New International Skeleton Tables for the Thermodynamic Properties of Ordinary Water Substance[a)]

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The current knowledge of thermodynamic properties of ordinary water substance is summarized in a condensed form of a set of skeleton steam tables, where the most probable values with the reliabilities on specific volume and enthalpy are provided in the range of temperatures from 273 to 1073 K and pressures from 101.325 kPa to 1 GPa and at the saturation state from the triple point to the critical point. These tables have been accepted as the IAPS Skeleton Tables 1985 for the Thermodynamic Properties of Ordinary Water Substance (IST-85) by the International Association for the Properties of Steam (IAPS). The former International Skeleton Steam Tables, October 1963 (IST-63), have been withdrawn by IAPS. About 17 000 experimental thermodynamic data were assessed and classified previously by Working Group 1 of IAPS. About 10 000 experimental data were collected and evaluated in detail and especially about 7000 specific-volume data among them were critically analyzed with respect to their errors using the statistical method originally developed at Keio University by the first three authors. As a result, specific-volume and enthalpy values with associated reliabilities were determined at 1455 grid points of 24 isotherms and 61 isobars in the single-fluid phase state and at 54 temperatures along the saturation curve. The background, analytical procedure, and reliability of IST-85 as well as the assessment of the existing experimental data and equations of state are also discussed in this paper.

Key words: density; enthalpy; error analysis; IAPS; IST-85; saturated steam; saturated water; specific volume; steam; thermodynamic property; vapor pressure; water.

Contents

[a)] This is the background report for the IAPS Skeleton Tables 1985 for the Thermodynamic Properties of Ordinary Water Substance issued by the International Association for the Properties of Steam.

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1. Introduction

Water[b] is the most abundant compound on the surface of the earth[1]; thus the knowledge of its thermodynamic properties is essential to understanding the mechanisms of nature. For practical applications, water has been used widely in industries as heating medium, working fluid of power generation, solvent, medium of hydrothermal reactions, and so on. The experimental data regarding the thermodynamic properties of water have been accumulated from the nineteenth century up to the present to form a large body of information. Industries have saved large amounts of energy and improved safety by means of the rational design and operation based on those experimental data.

Approximately 12 000 specific-volume data and 5000 other thermodynamic property data including heat capacity, internal energy, enthalpy, Joule–Thomson coefficient, and speed of sound, were reported for thermodynamic properties of water up to the present. Among them, about 6000 specific volume data and about 2000 other thermodynamic property data were reported after the establishment of the former International Skeleton Steam Tables(IST-63).

Although a large amount of experimental data has been accumulated, the use of them requires much effort even to collect and convert into common units. In addition, the fact that different investigators have often provided different values due to experimental errors for a property at the same state point, may lead users to be confused.

The objective of establishing skeleton tables is to extract the best value from those current experimental data and to provide it. A set of skeleton tables is the current information consisting of the most probable values and the reliabilities (tolerances) extracted from the experimental data by analyzing their errors on the basis of common criteria.

Straub, Scheffler, Rosner, Watanabe, Uematsu, and Sato have emphasized the importance of obtaining international agreement on the thermodynamic data[2]; they proposed skeleton tables for the specific volume of water in 1980.[3,4] Those efforts motivated the International Association for the Properties of Steam(IAPS) to issue the IAPS Skeleton Tables 1985(IST-85).

The IST-85 consists of three different tables. The first table gives the most probable specific-volume values with their associated tolerances in the range of temperatures from 273.15 to 1073.15 K and pressures up to 1 GPa, the second table gives the most probable enthalpy values with their associated tolerances in the same range as that of the specific-volume table, and the last one gives the thermodynamic properties along the saturation curve.

The original specific-volume and enthalpy tables for the single-fluid phase water were provided by the first three present authors, Sato, Uematsu, and Watanabe.[4–11] The specific-volume table was constructed on the basis of the experimental data by using the method of error analysis developed by Sato, Uematsu, and Watanabe,[4–7] whereas the enthalpy table was constructed from existing equations of state for water as described in Sec. 5.1.b. The table for the saturated water and saturated steam was calculated by the equations established by the last two present authors, Saul and Wagner,[12–14] whose equations have received international agreement to be released as Supplementary Release on Saturation Properties of Ordinary Water Substance.[15]

The present paper aims to provide the detailed background, procedure and assessment of IST-85, as well as the values of IST-85 and comparisons of the values of IST-85 with most of experimental data on specific volume and enthalpy of water, and with IST-63, existing equations of state including currently internationally agreed upon equations, the 1967 IFC Formulation for Industrial Use(IFC-67) and the IAPS Formulation 1984 for Scientific and General Use(IAPS-84).

2. Historical Background

In 1929, the First International Steam Table Conference was held in London in order to establish the International Skeleton Steam Tables for the purpose of providing the unified thermodynamic property values of water. Before 1929, there had already been much valuable research work on the thermodynamic properties of water and different steam tables had been used in different countries as shown in Table 1. But those steam tables do not agree at all grid points to within combined tolerances. The first conference had to start discussing the conversion factors of units regarding temperature, pressure, specific volume, and heat. The unit of heat, 1 kcal = 1/860 kW h, which was called "international steam table kilocalorie," was decided at this conference. This conference also decided that the final recommendations of the conference regarding thermodynamic properties of water should be given in the form of skeleton tables, and a set of basic skeleton tables was prepared. This set of skeleton steam tables consisted of a saturated steam table in the temperature range up to 623 K and a superheated steam table in the range of temperatures up to 823 K and pressures up to 25 MPa. But the set of skeleton steam tables was not completed at this conference.[16]

In 1930, the Second International Steam Table Confer-

[b] The single word "water" throughout this paper referred to ordinary water substance, light water, or H_2O, including both the liquid state and the gaseous state.

Table 1. List of Steam Tables

Year	Country	Prepared by	Title	T/K	P/MPa	Base
1763	UK	J. Watt				
1847	France	H.V. Regnault				
1859	UK	W.J.M. Rankine	Manual of the Steam Engine			
1860	Germany	G. Zeuner	Grundzüge der mechanischen Wärmetheorie mit besonderer Rücksicht auf das Verhalten des Wasserdampfes			
1900	UK	H.L. Callendar				Callendar-eq.
1904	Germany	R. Mollier	Neue Diagramme zur Technischen Wärmelehre			Callendar-eq.
1905	Germany	G. Zeuner	Technische Thermodynamik, 3			
1906	Germany	R. Mollier	Neue Diagramme zur Technischen Wärmelehre	773	2	Callendar-eq.
1923	Germany	O. Knoblauch E. Raisch H. Hausen	Tabellen und Diagramme für Wasserdampf berechnet aus der spezifischen Wärme	723	6	
1925	USA	G. E.				
1925	Germany	R. Mollier	The Mollier Steam Tables and Diagrams	823	15	Mollier-eq.
1930	USA	J.H. Keenan (ASME)	Steam Tables and Mollier Diagram			Davis-eq.
1932	Germany	R. Mollier	Neue Tabellen und Diagramme für Wasserdampf			Mollier-eq.
1932	Germany	A. Knoblauch E. Raisch H. Hausen W. Koch	Tabellen und Diagramme für Wasserdampf	823	25	Hausen-eq. (IST-30)
1934	Japan	(JSME)	Steam Tables and Diagrams of the JSME	823	25	Sugawara-eq. (IST-30)
1936	USA	J.H. Keenan F.G. Keyes	Thermodynamic Properties of Steam including Data for the Liquid and Solid Phases	1147	39	Keyes-Smith-Gerry-eq. (IST-34)
1937	Germany	W. Koch (VDI)	VDI-Wasserdampftafeln mit einem Mollier-Diagramm auf einer besonderen Tafel	823	30	Koch-eq. (IST-34)
1939	UK	G.S. Callendar A.C. Egerton	The 1939 Callendar Steam Tables	811	23	(IST-34)
1940	USSR	M.P. Vukalovich				Vukalovich-eq. (IST-34)
1943	USA	J.H. Keenan F.G. Keyes	Thermodynamic Properties of Steam	1147	39	(IST-34)
1944	UK	G.S. Callendar A.C. Egerton	The 1939 Callendar Steam Tables	811	23	(IST-34)
1946	USSR	M.P. Vukalovich		823	30	Vukalovich-eq. (IST-34)
1949	UK	G.S. Callendar A.C. Egerton	The 1939 Callendar Steam Tables	811	23	(IST-34)
1950	Japan	S. Niwa (JSME)	Revised Steam Tables and Diagrams of the JSME	873	30	Tanishita-eq. (IST-34)
1951	USSR	M.P. Vukalovich	Thermodynamic Properties of water and Steam	973	30	Vukalovich-eq. (IST-34)
1952	USSR	(Ministry of Electric Stations)	Tables of Thermodynamic Properties of Water and Steam based on experimental data	873	30	(IST-34)
1952	Germany	W. Koch (VDI)	VDI-Wasserdampftafeln	811	30	Koch-eq. (IST 34)
1953	Sweden	O.H. Faxén	Thermodynamic Tables in the Metric System for Water and Steam	923	25	Jůza-eq. (IST-34)

