The Molar Volume (Density) of Solid Oxygen in Equilibrium with Vapor

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Data from the literature on the molar volume of solid oxygen have been compiled and critically analyzed. A correlated and thermodynamically consistent set of molar volumes, including the volume changes at the various solid phase transitions, is presented. Evidence for the existence of a δ-solid phase is reviewed. Uncertainties in the data and in the recommended set of values are discussed.

Key words: Density; molar volume; oxygen; phase transition; solid.

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1. Introduction

Liquid oxygen has served as a thermometric fixed point in cryogenics for some time. In the International Practical Temperature Scale of 1968 (IPTS–68) both the triple point and the normal boiling point of oxygen are defined as primary fixed points [1, 2].[1] Solid oxygen is of considerable theoretical interest because it occurs in at least three, possibly four different solid modifications and has several isotopic components. The fourth solid modification, δ, has been investigated experimentally [3] but needs to be studied further. Details of the new phase are given in section 5.1.

Considerable experimental effort has gone into the investigation of the solid phase transition temperatures of oxygen because the transitions might be useful as secondary fixed points in thermometry. An appreciable effort has gone into the evaluation of low temperature entropy and enthalpy contributions to establish standard state values at 298.15 K, see for example [4, 5]. In contrast to entropy, enthalpy, specific heat, and the properties of the ideal gas, the molar volumes of solid oxygen have not been studied extensively. It is the purpose of this paper to review the data that are available from the literature, to critically evaluate the available data, and to present a correlated and thermodynamically consistent set of molar volumes for solid oxygen.

That the density (molar volume) of solid oxygen had not been related to liquid densities became evident during a task performed for NASA [6]. A compilation of Mullins et al. [7] was completed before the proper structures for both α and γ oxygen had been determined, and could not be used as source of volumetric data. Discrepancies of 10% indicated in a study by Jahnke [8] had not been removed in a subsequent study by Barrett et al. [9]. We had been asked to assemble thermodynamic properties of slush oxygen, that is a mixture of solid and liquid. Slush is being considered as an alternate to liquid oxygen in propulsion primarily because the density increases in going from liquid to mixtures of liquid

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[1] Figures in brackets indicate literature references at the end of this paper.

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and solid. Thus the density of solid oxygen became vitally important.

2. Approach, Sources of Data

The only molar volumes we will consider are those along the saturation boundary of solid-vapor, i.e., at temperatures below the triple point. We specifically exclude the very few measurements in the single phase where the solid is under pressure because to consider them would unduly complicate the paper. Values for the compressed solid have been measured [10] and compiled by Mills [11]. The approach will be to work from the triple point toward lower temperatures. The density of the liquid at the triple point is assumed to be known quite accurately and is used as a reference or starting value. The volume changes for the various phase transitions and each crystal thermal contraction are considered independently. They are combined algebraically to form a consistent set of molar volumes from the triple point to lower temperatures. Of course, the errors accumulate so the densities that are least well known are those at very low temperatures.

The sources of data that will be considered are those experimental papers that contain information on the transition temperatures, on direct volumetric measurements, on x-ray, neutron, or electron diffraction, on dilatometric measurements, on melting or transition curves, and on heats of transition. X-ray measurements yield both structures and volume values. Melting on transition curve derivatives and heats of transition are used in the Clausius-Clapeyron equation to obtain volume changes for a given transition.

3. Phases and Transition Temperatures

Oxygen occurs in at least three, possibly four solid modifications. Barrett et al. [12] using x-ray diffraction determined α-oxygen to be monoclinic. The structure of β-oxygen determined by Hörl [13] from electron diffraction data is rhombohedral. This structure has been confirmed by Alikhanov [14, neutron diffraction] and Curzon and Pawlowicz [15, electron diffraction]. The structure of γ-oxygen was determined by Jordan et al. [16] (x-ray) to be cubic. The structure of the δ-solid, if it is verified, is not known. The new transition occurs very close to the triple point. We will consider the δ-liquid and the γ-δ transsitions as if they were one. Thus the transitions of interest are α-β, β-γ, and γ-liquid.

