Journal of Physical and Chemical Reference Data

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Cite as: Journal of Physical and Chemical Reference Data **14**, 193 (1985); https://doi.org/10.1063/1.555746

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Assessment of Critical Parameter Values for H_2O and D_2O

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Recommendations for the most likely values of the critical parameters of light and heavy water as accepted by the International Association for the Properties of Steam are presented, together with an assessment of their reliability. The results are, for H_2O: $T_c = (647.14 + \delta_1)$K, $\delta_1 = 0.00 \pm 0.10$; $P_c = (22.064 + 0.27\delta_1 \pm 0.005)$ MPa; $\rho_c = (322 \pm 3)$ kg/m^3; and for D_2O: $T_c = (643.89 + \delta_2)$ K, $\delta_2 = 0.00 \pm 0.20$; $P_c = (21.671 + 0.27\ \delta_2 \pm 0.010)$ MPa; $\rho_c - (356 \pm 5)$ kg/m^3. Supporting material for these choices of values and the assessment of their reliability is provided. Temperature values are on the International Practical Temperature Scale of 1968 (IPTS 1968) unless otherwise indicated.

Key words: critical density; critical pressure; critical temperature; heavy water; steam; water.

Contents

1. Introduction

The values of the critical pressure P_c, the critical temperature T_c, and the critical volume V_c have played key roles in the formulation of the thermodynamic and transport properties of what is traditionally called "ordinary water substance" (which will be referred to as H_2O, light water, or steam if no confusion can arise). Experimental measurements of these critical parameters began with Cagniard de la Tour in 1822. Nowak *et al.*[1] summarize the experimental data obtained up to 1955. These older determinations have a low level of reliability for a variety of reasons having to do with the high value of the critical temperature of steam and the corrosive nature of the near-critical fluid. Our report will therefore limit itself to several recent high-quality determinations of the critical values of P_c and T_c of H_2O by Blank,[2] Reimann *et al.*,[3] and Scheffler *et al.*,[4,5] and to one determination of these values for heavy water by Blank.[2]

The critical parameter values used in the newer formulations of properties of steam have been obtained by an indirect method which localizes the state point at which the coexisting liquid and vapor phases become identical by an

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analysis of the fluid properties measured in the vicinity of that point. In the case of steam, the experimental information has principally consisted of the vapor pressure curve[6] and the latent heat data[7] measured with great accuracy by Osborne and co-workers at the National Bureau of Standards (NBS) in the 1930's. These authors analyzed their own data and reported $P_c = 225.65$ kgf/cm^3; $T_c = 374.15$ °C and $V_c = 3.1$ cm^3/g.[7] In SI units, and in Kelvin temperatures on the IPTS 1968,[8] the estimates of Osborne *et al.* are

$$\begin{aligned} P_c &= 22.129 \text{ MPa}, \\ T_c &= 647.37_7 \text{ K}, \\ V_c &= 0.0031 \text{ m}^3/\text{kg}, \\ (\rho_c &= 323 \text{ kg/m}^3). \end{aligned} \qquad (1)$$

In the course of the development of new skeleton tables, the 6th International Conference on the Properties of Steam (ICPS), in 1963, adopted the following values for the critical parameters (in current SI units)

$$\begin{aligned} P_c &= (22.12 \pm 0.01) \text{ MPa}, \\ T_c &= (647.37_7 \pm 0.10) \text{ K}, \\ V_c &= (0.003\ 17 \pm 0.000\ 15) \text{ m}^3/\text{kg}, \\ [\rho_c &= (315 \pm 15) \text{ kg/m}^3]. \end{aligned} \qquad (2)$$

This parameter set was also selected as the critical point for the 1967 IFC Formulation for Industrial Use.[9] The 1968 IFC Formulation for Scientific and General Use[10] gave as critical parameters in current SI units

$$\begin{aligned} P_c &= 22.1146 \text{ MPa}, \\ T_c &= 647.343 \text{ K}, \\ V_c &= (0.003\ 17 \pm 0.000\ 15) \text{ m}^3/\text{kg}, \\ (\rho_c &= 315 \text{ kg/m}^3). \end{aligned} \qquad (3)$$

In the mid sixties voices began to be heard that the internationally adopted formulations might not have the correct

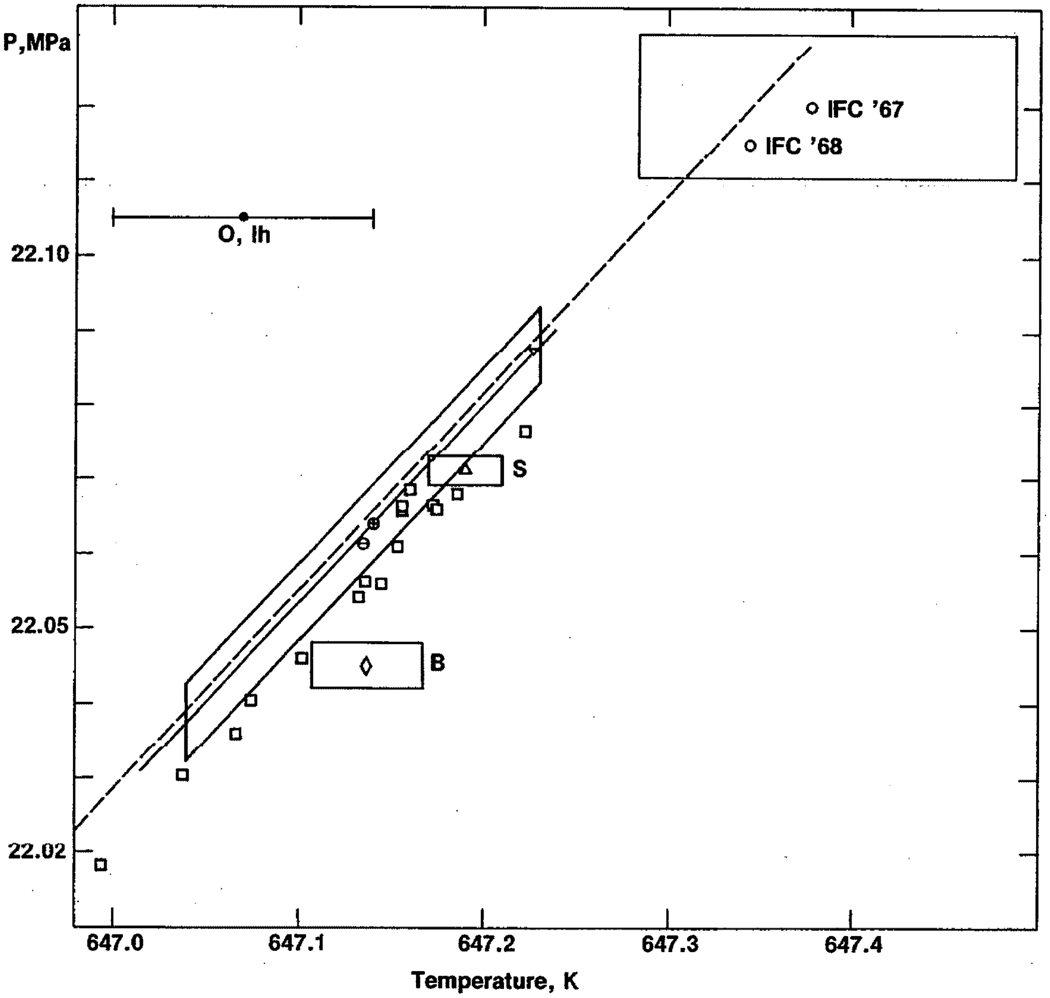

FIG. 1. The vapor pressure curve of steam near the critical point. The full curve is that determined by Osborne's, the dashed curve that by the scaled fit to Rivkin's data. Vapor pressures measured by Osborne (▽), Hanafusa *et al.* (⊖), and Scheffler (☐) are shown. Direct determinations of (P_c, T_c) by Blank (◊,*B*) and Scheffler (△,*S*) are indicated, with a rectangular area of uncertainty. The range of T_c consistent with Osborne's latent heat (O,lh) data is indicated in the upper left-hand corner. Our recommended value of (P_c, T_c) is marked by (⊕), with a rhomboidal region indicating its tolerance. For comparison, the selected value of IFC 67 and IFC 68 are marked.

critical point. For one thing, neither the IFC 67 nor the IFC 68 pair of P_c and T_c falls on the vapor pressure curve of Osborne *et al.* (Fig. 1). For another, reanalysis of the latent heat data leads to lower values of T_c than that estimated by Osborne. Thus, at the 6th ICPS in 1963, Juza[11] presented an estimate for T_c 80 mK below that of Osborne *et al.*, while Bridgeman and Aldrich,[12] in an extensive review of the Osborne data, estimated T_c 130 mK lower than Osborne's value. A scaled analysis of the latent heats by Levelt Sengers and Greer in 1972[13] gave a value of T_c 300 mK below that of Osborne *et al.* Since 1967, several new determinations have been made of the critical pressure and temperature of steam; detailed PVT, specific heat and speed of sound data were measured in the near vicinity of the critical point. After "heavy water substance" (to be referred to as D_2O or heavy water if no confusion can arise) became abundantly available, its thermophysical property and critical parameter values also became a subject of experimental study. In parallel with this growth in experimental knowledge, the modern theory of critical phenomena went through a period of stormy growth, resulting in the scaling laws that give a universal description of the critical anomalies of all systems that belong to the same universality class. For the class of three-dimensional Ising-like systems, to which molecular fluids belong, the behavior of the free energy near the critical point is accurately predicted by theory; for reviews, see Refs. 14–16. It is because of this growth in experimental knowledge and in theoretical understanding that the Executive Committee of the International Association for the Properties of Steam (IAPS) has requested the present authors to reassess the situation with respect to the critical parameter values of ordinary and heavy water substance. This report is a result of this reassessment. It contains the background material for the new estimates that have been adopted by the Executive Committee and national delegates, and that are given in the Appendix of this report.