Table 1. List of Steam Tables-continued

Year	Country	Prepared by	Title	T/K	P/MPa	Base
1955	Swiss	L.S. Dzung W. Rohrbach	Enthalpy-Entropy-Diagram for Steam and Water	1073	50	Vukalovich-eq. (IST-34)
1955	Japan	S. Sugawara (JSME)	Revised Steam Tables and Diagrams of the JSME	973	34	Tanishita-eq. (IST-34)
1955	USSR	(Moscow Institute of Energetics)		973	30	(IST-34)
1956	USSR	(Institute of Thermodynamics)		1073	40	(IST-34)
1956	Germany	W. Koch E. Schmidt	VDI-Wasserdampftafeln mit einem Mollier-Diagramm bis 800 °C	1073	30	Koch-eq. (IST-34)
1958	USSR	M.P. Vukalovich	Thermodynamic Properties of Water and Steam	1273	100	Vukalovich-eq. (IST-34)
1958	USSR	(Institute of Thermodynamics)	Tables for Thermodynamic Properties of Water and Steam			(IST-63)
1963	Germany	E. Schmidt	VDI-Wasserdampftafeln mit einem Mollier-Diagramm bis 800 °C und einem T,s-Diagramm	973	50	Koch-eq. (IST-34, IST-63)
1964	UK	R.W. Bain (NEL)	Steam Tables 1964, Physical Properties of Water and Steam	1073	100	(IST-63)
1963	USSR	M.P. Vukalovich	Tables of Thermodynamic Properties of Water and Water Vapor			
1965	USSR	M.P. Vukalovich	Tables of Thermodynamic Properties of Water and Water Vapor			
1967	UK	(ERA)	1967 Steam Tables	1073	100	(IST-63)
1967	USA	C.A. Meyer R.B. McClintock G.J. Silvestri R.C. Spencer, Jr., (ASME)	ASME Steam Tables, Thermodynamic and Transport Properties of Steam	1073	100	(IFC-67, IST-63)
1968	Japan	I. Tanishita (JSME)	1968 JSME Steam Tables	1073	100	(IFC-67, IST-63)
1968	USA	J.H. Keenan F.G. Keyes P.G. Hill J.G. Moore	Steam Tables, Thermodynamic Properties of Water including Vapor, Liquid, and Solid Phases	1573	100	Keenan-Keyes-Hill-Moore-eq.
1969	Germany	E. Schmidt (ASME, JSME, and VDI)	Properties of Water and Steam in SI Units	1073	100	(IFC-67, IST-63)
1969	USSR	M.P. Vukalovich S.L. Rivkin A.A. Alexandrov	Tables for Physical Properties of Water and Steam			
1970	UK	W.W. Campbell (Ministry of Technology)	UK Steam Tables in SI Units 1970	1073	100	(IFC-67, IST-63)
1975	USA	C.A. Meyer R.B. McClintock G.J. Silvestri R.C. Spencer, Jr., (ASME)	ASME Steam Tables, Thermodynamic and Transport Properties of Steam	1073	100	(IFC-67, IST-63)
1975	USSR	S.L. Rivkin A.A. Alexandrov	Thermophysical Properties of Water and Steam			
1979	Germany	E. Schmidt U. Grigull (ASME, JSME, and VDI)	Properties of Water and Steam in SI-Units	1073	100	(IFC-67, IST-63)
1980	Japan	I. Tanishita (JSME)	1980 SI JSME Steam Tables	1073	100	(IFC-67, IST-63)
1984	USA	L. Haar J.S. Gallahger G.S. Kell	NBS/NRC Steam Tables, Thermodynamic and Transport Properties and Computer Programs for Vapor and Liquid States of Water in SI Units	2273	3000	(IAPS-84)

ence was held in Berlin and the discussion for the establishment of International Skeleton Tables was continued under the chairmanship of Nobel prize winner W. Nernst. The revised set of skeleton tables was worked out at this conference. But additional experimental data available had made it possible to enlarge the effective range of the proposed skeleton tables.[17]

The first International Skeleton Steam Tables, 1934(IST-34) were finally adopted at the Third International Steam Table Conference held at three locations in the United States: Washington, D.C. on Monday, September 17th; Cambridge, Massachusetts on Tuesday, September 18th; and New York, N.Y. on Wednesday, September 19th, 1934. The IST-34 contains specific volumes and total heats, the latter name being used instead of enthalpy at that time. The specific-volume table provided 159 values covering temperatures up to 823 K and pressures up to 40 MPa, while the total-heat table provided 143 values covering up to 823 K and 30 MPa; the specific volumes and total heats for saturated water and saturated steam were provided at 10 K intervals between 273 and 643 K and at 1 K intervals between 643 and 647 K. Based on IST-34, many steam tables were published in different countries; Keenan and Keyes prepared the Steam Tables in 1936, in the United States; the VDI-Steam Tables were published based on the equation of state developed by Koch in 1937, in the Federal Republic of Germany; Callendar and Egerton prepared the Steam Tables in 1939, in the United Kingdom; the JSME-Steam Tables were derived from the equation of state developed by Tanishita in 1950, in Japan; and the Russian Steam Tables were derived from the equation of state developed by Vukalovich in 1940, in the Soviet Union.

The name of the International Steam Table Conference was changed into "International Conference on the Properties of Steam(ICPS)" at the fourth ICPS held in Philadelphia, 1954. At the fourth ICPS, the scope of conference was enlarged to other properties of water including viscosity and thermal conductivity.

The fifth ICPS held in London, 1956, considered tentative newer skeleton tables but could not agree to accept them because experimental work had not come to satisfactory completion at that time. An International Coordinating Committee was then established to prepare newer skeleton steam tables for both equilibrium and transport properties. The committee consisted of four countries, the Federal Republic of Germany, the United Kingdom, the United States, and the Soviet Union; it met four times between the fifth and sixth ICPS, including informal committee meeting held in London, 1957. At the fifth ICPS, the unit of energy was decided as $1\ J = 1\ Ws = 10^7$ erg, the unit of enthalpy as the J/kg. Furthermore, the reference state for steam tables was chosen to be liquid water at the triple point; at this point, the values of the internal energy and entropy were defined to be zero exactly.

The former International Skeleton Tables(IST-63), were adopted at the sixth ICPS held in New York, 1963, which provided specific-volume and enthalpy values at 580 points covering temperatures from 273 to 1073 K and pressures up to 100 MPa. The delegates and observers at the sixth ICPS consisted of 63 participants including the experts from Canada, ČSSR, France, FRG, Japan, Norway, Switzerland, the UK, the USA, and the USSR. The skeleton tables of viscosity and thermal conductivity were also authorized in 1964 under the name of "Supplementary Release on Transport Properties," November 1964(IST-64). At the sixth ICPS most members recognized it to be important that all countries use the same property values in design and performance calculations of power plants. Therefore, the International Formulation Committee of the Sixth International Conference on the Properties of Steam(IFC) was set up in 1963 in order to develop a unified international formulation for use with computers. The IFC consisted of six national formulation teams including ČSSR, FRG, Japan, the UK, the USA, and the USSR.

The 1967 IFC Formulation for Industrial Use(IFC-67),[18] which was formulated by combining separate equations in six subregions,[19–22] was established by IFC. The IFC-67 is being used effectively in most of the engineering calculations at present. The 1968 IFC Formulation for Scientific and General Use(IFC-68)[23] was also prepared by IFC. With the exception of the USSR, which base its steam tables on IFC-68, steam tables based on IFC-67 are used in many countries.[24] The computer software of IFC-67 is also currently available everywhere.

In 1968, the seventh ICPS held in Tokyo appointed a standing organization for the international cooperation on the properties of steam, the International Organization for the Properties of Steam(IOPS), by seven countries including ČSSR, France, FRG, Japan, the UK, the USA, and the USSR, which was renamed as the International Association for the Properties of Steam(IAPS) at the meeting of IOPS executive committee in Moscow, 1970. This executive committee in Moscow also agreed to set up three Working Groups, namely, Working Group 1 on the equilibrium properties, Working Group 2 on the transport properties, and Working Group 3 on the other properties of water and steam. Working Group 4 on the chemical thermodynamics in power cycles was established at the meeting of the IAPS executive committee in Ottawa, 1975. The meetings of the IAPS executive committee and working groups have been continuously held every year from the first executive committee meeting under the IOPS in Moscow, 1970, up to the present.

The revision of IST-63 was discussed at the eighth ICPS, held in Gien, France, in 1974, and many releases were issued by IAPS between the eighth and ninth ICPS; the former Dynamic Viscosity of Water Substance, 1975: the former Thermal Conductivity of Water Substance, 1977: The current Surface Tension of Water Substance, 1976: and the current Static Dielectric Constant of Water Substance, 1977.

The ninth ICPS was held in Munich in 1979 and commemorated the golden anniversary of Steam Property Conferences. White, the Executive Secretary of IAPS, reported the history of 50 years on international collaboration for the thermophysical properties of water.[25] The Japan National Committee on the Properties of Steam, the 139th Committee of the Japan Society for the Promotion of Science, compiled all reports and releases issued by ICPS and IAPS over a 50-

year period between 1929 and 1979 in two volumes.[26] At the ninth ICPS, Straub, as the chairman of Working Group 1, introduced the status of experimental study and the activity of IAPS on the equilibrium properties of water in the period between 1974 and 1979.[27] He reported that the number of experimental thermodynamic property data obtained from 1890 up to 1979 was about 12 000 specific-volume data and about 5000 caloric data. And he made it clear that, of these, about 6000 specific-volume data and 2000 caloric data were reported after 1961 and had not been taken into account for the establishment of IST-63. Then he concluded that the main task for Working Group 1 was the preparation of a new representation of the thermodynamic surface of water by developing revised international skeleton tables and a new formulation.

The requirement was satisfied at the tenth ICPS held in Moscow, 1984, with the acceptance of the IAPS Formulation 1984 for the Thermodynamic Properties of Ordinary Water Substance for Scientific and General Use (IAPS-84)[28] and the IAPS Skeleton Tables 1985 for the Thermodynamic Properties of Ordinary Water Substance (IST-85).[29] The IST-85 was proposed at the tenth ICPS and was accepted finally at the meeting of IAPS executive committee held in Gaithersburg (U.S.) 1985. The releases on the Dynamic Viscosity 1975 and Thermal Conductivity 1977 were also revised according to the revision of its density values at the meeting as the IAPS Formulation 1985 for the Viscosity of Ordinary Water Substance and the IAPS Formulation 1985 for the Thermal Conductivity of Ordinary Water Substance, respectively.

In addition, the following current releases were issued by IAPS between the ninth and tenth ICPS: the Ion Product of Water Substance, 1980; the 1983 IAPS Statement, Values of Temperature, Pressure, and Density of Ordinary and Heavy Water Substances at Their Respective Critical Points[30]; the IAPS Formulation 1984 for the Thermodynamic Properties of Heavy Water Substance; the Viscosity and Thermal Conductivity of Heavy Water Substance, 1984.

At present, IAPS are shifting emphasis to the study of the properties of aqueous mixtures and solutions. Accordingly, the four Working Groups of IAPS were reorganized into two Working Groups at the meeting of the IAPS executive committee in Moscow, 1984. Working Group A is responsible for thermophysical properties of ordinary and heavy water substance and aqueous systems not adopted for the study by Working Group B, whereas Working Group B is responsible for chemical thermodynamics of power cycles.