Transition temperatures have been measured by Hoge [17], Orlova [18], Muijlwijk et al. [19, 20], Weber [21], Kemp and Pickup [22], Cowan et al. [23], Kemp et al. [24] and Compton and Ward [25]. The values are collected for comparison in table 1. Values published prior to 1950 by other authors, as given in the reviews by Hoge [17] and Orlova [18], are not considered because the earlier temperature scales are simply not defined or achieved sufficiently well to permit meaningful comparison. The transition temperatures are shown to the nearest millikelvin, the original temperature and temperature scale is indicated whenever applicable. Conversions of temperatures to the IPTS–68 scale have been made according to the paper by Bedford et al. [27]. For this paper we adopt the values given in the last line of table 1. The uncertainty for the α-β transition is taken from the dispersion among the different experiments. The β-γ and γ-liquid transitions are realized in the national standards laboratories for calibration purposes to about 0.2 mK on the defined scale [23, 24, 25]. However, it should be recalled that the IPTS–68 scale as defined may still differ from the ideal thermodynamic scale by several mK. For example, the vapor pressure analysis by Prydz [28] invokes thermodynamic consistency. One of the conclusions that can be drawn from Prydz's paper is that the triple point and the normal boiling point of oxygen, both defined points on the IPTS–68, should probably be 5 millikelvin farther apart than they are on the IPTS. In other words, at one point, or perhaps both, the IPTS–68 and the ideal thermodynamic scale are not yet in exact agreement.

There are several explanations for the disagreement in temperature among the different experiments. The most logical one involves an error in temperature measurement. Specifically the thermal link between sample and thermometer may be inadequate. Low thermal conductivity of the solid [29], low vapor pressure, and incomplete conversion from one crystal structure to another all contribute to poor thermal linkage. The result is a temperature-time trace for any given transition which is not flat. As an example, see figure 2 in the paper by Muijlwijk et al. [20], where the authors even used helium gas to improve thermal contact for the α-β transition.

Another possible explanation is that the transition temperatures, certainly the triple point, are sensitive to impurities as shown by Ancsin [30, 31]. Differences of 2 millikelvin at the triple point can easily be the result of some very nominal impurities. Ancsin's results with helium gas show that the triple point pressure is considerably higher with helium present than without. Therefore, the practice of using helium to effect better thermal contact between solid oxygen and the thermometer may be a poor experimental procedure.

4. The Reference Volume—Liquid Density

For the liquid densities and in particular for the density of the liquid at the triple point we adopt the value published by Weber [21], $24.49_2 \pm 0.02$ cm^3/mol. For this paper Weber's value is the point of reference, that is all volumes at lower temperatures will be referred to it and adjusted as necessary. The uncertainty of Weber's value becomes crucial to the remainder of the paper and we will, therefore, examine it in more detail.

TABLE 1. Transition temperatures of oxygen

Transition $\alpha\longleftrightarrow\beta$			Transition $\beta\longleftrightarrow\gamma$			Triple point γ or $\delta\longleftrightarrow$liquid		
IPTS–68	Orig. scale	Ref.	IPTS–68	Orig. scale	Ref.	IPTS–68	Orig. scale	Ref.
23. 884	23. 886 NBS–39	[17] 1950	43. 806	43. 800 NBS–39	[17] 1950	54. 361	54. 363 NBS–39	[17] 1950
23. 866	23. 876 PRMI–54	[18] 1962	43. 811	43. 818 PRMI–54	[18] 1962	54. 365	54. 368 PRMI–54	[18] 1962
						54. 359	54. 350, CCT–64	[19] 1966
						54. 359	$54.\,350_7$ NBS–55	[21] 1969
23. 864	23. 858 CCT–64	[20] 1969	43. 803	43. 794 CCT–64	[20] 1969			
						Defined 54. 361		[1, 2] 1969
23. 880			43. 801			54. 361		[22] 1972
			$43.\,801_5$		[23] 1976			
						54. 361		[24] 1976
						54. 361		[25] 1976
$23.\,880^{+0.004}_{-0.016}$			43. 801 ± 0. 0002			54. 361 ± 0. 0002		