In Sec. 2, we outline the approach we have taken in this work. In Sec. 3, we discuss how well pressure and temperature can be measured at best under the conditions prevailing at the critical point of steam. After these general observations the report, in Sec. 4, describes the experiments which have been relevant to our work. These experiments fall into two categories: direct determinations of P_c and T_c by measuring these quantities at the point at which the meniscus is observed to disappear; and measurements of thermophysical properties in a region around the critical point, from which the values of the critical parameters can be inferred without the critical point being directly observed.

In Secs. 5 and 6, additional sources of error and their possible effects are discussed, namely, gravity and impurity.

In Sec. 7, estimates for the critical parameter values P_c, T_c, and ρ_c of H_2O are made, while those for D_2O are presented in Sec. 8. The Appendix to this paper contains the values of the critical parameters of light and heavy water substance, and their respective uncertainties, as recommended to the Executive Committee in September 1982, and as adopted by the national delegates of IAPS.

The cutoff date for input of experimental material to this work has been 31 August 1982.

2. Method of Assessment

The work presented here has the following components: (a) a study of the most important sources of error in experimentation near the critical point, (b) an assessment of the reliability of all experiments that have contributed to our determination of the critical parameter values, and (c) development of a procedure for determining critical parameter values by the indirect method.

As to point (a), the error sources we have considered are random and systematic errors in the measurement of temperatures near 647 K and pressures of about 22 MPa (Sec. 3), gravity (Sec. 5), and impurity (Sec. 6). These sources of error limit the reliability with which critical parameters can be determined *a priori*.

As to point (b), each experiment is assessed as to how closely those limits have been approached. Here, direct evidence (the author's report on the accuracy of his experiment, the materials used, access to and quality of calibration facilities, the likelihood of temperature gradients) and circumstantial evidence (agreement or consistency with work considered of proven accuracy) are used in the assessment.

As to point (c), a brief summary of the indirect method should help guide the reader through this report. Since the indirect method locates the critical point by analysis of property data near it, the results will depend on the model used, as the examples given in the Introduction illustrate. The advance made since the analysis of Bridgeman and Aldrich in the theoretical understanding and mathematical analysis of critical anomalies has motivated us to reanalyze the existing data by the modern tools of the scaling laws. These laws give the variation of any fluid property along a specified path to the critical point as an asymptotic power-law dependence on $T - T_c$ or $\rho - \rho_c$, with universal exponent. Also the lowest order corrections to these laws are known from theory. By fitting the appropriate power-law expression to the property of interest, with inclusion of the correction terms if needed, the relevant critical parameter value is obtained by searching for the minimum in the reduced chi square when this value is varied.

From considerable experience, we have learned that the value of P_c is poorly defined by analyzing one-phase properties such as the PVT relation. From the vapor pressure curve a definition of T_c is likewise not possible, because there is no change in the slope of the critical isochore at the critical point. In principle, the point where C_V or C_p diverges, or the speed of sound goes to zero should define T_c. In practice, the temperature scales of the relevant experiments were not always sufficiently defined, as we will explain (Sec. 4). We have found that by far the most reliable results are obtained by extrapolating to zero the values of any property that marks the difference between coexisting vapor and liquid phases.[13,17] Commonly, the difference of coexisting densities is considered, but any other extensive property (latent heat, refractive index, surface tension) is suitable. For steam, we have analyzed the latent heat data of Osborne *et al.*[7] For D_2O, we have used the sole directly determined value of T_c,[2] no other information being available.

Once the value of T_c is obtained, that of P_c follows readily from known vapor pressure and/or PVT data near the critical point. For H_2O, we have used Osborne's vapor pressures,[6] after establishing thermodynamic consistency of Osborne's vapor pressures, latent heats[7] and the more recent PVT data of Rivkin *et al.*[18,19] Determinations of the vapor pressure of steam, performed in recent years at Keio University in Japan,[20,21] confirm Osborne's vapor pressures with high accuracy. For D_2O, we determined P_c from Rivkin's PVT data.[22]

Values of the critical density may be obtained indirectly from the scaled analysis of PVT data and from coexistence properties. In the case of H_2O, we have done both and obtained results that are mutually consistent. For D_2O, we have obtained an estimate of ρ_c from a scaled analysis of Rivkin's PVT data.[22,23]

In what follows, temperatures will be reported in K on IPTS 1968.[8] At the critical point of steam, temperatures on this scale are 77 mK higher than on the 1929 and 1948 scales.

3. Realization of Pressure and Temperature Scales

Two questions have to be dealt with in assigning reliability to measured values of temperature and pressure: (1) how well could this have been done optimally at the time the experiments were done, and (2) how well was it done in practice? We will defer an answer to question (2) to Sec. 7 and answer question (1) by referring to established and documented practice at a Standards Laboratory such as NBS.

3.1. The Pressure Scale

We refer to the careful documentation of Meyers and Jessup[24] who established 1 part in 10^4 as the absolute reliability of their piston gauges in the range up to 75 atmospheres (7.6 MPa). In that range, the pressure dependence of the effective area was less than 3 parts in 100 000. Present-day calibrations at standards laboratories are guaranteed with not much greater reliability (but, of course, in much larger pressure ranges). Careful transfer of the pressure scale from standards to nonstandards laboratories does not have to result in serious degradation. Witness, for instance, seven independent determinations of the vapor pressure of CO_2 at 0 °C, at 3.48 MPa, between 1933 and 1971, which show a total spread of 1.5 parts in 10^4 in pressure, while this spread encompasses errors in temperature and in sample preparation in addition to uncertainty in pressure scale.[25]

Osborne *et al.*, in their work on steam in the thirties, used the gauges calibrated by Meyers and Jessup, and by recalibration with respect to the vapor pressure of CO_2 at the ice point made sure their effective area was unchanged.[6] The only remaining uncertainty is the dependence of the effective area on pressure, which one would expect to begin to be observable at 22 MPa, the critical pressure of steam. The establishment of this dependence is the only advantage present-day practice has over that in Meyer's days a half century ago. We have therefore assigned to Osborne's pressure scale around 22 MPa an uncertainty σ_P of

$$\sigma_P(\text{Osborne}) = \pm 0.01\% = \pm 2\ \text{kPa}. \tag{3.1}$$

In modern work, with reasonable care, the pressure can be measured with an accuracy of 1 part in 10^4.

3.2. The Temperature Scale

The temperature scale at the steam critical point, 647 K, if realized according to modern practices specified in the IPTS 1968 document,[8] can be established with no larger uncertainty than 2 mK. Before 1968, the temperature scale was based on the sulphur fixed point at 444.6 °C, and the temperature coefficients of the platinum resistance thermometers were lower and showed a larger spread than specified in Ref. 8. The work of Hoge and Brickwedde at NBS[26] documents the possible error of thermometry at the time of Osborne's work. Seven platinum resistance thermometers, calibrated at the fixed points of the 1929 scale, showed a spread of 8 mK at temperatures near the steam critical point, 5 mK of which to be ascribed to irreproducibility of the sulphur point. Thus, we conclude that Osborne's vapor pressure and latent heat data were obtained on a scale that was defined to 8 mK:

$$\sigma_T(\text{Osborne}) = 8\ \text{mK}. \tag{3.2}$$

Osborne himself used two independently calibrated thermometers and reported that their readings always agreed to well within 10 mK.

The transfer of a temperature scale from a standards to a nonstandards laboratory is wrought with peril. Not only does it involve transportation of a fragile instrument, but, afterwards, it requires continuous monitoring of the resistance of the thermometer at, at least, one fixed point (usually the triple point of water) after the thermometer is handled or cycled to high temperature. If no statement is made when the results are reported, there is no direct way of tracing the reliability of the reported temperatures.

