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New Equation of State for Ordinary Water Substance in the Critical Region*

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A new equation of state for ordinary water substance in the critical region was formulated based upon the International Skeleton Tables (1963). The new equation of state is given in a form of pressure as a function of temperature and specific volume, and is valid in the ranges of temperatures from 350°C to 650°C, of pressures from 165.37 bar to 1 000 bar, where the specific volume is less than about 10 cm³/g. The new equation has a comparatively simple functional form which is convenient for the practical computations with electronic computers and fulfils the condition of the thermodynamic consistency at the critical point in itself, and moreover it can cover the above mentioned entire region by a single formula.

The specific volume and specific enthalpy computed from the equation agree well with the Skeleton Table values within the tolerances.

The new equation was adopted as one of the subformulations of The 1967 IFC Formulation for Industrial Use.

1. Introduction

In many countries, hitherto, the equation of state for water substance was formulated separately, and the Steam Table and the Diagram were made in each country based upon it respectively. Therefore some slight discrepancies were found among the numerical values of the Steam Tables and inconveniences were sometimes arose.

On the other hand, according to the recent trend of the steam condition to increase temperatures and pressures, the Sixth International Conference on the Properties of Steam (ICPS), held in New York in October, 1963, adopted the new International Skeleton Tables (1963) for a wider range of temperatures and pressures up to 800°C and 1 000 bar^{(1) (2)}.

In addition to this, the Sixth ICPS established a committee, called the International Formulation Committee (IFC), which consisted of the delegations of Czechoslovakia, Federal Republic of Germany, Japan, U.S.A., U.K. and USSR, for the aim of developing at the earliest practical date a formulation,

for use with electronic computers, of the properties of ordinary water substance. This formulation shall provide the values that are, at all points, within the tolerances stated in the International Skeleton Tables (1963).

In cooperation with these tasks of the IFC, we made a complete set of formulations covering the states of compressed water, superheated steam, critical region and the saturation line in our Heat Engineering Laboratory of Keio University, and they were submitted to the second meeting of the IFC held in Glasgow in March, 1966.

Among these formulations, the equations of state for the critical region and the saturation pressure⁽³⁾ were adopted as the subformulations of The 1967 IFC Formulation for Industrial Use, combined with those of compressed water and superheated steam made in Federal Republic of Germany. In this paper, the new equation of state for the critical region will be described in detail.

Our new equation of state for the critical region was formulated so as to coincide continuously and smoothly with our equations of state for compressed water⁽⁴⁾ along the interregional boundary of 350°C isotherm, and also with that for superheated steam⁽⁵⁾ along an interregional boundary curve in the temperature range from 350°C to 650°C.

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2. Review of other investigations

A number of investigations relating to the formulation of the thermodynamic properties of ordinary water substance in the critical region have previously been reported. But in earlier periods, the experimental ranges of temperatures and pressures were narrow and the number of measured values was not enough. Therefore, we shall review in the following the investigations of late years which seem to be important.

L. Ziegler formulated an equation of state of ordinary water substance for the supercritical region⁽⁶⁾ and E. S. Nowak et al. investigated about the expression of the thermodynamic properties in the critical region^{(7) (8)}.

After these investigations, the trials of formulations in the critical region were carried out by H. D. Baehr et al.⁽⁹⁾, J. Juza et al.⁽¹⁰⁾, and T. Sato et al.⁽¹¹⁾ K. Miyabe et al.⁽¹²⁾ formulated an equation of state for a very narrow region just around the critical point. One of the common features in the formulations made by H. D. Baehr et al., J. Juza et al. and T. Sato et al. is that the whole critical region is divided into two or more subregions. These formulations are shown in the following.

H. D. Baehr et al. made the following equation for the critical region, in which the critical isotherm ($\theta=1$) is chosen as one of the interregional boundaries,

$$\beta(\theta, \chi) = \sum_{\nu=2}^{11} \alpha_{\nu} \chi^{-\nu} + \left(\sum_{\nu=1}^{11} \beta_{\nu} \chi^{-\nu} \right) \theta + (1-1/\theta)(\theta-1.34891086)C(\theta, \chi) + 4\beta(\theta, \chi)$$

where $C(\theta, \chi) = \chi^{-2}(7.27\theta-16.7)(\chi^{-1}-0.69\theta-0.236)(\chi^{-1}+1.346\theta-3.242)$
and

$$4\beta(\theta, \chi) = \begin{cases} 0, & \theta \geq 1 \\ 1.8764 \times 10^4 \chi^{-2} (\chi^{-1}-2.20)(\chi^{-1}-3.08)(\theta-1)^3(\theta-0.949), & \theta < 1 \end{cases}$$

T. Sato et al. formulated the thermodynamic properties in the same subregions described above as follows: For the subregion of $\theta \geq 1$,

$$\beta = 1 + \{F_0 + F_1 \chi^{-1} + \sum_{\nu=2}^9 (1-\nu) F_{\nu} \chi^{-\nu}\} + (\theta-1) \{G_0 + G_1 \chi^{-1} + \sum_{\nu=2}^9 (1-\nu) G_{\nu} \chi^{-\nu}\} \\ + (\theta-1)(\theta_1-\theta) [\theta^{-2} \{K_0 + K_1 \chi^{-1} + \sum_{\nu=2}^5 (1-\nu) K_{\nu} \chi^{-\nu}\} + (\theta-\theta_2)(-4L_1 \chi^{-5} - 5L_2 \chi^{-6})]$$

and for the subregion of $\theta < 1$,

$$\beta = 1 + \{F_0 + F_1 \chi^{-1} + \sum_{\nu=2}^9 (1-\nu) F_{\nu} \chi^{-\nu}\} + (\theta-1) \{J_0 + J_1 \chi^{-1} + \sum_{\nu=2}^{10} (1-\nu) J_{\nu} \chi^{-\nu}\}$$

In these equations, F_{ν} , G_{ν} , J_{ν} , K_{ν} and L_{ν} are the numerical constants, and θ_1 and θ_2 are the reduced temperatures corresponding to 350°C and 400°C respectively.

The formulation by J. Juza et al. has the interregional boundaries consisting of the critical isotherm and two isochores of 0.43 g/cm³ and 0.79 g/cm³. These subformulations are the same in their form but the numerical constants have different values in each subregion as follows:

$$\beta = \frac{I_{10}\theta}{\chi} \left\{ 1 + \sum_{n=1}^4 n I_n \left(\frac{1}{\chi} \right)^n + \sum_{n=5}^7 (n+8) I_n \left(\frac{1}{\chi} \right)^{n+8} \right\} \\ - \frac{1}{\chi^2} \left[\sum_{q=2}^{Y_0} \left\{ \sum_{n=1}^{Y_q} \frac{1-n}{3.17} Y_{q20} Y_{qn} Z_q^{n-2} \right\} N_q - \left\{ \sum_{n=2}^{Y_8} \frac{2n+Y_{822}}{3.17} Y_{820} Y_{8n} Z_8^{2n+Y_{822}-1} \right\} \frac{Y_{90}}{Y_{91}+Y_{92}\theta^{Y_{93}}} \right]$$

where $Z_w = Y_{w20} \left\{ \frac{1}{3.17\chi} - Y_{w21} \right\}$ ($w=q, \dots, 8$), $N_q = \frac{I_{q0} + \sum_{m=1}^{I_q} I_{qm} (1/\theta)^{I_{q11}(m-1) + I_{q12}}}{I_{q8} + I_{q9}\theta^{I_{q10}}}$

In these equations, I_{ν} , Y_{ν} , etc. are the numerical constants which have different sets of values corresponding to each subregion.

3. Symbols, units and basic quantities

P : pressure, bar
 v : specific volume, cm³/g
 t : temperature, °C
 T : absolute temperature, °K
 ρ : density, g/cm³
 h : specific enthalpy, J/g
 s : specific entropy, J/g °K
 u : specific internal energy, J/g
 f : specific free energy, J/g

g : specific free enthalpy, J/g
 c_p : specific isobaric heat capacity, J/g °K
 c_v : specific isochoric heat capacity, J/g °K
 k : isentropic exponent
 β : reduced pressure, P/P_{c1}
 χ : reduced specific volume, v/v_{c1}
 ε : reduced specific enthalpy, $h/P_{c1}v_{c1}$
 σ : reduced specific entropy, $sT_{c1}/P_{c1}v_{c1}$
 Ψ : reduced specific free energy, $\varepsilon - \beta\chi - \theta\sigma$

λ_ρ : reduced specific isobaric heat capacity,
 $c_p T_{c1}/P_{c1} v_{c1}$
 λ_v : reduced specific isochoric heat capacity,
 $c_v T_{c1}/P_{c1} v_{c1}$

Subscripts

c1: quantities at the critical point
 1: quantities along 350°C isotherm
 s: quantities at the saturated state

Constant quantities

0 °C=273.15°K
 triple point of ordinary water substance,
 0.01°C=273.16°K
 critical pressure, $P_{c1}=221.2$ bar
 critical specific volume, $v_{c1}=3.17$ cm³/g

critical temperature, $T_{c1}=647.30$ °K
 $A=a$ constant=1/10 J/bar cm³

4. Preliminary considerations

It is very difficult to obtain the equation of state for ordinary water substance in the critical region in a form of $v=v(P, T)$ which is very convenient for practical use. Therefore, in this case, specific volume and temperature were taken as the independent variables as a form of $P=P(v, T)$.