Weber establishes the liquid triple point density from the intersection of his high density *PVT* surface with the vapor pressure curve. The surface is derived from some 557 experimental *PVT* points in the single phase compressed liquid region. The lowest isotherm of experimental points is at 56 K; however measurements at lower temperatures along the melting line round out the set of experimental data. For the region in question Weber indicates an uncertainty of 0.1% in density. This estimate will not be changed appreciably by the 1.5 K extrapolation to the triple point. Changing the temperature scale from the experimental NBS–55 to IPTS–68 and changing the vapor pressure at the triple point to the value currently considered the best have negligible effect on the value of the liquid density at the triple point.

Weber's uncertainty of 0.1% for the liquid triple point density of oxygen can be verified indirectly through results obtained on other fluids. Nitrogen [32], methane [33], and ethane [34] have been measured in the same *PVT* system that Weber used for oxygen. Liquid densities for these gases measured by Haynes et al. [35, 36, 37] in a totally different apparatus, a magnetic densimeter, differ by no more than 0.1% at temperatures below 120 K.

5. Data, and Analysis of the Solid Volumes

5.1. The Volume Change on Fusion, and the δ-Solid

The volume change on fusion has not been measured directly; it must be calculated from the Clausius-Clapeyron equation using the heat of fusion [38, 39, 40, 41, 3] and the melting curve derivative. Except for the value of Aucsin [41] the heats of fusion reported by various authors differ by no more than 0.4%, thus the value calculated for the volume change on fusion depends primarily on which melting curve is used. Weber [21] has compared his own results to the melting curves published by other authors as shown in table 2.

The earliest value obtained by Lisman and Keesom [42] is seen to fall quite wide of the more recent results. Jahnke [8] attributes a value of 0.921 cm^3/mol to Lisman and Keesom. The origin of this value is unclear since a recalculation of Lisman and Keesom's value either through the melting pressure derivative or from their published density differences confirms their value of 1.01 cm^3/mol. The agreement between Mills and Grilly [43] and Weber [21] is surprisingly good considering that the former authors obtain all of their data at pressures greater than 35 MN/m^2.

TABLE 2. Values of the volume change on fusion calculated from the Clausius-Clapeyron equation

Author	Year	Calc. volume change, cm^3/mol
Lisman and Keesom [42]	*1935*	*1. 01 (0. 921 ?)* [a]
Mills and Grilly [43]	1955	0. 93
Jahnke [8]	1967	0. 918 ± 0. 02
Weber [21]	1970	0. 94 ± 0. 01

[a] See text.

Jahnke [8] pressurized his oxygen samples with helium gas, which may account for his results being slightly lower than the others. Weber's [21] melting pressures are closest in temperature to the triple point. If we adopt his calculated value of the volume change on fusion with a slightly increased uncertainty to cover all of the melting curves and the variation in the experimental heats of fusion, i.e., 0.94 ±0.02 cm^3/mol, then the molar volume for the γ-solid at the triple point becomes 23.55 ±0.04 cm^3/mol. If on the other hand we extrapolate a curve fit of the x-ray measurements of Barrett et al. [9] on the γ-solid to the triple point temperature, then we obtain a value of 23.69_2 ±0.05 cm^3/mol.

It is apparent that a systematic difference exists between the best x-ray measurements on the γ-solid on one hand and the liquid densities coupled with the volume change on fusion on the other. The size of the discrepancy is 0.14 cm^3/mol or about 0.6% in molar volume. The discrepancy has been recognized as early as 1936 [44] but has not been resolved. The individual errors do not overlap. To account for an error of this size experimentally we would have to postulate an error of 10% in the heat of fusion, unlikely, an error of 10% in the derivative of the melting curve, unlikely, or a systematic error of 2 K in the x-ray measurement, also unlikely [45]. A potential explanation of the discrepancy involves the existence of a new, as yet unrecognized, solid phase for oxygen. The review of the molar volumes of solid oxygen has thus led to a search for a δ-solid in oxygen. Experimental evidence of a new phase has been obtained very recently by Roder [3]. However, additional experiments are needed to confirm the new phase.