The major source of temperature uncertainty at the critical points of H_2O and D_2O, however, is probably not the imperfect realization of the scale, but rather the presence of temperature gradients in the sample, and between the sample and thermometer. These gradients are very hard to eliminate at the high temperatures involved. It is usually not possible to establish values for such gradients in specific experiments, and we have to use circumstantial evidence instead (Secs. 4 and 6).

4. The Experiments: Precision, Accuracy, Consistency

We group the experiments that will yield the values of the critical parameters in the following three classes:

(1) The vapor pressure relations of H_2O and D_2O, to which the critical parameters P_c, T_c have to be constrained, (Sec. 4.1).[3–6,18–21,27]

(2) The direct determinations of P_c, T_c, for H_2O and D_2O,[3–5] (Sec. 4.2).

(3) The determinations of ρ_c, T_c from latent heat data below T_c for H_2O, and those of ρ_c from PVT data mostly above T_c, for both H_2O and D_2O,[7,13,18,19,22] (Sec. 4.3).

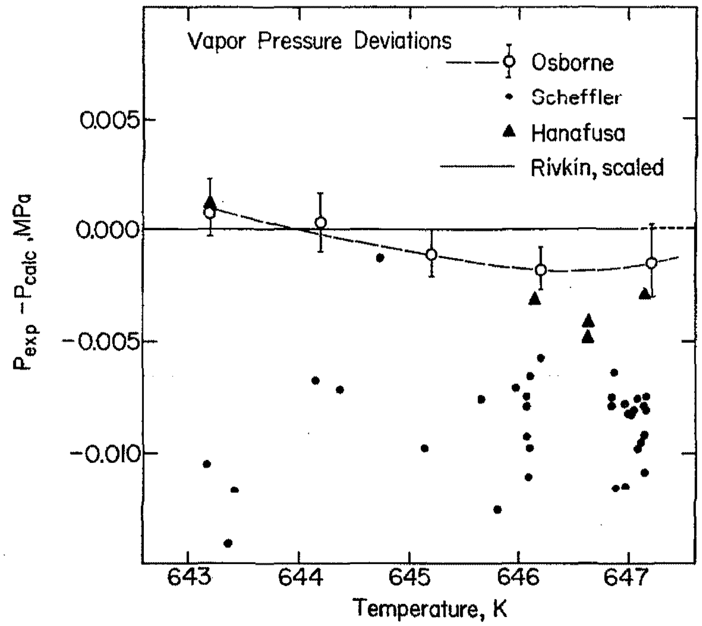

FIG. 2. A fit to the vapor pressures in the last few degrees from the critical point. The base line is a scaled fit to Rivkin's PVT data. Osborne's values, with their maximum spread around the mean, are shown as O. Recent Keio University data are shown as ▲. The vapor pressures of Scheffler *et al.* are given as ●. The dashed curve through Osborne's data is the one to which the recommended value is confined.

4.1. The Vapor Pressure Relation

(a) Osborne *et al.* measured vapor pressures[6] and latent heats[7] in the same calorimeter. The platinum thermometers were inserted in a silver reference block right above the calorimeter shell. Thirty-eight thermocouple junctions, five of which were located along the height of the calorimeter shell, monitored temperature differences throughout the calorimeter shell and the two isothermal shields. Thirty silver fins inside the calorimeter shell helped to equalize the temperature. Osborne mentions the presence of thermal gradients above 350 °C (Ref. 6, p. 165), but gives no actual values. The temperature value assigned to the measured vapor pressure was that measured near the liquid–vapor interface. In the range above 370 °C, the vapor pressure was measured as a function of the amount of water in the cell. The full curve in Fig. 1 represents the course of Osborne's vapor pressure data near the critical point. The quality of the experiments, and the documented accuracy of pressure and temperature measurements at the National Bureau of Standards in Osborne's time (cf. Sec. 3) lead us to expect an absolute accuracy of 1 part in 10^4, or 2 kPa in pressure, and better than 10 mK in temperature. Supportive evidence that this goal was obtained is the agreement, within 1 kPa or 5 mK, between the vapor pressure data of Osborne *et al.* and of Kell *et al.* at 350 °C,[27] the latter obtained at the National Research Council of Canada. These two sets of data are the only ones obtained at standards laboratories, where the relation to pressure and temperature standards is directly monitored.

(b) Rivkin and co-workers[18,19,22] determined the PVT relations of H_2O and D_2O with great detail near the critical point. A scaled analysis of the PVT data for H_2O,[15] mostly those in the supercritical region, determines a vapor pressure curve. This curve is the base line in the deviation plot of Fig. 2. Rivkin (Refs. 18,19, and private communication), assigns an uncertainty of 20 mK to his temperature measurements, and one of 1 kPa to his pressure measurements. Circumstantial evidence indicates that there may be more spread than 20 mK between various realizations of the temperature scale in his Institute. Thus Rivkin's viscosity and PVT data for near-critical H_2O have a discrepancy corresponding to 40 mK[28] and Sirota's C_p and Rivkin's PVT data have an inconsistency of about 50 mK.[29,15,a] We do, however, believe that Rivkin's PVT data for H_2O are accurate to the tolerance he quotes because the vapor pressure curve predicted from Rivkin's data agrees with Osborne's vapor pressures to well within 2 kPa (Table 1, Figs. 1 and 2); this points to a disagreement of the combined pressure and temperature scales the equivalent of less than 10 mK.

(c) Recently, Hanafusa *et al.* at Keio University determined PVT properties of H_2O very close to the critical point.[20,21] The measurements were performed in a spherical 304 stainless-steel piezometer immersed in a stirred molten-salt bath. The temperature uniformity of the bath was found to be within 2 mK. The temperature was measured by means of a platinum resistance thermometer that was calibrated at the National Research Laboratory of Metrology, and peri-

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[a] In a private communication, September, 1984, Dr. Sirota pointed out that a reevaluation of his temperatures, including a 50 mK shift of the desired sign near the critical point, was published by him in Teploenergetika 10, 84 (1963).

TABLE 1. Osborne's vapor pressure data (Ref. 6) for H_2O, and prediction (Ref. 15) based on Rivkin's PVT data (Refs. 18 and 19)

T,K	P_{exp} (MPa)	standard deviation of mean (kPa)	max spread of (n) detns (kPa)	P_{calc} (MPa)	$P_{exp} - P_{calc}$ (kPa)
643.22_7	21.0524	0.2	2.6 (19)	21.0517	+ 0.7
644.22_7	21.3056	0.2	2.7 (12)	21.3053	+ 0.3
645.22_7	21.5615	0.2	2.1 (9)	21.5625	− 0.1
646.22_7	21.8217	0.1_4	1.9 (12)	21.8235	− 1.8
[647.22_7	22.0873	0.3	3.1 (13)	22.0888	− 1.5]

odically checked at the triple point of water. The observed drift did not exceed 1 mK between repeat measurements. The total uncertainty of the temperature due to all sources of error is estimated to be 5 mK. The pressure was measured on a dead-weight piston gauge calibrated with the aid of an air pressure gauge. Hydrostatic heads and two separators add to the pressure uncertainty, which is estimated to be no larger than 3 kPa. The PVT measurements at the time this report was written (August 1982) include five points considered vapor pressures, although this designation could not be proven beyond doubt for the highest point. The Keio University data, in general, fall slightly (the equivalent of 4 kPa) below the scaled surface fitted to Rivkin's data. The deviations of the vapor pressure points are shown in Fig. 2. It is seen that they agree with Osborne's points to well within combined pressure error (2 kPa for Osborne's, 3 kPa for the Keio University data).

(d) The vapor pressures obtained as a by-product of the experiments in direct determination of the critical point of H_2O^{2-5} will be discussed in some detail in Sec. 4.2. In summary, the original determination of P_c, T_c by Blank[2] fell about 10 kPa below the vapor pressure curve of Osborne *et al.* The vapor pressures of Reimann *et al.*,[31] which were measured in Blank's apparatus, showed a departure of about − 7 kPa near T_c, but a few degrees lower the departure had grown to − 30 kPa. These worrisome discrepancies led Scheffler *et al.*[4,5] to a thorough redesign of the apparatus. In particular, a great deal of attention was given to improving the measurement of pressure.

The vapor pressure data reported with the improved instrument fall on the average about 6 kPa below Osborne's values in the range of 643–647 K (Figs. 1 and 2); this is well within the reported uncertainty of Scheffler's data, namely, 2 kPa direct pressure error, and 8 kPa from the propagated temperature error of 30 mK.[4] Thus, a vexing discrepancy has been resolved.

