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Equation of State for D₂O in the Liquid Region of up to 1000 bar[#]

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For D₂O in the compressed liquid state, several equations of state are available, but they do not fully represent more precise experimental data in very recent years. Present report describes a newly correlated equation of state for D₂O in the liquid (partly gaseous) region of up to 380 °C and 1000 bar. The latest experimental data have been fully taken into account. The newly correlated equation expresses the specific volume as a function of temperature and pressure, considering conveniences in industrial calculations and also in the calculation of derived functions. Equations of derived functions, namely the enthalpy, the entropy and the specific heat at constant pressure, have been obtained from the new equation of state. Properties of liquid D₂O were calculated with the aid of the new equation.

1. Nomenclature

c_p	specific heat	kJ/kg K
g	specific Gibbs function	kJ/kg K
h	specific enthalpy	kJ/kg
h_{P1}	specific enthalpy at P_1	kJ/kg
P	pressure	bar
P_1	reference pressure	bar
s	specific entropy	kJ/kg K
s_{P1}	specific entropy at P_1	kJ/kg K
v	specific volume	cm ³ /g
T	temperature (IPTS-68)	K
t	temperature	°C
ξ	reduced Gibbs function	$g/P_c v_c$
χ	reduced specific volume	v/v_c
π	reduced pressure	P/P_c
τ	$T/100$	

Suffix c critical

2. Introduction

Data on thermophysical properties of D₂O (heavy water) in extensive ranges of temperatures and pressures are increasingly needed in nuclear-power engineering and relating fields. At present, only a few equations of state are available for D₂O and even they do not represent reliable experimental data in the last decade. The most comprehensive data book on D₂O properties by Kirillin⁽¹⁾ is now 11 years old. Recently, a number of experimental investigations on PVT behavior of D₂O at high temperature and high pressure have been reported and they have made it possible to formulate a more precise equation of state based on these latest data and also to expand the region covered.

Present report describes a new equation of state for D₂O in the compressed liquid (partly gaseous) region of up to

380 °C and 1000 bar, in which the latest experimental data are fully taken into account. Derived functions, such as the enthalpy, the entropy and the specific heat, were calculated with the aid of new equation.

3. Existing correlation and available experimental PVT data for D₂O

Equations of state for liquid D₂O were reported by Mamedov⁽²⁾ in 1960, Plank⁽³⁾ in 1961 and Kirillin⁽¹⁾ in 1965. Mamedov's equation was simple and was based on Kirillin's data. Deviations of the equation from recent experimental data by Teederberg et al.⁽⁴⁾⁽⁵⁾ reach 2.6 % at 350 °C and 1000 bar, and are larger at 360 °C and saturation pressure. Deviations of Plank's equation from Teederberg's data are similar to those of Mamedov's. None of these two equations is satisfactorily

Fig.1 Ranges of PVT experiments of liquid D₂O

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precise by present-day standard. Kirillin's equation was based on his own measurements which considerably deviated from recent Tsederberg's data. Region higher than 540 bar was not covered by Kirillin's equation.

Experimental investigations of PVT relation for liquid D_2O include Bridgman(6), Kirillin and Ulybin(7), Rivkin et al.(8)(9)(10), Juza et al.(11), Kell et al.(12), Tsederberg et al.(4)(5) and Nevolina et al.(13). Bridgman's measurements at pressures up to 11768 bar are the earliest among works at high pressures. Nevolina's measurements were limited to 20 °C. Data by Kirillin, Rivkin and Tsederberg cover wide ranges of temperatures and pressures and can be considered basic data for correlating the equations of state. Regions of these measurements are shown in Figure 1.

Kirillin and Ulybin measured in the temperature range 250 - 500 °C and at pressures up to 490 bar. Their estimated precision was 0.2 - 0.25 %, but deviations of their data from Tsederberg's reached 0.7 % except in the vicinity of saturation line where deviation was larger. Purity of their sample D_2O was not reported. Rivkin's measurements were done in the temperature range 50 - 300 °C with estimated precision of 0.01 - 0.03 % (first report) and in the range 275 - 425 °C with estimated precision of 0.02 - 0.10 % (second report). Their highest pressure was 333 bar. Tsederberg's data were given in the temperature range 20 - 425 °C and at pressures up to 1000 bar. Their estimated precision was 0.03 - 0.12 % and the purity of D_2O was 99.70 %. Agreement between Rivkin's and Tsederberg's data is very good and deviations rarely exceed 0.05 %.

Fig.2 Region of equations of state for D_2O

4. Basic data for formulation

After preliminary critical evaluation of these available data, those by Rivkin and Tsederberg were selected as basic data for present formulation. Kirillin's data were used only for comparison, since their data had larger experimental uncertainty and showed systematic deviations of up to 0.4 % from the latest Tsederberg's. Purity of D_2O specimen was different in each investigation mentioned above. Small corrections were made to experimental PVT data by extrapolating to 100 % D_2O . The specific volume of the mixture was assumed to be proportional to mole fraction since the fraction of H_2O was very small. Also because temperature scale in Rivkin's measurements was IPTS-48, their temperature data were corrected to IPTS-68. The largest magnitude of this correction in temperature corresponds to a difference of 0.06 % in the specific volume in the vicinity of the critical point.