The basic form of the equation of state is given as follows, using density ρ instead of specific volume v ,
 $P=P(\rho, T)$ (1)

Expanding pressure P in double Taylor series around the critical point, the following equation can be derived from Eq. (1),

$$\begin{aligned}
 P = & P_{c1} + \left(\frac{\partial P}{\partial \rho} \right)_{c1} \Delta \rho + \left(\frac{\partial P}{\partial T} \right)_{c1} \Delta T \\
 & + \frac{1}{2!} \left\{ \left(\frac{\partial^2 P}{\partial \rho^2} \right)_{c1} (\Delta \rho)^2 + 2 \left(\frac{\partial^2 P}{\partial \rho \partial T} \right)_{c1} (\Delta \rho) (\Delta T) + \left(\frac{\partial^2 P}{\partial T^2} \right)_{c1} (\Delta T)^2 \right\} \\
 & + \frac{1}{3!} \left\{ \left(\frac{\partial^3 P}{\partial \rho^3} \right)_{c1} (\Delta \rho)^3 + 3 \left(\frac{\partial^3 P}{\partial \rho^2 \partial T} \right)_{c1} (\Delta \rho)^2 (\Delta T) + \dots \right\} \\
 & + \frac{1}{4!} \left\{ \left(\frac{\partial^4 P}{\partial \rho^4} \right)_{c1} (\Delta \rho)^4 + \dots \right\} + \dots \dots \dots (2)
 \end{aligned}$$

where, $\Delta \rho = \rho - \rho_{c1}$, $\Delta T = T - T_{c1}$ and $\rho_{c1} = 1/v_{c1}$.

Owing to the fact that the critical isotherm has an inflection point and horizontal gradient at the critical point on P vs. v plane, we have

$$\left(\frac{\partial P}{\partial v} \right)_{T_{c1}} = 0; \quad \left(\frac{\partial^2 P}{\partial v^2} \right)_{T_{c1}} = 0 \dots \dots \dots (3)$$

From $d\rho = -dv/v^2$, above equations become

$$\left(\frac{\partial P}{\partial \rho} \right)_{T_{c1}} = -v^2 \left(\frac{\partial P}{\partial v} \right)_{T_{c1}} = 0; \quad \left(\frac{\partial^2 P}{\partial \rho^2} \right)_{T_{c1}} = 2v^3 \left(\frac{\partial P}{\partial v} \right)_{T_{c1}} + v^4 \left(\frac{\partial^2 P}{\partial v^2} \right)_{T_{c1}} = 0 \dots \dots \dots (4)$$

Substituting above equations into Eq. (2), we have the following expression:

$$P = P_{c1} + (\Delta \rho)^3 f(\Delta \rho) + \Delta T F(\Delta \rho, \Delta T) \dots \dots \dots (5)$$

In this equation, $f(\Delta \rho)$ is a function of the density difference $\Delta \rho = \rho - \rho_{c1}$ alone and $F(\Delta \rho, \Delta T)$ is another function of the density difference and the temperature difference $\Delta T = T - T_{c1}$. If these two functions are suitably determined from the experimental data, then Eq. (5) becomes an equation of state in the critical region.

5. Formulation of the new equation of state

Initially, the values of the product Pv of pressure P and specific volume v were calculated for the grid points given in the International Skeleton Tables (1963), in the region where this formulation is aimed to be valid. From these calculated results, a diagram of Pv vs. ρ was drawn as precisely as possible on a large scale, the reduced scale diagram of which is shown in Fig. 1. From Fig. 1, the basic property values for 16 isochores were determined as shown in Table 1. In this procedure of determining the property values, the following methods were applied for the saturated states corresponding to these 16 isochores. It was found too difficult to determine

Fig. 1 Pv vs. ρ diagram based upon the International Skeleton Tables (1963)

graphically the precise intersections of the saturated water curve with the isochores on v vs. t diagram especially in the range of temperatures from 300°C to 374.15°C. Then another diagram on ρ vs. t plane, Fig. 2, was used to determine graphically the saturation temperature which corresponds to each isochore given in Table 1.

On the other hand, the numerical values of the saturation pressure and temperature are given in the International Skeleton Tables (1963). Hence, we can determine the saturation pressure corresponding to the temperature obtained in the manner described above.

In Fig. 3, 16 isochores listed in Table 1 are shown on P vs. t plane. Among these 16 isochores, the minimum density of $\rho=0.092\,773\text{ g/cm}^3$ corresponds to the specific volume of $10.779\text{ cm}^3/\text{g}$ given for the saturated steam of 340°C isotherm in the International Skeleton Tables (1963), and also the maximum density of $\rho=0.761\,04\text{ g/cm}^3$ corresponds to $1.314\text{ cm}^3/\text{g}$ for the grid point of 350°C and 1 000 bar.

Observing the P vs. t diagram of Fig. 3 in detail, it is found that the tendency of each isochore is nearly a straight line in the almost entire region, except in the high pressure region and in the very

Table 1 Basic property values for 16 isochores

$\rho=0.092\,773\text{ g/cm}^3$		773.15	491.10	698.15	381.38	$\rho=0.590\text{ g/cm}^3$	
$T\text{ }^\circ\text{K}$	$P\text{ bar}$	823.15	594.53	723.15	463.32	$T\text{ }^\circ\text{K}$	$P\text{ bar}$
613.15	146.08	873.15	695.95	748.15	545.98	619.03	157.17
623.15	154.24	923.15	795.13	773.15	629.28	623.15	184.143
648.15	173.32	$\rho=0.280\text{ g/cm}^3$		$\rho=0.400\text{ g/cm}^3$		648.15	357.18
673.15	190.84	$T\text{ }^\circ\text{K}$	$P\text{ bar}$	$T\text{ }^\circ\text{K}$	$P\text{ bar}$	673.15	531.71
698.15	208.23	647.05	220.62	646.08	218.08	698.15	712.60
723.15	224.73	673.15	284.37	648.15	225.04	723.15	897.63
748.15	240.65	698.15	345.24	673.15	312.80	$\rho=0.650\text{ g/cm}^3$	
773.15	256.24	723.15	405.92	698.15	404.52	$T\text{ }^\circ\text{K}$	$P\text{ bar}$
823.15	286.15	748.15	466.51	723.15	498.72	599.64	122.89
873.15	315.30	773.15	526.74	748.15	594.28	623.15	321.62
923.15	343.77	823.15	646.16	773.15	690.64	648.15	540.02
$\rho=0.120\text{ g/cm}^3$		923.15	878.61	823.15	883.52	673.15	759.07
$T\text{ }^\circ\text{K}$	$P\text{ bar}$	$\rho=0.300\text{ g/cm}^3$		$\rho=0.450\text{ g/cm}^3$		698.15	980.33
625.67	170.63	$T\text{ }^\circ\text{K}$	$P\text{ bar}$	$T\text{ }^\circ\text{K}$	$P\text{ bar}$	638.15	453.30
673.15	218.95	647.25	221.14	643.18	211.28	658.15	627.10
698.15	242.75	673.15	288.28	673.15	334.13	688.15	891.90
723.15	265.34	698.15	353.76	698.15	443.66	$\rho=0.690\text{ g/cm}^3$	
748.15	287.35	723.15	419.25	723.15	556.09	$T\text{ }^\circ\text{K}$	$P\text{ bar}$
773.15	308.74	748.15	485.19	748.15	669.83	583.52	99.18
823.15	350.21	773.15	550.80	773.15	785.07	623.15	484.66
873.15	390.36	823.15	681.18	$\rho=0.500\text{ g/cm}^3$		648.15	739.68
923.15	429.37	873.15	809.61	$T\text{ }^\circ\text{K}$	$P\text{ bar}$	673.15	992.84
$\rho=0.190\text{ g/cm}^3$		923.15	936.18	637.655	197.126	593.15	190.90
$T\text{ }^\circ\text{K}$	$P\text{ bar}$	$\rho=0.320\text{ g/cm}^3$		648.15	247.65	603.15	287.00
641.71	206.93	$T\text{ }^\circ\text{K}$	$P\text{ bar}$	673.15	372.75	613.15	384.80
673.15	260.09	647.27	221.20	698.15	503.60	638.15	637.40
698.15	300.75	673.15	292.19	723.15	637.90	658.15	840.80
723.15	340.01	698.15	362.69	748.15	772.85	$\rho=0.761\,04\text{ g/cm}^3$	
748.15	378.54	723.15	433.28	773.15	910.70	$T\text{ }^\circ\text{K}$	$P\text{ bar}$
773.15	416.42	748.15	504.29	$\rho=0.540\text{ g/cm}^3$		547.21	58.68
823.15	490.01	773.15	575.20	$T\text{ }^\circ\text{K}$	$P\text{ bar}$	573.15	355.70
873.15	561.45	823.15	717.57	630.86	181.73	623.15	1 000.00
923.15	630.90	873.15	857.44	648.15	279.33	555.15	147.60
$\rho=0.250\text{ g/cm}^3$		923.15	995.84	673.15	424.98	565.15	261.80
$T\text{ }^\circ\text{K}$	$P\text{ bar}$	$\rho=0.360\text{ g/cm}^3$		698.15	575.37	583.15	477.60
646.275	218.585	$T\text{ }^\circ\text{K}$	$P\text{ bar}$	723.15	729.97	593.15	605.20
673.15	277.78	647.11	220.778	748.15	885.74	603.15	737.20
698.15	332.05	673.15	301.32	$\rho=0.540\text{ g/cm}^3$		613.15	868.90
723.15	385.43	$\rho=0.360\text{ g/cm}^3$		$T\text{ }^\circ\text{K}$	$P\text{ bar}$		
748.15	433.60	$T\text{ }^\circ\text{K}$	$P\text{ bar}$				