The historical progress on Steam Tables published in various countries and three International Skeleton Tables (IST) for the thermodynamic properties of water is summarized in Tables 1 and 2, separately. Note that while the IST has been revised three times, the International Practical Temperature Scale has been also changed three times from the International Temperature Scale of 1927 (ITS-27) to the International Practical Temperature Scale of 1948 (IPTS-48)[31], and to IPTS-68.[32]

Table 2. Historical progress of International Skeleton Tables

International Skeleton Tables (IST)	Property	Range: Temperature K	Range: Pressure MPa	Grid points	Temp. scale
IST-34	volume(v)	273 – 823	0.1 – 40	159	ITS-27
	enthalpy(h)	273 – 823	0.1 – 30	143	ITS-27
IST-63	v, h	273 – 1073	0.1 – 100	580	IPTS-48
IST-85	v, h	273 – 1073	0.1 – 1000	1455	IPTS-68

3. Experimental Situation

3.1. Single-Fluid Phase State

A detailed data survey on the thermodynamic properties of water was conducted in 1974 by Watanabe and Uematsu.[33] Many experimental data were summarized and discussed in this survey. In addition, most of those data were compared with IFC-67, the so-called MIT Formulation devised by Keenan, Keyes, Hill, and Moore,[34] IFC-68, and the equation of state devised by Jůza in 1966.[35] The work performed by Watanabe led to IAPS discussions on the necessity of revisions of IST-63 and IFC-68 at Working Group meetings in Schliersee, 1975. The discussion was continued at meetings of IAPS in Ottawa, 1975, in Kyoto, 1976, in Moscow, 1977, and in Washington, 1978.

The "International Input," critically evaluated and internationally agreed upon thermodynamic properties data set for the establishment of new standards, was prepared by members of Working Group 1 of IAPS, namely, Alexandrov, Jůza, Levelt Sengers, Straub, Uematsu, and Watanabe for the experimental specific-volume data as well as Alexandrov, Jůza, and Straub for the caloric property data including heat capacity, enthalpy, and internal energy. The results were compiled and reported by Straub and Rosner as an internal IAPS report in 1977.[36,37] The report lists more than 170 papers as primary data base; 91 papers for the specific volume and 38 papers for the caloric properties were selected, with the evaluated results ranked, in order of decreasing reliability, from A to D.

3.1.a. Specific Volume

Concerning the specific volume at high temperatures and high pressures, 44 experimental data sets were collected. They are listed in Table 3, which begins with the data reported by Amagat in 1893[38] and ends with that by Hanafusa *et al.* in 1984.[104] The total number of the experimental data listed in Table 3 is 10 490 including 4476 data points classified with rank A, 1441 points with rank B, 3186 points with rank C and additional 1387 unclassified data points reported more recently.

The distribution of 6597 experimental data points which are affixed with an asterisk to the authors' name in Table 3 and 231 specific-volume data derived by Chen *et al.*[85] from speed-of-sound data, is shown in Figs. 1 and 2 on the pressure–temperature diagram with different symbols for different series of measurements. Figure 1 shows the distribution of 1422 data points reported prior to 1963 when the former international skeleton tables were issued, and Fig. 2 shows the distribution of 5406 data points reported after 1964. Most of specific-volume data in the range correspond-

Table 3. Experimental studies on the specific volume of water

Authors	Year	Ref.	Temperature K	Pressure MPa	No. of data	Error in volume %	Evaluation[a], % Regions 1	2	3
Amagat	1893	38	273 -- 423	0.1 -- 300	611				
Bridgman	1912	39	253 -- 298	0.1 -- 981	142				
Bridgman	1913	40	253 -- 353	0.1 -- 1226	415				
Bridgman	1931	41	273 -- 368	0.1 -- 1079	31				
Bridgman	1935	42	253 -- 373	0.1 -- 1177	124				
*Smith/Keyes	1934	43	303 -- 647	0.4 -- 35	307	0.01	0.012	0.055	
*Keyes/Smith/Gerry	1935	44	468 -- 733	1.3 -- 36	289				
Kennedy	1957	45	473 -- 1274	1 -- 10	741				
Kennedy/Knight/Holser	1958	46	273 -- 373	0.1 -- 140	165				
Holser/Kennedy	1958	47	393 -- 673	10 -- 140	270				
Holser/Kennedy	1959	48	693 -- 1274	15 -- 140	510				
Kirillin/Ulybin	1959	49	571 -- 923	8.1 -- 95	488	0.2			
Vukalovich/Zubarev/ Alexandrov	1959	50	423 -- 573	2.5 -- 123	77	0.1			
*Vukalovich/Zubarev/ Alexandrov	1961	51	673 -- 923	4.8 -- 121	175	0.2		0.066	
*Vukalovich/Zubarev/ Alexandrov	1962	52	973 -- 1173	4.7 -- 121	148	0.2			
*Jůza/Kmoníček/Šifner	1961	53	347 -- 623	26.6 -- 350	64	0.2			0.12
*Rivkin/Akhundov	1962	54	633 -- 693	5.0 -- 38	249	0.05		0.081	
*Rivkin/Akhundov	1963	55	647 -- 773	4.8 -- 60	190	0.05			
*Rivkin/Troyanovskaya/ Akhundov	1964	56	633 -- 660	9.0 -- 34	121	0.04			
*Rivkin/Troyanovskaya	1964	57	645 -- 662	22.2 -- 27	316	0.04			
*Rivkin/Akhundov/ Kremenevskaya/ Asadullaeva	1966	58	645 -- 647	14.6 -- 24	103	0.04			
Tanishita/Watanabe	1963	59	873 -- 1173	8.5 -- 88	79	0.2			
Tanishita/Watanabe/ Kijima/Uematsu	1968	60	643 -- 693	9.4 -- 72	132	0.2			

Table 3. Experimental studies on the specific volume of water-continued

Authors	Year	Ref.	Temperature K	Pressure MPa	No. of data	Error in volume %	Evaluation[a], % Regions 1	2	3
*Tanishita/Watanabe/ Kijima/Ishii/Oguchi/ Uematsu	1976	61	423 -- 773	1.7 -- 195	158	0.03	0.029	0.085	0.069
Sugawara/Sato/Minamiyama	1964	62	869 -- 1108	6.1 -- 14	108	0.2			
*Maier/Franck	1966	63	473 -- 1123	93 -- 600	196	1		0.58	
*Köster/Franck	1969	64	298 -- 873	50 -- 1000	288	1		0.35	
*Vedam/Holton	1968	65	303 -- 353	0.1 -- 1000	120	0.2		0.050	
*Borzunov/Razumikhin/ Stekol'nikov	1970	66	293 -- 338	0.1 -- 923	66	0.05		0.15	
*Grindley/Lind	1971	67	298 -- 423	0.1 -- 300	560	0.01	0.012	0.034	
*Garnjost	1974	68	374 -- 573	9.2 -- 74	68	0.006	0.016		
*Grigoryev/Murdaev/	1974	69	293 -- 633	1.6 -- 83	123	0.018	0.008		
Rastorguyev						0.043	0.037	0.081	
*Kell/McLaurin/Whalley	1974	70	648 -- 773	4.2 -- 103	426			0.030	
*Kell/Whalley	1975	71	273 -- 423	0.1 -- 103	596	0.003	0.004		
*Kell/McLaurin/Whalley	1978	72	423 -- 623	0.5 -- 103	196	0.01	0.025	0.029	
*Alexandrov/Khasanshin/ Larkin	1976	73	264 -- 278	5 -- 102	60	0.005	0.018	0.077	
*Alexandrov/Khasanshin/ Larkin	1976	74	423 -- 653	5 -- 101	96				
*Zubarev/Prusakov/ Barkovskii	1977	75	673 -- 873	30 -- 200	58	0.1 }		0.1	0.079
*Zubarev/Prusakov/ Barkovskii	1977	76	923 -- 1123	30 -- 200	54	0.1 }			
*Burnham/Holloway/ Davis	1977	77	293 -- 1173	100 -- 810	1321			0.25	
*Hilbert/Tödheide/ Franck	1981	78	293 -- 873	10 -- 400	134	0.2	0.050	0.099	0.15
*Hanafusa/Tsuchida/Araki/ Sato/Uematsu/Watanabe	1984	104	43 -- 653	20 -- 40	115	0.04			

* The data used to establish the skeleton tables in the present study.

[a] Evaluated errors for the specific-volume values due to the statistical method proposed by Sato et al. as described in Sec. 5.1.a. The regions are corresponding to those in Fig. 5.

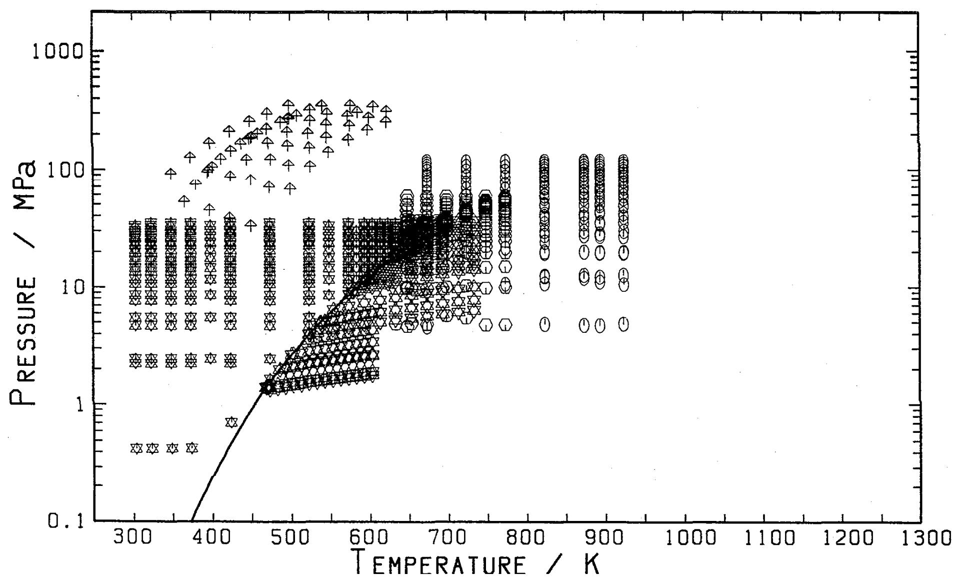

Fig. 1. Experimental data of the specific volume of water published prior to 1963 on the pressure-temperature plane. Specific volume measured by Smith and Keyes (), Keyes et al.(), Vukalovich et al. in 1961 (), in 1962(), Jůza et al.(), Rivkin et al. in 1962() and in 1963() are shown.

ing to the temperatures from 273 to 1173 K and pressures up to 1 GPa have been replaced with newer data reported after 1964 as shown in Fig. 2.