5. New equation of state

5.1 Equation of state

For fluids over a wide range of temperatures and pressures, satisfactory equations of state which are derived purely theoretically are not known. Various kinds of empirical or semi-empirical equations of state have been proposed for many industrially important substances. These equations include Van der Waals equation, Berthelot equation, Dietric equation, Beattie-Bridgeman equation, B-W-R equation, virial form equation and many others. (For general discussion of these equations of state, see, for example, References[14] and [15].) With empirically determined coefficients, many of these equations are known to give reasonably acceptable results in each specified region and for specified substance, but are not precise enough for present purpose. Equations, such as B-W-R equation and virial form equation, may give more precise values but do not explicitly express the specific volume (or the density). Simple polynomial expansion of the specific volume in temperature and pressure usually requires an enormous number of terms which leads to loss of the number of effective digits in the final value and to unfavorable "ripples" in derived functions. The polynomial of very high power often gives an unrealistic increase or decrease in derived functions. In the case of present study, a new equation of state has been proposed in which an exponential term has newly been introduced in order to replace the terms of high power in the polynomial expansion. The detail of the exponential term was determined after repeating trial-and-error calculations, since the fitting procedure of the nonlinear term was complicated. The form of other terms were selected with a view to simplifying the equation and minimizing the number of coefficients. The highest pressure in the effective region has been limited to 1000 bar, since this

Table 1. Coefficients of equations (1) and (5)

$C_{10} = 1.07811946 \times 10^2$	$C_{20} = -3.6976916 \times 10^3$
$C_{11} = -2.12905715 \times 10^0$	$C_{21} = 2.2524786 \times 10^1$
$C_{12} = 1.86690123 \times 10^{-2}$	$C_{22} = 3.6125594 \times 10^{-1}$
$C_{13} = -9.53573030 \times 10^{-5}$	$C_{23} = -1.7431798 \times 10^{-3}$
$C_{14} = 3.14090654 \times 10^{-7}$	$C_{24} = 2.6126347 \times 10^{-6}$
$C_{15} = -6.94086874 \times 10^{-10}$	$C_{25} = -1.3021275 \times 10^{-9}$
$C_{16} = 1.03063843 \times 10^{-12}$	
$C_{17} = -9.91306878 \times 10^{-16}$	$C_{40} = 2.41343799 \times 10^3$
$C_{18} = 5.59400461 \times 10^{-19}$	$C_{41} = +2.62949679 \times 10^1$
$C_{19} = -1.40713627 \times 10^{-22}$	$C_{42} = 1.10027165 \times 10^{-1}$
	$C_{43} = -2.23456891 \times 10^{-4}$
$C_{30} = -6.44602781 \times 10^5$	$C_{44} = 2.21327188 \times 10^{-7}$
$C_{31} = 1.17837622 \times 10^4$	$C_{45} = -8.57199889 \times 10^{-11}$
$C_{32} = -9.21290436 \times 10^1$	
$C_{33} = 4.03846838 \times 10^{-1}$	$C_{50} = -1.055 \times 10^1$
$C_{34} = -1.08637769 \times 10^{-3}$	$C_{51} = 1.030 \times 10^{-2}$
$C_{35} = 1.83783022 \times 10^{-6}$	
$C_{36} = -1.91134677 \times 10^{-9}$	$C_{60} = -8.00 \times 10^{-10}$
$C_{37} = 1.11862710 \times 10^{-12}$	$C_{61} = 2.00 \times 10^{-32}$
$C_{38} = -2.82414921 \times 10^{-16}$	
$a_0 = 9.090 \times 10^{-1}$	$a_4 = 1.315 \times 10^{-32}$
$a_1 = 4.44063 \times 10^{-2}$	$a_5 = 6.91170 \times 10^{-7}$
$a_2 = -2.4065934 \times 10^{-3}$	$a_6 = 6.8941 \times 10^0$
$a_3 = 1.2521189 \times 10^{-5}$	
	$C_{10}^* = 1.07812220 \times 10^2$

Fig.3 Comparison with experimental PvT data (Teederberg)

Fig.4 Comparison with experimental PvT data (Rivkin 1962)

is considered to be sufficient for practical calculations.

The form of equation was determined considering following items;

- (i) For practical convenience, pressure and temperature were selected as independent variables, that is, the specific volume was expressed as $v = v(T, P)$.
- (ii) Agreement with experimental data was judged by referring to the tolerance listed in the ICPS Skeleton Table(1963)(16) for ordinary water at respective temperatures and pressures.
- (iii) For easier calculation of derived function, the form of equation was selected considering convenience in differentiation and integration.