4.2. The Direct Determination of T_c and P_c

All direct determinations that are relevant to our task were made with the same basic instrument designed by Blank,[2] i.e., a pressure cell provided with sapphire windows through which a passage through the critical point could be observed, through the coincidence of two slit images shifted with respect to each other because of the difference in refractive index between vapor and liquid. A great deal of effort was made to ensure temperature homogeneity. The cell was surrounded by two heavy concentric copper cylinders, both maintained at the control temperature. Six quartz windows on each side, in good thermal contact with the copper cylinders, guarded against heat losses from the sapphire windows. The outer two quartz windows were provided with heaters. The temperature distribution along the cell and at the sapphire windows was monitored by thermocouples. Blank mentions the presence of strong convection currents in the cell near T_c; these were caused by the fact that he operated the instrument in a ramping mode. Scheffler, however, reports that no convection was observed in his experiment because he kept the temperature constant.

The temperature was measured on two 100 Ω capsule-type platinum thermometers located at the top and bottom of the cell. The two thermometers agreed to within 10 mK at all temperatures. Blank had his thermometers calibrated at the Physikalisch-Technische Bundesanstalt (PTB) after completion of the experiment. Scheffler *et al.* calibrated the thermometers *in situ* with respect to a long-stem standard calibrated at PTB. They estimate the maximum uncertainty in the establishment of the sample temperature as 30 mK.

The values of T_c reported with this instrument have ranged from 647.14 K[2,3] to 647.19 K.[4,5]

As discussed in Sec. 4.1(d), the initial vapor pressures obtained in this apparatus were quite low. Scheffler redesigned the pressure measurement instrumentation. He replaced the mercury U tube used by Blank as a separator by a high-temperature differential pressure transducer, thus obtaining a reduction of noxious space and liquid heads. A high-quality piston gauge was used, guaranteed by the manufacturer to be accurate to 1 part in 10^4. The vapor pressure data reported with the redesigned apparatus were discussed in Sec. 4.1(d). The direct determinations made by Blank and by Scheffler *et al.* are marked in the P–T diagram, Fig. 1.

The value of T_c reported by Scheffler *et al.* is high compared to estimates obtained indirectly from the latent heat data of Osborne. This will be discussed further in Sec. 4.3.

For D_2O, the only direct determination of P_c,T_c we have is that of Blank.[2] From the experience with Blank's values for H_2O, we expect the critical temperature to be acceptable while the critical pressure may be on the low side.

4.3. The Experiments Leading to Indirect Determinations of T_c and P_c

As outlined in Sec. 2, estimates of T_c can be obtained indirectly by power-law analysis of properties of coexisting phases. We will consider latent heat. The critical density is obtained as a by-product of the analysis of the latent heat.

Alternatively, it follows from a scaled analysis of the PVT data in the supercritical region. The details of these analyses are given in Secs. 7 and 8. Here, we discuss the reliability and consistency of the relevant experiment.

(a) The latent heat data for H_2O of Osborne *et al.*[7] were measured in the calorimeter discussed in Sec. 4.1(a). The latent heats b and g, accompanying isothermal extraction of unit mass of liquid and vapor, respectively, from a calorimeter containing coexisting phases, were measured repeatedly at each of about 20 temperatures between 373 and 647 K on Osborne's scale, and at 1 and 0.5 K intervals above 643 K. At each temperature, a large number of determinations of latent heats were made so that the statistical distribution and spread of the data are well known.

The principal difficulty encountered in the experiment was reported as "mixing of phases" at 647.23_7 K and to a lesser extent at 646.72_7 K; this leads to a large scatter in the values of g and b at 647.23_7 K. The analysis by means of the scaling laws to be given in Sec. 7 has led to two conclusions: (1) The 647.23_7 K point is not consistent with the other data, for the reason, we believe, that it might have been slightly supercritical; (2) the critical temperature consistent with the latent heat data is 647.06_7 K. With this choice of T_c, the latent heat data can be predicted to well within their spread and to within a few standard deviations of the mean by a surface fitted to Rivkins's PVT data.

(b) One-phase properties that either diverge or go to zero at the critical point are compressibility and C_P (strong divergence), C_V (weak divergence) and speed of sound (weak approach to zero). Although, in principle, these properties could be used to obtain estimates for T_c, in practice the results have been disappointing. Sirota's[30] values of the C_P maxima of H_2O can be represented well by the scaled fit to Rivkin's data, but do require a value of T_c lower by about 70 mK than that derived from Osborne's latent heat data. The latter value is already at the low end of the range obtained in direct observations of meniscus disappearance.

The weak character of the anomaly makes Erokhin's[31] speed-of-sound data for H_2O insensitive to the choice of T_c. Moreover, there is an inconsistency between the Rivkin surface and the Erokhin data that is manifested in a density shift of the speed-of-sound minima. Expressed in temperature, it would amount to a 50 mK discrepancy.[15]

Data for the specific heat C_V, on the other hand, are extremely sensitive indicators of the location of the phase boundary, because this quantity, if measured along isochores, jumps from the high two-phase to the lower one-phase value. The data of Baehr *et al.*,[32] however, lack the resolution for such a determination, since they were taken over heating intervals of several K. The data of Amirkhanov, Kerimov, and co-workers[33] have the fine detail required but have been plagued by internal inconsistencies, due, in part, to the presence of air in some of the earlier experiments. According to Ref. 33, thermal differences inside the calorimeter were carefully monitored with differential thermocouples. The platinum resistance thermometer used was repeatedly checked at the Leningrad Metrology Institute, and its fixed point values reproduced to ± 3 mK. The data considered most reliable by Amirkhanov *et al.* indicate that the transition of C_V from its two-phase to its one-phase value on the critical isochore ($V = 3.17$ cm^3/g) occurs between 647.32_7 and 647.40_7 K, which is well above other directly determined values, and considerably above the values determined indirectly by scaling-law analysis. An adjustment of 0.31 K is required[15] to achieve consistency between a scaled analysis of Rivkin's PVT data and Amirkhanov's C_V data. Although the effect of gravity on the near-critical states cannot be ignored in this experiment, it would shift the location of the maximum value of C_V observed along the critical isochore to a value *below* T_c, so that the reported value would be a lower bound for T_c. We have no plausible explanation for this large discrepancy other than the presence of a low-volatility impurity and have decided to not use the T_c value from C_V measurements for our present assessment.

(c) An assessment of the reliability of the Rivkin PVT data to be used for the determination of the critical densities of H_2O and D_2O was given in Sec. 4.1(b). There is complete consistency with the Osborne vapor pressures, to the equivalent of better than 10 mK, well within the estimated accuracy of 20 mK in temperature and 1 kPa of pressure of Rivkin's PVT data; there is also consistency with the latent-heat data after appropriate choice of T_c. This implies consistency of the critical densities of H_2O derived from latent heats and from Rivkin's data (Sec. 7).

5. Gravity

Gravitational forces interacting with the highly compressible near-critical fluid cause large density gradients near a critical point.[34] These gradients will be a source of error. In conventional PVT measurements, the density at the level where the pressure is measured may not correspond to the measured average bulk density. In specific-heat measurements, not only do the different layers in the cell have different heat capacity, there is an additional heat effect because of the change in distribution of material in the cell. Estimates of the error introduced by gravity were made by Moldover *et al.*[35] These authors give the range in temperature from the critical, at $\rho = \rho_c$, within which the error due to gravity in the property of interest exceeds 1%, if the density gradient is fully developed. The estimates were made for Xe in a cell 1 cm high. By use of the characteristic parameters listed in that paper, we can estimate the ranges of the case of interest to us, namely, H_2O and D_2O in a cell typically 10 cm high. For less than 1% error in density in a PVT experiment, a range of 300 mK above critical, at $\rho = \rho_c$, is to be excluded. For less than 1% error in a C_V experiment, a range of 150 mK, at $\rho = \rho_c$, must be excluded. The excluded range is smaller in temperature below T_c. In the cases of practical interest to us, these limitations are usually unimportant. In the Rivkin PVT experiments, for instance, the intrinsic pressure uncertainty of 1 kPa exceeds by a factor of about 5 the hydrostatic head in the cell, and is therefore the dominant source of error in density assignment. Likewise, in the Keio University experiments, the intrinsic pressure uncertainty of 3 kPa exceeds the hydrostatic head by more than a factor of 10. In the Osborne latent heat experiments, the closest point we consider is more than 0.3 K from critical. In his vapor pressure measurements, the gravity effect is irrelevant.

6. Impurity

6.1. General Remarks

Water near its critical point is a corrosive fluid and a strong solvent. In the experiments we are dealing with, water samples are retained at near-critical conditions for prolonged periods. It is to be expected that steam will attack the container walls and that contamination of the sample will result. On the other hand, it is well known that critical parameters are quite sensitive to the presence of impurity. It is therefore necessary to make an assessment of the possible size of impurities and their effects on critical parameter determinations in the experiments considered.