Exactly how the δ-solid affects the volume changes near the triple point remains to be determined. Several possibilities have been indicated by Roder [3]. For this paper we ignore the δ-solid and take the volume change in going from the liquid to the γ-solid to be 0.80±0.03 cm^3/mol, i.e., we accept the x-ray determination of Barrett et al. [9] and the liquid values of Weber [21] as representing the best possible values for the molar volume of the γ-solid and the liquid at the temperature of the triple point. Some of Weber's liquid densities, the volume change in going from liquid to γ-solid and the best value for the γ-solid at 54.361 K, 23.69± 0.05 cm^3/mol, are shown in figure 1.

5.2. The γ-Solid

Density data for the γ-solid can be obtained from several sources. Tolkachev and Manzhelii [46] made a single determination of density; Manzhelii et al. [47] reported thermal expansion measurements made with a quartz dilatometer; Jordan et al. [16] reported on the x-ray structure determination from which a density can be calculated; Cox et al. [48] reported a refinement in structure; and Barrett et al. [9] made x-ray measurements at a number of temperatures from which they determined expansion coefficients as well as molar volumes. The published experimental data as well as the results of Schuch and Mills [10] are shown in figure 1. The thermal expansion meas-

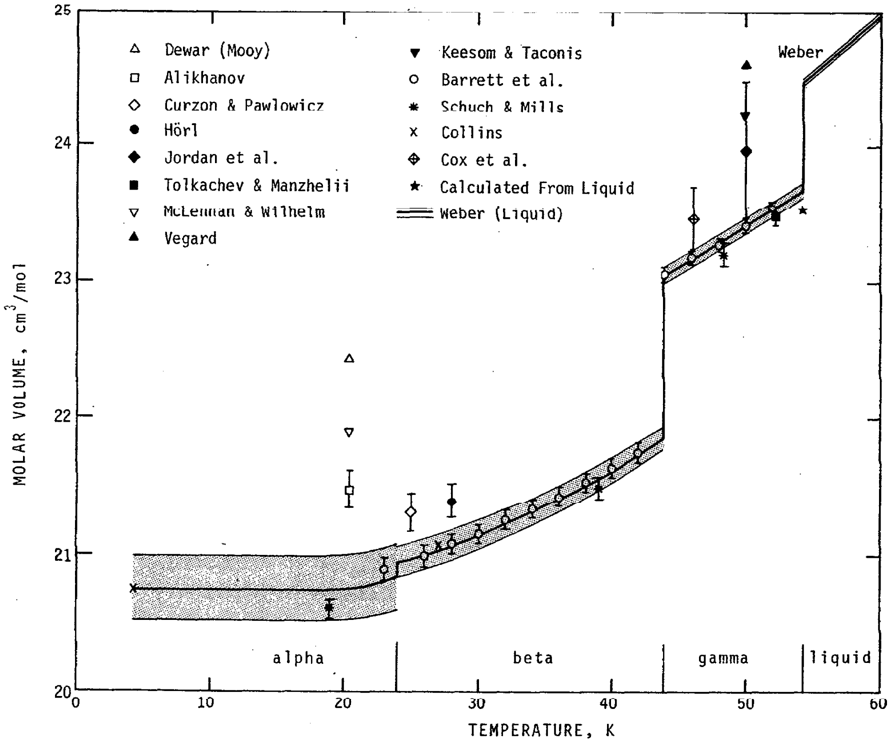

FIGURE 1. The molar volume of solid oxygen.

urements of Manzhellii et al. [47] are not plotted because the method is relative to a known or reference value, however, volume changes obtained from their results are used in the analysis below.

