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Sixteen Thousand Evaluated Experimental Thermodynamic Property Data for Water and Steam

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As part of the activities of the International Association for the Properties of Water and Steam, all reliable sources of experimental data on the thermodynamic properties of ordinary (light) water and steam have been collected and converted to common temperature, pressure, volume, mass and heat scales. The data are grouped by state or phase: ideal-gas properties; sublimation and melting curves; saturation properties; properties of liquid water at ambient pressure; thermodynamic properties of the single-phase state; and those of metastable states. In each category, a subdivision is made by property. Properties include the volume, enthalpy, heat capacities, sound velocity, internal energy and Joule-Thomson and related coefficients. The total data collection contains approximately 16 000 data points and covers a century of experimental work at temperatures from 253 to 1273 K and pressures up to 1 GPa. This report characterizes the data and gives the literature references. The actual data collection is available in computerized form.

Key words: density; enthalpy; equation of state; heat capacity; international input; metastable states; pressure; saturation properties; sound velocity; steam; temperature; vapor pressure; water.

Contents

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Nomenclature

specific heat capacity
density
specific enthalpy
compressibility
pressure
temperature
specific internal energy
specific volume
sound velocity

Greek Symbols

throttling coefficient
temperature-pressure coefficient
Joule-Thomson coefficient

Subscripts

isobaric
isothermal
isenthalpic
isentropic

1. Introduction

1.1 Historical

The data taking, collecting, sifting, graphing and formulating of properties of water and steam has been an ongoing effort since steam emerged as the working fluid in mechanical and electric power generation. In the early part of this century, data were presented in the form of thermodynamic tables and charts.

Traditionally, the needs of the power engineers for property values of water and steam were met by so-called Skeleton Tables. These are tables of values of the specific volume and of the enthalpy of water and steam, on grid points in pressure-temperature space, sufficiently closely spaced that linear interpolations are adequate. The grid-point values are obtained by interpolating in the relevant experimental data sets; data that appear discrepant are rejected, and a tolerance based on the scatter of the existing data sets is assigned to each grid point.

The first International Steam Table Conference was held in London in 1929 with the purpose of obtaining international agreement on the properties of steam. In 1934, agreement was reached on the first International Skeleton Steam Tables (IST 34). A substantial effort to expand and improve the experimental data base for steam was already under way, most notably by Osborne and coworkers at NBS, the National Bureau of Standards, presently NIST, the National Institute of Standards and Technology, in the U.S.A. A collection of data and tables for thermodynamic properties of water and steam was part of a comprehensive study by Dorsey in 1940[1]. After the second world war, the acquisition, evaluation and correlation of steam properties gained new impetus in several countries. At the Sixth International Conference on the Properties of Steam (ICPS) in New York, 1963, the International Skeleton Tables of the Thermodynamic Properties of Water Substance, 1963, were adopted.

The Skeleton Tables do not permit the imposition of thermodynamic consistency requirements on volume, enthalpy, and their derivatives. Deriving both volume and enthalpy from an accurate thermodynamic fundamental equation could assure such consistency, but devising such an equation was not feasible before computational power became widely available, in the late 1950's. The 1963 Sixth ICPS, therefore, also established an International Formulation Committee (IFC) which proceeded to develop a formulation of the thermodynamic properties of water and steam of the highest possible accuracy, for scientific and general use, and another one suited for computerized industrial calculations.

In 1968, at the Seventh ICPS in Tokyo, the 1967 IFC Formulation (IFC 67) for Industrial Use and the 1968 IFC formulation for Scientific and General Use (IFC 68) were formally adopted[3].

The IFC 67, which is still in use, is thus a first attempt at insuring thermodynamic consistency. It was found, however, that a fundamental equation based on temperature and pressure as independent variables could not be used over ranges including near- and supercritical steam. The IFC 67 therefore consists of formulations for several subregions, some with pressure and temperature, others with density and temperature as independent variables; and great effort was spent to assure smoothness of first and second derivatives across the boundaries of these subregions.

For applications that include near and supercritical steam, a formulation solely in terms of density and temperature as independent variables is much more suitable. At the time that the IFC 67 was adopted, the first Helmholtz free energy formulation of the properties of steam appeared, the equation of Keenan *et al.*[2] In the two decades since that prototype equation appeared, computer capabilities and computer-based regression techniques have increased in power by leaps and bounds. The selected bibliography on formulations for water and steam that accompanies this section bears witness to the ongoing activities, mostly but not exclusively associated with the appropriate working groups of the International Association for the Properties of Water and Steam (IAPWS).

Shortly after the 1968 Conference, the International Association for the Properties of Steam (IAPS) was established as a standing organization for the international cooperation on the properties of steam. IAPS began with the task of collecting and updating the experimental data on thermodynamic properties of ordinary (light) water and steam. This work was taken on because many new high-quality experimental data had been obtained in much wider ranges of temperature and pressure since 1963, which was the termination date for the input to IFC 67 and IFC 68. Thus, IAPS was preparing for an extension to higher pressures and temperatures of the Skeleton Tables, and also for an eventual replacement of the IFC 68 by a formulation that would be more accurate and valid over a larger range. These activities culminated in the formulation that is the basis of the 1984 NBS/NRC Steam Tables,[7] presently the accepted international scientific formulation of the properties of water and steam. Since 1984, there have been several efforts to extend and improve the formulation,[9,11] to obtain more precise formulations in more limited regions,[6,10] and to produce the more accurate Skeleton Tables that are currently accepted by IAPWS.[8]

The bulk of the work of collecting the data base on which all these formulations are built, fell on the shoulders of the Japanese group headed by Watanabe[4] and of the German group headed by Straub[5]. Many members of what then was IAPS Working Group 1 were involved in the task of ranking the data in four categories of descending reliability. In general, only the best category data were used in further development of skeleton tables and formulations. The lower-quality data were used only in regions where better data were absent. The present collection of data includes only that latter part of the lower-quality data. The so-called International Input contained roughly 9000 *PVT* and 7000 other property data points. The present collection contains this International Inp with, in addition, all other thermodynamic property da published since 1979. The closing date on the collecti is Dec. 31, 1987; a few data sets of exceptional qual that were obtained after that date have been include

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[8]Release on the IAPS Skeleton Tables 1985 for the Thermodynam Properties of Ordinary Water Substance, (November, 1985) IAP Secretariat. H. Sato, M. Uematsu, K. Watanabe, A. Saul, and Wagner, J. Phys. Chem. Ref. Data 17, 1439 (1988).

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1.2 Organization of the Data

In the paper, the data sources have been grouped l state or phase in the following categories: ideal-gas pro erties, Sec. 2; sublimation and melting properties, Sec. saturation properties, Sec. 4; properties of liquid water ambient pressure, Sec. 5; properties of the single-pha state, Sec. 6; properties of metastable states, Sec. 7. Tl actual data sets are available in computerized form. Ea reference to experimental data contains a code numb identical to the file number of the relevant computeriz file. The properties whose values we have collected i clude fixed points, virial coefficients, density, enthalp sound velocity, specific heats at constant pressure or vo ume, internal energy and Joule-Thomson coefficien With very few exceptions which are clearly noted in t text, the property data are measured data which are avai able in computerized form as explained below.

In the body of the report, we describe each data set i a single line in a table in the appropriate subsection; th line contains the authors' names, the date of publicatio the file name, the reference to the data source, the a thors' estimate of uncertainty (for which we take no r sponsibility) and one of the characters S, A or B, th reflects our judgement of reliability. Data of prove highest reliability are in category S. Category A is that ata that are of sufficient reliability to be used in formu- ıtions. Category B labels data that lack assurance of suf- cient reliability; confirming information may be absent; o information or uncertainty may have been given in the ɔurce; or there may be reason to believe that the uncer- ıinty is much larger than stated. It is the ongoing activity f formulation that provides the connection between the arious properties, and permits judgment about consis- ɜncy of various types of data. We have deemed it essen- :al to provide, to the extent possible, this type of ıformation about internal and mutual consistency of ata sets to the reader. In addition, we have added a few ɜts of correlated data of superior quality to our collec- :on. These sets are labeled as SC.