The first accurate measurements for the density of water in a large pressure range were reported by Amagat in 1893.[38] According to the description by Dorsey in 1940,[80] the original specific-volume values reported by Amagat should be multiplied by 1.000 159 in order to get specific-volume values in dm^3/kg.

Similarly, a conversion factor of 0.055 509 6 should be

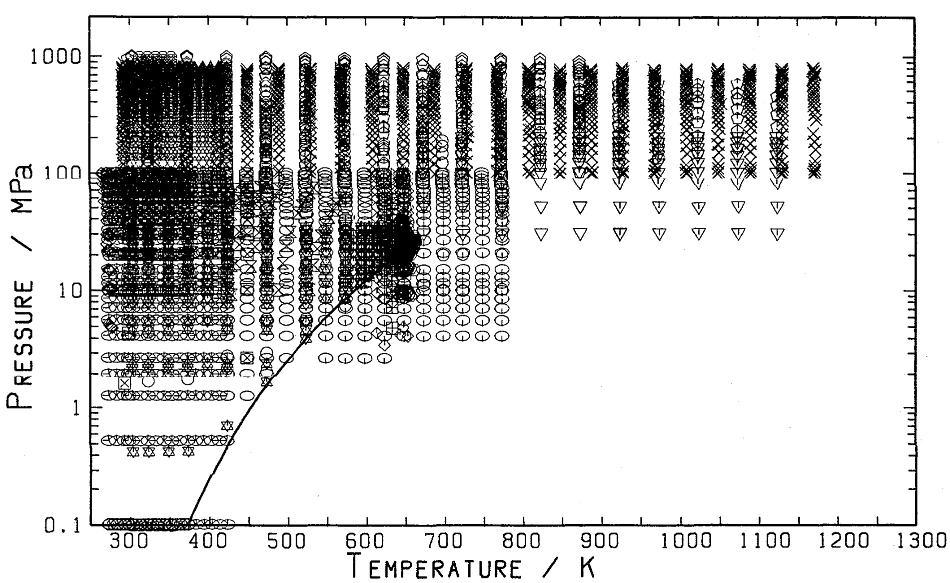

Fig. 2. Experimental data of the specific volume of water published after 1964 on the pressure-temperature plane. Specific volumes measured by Rivkin et al. in 1964(), (), and in 1966(), Tanishita et al. (), Maier and Franck(), Köster and Franck(), Vedam and Holton(), Borzunov et al.(), Grindley and Lind(), Garnjost(), Grigoryev() and (), Kell et al. in 1974(), Kell and Whalley(), Kell et al. in 1978(), Alexandrov et al.(), Alexandrov et al.(), Zubarev et al. in 1977(), (), Burnham et al. (), Chen et al. (), Hilbert et al.(), Hanafusa et al.(), are shown.

multiplied to the original molar-volume values measured by Bridgman in 1912,[39] 1913,[40] 1931,[41] and 1935.[42] Bridgman's 1912 data[39] seemed to be preferable to those of 1935[42] as described by Vedam and Holton.[65] The specific-volume data determined by Vedam and Holton agree with Bridgman's 1912 data to within $\pm 0.1\%$. They pointed out that Bridgman had used the incorrect data in his calibration of pressure at 273 K. The same conclusion was reached by Grindley and Lind,[67] whose specific-volume data agreed with Bridgman's earlier measurements[40] to within $\pm 0.17\%$, after correcting Bridgman's pressure scale; while Bridgman's later data obtained with the sylphon-bellows techniques[42] lie 0.6% above those of Grindley and Lind.

Similar correction must be made to the pressure scale for the measurements of Burnham et *al.* in 1969[81] as pointed out by Grindley and Lind. The corrected Burnham's data were circulated to members of Working Group 1 of IAPS in 1977.[77]

Smith and Keyes reported specific volumes of liquid water in 1934[43] and those of steam and at saturation in 1935.[44] During the course of their experimental work on liquid water, three independent series of measurements were made in three cylindrical vessels made of different materials, a nickel vessel at temperatures from 303 to 573 K, a chrome-vanadium vessel at temperatures from 423 to 633 K, and a number 1B Nirosta 18/8 vessel at temperatures from 303 to 633 K, respectively. These data are still valuable, except for those measured by using the nickel vessel which are lower by about 0.05% in specific volume than those measured by using other vessels.

Kennedy in 1957,[45] Kennedy *et al.* in 1958,[46] and Holser and Kennedy in 1958[47] and 1959[48] added an oxidizing agent (CuO) to water so as to prevent the reaction between water and experimental bomb wall at high temperatures. Their data have systematic errors along the 323, 473, 673, and 773 K isotherms as shown in the figures prepared by Tanishita *et al.*[61]

Kirillin and Ulybin[49] summarized a series of their data reported from 1953 to 1959 in various papers. Their work was followed by that of Vukalovich *et al.*, who reported experimental data in the extended range including liquid water[50] and steam,[51,52] at temperatures up to 1173 K and pressures up to 120 MPa in 1959 to 1962. In addition, Zubarev *et al.* extended the pressure range to 200 MPa in 1977.[75,76]

Alexandrov *et al.* measured specific volumes at two special regions, namely, a region near the critical point and a region including the locus of maximum density. The experimental data were reported at the states adjacent to the critical point along every 10 K interval between 613 and 653 K at pressures up to 101 MPa in 1974.[82] They reported later that those data, because of the incorrect treatment of their measured pressures, required corrections of up to 0.072% in specific volume. The corrected values were presented to members of Working Group 1 in 1976.[74] Another set of experimental data reported by Alexandrov *et al.*[73] is valuable information for revealing the behavior in the region where a density maximum is present on isobars below about 40 MPa. They measured specific volumes along isotherms at 1 K intervals between 264 and 278 K in the pressure range from 5 to 102 MPa.

Jůza *et al.* reported specific volumes at high pressures from 27 to 350 MPa and temperatures from 347 to 623 K with an uncertainty of $\pm 0.2\%$ in 1961[53]; smoothed specific-volume values were given in an appendix to their 1966 publication on their equation of state[35] at temperatures from 373 to 623 K and pressures from 100 to 450 MPa with an uncertainty of $\pm 0.3\%$ in specific volume.

Maier and Franck in 1966,[63] Vedam and Holton in 1968,[65] Köster and Franck in 1969,[64] Borzunov *et al.* in 1970,[66] Grindley and Lind in 1971,[67] and Hilbert *et al.* in 1981[78] reported experimental data at very high pressures with the claimed uncertainty of $\pm 1\%$, $\pm 0.2\%$, $\pm 1\%$, $\pm 0.05\%$, $\pm 0.01\%$, and $\pm 0.02\%$ in specific volume, respectively.

Maier and Franck used a corrosion resistant nickel-base alloy for their constant-volume vessel for measurements at temperatures from 473 to 1123 K and pressures up to 600 MPa. Köster and Franck improved the apparatus of Maier and Franck and measured specific volumes at temperatures from 298 to 873 K and pressures up to 1 GPa.

Vedam and Holton measured speed of sound at temperatures from 303 to 353 K and pressures from 0.1 MPa to 1 GPa in 1968 and developed a computer-aided procedure for obtaining specific-volume values from speed-of-sound data.

Borzunov *et al.* used a glass pycnometer to measure the density of liquid water at temperatures up to 338 K and pressures up to 923 MPa in 1970; although their claimed uncertainty was reported as $\pm 0.05\%$, their specific volumes deviate systematically by about 0.2% from other measurements.

Grindley and Lind measured specific volumes up to 800 MPa between 298 and 423 K by electromagnetic detection of the change in length of a water column.

Hilbert *et al.* used an internally heated pressure vessel including a nickel bellows to measure specific volumes of water and aqueous electrolyte solutions in the range from 293 to 873 K and from 10 to 400 MPa.

Tanishita *et al.* reported specific volumes of steam in 1963,[59] those in the region near the critical point in 1968,[60] and those in the extended range, temperatures from 423 to 773 K and pressures up to 195 MPa, in 1976[61] by using a constant volume vessel made of platinum; its inner volume was 240 cm^3. The data reported in 1976, with an uncertainty of $\pm 0.03\%$ in specific volume, give information at high pressures up to 200 MPa over a wide temperature range up to 773 K where accurate data have scarcely been available.

Sugawara *et al.*[62] measured specific volumes of superheated steam at high temperatures between 869 and 1108 K, and at moderate pressures below 14 MPa with an uncertainty of $\pm 0.2\%$ by using a 70-cm^3 quartz-glass vessel in 1964.

Garnjost[68] reported specific volumes along isochores in the temperature range from 374 to 573 K and the pressure range from 9.2 to 74 MPa in 1974 with uncertainty of $\pm 0.012\%$ in pressure, ± 0.01 K in temperature, and from $\pm 0.006\%$ to $\pm 0.037\%$ in specific volume, respectively.

In the region near the critical point, Rivkin *et al.*,[54–58]

Grigoryev *et al.*,[69] and Hanafusa *et al.*[104] have reported specific volumes. Rivkin *et al.* measured 979 experimental data in the immediate vicinity of the critical point with uncertainty of $\pm 0.04\%$ to $\pm 0.05\%$ in specific volume, which were reported in five different publications from 1962 to 1966. Grigoryev *et al.* reported data in 1974 which were measured by using two different vessels made of Kh18N10T steel, one of 185 cm^3 and the other 804 cm^3 in inner volume. The data at 298, 523, 573, 623, and 633 K were measured in the small vessel with an uncertainty of $\pm 0.043\%$ in specific volume and the data along eight isotherms between 298 and 448 K were measured in the large vessel with an uncertainty of $\pm 0.018\%$. Hanafusa *et al.* reported 115 specific volumes and eight vapor pressures in the temperature range from 643 to 653 K, the pressure range from 20 to 40 MPa, and the density range from 136 to 617 kg/m^3, with an uncertainty of $\pm 0.04\%$ in specific volume. Part of the results, namely, 66 specific volumes and four vapor pressures, were reported in advance in 1983.[79] The measurements were conducted by using a 188 cm^3 spherical vessel made of 304 stainless steel.