The newly formulated equation of state for liquid D₂O is as follows,

$$v(T, P) = C_1(T) + C_3(T) / \{P + C_2(T)\} + C_4(T) \exp(C_5(T)P) + C_6(T)(P/1000)^{12} \quad (1)$$

where

$$\begin{aligned} C_1(T) &= \sum_{i=0}^9 C_{1i} T^i \\ C_2(T) &= \sum_{i=0}^5 C_{2i} T^i \\ C_3(T) &= \sum_{i=0}^8 C_{3i} T^i \\ C_4(T) &= \exp\left(\sum_{i=0}^5 C_{4i} T^i\right) \end{aligned}$$

$$\begin{aligned} C_5(T) &= -\exp\left(\sum_{i=0}^1 C_{5i} T^i\right) \\ C_6(T) &= C_{60} T^8 + C_{61} T^{35} \end{aligned}$$

and constants C_{1i} are given in Table 1. C_{10}^* in Table 1 can be used instead of C_{10} in order to reproduce original experimental data which are not corrected to 100 % pure D₂O. Equation(1) is valid in the liquid and dense-gas regions of temperatures 3.81 - 380°C and of pressures 0 - 1000 bar as shown in Figure 2. The valid region has been made wider than that of Kirillin's equation. In the vicinity of the critical point, the boundary of valid region is given by the isotherm of 380°C and the following equation,

$$P_1(T) = 8455.39 - 29.9306T + 0.026705T^2 \quad (2)$$

This boundary is shown as line A in Figure 2. In equation(1) the third term is necessary only in the narrow region near saturation pressure at high temperatures and the fourth term is a small correction term at about 370°C and 1000 bar. The term $C_4(T) \exp(-C_5(T)P)$ in equation(1) is unique in this kind of equations of state and is found to be quite useful to get better fit with a less number of terms.

5.2 Derived functions

Applying ordinary thermodynamic relations to the new equation of state, the specific heat at constant pressure, c_p , is

given as,

$$c_p = c_{p1}(T) - T \int_{P_1}^P \left(\frac{\partial^2 v}{\partial T^2} \right)_P dP \quad (3)$$

In usual case, in order to calculate c_p we need the equation of state in the gaseous region, the equation of saturation pressure and c_{p0} at the ideal gas state. Instead, here the term $c_{p1}(T)$ denotes c_p at reference pressure P_1 , determined from the experimental data of c_p by Rivkin et al. (17) at 294.2 bar (300 at). Using the relation (3) with equation (1) we get,

$$\begin{aligned} c_p = c_{p1}(T) - \frac{T}{10} [C_1''P + C_3'' \ln(P+C_2) \\ + \frac{2C_3'C_2 + C_3C_2''}{(P+C_2)} - \frac{C_3(C_2')^2}{(P+C_2)^2}]_{P_1}^P \\ - \frac{T}{10C_5} [\exp(C_5P) \cdot \{C_4'' + (2C_4C_5' \\ + C_4C_5'')(P - \frac{1}{C_5}) + C_4(C_5'')^2 \cdot (P^2 - 2P \\ + \frac{2}{C_5})\}]_{P_1}^P - \frac{T}{10} [\frac{1000C_6''}{13} \cdot (\frac{P}{1000})^{13}]_{P_1}^P \end{aligned}$$

where $P_1 = 294.2$ bar. C_i with prime "1" and double prime "''" denote the first and the second derivative of functions $C_i(T)$. The term $c_{p1}(T)$ was determined as,

$$c_{p1}(T) = 4.1868 \{ a_0 + a_1T + a_2T^3 + a_3T^6 + a_4T^{39} + a_5T/(a_6 - T)^{10} \} \quad (5)$$

Constants a_i are also given in Table 1. The region of validity for the specific heat is almost similar to that for the

specific volume but there exists a very narrow region in the vicinity of the critical point where equation (4) fails to reproduce the experimental data. More precisely, therefore, the boundary for the specific heat is described by the isotherm of 380°C and the following relation which is close to equation (2);

$$P_2(T) = 4.3423T - 2526.23 \quad (6)$$

The enthalpy is calculated with the aid of the following equation derived from equation (1),

$$\begin{aligned} h = h_{p1}(T) - \frac{T^2}{10} \left[\frac{(C_1'T - C_1)P}{T^2} + \left(\frac{C_3'}{T} - \frac{C_3}{T^2} \right) \ln(P \right. \\ \left. + C_2) + \frac{C_3C_2'}{T(P+C_2)} \right]_{P_1}^P - \frac{T^2}{10C_5} \left[\frac{\exp(C_5P)}{C_5T} \{ C_4' \right. \\ \left. + C_4C_5'(P - \frac{1}{C_5}) \} - \frac{C_4}{T} \right]_{P_1}^P \\ - \frac{T^2}{10} \left[\frac{1000}{13} \cdot \frac{(C_6'T - C_6)}{T^2} \left(\frac{P}{1000} \right)^{13} \right]_{P_1}^P \quad (7) \end{aligned}$$