At the end of each subsection, we list in chronological rder the complete bibliography for the material cited in ıe particular subsection. By the way we have organized ıe data, it is possible for a single paper to be referred to ı more than one subsection. In those cases, we have pro- ided cross-references.

On the diskettes which are available from AIP[a], the data are listed in ASCII format. For each data set, a seven- or eight-letter file name is used, composed of the first letter of the property name, and the first four letters of the first author's family name, followed by the last two digits of the year of publication and, if necessary, a letter such as A, B, etc. for ordering within that year. All states except the one-phase state are indicated by an additional two-letter extension, separated from the file name by a period. A data file begins with a few lines of information, giving the file name, author names, journal reference, the types and units of the property data and independent variables, and the number of data points to follow. After this the data set follows, in general consisting of three columns (one dependent and two independent variables). In the case of saturation data, two columns may suffice. The explanation of the file name organization and an example of file content are shown in Tables 1.2.1 and 1.2.2. Instructions for locating sets of related files by property, author, etc. are given in the "README" file on the first disk.

TABLE 1.2.1. Explanation of the file name organization

DKELL75A.AT	
	data in the single phase
.AT	data at atmospheric pressure
.SC	data for supercooled water
.SH	data for superheated water
.SL	data for saturated liquid
.SV	data for saturated vapor
A	
B	for ordering the same file name
C	
75	the last two digits of the year of publication
KELL	first four letters of the first author's family name
B	virial coefficients (2nd and 3rd) data
C	specific heat at constant pressure data
D	density data
E	specific heat at constant volume data
H	enthalpy data
J	Joule-Thomson coefficient data
P	vapor pressure data
U	internal energy data
W	speed of sound data

[a]See AIP Document No. PAPS JPCRD-20-1023-disk for files of these data in machine-readable form. The data are available from AIP on disk as ASCII files, formatted by MS-DOS for IBM-compatible computers; the files total 800 kB. When ordering, please indicate whether 3½ inch or 5¼ inch disks are preferred.

Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, NY 10017. The price is $10.00 in either format. Airmail additional. Make checks payable to American Institute of Physics.

TABLE 1.2.2. An example of the file contents in the case of DKELL75.AT

DKELL75.AT
Kell,G. S.
J. Chem. Eng. Data, 20 (1) 97 (1975).

	T90(K)	P(MPa)	d(kg/m3)
25			
	273.150	.101325	999.84260
	278.147	.101325	999.96690
	283.144	.101325	999.70311
	288.141	.101325	999.10362
	293.138	.101325	998.20874
	298.136	.101325	997.05027
	303.134	.101325	995.65331
	308.132	.101325	994.03845
	313.130	.101325	992.22289
	318.128	.101325	990.22074
	323.137	.101325	988.03930
	328.125	.101325	985.70316
	333.134	.101325	983.20192
	338.124	.101325	980.56279
	343.132	.101325	977.77266
	348.124	.101325	974.85613
	353.123	.101325	971.80450
	358.123	.101325	968.62628
	363.123	.101325	965.32527
	373.124	.101325	958.36664
	383.126	.101325	950.94723
	393.127	.101325	943.07942
	403.130	.101325	934.76863
	413.132	.101325	926.01485
	423.134	.101325	916.81308

1.3. Units

The property units are compatible with the SI. They are summarized in Table 1.3.

TABLE 1.3. Properties and units

Property	Symbol	Unit
Temperature	T	K (ITS–90)
Pressure	p	MPa
Density	d	$kg\ m^{-3}$
Specific Volume	v	$m^3\ kg^{-1}$
Sound Velocity	w	$m\ s^{-1}$
Specific Enthalpy	h	$kJ\ kg^{-1}$
Specific Internal Energy	u	$kJ\ kg^{-1}$
Specific Heat Capacity at Constant Pressure	c_p	$kJ\ kg^{-1}\ K^{-1}$
Specific Heat Capacity at Constant Volume	c_v	$kJ\ kg^{-1}\ K^{-1}$
Joule-Thomson Coefficient	μ	$K\ MPa^{-1}$

1.4. The International Temperature Scale

All data in this report have been converted to and are reported on the International Temperature Scale of 1990 (ITS–90)[3]. This scale has been very recently adopted. is much closer to the thermodynamic scale than IPTS–68.[1] Since the temperature scale has only one fi point, the triple-point temperature of water, a chang scale will result in changes in values assigned to all ot fixed points of water. Thus the boiling point of wa which was equal to 373.15 on IPTS–68, is assigned a va of 373.124 on the new scale. For most properties, temperature values have simply been shifted by known difference[3] between the ITS–90 and the scale which the temperature data had been reported. In case of heat capacity and Joule-Thomson coefficient, procedure developed by Douglas[2] was employed for c recting not only the temperature scale itself, but also temperature differential.

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2. Thermodynamic Properties of Steam in the Ideal-Gas State

Ideal-gas properties of steam are calculated from sp troscopic data. The authorative calculation of Friedm and Haar[1] in 1954 gives references to earlier work a covers the range of 50–5000 K. It was followed by that Woolley[2] in 1980, who calculated ideal-gas Gibbs free e ergy, enthalpy, entropy and specific heat for the range to 4000 K both for pure isotopic water and for the is topic mixture as occurring in standard mean ocean wat (SMOW). This correlation was the basis for the ideal-g input to the NBS/NRC Steam Tables adopted by IAPS 1985. Since 1979, improvements have been made in t formulation by Cooper[3] and by Woolley[4]. Cooper i proved the mathematical behavior at high-temperatu The improvements made by Woolley mainly address t effects of anharmonicities that are noticeable only at ve high temperatures. In his latest paper,[4] for instanc Woolley, calculating the effects of refinements in t treatment of centrifugal influences on vibrations and r tations, finds differences in the ideal-gas heat capacity less than 0.1% for temperatures up to 1000 K; the diffe ences grow to almost 1% at 2000 K. The ideal-gas dat being calculated data, are not available in computeriz form in the present work.

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3. Sublimation and Melting Curves

If solid phases are included, the phase diagram of water is quite complex (Fig.1). Recently, Saul and Wagner[12] have developed formulations for all known melting and sublimation curves. Their formulation has been adopted by IAPWS as a release.[13] The paper, including the text of the IAPWS release, will be published.[14] In Fig. 1, we indicate the locations of all triple points according to their evaluation. Their correlations and reevaluation of the triple points were based on the experimental data of Refs. 1–3, 5–11, corrected according to the advice of Babb[4]. In the ice-VII region, Mishima and Endo[10] correlated their own measurements in 1978. None of the data referred to here are available in computerized form in the present work.

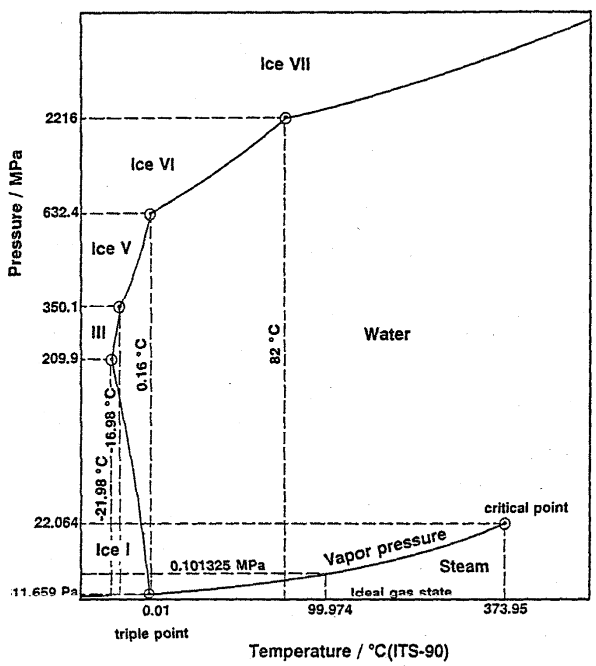

FIG. 1. Phase boundaries for ice, water, and steam.

