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Isochoric Heat Capacity Measurements for Light and Heavy Water Near the Critical Point[1]

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The isochoric heat capacity was measured for D_2O at a fixed density of $356.075\ \mathrm{kg \cdot m^{-3}}$ and for H_2O at $309.905\ \mathrm{kg \cdot m^{-3}}$. The measurements cover the range of temperatures from 623 to 661 K. The measurements were made with a high-temperature, high-pressure, adiabatic calorimeter with a nearly constant inner volume. The uncertainty of the temperature is 10 mK, while the uncertainty of the heat capacity is estimated to be 2 to 3%. Measurements were made in both the two-phase and the one-phase regions. The calorimeter instrumentation also enables measurements of PVT and the temperature derivative $(\partial P/\partial T)_V$ along each measured isochore. A detailed discussion is presented on the experimental temperature behavior of C_V in the one- and two-phase regions, including the coexistence curve near the critical point. A quasi-static thermogram method was applied to determine values of temperature at saturation $T_S(\rho)$ on measured isochores. The uncertainty of the phase-transition temperature measurements is about ± 0.02 K. The measured C_V data for D_2O and H_2O are compared with values predicted from a recent developed parametric crossover equation of state and IAPWS-95 formulation.

KEY WORDS: adiabatic calorimeter; critical point; coexistence curve; crossover equation of state; density; heavy water; isochoric heat capacity; light water; quasi-static thermogram method.

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1. INTRODUCTION

Previously, isochoric heat capacity measurements of heavy water were reported by Amirkhanov et al. [1, 2], Mursalov [3], and Mursalov et al. [4]. Isochoric heat capacities for D_2O for 11 liquid isochores between 303.03 and 1104.97 $kg \cdot m^{-3}$ in the temperature range from 293 to 733 K have been reported by Amirkhanov et al. [1]. Amirkhanov et al. [2] also reported two- and one-phase isochoric heat capacities of D_2O (isotopic purity, 99.8 mass%) at two densities, 370.37 and 400.00 $kg \cdot m^{-3}$. The measured data of Ref. 2 were presented graphically. A comprehensive set of 23 liquid and vapor isochores was reported by Mursalov et al. [3, 4]. These measurements cover the temperature range from 294 to 746 K and densities between 52 and 1105 $kg \cdot m^{-3}$. Two crossover equations of state for D_2O have been developed by Kiselev et al. [5] and Wyczalkowska et al. [6]. Hill et al. [7] have developed a fundamental equation of state (EOS) for D_2O which is valid for states in the range up to 100 MPa and 873 K. A detailed review of the available experimental C_V data for light water in the critical region has been reported by Abdulagatov et al. [8]. In this paper we present two- and one-phase isochoric heat capacity measurements along near-critical isochores for D_2O at a density of 356.075 $kg \cdot m^{-3}$ and for H_2O at 309.905 $kg \cdot m^{-3}$. The measurements cover the temperature range from 623 to 661 K.

There are some important differences between IAPWS-85 [9] accepted values of critical parameters [$T_C = 643.89 \pm 0.2$ K (IPTS-68) or 643.847 K (ITS-90), $\rho_C = 356 \pm 5\ kg \cdot m^{-3}$] and published experimental saturated temperature and density data near the critical point [3, 10, 11] which indicate that T_C should be 0.45 K higher than the accepted value. New measurements near the coexistence curve of D_2O in the immediate vicinity of the critical point are needed to resolve this long-standing discrepancy. Isochoric heat capacity measurements in the two-phase and one-phase regions are very sensitive to the location of a phase-transition boundary, especially near the critical point. The discontinuity of C_V measurements near a phase-transition curve, when approached from either the two-phase or the one-phase region along various near-critical isochores, can provide very reliable (T_S, ρ_S) data on the coexistence curve. These data can be used to estimate values of critical parameters (T_C, ρ_C). An additional measurement of C_V for light water along a single near-critical isochore at a density of 309.905 $kg \cdot m^{-3}$will provide a performance check of our experimental equipment and verify calculation procedures.