Before going into detail, we want to make some general remarks regarding the order of magnitude of effects that could cause concern. We have to consider two types of impurities: (1) dissolved solids, such as salts and oxides, and (2) volatiles, such as dissolved air and hydrogen as a reaction product of corrosion.

If sodium chloride is taken as a prototype for a solid impurity, an impurity concentration of 5 g/m^3, which is typical and probably unavoidable in the water samples of the experiments we are interested in, we estimate from data on the critical line[36,37] that the critical temperature is raised by 5 mK, the critical pressure by 1.3 kPa, both quantities on the borderline of detection. If hydrogen is taken as a prototype volatile impurity, we conclude from data of Seward and Franck[38] that the effect on the critical temperature is negligible, but that 1 mol % of H_2 raises the critical pressure by about 1 MPa. If the volatiles are at the ppm level, they will have negligible effect but a 10 ppm volatile impurity will have a 1 kPa effect on the critical pressure.

Most experimenters have been quite aware of the need for careful purification and of the dangers of corrosion. The problem is in assessing how much impurity was actually present in each of the experiments, because there is, in general, no good way of establishing impurity content after the experiment is completed. If the sample is cooled down, taken out of the cell, and analyzed for impurity (which was done by Blank), the danger is that solutes are deposited in the cell, stay behind, and escape detection. If the water is taken out and the cell checked for volatiles (as was done by Osborne), most of the volatiles have dissolved and disappeared with the water. So we are left with mostly circumstantial evidence: the purity of the sample before the experiment, the materials used, and signs of corrosion after the experiment. If corrosion is seen, it means that a surface layer of the order of 1 μm thickness is present. In a typical vessel of 150 cm^3 volume, 360 cm^2 surface area, the creation of such a surface layer would generate of the order of 3.10^{-3} mol of hydrogen, which would constitute a 1000 ppm molar impurity and affect the pressure by 100 kPa. Thus, the presence of a visible contamination is a danger signal. The effect can be minimized by a pretreatment of the vessel wall or by repeated filling with fresh water samples. The signs of a corrosion process going on are drift in the pressure readings with time and dependence of the vapor pressure on the liquid/vapor volume ratio.

6.2. The Individual Experiments

(a) Osborne *et al.* purified their samples by continuous low-pressure distillation. They found no measurable partial pressure of air (Ref. 6, p. 168; Ref. 7, p. 401). They tested for the presence of volatiles during the experiment by measuring the vapor pressure with various amounts of liquid in the cell—the vapor pressure did not change. This is necessary but not sufficient evidence for the absence of volatiles.[37] Osborne used a "special alloy steel" with 19% Cr, 7.5% Ni, 4.5% W, 1.3% Si, 0.15% Mn, and 0.46% C. The calorimeter was made in two halves with a silver gasket. After carrying a charge of water at 300 °C, the inner surface showed a very thin film of light straw color. As we mentioned, this may be of little consequence if the cell content is changed repeatedly. It was in the nature of the calorimetric experiments that this was done. In the vapor pressure measurements there is no explicit statement about repeated fillings. In describing the tests for absence of volatiles (measuring the vapor pressure before and after liquid is withdrawn), however, Osborne implies that the calorimeter was repeatedly refilled. Repeated vapor pressure measurements showed no sign of drift over periods of weeks. The vapor pressure did not depend on the amount of liquid present.

(b) Rivkin used a nickel-based stainless-steel alloy. The surface showed no sign of corrosion. Fresh water samples were used for each isotherm. Rivkin reports exceedingly long equilibration times for points near critical.[19] Conceivably, these long times were due to slow diffusion of impurities.

(c) Kell used 304 stainless steel that became corrosion resistant after pickling. Even after use at 500 °C, there was no sign of contamination on the vessel wall. There was no evidence of drift in sample properties even at 500 °C. Each isotherm was measured with a fresh water sample.

(d) The cell used by Blank and Scheffler was made out of Inconel X-750, which is expected to be more corrosion resistant than the steels used by Osborne, Rivkin, and Kell.The cell wall was preoxydized at 350 °C by two fillings of water which were then discarded. The cell contained silver washers and sapphire windows. The sapphire windows did show signs of degradation after prolonged use. The solubility of aluminum oxide in water, however, is so low that no effect on the critical parameters is expected.

The presence of silver gaskets in the Blank, Scheffler, and Osborne experiments is believed to be beneficial because it allows for any hydrogen generated to diffuse outward, and because silver absorbs oxygen. (e) The Keio University group used 304 stainless-steel and filled ion-exchanged, twice-distilled deaerated water into the evacuated cell. Each isotherm required a new filling of water, which minimizes the effect of corrosion.

6.3. Summary of Results

(1) The presence of dissolved solid contaminants on the level of 5 g/m^3 of liquid water is to be expected in all experiments. Their effect on the values of the critical parameters *T_c and P_c should be, at most, marginal.*

(2) The steels in the Osborne, Rivkin, and Kell experiments are not fully corrosion resistant. Corrosion effects are potentially serious because of the generation of hydrogen which would affect the value of P_c. Corrosion effects can be minimized by pretreating cell walls (Kell) or by repeated refilling with fresh water samples (Kell, Rivkin, Osborne, Scheffler, Hanafusa).

The alloys used by Blank and Scheffler have better corrosion resistance. The observed corrosion of the sapphire windows is not believed to have caused an appreciable effect on the critical parameter values.

(3) Circumstantial evidence that no appreciable amounts of hydrogen were present in the Kell, Osborne, Rivkin, and Keio University experiments is obtained from (a) the reproducibility and absence of drift in the Kell and Osborne experiments, (b) the independence of the Osborne vapor pressure data on the mass of liquid present, and (c) the complete consistency of the four data sets.

6.4. Conclusions

Notwithstanding the difficulty of the task of keeping water substance near its critical conditions free of contamination, we have presented mostly circumstantial evidence that the experiments of interest to us are sufficiently free of contaminants to exclude more than marginal effects on the critical parameters.

6.5. Isotope Effects

The most obvious impurity effect in D_2O is the presence of some H_2O. In Blank's[2] work there was about 3% of H_2O present. His procedure of linear extrapolation of the critical parameters to 100% pure D_2O seems reasonable, in the absence of further knowledge about the course of the critical parameters of the two pure substances, the similarity of the species and the relatively short distance of extrapolation (the equivalent of 100 mK), no important error would be expected.

In the case of the Rivkin PVT data, the D_2O impurity was much smaller—only 0.13%. We have corrected for this impurity by a corresponding states model.[23,39,40] The corrections were within the estimated uncertainty of the Rivkin data.

A more difficult and more subtle question is that of the isotopic composition of D_2O itself. A comprehensive treatment of this question for H_2O and D_2O was given by Kell,[41] who pointed out that in addition to the presence of the other hydrogen isotope, attention needs to be given to the variable amounts of the heavier oxygen isotopes ^{17}O and ^{18}O. For our purpose, the principal effect of the presence of these heavier isotopes would be on the critical density itself. The ^{17}O isotope is present on the 0.04%, the ^{18}O isotope on the 0.2% weight fraction level. Even a factor of 3 variation in the ^{18}O fraction, as seems to be a possibility in D_2O, would introduce an error of less than 3 parts in 10^4, way below the confidence level of our estimate of ρ_c.

7. The Critical Parameters of Light Water Substance

7.1. Direct Determinations

The results of the direct determinations of relevance here are

	T,K	P_c,MPA
Blank[2]	647.14 ± 0.03	22.045 ± 0.003
Reimann *et al.*[3]	647.14	22.048
Scheffler *et al.*[4,5]	647.19 ± 0.03	22.071 ± 0.002

where the tolerances quoted are those given by the respective experimenters. The values obtained by Blank and by Scheffler *et al.* are indicated in the vapor pressure plot, Fig. 1.