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4. Thermodynamic Properties of the Saturation States

4.1. The Triple Point

According to the measurements of Guildner *et al.*[2] in 1976, the triple point of water, by definition at 273.16 K on both IPTS–68 and on ITS–90, is at (611.657±0.010) Pa. The earlier determination by Douslin[1] resulted in a pressure value about 0.4 Pa greater than that of Guildner *et al*.

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4.2. The Critical Point

Critical-point parameters have been directly observed[6-9] or derived from property measurements close to the critical point.[1-5, 10, 11, 13] The IAPS statement of 1983 gives the following values:[12]

critical density	(322 ± 3)	kg m^{-3}
critical temperature	$(647.14 + \delta)$	K (IPTS–68)
critical pressure	$(22.064 + 0.27\delta \pm .005)$MPa	
	with $\delta = (0.00 \pm 0.10)$	

The critical temperature equals 647.10 K on ITS–90.

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4.3. Vapor Pressure

Although the vapor pressure of water has been measured since the days of Fahrenheit (1793), our data collection begins with the comprehensive and definitive original data set of Osborne *et al.*[1] in 1933, which supersedes all previous work. The other Osborne references[2,3] contain smoothed data. In recent years, a number of experimenters have added detail, especially in the region below room temperature[7] and in the critical region.[10,11,14] Saul and Wagner[13] have recently formulated the saturation properties of water, including the vapor pressure. Their formulation has been adopted by IAPWS as a supplementary release.[12] The sources of experimental data that we have collected are listed in Table 4.3. The data of Douslin *et al.*,[5] though very precise, have been assigned to category B because of lack of consistency with Guildner's triple point determination (Sec. 4.1). A total of 281 vapor pressure data, from Refs. 1, 2, 4, 6, 7, 10, 11, 14, are available in computer-accessible form.

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4.4. Density, Enthalpy and Sound Velocity of the Saturation States

In addition to the vapor pressure (Sec. 4.3) the fol ing properties have been measured in saturated phase

TABLE 4.3. Vapor pressures

Authors	Year	File name	Ref.	Temperature K	No. of data	Uncertainty in pressure	Categ
Osborne/Stimson/Fiock/Ginnings	1933	POSBO33	1	383 – 647	38	0.03 %	S
Osborne/Stimson/Ginnings	1937	POSBO37	2	373 – 647	64	–	SC
Osborne/Stimson/Ginnings	1939	POSBO39	3	273 – 647	84	–	SC
Rivkin/Troyanovskaya/Akhundov	1964	PRIVK64	4	646 – 647	18	0.3 kPa	A
Stimson	1969	PSTIM69	6	298 – 373	7	0.002 %	S
Douslin	1971	PDOUS71	7	271 – 293	14	0.3 – 0.8 Pa	B
Hanafusa/Tsuchida/Kawai/Sato/Uematsu/ Watanabe	1984	PHANA84	10	643 – 647	8	3 kPa	A
Kell/McLaurin/Whalley	1985	PKELL85	11	423 – 623	22	0.1 – 0.5 kPa (<600 K)	A
						1 – 2 kPa (>600 K)	A
Morita/Sato/Uematsu/Watanabe	1989	PMORI89	14	638 – 647	26	3 kPa	A
Total					281		

ter and steam: specific volumes or densities,[3,4,9,10] enilpies,[1,4,5] heat capacity,[8] and sound velocity.[2,7,11] The mprehensive and highly accurate enthalpy measure-ents of Osborne, Stimson and Fiock[1] in 1930 supersede previous work and form the beginning of our data col-tion. Fiock[2] reviewed caloric measurements prior to 30. The caloric properties measured by Osborne *et al.*[1] the enthalpies required to extract isothermally a unit ass of vapor or liquid at coexistence, and the constant-lume heat capacity of the two-phase sample. From ese, and from the vapor pressures obtained by the same thors (Sec. 4.3, Ref. 1), the enthalpies, entropies, vol-nes and heat capacities of coexisting phases were rived;[4,5] they are summarized in Table 2 of Ref. 6.

The paper of Saul and Wagner and the supplementary PWS release referred to in Sec. 4.3, Refs. 12 and 13 so contain correlating equations for the orthobaric den-ies, enthalpy and entropy of saturated vapor and liquid. The paper of Smith and Keyes contains, in addition to e measured saturation volumes that are part of our ta collection, values of constant-volume and constant-essure heat capacities derived from their own and Os-rne's data between 273 and 533 K. Several of the turation properties vary over many orders of magni-de, which makes the assessment of the reliability difficult. Our judgement was based primarily on the degree of continuity of the saturation data with the best data in adjacent one-phase regions.

All experimental data[1,3-5,7-11] listed in Table 4.4 are available in computer-accessible form.

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TABLE 4.4. Saturation properties

uthors	Year	File name	Ref.	Temperature K	No. of data	Properties	Uncertainty	Category
borne/Stimson/Fiock	1930	HOSBO30.SL	1	273 – 543	28	h'	–	A
		HOSBO30.SV	1	273 – 543	28	h''	–	A
iith/Keyes	1934	DSMIT34.SL	3	303 – 633	13	ρ'	–	A
borne/Stimson/Ginnings[a]	1937	HOSBO37.SL	4	373 – 647	64	h'	–	SC
		HOSBO37.SV	4	373 – 647	64	h''	–	SC
borne/Stimson/Ginnings	1939	HOSBO39A.SL	5	273 – 368	20	h'	–	A
borne/Stimson/Ginnings	1939	DOSBO39B.SL	6	273 – 647	84		–	SC
		DOSBO39B.SV	6	273 – 647	84		–	SC
		HOSBO39B.SL	6	273 – 647	84		–	SC
		HOSBO39B.SV	6	273 – 647	84		–	SC
:Dade/Pardue/Hedrich/Vrataric	1959	WMCDA59.SL	7	366 – 561	36	w'	1 %	A
ota	1963	CSIRO63.SL	8	273 – 645	44	C_p'	–	A
		CISRO63.SV	8	273 – 645	44	C_p''	–	A
ll[c]	1975	DKELL75.SL	9	273 – 423	33	ρ'	10 ppm	SC
ll/McLaurin/Whalley	1985	DKELL85.SL	10	423 – 623	22	ρ'	0.08 kg/m^3	SC
		DKELL85.SV	10	423 – 623	22	ρ''	0.08 kg/m^3	SC
iavez/Sosa/Tsumura	1985	WCHAV85.SL	11	273 – 535	108	w'	0.05 %	A
Total					862			

sborne *et al.* measured several latent heat and the vapor pressure, then derived v', v'', h', h'', s', s'', and C_p'.
ell derived v' from evaluated density and sound velocity data at atmospheric pressure with an accuracy of better than 10 ppm.

saturated water.
saturated steam.

5. Thermodynamic Properties of Liquid Water at Ambient Pressure

5.1. Density at Ambient Pressure

Accurate absolute determinations of the density and expansion coefficient of liquid water at ambient pressure were carried out in the early half of the century.[1-3] Owen *et al.*,[4] and Steckel and Szapiro,[5] did very careful measurements of the ratio ρ/ρ_{max}. For reviews, see Refs. 14, 28. In 1967, Menaché[6] drew attention to the fact that the absolute density of water was not known to better than 10 g m^{-3}, principally because of the effect of variations in the isotopic composition of the samples used. In 1969, the International Association for the Physical Sciences of the Ocean (IAPSO) adopted a recommendation for a new study of the density of water. The International Union for Geodesy and Geophysics (IUGG) passed the text recommending such a study to the Comité International des Poids et des Mesures (CIPM). Also, Commission I.4 on Physicochemical Measurements and Standards of the International Union of Pure and Applied Chemistry (IUPAC) has been concerned with the same subject since 1965, as stated in Ref. 28. As a consequence, many new studies have been carried out or are in progress at present.[6,10-12,17-27,30,32,33] Careful attention has been given to isotopic composition,[5,6,8,10,15,16,25,33] and to the effects of dissolved gases[16,19,20] and of temperature.[1,2,8,10,14,32,33] The principal sources of highly accurate new density data are the National Research Laboratory of Metrology in Japan, and the Council for Scientific and Industrial Research in Australia. Masui and coworkers[30,32,33] in Japan have made precise measurements of the density of standard mean ocean water in the past decade. By measuring the thermal expansion between 0 and 85 °C, Takenaka and Masui subsequently derived values for the density of water at ambient pressure for this entire temperature range.[32] These most recent values supersede the earlier data,[25] and form part of our collection. Watanabe[33] has measured the thermal dilatation of water at ambient pressı between 0 °C and 44 °C. He reported a correlation density developed from their careful measurements a derived the maximum density temperature as 3.9834 °C terms of the ITS–90. Watanabe only reported a corre tion, so our collection does not include it.