narrow vicinity of the critical point. Therefore, on each isochore, the basic data in Table 1 are fitted by the least square method for various simple equations, for example, as shown in the following:

$$P = a_1(\rho)/T^2 + b_1(\rho)/T + c_1(\rho) + d_1(\rho)T \dots\dots\dots (6)$$

$$P = a_2(\rho)/T + b_2(\rho) + c_2(\rho)T \dots\dots\dots (7)$$

$$P = a_3(\rho) + b_3(\rho)T + c_3(\rho)T^2 \dots\dots\dots (8)$$

$$P = a_4(\rho) + b_4(\rho)T + c_4(\rho)T^2 + d_4(\rho)T^3 \dots\dots\dots (9)$$

In these equations, the coefficients $a_1(\rho)$, $b_1(\rho)$, $c_1(\rho)$, $d_1(\rho)$,..... etc. are the functions of density ρ alone. Among these equations, Eq. (9) is found to be the most suitable one for the present purpose.

As is clear from Eqs. (4) and (5), each term including temperature T in Eq. (9) has to be expressed as a term of temperature difference $T - T_{c1}$. Then, Eq. (9) can be rewritten in the following form:

$$P = P_{c1} + a_5(\rho) + b_5(\rho)(T - T_{c1}) + c_5(\rho)(T - T_{c1})^2 + d_5(\rho)(T - T_{c1})^3 \dots\dots\dots (10)$$

From this equation, the critical isotherm $T = T_{c1}$ is found to be as follows:

$$(P)_{T=T_{c1}} = P_{c1} + a_5(\rho) \dots\dots\dots (11)$$

Comparing Eq. (11) with Eq. (5), the coefficient $a_5(\rho)$ must be taken a functional form in which $\rho = \rho_{c1}$ is a real triple root. For the further analysis of the function $a_5(\rho)$, the property values along the critical isotherm of 374.15 °C are obtained graphically from a Pv vs. t diagrams which are drawn for the several isobars such as 200, 225, 250 bar etc. in the critical region, based on the International Skeleton Tables (1963) and other experimental data.

Applying the least square method, we expressed the numerical values of the thermodynamic property

Fig. 2 ρ vs. t diagram for the saturated states in the critical region

along the critical isotherm by the function $a_5(\rho)$ in Eq. (11) as follows:

$$a_5(\rho) = (\rho - \rho_{c1})^3 \sum_{j=0}^8 a_j \rho^j \dots\dots\dots (12)$$

The values of the numerical constants a_j ($j=0 \sim 8$) are given in Table 2.

At the next step, by substituting Eq. (12) into Eq. (10) and arranging the already determined terms in the left hand side of the equation, the following expression was obtained:

Table 2 Numerical constants in Eqs. (12) to (17) and (21)

a_0	+6.924 7	5.128×10^3	c_4	+6.463 9	6.399×10^3
a_1	-3.045 2	1.976×10^4	c_5	+1.051 4	5.325×10^4
a_2	+5.194 2	1.692×10^4	c_6	-4.461 6	2.941×10^4
a_3	-2.549 4	8.623×10^5	c_7	+3.310 2	7.839×10^4
a_4	+9.482 8	5.557×10^5	d_0	-6.482 5	9.699×10^{-6}
a_5	-6.261 0	8.589×10^5	d_1	-2.153 3	1.520×10^1
a_6	-1.674 9	6.290×10^6	d_2	+6.629 1	8.364×10^2
a_7	+2.807 7	7.247×10^6	d_3	-4.344 7	2.241×10^3
a_8	-1.217 6	7.478×10^6	d_4	+8.860 9	6.688×10^3
b_0	-2.421 6	0.207×10^1	d_5	+7.852 0	3.727×10^3
b_1	+8.392 5	9.851×10^2	d_6	-5.220 5	6.807×10^4
b_2	+4.247 1	3.049×10^3	d_7	+1.727 0	7.079×10^4
b_3	-2.621 0	4.285×10^4	d_8	+1.235 0	2.073×10^5
b_4	+5.594 7	8.282×10^4	d_9	-1.152 6	7.085×10^5
b_5	-4.348 7	3.790×10^4	e	-3.992 2	2.453×10^{20}
b_6	+1.088 0	1.496×10^4	u_0	+2.510 9	7.946×10^3
c_0	+2.269 4	7.965×10^1	u_1	+2.998 8	0.480×10^2
c_1	-4.914 4	0.621×10^2	u_2	-3.446 5	0.024×10^1
c_2	+2.288 7	7.613×10^3	u_3	-2.711 0	8.766×10^0
c_3	-4.763 2	5.876×10^3	u_4	+2.476 8	4.921×10^0

Fig. 3 16 isochores on P vs. t diagram

$$\begin{aligned}
 P - P_{c1} - (\rho - \rho_{c1})^3 \sum_{j=0}^8 a_j \rho^j \\
 = b_5(\rho)(T - T_{c1}) + c_5(\rho)(T - T_{c1})^2 \\
 + d_5(\rho)(T - T_{c1})^3 \dots\dots\dots(13)
 \end{aligned}$$

Applying the least square method, we expressed the numerical values of the first term in the right hand side of the above equation, by the following function $b_5(\rho)$:

$$b_5(\rho) = \sum_{j=0}^6 b_j \rho^j \dots\dots\dots(14)$$

In the similar manner, the functions $c_5(\rho)$ and $d_5(\rho)$ were determined as follows:

$$c_5(\rho) = \sum_{j=0}^7 c_j \rho^j \dots\dots\dots(15)$$

(a) Function $a_j(\rho)$ (b) Function $b_j(\rho)$

$$d_5(\rho) = \sum_{j=0}^9 d_j \rho^j \dots\dots\dots(16)$$

The values of the numerical constants in the above equations are given in Table 2.

After examining the computed results of the thermodynamic property values of ordinary water substance in the critical region by Eqs. (13) to (16), it was found that some slight modifications were necessary for the values of specific enthalpy and those of specific isobaric heat capacity along 350°C isotherm. Then, adding one term to Eq. (10) for this improvement, the new equation of state for

(c) Function $c_j(\rho)$ (d) Function $d_j(\rho)$

Fig. 4

ordinary water substance in the critical region was finally determined as follows:

$$P = P_{c1} + (\rho - \rho_{c1})^3 \sum_{j=0}^8 a_j \rho^j + (T - T_{c1}) \sum_{j=0}^6 b_j \rho^j + (T - T_{c1})^2 \sum_{j=0}^7 c_j \rho^j + (T - T_{c1})^3 \sum_{j=0}^9 d_j \rho^j + (T - T_{c1}) T^{-23} e \rho^6 \dots (17)$$

The numerical value of e in the above equation is also given in Table 2. In Fig. 4, the functions of density given in each term of the right hand side of Eq. (17) are shown against ρ . As is clear in Fig. 4 (a), the function $a_5(\rho)$ of the critical isotherm becomes nearly axially symmetric with respect to the critical isochore $\rho = \rho_{c1}$ in this figure.

6. Canonical functions and derived functions of the new equation of state

6.1 Canonical functions of the new equation of state

In order to derive the thermodynamic functions such as enthalpy, entropy, isobaric and isochoric heat capacities from the new equation of state given as Eq. (17), the transformation of the new equation of state into the canonical form $f = f(v, T)$ was performed according to the resolution of the IFC⁽¹³⁾.

Here, the equations of internal energy, enthalpy and entropy can be derived from Eq. (17) as follows:

$$h = u_1(T) - AT^2 \int_{\rho_1}^{\rho} \frac{\partial(P/T)}{\partial T} \frac{d\rho}{\rho^2} + A \frac{P}{\rho} \dots (18)$$

$$s = s(T_1, \rho_1) + \int_{T_1}^T \frac{du_1}{dT} \frac{dT}{T} - A \int_{\rho_1}^{\rho} \frac{\partial P}{\partial T} \frac{d\rho}{\rho^2} \dots (19)$$

$$u = h - APv \dots (20)$$

In the above Eqs. (18) and (19), the values of $u_1(T)$ and $s(T_1, \rho_1)$ were determined based upon the property values along 350°C isotherm. In addition, the necessity for the smoothness in the continuity at the interregional boundaries of the new equation of state with those of compressed water⁽⁴⁾ and of superheated steam⁽⁵⁾ must be taken into consideration. Thus the determined values of $u_1(T)$ and $s(T_1, \rho_1)$ are as follows:

$$u_1(T) = \sum_{j=0}^4 u_j \rho^j \dots (21)$$

$$s(T_1, \rho_1) = 5.24614 \text{ J/g}^\circ\text{K} \dots (22)$$

In Eq. (22), the value of density ρ_1 corresponds to the isochore $v_1 = 9 \text{ cm}^3/\text{g}$. The values of the numerical constants u_j in Eq. (21) are also given in Table 2.