2. EXPERIMENTAL

Only a brief description of the calorimeter, the method, and the appropriate working equations is necessary, since they have been described in detail previously [4, 12–16]. The calorimeter is made of a multilayered system which consists of an internal thin-walled vessel and an outer adiabatic shell, with a 3.5-mm-thick semiconductor layer (cuprous oxide) between them. The calorimeter vessel was constructed from heat- and corrosion-resistant high-strength stainless steel (1X18H9T). The heat capacity of the empty calorimeter C_0 was measured using helium [17] as a reference substance. The temperature dependence of C_0 can be described within ±0.9% by the equation

$$C_0 = 67.36 + 0.0175T - 23 \times 10^{-6}T^2 \tag{1}$$

where T (K) is the temperature and C_0 ($\mathrm{J \cdot K^{-1}}$) is the empty calorimeter heat capacity.

The temperature dependence of the volume of the calorimeter was measured with an uncertainty of 0.05% by filling the calorimeter with water [18]. Changes in the volume of the calorimeter due to changes in temperature $V(T)$ can be represented by

$$V(T) = V_{297}[1 + 3\alpha(T)(T - 297.15)] \tag{2}$$

where $V_{297} = 104.441 \pm 0.002\ \mathrm{cm}^3$ is the volume of the calorimeter at 297.15 K and at a pressure 0.1 MPa from the water calibration, and $\alpha(T)$ is the thermal expansion coefficient of the calorimeter material as a linear function of temperature. The pressure dependence of the volume $V(P)$ was determined by calculation using a formula for a spherical vessel [19]. The correction to the calorimeter volume $\Delta V(T) = V(T) - V_{297}$ due to temperature change is $2.39\ \mathrm{cm}^3$ at 673 K, which results in a 1.7% uncertainty. The pressure correction $\Delta V(P)$ at a pressure of 25 MPa is $0.036\ \mathrm{cm}^3$. The maximum uncertainty of $\Delta V(P) = V(P) - V_{0.1}$ is $0.004\ \mathrm{cm}^3$.

Measurements of C_V were made with the continuous-heating method. This method enables one to determine the transition temperature T_s of the system from the two-phase to a single-phase state (i.e., to determine T_s and ρ_s data corresponding to the coexistence curve), the jump in the heat capacity ΔC_V, and reliable C_V data in the single- and two-phase regions. The method of quasi-static thermograms was used to determine T_s and ρ_s at the coexistence curve. The method of quasi-static thermograms gives reliable data under all conditions, including close to T_c. In this method, the calorimeter is filled to a desired fluid density, then the apparatus is raised to the working temperature and held until adiabatic conditions are sustained. After this, thermograms are recorded. These simultaneously display the time-dependence of the sample temperature and the potential difference for the thermocouple between the inner and the outer calorimetric vessels. At each density, thermograms are recorded several times while both heating and cooling. This method efficiently determines the whole phase transition curve at densities near the critical point. This method loses some sensitivity at densities well below or above ρ_c. The smaller is the sample mass, the smaller is its contribution to the total heat capacity of the calorimetric system. Therefore, for small mass, the breaks displayed in thermograms, which are a consequence of the discontinuity in heat capacity of the sample, become less distinct. At high sample densities, the jump in heat capacity ΔC_V at the phase transition point is relatively small, and this may also lead to a loss of sensitivity. At a phase transition point, the slope of a thermogram ordinarily changes by 20 to 30% which makes it possible easily to determine the transition temperature.

The rate of temperature change, determined by the power supplied to the internal heater, varied from $10^{-3}\ \mathrm{K\cdot s^{-1}}$ far from the critical point to $5\times10^{-5}\ \mathrm{K\cdot s^{-1}}$ in the critical region. Near the critical point and the phase transition curve, the measurements were performed using lower temperature ramp rates. In the region of regular behavior of C_V, the measurements were carried out in temperature steps of 0.1 to 0.2 K; in the region of critical anomalies, the step was decreased to 0.02 K. The heat capacity C_V is calculated from the measured quantities with

$$C_V=\frac{1}{m}\left\{\frac{\Delta Q}{\Delta T}-C_0\right\} \tag{3}$$

where m is the mass of the sample in the calorimeter, ΔQ is the amount of heat released by the internal heater, and C_0 is the heat capacity of the empty calorimeter.