The total volume change for the γ-solid between triple point and the β-γ transition is 0.64 cm^3/mol from the paper of Barrett et al. [9] obtained by extrapolating a linear least squares fit of the published volume data to the respective temperatures. We note that the expansion coefficient published by Barrett et al. [9] for the γ-solid, $\Delta\ell/\ell=780\times10^{-6}$ K^{-1}, must have suffered a digit reversal. A value of 870×10^{-6} K^{-1} is probably correct. The value obtained by integrating the thermal expansion values of Manzhelii et al. [47] is 0.65 cm^3/mol. The agreement in volume change between the two radically different methods is very satisfactory.

To obtain a curve of recommended values we apply the volume change of 0.64 ± 0.01 cm^3/mol to the molar volume obtained for the triple point solid in the previous section. Thus the molar volume of γ-solid at the β-γ transition becomes 23.05 ± 0.06 cm^3/mol. Values at intermediate temperatures are interpolated from our curve fit to the volumes of Barrett et al. [9]. Experimental precision plotted in figure 1 as error bars were obtained as follows: calculated from the error given for the lattice constant by Jordan et al. [16] and Cox et al. [48], stated to be $\pm0.03\%$ in density by Tolkachev and Manzhelii [46], and estimated to be ±0.05 cm^3/mol for the measurements of Barrett et al. [9]. The last estimate is calculated from a precision of ±0.005 Å in the lattice constant of α-oxygen by Barrett et al. [12] since the authors did not give an explicit uncertainty in their paper on γ-oxygen. Uncertainties of the recommended values were obtained by adding the error estimate applicable to each separate element.

We note that the direct determination of density [46] lies somewhat below the recommended values, whereas the values derived from the x-ray experiment of Jordan et al. [16] and the neutron diffraction experiment of Cox et al. [48] fall considerably higher than the ones recommended.

5.3. The β-γ Transition

The volume change for the β-γ transition has been measured directly at elevated pressures by Stevenson [49] and Stewart [50]. A value of 1.19 cm^3/mol is obtained from the measurements of Barrett et al. [9] using the linear curve fit of the previous section for the γ-solid and a parabolic fit for the molar volumes of the β-solid. The volume change can also be established from heats of fusion [39, 40, 41] and the pressure dependence of the β-γ transition [49, 50, 8]. The values to be considered are given in table 3.

TABLE 3. Volume changes for the β-γ transition

Author	Year	Method	Value cm^3/mol
Stevenson [49]	1957	Clausius-Clapeyron eq.	0.759 (0.959 ?) [a]
Stewart [50]	1959	Clausius-Clapeyron eq.	1.16 ± 0.14
		Extrapolation of ΔV to zero pressure.	1.18 ± 0.06
Jahnke [8]	1967	Clausius-Clapeyron eq.	1.08 ± 0.05
Barrett et al. [9]	1967	Extrapolation of volumes (x-ray).	1.19

[a] See text.

The value published by Stevenson [49] is 0.759 cm^3/mol. Since this value is so very much different from the others we checked it in detail. We obtain a slope of 175 atm/K from his figure 6. Using a value of 177.6 cal/mol [39] for the heat of transition the recalculated value becomes 0.96 cm^3/mol. We suspect a digital error in the printing of Stevenson's paper, i.e., 0.759 should have been 0.959 cm^3/mol.

The agreement between the values of Stewart [50] and Barrett et al. [9] is excellent. The value contributed by Jahnke [8] is a little wide, again perhaps becasue of pressurization with helium gas. We adopt the value of 1.18 ± 0.02 cm^3/mol from the values presented in table 3. Thus the molar volume of the β-solid at the β-γ transition becomes 21.87 ± 0.08 cm^3/mol.

5.4. The β-Solid

Density data for the β-solid can be obtained from several sources. Hörl [13] reported the structure to be rhombohedral and calculated a density of 1.495 g/cm^3 for a temperature of 28 K. A subsequent paper by Hörl [51] has not been used in this compilation. A value of 21.32 cm^3/mol has been calculated from the paper by Curzon and Pawlowicz [15] and assigned a temperature of 25 K. Mills [11] has calculated a value of 21.05 cm^3/mol from the paper of Collins [52] for a temperature of 27 K. The papers by Manzhelii et al. [47] and Barrett et al. [9] discussed in the section on the γ-solid also contain β-solid data that are used here. Experimental values including the value from Schuch and Mills [10] that can be plotted are shown in figure 1.