The term $h_{p1}(T)$ is given as,

$$\begin{aligned} h_{p1}(T) = h_{p10} + 418.68 \left[a_0T + \frac{a_1}{2}T^2 + \frac{a_2}{4}T^4 \right. \\ \left. + \frac{a_3}{7}T^7 + \frac{a_4}{40}T^{40} - \frac{a_5}{8(a_6 - T)^8} \right. \\ \left. + \frac{a_5a_6}{9(a_6 - T)^9} \right]_{T_0}^T \quad (8) \end{aligned}$$

where

$$T_0 = 2.7697$$

Table 2. The specific volume of D₂O

		v (cm ³ /g)										
P (BAR)	T (C)	3.81	20.00	50.00	100.00	150.00	200.00	250.00	300.00	350.00	370.00	380.00
1.0		.90405	.90478	.91266	.94057							
5.0		.90387	.90461	.91250	.94039	.98285						
10.0		.90365	.90440	.91229	.94016	.98255						
25.0		.90298	.90376	.91168	.93947	.98165	1.04329					
50.0		.90186	.90269	.91066	.93834	.98017	1.04096	1.13096				
75.0		.90076	.90164	.90965	.93721	.97871	1.03867	1.12663				
100.0		.89967	.90060	.90865	.93609	.97726	1.03643	1.12247	1.26873			
125.0		.89858	.89956	.90766	.93498	.97583	1.03424	1.11849	1.25910			
150.0		.89750	.89853	.90667	.93388	.97441	1.03209	1.11465	1.25018			
175.0		.89643	.89751	.90569	.93279	.97301	1.02998	1.11096	1.24187			
200.0		.89537	.89649	.90472	.93171	.97163	1.02791	1.10739	1.23408	1.52836		
210.0		.89495	.89609	.90433	.93128	.97107	1.02709	1.10600	1.23110	1.51231		
220.0		.89453	.89569	.90395	.93085	.97053	1.02628	1.10463	1.22918	1.49769		
225.0		.89431	.89549	.90376	.93064	.97025	1.02588	1.10325	1.22675	1.49085		
230.0		.89410	.89529	.90356	.93043	.96998	1.02547	1.10327	1.22534	1.48431		
250.0		.89327	.89449	.90280	.92958	.96890	1.02388	1.10161	1.21982	1.46068		
275.0		.89223	.89350	.90185	.92853	.96755	1.02192	1.09738	1.21325	1.43575		
300.0		.89120	.89251	.90091	.92748	.96622	1.01999	1.09424	1.20700	1.41463	1.58658	1.73008
325.0		.89018	.89154	.89997	.92645	.96491	1.01810	1.09119	1.20102	1.39633	1.54525	1.66101
350.0		.88916	.89057	.89904	.92542	.96360	1.01624	1.08822	1.19531	1.38017	1.51246	1.60979
375.0		.88815	.88960	.89812	.92440	.96231	1.01441	1.08533	1.18983	1.36568	1.48545	1.56995
400.0		.88715	.88865	.89721	.92339	.96104	1.01261	1.08252	1.18457	1.35250	1.46252	1.53761
450.0		.88517	.88675	.89540	.92140	.95853	1.01090	1.07710	1.17462	1.32919	1.42477	1.48683
500.0		.88322	.88489	.89361	.91943	.95606	1.00568	1.07193	1.16536	1.30897	1.39412	1.44731
550.0		.88129	.88305	.89185	.91750	.95365	1.00237	1.06699	1.15671	1.29109	1.36818	1.41479
600.0		.87940	.88124	.89012	.91560	.95128	.99916	.96226	1.14860	1.27508	1.34570	1.38718
650.0		.87753	.87945	.88841	.91373	.94896	.99604	1.05772	1.14097	1.26063	1.32595	1.36333
700.0		.87568	.87769	.88673	.91189	.94668	.99300	1.05335	1.13377	1.24749	1.30840	1.34244
750.0		.87366	.87595	.88507	.91008	.94444	.99005	1.04915	1.12696	1.23548	1.29268	1.32398
800.0		.87207	.87424	.88343	.90829	.94225	.98717	1.04509	1.12050	1.22443	1.27848	1.30750
850.0		.87030	.87255	.88162	.90653	.94009	.98435	1.04116	1.11434	1.21419	1.26556	1.29267
900.0		.86856	.87088	.88022	.90480	.93796	.98160	1.03734	1.10842	1.20461	1.25366	1.27916
950.0		.86683	.86923	.87865	.90308	.93567	.97888	1.03359	1.10269	1.19552	1.24253	1.26666
1000.0		.86513	.86760	.87709	.90139	.93370	.97619	1.02988	1.09783	1.18670	1.23189	1.25488