In the liquid water region, four different specific-volume data sets have been reported in the range of temperatures up to 773 K and pressures up to 100 MPa by Kell *et al.* in 1974,[70] 1975,[71] and 1978,[72] and by Chen *et al.* in 1977.[85] Kell *et al.* reported 1218 experimental data at temperatures from 273 to 773 K and pressures from 0.1 to 103 MPa with a 250 cm^3 cylindrical vessel made of 304 stainless steel for the measurements at temperatures below 623 K, while a 35-cm^3 vessel was used for the measurements at temperatures between 623 and 773 K. Detailed description concerning their apparatus was reported in 1965[84] together with the data at temperatures from 273 to 423 K and pressures up to 103 MPa. But the data reported in 1965 were revised due to the recalculation of the compressibility of their vessel on the basis of newly obtained speed of sound data in 1975.[71] The revised values exceed the original specific-volume data by about 0.01%.

Very precise thermodynamic data have been obtained at atmospheric pressure in the temperature range from 273 to 423 K including metastable states between 373 and 423 K. Those are specific-volume data measured by Gildseth *et al.* in 1972[86] at temperatures from 278 to 353 K, those by Kell in 1975[87] at temperatures from 273 to 423 K, speed-of-sound data by Del Grosso and Mader in 1970[88] and 1972[89] at temperatures from 273 to 368 K, and heat capacity data by de Haas in 1950[90] at temperatures up to 373 K. Based on such precise experimental data, Chen *et al.* in 1977[85] and Sato *et al.* in 1985[91] reported equations of state, respectively.

Chen *et al.* derived specific-volume data at temperatures from 273 to 373 K and pressures up to 100 MPa with a claimed uncertainty of ± 20 ppm from the speed-of-sound data measured by Wilson[92] and by Del Grosso and Mader. This equation includes the correlation developed by Kell[87] for density of liquid water at atmospheric pressure.

Sato *et al.* reported an equation of state for liquid water from 273 to 423 K and pressures up to 1 GPa from which all thermodynamic properties can be derived with high reliability reflecting precise experimental data. At atmospheric pressure, this equation represents specific volumes measured by Gildseth *et al.*[86] at temperatures from 278 to 353 K with an absolute average deviation of 2 ppm and a maximum absolute deviation of 4 ppm, specific volumes measured by Kell[87] at temperatures from 273 to 423 K with an absolute average deviation of 2 ppm and a maximum absolute deviation of 7 ppm, speed-of-sound data measured by Del Grosso and Mader[88,89] within ± 50 ppm at temperatures from 273 to 368 K, and heat capacity data reported by de Haas[90] within ± 5 J/(kg K) at temperatures up to 353 K and ± 7 J/(kg K) at temperatures up to 373 K, respectively. This equation can represent all well-known thermodynamic singularities of liquid water such as maximum density, minimum isobaric specific heat, maximum speed of sound, etc.

3.1.b. Enthalpy

Comparing with the amount of available specific-volume data, the total amount of enthalpy data is very limited. Working Group 1 of IAPS selected seven experimental data sets as "International Input" listed in Table 4. The distribution of these data, which include Osborne's data along the

Table 4. Experimental studies on the enthalpy of water

Authors	Year	Ref.	Temperature K	Pressure MPa	No. of data	Uncertainty in enthalpy
Havliček/Miškovský	1936	93	293 -- 823	0.1 -- 39.2	104	0.25 %
Vukalovich/Zubarev/Prusakov	1958	94	720 -- 823	20 -- 40	48	6 kJ/kg
Callendar/Egerton	1960	97	473 -- 873	0.5 -- 22	120	2.1 kJ/kg
Vukalovich/Zubarev/Prusakov	1962	95	673 -- 883	20 -- 54	56	6 kJ/kg
Vukalovich/Zubarev/Prusakov	1963	96	673 -- 983	2.5 -- 49	48	
Sheindlin/Gorbunova	1964	98	618 -- 734	20 -- 49	72	
Angus/Newitt	1966	99	673 -- 973	6 -- 100	16	0.1 %

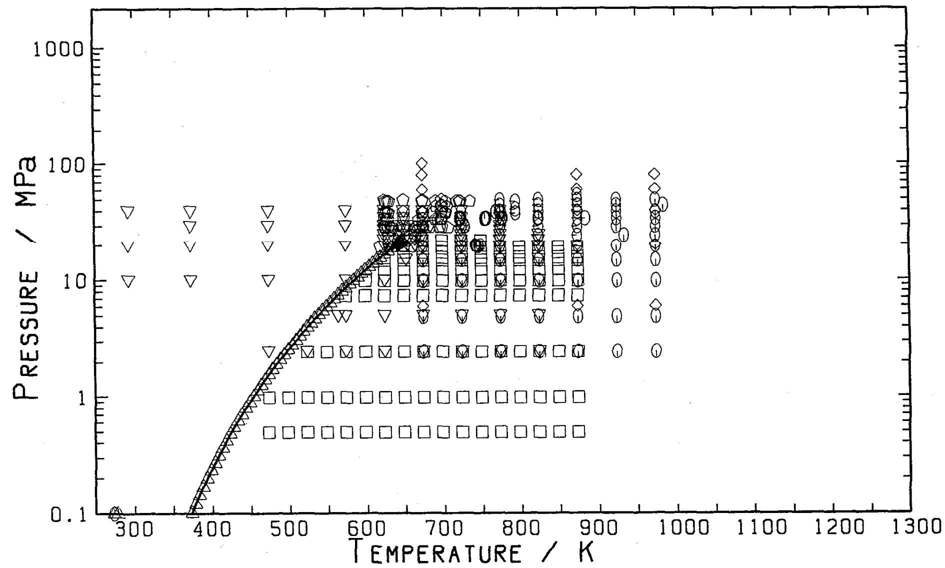

Fig. 3. Experimental data of the enthalpy on the pressure-temperature plane. Enthalpies measured by Havliček and Miškovský(▽), Osborne et al. in 1937(△) and in 1939(⧋), Vukalovich et al. in 1958(◯), in 1962(⦶) and in 1963(⊖), Callendar and Egerton(□), Sheindlin and Gorbunova(⬠), and Angus and Newitt (◇) are shown.

saturation curve,[105,107] is shown on a pressure–temperature diagram in Fig. 3. The total number of experimental data listed in Table 4 is 464 excluding Osborne's data; they cover the temperature range from 293 to 983 K and pressure range up to 100 MPa.

Angus and Newitt[99] reported 16 enthalpy values with an uncertainty of $\pm 0.1\%$ at temperatures from 673 to 973 K and pressures from 6 to 100 MPa in 1966; they were derived from 382 experimental measurements performed between 1959 and 1964. Their data agree in the range of overlap with the data of Havliček and Miškovský in 1936,[93] the data of Vukalovich *et al.* in 1958[94] and 1962,[95] and the data of Callendar and Egerton in 1960[97] within the respective claimed uncertainty.

The scarceness of experimental data on enthalpy is mainly understood as a result of difficulty in measuring the caloric properties precisely. Sato *et al.*[9] have pointed out that in the case of water the reliability of enthalpy values derived from equations of state might be higher than the reliability of experimental enthalpy data, since many accurate experimental data regarding specific volume and heat capacity are available at present for formulating equations of state.

3.2. Saturation State

3.2.a. Vapor Pressure

In 1974, Wagner[12] reviewed and evaluated most of vapor-pressure data of water in order to establish his vapor-

Table 5. Experimental studies on the vapor pressures of water

Authors	Year	Ref.	Temperature K	No. of data	Uncertainty in pressure
Osborne/Stimson/Fiock/ Ginnings	1933	100	373 -- 647	382	0.03 %
Rivkin/Troyanovskaya/ Akhundov	1964	101	646 -- 647	13	
Stimson	1969	102	298 -- 373	7	0.002 %
Kell/McLaurin/Whalley	1974	70	423 -- 623	22	0.2-0.3 kPa
Guildner/Johnson/Jones	1976	103	273.16	1	0.010 Pa
Hanafusa/Tsuchida/ Kawai/Sato/Uematsu/ Watanabe	1984	104	643 -- 646	7	3 kPa

pressure equation. Based on that review, six experimental data sets were selected for representing the vapor-pressure curve of water as listed in Table 5. Guildner *et al.* measured the triple-point pressure with an uncertainty of ± 0.010 Pa in 1976.[103] Stimson measured vapor pressures up to 373 K with an uncertainty of $\pm 0.002\%$ in 1969.[102] Osborne *et al.* measured vapor pressures with an uncertainty of $\pm 0.03\%$ in 1933,[100] which are still valuable information at temperatures between 373 and 647 K.

3.2.b. Specific Volume

Concerning specific volumes of saturated water, very few reliable data are available as listed in Table 6. Smith and Keyes[43] measured specific volumes of saturated water at temperatures between 303 and 633 K. The specific-volume values below 593 K are valuable input, but the data above 593 K deviate systematically from other data.

Kell[87] derived correlations of density and of isothermal compressibility of liquid water at atmospheric pressure based on precise experimental data. Those correlations are effective in the temperature range from 273 to 423 K. The saturated liquid density of water can be derived from these correlations by means of the relation,

$$\rho' = \rho(T,P_0)\{1 + \kappa_T(T,P_0)[P_s(T) - P_0]\}, \tag{1}$$

where ρ', κ_T, P_s, and P_0 and are saturated water density, isothermal compressibility, vapor pressure, and atmospheric pressure, respectively.

Osborne, Stimson, and Ginnings[105] determined specific-volume values from measurements of the caloric quantity β by means of the relation,

$$v' = \beta \Big/ \left(T\frac{dP_s}{dT}\right), \tag{2}$$

where v' and T are specific volume of saturated water and temperature, respectively. Their β data cover the temperature range from 373 to 647 K.