The total volume change for the β-solid between the α-β and the β-γ transitions is found to be 0.94 cm^3/mol from the paper by Barrett et al. [9]. This value was obtained by extrapolating a parabolic least squares fit of the molar volumes to the respective temperatures. A parabolic fit is indicated because both the molar volumes of Barrett et al. [9] and the thermal expansion results by Manzhelii et al. [47] show a distinct temperature dependence. The total volume change obtained by integration of the thermal expansion values of Manzhelii et al. [47] is 0.89 cm^3/mol. Again, the agreement between the two different experiments is quite good. The difference probably arises because the thermal expansion measures the property of the bulk material while the calculation of density from the lattice constants assumes a fairly ideal, defect-free crystal.

To obtain a curve of recommended values it is appropriate to apply the average of the two total volume changes, 0.92 ± 0.03 cm^3/mol, to the molar volume obtained for the β-solid at the β-γ transition. Thus the molar volume of the β-solid at the α-β transition becomes 20.95 ± 0.11 cm^3/mol. Values at intermediate temperatures are interpolated parabolically.

The error bars plotted in figure 1 for the electron diffraction experiments by Hörl [13] and Curzon and Pawlowicz [15] are calculated from the experimental precision indicated in these papers, and represent only the experimental precision. We have assigned a temperature of 25 K to the value of Curzon and Pawlowicz because they had to deposit their sample at 25 K to obtain a definite ring pattern for the β-solid. They state that they see no change in lattice parameters on cooling from 25 to 7 K, and therefore calculate their lattice parameter at 7 K. This paper illustrates clearly that considerable error in assigning a valid temperature to the published lattice parameters is possible. The experimental precision for the measurements of Barrett et al. [9] is estimated to be ± 0.07 cm^3/mol from the uncertainties given by Barrett et al. [12] for the α-solid. The disagreement between Hörl, Curzon and Pawlowicz, and Barrett et al. is larger than the combined experimental precision for the different experiments. Barrett et al. indicate that Hörl's lattice parameters fit a temperature of 35 K. This is true for the value of a_o at 36 K, however the C_o values at that temperature still differ by two parts in 1,000. In other words, systematic differences between the three different experiments remain unaccounted for.

5.5. The α-β Transition

Considerable confusion as to whether this transition is first or second order exists in the literature. Barrett et al. [9] point out that the transformation cannot be second order for quite general, theoretical reasons. Their conclusion is that the transition is first order and of a martensitic type, and that "Martensitic transformations are sensitive to strain and can easily imitate second-order transformations. Residual strains can aid or inhibit such a transformation so that the transformation of a strained sample does not take place at the transition temperature itself, but is spread out over a range of temperatures."

A martensitic transformation explains the rather diverse results and interpretations obtained by Eucken [53], Clusius [38], Giauque and Johnson [39], Hoge [17], Borovik-Romanov et al. [34], Fagerstroem and Hollis Hallett [40], Muijlwijk et al. [20], Ancsin [41], and Dundon [55] when these authors attempt to measure a heat of transformation. As mentioned earlier, the heating curve of Muijlwijk et al. (their figure 2) is not flat. Nevertheless, a distinct heat of transition is indicated by this curve and could have been evaluated by the authors. Thus their conclusion of "no evidence of a latent heat" is invalid. Fagerstroem and Hollis Hallet show a λ-like transition and presume a second order transition. Hoge is uncertain about the transformation but places the heat of transition as "about one-fifth the heat of fusion." The reported values for a heat of transition are those of Eucken −17.5 cal/mol, Clusius −21.1 cal/mol, Giauque and Johnston -22.42 ± 0.1 cal/mol, and Ancsin −103.13 J/mol. A totally different result can be obtained from the recent paper of Kemp and Pickup [22]. In contrast to most other authors who show the transition as a λ-like curve of C_{sat} vs. temperature, Kemp and Pickup present a temperature-time trace which is flat (their figure 2). They obtain the temperature-time trace by using a power input which is constant and appropriate to this transition, i.e., very small, 1.6 mW. Their loading is uncertain, around 10 cm^3 of liquid, i.e., approximately 0.41 moles. The heat of transition estimated from this paper is 10 J/mol, nearly a factor of ten smaller than the other values!