The heat capacity was obtained from the measured quantities m, ΔQ, ΔT, and C_0. The accuracy of the heat capacity measurements was assessed by analyzing the sensitivity of Eq. (3) to the experimental uncertainties of the measured quantities. The temperature was measured with a 10-Ω PRT mounted in a tube inside the calorimetric sphere. The thermometer was calibrated on the IPTS-68, and the measurements were converted to the ITS-90. The uncertainty of temperature measurements was less than 10 mK. The density of the sample $\rho=m/V_{PT}$ was obtained from the measured mass of the sample m and the working volume V_{PT} of the calorimetric vessel. The uncertainty in fluid mass measurement is 5×10^{-4} g. The uncertainty in density measurements is about 0.1%. The correction associated with deviations from a strictly isochoric path of the process can be estimated by

$$C_V=C_V^{\exp}-T\left(\frac{\partial P}{\partial T}\right)_V\left\{\left(\frac{dV}{dT}\right)+\left(\frac{\partial P}{\partial T}\right)_V\frac{dV}{dP}\right\}\left\{1-\frac{dV}{dP}\left(\frac{\partial P}{\partial V}\right)_T\right\}^{-1} \tag{4}$$

where the partial derivatives correspond to the sample and the total derivatives correspond to the calorimetric vessel. The correction in Eq. (4) was calculated with an uncertainty of between 4.0 and 9.5%, depending on density. The standard deviation for this correction $C_V - C_V^{\exp}$ is 11%. The uncertainty in C_V due to spurious heat leakage is $0.013\ \mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$. The uncertainty propagated to C_V from absolute uncertainties of the specific volume $\Delta V = 4 \cdot 10^{-4} V$ and temperature $\Delta T = 0.01$ K within 0.5 K of the phase transition point is 0.16%. It is 0.05% when the measurment is far from a phase transition.

When they exist, surface temperature gradients of about $0.1\ \mathrm{K \cdot m^{-1}}$ can result in systematic uncertainties in C_V ofup to 5%. In order to minimize temperature gradients, all thermal screens were made from copper and were furnished with additional heaters. Control of surface temperature gradients was performed by driving to zero the emfs of differential copper–constantan thermocouples. This approach reduced the temperature gradients on the surface of the calorimeter vessel to $0.02\ \mathrm{K \cdot m^{-1}}$. The sample of D_2O was used as supplied and had a purity of 99.8 mol%.

Based on a detailed analysis of all sources of uncertainties likely to affect the determination of C_V with the present system, the combined standard uncertainty of the measured heat capacity is 2 to 3 %.

3. RESULTS AND DISCUSSION

Measurements of the isochoric heat capacity were performed along the near-critical isochores $356.075\ \mathrm{kg \cdot m^{-3}}$ (D_2O) and $309.905\ \mathrm{kg \cdot m^{-3}}$ (H_2O) in the one- and two-phase regions. The temperature range was 623 to 661 K for heavy water and 627 to 658 K for light water. In total, 72 C_V measurements were made in the one- and two-phase regions for D_2O and 61 measurements for H_2O. Phase transition temperatures $T_S = 643.883$ (D_2O) and $T_S = 647.02$ K (H_2O) and one- C_{V1} and two-phase C_{V2} isochoric heat capacities on the coexistence curve were determined. The experimental values are given in Tables I and II and shown in Fig. 1. As shown in Fig. 1, detailed measurements were made near the phase transition points in order to determine exactly the phase transition T_S temperatures. Figure 1 shows the experimental behavior of C_V as a function of temperature for D_2O and H_2O on near-critical isochores together with values calculated from CREOS [5] and IAPWS-95 formulations [18]. The present data were not used to develop these formulations. Considering this fact, the deviations plotted in Fig. 2 show good agreement with the models. The deviation statistics are given in Table III. The absolute average deviation (AAD) for one-phase C_V is 1.6% for H_2O and 3.8% for D_2O, while two-phase C_V show a systematic bias of +6.5% for H_2O and small

Table I. One-Phase and Two-Phase Isochoric Heat Capacity Measurements of Light and Heavy Water at Near-Critical Densities