The density of water at ambient pressure is often ‹ tained from correlations valid in larger pressure rang Many such correlations are available.[7-9, 13, 14, 16, 29, 31] K‹ derived the density and other properties of water at a bient pressure from a correlation of highly precise P data of Kell and Whalley for liquid water up to 1 kl (Sec. 6.3). Later, Kell[14] reviewed density, thermal exp‹ sivity, and compressibility of liquid water at ambient pr sure and at temperatures from 273 to 425 K. Since consider this correlation very accurate, we have made part of our collection. The equation of state of Sato[31] : liquid water from 240 to 423 K and at pressures up to 1 MPa reproduces the thermodynamic property values ambient pressure mostly within experimental error.

The sources of data on the density of water at atn spheric pressure that we have collected in computer-‹ cessible form are listed in Table 5.1.

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TABLE 5.1. Density of water at ambient pressure

Authors	Year	File name	Ref.	Temperature K	No. of data	Uncertainty	Catego
Owen/White/Smith	1956	DOWEN56.AT	4	313 – 358	10	0.2 ppm	B
Steckel/Szapiro	1963	DSTEC63.AT	5	275 – 351	40	–	B
Gildseth/Habenschuss/Spedding	1972	DGILD72.AT	10	293 – 352	45	3 ppm	A
Kell[a]	1975	DKELL75.AT	14	273 – 423	25	–	SC
Watanabe/Iizuka	1982	DWATA82.AT	20	273 – 317	45	1.8 ppm	A
Takenaka/Masui	1990	DTAKE90.AT	32	274 – 359	79	1 ppm	S
Total					244		

[a] Kell reported density values based on his critical review as described in Sec. 5.1

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5.2 Sound Velocity at Ambient Pressure

After early work by Randall[1] in the 1930's, there has ɜen a surge in precise sound velocity determination in ater at ambient pressure in the past three decades.[2–18] A rge number of reliable data are available; the sources of ɹr computerized collection are listed in Table 5.2. Some marks about the precision and reliability of several of ese sources are in order. Greenspan and Tschiegg[2] easured sound velocity in water between 272 and 373 K th a claimed accuracy of 0.05 $m\,s^{-1}$ in 1957. Wilson[3] easured the sound velocity between 274 and 364 K with claimed accuracy of 0.15 $m\,s^{-1}$ in 1959. In Table 1 of eir 1976 paper, Kroebel and Mahrt[13] showed on the ba- of Fig. 5 of Carnvale's paper[8] that the data of eenspan and Tschiegg were about 0.3 $m\,s^{-1}$ and those Wilson about 0.6 $m\,s^{-1}$ above other data obtained later.[4–13] We have therefore not included the data of Refs. 2 and 3 in our collection.

Wilson[3], and Barlow and Yazgan[7] extended their measurements to pressures of 97 and 80 MPa, respectively. We refer to Sec. 6.4 for these data.

Several authors extended their measurements into the supercooled water regime. Rouch *et al.*[15] and Petitet *et al.*[17] reported data, while Trinh and Apfel[16] reported graphs of their data at ambient pressure. For further discussion, we refer to Sec. 7.1. Trinh and Apfel as well as Evstefeev *et al.*, also reported sound velocity data in superheated water at ambient pressure. We refer to Sec. 7.2 for these results. We confirmed that the recent measurements by Fujii and Masui[18] agree with the data of Del Grosso and Mader within the respective experimental uncertainties of ±0.015 m/s. The data sources on sound velocity at ambient pressure that are available in computer-accessible form are listed in Table 5.2.

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5.3. Heat Capacities at Ambient Pressure

Most data for the heat capacity of liquid water at ambient pressure were obtained long ago, between 1879 and 1935.[1–11] Fiock[9] reviewed the calorimetric measurements reported before 1930, including the work of Barnes[3,4] and of Jaeger and von Steinwehr[6]. The calorimetric data of Osborne and coworkers[8,12] at NBS for saturated water and steam, topic of Sec. 4.4, form to this very day essential input to formulations of the properties of steam. Osborne *et al.*[12] compared their data with those of Rowland[1] and with Day's revision of Rowland's data;[2] with

TABLE 5.2. Sound velocity in water at ambient pressure

Authors	Year	File name	Ref.	Temperature K	No. of data	Uncertainty m/s	Categ
Randall	1932	WRAND32.AT	1	273 – 359	10	–	B
Neubauer/Dragonette	1964	WNEUB64.AT	4	290 – 296	45	0.23	B
McSkimin	1965	WMCSK65.AT	5	297 – 352	37	0.1	B
Barlow/Yazgan	1966	WBARL66.AT	6	297 – 353	43	0.038 – 0.024	A
Barlow/Yazgan	1967	WBARL67.AT	7	290 – 366	8	0.2 – 0.3	A
Carnvale/Bowen/Basileo/Sprenke	1968	WCARN68.AT	8	308	9	0.18	A
Del Grosso	1969	WDELG69.AT	9	273 – 363	19	0.02	B
Williamson	1969	WWILL69.AT	10	296 – 348	19	0.20	A
Del Grosso	1970	WDELG70.AT	11	273 – 347	36	–	A
Del Grosso/Mader	1972	WDELG72.AT	12	273 – 368	148	0.015	S
Kroebel/Mahrt	1976	WKROE76.AT	13	276 – 307	20	0.04	A
Gupta/Jain/Nanda	1976	WGUPT76.AT	14	277 – 353	15	–	B
Fujii/Masui	1990	WFUJI90.AT	18	293 – 348	41	0.015	S
Total					450		

Barnes's[3] original data of 1902 and with Barnes's[4] revised data; with Callendar's 1912 data[5]; and with their own earlier data.[8] Laby and Hercus[11] discussed the effect of dissolved air on the heat capacity.

There are many studies of the heat capacity of supercooled water. Rasmussen *et al.* measured specific heat capacities c_p and c_v in 1973. Trinh and Apfel derived heat capacity values from their sound velocity measurements in 1978. Oguni and Angell published graphs of their measurements of c_p. Angell *et al.* reported c_p measurements for supercooled water. For data and references on heat capacities of supercooled water, we refer to Sec. 7.1.

McCullough *et al.*[14] is the only source for c_p data for water *vapor* at ambient pressure and below. His temperature range was from 361 to 487 K , and his accuracy $\pm 0.1\%$. His work, which includes evaluation of second and third equation-of-state virials, is discussed in Sec. 6.1.

Our collection consists of only two data sets, the d of Osborne *et al.*[12] for c_p, and the data of Steckel a Cagnasso[15] for c_v. The commonly accepted value of c_p 288.15 K and ambient pressure, which defines the calo unit, is that given by de Haas[13], namely 4.1855 J/(kg] The data, reported as NBS 1939 in Table 11 of Ref. (1 are available in computer-accessible form.

Correlations for c_p at ambient pressure are available Refs. 16 and 17.