The specific volume of saturated steam v'' is derived from Osborne's measurements of the caloric quantity γ as listed in Table 7 by means of the relation,

$$v'' = \gamma \Big/ \left(T\frac{dP_s}{dT}\right). \tag{3}$$

The γ values obtained by Osborne *et al.* at temperatures beyond 645 K are not recommended to be used because they are not consistent with the critical parameters accepted by IAPS.[30]

Table 6. Experimental studies on the specific volume of saturated water

Authors	Year	Ref.	Temperature K	No. of data	Uncertainty in volume
Smith/Keyes	1934	43	303 -- 593	9	0.05 %
Osborne/Stimson/ Ginnings	1937	105	373 -- 647	29	
Kell/McLaurin/Whalley	1974	70	423 -- 623	22	
Kell	1975	87	273 -- 423	32	10 ppm

Table 7. Experimental studies on the specific volume of saturated steam

Authors	Year	Ref.	Temperature K	No. of data
Osborne/Stimson/ Ginnings	1937	105	373 -- 645	189
Osborne/Stimson/ Ginnings	1939	107	273 -- 373	146

3.2.c. Enthalpy

As described in the previous section, Osborne and his co-workers at the National Institute of Standards and Technology[105,107] listed in Table 8 carried out calorimetric measurements along saturation curve. They used the international joule which is equal to 1.000 165 J according to the analysis of Stimson.[110] They measured the caloric quantities α, β, and γ. The α depends only on temperature, which is defined by the following expression;

$$\alpha = h' - \beta = h'' - \gamma, \tag{4}$$

where h' and h" are enthalpies of saturated water and steam; β and γ are experimental values defined by Eqs. (2) and (3). The enthalpy values and latent heat can be derived from Osborne's calorimetric measurements of α, β, and γ according to Eq. (4). Near the critical point Baehr *et al.* measured the internal energy in 1974.[109] The α values derived from internal-energy data by Baehr *et al.* differ from Osborne's data by about 1%.

4. Statistical Treatment

4.1. Basic Concept

In order to establish skeleton tables from the large number and variety of experimental data reported by different investigators, the uncertainty of the data must be evaluated with a common set of criteria because the different investigators have reported the uncertainty of their measurements in different ways. In addition, it is virtually impossible to evaluate, from the limited information given in the literature, all factors which cause the uncertainty of measurements, such

Table 8. Experimental studies on the caloric property of saturated water and steam

Authors	Year	Ref.	Temperature K	No. of data
Osborne/Stimson/ Ginnings	1937	105	373 -- 645	142
Osborne/Stimson/ Ginnings	1939	107	273 -- 373	256

as the effect of isotopic composition, of impurities and environmental conditions. Therefore, statistical treatment is the only possible method for treating the uncertainty of experimental data under these circumstances.

Two different types of errors, systematic error and random error, should be evaluated for the uncertainty of measurements. The random error is caused by inevitable fluctuations of experimental conditions, which cause random variations of results of repeated measurements conducted by the same apparatus and the same experimenters. The systematic error, on the other hand, shows up as the difference among results in different measuring procedures; it may be a result of uncertainty caused by limited reliability of instruments, processing of scanty experimental data, and systematic error in physical factors such as temperature and pressure.

Since systematic errors and random errors are distinctly different components of uncertainty, different treatments are necessary to analyze those two errors independently. The random error is generally assigned as a standard deviation from the correlation of an individual data set, while the systematic error is estimated as a difference (bias) between the data and the weighted average of several independent measurements performed by different methods and different experimenters.

Even though more than 10 000 specific-volume data are available for water, very few measurements are performed at the same state point; this causes difficulty in treating those data statistically. Statistical treatment requires an appropriate amount of sampling at a single condition. Hence, prior to the statistical analysis, experimental data at different state parameters, but within a limited domain, are converted into values at a common state point (grid point) with the aid of available equations of state. The procedures will be described in the succeeding sections.

4.2. Error Analysis

There are 10 490 experimental specific-volume data as listed in Table 3. Some independent experimental data sets overlap in their temperature and/or pressure ranges. Due to the uncertainty of measurements, however, the different data sets give different volume values at the same temperature and pressure; this makes it necessary to analyze the uncertainty in order to obtain a most probable value with estimated reliability.

In this section the statistical treatment of experimental data for the specific volume of water will be summarized briefly. The details of this treatment have been reported in earlier publications by the present authors at Keio University.[4–7]

The calculation of the random and systematic errors are fairly simple. The random error at a certain grid point y is estimated as a standard deviation, $\delta_{j,y}$, by

$$\delta_{j,y} = \sqrt{\sum_{i=1}^{n} (x_{i,y} - \bar{x}_{j,y})^2/(n-1)}\ , \tag{5}$$

where n denotes the total number of the experimental data measured by a single research group, j, within a limited domain prepared for the grid point, y; $x_{i,y}$ denotes a single datum converted into the value at the grid point with the aid of the available equation of state; and $\bar{x}_{j,y}$ denotes the average value of $x_{i,y}$ calculated by

$$\bar{x}_{j,y} = \sum_{i=1}^{n} x_{i,y}/n. \tag{6}$$

The $\delta_{j,y}$ and $\bar{x}_{j,y}$ are calculated at each grid point y for each data set j by Eqs. (5) and (6).

The systematic error is evaluated as a difference $E_{j,y}$ by

$$E_{j,y} = |\bar{x}_{j,y} - \mu_{y,k}|, \tag{7}$$

where $\mu_{y,k}$ is a weighted average, and k denotes the number of times of iteration which will be discussed below. The $\mu_{y,k}$ is given by

$$\mu_{y,k} = \sum_{j=1}^{N} w_{j,y}\bar{x}_{j,y} / \sum_{j=1}^{N} w_{j,y}, \tag{8}$$

where N denotes the total number of data sets available at the grid point y and $w_{j,y}$ is the weighting factor for average value of $\bar{x}_{j,y}$. The weighting factor $w_{j,y}$ is defined by

$$w_{j,y} = |A\bar{x}_{j,y}/(\delta_{j,y} + E_{j,y})|, \tag{9}$$

where A is an amplitude.

In the course of the calculation, $E_{j,y}$ and $\mu_{y,k}$ are related to each other as given in Eqs. (7)–(9), so that an iteration procedure is required. As an initial guess $w_{j,y}$ is derived on the basis of relative comparison of the uncertainty of experimental data claimed by the experimenters, or all of them are set equal to unity if uncertainty is not claimed. Then, the first estimate of $\mu_{y,k=1}$ is obtained by means of Eq. (8) after which $E_{j,y}$ and $w_{j,y}$ are obtained by Eqs. (7) and (9), respectively. This procedure is repeated several times until the condition described below is satisfied.

The weighting factor $w_{j,y}$ is calculated for each data set at each grid point by means of Eq. (9). When A is fixed to 0.01, the weighting factor is equivalent to the reciprocal of a sum of evaluation for percentage random error and percentage systematic error of $\bar{x}_{j,y}$. As an index for evaluating experimental errors of overall measurements for a single data set j, a new parameter Δ_j is introduced:

$$\Delta_j = \sum_{y=1}^{Y} \frac{\delta_{j,y}}{Y} + \sum_{y=1}^{Z} \frac{E_{j,y}}{Z}\,, \tag{10}$$

where Y is the total number of $\delta_{j,y}$ and Z is the total number of $E_{j,y}$, respectively. The Δ_j is calculated for each data set and compared with the respective claimed uncertainty. The condition for terminating the iteration procedure is when most of the Δ_j show the respective claimed uncertainty at the best relationship. There is, of course, a possibility of finding inconsistency between Δ_j and the claimed uncertainty for some data sets in the course of this evaluation.

4.3. Skeleton Tables

The overall process as to establishing skeleton tables on specific volume is summarized in a flow chart in Fig. 4. At the first step literature values of thermodynamic properties of water are collected and evaluated with respect to the claimed uncertainty, then the data sets are classified into several ranks of priority for the data source(step 2). The

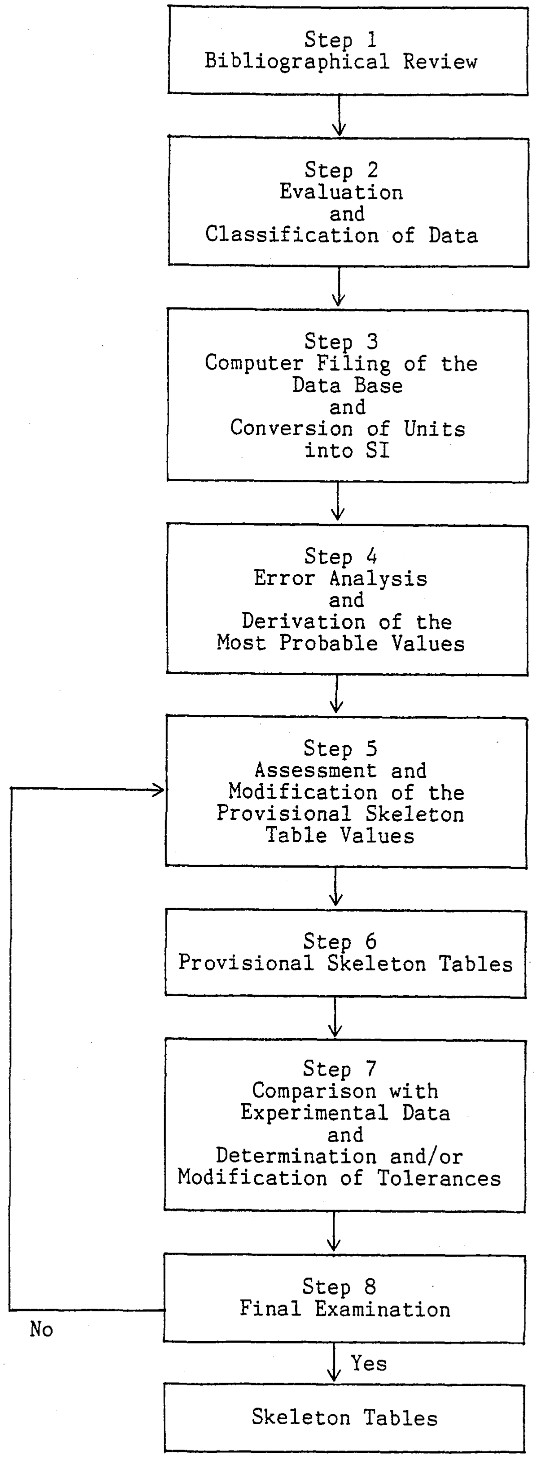

FIG. 4. Process for the establishment of the present skeleton tables.

selected data sets are stored in a computer file and then these data are converted to SI units, namely Pa for pressure, K(IPTS-68) for temperature, m^3/kg for specific volume (step 3), respectively. The data sets are analyzed by the original statistical error treatment described in the preceding section (step 4).