Using the thermodynamic relation $f = u - Ts$, the equation of the canonical function, i.e., that of the dimensionless free energy (Helmholtz function) Ψ , can be derived from Eqs. (18) to (22) in the following form:

$$\begin{aligned} \Psi = & C_{00} + C_{01}\chi + \sum_{j=2}^{11} C_{0j}\chi^{1-j} + C_{012} \ln \chi \\ & + (C_{10} + C_{11}\chi + \sum_{j=2}^6 C_{1j}\chi^{1-j} + C_{17} \ln \chi)(\theta - 1) \\ & + (C_{20} + C_{21}\chi + \sum_{j=2}^7 C_{2j}\chi^{1-j} + C_{28} \ln \chi)(\theta - 1)^2 \\ & + (C_{30} + C_{31}\chi + \sum_{j=2}^9 C_{3j}\chi^{1-j} + C_{310} \ln \chi)(\theta - 1)^3 \\ & + C_4(\theta - 1)^4 + (C_{50} + C_{51}\chi^{-5})\theta^{-23}(\theta - 1) \\ & + C_6 \theta \ln \theta \dots (23) \end{aligned}$$

The values of the numerical constants in the above equation are tabulated in Table 3.

From Eq. (23), the following thermodynamic functions can be derived from the general thermodynamic relations.

$$\sigma = -(\partial \Psi / \partial \theta)_\chi \dots (24)$$

$$\beta = -(\partial \Psi / \partial \chi)_\theta \dots (25)$$

$$\varepsilon = \Psi + \beta\chi + \theta\sigma \dots (26)$$

$$\lambda_\theta = -\theta(\partial^2 \Psi / \partial \theta^2)_\chi + \theta(\partial^2 \Psi / \partial \chi \partial \theta)^2 / (\partial^2 \Psi / \partial \chi^2)_\theta \dots (27)$$

$$\lambda_\chi = -\theta(\partial^2 \Psi / \partial \theta^2)_\chi \dots (28)$$

6.2 Equation of the reduced pressure

From Eqs. (23) and (25), the equation of the reduced pressure β is given as follows:

$$\begin{aligned} \beta = & -\{C_{01} + \sum_{j=2}^{11} (1-j)C_{0j}\chi^{-j} + C_{012}\chi^{-1}\} \\ & -\{C_{11} + \sum_{j=2}^6 (1-j)C_{1j}\chi^{-j} + C_{17}\chi^{-1}\}(\theta - 1) \\ & -\{C_{21} + \sum_{j=2}^7 (1-j)C_{2j}\chi^{-j} + C_{28}\chi^{-1}\}(\theta - 1)^2 \\ & -\{C_{31} + \sum_{j=2}^9 (1-j)C_{3j}\chi^{-j} + C_{310}\chi^{-1}\}(\theta - 1)^3 \\ & + 5C_{51}\chi^{-6}\theta^{-23}(\theta - 1) \dots (29) \end{aligned}$$

In this equation, for the reduced temperature range

Table 3 Numerical constants in Eq. (23)

C_{00}	-6.842 1	3.780×10^0	C_{22}	+4.314 3	0.538×10^1
C_{01}	-1.725 4	0.326×10^{-2}	C_{23}	-1.416 1	9.313×10^1
C_{02}	-7.771 7	5.039×10^0	C_{24}	+4.041 7	2.459×10^0
C_{03}	+4.204 6	0.752×10^0	C_{25}	+1.555 4	6.326×10^0
C_{04}	-2.768 0	7.038×10^0	C_{26}	-1.665 6	8.935×10^0
C_{05}	+2.104 1	9.707×10^0	C_{27}	+3.248 8	1.158×10^{-1}
C_{06}	-1.146 4	9.588×10^0	C_{28}	+2.936 5	5.325×10^1
C_{07}	+2.231 3	8.085×10^{-1}	C_{30}	+1.815 9	2.366×10^1
C_{08}	+1.162 5	0.363×10^{-1}	C_{31}	+7.948 4	1.842×10^{-6}
C_{09}	-8.209 0	0.544×10^{-2}	C_{32}	+8.088 5	9.747×10^1
C_{010}	+1.941 2	9.239×10^{-2}	C_{33}	-8.361 5	3.380×10^1
C_{011}	-1.694 7	0.576×10^{-3}	C_{34}	+3.586 3	6.517×10^1
C_{012}	-4.311 5	5.370×10^0	C_{35}	+7.518 9	5.954×10^0
C_{10}	-2.571 5	7.554×10^2	C_{36}	-1.261 6	0.640×10^1
C_{11}	+7.086 3	6.085×10^{-1}	C_{37}	+1.097 1	7.462×10^0
C_{12}	+1.236 7	9.455×10^1	C_{38}	+2.121 4	5.492×10^0
C_{13}	-1.203 8	9.004×10^1	C_{39}	-5.465 2	9.566×10^{-1}
C_{14}	+5.404 3	7.422×10^0	C_{310}	+8.328 7	5.413×10^0
C_{15}	-9.938 6	5.043×10^{-1}	C_4	-2.067 0	7.558×10^1
C_{16}	+6.275 2	3.182×10^{-2}	C_{50}	+2.759 7	1.776×10^{-6}
C_{17}	-7.747 4	3.016×10^0	C_{51}	-5.090 7	3.985×10^{-4}
C_{20}	-1.512 2	8.479×10^2	C_6	+2.106 3	6.332×10^2
C_{21}	-4.298 8	5.092×10^0			

0.962 691 179 $\leq \theta < 1$, the least root of χ should be $\chi < 1$ and the largest one should be $\chi > 1$.

6.3 Equation of the reduced entropy

From Eqs. (23) and (24), the equation of the reduced entropy σ is given as follows:

$$\begin{aligned} \sigma = & -(C_{10} + C_{11}\chi + \sum_{j=2}^6 C_{1j}\chi^{1-j} + C_{17} \ln \chi + C_6) - 2(C_{20} + C_{21}\chi + \sum_{j=2}^7 C_{2j}\chi^{1-j} + C_{28} \ln \chi)(\theta - 1) \\ & - 3(C_{30} + C_{31}\chi + \sum_{j=2}^9 C_{3j}\chi^{1-j} + C_{310} \ln \chi)(\theta - 1)^2 - 4C_4(\theta - 1)^3 + (C_{50} + C_{51}\chi^{-5})(22\theta^{-23} - 23\theta^{-24}) \\ & - C_6 \ln \theta \dots \dots \dots (30) \end{aligned}$$

6.4 Equation of the reduced enthalpy

From Eqs. (23) and (26), the equation of the reduced enthalpy ϵ is given as follows:

$$\begin{aligned} \epsilon = & \{(C_{00} - C_{012} - C_{10} - C_6) - C_{11}\chi + \sum_{j=2}^{11} jC_{0j}\chi^{1-j} - \sum_{j=2}^6 C_{1j}\chi^{1-j} + (C_{012} - C_{17}) \ln \chi\} \\ & + \{(-C_{17} - 2C_{20} - C_6) - (C_{11} + 2C_{21})\chi + \sum_{j=2}^6 (j-1)C_{1j}\chi^{1-j} - 2\sum_{j=2}^7 C_{2j}\chi^{1-j} - 2C_{28} \ln \chi\}(\theta - 1) \\ & + \{(-C_{20} - C_{28} - 3C_{30}) - (2C_{21} + 3C_{31})\chi + \sum_{j=2}^7 (j-2)C_{2j}\chi^{1-j} - 3\sum_{j=2}^9 C_{3j}\chi^{1-j} - (C_{28} + 3C_{310}) \ln \chi\}(\theta - 1)^2 \\ & + \{(-2C_{30} - C_{310} - 4C_4) - 3C_{31}\chi + \sum_{j=2}^9 (j-3)C_{3j}\chi^{1-j} - 2C_{310} \ln \chi\}(\theta - 1)^3 - 3C_4(\theta - 1)^4 \\ & + (23C_{50} + 28C_{51}\chi^{-5})\theta^{-22} - (24C_{50} + 29C_{51}\chi^{-5})\theta^{-23} \dots \dots \dots (31) \end{aligned}$$

6.5 Equation of the reduced isobaric heat capacity

From Eqs. (23) and (27), the equation of the reduced isobaric heat capacity λ_p is given as follows:

$$\begin{aligned} \lambda_p = & -2(C_{20} + C_{21}\chi + \sum_{j=2}^7 C_{2j}\chi^{1-j} + C_{28} \ln \chi)\theta - 6(C_{30} + C_{31}\chi + \sum_{j=2}^9 C_{3j}\chi^{1-j} + C_{310} \ln \chi)\theta(\theta - 1) \\ & - 12C_4\theta(\theta - 1)^2 - (C_{50} + C_{51}\chi^{-5})(506\theta^{-23} - 552\theta^{-24}) - C_6 \\ & + \theta \{C_{11} + \sum_{j=2}^6 (1-j)C_{1j}\chi^{-j} + C_{17}\chi^{-1}\} + 2\{C_{21} + \sum_{j=2}^7 (1-j)C_{2j}\chi^{-j} + C_{28}\chi^{-1}\}(\theta - 1) \\ & + 3\{C_{31} + \sum_{j=2}^9 (1-j)C_{3j}\chi^{-j} + C_{310}\chi^{-1}\}(\theta - 1)^2 - 5C_{51}\chi^{-6}(-22\theta^{-23} + 23\theta^{-24})^2 \\ & / \{ \sum_{j=2}^{11} j(j-1)C_{0j}\chi^{-j-1} - C_{012}\chi^{-2} \} + \{ \sum_{j=2}^6 j(j-1)C_{1j}\chi^{-j-1} - C_{17}\chi^{-2} \}(\theta - 1) \\ & + \{ \sum_{j=2}^7 j(j-1)C_{2j}\chi^{-j-1} - C_{28}\chi^{-2} \}(\theta - 1)^2 + \{ \sum_{j=2}^9 j(j-1)C_{3j}\chi^{-j-1} \\ & - C_{310}\chi^{-2} \}(\theta - 1)^3 + 30C_{51}\chi^{-7}(\theta^{-22} - \theta^{-23}) \dots \dots \dots (32) \end{aligned}$$