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TABLE 5.3. Heat capacities of water at ambient pressure

Authors	Year	File name	Ref.	Temperature K	No. of data	Property	Uncertainty	Category
Osborne/Stimson/Ginnings	1939	COSBO39.AT	12	273 – 373	21	C_p	–	A
Steckel/Cagnasso	1966	ESTEC66.AT	15	311 , 363	2	C_v	–	B
Total					23			

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6. Thermodynamic Properties of the Single-Phase State

6.1. Virial Coefficients

The direct measurement of the nonideality of water 'apor by static methods is very difficult for temperatures ›elow 425 K, because sorption effects tend to dominate ›ver nonideality effects at these relatively low pressures. ʗell *et al.*[5,7,11,13,15] who did the most careful *pVT* measure-nents in the vapor phase, do not believe their data for the econd virial coefficient can be trusted below 425 K.)ymond and Smith[10] compiled the data of Refs. 2, 5–8. Ɉew data by Eubank and coworkers,[12] by means of the Ǝurnett method of *pVT* measurement in the range from 48 to 498 K, show evidence of considerable sorption ef-ects, for which the authors have made careful correc-ions. We have included their set III in our data ollection. Other experimental sources of virial data are measurements of sound velocity or calorimetry,[1] from which information on gas imperfection can be deduced. Wormald[4] derived virial coefficients from his measurements of the isothermal throttling coefficient. Le Fevre *et al.*[8] did the most recent data assessment and correlation of the second virial coefficient of steam; their formulation agrees well with the second virial coefficients that follow from the NBS/NRC Steam Tables discussed before (Sec. 1.1). Eubank *et al.*[12,14] reviewed all previous work. The data of Eubank *et al.* agree with the correlation of Le Fevre *et al.* to within 2%. The references to virial coefficient data available on disk are summarized in Table 6.2.

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TABLE 6.1. Virial coefficients of steam

Authors	Year	File name	Ref.	Temperature K	No. of data	Virials[a]	Category
:eyes/Smith/Gerry	1936	BKEYE36	2	323 – 723	9	*B*	A
:ell/McLaurin/Whalley	1965	BKELL65	5	523 – 723	6	*B*,*C*	A
'ukalovich/Trakhtengerts/Spiridonov	1967	BVUKA67	6	353 – 1173	18	*B*,*C*	A
:ell/McLaurin/Whalley	1968	BKELL68	7	423 – 723	28	*B*,*C*	A
eFevre/Nightingale/Rose	1975	BLEFE75	8	293 – 1248	25	*B*	A
ubank/Joffrion/Patel/Warowny	1988	BEUBA88	12	373 – 498	8	*B*,*C*	A
ell/McLaurin/Whalley	1989	BKELL89	13	423 – 773	31	*B*,*C*	S
Total					125		

ʒ: second viral coefficient; *C*: third viral coefficient

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6.2. Density

There is a century of effort of measurement of the equation of state of water and steam. This is an activity that shows no signs of abating: more than half the data sources date to the past twenty years. In the case of the equation of state, a detailed review of each individual data source seems unnecessary: three recent formulations of the properties of water and steam listed in Sec. 1.1 (Refs. 7,9,11) perform extensive comparisons with all or parts of the data sets. Be it sufficient to state the following generalities. The work of Amagat[1] and of Bridgman[2–4,6] was essential in opening up the high-pressure region for study. Further push towards high pressures came from Franck and his coworkers,[29,31,49] Vedam and Holton,[30] Grindley and Lind,[35] and Burnham *et al.*[32] Walsh and Rice,[8,9] and Mitchell and Nellis,[50] enter shock-wave regime. Keyes *et al.,*[5,7] and Kenned coworkers[10–13] set the stage for systematic investiga the U.S.A., while Kirillin,[14,15] Vukalovich and coworkers,[16,17,19] Alexandrov and coworkers,[39,41,4 Zubarev *et al.*[45,46,48] fulfilled that role in the U.S Tanishita and coworkers in Japan,[23,33,43] and Jůza *et* in Czechoslovakia. It is generally agreed, howeve the extensive and highly accurate *pVT* data of Ke coworkers[27,38,40,47,53,56,57] in Canada provide the key t new formulations of the properties of compressed and of water vapor above 425 K (see Chen *et al.*[4 discussion of consistency of ambient-pressure sou locity and compressibility data). The earlier wo Rivkin *et al.*[20,22,24,25,28] in the U.S.S.R., and the recen of Hanafusa *et al.*[52] and of Morita *et al.*[55] in Japan a the near- and supercritical regime. This brief sun does not do full justice to the references listed belo refer to the detailed comparisons in the publicati Haar *et al.*, Wagner and Saul, Hill, and Sato *et al.* in Sec. 1.1 (Refs. 7,8,9,11) for those who need to fu preciate and appraise the enormous effort that has invested in measuring the equation of state of wat steam. Recent measurements for the density of stea Eubank *et al.*[54] and by Kell,[56,57] do not agree perfectl each other. As discussed in Sec. 6.1, sorption effe low-density water vapor are substantial and may re further study.

Data that have been historically important but a available on disk are summarized in Table 6.2.1. Th erences to the data available on disk are summari Table 6.2.2.

TABLE 6.2.1. Density data for water and steam, of historical significance

Authors	Year	Ref.	Temperature K	Pressure MPa	No. of data	Uncertainty in volume, %
Amagat	1893	1	273 – 423	0.1 – 300	611	–
Bridgman	1912	2	253 – 298	0.1 – 981	142	–
Bridgman	1913	3	253 – 353	0.1 – 1226	415	–
Bridgman	1931	4	273 – 368	0.1 – 1079	31	–
Bridgman	1935	6	253 – 373	0.1 – 1177	124	–
Kennedy/Knight/Holser	1958	11	273 – 373	0.1 – 140	165	–
Holser/Kennedy	1958	12	393 – 673	10 – 140	270	–
Holser/Kennedy	1959	13	693 – 1274	15 – 140	510	–
Kirillin/Ulybin	1959	14,15	571 – 923	8.1 – 95	488	0.2
Vukalovich/Zubarev/Alexandrov	1959	16	423 – 573	2.5 – 123	77	0.1
Tanishita/Watanabe	1963	23	873 – 1173	8.5 – 88	79	0.2
Tanishita/Watanabe/Kijima/ Uematsu	1968	33	643 – 693	9.4 – 72	132	0.2
Total					3044	