The α-β transition has been measured at elevated pressure by both Stevenson [49] and Stewart [50]. Evidence that a volume change does indeed exist is found in figure 7 by Stevenson who calculates the volume change to be 0.117 cm^3/mol from the Clausius-Clapeyron equation using the transition heat from Giauque and Johnston [39]. Stewart erroneously assumed the transition to be second order and did not present a volume change. However, using the derivative of his phase transition curve and the heat of transition from Giauque and Johnston we can calculate a value of 0.12_5 cm^3/mol from his paper, which is in excellent agreement with the value by Stevenson. In both cases it would be preferable to extrapolate the measured volume changes to zero pressure. However, the required values have not been published in these papers.

Manzhelii et al. [47] state that the volume change observed in their thermal expansion experiment is on the order of 0.5% even though they are not able to establish a reproducible value. The volume jump given by Dundon [55] is 0.135 cm^3/mol ± 10%. The volume jump can not be established unambiguously from the x-ray diffraction experiments because the α-oxygen volumes of Barrett et al. [12] and Schuch and Mills [10] differ by 1%.

We adopt a value of 0.13 ± 0.11 cm^3/mol for the volume change of the α-β transition as a composite of the results of the more recent experiments [10, 41, 49, 50, 55]. The uncertainty of the volume change is deliberately estimated as quite large because we feel strongly that the heat of transition could be in error by a factor of ten. Since the value of the β-solid at the α-β transition had been established at 20.95 ± 0.11 cm^3/mol the molar volume of the α-solid at the α-β transition becomes 20.82 ± 0.22 cm^3/mol. We note that the uncertainty of 0.22 cm^3/mol, nearly 1% of the molar volume, arises in equal parts from the cumulative error in the molar volume and the uncertainty for the heat of transition for the α-β transition.

5.6. The α-Solid

The direct density measurement of Dewar [56] made at the boiling point of hydrogen falls into the temperature range of the α-solid. It is clear from figure 1 that this value is about 8% wide of the more recent measurements. Molar volumes and experimental imprecisions derived from the papers of Alikhanov [14] Barrett et al. [12] and Schuch and Mills [10] are plotted in figure 1. From the neutron diffraction experiment of Collins [52] we have calculated a value of 20.74 cm^3/mol at 4.2 K. The uncertainty for this value cannot be calculated, but is taken to be the same as for that of Alikhanov. The thermal expansion measurements of Manzhelii et al. [47] are used to provide a volume variation down to 18.75 K. At that temperature the values extrapolate to zero expansion. At temperatures below 18.75 K the molar volume is assumed to remain contant. Thus the total volume change for the α-solid becomes 0.06 cm^3/mol and the molar volume at 4.2 K becomes 20.75±0.22 cm^3/mol, or very nearly identical to the results of Collins [52]. The uncertainty for the volumes of the α-solid were established in the previous section as ±0.22 cm^3/mol.

6. Results

The results of this study are presented in graphical form in figure 1. Recommended values of molar volumes and densities are given in table 4. As far as errors are concerned, we have followed the suggestion of Rosenfeld [57], that is we assume the errors given in most papers to indicate experimental imprecision, and we establish an actual uncertainty whenever possible from the dispersion among several different experiments. By breaking the problem into several parts, each part can be assessed individually and an uncertainty for it established. The sum of the parts yields a thermodynamically consistent set of values and a consistent set of uncertainties. The uncertainty in recommended values in table 4 increases from 0.2% at the triple point to no more than 1.1% at the very lowest temperature.