TABLE 2. Latent heat data (Ref. 7) for H_2O, and prediction (Ref. 15) based on Rivkin's PVT data (Refs. 18 and 19)

T,K	g_{exp} (kJ/kg)	standard deviation of mean	max spread of (n) detns	g_{calc}	$g_{exp} - g_{calc}$
643.22_7	800.44	0.3	4.6 (18)	802.07	− 1.63
644.22_7				771.25	
645.22_7	733.65	0.7	10.8 (5)	733.93	− 0.28
646.22_7	683.05	0.5	3.0 (5)	682.34	+ 0.71
646.72_7	642.98	2.1	8.6 (4)	640.54	+ 2.44
647.22_7	586.62	5.8	49.4 (8)		
T,K	b_{exp} kJ/kg	standard deviation of mean	max spread of (n) detns	b_{calc}	$b_{exp} - b_{calc}$
643.22_7	359.35	0.5	2.91 (6)	359.94	− 0.59
644.22_7	374.29		(1)	376.11	− 1.82
645.22_7	395.48	0.21	0.86 (4)	396.57	− 1.09
646.22_7	427.56	0.64	2.03 (3)	426.72	+ 0.84
646.72_7	452.35	1.8	10.8 (5)	453.23	− 0.88
647.22_7	504.3	5.3	32 (6)		

TABLE 3. Power-law analysis of latent heat data (Ref. 7) of H_2O with varying T_c

T_c,K	Fit to uncorrected data in the range 603–646.73 K (Ref. 13)		Fit to corrected data in the range 643–646.73 K (Ref. 15)	
	χ^2	β	χ^2	β
647.04_7			1.98	0.320
647.05_7	2.19	0.3357	1.84	0.322
647.06_7	1.06	0.3359	1.84	0.324
647.07_7	0.55	0.3361	1.96	0.326
647.08_7	0.66	0.3363	2.19	0.327
647.09_7	1.35	0.3365	2.53	0.329

7.2. Indirect Determinations

(a) The vapor pressure curve and its extension, the critical isochore, are plotted in Fig. 1 for the range within 0.5 K from the critical point. The origins of the various data sets and curves are the following. The data of Osborne *et al.* in our range of interest are tabulated in Table 1. At each temperature, a large number of determinations are available, which permits evaluation of the spread of the data, the mean and the standard deviation of the mean. We believe that the highest point may have been slightly (0.15 K) supercritical.[b] The full curve in Fig. 1 passes through this highest point and has a slope determined by this and the next lower point. The deviation plot of Fig. 2 shows that the roughly 50 data points (represented by their mean and spread at each of five temperatures) do not depart from the average by more than 1.6 kPa. We estimate the total inaccuracy, resulting from uncertainty in temperature (8 mK) and pressure (1 part in 10^4) as 4 kPa.

A vapor pressure relation can also be obtained by fitting a scaled equation to the PVT data of Rivkin *et al.*[15,18,19] From the comparison in Table 1 and from the deviation plot in Fig. 2, it can be seen that this predicted curve agrees with the data of Osborne *et al.* in the range of overlap to better than 2 kPa.

In Fig. 1, the recent vapor pressure measurements of Scheffler *et al.*[4,5] are indicated. As noted in Sec. 4.1(d), Scheffler estimates the maximum uncertainty due to combined maximum errors in pressure (2 kPa) and temperature (30 mK) as 10 kPa. In the deviation plot, Fig. 2, these data can be seen to fall about 6 kPa below Osborne's data. In this same plot, five vapor pressure data obtained at Keio University[20,21] are also indicated. The authors estimate the uncertainty as 5 mK, or, with the combined uncertainty expressed in terms of pressure alone, 4 kPa. These data fall below Osborne's by 0–3 kPa. Since all later determinations, within their estimated uncertainty, are consistent with Osborne's data, which appear to be the most precise, we have decided that the most likely course of the vapor pressure curve of water substance near the critical point is that defined by Osborne's data.

(b) The determination of a value for the critical temperature from the latent heat data of Osborne *et al.*[7] proceeds as follows. The experiment consisted of measuring the latent heats b and g accompanying isothermal extraction of a unit mass of liquid and vapor, respectively, from a calorimeter containing coexisting phases. These latent heats are related to the coexisting densities ρ_L, ρ_V and the vapor pressure by

$$b = (T/\rho_L)(dP/dT)_{vap},$$
$$g = (T/\rho_V)(dP/dT)_{vap}. \qquad (7.2)$$

Osborne *et al.* determined these quantities from 273.15 K to the critical point. Again, many determinations were made at each temperature, so that there are more than 20 measurements each of g and b within the last 4 K from the critical point (Table 2).

For the analysis it is important to note that g and b become equal at the critical point, so that the asymptotic behavior of their difference will yield a value of T_c. The behavior of the sum of g and b, on the other hand, allows us to estimate ρ_c. As to the first point, the quantity $(g-b)/(g+b)$ behaves as

$$(\rho_L - \rho_V)/(\rho_L + \rho_V),$$

that is asymptotically as $B[T-T_c]^\beta$. Levelt Sengers and Greer[13] analyzed the quantity

$$[(g-b)/(g+b)][\rho_L + \rho_V]$$

by a simple power law with free exponent β, in the range 602.23–647.23 K, assuming that $\rho_L + \rho_V$ follows the law of the rectilinear diameter and varying T_c in steps. They concluded (1) that the data point at 647.29_7 K is out of line with the other data, and (2) that, with this point omitted, a properly weighted fit reaches a minimum χ^2 at 647.07_7 K (Table 3). A change of no more than 10 mK doubles χ^2. For the present purpose, we have refined the analysis considerably. It is now recognized that corrections to scaling become important within a few degrees from the critical point. We have calculated these corrections, using the potential of Ref. 29 for the range 643.22_7–647.72_7 K. Their largest contribution was 1.5% at 643.22_7 K (Table 4). After subtraction of the correction terms, the remaining asymptotic part was fitted again to the asymptotic power law with free exponent β. The data

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[b] On the basis of the scaled equation of state, Table 5 and Ref. 15, it is readily checked that 0.15 K above the critical point, a 10% variation in density causes no more than 1 kPa change in pressure, which is barely above the limit of detection for Osborne's experiment. A slightly supercritical pressure thus would appear to have the nonvariance typical of vapor pressure.

TABLE 4. "Best" fit to latent heat function $(g-b)/(g+b)$

T,K IPTS 1968	$(g-b)/(g+b)$ exp.	Corr. to scaling	Asympt. term exp.	Prediction (power law)
643.22_7	0.380 32	0.005 68	0.374 64	0.374 80
645.22_7	0.299 50	0.003 61	0.295 89	0.295 11
646.22_7	0.230 04	0.002 11	0.227 94	0.228 86
647.72_7	0.174 04	0.001 08	0.172 95	0.170 75

were weighted in accordance with the error of the mean derived from Osborne's data, just as in Ref. 13. We have found (1) that the inclusion of the 647.22_7 K point led to a tenfold increase in χ^2; (2) the omission of this point[c] led to reasonable χ^2 values (not greatly exceeding unity); (3) the minimum χ^2 was obtained for $T_c = 647.06_7$ K (Table 4) a value only 10 mK different from that obtained before,[13] while the value 0.324 ± 0.002 obtained for the exponent β is in excellent agreement with the theoretical value of 0.325. A doubling of χ^2 occurs when T_c is changed from the optimum by 70 mK. The present minimum is far less sharp because of the smaller size of the data range. The location of the minimum is apparently insensitive to the precise form of the correlating equation and the size of the range: the different approaches locate T_c to 10 mK. We take as our best estimate from Osborne's latent heat data:

$$T_c = (647.06_7 \pm 0.07)\ \text{K}. \tag{7.3}$$

(c) In order to obtain values of P_c and ρ_c from Rivkin's PVT data, we fitted these data with a scaled equation imposing the above T_c value.[15] The optimum parameter values for the scaled potential are listed in Table 5. The consistency of the Osborne and Rivkin data was proved by prediction of the vapor pressures and latent heats at Osborne's temperatures on the basis of the equation fitted to Rivkin's data. The results are given in Table 1 for the vapor pressure and in Table 2 for the latent heat. The vapor pressures are fitted to 2 kPa and the latent heats to 2 kJ/kg. For this choice of T_c, we then obtain as the values of P_c and ρ_c from the fit to Rivkin's data

$$\begin{aligned} P_c &= 22.0460\ \text{MPa}, \\ \rho_c &= 322.78\ \text{kg/m}^3. \end{aligned} \tag{7.4}$$

If we use Osborne's vapor pressure curve instead, a slightly lower value of P_c results, namely,

$$P_c = 22.0446\ \text{MPa}. \tag{7.5}$$

(d) The value of ρ_c can be inferred from Osborne's vapor pressures and latent heats because of the relation

$$g_c = b_c = T_c \left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_c \frac{1}{\rho_c}, \tag{7.6}$$

where $(\mathrm{d}P/\mathrm{d}T)_c$ is the limiting slope of the vapor pressure curve, and g_c, b_c are the values of the latent heats g and b at the critical point.