6.6 Equation of the reduced isochoric heat capacity

From Eqs. (23) and (28), the equation of the reduced isochoric heat capacity λ_v is given as follows:

$$\begin{aligned} \lambda_v = & -2(C_{20} + C_{21}\chi + \sum_{j=2}^7 C_{2j}\chi^{1-j} + C_{28} \ln \chi)\theta - 6(C_{30} + C_{31}\chi + \sum_{j=2}^9 C_{3j}\chi^{1-j} + C_{310} \ln \chi)\theta(\theta - 1) \\ & - 12C_4\theta(\theta - 1)^2 - (C_{50} + C_{51}\chi^{-5})(506\theta^{-23} - 552\theta^{-24}) - C_6 \dots \dots \dots (33) \end{aligned}$$

6.7 Equation of the isentropic exponent

The isentropic exponent k of the steam can be expressed by the following equation⁽¹⁴⁾,

$$k = -\frac{v}{P} \left(\frac{\partial P}{\partial v} \right)_s = -\frac{c_p}{c_v} \frac{v}{P} \left(\frac{\partial P}{\partial v} \right)_T \dots \dots \dots (34)$$

Using the dimensionless quantities, the above equation can be rewritten as follows:

$$k = -\frac{\lambda_p}{\lambda_v} \frac{\chi}{\beta} \left(\frac{\partial \beta}{\partial \chi} \right)_\theta \dots \dots \dots (35)$$

7. Computed results of the new equation of state

7.1 Computed results of the specific volume

For the computations of the thermodynamic property values from the new equation of state, an electronic computer IBM 7090 was used, and a part of those computed results was reported to the IFC⁽¹⁵⁾.

In computing the specific volume, the numerical calculations with Newton-Raphson's iterative method were applied, because the formulated new equation of state, Eq. (17) is given in such a functional form as $P = P(v, T)$. The computed results of the specific volume are tabulated in Table 4. Also the computed values for the saturated states are tabulated with other property values in Table 10.

7.2 Computed results of the specific enthalpy

Using the computed values of the specific volume described in the preceding section 7.1, the values of specific enthalpy h were computed by Eqs. (17), (18) and (21). These computed results at the grid points of the International Skeleton Tables (1963) are tabulated in Table 5 and those for the saturated states are also tabulated in Table 10. In Fig. 5, comparisons of the computed values of specific volume and

Table 4 Computed specific volume v (cm^3/g)
 upper figures: computed values, lower figures: (computed values-Skeleton Table values)/tolerance

$t^\circ\text{C}$ P bar	350	375	400	425	450	475	500	550	600	650
175	1.716 32 0/2	10.550 6 -2/4								
200	1.666 19 1/2	7.655 7 -2/3	9.942 8 -1/3							
225	1.629 01 -1/2	2.511 7 -2/4	7.872 7 1/3							
250	1.599 29 -1/2	1.983 4 0/2	6.014 6 1/3							
275	1.574 46 -1.54/2	1.863 60 -1/10	4.171 9 -2/3							
300	1.553 12 -1.88/2	1.792 33 -5/8	2.830 81 1/2	5.312 16 14/20						
350	1.517 72 -1/3	1.701 62 -3/6	2.110 97 0/10	3.419 61 -10/12	4.964 94 -9/14					
400	1.488 93 0/3	1.641 47 -3/5	1.909 21 -3/7	2.548 40 2/9	3.674 86 -9/12	4.762 38 4/12				
450	1.464 66 1/3	1.596 46 -3/5	1.801 39 -3/6	2.190 04 -1/7	2.913 46 -3/9	3.804 09 -9.91/10	4.628 91 1/10	5.943 22 9/11	6.976 97 -5/13	7.872 46 -13/15
500	1.443 68 1/3	1.560 49 -4/5	1.729 14 -2/5	2.006 79 -3/6	2.492 14 0/6	3.164 76 -5/8	3.876 46 -7.54/8	5.116 12 2/10	6.108 09 0/12	6.957 00 -3/14
550	1.425 19 1/3	1.530 61 -2/5	1.675 26 -2/5	1.892 92 -3/5	2.243 52 -1/5	2.750 38 0/6	3.335 96 -6/7	4.460 78 -3/8	5.404 33 0/10	6.213 44 4/12
600	1.408 67 2/3	1.505 04 -2/5	1.632 47 -2/4	1.812 86 -3/4	2.083 70 -1/4	2.474 00 0/5	2.951 59 1/6	3.944 77 -5/8	4.828 73 -2/9	5.598 15 6/11
650	1.393 76 1/3	1.482 72 -1/5	1.597 13 -2/4	1.752 06 -3.94/4	1.972 34 -3.66/4	2.281 97 -1/5	2.673 38 1/5	3.540 37 -3/7	4.356 38 -4/8	5.083 30 3/10
700	1.380 14 0/3	1.462 92 -1/5	1.567 08 -2/4	1.703 50 -2/4	1.889 54 -2/4	2.142 97 -1/4	2.466 87 1/5	3.222 14 1/6	3.968 18 -3/7	4.649 79 2/9
750	1.367 62 1/3	1.445 12 -1/4	1.541 00 -2/4	1.663 28 -2/4	1.824 76 -2/4	2.038 32 -2/4	2.309 94 0/5	2.968 72 4/6	3.648 01 0/7	4.283 36 0/8
800	1.356 04 1/3	1.428 99 -1/4	1.517 97 -1/3	1.629 06 -2/3	1.772 17 -3/4	1.956 60 -1/4	2.188 06 -1/4	2.763 96 4/6	3.382 04 2/7	3.972 40 0/8
850	1.345 28 0/4	1.414 25 -1/4	1.497 41 -1/3	1.599 38 -2.62/3	1.728 19 -2.81/3	1.890 72 -1/4	2.091 36 -1/4	2.596 36 2/5	3.158 87 4/6	3.707 05 1/8
900	1.335 19 1/4	1.400 67 0/4	1.478 83 -1/3	1.573 24 -2.76/3	1.690 60 -2/3	1.836 18 -1/4	2.012 95 -1/4	2.457 81 0/5	2.969 59 4/6	3.478 94 1/7
950	1.325 72 2/4	1.388 08 0/4	1.461 90 -1/3	1.549 92 -2/3	1.657 88 -2/3	1.790 00 0/4	1.948 08 0/4	2.342 41 -2/5	2.807 46 1/6	3.281 14 -1/7
1 000	1.316 77 3/4	1.376 36 0/4	1.446 38 -1/3	1.528 89 -1/3	1.628 98 -1/3	1.750 18 0/4	1.893 38 1/4	2.245 67 -2/5	2.667 52 -2/5	3.108 05 -3/6

Fig. 5 Comparison of the computed values of specific volume and enthalpy with the values of the International Skeleton Tables (1963)

of specific enthalpy with the Skeleton Table values are made, in which the solid line curve and the broken line curve are corresponding to specific volume and specific enthalpy respectively.

7.3 Computed results of the specific entropy

In the same way as for the computations of specific enthalpy, the values of specific entropy were computed by Eqs. (17), (19) and (22). The computed results are tabulated in Table 6 and in Table 10.

7.4 Computed results of the specific isobaric and isochoric heat capacities and the isentropic exponent

The specific isobaric and isochoric heat capacities were computed using the following thermodynamic relations:

$$c_p = c_v - AT \frac{(\partial P / \partial T)_v^2}{(\partial P / \partial v)_T} \dots \dots \dots (36)$$

$$c_v = \frac{du_1(T)}{dT} - AT \int_{\rho_1}^{\rho} \left(\frac{\partial^2 P}{\partial T^2} \right) \frac{d\rho}{\rho^2} \dots \dots \dots (37)$$

The computed results of these specific heat capacities are tabulated in Tables 7 and 8 respectively. And the computed results for the specific isobaric heat capacity c_p are shown against pressure P in Fig. 6.

The values of the isentropic exponent k were computed by Eq. (34) and their computed results are tabulated in Table 9. And the computed results of the isentropic exponent k are shown against the temperature t in Fig. 7⁽¹⁶⁾.

7.5 Computed results of the thermodynamic property values at the saturated states

The computed results of v , h , s , c_p , c_v and k for the saturated water and steam are tabulated in Table 10. In these computations, the values of the saturation pressure P_s were obtained by the new equation of the saturation pressure formulated at Keio University⁽³⁾.

