point above the thermometers. The pressure in the vacuum jacket was less than 10^{-6} Torr at all times when data were being taken. The mutual inductance coils were mounted outside of a glass vacuum jacket tail in the liquid-helium bath and were kept at a constant temperature; only the thermometer block and the paramagnetic salt changed temperature. "Blank" runs (with no salt in the nylon container) gave a mutual inductance versus temperature correction which corresponded to less than 1 mK at any temperature. This was achieved by careful coil design and by the insertion of a superconducting lead shield between the block and the coils to eliminate effects due to temperature-dependent eddy currents in the block.

All vapor-pressure and susceptibility data were recorded in terms of the resistances of the platinum thermometer and the four germanium thermometers. Measuring currents were limited to reduce thermometer heating effects and standard potentiometric and current-reversal techniques were used in the resistance determinations. No detectable shifts in thermometer calibrations (greater than ± 0.2 mK) were observed in the course of the vapor-pressure measurements and data taking with both CMA and MAS. MAS has roughly 3 times the volume susceptibility of CMA and hence 3 times the temperature sensitivity. CMA, however, has smaller absolute values of Δ (+1.9 mK vs -36 mK) and δ ($2.8 \times 10^{-3} \text{ K}^2$ vs $8.4 \times 10^{-3} \text{ K}^2$). When these sets of parameters were used (with appropriate values of A and B) the temperatures obtained using the two different paramagnetic salts were identical to within better than 1 mK down to 5 K and to ± 0.3 mK below 5 K. We have designated the temperature scale which results from a combination of the two sets of data as T_M ; this scale is "stored" in the resistance-temperature relationships of our germanium thermometers.

Our results are compared with the liquid heli-

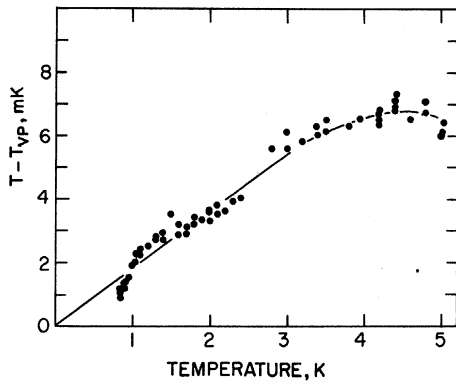


FIG. 2. The deviation of T_M from the liquid helium vapor pressure scales.

um vapor-pressure scales in Fig. 2; here, T_{58} has been used from 5 to approximately 1.4 K and T_{62} from 1.6 to 0.9 K with no detectable differences in the overlap region. The solid dots represent deviations from T_M of vapor pressure temperatures taken over the course of a year and recorded in terms of thermometer resistances. We do not believe that the systematic deviation about the straight line is a real effect. The smooth curve through these points is plotted also in Fig. 1 where the agreement appears to be within the stated uncertainties in the other less precise data. A similar conclusion that $T - T_{58} = 7 \pm 3$ mK near 4 K follows from a compilation of the results of various CVGT determinations.^{9,16}

Unfortunately, there is no reason to believe that the $T - T_{58}$ relation which we give in Fig. 2 is correct in a thermodynamic sense, since the basic input data, the N.B.S.-1955 scale, may not represent the thermodynamic scale. Indeed, if we had used IPTS-68¹³ to calibrate our thermometers from 18 to 30 K, the value of $T - T_{58}$ which we give for 4.2 K (6.7 mK) would increase to approximately 8.5 mK, in better agreement with the acoustic results. The gas thermometer results would increase correspondingly. We appear to be in the unfortunate position of being able to relate the liquid helium temperature region to the 20 K region with a greater accuracy than thermodynamic temperatures can be realized at present from 18 to 30 K. In any event, it is obvious that T_{58} deviates significantly, although almost linearly below 4 K, from thermodynamic temperatures.

Figure 3 compares our temperature scale with the N.B.S. Provisional Temperature Scale 2-20 (1965)¹⁰ which we will designate as N.B.S. acoustic, the RTAS CVGT scale,⁹ and the two scales on which our platinum resistance thermometer

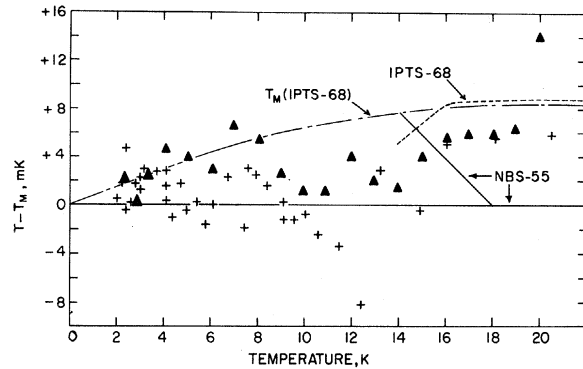


FIG. 3. The deviation of various temperature scales from T_M . Crosses, RTAS (Ref. 9); triangles, N.B.S. acoustic (Rev. 10).

has been calibrated, N.B.S.-1955 and IPTS-68. T_M , by definition, is identical with N.B.S.-1955 above 18 K. One of our thermometers, GR803, was calibrated in the RTAS experiment, and also has been calibrated at N.B.S. on the acoustic scale. Hence, it is the source of the comparisons with these two scales shown in Fig. 3. There are a number of annoying inconsistencies, but various checks including thermometer calibration comparisons and vapor-pressure measurements on hydrogen and neon lead us to believe that our thermometer calibrations (GR803 and platinum resistance) correspond to the N.B.S. scales with an accuracy of 2 mK.