Osborne *et al.*[7] analyzed the difference $g-b$ by means of an empirical function of $T-T_c$, with T_c adjustable; from this analysis, and another empirical expression fitted to the vapor pressure data, they concluded that

$$\begin{aligned} T_c &= 647.37_7\ \text{K}, \\ g_c = b_c &= 535.08\ \text{kJ/kg}, \\ T_c(\mathrm{d}P/\mathrm{d}T)_c &= 173\ \text{MPa}. \end{aligned} \tag{7.7}$$

The values of g and b change by 10% in the range 370–374 °C; the value of $T\,\mathrm{d}P/\mathrm{d}T$ changes by 5%. Thus it is to be expected that the extrapolated values should depend sensitively on the method of extrapolation used. This is demonstrated by the correlation of Bridgeman and Aldrich,[12] who challenged Osborne's method of extrapolation and deduced, on the basis of the same data set,

$$\begin{aligned} T_c &= 647.24_7\ \text{K}, \\ g_c = b_c &= 541.38 \pm 0.07\ \text{kJ/kg}, \\ T_c(\mathrm{d}P/\mathrm{d}T)_c &= 171.6\ \text{MPa}. \end{aligned} \tag{7.8}$$

The scaling laws can help in reducing the uncertainty of

TABLE 5. Parameters in the revised and extended scaled potential for H_2O fitted to Rivkin's data (Refs. 15, 18, and 19)

Critical exponents (fixed)	Critical temperature (fixed)
$\beta = 0.325$	$T_c = 647.06_7$ K
$\delta = 4.82$	
$\Delta = 0.50$	
Fitted parameters	Derived parameters
$\rho_c = 322.78\ \text{kg/m}^3$	$\tilde{P}_{11} = 0.4918$
$b^2 = 1.3757$	$P_c = 22.0460$ MPa
$a = +\ 23.667$	
$k_0 = +\ 1.4403$	
$k_1 = +\ 0.2942$	
$d = -\ 0.01776$	
$\tilde{P}_1 = +\ 6.8445$	
$\tilde{P}_2 = -\ 25.4915$	
$\tilde{P}_3 = +\ 5.238$	

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[c] The average values of g and b at the 647.22_7 K point differ by about 16%; the spread around each average is ±4%. We have no completely satisfactory explanation for a persisting density difference 150 mK above the critical point. Gravity effects in a cell of the height of Osborne's would give rise to about 2% difference in density between top and bottom. Unequilibrated impurities of volatility greatly different from that of steam even if present at only a 5 ppm level, could, in principle, lead to substantial density gradients at a temperature 150 mK above the critical point while causing only marginal changes in the pressure (Ref. 42) and would have the tendency to persist for a long time in an unstirred vessel. In the absence of knowledge about the nature of the impurities, however, no quantitative estimates can be made of their effects. A temperature gradient of only 4 mK over the height of the cell will give a 10% density gradient 150 mK above T_c, and is the most likely explanation for a spurious density difference.

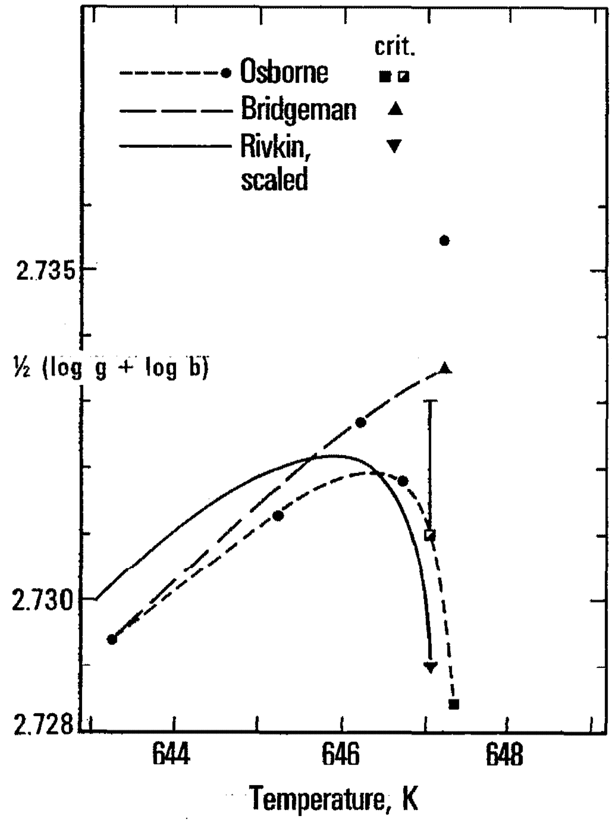

FIG. 3. A "Bridgeman and Aldrich plot" of the sum $(\log g + \log b)/2$ of latent heats. We show Osborne's experimental data, ●, our predicted curve based on Rivkin's PVT data (solid curve), an extrapolation due to Osborne - - - -, and that due to Bridgeman and Aldrich — —. Note that scaling confirms Osborne's method of extrapolation. Note also that Osborne rejected his own highest point. The symbols ▲ and ▼ indicate various estimates for the critical value of the sum, as referenced in the figure. The symbol ■ indicates Osborne's estimate, the symbol ◪ our estimate of $(\log g + \log b)/2$ based on Osborn's data, the vertical bar a conservative estimate of its uncertainty.

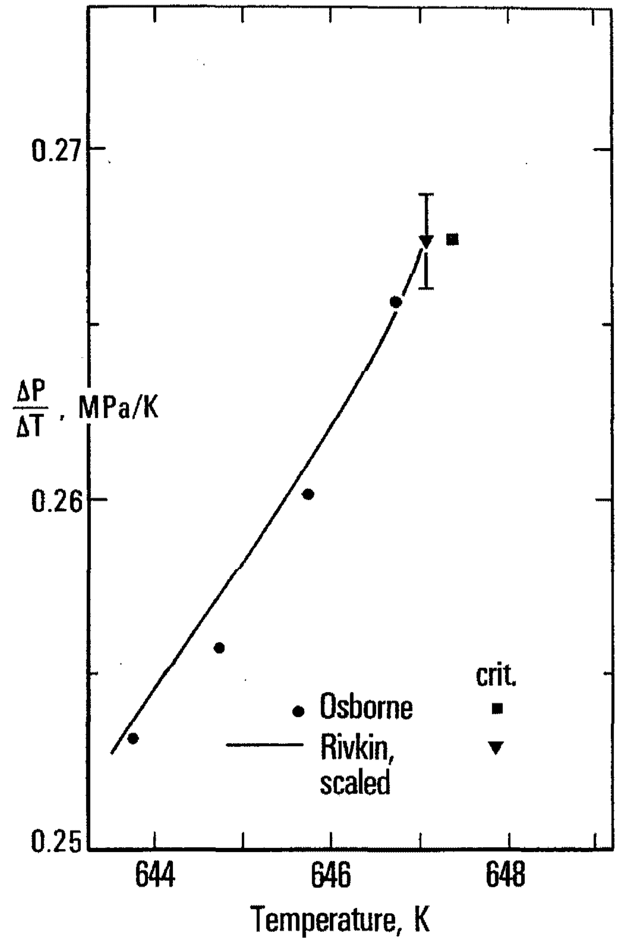

FIG. 4. A plot of $\Delta P/\Delta T$ for Osborne's vapor pressure data (●) and a full curve through our values of $\Delta P/\Delta T$ predicted from Rivkin's PVT data (Ref. 15). The limiting slope at 647.06_7 K (▼) is defined to better than the tolerance of ± 0.5% indicated.

the extrapolations of the latent heats and the slope of the vapor pressure curve. As to the latent heats, we have with Bridgeman and Aldrich,[12] plotted the quantity $(1/2)(\log b + \log g)$ versus temperature (Fig. 3). We show the experimental data, the prediction of the scaling laws based on Rivkin's PVT data, the extrapolation by Osborne *et al.*, and that of Bridgeman and Aldrich. In order to obtain the limiting slope of the vapor pressure curve, we plot the values of $\Delta P/\Delta T$ obtained from Osborne's vapor pressure data[6] and his estimate of the limiting slope in Fig. 4. We also plot the smooth curve through our predicted values of $\Delta P/\Delta T$, and our limiting slope, based on Rivkin's data. An unbiased curve through Osborne's data, with the general shape dictated by the scaling laws, would readily extrapolate through our predicted limiting slope, with a maximum uncertainty of ± 0.5% as indicated. (Our limiting slope agrees within the 1 part in 1000 level with that derived from Wagner's equation[43] at 647.06_7 K.) Note that Osborne *et al.* obviously disregarded the point at 647.22_7 K, while Bridgeman and Aldrich did not. Note also that the trend assumed by Osborne *et al.* is in accordance with scaling while the trend assumed by Bridgeman and Aldrich is not. At the value of $T_c = 647.06_7$ K following from Osborne's latent heats with omission of the 647.22_7 point, we deduce from Osborne's data, on the basis of Figs. 3 and 4:

$$\log g_c = \log b_c = 2.731 \pm 0.002,$$

$$g_c = b_c = 538.3 \pm 2.5 \text{ kJ/kg}, \tag{7.9}$$

$$(dP/dT)_c = (0.2673 \pm 0.0013) \text{ MPa/K},$$

$$T_c(dP/dT)_c = (172.9 \pm 0.8) \text{ MPa}. \tag{7.10}$$

Combining Eqs. (7.6), (7.9), and (7.10), we obtain, for the critical density,

$$\rho_c = 321.2 \pm 3.1 \text{ kg/m}^3. \tag{7.11}$$

Here the error estimates are maximum uncertainties expected in the quantities of interest. This value is in very good agreement with the value we deduced from Rivkin's PVT data, $\rho_c = 322.8$ kg/m^3.