TABLE 6.2.2. Density of water and steam

Authors	Year	File name	Ref.	Temperature K	Pressure MPa	No. of data	Uncertainty in volume, %	Category
ıith/Keyes	1934	DSMIT34	5	303 – 647	0.4 – 35	434	0.01	A
ːyes/Smith/Gerry	1936	DKEYE36	7	468 – 733	1.3 – 36	289	–	A
alsh/Rice	1957	DWALS57	8,9	293	3.1 GPa – 42 GPa	16	–	B
ːnnedy	1957	DKENN57	10	473 – 1274	1 – 10	736	–	B
ıkalovich/Zubarev/Alexandrov	1961	DVUKA61	17	673 – 923	4.8 – 121	175	0.2	A
za/Kmoníček/Šifner	1961	DJUZA61	18	348 – 623	26.6 – 350	64	0.2	B
ıkalovich/Zubarev/Alexandrov	1962	DVUKA62	19	972 – 1174	4.6 – 118	148	0.2	A
vkin/Akhundov	1962	DRIVK62	20	633 – 693	4.9 – 37	249	0.05	S
vkin/Akhundov	1963	DRIVK63	22	647 – 773	4.7 – 60	190	0.05	S
vkin/Troyanovskaya/Akhundov	1964	DRIVK64A	24	646 – 662	21.8 – 27	121	0.04	S
vkin/Troyanovskaya	1964	DRIVK64B	25	633 – 660	9.0 – 33	316	0.04	S
gawara/Sato/Minamiyama	1964	DSUGA64	26	866 – 1109	3.2 – 14	108	0.2	B
ıier/Franck	1966	DMAIE66	29	473 – 1124	93 – 604	196	1	B
vkin/Akhundov/Kremenevskaya/ Asadullaeva	1966	DRIVK66	28	645 – 648	14.6 – 24	103	0.04	S
dam/Holton	1968	DVEDA68	30	303 – 353	0.1 – 981	121	0.2	B
ster/Franck	1969	DKOES69	31	298 – 873	50 – 1006	288	1	B
rzunov/Razumikhin/Stekol'nikov	1970	DBORZ70	34	293 – 338	0.1 – 905	66	0.05	B
indley/Lind	1971	DGRIN71	35	298 – 423	20 – 800	560	0.01	A
rnjost	1974	DGARN74	36	374 – 573	9.2 – 74	68	0.006	A
igoryev/Murdaev/Rastorguyev	1974	DGRIG74	37	293 – 633	1.6 – 83	123	0.018	A
ll/Whalley	1975	DKELL75	40	273 – 423	0.1 – 103	252	0.003	S
ːxandrov/Khasanshin/Larkin	1976	DALEX76A	41	264 – 278	5 – 101	60	0.005	A
ːxandrov/Khasanshin/Larkin	1976	DALEX76B	42	423 – 653	3.5 – 101	96	–	A
ıishita/Watanabe/Kijima/Ishii/ Oguchi/Uematsu	1976	DTANI76	43	323 – 773	1.7 – 195	158	0.03	A
ɔarev/Prusakov/Barkovskii	1977	DZUBA77A	45	673 – 873	30 – 200	58	0.1	A
ɔarev/Prusakov/Barkovskii	1977	DZUBA77B	46	923 – 1123	30 – 200	54	0.1	A
·nham/Holloway/Davis	1977	DBURN77	32	293 – 1173	100 – 810	1321	–	B
ːn/Fine/Millero	1977	DCHEN77	44	273 – 373	0.1 – 100	231	–	SC
l/McLaurin/Whalley	1978	DKELL78	47	423 – 623	0.5 – 103	196	0.01	S
ɔert/Tödheide/Franck	1981	DHILB81	49	293 – 873	10 – 400	134	0.2	A
chell/Nellis	1982	DMITC82	50	293 – 298	34 GPa – 83 GPa	7	–	B
enga/Ahrens/Nellis/Mitchell	1982	DLYZE82	51	3278 – 5270	49 GPa – 80 GPa	5	–	B
ıafusa/Tsuchida/Araki/Sato/ Jematsu/Watanabe	1984	DHANA84	52	643 – 653	20 – 40	114	0.04	S
l/McLaurin/Whalley	1985	DKELL85	53	648 – 773	4.2 – 103	426	0.043	S
ıank/Joffrion/Patel/Warowny	1988	DEUBA88	54	373 – 498	0.0 – 1.9	73	–	A
ːita/Sato/Uematsu/Watanabe	1989	DMORI89	55	641 – 652	20 – 38	93	–	S
l/McLaurin/Whalley	1989	DKELL89	56	423 – 773	0.1 – 36	630	–	S
otal						8279		

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6.3. Enthalpy

All enthalpy data sources were reviewed by Watanal The older work, around 1900, was principally concerı with the determination of the mechanical equivalent heat. Our collection begins with data obtained in 1930's. Direct enthalpy measurements have been mo limited to the vapor phase and to superheated steam. exception is the work of Havlicek and Miskovsky,[1] w covered the range of water, steam and supercritical ter. The bulk of the fairly restricted number of entha measurements in steam was performed in the U.S.S and in the U.K. The earliest systematic and extensive vestigations of the enthalpy of superheated steam, up 873 K, were those of Callendar and Egerton[3] in the U This work began in the 1930s and was extended and c rected up to 1960, in which year a comprehensive revi appeared.[3] Vukalovich and coworkers,[2,4,5] and Sheind and Gorbunova[7] covered a large part of the supercriti regime in the 1950s and early 1960s. Angus and Newi extended those measurements to higher pressures, w superb accuracy. Very recently, Castro-Gomez *et al* measured the enthalpy increment of water at tempe tures from 356 to 408 K and at pressures from 0.17 to 1 MPa; they claim an uncertainty of ±0.5%. The late heat measurements of Osborne and coworkers in sa rated water and steam, described in Sec. 4.4, have yielded the enthalpy of evaporation, and therefore also the enthalpy of saturated water, once that of steam is known. The many new sources of excellent isobaric heat capacity data, to be discussed in the next section, also contribute to our knowledge of the enthalpy of water and steam. Presently, enthalpy values of water and steam are usually derived from a thermodynamic free energy formulation based on the latent heat data and on *pVT* data. It is still a matter of debate whether direct measurements can give more reliable enthalpy values than those derived from an accurate formulation.

The sources available on disk are summarized in Table 6.3.

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TABLE 6.3. Enthalpy of water and steam

Authors	Year	File name	Ref.	Temperature K	Pressure MPa	No. of data	Uncertainty in enthalpy	Category
Havlíček/Miškovský	1936	HHAVL36	1	293 – 823	0.1 – 39.2	101	0.25 %	B
Vukalovich/Zubarev/Prusakov	1958	HVUKA58	2	720 – 823	20 – 40	48	6 kJ/kg	B
Callendar/Egerton	1960	HCALL60	3	473 – 873	0.5 – 22	120	2.1 kJ/kg	B
Vukalovich/Zubarev/Prusakov	1962	HVUKA62	4	673 – 883	20 – 54	55	6 kJ/kg	B
Vukalovich/Zubarev/Prusakov	1963	HVUKA63	5	673 – 983	2.5 – 49	48	–	B
Sheindlin/Gorbunova	1964	HSHEI64	7	618 – 734	19 – 49	72	–	B
Angus/Newitt	1966	HANGU66	8	673 – 974	6 – 100	16	0.1 %	A
Total						460		

6.4 Sound Velocity

Until the early 1970s, sound velocity measurements were carried out solely in pressurized water below the boiling point[2–4,6,7] and in superheated steam[1,5,8,9] up to 400 °C. Of these older, often quite excellent data in the liquid, those of Wilson[4] claimed the highest accuracy, of 0.01%. The data of Holton *et al.*,[7] and those of Smith and Lawson,[2] of a somewhat larger tolerance of 0.2%, agree with the data of Wilson to within that tolerance. Fine and Millero,[10] however, have pointed out that the Wilson data are not fully consistent with their own highly precise data in water, nor with the accurate data at ambient pressure. Chen *et al.* (Ref. 44 in Sec. 6.2) showed that all of the Wilson data need to be shifted, due to an error in the reference value at ambient pressure. As a consequence, the Wilson data are believed to be accurate to ±0.1%, while the corrected data are accurate to ±0.05%.

Since the early 1970s, several groups in the U.S.S.R., associated with Alexandrov,[12–14] Mamedov,[15] and Erokhin,[16,17] and one in France, with Le Neindre,[18,20] have actively expanded the range of pressures and temperatures, so that quality data are now available in high-temperature and supercritical water. In the process, the number of data points available has tripled.

The data from the French group connect smoothly with the Alexandrov data both at high and low temperatures. They also are consistent with data obtained in supercooled water by Kanno and Angell, and by Ter Minassian *et al.*, that are discussed in Sec. 7. The data of Alexandrov *et al.*, those of Mamedov, and those of Erokin *et al.*, have been demonstrated to be consistent with the *pVT* data (see Refs. 6,7,9,11 in Sec. 1.1), and with critical-point scaling.[19,21]

Because of their high accuracy, sound velocity data provide a sensitive check on the behavior of derivatives during the development of thermodynamic formulations for water and steam. The data available on disk are listed in Table 6.4.