Table 3. The specific heat of D₂O

		CP (KJ/KG.K)										
P (BAR)	T (C)	3.81	20.00	50.00	100.00	150.00	200.00	250.00	300.00	350.00	370.00	380.00
1.0	4.1967	4.2114	4.1942	4.1731								
5.0	4.1958	4.2103	4.1932	4.1723	4.2098							
10.0	4.1947	4.2089	4.1920	4.1712	4.2082							
25.0	4.1913	4.2046	4.1882	4.1682	4.2036	4.3272						
50.0	4.1857	4.1974	4.1821	4.1631	4.1961	4.3135	4.6527					
75.0	4.1801	4.1903	4.1760	4.1581	4.1888	4.3004	4.6221					
100.0	4.1745	4.1833	4.1701	4.1532	4.1816	4.2879	4.5932	5.4109				
125.0	4.1688	4.1763	4.1642	4.1484	4.1745	4.2760	4.5658	5.3066				
150.0	4.1632	4.1694	4.1584	4.1436	4.1676	4.2646	4.5397	5.2157				
175.0	4.1575	4.1625	4.1526	4.1390	4.1608	4.2536	4.5149	5.1358	9.0704			
200.0	4.1518	4.1556	4.1470	4.1343	4.1541	4.2430	4.4913	5.0647	7.9829			
210.0	4.1496	4.1529	4.1447	4.1325	4.1515	4.2389	4.4821	5.0383	7.6540			
220.0	4.1473	4.1502	4.1425	4.1307	4.1489	4.2349	4.4731	5.0131	7.3709			
225.0	4.1461	4.1488	4.1414	4.1298	4.1476	4.2329	4.4686	5.0009	7.2442			
230.0	4.1450	4.1475	4.1403	4.1289	4.1463	4.2309	4.4642	4.9889	7.1262			
250.0	4.1404	4.1421	4.1358	4.1253	4.1411	4.2230	4.4470	4.9431	6.7279			
275.0	4.1347	4.1354	4.1304	4.1209	4.1348	4.2135	4.4264	4.8906	6.3549	8.5983		
300.0	4.1290	4.1287	4.1250	4.1166	4.1286	4.2043	4.4065	4.8425	6.0755	7.7440	9.8455	
325.0	4.1233	4.1221	4.1198	4.1123	4.1225	4.1953	4.3876	4.7981	5.8584	7.1547	8.8917	
350.0	4.1175	4.1155	4.1145	4.1081	4.1165	4.1867	4.3694	4.7571	5.6838	6.7256	8.2083	
375.0	4.1117	4.1090	4.1094	4.1039	4.1106	4.1782	4.3519	4.7191	5.5391	6.3972	7.6916	
400.0	4.1060	4.1025	4.1043	4.0998	4.1048	4.1700	4.3351	4.6836	5.4160	6.1355	7.2852	
450.0	4.0944	4.0896	4.0944	4.0918	4.0934	4.1541	4.3036	4.6193	5.2148	5.7406	6.6885	
500.0	4.0827	4.0762	4.0847	4.0841	4.0824	4.1390	4.2744	4.5626	5.0546	5.4559	6.2832	
550.0	4.0710	4.0643	4.0753	4.0765	4.0717	4.1246	4.2475	4.5121	4.9223	5.2443	6.0071	
600.0	4.0592	4.0519	4.0661	4.0692	4.0612	4.1107	4.2225	4.4667	4.8105	5.0854	5.8237	
650.0	4.0474	4.0397	4.0572	4.0621	4.0511	4.0973	4.1993	4.4255	4.7143	4.9662	5.7091	
700.0	4.0355	4.0275	4.0486	4.0552	4.0412	4.0845	4.1778	4.3881	4.6304	4.8777	5.6462	
750.0	4.0236	4.0156	4.0402	4.0485	4.0315	4.0720	4.1578	4.3536	4.5561	4.8132	5.6230	
800.0	4.0116	4.0038	4.0321	4.0420	4.0220	4.0600	4.1391	4.3218	4.4896	4.7677	5.6304	
850.0	3.9995	3.9921	4.0241	4.0356	4.0128	4.0483	4.1217	4.2921	4.4293	4.7373	5.6619	
900.0	3.9873	3.9805	4.0165	4.0295	4.0037	4.0370	4.1055	4.2643	4.3741	4.7190	5.7123	
950.0	3.9751	3.9691	4.0090	4.0235	3.9948	4.0260	4.0903	4.2382	4.3229	4.7104	5.7774	
1000.0	3.9629	3.9578	4.0014	4.0177	3.9862	4.0154	4.0761	4.2135	4.2750	4.7092	5.8535	