Throughout the data processing from steps 1–4, skeleton table values are primarily determined on the basis of the experimental data. Next, the following items are investigated (step 5):

(1) Relation between determined table values and other parameters such as the critical parameters, the triple-point temperature and pressure, the thermodynamic properties at atmospheric pressure and along the saturation line, the thermodynamic properties at the ideal-gas state, second virial coefficient, etc.

(2) Relation between determined table values and the experimental data; this assessment requires equations of state as a base for comparing them.

(3) Randomness of the grid-point values which have a scatter reflecting the reliability of experimental data sources.

After the above assessment, the provisional skeleton tables are established (step 6). Finally, the reliabilities of the most probable values called "tolerances" are determined on the basis of the consistency with the experimental data and of the results of the error analysis (step 7), and all of the most probable values determined as the provisional skeleton tables are compared again with all of the available experimental data taking the associated tolerances into consideration (step 8).

The detailed procedures for the establishment of the present specific volume and the enthalpy tables are given in the following section.

5. Data Processing

5.1. Single-Fluid Phase State

5.1.a. Specific Volume

The actual data processing for establishing the present skeleton tables is described in this section. The data with an asterisk in Table 3 and 231 specific-volume values derived by Chen *et al.*[83] from speed-of-sound data are the the data used to establish the present specific-volume skeleton table in the single-fluid-phase state. The distribution of these data is shown in Figs. 1 and 2. The data reported by Hanafusa *et al.* in 1984[104] were only used in the process after step 5 of the flow chart in Fig. 4, because they were published after the establishment of the most probable values at step 4. Therefore, 6713 data points become the data base in the statistical treatment at step 4.

Figure 5 shows five distinct subregions of statistical

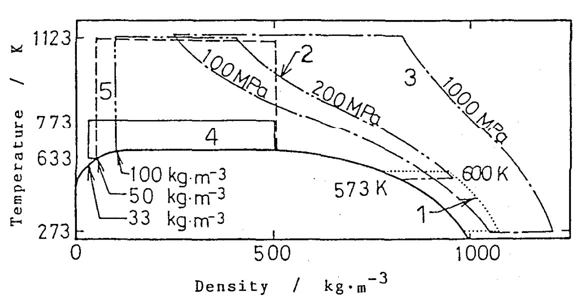

FIG. 5. Five subregions for the error analysis of the experimental specific volume data.

treatment in accordance with the difference of pressure dependence of specific volume. The subregion 1 in Fig. 5 is prepared for liquid phase; subregion 2 for supercritical-fluid phase; subregion 3 for high-pressure phase; subregion 4 for critical region; and subregion 5 for single-fluid phase at high temperatures.

In subregions 1, 2, and 3, the errors in specific-volume values were analyzed as a function of temperature and pressure, whereas the errors in pressure values were analyzed as a function of temperature and specific volume in subregions 4 and 5. The experimental data were converted into the grid-point values by the equation of state developed by Pollak[111] in subregions 1, 2, 4, and 5, whereas by the equation of state developed by Jůza[35] in subregion 3.

The evaluated errors for the specific volume values are given in Table 3, which were calculated by Eq. (10). The evaluated pressure errors in subregions 4 and 5 have been given in a previous publication.[4]

The size of a domain prepared for a grid point was chosen case by case according to the distribution of data points and the behavior of the thermodynamic state surface, namely, how strongly specific volume depends on temperature and pressure or how strongly pressure depends on temperature and specific volume. The domains were overlapped with each other as widely as possible in order to get smoother behavior among grid-point values.

The result and some detailed discussion of the error analysis have been presented by Sato *et al.*,[4] and the original most probable values obtained directly by the present error analysis are summarized in Tables 2 and 3 of a previous publication.[7]

5.1.b. Enthalpy

Regarding the enthalpy of water in the single-fluid phase, only 464 experimental data in seven references[93–99] are available as mentioned in Sec. 3.1.b. Due to the scarcity of enthalpy data, the statistical method used for establishing the specific-volume table can not be applied to the case of enthalpy.

The enthalpy table was constructed on the basis of derived values from four equations of state of water, namely, the equation developed by Pollak in 1974,[111] the equation developed by Haar, Gallagher, and Kell,[112] whose equation was accepted as IAPS-84,[28] and two independent equations developed by Sato *et al.* in 1981[113] and in 1985.[91] The reliabilities of those equations were carefully examined on the basis of the present specific-volume table and by comparing them with experimental data regarding specific volume, heat capacity, and speed of sound, so on.[8,9] These four equations agree well with the present specific-volume table values and with experimental data in most of the respective ranges except at high pressures along the isotherm of 273 K. The discrepancies among the derived values regarding specific volume, enthalpy, speed of sound, and heat capacity at constant pressure along the 273 K isotherm are listed in Table 9.

Table 9. Discrepancies among derived thermodynamic property values from four equations of state; equation developed by Pollak, IAPS-84, and two equations developed by Sato et al., along 273 K isotherm

Property	Pressure 100 MPa	200 MPa	300 MPa
Specific volume	0.012 %	0.27 %	1.0 %
Enthalpy	0.7 %	0.3 %	2.2 %
Speed of sound	0.7 %	9 %	20 %
Heat capacity, C_p	2.8 %	7 %	15 %

Enthalpy values calculated from the equations of state are to be preferred over available experimental data in case of water. That good equations of state can reliably predict enthalpy values, is apparent from the excellent agreement of thermodynamic surfaces fitted to specific-volume data and other thermodynamic property data such as the heat capacity at constant pressure data of Sirota *et al.*[114–126] For example, in the case of the enthalpy data of Havlíček and Miškovský[93] on the 473.15 K isotherm, where the three equations agree to within $\pm 0.05\%$ but differ from the data by more than 0.4% as shown in Fig. A.III.9a in Appendix III, we have given preference to the equations.

The tolerances for the enthalpy values at pressures below 100 MPa were determined by taking the consistency of the experimental data and the agreement among the four equations into consideration. The tolerances above 100 MPa were determined from the analysis of three equations excluding the equation by Pollak. The detailed discussions have been reported in another publication[9] and the reliability of each equation of state will be discussed in Sec. 9.2. Comparison of the skeleton table values with available experimental data and four equations is given schematically along 24 isotherms in Appendix III.

5.2. Saturation State

The skeleton table values at the saturation state were calculated by the equations for the vapor pressure, densities of saturated water and steam, and the caloric property α from which the enthalpy values of saturated water and steam were derived by using relations of Eqs. (2)–(4) as previously described in Sec. 3.2. These equations are given in the supplementary release[15] issued by IAPS.

In order to obtain these equations, Wagner and Saul[13] and Saul and Wagner[14] applied an optimization method developed by Ewers and Wagner.[127,128] All equations have been fitted to the data by weighted least squares according to the method of maximum likelihood by Saul and Wagner.[14] The variance of the data from their respective equations is the basis for evaluating the tolerance. Each equation covers the entire range of the vapor–liquid equilibrium and represents the experimental data within the claimed uncertainty. More detailed discussions have been given by Saul and Wagner.[14]

6. Common Requirements

6.1. Critical Point

6.1.a. Temperature, Pressure, and Density

The values of critical temperature, critical pressure, and critical density of water which have been given in a 1983 IAPS Statement,[30] have been determined on the basis of international cooperative study conducted by Levelt Sengers, Straub, Watanabe, and Hill.[83] We adopted these values for the most probable values of present skeleton steam tables at the critical point.

6.1.b. Enthalpy

The enthalpy values at the saturation state above 373 K were determined on the same data base as for IST-63, since no essential experimental data had been accumulated since then except the internal energy data by Baehr *et al.* In the course of redetermination of the enthalpy at the critical point, not only the effect of replacement of the temperature scale from IPTS-48 to IPTS-68, but also the effect of the newly determined critical parameters were taken into consideration.

6.2. Saturation State

6.2.a. Triple Point

The temperature of the triple point of water, 273.16 K, is defined as the fundamental standard of IPTS-68. The internal energy and the entropy of saturated water at the triple point are assigned a value of zero as adopted at the fifth ICPS in London, 1956. The triple-point pressure was measured very precisely by Guildner *et al.* in 1976.[103] They proposed 611.657 ± 0.010 Pa.

6.2.b. Boiling Point

The normal boiling point is defined as being 373.15 K in the current standard, IPTS-68. On the other hand, it should be remembered that there exists a temperature difference between the IPTS-68 and the thermodynamic temperature. Guildner and Edsinger have reported the thermodynamic temperature of the boiling point of water as being 373.1248 K with the random error of ± 0.0018 K and the systematic error of $\pm 0.000\,54$ K in 1976.[129]

6.2.c. Clapeyron's Equation

The relation among temperature, vapor pressure, specific volume, and enthalpy at the saturated state must satisfy Clapeyron's equation. In the present skeleton tables, this thermodynamic consistency is assured, since the most probable values for the enthalpy at the saturated state were derived from the vapor pressure, and the densities of saturated water and saturated steam as discussed in Sec. 5.2.

6.3. Single-Fluid Phase State

6.3.a. Second Virial Coefficient

The study performed by Le Fevre *et al.* about the second virial coefficient of water in 1975[130] is reliable. The most probable specific-volume values at pressures below 2.5 MPa have been determined by the careful consideration of Le Fevre's second virial coefficient.