T (K)	C_V ($\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$)	T (K)	C_V ($\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$)
H_2O $\rho = 309.905\ \mathrm{kg \cdot m^{-3}}$		D_2O $\rho = 356.075\ \mathrm{kg \cdot m^{-3}}$	
627.11	9.411	623.80	7.489
627.29	9.437	623.88	7.409
627.47	9.534	623.97	7.482
627.65	9.610	624.05	7.473
627.83	9.646	624.15	7.499
628.01	9.765	624.24	7.495
628.10	9.801	624.53	7.508
628.36	9.860	628.13	7.976
641.47	10.961	628.30	7.894
641.65	10.933	628.49	7.942
641.99	10.942	628.67	7.955
642.17	10.933	628.85	8.070
644.41	11.510	629.74	7.893
644.49	11.746	629.92	7.885
644.59	12.051	630.01	7.843
644.67	12.089	630.18	7.899
644.77	12.052	639.15	9.479
644.86	12.078	639.32	9.273
644.95	12.081	639.59	9.348
645.04	12.002	641.91	10.160
645.13	12.075	641.99	10.340
645.22	12.180	642.09	10.410
645.30	12.300	642.17	10.380
645.40	12.356	642.36	10.721
645.58	12.388	642.45	10.876
645.67	12.715	642.54	11.039
645.74	12.582	642.63	11.114
645.84	12.953	642.72	11.165
645.92	13.037	642.80	11.255
646.02	13.465	642.90	11.345
646.11	13.341	642.98	11.636
646.20	13.547	643.08	11.600
646.29	13.205	643.16	11.944
646.38	13.711	643.24	12.185
646.47	14.151	643.34	12.493
646.55	14.726	643.42	12.694

Table I. *(Continued)*

T (K)	C_V ($\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$)	T (K)	C_V ($\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$)
H_2O		D_2O	
$\rho = 309.905\ \mathrm{kg \cdot m^{-3}}$		$\rho = 356.075\ \mathrm{kg \cdot m^{-3}}$	
646.65	15.090	643.52	12.879
646.74	15.318	643.61	13.424
646.83	16.014	643.70	13.660
646.91	16.883	643.79	14.250
646.99	19.324	643.88	16.365
647.02	27.719	643.88	21.239
647.02	11.431	643.88	8.347
647.17	8.582	644.05	7.027
647.27	8.295	644.15	6.383
647.36	7.835	644.24	6.138
650.57	4.610	644.33	5.969
650.74	4.569	644.42	5.747
650.92	4.553	644.49	5.796
651.11	4.541	644.59	5.574
651.28	4.476	644.67	5.524
651.46	4.360	644.77	5.400
651.64	4.344	644.86	5.313
651.82	4.352	651.55	4.400
657.16	4.026	651.64	4.321
657.24	4.068	651.73	4.394
657.34	4.054	651.82	4.313
657.52	4.047	651.91	4.277
657.70	3.950	651.99	4.235
657.79	4.132	652.09	4.216
657.88	3.970	652.30	4.255
		652.43	4.318
		652.53	4.363
		652.61	4.350
		652.71	4.335
		652.80	4.300
		660.01	3.940
		660.10	3.946
		660.18	3.891
		660.28	3.917
		660.36	3.867
		660.46	3.844
		660.54	3.810

Table II. Isochoric Heat Capacity Measurements (C_{V1}, C_{V2}), Temperatures (T_S), Densities (ρ_S), and Vapor-Pressure Temperature Derivatives (dP_S/dT_s) for H_2O and D_2O on the Coexistence Curve

T_S (K)	ρ_S ($\mathrm{kg \cdot m^{-3}}$)	C_{V1} ($\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$)	C_{V2} ($\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$)	(dP_S/dT_s) ($\mathrm{MPa \cdot K^{-1}}$)
		H_2O		
647.020	309.905	11.431	27.719	0.263
		D_2O		
643.883	356.075	8.347	21.239	0.276

nonsystematic deviations, within 3.6%, for D_2O. The maximum deviations of about ±11 to 25% were found in the immediate vicinity of the phase transition temperatures, at 643.83 K for D_2O and at 647.065 K for H_2O. The experimental temperatures T_S and densities ρ_S along the coexistence curve are presented in Table II and Fig. 3 together with published values. Our results for D_2O $T_S = 643.883$ K (ITS-90) show excellent agreement with the IAPWS-85 recommendation $T_C = 643.89 \pm 0.2$ K (IPTS-68) [9], which is from a direct visual observation by Blank [20], and were supported by measurements of Marshall and Simonson [21], which gave