Table 4. The specific enthalpy of D₂O

		H (KJ/KG)										
P (BAR)	T (C)	3.81	20.00	50.00	100.00	150.00	200.00	250.00	300.00	350.00	370.00	380.00
1.0	0.091	68.196	194.337	403.342								
5.0	4.456	68.543	194.651	403.613	612.805							
10.0	9.12	68.977	195.044	403.952	613.354							
25.0	2.277	70.279	196.222	404.965	613.922	927.147						
50.0	4.549	72.444	198.184	406.662	615.323	927.979	1050.157					
75.0	6.816	74.605	200.143	408.358	616.731	928.839	1050.115					
100.0	9.077	76.760	202.099	410.056	618.144	929.725	1050.138	1296.636				
125.0	11.334	78.912	204.053	411.755	619.564	930.635	1050.222	1293.991				
150.0	13.586	81.059	206.005	413.455	620.989	931.568	1050.361	1291.645				
175.0	15.833	83.201	207.954	415.156	622.419	932.524	1050.551	1289.556	1602.068			
200.0	18.076	85.339	209.900	416.859	623.856	933.500	1050.790	1287.694	1586.141			
210.0	18.971	86.193	210.678	417.540	624.432	933.895	1050.898	1287.006	1580.588			
220.0	19.866	87.046	211.455	418.222	625.008	934.294	1051.014	1286.348	1575.569			
225.0	20.313	87.472	211.844	418.563	625.297	934.495	1051.074	1286.030	1573.236			
230.0	20.760	87.898	212.233	418.904	625.586	934.696	1051.136	1285.720	1571.011			
250.0	22.546	89.601	213.786	420.268	626.743	935.509	1051.400	1284.546	1563.044			
275.0	24.774	91.726	215.725	421.974	628.195	936.540	1051.767	1283.221	1554.766	1700.531		
300.0	26.998	93.846	217.661	423.682	629.651	937.587	1052.171	1282.042	1547.872	1683.352	1749.679	
325.0	29.217	95.962	219.596	425.390	631.112	938.651	1052.611	1280.995	1542.005	1670.051	1748.797	
350.0	31.431	98.073	221.528	427.100	632.578	939.729	1053.085	1280.070	1536.924	1659.318	1732.631	
375.0	33.641	100.181	223.457	428.810	634.048	940.822	1053.592	1279.257	1532.460	1650.425	1719.584	
400.0	35.846	102.284	225.384	430.522	635.522	941.928	1054.130	1278.548	1528.497	1642.820	1708.715	
450.0	40.243	106.477	229.231	433.947	638.483	944.178	1055.292	1277.413	1521.750	1630.385	1691.430	
500.0	44.622	110.655	233.069	437.377	641.463	946.474	1056.562	1276.615	1516.228	1620.554	1678.219	
550.0	48.985	114.816	236.897	440.809	644.453	948.814	1057.931	1276.113	1511.652	1612.615	1667.857	
600.0	53.330	118.960	240.716	444.245	647.459	951.193	1059.392	1275.873	1507.836	1606.097	1659.630	
650.0	57.658	123.090	244.526	447.683	650.479	953.607	1060.936	1275.866	1504.645	1600.712	1651.062	
700.0	61.970	127.203	248.326	451.124	653.511	956.054	1062.559	1276.066	1501.973	1596.241	1647.810	
750.0	66.266	131.301	252.118	454.567	656.556	958.532	1064.253	1276.452	1499.739	1592.519	1643.617	
800.0	70.546	135.384	255.901	458.012	659.612	961.038	1066.015	1277.015	1497.874	1589.815	1640.286	
850.0	74.810	139.452	259.675	461.460	662.679	963.570	1067.839	1277.708	1496.325	1586.826	1637.663	
900.0	79.056	143.505	263.440	464.909	665.756	966.127	1069.722	1278.548	1495.049	1584.670	1635.624	
950.0	83.291	147.543	267.196	468.361	668.843	968.708	1071.661	1279.515	1494.009	1582.879	1634.071	
1000.0	87.509	151.568	270.944	471.814	671.940	971.311	1073.654	1280.600	1493.181	1581.401	1632.923	

$$h_{p10} = 26.5236 \text{ kJ/kg}$$

The term $s_{p1}(T)$ is given as,

$$s_{p1}(T) = s_{p10} + 4.1868 \left[a_0 \ln T + a_1 T + \frac{a_2}{3} T^3 + \frac{a_3}{6} T^6 + \frac{a_4}{39} T^{39} + \frac{a_5}{9(a_6 - T)^9} \right] T_0 \quad (10)$$

where

$$P_1 = 294.1995 \text{ bar}$$

$$T_0 = 2.7697$$

$$s_{p10} = 0.0004 \text{ kJ/kg K}$$

The entropy is calculated with the aid of the following equation,

$$s = s_{p1}(T) - \frac{1}{10} \left[C_1 P + C_2 \ln(P + C_2) + \frac{C_3 C_2}{P + C_2} \right]_{P_1} - \frac{1}{10} \left[\frac{\exp(C_5 P)}{C_5} \left\{ C_4 + C_4 C_5 \left(P - \frac{1}{C_5} \right) \right\} \right]_{P_1} - \frac{1}{10} \left[\frac{1000}{13} C_6 \left(\frac{P}{1000} \right)^{13} \right]_{P_1} \quad (9)$$

6. Calculated results and comparisons

Specific volumes of D_2O calculated with the aid of equation (1) are listed in Table 2. Figures 3 and 4 show deviations of experimental data of Tsederberg et al. and Rivkin et al., respectively, from equation (1). These two sets of data were used as the basic data for present formulation. Tsederberg's data fell within 0.05 % from equation (1) except several points on near-critical isotherms. The agreement is satisfactory since precision of their experiment was 0.2 - 0.3 %. Deviations of Rivkin's data are mostly less than 0.2 %. Although they are larger than those of Tsederberg's, this is satisfactorily because Rivkin's measurements are limited to the critical region. Deviations of Kirillin's data are shown in Figure 5. The equation by Kirillin was mainly based on these data which showed systematic deviations from our equation, that is, from Rivkin's and Tsederberg's data. Deviations of older data including Kirillin's were larger. The reliability of those older data is lower.