6.3.b. Precise Data at Atmospheric Pressure

Very precise experimental data for the thermodynamic properties of liquid water at atmospheric pressure are available as described in Sec. 3.1. Some of such precise experimental data are reported by Gildseth *et al.* in 1972,[86] and by Del Grosso in 1970[88] and Del Grosso and Mader in 1972.[89] Sato *et al.*[91] proposed an equation of state for representing these experimental data precisely which is effective in the temperature range from 273 to 423 K. The most probable values in the present skeleton tables both for the specific volume and enthalpy at atmospheric pressure agree with Sato's equation within their associated tolerances in the temperature range between 273 and 373 K. This fact proves the good relationship between the most probable values and the precise experimental data at atmospheric pressure.

7. Skeleton Tables

The present skeleton tables were adopted as "The IAPS Skeleton Tables 1985 for the Thermodynamic Properties of Ordinary Water Substance (IST-85)." The IST-85 is reproduced in Appendix I.

The IST-85 consists of two parts, one is for the single-fluid phase state and the other is for the saturation state. Part I of IST-85 contains two skeleton tables. Table 1 (IST-85) gives the most probable specific-volume values with their associated tolerances in the temperature range from 273.15 to 1 073.15 K and pressure range up to 1 GPa, whereas Table 2 (IST-85) gives the most probable enthalpy values with their associated tolerances in the same range as that of the specific-volume table. The boundary line between liquid water and steam is indicated, beginning at 398.15 K and 101.325 kPa and disappears at 623.15 K and 15 MPa. No entries are given in the range of the solid phase at the pressures above 650 MPa along the 273.15 K isotherm and above 900 MPa along the 298.15 K isotherm. Part II of IST-85 contains skeleton table of thermodynamic properties at the saturation state of water. Table 3 (IST-85) gives the most probable thermodynamic property values with their associated tolerances for the coexisting vapor–liquid phases between the triple point and the critical point.

8. Comparisons

8.1. Single-Fluid Phase State

8.1.a. Specific Volume

Complete comparison of the most probable specific-volume values with the essential experimental data and five equations of state for water, namely, IFC-67,[18] Pollak's equation,[111] Sato's equations[91,113] and IAPS-84,[28] is shown in Appendix II. Percent deviation, Δv, is calculated by the following equation:

$$\Delta v = 100(v - v_{\mathrm{cal}})/v_{\mathrm{cal}}, \qquad (11)$$

where v is the experimental or derived specific-volume value including the most probable value and v_{cal} is the IAPS-84 value. The experimental data plotted in the figures of Appendix II are reported at temperatures within ± 1 K around the nominal temperature. The top figures are plotted on a logarithmic pressure scale, whereas the bottom figures are plotted on an ordinary pressure scale up to 1 GPa.

Regarding the specific volumes of liquid water in the pressure range below 200 MPa (Figs. A.II.1a–12a), the experimental data by Kell *et al.*[70–72] and the data by Chen *et al.*[85] are the most precise data. The most probable specific-volume values agree with those data completely within a few tenths of the associated tolerances.

For the superheated steam, the data measured by Kell[70] and by Keyes *et al.*[44] deviate from the most probable values beyond the tolerance at 573.15 and 623.15 K (Figs. A.II.11a and 12a).

In the pressure range above 200 MPa (Figs. A.II.1b–24b), the experimental data reported by Jůza *et al.*,[53] Vedam and Holton,[65] Borzunov *et al.*,[66] Grindley and Lind,[67] Hilbert *et al.*,[78] Tanishita *et al.*,[61] and Zubarev *et al.*,[75,76] are the major sources of information. The most probable values agree with those data within their tolerances. The experimental data reported by Maier and Franck,[63] Köster and Franck,[64] and Burnham *et al.*[77] are measured over a wide temperature and pressure range with an uncertainty of about $\pm 1\%$ in specific volume. The most probable values are larger than most of the data reported by Maier and Franck and Köster and Franck (see, e.g., Figs. A.II.9b–12b), but, on the other hand, they are smaller than the data reported by Burnham *et al.* (see, e.g., Figs. A.II.13b).

8.1.b. Enthalpy

The complete comparison of the most probable enthalpy values with the essential experimental data and five equations of state is shown in Appendix III. The percent deviation Δh is calculated by the following equation:

$$\Delta h = 100(h - h_{\text{cal}})/h_{\text{cal}}, \tag{12}$$

where h is the experimental or derived enthalpy value including the most probable value and h_{cal} is the IAPS-84 enthalpy value. The temperature range of the experimental data plotted in the figures is ± 1 K around the nominal temperature.

As described in Sec. 5.1.b., the most probable enthalpy values are determined from the equation developed by Pollak, IAPS-84, and two independent equations developed by Sato *et al.*

In most of the range up to 973 K and below 200 MPa (Figs. A.III.5a–22a), the differences among the four equations of state are smaller than the scatter among the experimental data. Since some of these equations of state have been developed on the basis of not only the precise specific-volume data but also the experimental heat capacity and speed-of-sound data, they agree with each other very well. This agreement justifies small tolerances assigned to the most probable enthalpy values in comparison with discrepancies among experimental data.

8.2. Saturation State

The comparison of the equation for the vapor pressure with experimental data is shown in Fig. 6. The experimental data reported by Stimson[102] between 298 and 373 K and those reported by Osborne *et al.*[100] between 373 and 647 K have been used to determine the associated tolerances.

The comparison of the equation of the saturated water density with experimental data is shown in Fig. 7. The tolerances of the most probable specific volumes between 273 and 423 K are determined from 10 to 30 ppm as shown in the lower plot in Fig. 7. The tolerance of specific volume of saturated steam includes all of the derived data reported by Osborne *et al.*[105,107] as shown in Fig. 8.

As described in Sec. 5.2., the enthalpy values for saturated water and saturated steam were calculated by Eqs. (2)–(4). The enthalpy values were determined on the basis of α-values measured by Osborne *et al.*[105,107] These α-values are plotted in Fig. 9. Osborne's data agree with the equation within $\pm 0.07\%$ up to 373 K and $\pm 0.3\%$ above 373 K. The tolerances for enthalpy values of saturated water and saturated steam were decided so as to include the majority of Osborne's α-data and those tolerances are shown in Figs. 10 and 11, respectively.

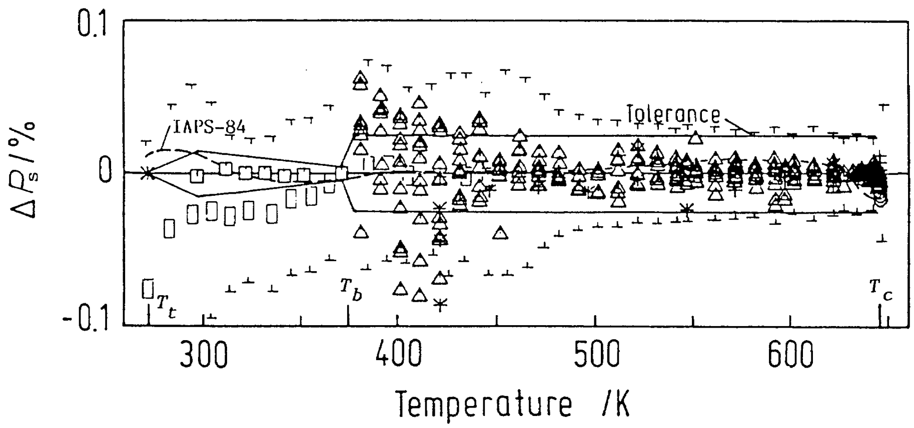

Fig. 6. Percent deviations of the vapor pressure values from the equation developed by Wagner and Saul. The data measured by Osborne et al.(△), Stimson (□), Guildner et al.(✳), Rivkin et al.(+), Kell et al.(✳), Hanafusa et al.(○) and the values of the International Skeleton Steam Tables, 1963(▯) and the associated tolerances (⊤ , ⊥) are shown. T_t, T_b, and T_c are the triple, boiling, and critical points of water, respectively.

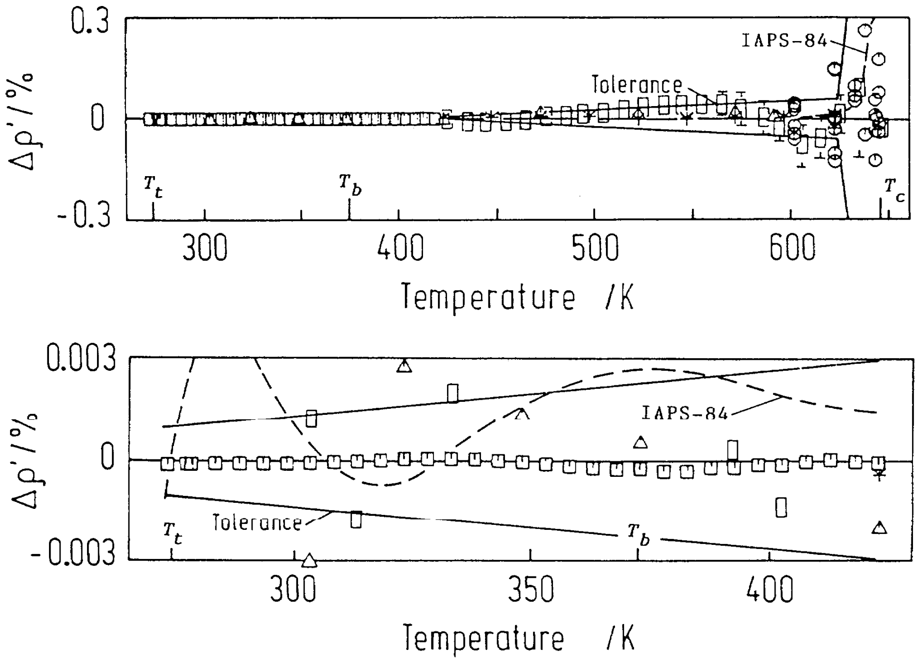

Fig. 7. Percent deviations of the density values of saturated water from the equation developed by Wagner and Saul. The data measured by Smith and Keyes(△), Kell et al.(✳), Osborne et al.(○), Kell(□) and the values of the International Skeleton Steam Tables, 1963(▯), and the associated tolerances(⊤ , ⊥) are shown. T_t, T_b, and T_c are the triple, boiling, and critical points of water.