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TABLE 6.4. Sound velocity in water and steam

Authors	Year	File Name	Ref.	Temperature K	Pressure MPa	No. of data	Uncertainty %	Cat
Woodburn	1949	WWOOD49	1	422 – 644	0.2 – 0.7	10	–	]
Smith/Lawson	1954	WSMIT54	2	261 – 402	0.1 – 923	110	–	[illegible]
Litovitz/Carnevale	1955	WLITO55	3	273 , 303	0.1 – 196	10	–	]
Wilson	1959	WWILS59	4	274 – 364	0.1 – 97	88	0.01	[illegible]
Woodburn	1964	WWOOD64	5	593 – 673	1.5 – 7	9	0.15	I
Barlow/Yazgan	1967	WBARL67	6	290 – 366	0.1 – 80	72	–	[illegible]
Holton/Hagelberg/Kao/Johnson	1968	WHOLT68	7	323	0.1 – 983	34	0.2	[illegible]
Novikov/Avdonin	1968	WNOVI68	8	423 – 603	0.2 – 10	99	–	[illegible]
Woodburn/Fostyk	1968	WWOOD68	9	563 – 662	3.6 – 23	9	–	E
Dibelius/Reiman/Scholtholt	1974	WDIBE74	11	490 – 1033	1.4 – 24	34	0.2	B
Alexandrov/Larkin	1976	WALEX76	12	270 – 647	0.1 – 71	195	–	A
Alexandrov/Kochetov	1979	WALEX79A	13	266 – 423	6 – 99	59	–	A
Alexandrov/Kochetov	1979	WALEX79B	14	473 – 673	50 – 99	36	–	A
Mamedov	1979	WMAME79	15	273 – 623	0 – 70	83	0.2	A
Erokin/Kalyanov	1979	WEROK79	16	452 – 650	1 – 50	239	–	A
Erokin/Kalyanov	1980	WEROK80	17	648 – 773	1 – 52	219	–	A
Petitet/Danielou/Tufeu/Le Neindre	1986	WPETI86	20	479 – 967	50 – 300	73	0.5	A
Total						1379		

6.5. Isobaric Heat Capacity

Virtually all data on the isobaric heat capacity of water and steam originate from the laboratory of Sirota in the U.S.S.R.,[2-12,15] where an active program of flow calorimetry existed from the mid-1950s to 1970, and a range of state variables up to 960 K and 100 MPa was covered with exemplary accuracy in vapor, liquid and supercritical conditions. Sirota derived the heat capacity of saturated water and steam from his data.[9] Also, the locus of c_p maxima along isotherms was determined by Sirota *et al.*[13] This group also developed an equation of state for water and steam based on the c_p data and calculated c_p from it in the range of 273–423 K and 5–100 MPa.[14] Czarnota[16] measured c_p at very high pressures in 1984. It is not yet possible to confirm the reliability of these data. Recently, Philippi developed a wide-range flow calorimeter in Germany and measured a large number of c_p data for water and steam.[17,18]

Accurate heat capacity data serve as a powerful tool for checking derivative behavior of thermodynamic formulations. The data of Sirota *et al.* in near- and supercritical steam have been demonstrated to be consistent with the critical-point scaling laws (see Ref. 19, 21 in Sec. 6.4).

The sources of the data that are available on disk are summarized in Table 6.5.

References

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[2]A. M. Sirota and D. T. Timrot, Teploenergetika 3(7), 16 (1956).

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TABLE 6.5. Isobaric heat capacity of water and steam

Authors	Year	File name	Ref.	Temperature K	Pressure MPa	No. of data	Uncertainty[a] %	Category
Sirota/Timrot	1956	CSIRO56	2	487 – 654	2 – 12	62	0.2 – 0.3/1.5	A
Sirota	1958	CSIRO58	3	587 – 827	2 – 15	28	0.3/–	A
Sirota/Mal'tsev	1959	CSIRO59	4	285 – 774	2.5 – 49	230	0.2/0.15 – 0.9	A
Sirota/Mal'tsev	1960	CSIRO60	5	736 – 872	29 – 49	26	0.2 – 0.3/0.6	A
Sirota/Mal'tsev	1962	CSIRO62A	6	579 – 775	12 – 27	252	0.4/0.6	A
Sirota/Mal'tsev	1962	CSIRO62B	7	635 – 869	6 – 22	44	1/–	A
Sirota/Mal'tsev/Grishkov	1963	CSIRO63	8	613 – 875	59 – 78	58	0.2 – 0.3/0.5	A
Sirota/Grishkov	1966	CSIRO66A	10	453 – 962	39 – 98	60	–/–	A
Sirota/Beljakova/Shrago	1966	CSIRO66B	11	579 – 872	12 – 69	138	0.2 – 0.3/–	A
Sirota/Grishkov	1968	CSIRO68	12	277 – 306	29 – 98	18	0.05 – 0.1/0.3	A
Sirota/Grishkov/Tomishko	1970	CSIRO70	15	273 – 306	20 – 98	52	0.05 – 0.1/0.3	A
Czarnota	1984	CCZAR84	16	299 , 300	224 – 1003	9	0.5 – 1.4	B
Philippi	1987	CPHIL87	17	298 – 673	20 – 50	100	–/–	A
Total						1077		

[a]Random error/systematic error

6.6. Isochoric Heat Capacity

Isochoric heat capacity measurements in steam are very difficult. Contrary to the short residence times of flow calorimetry, the sample resides in the calorimeter for long periods, which makes contamination a serious problem. Also, because of the high temperatures and pressures involved, the heat capacity of the container far exceeds that of its contents. One has to expect lower accuracy in c_v than in c_p. Direct measurements of c_v are most informative in the near-and supercritical regime, where a weak divergence develops in c_v. They also can be used to locate the phase boundary, where a jump occurs in the value of c_v.

In the period 1962–1975, Amirkhanov, Kerimov and coworkers[1–4] in the U.S.S.R. have produced a large number of isochoric heat capacity data over a temperature range from ambient up to over 1000 K. They performed many detailed measurements in the critical region. These authors have published a book on their data.[3]

Baehr and Schomäcker in Germany measured c_v in the near- and supercritical regime in the mid-1970s.[5]

Lyzenga *et al.*[6] derived some information on c_v at extreme pressures and temperatures from their shock-wave data.

The c_v data of Baehr and Schomäcker have been sh to be consistent with accurate formulations of the t modynamic properties of steam based on *pVT* data (R 9, 11 in Sec. 1.1) and with the scaling laws (Refs. 19 in Sec. 6.4). The U.S.S.R. data show a more checke picture: they do not always agree with the ph boundary data derived from *pVT* and latent heat infor tion, and they do not seem to be fully consistent intern (Ref. 19, Sec. 6.4).

The references to the data sources available on are given in Table 6.6.

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TABLE 6.6. Isochoric heat capacity of water and steam

Authors	Year	File Name	Ref.	Temperature K	Density kg/dm^3	No. of data	Uncertainty	Cate
Amirkhanov/Kerimov	1962	EAMIR62	1	573 – 633	46 – 144	4	–	E
Kerimov	1968	EKERI68	2	574 – 723	46 – 93	44	–	E
Amirkhanov/Stepanov/Alibekov	1969	EAMIR69	3	287 – 1075	45 – 999	1030	–	E
Kerimov/Alieva	1975	EKERI75	4	523 – 873	20 – 50	314	–	E
Baehr/Schomäcker	1975	EBAEH75	5	552 – 693	213 – 366	491	–	A
Total						1883		

6.7. Internal Energy

Only a single source of internal energy data exists, that of Baehr and coworkers[1] in Germany (Table 6.7). These data cover a substantial range around the critical point.

References

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TABLE 6.7. Internal energy of water and steam

Authors	Year	File Name	Ref.	Temperature K	Density kg/dm^3	No. of data	Uncertainty %	Cate
Baehr/Schomäcker/Schultz	1974	UBAEH74	1	552 – 693	213 – 396	367	1.5 – 2.5	A
Total						367		

6.8 Joule-Thomson and Related Coefficients

There are a number of thermodynamic derivatives that, like the isobaric heat capacity and sound velocity, can be measured with relative ease and high accuracy, and therefore provide checks on the accuracy of formulations of thermodynamic properties of water and steam. These derivatives are the Joule-Thomson coefficient, $\mu = (\partial T/\partial P)_h$, the isothermal throttling coefficient, $\delta_T = (\partial h/\partial P)_T$; and the isentropic temperature-pressure coefficient, $\beta_S = (\partial T/\partial P)_S$, which equals $VT\alpha_p/c_p$, with α_P the thermal expansion coefficient.

Since the beginning of this century, values of μ, δ_T and β_S have been measured in water and steam by seven groups in Czechoslovakia, Germany, U.K. and U.S.S.R.

By comparing with the accurate formulation of Hill (Ref. 11, Sec. 1.1), we find that the data of Peake[1] depart by 1.4 to 10%; the point of Trueblood[2] by only −0.1%; those of Reamer *et al.*[3] by −4 to 20%; those of Jûza *et al.*[4] by −6 to 3%; those of Franz and Grigull[5] by −44 to 9%; those of Ertle[6] by −11 to 10%; those of Rögener and Soll[8] mostly by ± 0.4%; those of Stasenko *et al.*[9] by −8.6 to 7.1%.