The isentropic exponent at the critical point k_{c1} was calculated by the following equation which could

Table 5 Computed specific enthalpy h (J/g)
upper figures: computed values, lower figures: (computed values-Skeleton Table values)/tolerance

t °C	350	375	400	425	450	475	500	550	600	650
P bar										
175	1 661.61 -1/3	2 754.20 -1/8								
200	1 644.91 -1/3	2 602.92 -2/8	2 818.49 -1/8							
225	1 632.44 -1/3	1 982.68 -3/12	2 714.52 0/8							
250	1 622.49 -1/3	1 848.77 -1/8	2 578.12 -2/8							
275	1 614.24 -1/3	1 812.64 -1/8	2 376.13 -7/8							
300	1 607.23 -2/3	1 790.16 -1/6	2 157.84 1/8	2 612.61 -1/6						
350	1 595.91 -2/3	1 760.84 -1/6	1 989.14 -3/8	2 370.02 5/6	2 673.49 1/6					
400	1 587.11 -2.89/3	1 741.28 -2/6	1 930.17 -4/8	2 201.94 -1/6	2 510.80 -3/6	2 743.62 3/6				
450	1 580.11 -2/3	1 726.85 -2/6	1 896.61 -4/8	2 112.82 -2/6	2 379.41 -1/6	2 624.62 1/6	2 816.23 3/6	3 089.31 1/8	3 295.04 -3/10	3 484.43 6/10
500	1 574.45 -2.55/3	1 715.62 -1/6	1 873.69 -4/8	2 061.01 -3/6	2 288.46 0/6	2 522.29 0/6	2 724.31 1/6	3 024.60 2/8	3 246.82 -2/10	3 444.89 6/10
550	1 569.85 -2/3	1 706.62 -2/6	1 856.65 -3/8	2 026.77 -3/8	2 226.21 -2/8	2 441.80 3/8	2 642.63 2/8	2 960.61 1/8	3 198.26 -2/10	3 405.42 5/10
600	1 566.10 -2/3	1 699.24 -3/6	1 843.33 -4/8	2 002.01 -3/8	2 182.31 -1/8	2 379.86 2/8	2 573.87 3/8	2 899.80 0/8	3 150.20 -3/10	3 366.10 4/10
650	1 563.07 -2/3	1 693.12 -3/6	1 832.60 -3/8	1 983.05 -3/8	2 149.97 -1/8	2 332.17 2/8	2 517.07 3/8	2 843.98 0/8	3 103.71 -3/10	3 327.37 3/10
700	1 560.64 -1/3	1 688.01 -3/6	1 823.78 -4/8	1 967.98 -3/8	2 125.15 -1/8	2 295.11 1/8	2 470.40 2/8	2 793.86 1/8	3 059.69 -2/10	3 289.77 2/10
750	1 558.72 -1/4	1 683.71 -3/6	1 816.43 -4/8	1 955.68 -2/8	2 105.42 -1/8	2 265.84 1/8	2 432.13 2/8	2 749.32 1/8	3 018.68 -2/10	3 253.81 1/10
800	1 557.25 -2/4	1 680.10 -4/6	1 810.25 -4/8	1 945.44 -3/8	2 089.32 -1/8	2 242.26 1/8	2 400.71 3/8	2 709.95 1/8	2 980.87 -2/10	3 219.83 1/10
850	1 556.17 -1/4	1 677.07 -4/6	1 805.02 -3/8	1 936.82 -1/8	2 075.92 -1/8	2 222.89 1/8	2 374.78 2/8	2 675.28 1/8	2 946.17 -2/10	3 188.00 1/10
900	1 555.44 -2/4	1 674.53 -3/6	1 800.58 -3/8	1 929.49 -3/8	2 064.58 0/8	2 206.69 1/8	2 353.17 2/8	2 644.94 1/8	2 914.41 -2/10	3 158.31 1/10
950	1 555.02 -1/5	1 672.43 -4/6	1 796.82 -2/8	1 923.22 -2/8	2 054.87 -1/8	2 192.92 0/8	2 334.97 2/8	2 618.54 1/8	2 885.43 -2/10	3 130.68 2/10
1 000	1 554.88 0/5	1 670.10 -3/6	1 793.63 -2/8	1 917.83 -2/8	2 046.48 -1/8	2 181.08 0/8	2 319.44 1/8	2 595.69 1/8	2 859.09 -2/10	3 104.98 2/10

be derived from Eqs. (34), (36) and (3).

$$k_{e1} = \frac{v_{e1}}{P_{e1}} \left\{ \frac{AT_{e1}}{(c_v)_{e1}} \left[\left(\frac{\partial P}{\partial T} \right)_{v_{e1}} \right]^2 \right\} \dots \dots \dots (38)$$

In Tables 4 to 10, the regions just outside of the bold solid lines show the regions where the present new equation of state is not applied although it is valid, taking into consideration the practical applicability and also the combinations with other sub-

formulations devised at Keio University^{(3)~(5)}.

7.6 Computed results at the interregional boundaries

The interregional boundary between the present new equation of state for the critical region and the subformulation for the compressed water⁽⁴⁾ was determined along 350°C isotherm in the range of pressures from the saturation pressure to 1 000 bar.

Table 6 Computed specific entropy s (J/g°K)

$t^\circ\text{C}$ P bar	350	375	400	425	450	475	500	550	600	650
175	3.761 54	5.497 09								
200	3.727 97	5.228 64	5.555 68							
225	3.701 34	4.248 99	5.368 23							
250	3.678 90	4.034 21	5.139 86							
275	3.659 29	3.971 04	4.820 87							
300	3.641 78	3.929 32	4.483 91	5.148 99						
350	3.611 31	3.870 62	4.215 70	4.770 83	5.198 57					
400	3.585 13	3.827 57	4.113 26	4.509 20	4.944 05	5.260 89				
450	3.562 04	3.792 83	4.049 66	4.364 75	4.739 85	5.073 39	5.325 50	5.668 45	5.911 29	6.122 20
500	3.541 30	3.763 33	4.002 52	4.275 57	4.595 53	4.913 48	5.179 23	5.556 34	5.818 69	6.039 30
550	3.522 41	3.737 52	3.964 57	4.212 58	4.493 14	4.786 23	5.050 37	5.449 60	5.730 18	5.960 94
600	3.505 03	3.714 44	3.932 50	4.163 86	4.417 51	4.686 04	4.941 18	5.350 25	5.645 90	5.886 41
650	3.488 93	3.693 49	3.904 57	4.123 95	4.358 79	4.606 44	4.849 57	5.259 76	5.566 40	5.815 58
700	3.473 90	3.674 25	3.879 73	4.090 01	4.311 13	4.542 14	4.772 62	5.178 37	5.492 18	5.748 52
750	3.459 80	3.656 38	3.857 27	4.060 33	4.271 01	4.489 06	4.707 69	5.105 49	5.423 44	5.685 40
800	3.446 51	3.639 73	3.836 72	4.033 88	4.236 33	4.444 21	4.652 52	5.040 27	5.360 03	5.626 26
850	3.433 97	3.624 09	3.817 76	4.009 96	4.205 68	4.405 47	4.605 16	4.981 89	5.301 57	5.571 00
900	3.422 05	3.609 33	3.800 12	3.988 11	4.178 19	4.371 37	4.563 95	4.929 69	5.247 67	5.519 40
950	3.410 70	3.595 33	3.783 60	3.967 95	4.153 19	4.340 86	4.527 60	4.883 05	5.197 95	5.471 17
1 000	3.399 86	3.582 01	3.768 06	3.949 22	4.130 24	4.313 20	4.495 10	4.841 37	5.152 12	5.426 04

Table 7 Computed specific isobaric heat capacity c_p (J/g°K)

$t^\circ\text{C}$ P bar	350	375	400	425	450	475	500	550	600	650
175	9.238	7.321								
200	8.056	12.805	6.399							
225	7.377	105.12	8.693							
250	6.920	14.015	13.361							
275	6.584	10.253	24.712							
300	6.323	8.759	24.340	11.251						
350	5.935	7.374	12.015	15.438	9.236					
400	5.651	6.684	8.794	12.744	11.064	7.764				
450	5.428	6.257	7.495	9.961	10.697	8.733	6.706	4.561	3.825	3.860
500	5.245	5.960	6.782	8.325	9.592	8.846	7.292	4.996	4.065	3.975
550	5.088	5.740	6.323	7.366	8.508	8.495	7.489	5.371	4.305	4.105
600	4.949	5.568	5.999	6.751	7.654	7.987	7.425	5.641	4.525	4.236
650	4.825	5.429	5.756	6.324	7.027	7.458	7.225	5.800	4.709	4.359
700	4.711	5.314	5.565	6.007	6.567	6.980	6.957	5.873	4.850	4.468
750	4.605	5.216	5.410	5.761	6.220	6.582	6.662	5.884	4.953	4.558
800	4.506	5.131	5.282	5.563	5.949	6.261	6.375	5.849	5.023	4.632
850	4.411	5.058	5.174	5.399	5.732	6.004	6.118	5.777	5.069	4.691
900	4.320	4.993	5.081	5.260	5.553	5.796	5.899	5.677	5.093	4.738
950	4.233	4.934	5.001	5.140	5.401	5.625	5.716	5.559	5.096	4.777
1 000	4.147	4.882	4.930	5.034	5.269	5.481	5.566	5.435	5.079	4.807

In Table 11, the computed results of v , h , s , c_p and g at the interregional boundary with two subformulations and their differences are tabulated. In Table 11, the term "Prague Value" means the recommended values for the allowable discrepancies of the property values given at the first meeting of the IFC⁽¹³⁾.