In the case of D_2O , there are no such recognized standard "tolerances" as those in International Skeleton Tables for H_2O . But deviations of experimental data for D_2O from equation (1) are comparable to those tolerances, that is, about 0.03 % at 200 °C and about 0.1 % at 300 °C in International Skeleton Tables (14) for H_2O .

Root mean square errors of major experimental data from the new equation are summarized;

Author	Year	Number of data	RMSE (%)
Bridgman	1935	14	0.08
Juza et al.	1966	13	0.15
Kirillin et al.	1958	46	0.27
Rivkin et al.	1962	58	0.13
Tsederberg et al.	1972	71	0.01
Tsederberg et al.	1973	95	0.03

Calculated results of the specific heat at constant pressure with the aid of equation (4) are listed in Table 3. Since the second derivative of the equation of state is included in the derivation of the specific heat, the calculated specific heat can be one of the means for judging the quality of the equation of state. As seen in Figure 6, the specific heat at constant pressure calculated with the aid of the new equation agrees very well with experimental data by Rivkin et al. (17) which are supposed to be the most reliable at present. Deviations are less than 0.05 % at temperature below 300 °C and less than 1 % except in immediate vicinity of the critical point. The specific heat calculated with Kirillin's equation of state showed deviations of up to 2 %, or more in some regions, from present results and Rivkin's data. This is one of the reasons for supporting the necessity of present formulation.

The enthalpy and the entropy of D_2O calculated with the aid of equations (7) and (9) are listed in Tables 4 and 5. The enthalpy calculated with present formulation agrees with those in Kirillin's table, the deviations being less than 1 %. Properties of saturated liquid are calculated in Table 6. Saturation pressure was calculated with the equation in reference [18].

The uncertainties of properties calculated with present formulation are estimated to be;

For the specific volume
 $3.81 \leq t \leq 15^\circ\text{C} : 0.1 \%$
 $15 < t \leq 100^\circ\text{C} : 0.03 \%$
 $100 < t \leq 200^\circ\text{C} : 0.05 \%$
 $200 < t \leq 300^\circ\text{C} : 0.1 \%$
 $300 < t \leq 380^\circ\text{C} : 0.2 \%$

For the enthalpy, the entropy and the specific heat

$3.81 \leq t < 300^\circ\text{C} : 0.5 \%$
 $300 \leq t \leq 380^\circ\text{C} : 1.0 \%$

Table 5. The specific entropy of D_2O

S (KJ/KG K)

T(°C)	3.81	20.00	50.00	100.00	150.00	200.00	250.00	300.00	350.00	370.00	380.00
P(3.3)											
1.0	-0.000	.239	.649	1.250							
5.0	.002	.239	.648	1.250	1.776						
10.0	.002	.239	.648	1.249	1.775						
25.0	.000	.239	.648	1.248	1.774	2.250					
50.0	.000	.238	.647	1.247	1.771	2.246	2.692				
75.0	.000	.238	.646	1.245	1.769	2.243	2.687				
100.0	.000	.238	.645	1.243	1.766	2.239	2.682	3.131			
125.0	.000	.237	.644	1.241	1.764	2.235	2.676	3.121			
150.0	.000	.237	.643	1.240	1.762	2.232	2.671	3.111			
175.0	.000	.237	.642	1.238	1.759	2.228	2.666	3.102	3.625		
200.0	.000	.236	.641	1.236	1.757	2.225	2.661	3.094	3.591		
210.0	.000	.236	.640	1.235	1.756	2.224	2.660	3.090	3.580		
220.0	.000	.236	.640	1.235	1.755	2.222	2.658	3.087	3.570		
225.0	.000	.236	.640	1.235	1.755	2.222	2.657	3.085	3.565		
230.0	.000	.236	.640	1.234	1.754	2.221	2.656	3.084	3.560		
235.0	.000	.236	.639	1.233	1.752	2.219	2.652	3.077	3.542		
240.0	.000	.235	.638	1.231	1.750	2.215	2.648	3.070	3.523	3.753	
245.0	.000	.235	.637	1.230	1.748	2.212	2.643	3.062	3.506	3.720	3.853
250.0	.000	.234	.636	1.228	1.745	2.209	2.639	3.055	3.491	3.694	3.815
255.0	.000	.234	.635	1.226	1.743	2.206	2.634	3.048	3.478	3.671	3.784
260.0	.000	.234	.634	1.225	1.741	2.203	2.630	3.042	3.465	3.651	3.758
265.0	.000	.233	.633	1.223	1.739	2.200	2.626	3.035	3.453	3.634	3.735
270.0	.000	.232	.631	1.220	1.734	2.194	2.618	3.023	3.432	3.603	3.697
275.0	.000	.232	.629	1.217	1.730	2.188	2.610	3.012	3.412	3.577	3.666
280.0	.000	.231	.627	1.214	1.726	2.182	2.602	3.001	3.394	3.554	3.639
285.0	.001	.230	.625	1.211	1.722	2.177	2.595	2.990	3.378	3.533	3.616
290.0	.001	.229	.623	1.208	1.718	2.171	2.588	2.980	3.363	3.514	3.595
295.0	.001	.228	.621	1.205	1.714	2.166	2.581	2.971	3.348	3.497	3.577
300.0	.001	.227	.619	1.202	1.710	2.161	2.574	2.961	3.335	3.481	3.560
305.0	.002	.226	.617	1.199	1.706	2.156	2.567	2.953	3.322	3.466	3.545
310.0	.002	.225	.615	1.196	1.702	2.151	2.561	2.944	3.310	3.453	3.531
315.0	.002	.224	.613	1.193	1.698	2.146	2.555	2.936	3.298	3.439	3.518
320.0	.003	.223	.611	1.190	1.694	2.141	2.548	2.928	3.287	3.427	3.506
325.0	.003	.222	.609	1.187	1.691	2.136	2.542	2.920	3.276	3.415	3.494