The δ_T data of Wormald were used by him to compute virial coefficients of steam (Ref. 4 in Sec. 6.1).

These data sources are summarized in Table 6.8, and they are available on disk.

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TABLE 6.8. Joule–Thomson and related coefficients of water and steam

Authors	Year	File name	Ref.	Temperature K	Pressure MPa	No. of data	Property	Uncertainty	Category
Peake	1905	JPEAK05	1	449 – 459	0.8 – 1.1	10	$\mu = (\partial T/\partial P)_h$	–	B
Trueblood	1917	JTRUE17	2	438	0.38	1	μ	–	B
Reamer/Richter/DeWitt/Sage	1957	JREAM57	3	589 – 700	0.7 – 21	32	μ	–	B
Jûza/Kmoniček/Schovanec	1963	JJUZA63	4	403 – 463	0.12 – 0.19	16	μ	1 %	B
Franz/Grigull	1972	JFRAN72	5	293 – 359	0.1 – 50	22	μ	–	B
				379 – 655	0.1 – 22	47	μ	–	B
				638 – 651	22 – 40	13	μ	–	B
Ertlea	1979	JERTL79A	6	296 – 347	0.16 – 35	38	μ	6.5 %	B
		JERTL79B	6	432 – 1074	0.1 – 5	234	μ	1.4 – 1.7 %	B
Rögener/Soll	1980	JROEG80	8	276 – 353	3 – 84	89	$\beta_s = (\partial T/\partial P)_s$	0.4 – 0.8 %	A
Stasenko/Philippov/Blagonravov	1984	JSTAS84	9	295 – 495	10, 20	8	β_s	–	B
Total						510			

7. Thermodynamic Properties of Metastable Water

Beginning in the early 1970s, there has been a revival of interest in the properties of supercooled and superheated water. A strong scientific impetus was generated by Angell and coworkers in the U. S. A, who first suggested the presence of a nonanalyticity in the thermodynamic properties of supercooled water at approximately 5 K below the freezing point, as evidenced by rapidly increasing compressibility, heat capacity, dielectric constant and viscosity. In the same time period, Skripov and coworkers in the USSR measured properties of superheated water, that is, metastable water heated above its boiling temperature.

7. 1 Density, Sound Velocity and Heat Capacities of Supercooled Water

A large number of anomalous thermodynamic properties of supercooled water, such as density, heat capacities, compressibility and sound velocity, have been measured by the pioneers of this work, Angell, Speedy and coworkers,[3,4,11,13,14,17,20,22] and also by Trinh and Apfel. [8,9,12] All of this work was done at ambient pressure, except for the compressibility measurements of Kanno and Angell,[11] which extended to 190 MPa. Angell *et al.* [4] complemented the thermodynamic measurements with measurements of the chemical shift in proton magnetic resonance. Rasmussen and MacKenzie[5] analyzed the heat capacity and density data of supercooled water and concluded that ice-like clusters incorporating six or more monomers are present in this medium. Speedy and Angell[6] concluded that at a temperature of about 228 K a lambda transition might occur, associated with the formation of an open hydrogen-bonded network. On the other hand, the homogeneous nucleation temperature is estimated to be of the same order, so that the transition temperature might correspond to the limit of stability of the supercooled liquid phase. Rouch *et al.* [7] also suggested the existence of a singularity at about 228 K, on the basis of their sound velocity measurements. D'Arrigo,[10] by an analysis of the available experimental data, concluded that asympt power law behavior will be restricted to the range tween 247 and 263 K.

Sound velocity data were reported also by Co *et al.* [18] and Petitet *et al.*[19] The heat-of-compression n surements of Ter Minassian *et al.* [16] and the sound ve ity data of Petitet *et al.* [19] extend to high pressures.

Many of the reports mentioned contain only graph representations or correlations, which we have included in computerized form. The sources of data av able on disk are summarized in Table 7. 1. We h categorized all data as category B because the reliabi of data obtained in metastable states is generally known.

Several of these authors[9,16] developed correlating eq tions that permitted calculation of other thermodynai properties beside those measured. In particular, 7 Minassian *et al.* [16] developed an equation for the coe cient of thermal expansion, from which they derived t pressure dependence of the isobaric heat capacity.

TABLE 7.1. Thermodynamic properties of supercooled water

Authors	Year	File name	Ref.	Temperature K	Pressure MPa	No. of data	Property	Uncertainty	Categ
Schufle	1965	DSCHU65.SC	1	250 – 277	0.1	25	d	–	B
Zheleznyi	1969	DZHEL69.SC	2	239 – 277	0.1	36	d	–	B
Rasmussen/MacKenzie/Angell/Tucker	1973	CRASM73.SC	3	235 – 273	0.1	31	C_p	–	B
		ERASM73.SC		235 – 277	0.1	9	C_v	–	B
Rouch/Lai/Chen	1977	WROUC77.SC	7	264 – 313	0.1	7	w	–	B
Trinh/Apfel	1978	WTRIN78.SC	9	238 – 268	0.1	7	w	–	B
Angell/Oguni/Sichina	1982	CANGE82.SC	17	236 – 290	0.1	17	C_p	–	B
Petitet/Tufeu/Le Neindre	1983	WPETI83A.SC	19	253 – 296	0.1	12	w	–	B
		WPETI83B.SC	19	253 – 296	0.1 – 462	105	w	–	B
Hare/Sorensen	1986	DHARE86.SC	21	239 – 313	0.1	13	d	0.01%	B
Hare/Sorensen	1987	DHARE87.SC	21	240 – 268	0.1	49	d	0.01%	B
Total						311			

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[21]D. E. Hare and C. M. Sorensen, J. Chem. Phys. **84**, 5085 (1986); 8 4840 (1987).
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Recent developments include highly accurate density measurement in glass capillaries down to −34 °C, by Hare and Sorensen[21]. Speedy[22], at various times, reviewed the available data and developed correlation procedures that properly incorporate the anomaly at the stability limit. In his most recent review, he also gave a careful treatment of capillary effects.

The formulations of the properties of water and steam are usually restricted to the stable range. It is becoming clear that incorporation of knowledge about supercooled water will have important benefits, by improving the accuracy of derivatives in liquid water near its freezing line. These derivatives play an important role in the formulation of the limiting-law behavior of electrolyte solutions.

7.2. Density, Sound Velocity, and Heat Capacities of Superheated Water

Skripov and coworkers measured the density and sound velocity for superheated water.[1–4,5,7,8,10] They were able to superheat water at atmospheric pressure to 493 K, which is 120 K above the boiling point.[2] They also measured at pressures up to 4 MPa.[2] In 1977, they extended this work to even higher pressures and temperatures.[3] Evstefeev and Skripov[7] measured sound velocity by a pulse method in 1979 up to 573 K and 10 MPa. Trinh and Apfel obtained sound velocity data by a Schlieren optics nethod.[6]

Amirkhanov and Abdulagatov,[9] on the basis of their c_v data, developed a formulation from which they were able to obtain a number of thermodynamic functions in superheated water from 615 to 646 K.

For the same reason as in Sec. 7.1, we have judged all data to be of category B. All data sources available on disk are listed in Table 7.2.

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TABLE 7.2. Thermodynamic properties of superheated water

Authors	Year	File name	Ref.	Temperature K	Pressure MPa	No. of data	Property	Uncertainty	Category
hukanov/Skripov	1971	DCHUK71.SH	2	413 – 504	0.1 – 4	123	*d*	–	B
vstefeev/Chukanov/Skripov	1977	DEVST77.SH	4	508 – 571	0.1 – 9	56	*d*	–	B
vstefeev	1978	WEVST78.SH	5	423 – 573	0.1 – 10	106	*w*	–	B
inh/Apfel	1978	WTRIN78.SH	6	383 – 443	0.1	7	*w*	–	B
stefeev/Skripov/Chukanov	1979	WEVST79.SH	7	423 – 573	0.1 – 10	53	*w*	–	B
Total						345			

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