Another boundary between the present new equation of state for the critical region and the sub-

formulation for the superheated steam was also given by the following equation, in the range of temperatures from 350°C to 600°C,

$$\beta_L = M_0 + M_1\theta + M_2\theta^2 \dots\dots\dots(39)$$

Fig. 6 Computed specific isobaric heat capacity along isotherms

Fig. 7 Computed isentropic exponent along isobars

Table 8 Computed specific isochoric heat capacity c_v (J/g·K)

$t^\circ\text{C}$	350	375	400	425	450	475	500	550	600	650
P bar										
175	3.000	2.834								
200	2.954	3.168	2.721							
225	2.922	3.498	2.952							
250	2.896	3.198	3.214							
275	2.876	3.117	3.452							
300	2.859	3.070	3.409	3.102						
350	2.831	3.017	3.148	3.257	2.933					
400	2.808	2.987	3.042	3.145	3.039	2.754				
450	2.787	2.969	2.986	3.033	3.016	2.829	2.587	2.243	2.206	2.537
500	2.767	2.958	2.950	2.962	2.953	2.839	2.643	2.298	2.227	2.519
550	2.748	2.951	2.925	2.915	2.898	2.816	2.664	2.343	2.248	2.506
600	2.729	2.946	2.908	2.881	2.858	2.789	2.664	2.376	2.269	2.498
650	2.709	2.944	2.895	2.853	2.828	2.767	2.658	2.401	2.291	2.496
700	2.689	2.943	2.885	2.831	2.802	2.750	2.654	2.420	2.313	2.501
750	2.667	2.942	2.879	2.812	2.780	2.736	2.653	2.438	2.336	2.511
800	2.644	2.942	2.874	2.796	2.759	2.724	2.654	2.456	2.360	2.526
850	2.621	2.943	2.871	2.782	2.740	2.711	2.655	2.477	2.386	2.547
900	2.596	2.943	2.870	2.770	2.721	2.697	2.655	2.501	2.416	2.572
950	2.569	2.944	2.870	2.759	2.704	2.683	2.654	2.527	2.449	2.602
1 000	2.541	2.945	2.871	2.751	2.687	2.667	2.650	2.553	2.486	2.637

where

$$M_0 = 1.303\,440\,24 \times 10^1,$$

$$M_1 = -2.884\,429\,19 \times 10^1,$$

$$M_2 = 1.670\,445\,79 \times 10^1.$$

The computed results of v , h , s , c_p and g with these two subformulations along the boundary, Eq. (39), and their differences were also obtained for the temperature intervals of 5°C between 350°C and 600°C. Those results are reported in another paper⁽⁵⁾.

8. Inclination of the critical isochore at the critical point

As an example to check the new equation of state for ordinary water substance in the critical region, the first partial derivative at the critical point $[(\partial P/\partial T)_v]_{c1}$ is examined below.

This first derivative means the inclination of the critical isochore at the critical point on the P vs. T diagram, and it is well known that it is equal to the inclination of the saturation curve at the critical point,^{(18) (19)} i.e.,

$$[(\partial P/\partial T)_v]_{c1} = (dP_s/dT)_{c1} \dots\dots\dots (40)$$

Equation (40) can be written in the dimensionless expression as follows:

$$\left[\frac{T}{P} \left(\frac{\partial P}{\partial T} \right)_v \right]_{c1} = \left(\frac{T}{P_s} \frac{dP_s}{dT} \right)_{c1} \dots\dots\dots (41)$$

The left hand side of the above equation was calculated by the new equation of state and was compared with the reported values by other investigators in Table 12. In this comparison, the computations were conducted using the agreed value

of the critical pressure $P_{c1} = 221.2$ bar. As is clear from Table 12, the dimensionless value of the left hand side of Eq. (41) was found to be nearly equal to 7.8, and also a good coincidence with those by other investigators was also observed.

According to the indications by H.D. Baehr^{(18) (19)}, and also by L. Ziegler⁽⁶⁾, the second partial derivative at the critical point $[(\partial^2 P/\partial T^2)_v]_{c1}$ must satisfy the following conditions,

$$[(\partial^2 P/\partial T^2)_v]_{c1} = 0$$

or

$$[(\partial^2 P/\partial T^2)_v]_{c1} \neq 0 \dots\dots\dots (42)$$

The calculated results of this second partial derivative in Eq. (42) by the new equation of state was 1.816×10^{-3} bar/°K².

9. Conclusions

The new equation of state for ordinary water substance in the critical region was formulated, which is valid in the ranges of temperatures from 350°C to 650°C and of pressures from 165.37 bar to 1 000 bar, where the specific volume is less than about 10 cm³/g. The new equation of state coincides satisfactorily with the International Skeleton Tables (1963) within the tolerances.

The functional form of the new equation of state is comparatively simple, because only one term is added to the power series of the temperature difference $T - T_{c1}$ in which the order of polynomials is up to only the third.

The equations of state by H. D. Baehr et

Table 9 Computed isentropic exponent

$t^\circ\text{C}$	350	375	400	425	450	475	500	550	600	650
P bar										
175	12.553	1.274								
200	13.422	1.352	1.302							
225	13.901	2.522	1.335							
250	14.168	5.127	1.371							
275	14.309	6.390	1.503							
300	14.372	7.241	2.069	1.395						
350	14.362	8.328	3.773	1.718	1.432					
400	14.256	8.976	5.014	2.457	1.659	1.478				
450	14.107	9.387	5.866	3.300	2.070	1.659	1.525			
500	13.939	9.656	6.476	4.042	2.566	1.935	1.677			
550	13.764	9.835	6.928	4.650	3.071	2.259	1.883			
600	13.589	9.954	7.270	5.144	3.548	2.595	2.114			
650	13.418	10.031	7.534	5.547	3.978	2.928	2.350	1.841	1.611	1.448
700	13.251	10.079	7.741	5.878	4.360	3.253	2.583	1.975	1.690	1.491
750	13.090	10.106	7.904	6.153	4.697	3.563	2.814	2.106	1.772	1.539
800	12.935	10.117	8.033	6.383	4.993	3.857	3.044	2.229	1.853	1.588
850	12.788	10.116	8.136	6.576	5.254	4.131	3.273	2.344	1.926	1.636
900	12.645	10.106	8.217	6.737	5.483	4.387	3.500	2.457	1.990	1.680
950	12.509	10.090	8.281	6.873	5.684	4.623	3.723	2.573	2.045	1.717
1 000	12.378	10.068	8.331	6.986	5.860	4.840	3.939	2.696	2.094	1.746

Table 10 Computed thermodynamic property values for the saturated water and steam

Temperature C°	Saturation pressure		Specific volume of the saturated water		Specific volume of the saturated steam		Specific enthalpy of the saturated water	
	Computed values	(Computed values—Skeleton Table values)/Tolerance	Computed values	(Computed values—Skeleton Table values)/Tolerance	Computed values	(Computed values—Skeleton Table values)/Tolerance	Computed values	(Computed values—Skeleton Table values)/Tolerance
	bar		cm³/g		cm³/g		J/g	
350	165.3513	-2/4	1.74171	0.71/1	8.79780	-7/35	1669.97	-2/3
360	186.7507	1/5	1.89355	0/4	6.92839	-15/40	1759.32	-2.68/3
370	210.5403	1/5	2.2088	-1/2	4.9697	4/10	1889.34	-3/6
371	213.0644	0/10	2.2740	-1.6/2	4.7171	4/10	1909.97	-3/6
372	215.6164	-1/11	2.3610	-2/3	4.4367	4/11	1935.27	-2/9
373	218.197	0/1	2.4951	-1/4	4.0822	3/12	1970.27	1/14
374	220.805	-0.95/1	2.8420	4/15	3.4618	-1/12	2046.28	14/20
374.15	221.200	0/1	3.1700	0/15	3.1700	0/15	2107.04	12/30

Temperature °C	Specific enthalpy of the saturated steam		Specific entropy of the saturated water	Specific entropy of the saturated steam	Isobaric heat capacity of the saturated water	Isobaric heat capacity of the saturated steam	Isochoric heat capacity of the saturated water	Isochoric heat capacity of the saturated steam	Isentropic exponent of the saturated steam
	Computed values	(Computed values—Skeleton Table values)/Tolerance	Computed values	Computed values	Computed values	Computed values	Computed values	Computed values	Computed values
	J/g		J/g°K	J/g°K	J/g°K	J/g°K	J/g°K	J/g°K	
350	2572.88	7.88/8	3.77762	5.22604	9.998	15.365	3.024	3.185	1.336
360	2487.06	6/8	3.91366	5.06278	14.512	24.704	3.172	3.386	1.394
370	2342.72	11.72/12	4.10969	4.81456	42.9	76.9	3.370	3.616	1.460
371	2317.28	12/14	4.14087	4.77313	56.6	102	3.404	3.642	1.479
372	2286.65	14/16	4.17919	4.72381	84.2	151	3.446	3.667	1.506
373	2243.63	14/18	4.23244	4.65548	164	298	3.504	3.692	1.554
374	2155.24	9/30	4.34890	4.51727	1.4×10^8	3.7×10^8	3.615	3.698	1.705
374.15	2107.04	12/30	4.44260	4.44260	4×10^{17}	4×10^{17}	3.674	3.674	1.83