7.3. Recommended Values of the Critical Parameters

The various estimates of the critical parameters of H_2O that we have discussed are summarized in Table 6. Our rec-

TABLE 6. Estimates for, and proposed best values of, the critical parameters of H_2O

References	T_c,K	P_c,MPa	ρ_c,kg/m^3
Direct observation			
2	647.14 ± 0.03	22.045 ± 0.003	
3	647.14	22.048	
4,5	647.19 ± 0.03	22.071 ± 0.002	
Derived values			
18,19,15	647.07 ± 0.07	22.0460	322.8
6,7, this work	647.07 ± 0.07	22.0446	$321.2 + 3.1$
Recommended "best" values	$647.14 + \delta_1$ $\delta_1 = 0.00 \pm 0.10$	$22.064 \pm 0.27\,\delta_1 \pm 0.005$	322 ± 3

ommended values are the following:

(1) For T_c, we choose an average of the values in Table 6, with an uncertainty large enough to encompass the extremes

$$T_c = (647.14 \pm 0.10)\ \text{K}. \tag{7.12}$$

(2) For P_c, we choose the corresponding value compatible with Eq. (7.12) and the vapor pressure curve defined by Osborne's data. The tolerance of the pressure shall be composed of two parts—one proportional to the uncertainty in T_c, estimated above as 0.1 K maximum, and the other the uncertainty the pressure itself, which we estimate as no larger than 5 kPa. It is to be understood that for any choice of T_c departing from the recommended value by $|\delta T| < 0.1$ K, a corresponding shift in P_c, equal to

$$(\delta T)(dP/dT)_c = 0.27(\delta T)\ \text{MPa}$$

is to be made. Thus we adopt

$$P_c = (22.064 + 0.27\delta_1 \pm 0.005)\ \text{MPa},$$

with

$$\delta_1 = 0.00 \pm 0.10. \tag{7.13}$$

(3) For ρ_c, we propose to accept an average of the values derived from Rivkin's PVT and Osborne's latent heat data,[d] namely,

$$\rho_c = 322 \pm 3\ \text{kg/m}^3,$$

$$[V_c = (0.003\,15 \pm 0.000\,03)\text{m}^3/\text{kg}], \tag{7.14}$$

where the uncertainty estimate reflects the maximum spread obtained when fitting PVT data with a variety of scaled equations, and the maximum error that can be incurred by extrapolations of Osborne's latent heats based on the scaling laws.

These "best" values are the ones given in the Abstract and in the Appendix.

Our proposed value for ρ_c falls within the tolerance of the value adopted in the Skeleton Tables and in IFC 67. The fivefold decrease in tolerance is evidence of the increased availability of high quality data and sophistication of data analysis. Our proposed values for the pair (T_c,P_c) do not fall within the tolerances set in IFC 67 (Fig. 1). Our proposed values fall within the rhomboidal area, indicated in Fig. 1, which has no points in common with the rectangular area around the IFC 67 choice. The downward shift in T_c is a consequence of the availability of a number of direct determinations and of more refined data analysis. That our tolerances on T_c and P_c have not decreased appreciably since IFC 67 was adopted is a consequence of a greater experimental experience with, and a more realistic appraisal of, the many sources of error that can affect the determination of the critical point under conditions as severe as 650 K, 22 MPa in a corrosive fluid. It is a tribute to the many fine experimenters that have provided input to this work, that their measurements, extending over a period of 50 years, are as close as shown in Fig. 1, and that they all agree to within the narrow tolerances claimed by their respective authors.

8. The Critical Parameters of Heavy Water Substance

8.1. Direct Determination

The critical parameters of a 97.1% D_2O–2.9% H_2O mixture were observed directly by Blank.[2] He obtained the values $T_c = (643.98 \pm 0.03)$ K, $P_c = (21.671 \pm 0.003)$ MPa. By assuming that the critical line of the D_2O/H_2O mixture is linear in $P(x)$ and $T(x)$, Blank concluded for pure D_2O:

$$T_c = (643.89 \pm 0.03)\ \text{K},$$

and (8.1)

$$P_c = (21.659 \pm 0.003)\ \text{MPa}.$$

We have accepted Blank's value of T_c for D_2O as the only result available; also, in the case of H_2O, his T_c value was equal to the value we have recommended here, and within 0.1 K from all values obtained directly and indirectly.

8.2. Indirect Determinations

We have deduced values for P_c and ρ_c from a scaled fit[23] to Rivkin and Akhundov's PVT data[22] for 99.87% D_2O, after correcting these data for the small H_2O impurity by a method described elsewhere.[39,40] We used the fit of Table 6

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[d] In principle, we should correct these ρ_c values for the 0.07 K difference in T_c between our recommended value and that derived from Osborne's data. In practice, such a correction would be 2 orders smaller than our stated uncertainty in ρ_c.

TABLE 7. Parameters in the revised and extended scaled potential for D_2O fitted to Rivkin's data (Refs. 22 and 23)

Critical exponents (fixed)		Critical temperature (fixed)	
β	$= 0.325$	T_c	$= 643.89$ K
δ	$= 4.82$		
Δ	$= 0.50$		
Parameters taken from Table 5		Fitted parameters	
b^2	$= 1.3757$	r_c	$= 356.24$ kg/m^3
a	$= +23.667$	P_c	$= 21.6713$ MPa
k_0	$= +1.4403$	$\tilde{P}_1$	$= +6.9107$
k_1	$= +0.2942$	$\tilde{P}_2$	$= -25.2370$
d	$= -0.01776$	$\tilde{P}_3$	$= +8.6180$
Derived parameters			
$\tilde{P}_{11} = 0.54764$			

for H_2O as a starting point, imposed Blank's value of T_c, and allowed the nonuniversal parameters (the analytic background, the mixing parameter and the correction-to-scaling amplitude) to vary until a minimum χ^2 was obtained. The weights in the fit were assigned in the same way as in the case of H_2O. The optimized parameters are listed in Table 7. The point to note is that, just as in the case of H_2O, the optimized value of P_c is about 10 kPa higher than the value reported by Blank. The same offset was noted by Hill *et al.*[40,44]

Our fit also results in a value of ρ_c. Since the data base and the method of fitting are similar to the case of H_2O, while the standard deviation of the fit is a factor of 1.7 higher, we have correspondingly enlarged our uncertainties in the random error in pressure and in ρ_c. Thus we recommend

$$\begin{aligned} &T_c = (643.89 \pm 0.20)\ \mathrm{K}, \\ &P_c = (21.671 + 0.27\delta_2 \pm 0.010)\ \mathrm{MPa}, \\ &\text{with } \delta_2 = 0.00 \pm 0.20, \\ &\rho_c = (356 \pm 5)\ \mathrm{kg/m^3}, \\ &[V_c = (0.002\,74 \pm 0.000\,04)\ \mathrm{m^3/kg}]. \end{aligned} \tag{8.2}$$

These best values are the ones given in the Abstract and in the Appendix.

9. Acknowledgments

We have profited from the insights of Professor E. U. Franck and Dr. Robert W. Potter II on the matter of impurity effects. B. Kamgar-Parsi gave valuable assistance in the analysis of the vapor pressure and caloric data for light and heavy water. IAPS members L. Haar, G. S. Kell, J. Kestin, E. Le Fevre, M. Uematsu, J. V. Sengers, and W. Wagner have offered useful suggestions and ideas.

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Appendix

IAPS Statement, 1983, of the Values of the Temperature, Pressure, and Density of Pure Ordinary and Heavy Water Substances at Their Respective Critical Points

Ordinary water substance, called H_2O, is of normal isotropic constitution. Heavy water substance, called D_2O, is ^2H_2O with the oxygen isotopes in the same abundance as in ordinary water substance. (See G. S. Kell, J. Phys. Chem. Ref. Data **6**, 1109, 1977).

Statement

H_2O Ordinary Water Substance		D_2O Heavy Water Substance
$(647.14 + \delta_1)$ K	T_c	$(643.89 + \delta_2)$ K
$\delta_1 = 0.00 \pm 0.10$		$\delta_2 = 0.00 \pm 0.20$
$(22.064 + 0.27\,\delta_1 \pm 0.005)$ MPa	P_c	$(21.671 + 0.27\,\delta_2 \pm 0.010)$ MPa
(322 ± 3) kg/m^3	ρ_c	(356 ± 5) kg/m^3

T_c is temperature at the critical point.
P_c is pressure at the critical point.
ρ_c is density at the critical point.