The RTAS data appear to scatter randomly about T_M with a maximum deviation of ± 3 mK except at 12 K and above 15 K, while differences from the acoustic scale appear to be small but systematic. If T_M is proportional to thermodynamic temperatures, the acoustic scale also can be considered to be proportional to thermodynamic temperatures if a systematic linear difference of 0.03% is assumed between the two scales. Below 20 K the acoustic data in Fig. 3 scatter about a line with this slope with a mean absolute deviation of less than 2 mK and a maximum deviation of 5 mK. This would suggest a value for the thermodynamic temperature at 20 K which is somewhere between N.B.S.-1955 and IPTS-68. The dot-dash line indicates the change in T_M which would result if our salt thermometers had been calibrated using IPTS-68.

Astrov, Orlova, and Kytin¹⁷ report much larger differences between the Physicotechnical and Radiotechnical Measurements Institute (PRMI) CVGT scale and the N.B.S.-acoustic scale. These differences vary from $T_{PRMI} - T_{AC} = +10$ mK near 7 K to -8 mK near 11 K. This indicates

a discrepancy between the scales compared in Fig. 3 and the PRMI scale.

We believe that we have established a temperature scale from 0.9 to 18 K which is consistent with N.B.S.-1955 to better than ± 1 mK over this temperature region. The absolute accuracy of our scale is limited by the uncertainties in the temperature scales above 20 K. Experiments to realize these temperatures more precisely must be performed before an "accepted" temperature scale can be established in this temperature region below the boiling point of liquid hydrogen and before T_{58} and T_{62} are revised. The relationship between such a new scale and the existing scales (N.B.S.-1955 and IPTS-68, for instance) can be used to recalculate our scale on a more firm thermodynamic basis.

The authors are indebted to Dr. H. H. Plumb for numerous conversations and for practical assistance with unpublished data, and to Dr. M. Durieux for providing us with a copy of his invaluable Ph.D. thesis. A preliminary (and in retrospect somewhat inaccurate) account of this work appears in a summary article on thermometry from 1 to 30 K.¹⁶ A complete description of these measurements will be submitted elsewhere.

*Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

¹F. G. Brickwedde, H. van Dijk, M. Durieux, J. R.

Clement, and J. K. Logan, *J. Res. Nat. Bur. Stand., Sect. A* **64**, 1 (1960).

²H. van Dijk, *Progr. Cryog.* **2**, 123 (1960).

³S. G. Sydoriak and R. H. Sherman, *J. Res. Nat. Bur. Stand., Sect. A* **68**, 547 (1964).

⁴S. G. Sydoriak, T. R. Roberts, and R. H. Sherman, *J. Res. Nat. Bur. Stand., Sect. A* **68**, 559 (1964).

⁵T. R. Roberts, R. H. Sherman, and S. G. Sydoriak, *J. Res. Nat. Bur. Stand., Sect. A* **68**, 567 (1964).

⁶R. H. Sherman, S. G. Sydoriak, and T. R. Roberts, *J. Res. Nat. Bur. Stand., Sect. A* **68**, 579 (1964).

⁷G. Cataland and H. H. Plumb, *J. Res. Nat. Bur. Stand., Sect. A* **69**, 531 (1965).

⁸D. T. Grimsrud and J. H. Wernitz, Jr., *Phys. Rev.* **157**, 181 (1967).

⁹J. S. Rogers, R. J. Tainsh, M. S. Anderson, and C. A. Swenson, *Metrologia* **4**, 47 (1968) (RTAS, hereafter).

¹⁰H. H. Plumb and G. Cataland, *Metrologia* **2**, 127 (1966).

¹¹M. Durieux, thesis, University of Leiden, The Netherlands, 1960 (unpublished).

¹²M. Durieux, H. van Dijk, H. ter Harmsel, and C. van Rijn, in *Temperature, Its Measurement and Control in Science and Industry*, compiled by the American Institute of Physics (Reinhold, New York, 1962), Vol. 3, Pt. 1, p. 383.

¹³Comité International des Poids et Mesures, *Metrologia* **5**, 35 (1969).

¹⁴P. W. Sparks and C. A. Swenson, *Phys. Rev.* **163**, 779 (1967).

¹⁵E. Maxwell, *Rev. Sci. Instrum.* **36**, 553 (1965).

¹⁶C. A. Swenson, *Critical Rev. Solid State Sci.* **1**, 99 (1970).

¹⁷D. N. Astrov, M. P. Orlova, and G. A. Kytin, *Metrologia* **5**, 111 (1969).

XENON SELF-DIFFUSION NEAR THE CRITICAL POINT AND ON THE LIQUID BRANCH OF THE COEXISTENCE CURVE*

R. S. Ehrlich† and H. Y. Carr

Department of Physics, Rutgers University, New Brunswick, New Jersey 08903
(Received 6 July 1970)

NMR measurements ($\pm 5\%$) of self-diffusion in xenon to within 10 ppm of the critical temperature show no anomaly relative to the behavior on the liquid branch of the coexistence curve between 177 and 281°K. In this lower temperature range we observe $\rho D \propto T^{2.74 \pm 0.08}$. This same temperature dependence also describes similar data of Trappeniers and Oosting for the nearly spherical molecule methane.

Whether or not the simplest of the transport properties, self-diffusion, behaves anomalously near the liquid-vapor critical point still remains to be answered definitively. Noble and Bloom,¹ using a NMR technique,² have observed an anomalous 15 to 20% decrease in the product of density ρ and diffusion coefficient D for liquid ethane on the coexistence curve in the region several de-

grees below the critical temperature T_c . Diffusion in the vicinity of the critical point has been observed in several other experiments on simple fluids using tracer methods³ and neutron scattering,⁴ but no similar anomaly has been reported.

We have recently used the NMR technique to measure the self-diffusion coefficient of xenon in the temperature region corresponding to that of