Table 11 Computed thermodynamic property values at the interregional boundary of 350°C isotherm

Pressure	Specific volume				Specific enthalpy			Specific entropy			Specific free enthalpy			Specific isobaric heat capacity			
	v_1	v_2	$(v_1 - v_2) \times 10^4$	$\frac{v_1 - v_2}{\frac{1}{2}(v_1 + v_2)} \times 10^4$	h_1	h_2	$h_1 - h_2$	s_1	s_2	$(s_1 - s_2) \times 10^4$	g_1	g_2	$g_1 - g_2$	c_{p1}	c_{p2}	$(c_{p1} - c_{p2})$	$\frac{c_{p1} - c_{p2}}{\frac{1}{2}(c_{p1} + c_{p2})}$
	bar	cm³/g	cm³/g		J/g	J/g	J/g	J/g°K	J/g°K	J/g°K	J/g	J/g	J/g	J/g°K	J/g°K	J/g°K	
Prague value				5			0.2			2			0.2				0.01
$P_s = 165.37$	1.74149	1.74171	-2.2	-1.3	1669.01	1669.97	-0.96	3.77530	3.77762	-23.2	-683.56	-684.06	0.50	9.894	9.998	-0.104	-0.01
175	1.71566	1.71632	-6.6	-3.8	1660.55	1661.61	-1.06	3.75904	3.76154	-25.0	-681.90	-682.39	0.49	9.125	9.238	-0.113	-0.01
200	1.66622	1.66619	0.3	0.2	1643.88	1644.91	-1.03	3.72551	3.72797	-24.6	-677.67	-678.17	0.50	7.819	8.056	-0.237	-0.03
225	1.62966	1.62901	6.5	4.0	1631.84	1632.44	-0.60	3.69958	3.70134	-17.6	-673.56	-674.05	0.49	7.066	7.377	-0.311	-0.04
250	1.60044	1.59929	11.5	7.2	1622.60	1622.49	0.11	3.67827	3.67890	-6.3	-669.52	-670.02	0.50	6.614	6.920	-0.306	-0.05
275	1.57608	1.57446	16.2	10.3	1615.18	1614.24	0.94	3.66000	3.65929	7.1	-665.55	-666.05	0.50	6.337	6.584	-0.247	-0.04
300	1.55514	1.55312	20.2	13.0	1609.01	1607.23	1.78	3.64382	3.64178	20.4	-661.64	-662.14	0.50	6.164	6.323	-0.159	-0.03
350	1.52022	1.51772	25.0	16.5	1599.14	1595.91	3.23	3.61565	3.61131	43.4	-653.95	-654.47	0.52	5.982	5.935	0.047	0.01
400	1.49147	1.48893	25.4	17.0	1591.38	1587.11	4.27	3.59112	3.58513	59.9	-646.48	-646.96	0.48	5.891	5.651	0.240	0.04
450	1.46687	1.46466	22.1	15.1	1585.00	1580.11	4.89	3.56901	3.56204	69.7	-639.03	-639.58	0.55	5.825	5.428	0.397	0.07
500	1.44531	1.44368	16.3	11.3	1579.60	1574.45	5.15	3.54866	3.54130	73.6	-631.75	-632.31	0.56	5.757	5.245	0.512	0.09
550	1.42611	1.42519	9.2	6.5	1574.96	1569.85	5.11	3.52969	3.52241	72.8	-624.57	-625.14	0.57	5.678	5.088	0.590	0.11
600	1.40883	1.40867	1.6	1.1	1570.92	1566.10	4.82	3.51184	3.50503	68.1	-617.49	-618.06	0.57	5.584	4.949	0.635	0.12
650	1.39315	1.39376	-6.1	-4.4	1567.38	1563.07	4.31	3.49492	3.48893	59.9	-610.48	-611.05	0.57	5.475	4.825	0.650	0.13
700	1.37886	1.38014	-12.8	-9.3	1564.24	1560.64	3.60	3.47876	3.47390	48.6	-603.55	-604.12	0.57	5.350	4.711	0.639	0.13
750	1.36578	1.36762	-18.4	-13.5	1561.44	1558.72	2.72	3.46325	3.45980	34.5	-596.69	-597.25	0.56	5.211	4.605	0.606	0.12
800	1.35378	1.35604	-22.6	-16.7	1558.90	1557.25	1.65	3.44828	3.44651	17.7	-589.89	-590.44	0.55	5.088	4.506	0.582	0.12
850	1.34276	1.34528	-25.2	-18.7	1556.60	1556.17	0.43	3.43376	3.43397	-2.1	-583.15	-583.71	0.56	4.891	4.411	0.480	0.10
900	1.33262	1.33519	-25.7	-19.3	1554.46	1555.44	-0.98	3.41960	3.42205	-24.5	-576.46	-577.01	0.55	4.712	4.320	0.392	0.09
950	1.32331	1.32572	-24.1	-18.2	1552.46	1555.02	-2.56	3.40574	3.41070	-49.6	-569.82	-570.35	0.53	4.519	4.233	0.286	0.07
1000	1.31477	1.31677	-20.0	-15.2	1550.56	1554.88	-4.32	3.39210	3.39986	-77.6	-563.23	-563.74	0.51	4.315	4.147	0.168	0.04

al.⁽⁹⁾ (17), T. Sato et al.⁽¹¹⁾ are valid in the ranges of the state parameters which are nearly the same as that of the present work. Although the equations of state by H. D. Baehr et al. and T. Sato et al. have some supplementary terms which are dissimilar to the subregions divided by the interregional boundary of the critical isotherm, the present formulation can cover the aimed entire region with a single formula.

The given entire region of the International Skeleton Tables (1963) can be covered completely by the present formulation combined with the subformulations for the compressed water⁽⁴⁾, superheated steam⁽⁵⁾ and with the equation of the saturation pressure⁽³⁾.

The thermodynamic property values, such as specific entropy, specific isobaric and isochoric heat capacities and isentropic exponent, are computed by the new equation of state. And the discontinuities in the property values at the interregional boundaries are also examined.

In order to know the characteristics of the present formulation at the critical point, the first and second partial derivatives of pressure with respect to temperature were examined.

10. Additional remarks

As it is mentioned above, the present new equation of state for ordinary water substance in the critical region was adopted as a subformulation of the 1967 IFC Formulation for Industrial Use, in association with the other subformulations of the compressed water and of the superheated steam which were formulated by Federal Republic of Germany⁽¹⁷⁾, and also with the new equation of the saturation pressure which was formulated by Keio University⁽³⁾. Therefore, in order to improve the smoothness of the thermodynamic property values at the interregional boundaries, a working party was established between the delegation of Federal Republic of Germany and the authors, by request of the IFC.

Table 12 Inclination of the critical isochore and that of the saturation line at the critical point

Eq. of state for the critical region	Investigators	$\left[\frac{T}{P} \left(\frac{\partial P}{\partial T} \right)_v \right]_{cl}$
	present work K. Miyabe et al. ⁽¹²⁾ L. Ziegler ⁽⁶⁾	7.8778 7.7929 7.8
Eq. of the saturation pressure	Investigators	$\left(\frac{T}{P_s} \frac{dP_s}{dT} \right)_{cl}$
	I. Tanishita et al. ⁽⁸⁾ N. S. Osborne et al. ⁽²⁰⁾ O. C. Bridgeman et al. ⁽²¹⁾ M. R. Gibson et al. ⁽²²⁾ E. Schmidt et al. ⁽¹⁷⁾	7.6912 7.8268 7.7717 7.7427 7.8494

Through these contacts, some slight modifications were added to the present new equation of state. The items of these modifications are shown in the following paragraphs.

(i) For the interregional boundary between the critical region and the superheated steam region, a boundary equation which is slightly different from Eq. (39) was newly determined. In connection with this revision, one term is added to the equation of the reduced pressure β , Eq. (29), in order to avoid the discontinuities of the thermodynamic property values at this interregional boundary.

(ii) The interregional boundary between the critical region and the compressed water region is 350°C isotherm, in which the pressure varies from the saturation pressure to 1000 bar. Two additional polynomials were added to the equation of the reduced pressure β , Eq. (29), in order to improve the smoothness in the continuities of the thermodynamic property values along this isotherm. The added two terms mentioned above are effective only in the range of temperatures less than the critical temperature, i.e., $350^\circ\text{C} \leq t < 374.15^\circ\text{C}$ ($0.962691179 \leq \theta < 1$), and they vanish exactly at the critical temperature.

(iii) In accordance with the minor changes described above in (i) and (ii), a part of the equation of the reduced free energy ψ , Eq. (28), was modified and also the values of the several numerical constants were revised.

(iv) An additional term was added to the equation of the saturation pressure⁽³⁾, in order to improve the thermodynamic consistency especially in a very narrow region close to the critical point. Therefore, the values of two numerical constants in the expression for the reduced free energy ψ , Eq. (28), were slightly changed.

As for the contents of The 1967 IFC Formulation for Industrial Use, the details are explained in the references⁽²³⁾ (24).

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