Table 6. Properties of saturated liquid D₂O

T(°C)	PS(BAR)	V ^c (CM ³ /G)	H ^c (KJ/KG)	S ^c (KJ/KG K)	CP ^c (KJ/KG K)
3.81	.007	.90410	.001	.000	4.197
10.00	.010	.90409	26.011	.093	4.206
20.00	.020	.90483	68.111	.239	4.212
30.00	.037	.90654	110.220	.380	4.209
40.00	.066	.90919	152.280	.517	4.202
50.00	.111	.91271	194.267	.649	4.194
60.00	.182	.91699	236.179	.776	4.187
70.00	.288	.92198	278.025	.900	4.181
80.00	.442	.92760	319.822	1.020	4.176
90.00	.661	.93381	361.586	1.137	4.174
100.00	.963	.94058	403.340	1.250	4.173
110.00	1.371	.94790	445.103	1.360	4.175
120.00	1.912	.95577	486.900	1.468	4.178
130.00	2.616	.96421	528.756	1.573	4.185
140.00	3.517	.97323	570.703	1.675	4.195
150.00	4.654	.98287	612.786	1.776	4.210
160.00	6.068	.99323	655.064	1.874	4.232
170.00	7.804	1.00441	697.599	1.971	4.259
180.00	9.913	1.01656	740.423	2.066	4.287
190.00	12.446	1.02981	783.516	2.160	4.311
200.00	15.460	1.04420	826.837	2.251	4.333
210.00	19.015	1.05967	870.402	2.342	4.362
220.00	23.173	1.07615	914.330	2.431	4.408
230.00	28.002	1.09368	958.817	2.519	4.476
240.00	33.569	1.11245	1004.055	2.607	4.563
250.00	39.950	1.13276	1050.193	2.695	4.665
260.00	47.220	1.15504	1097.337	2.782	4.782
270.00	55.461	1.17976	1145.578	2.870	4.913
280.00	64.758	1.20741	1195.020	2.958	5.064
290.00	75.201	1.23861	1245.806	3.047	5.245
300.00	86.888	1.27411	1298.158	3.137	5.472
310.00	99.925	1.31502	1352.443	3.228	5.775
320.00	114.428	1.36310	1409.291	3.321	6.210
330.00	130.528	1.42138	1469.767	3.418	6.874
340.00	148.380	1.49500	1535.513	3.522	7.910
345.00	158.020	1.53991	1570.985	3.577	8.614

7. Conversion to the equation of Gibbs function

The new equation of state was converted into the following equation of Gibbs function, so-called the equation of canonical function. Derived functions can be calculated from it with differentiating procedures(19).

$$\xi = g/P_c v_c = (h - Ts)/P_c v_c \quad (11)$$

$$(P_c v_c = 64.0023 \text{ kJ/kg})$$

where h and s are those given in equations (7) and (9).

8. Concluding remarks

The recent experimental data of PvT relation for liquid D₂O have been analysed and correlated into a new equation of state. The new equation has a comparatively simple form which is suitable for computer calculations of engineering and industrial purposes, and valid in the compressed liquid region of temperatures 3.81 - 380 °C and of pressures 0 - 1000 bar. The equation reproduces the best experimental data of specific volume and the specific heat within their estimated reliability.

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Fig.5 Comparison with experimental data (Kirillin 1959)

Fig.6 Comparison with experimental data (Rivkin 1962 & 1963)

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