7. Conclusion

One way to state the results of this study is as follows: The molar volumes obtained, or obtainable from the papers of Dewar [56], McLennan and Wilhelm [58], Mooy [59], Ruhemann [60], Vegard [61, 62], Keesom and Taconis [44], Jordan et al. [16], Cox et al. [48], Hörl [13], Curzon and Pawlowicz [15] and Alikhanov [14] should be rejected. The values are simply not accurate enough to be included in a critical compilation of the molar volumes of solid oxygen. The recommended values are essentially the average between the thermal expansion results of Manzhelii et al. [47] and the x-ray measurements of Barrett et al. [9, 12] except for the α-solid where the values of Manzhelii et al. [47], Collins [52], and Schuch and Mills [10] are preferred. The direct implication is that nearly all values presently cited in handbooks of physical data need to be revised.

Many of the handbook values can be traced to the International Critical Tables, 1.4256 g/cm^3 at 20.5 K, that is, the value published by Dewar. This value was supposedly confirmed by Mooy [59] with x-rays, however we now know Mooy's structural assignment to be in error. Dewar's value differs by nearly 8% from the one recommended. This is not surprising; since he condensed his samples from the vapor state the formation of voids is likely. Similar more recent experiments with solid nitrogen were shown to contain up to 30% voids by measuring the dielectric constant of the condensed material [63]. Another value quite often cited in handbooks is 1.46 g/cm^3 at 20.5 K [64, for example]. This value can be traced to the x-ray work of McLennan and Wilhelm [58] whose assigned structure we now know to be incorrect. This value is about 6% different from the recommended one. A quite different value, 1.568 g/cm^3 at 0 K is cited in yet another handbook [65]. This value can be traced to the Smithsonian Tables [66], it is most likely an extrapolation of Dewar's values for liquid and solid to 0 K. Only by accident is this value close to the recommended values.

For the β-crystal Ruhemann [60] was not able to assign a definite structure, he did, however, state that McLennan and Wilhelm's structure should not be considered final. For the γ-crystal Vegard [61,62], Keesom and Taconis [44] and Jordan et al. [16] all cite the same structure, cubic. Their lattice parameters are identical, 6.83 Å, however their published densities vary by 2.5%, i.e., 1.30, 1.32, and 1.334 g/cm^3. Even the best of these values, Jordan et al. [16], differs by 2.5% from the work recommended, Barrett et al. [9]. Thus the densities cited by another compilation of x-ray structures [67] are in error by about 2.5%.

The papers rejected do, however, yield a clue about systematic differences. It appears that structural assignments, temperature control, and temperature measurement have improved as time has passed.

Two items remain in question: the precise value of the volume change for the α-β transition, and volume changes from the γ-solid to the liquid, involving as

TABLE 4. Molar volumes and densities of solid oxygen

Temperature K	Solid type	Molar volume cm³/mol est. error	Density	
			mol/cm³	g/cm³ [a]
4.2	Alpha	20.75 ±0.22	.04819	1.542
18.75		20.75 ±0.22	.04819	1.542
20.		20.75	.04819	1.542
22.		20.78	.04812	1.540
23.880		20.82 ±0.22	.04803	1.537
23.880	Beta	20.95 ±0.11	.04773	1.527
24.		20.95	.04773	1.527
26.		21.02	.04757	1.522
28.		21.08	.04744	1.518
30.		21.16	.04726	1.512
32.		21.24	.04708	1.507
34.		21.33	.04688	1.500
36.		21.42	.04669	1.494
38.		21.52	.04647	1.487
40.		21.63	.04623	1.479
42.		21.75	.04598	1.471
43.801		21.87 ±0.08	.04572	1.463
43.801	Gamma	23.05 ±0.06	.04338	1.388
44.		23.06	.04337	1.388
46.		23.18	.04314	1.380
48.		23.30	.04292	1.373
50.		23.43	.04268	1.366
52.		23.55	.04246	1.359
54.		23.67	.04225	1.352
54.361		23.69 ±0.05	.04221	1.351
54.361	Liquid	24.49_2 ±0.02	.04083	1.307

[a] Molecular weight 31.9988 g/mol.

they do the δ-solid. Both are deserving of further careful research.

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