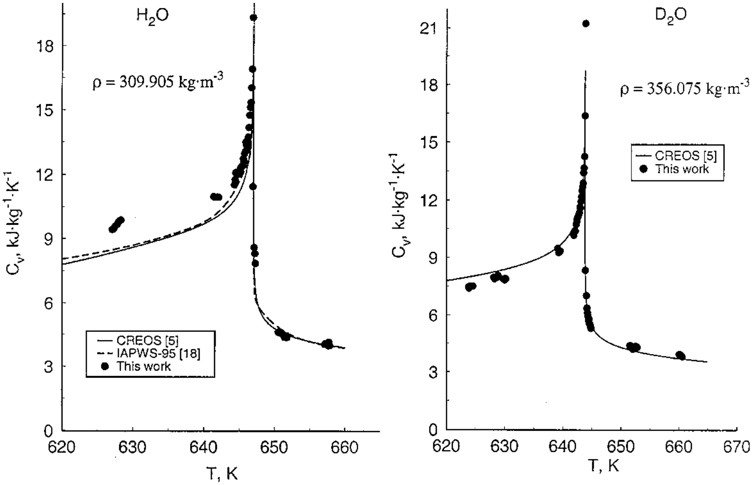

Fig. 1. Temperature dependence of the experimental isochoric heat capacity of light and heavy water along the neat-critical isochortes together with values calculated from CREOS [5] and IAPWS-95 [18].

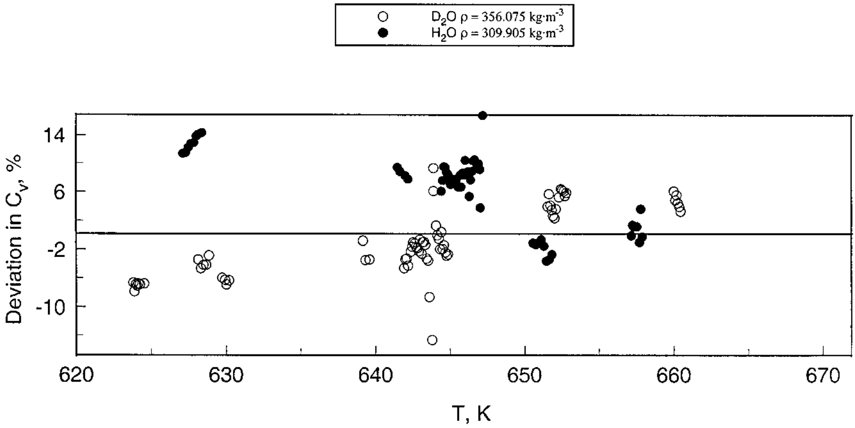

Fig. 2. Percentage deviations of measured isochoric heat capacities of light and heavy water with the values calculated from CREOS [5] and IAPWS-95 [18].

$T_C = 643.847 \pm 0.1$ K (ITS-90). Therefore, our new experimental result conforms with the IAPWS-85 recommendation [9] of $T_C = 643.847$ K (ITS-90) and is also consistent with the available experimental *PVT* data for heavy water [22–25]. The critical temperature derived from previous C_V measurements by Mursalov et al. [4], Hebert et al. [10], and Reisenfeld and Chang [11] gives a systematic deviation from present results of about

Table III. Deviation Statistics for Measured C_V Data Compared with a Model [5] Developed Without These Results for D_2O and H_2O

ρ_S (kg · m^{-3})	AAD (%)	Bias (%)	SD (%)	SE (%)	Max. dev. (%)
H_2O (all data, one- and two phase regions)					
309.905	6.8	6.3	4.75	0.6	23.3
H_2O (one- phase region)					
309.905	1.6	−0.6	1.9	0.5	3.6
D_2O (all data, one and two-phase regions)					
356.075	3.9	−0.8	4.4	0.5	9.3
D_2O (one-phase region)					
356.075	3.8	2.9	3.3	0.6	9.3

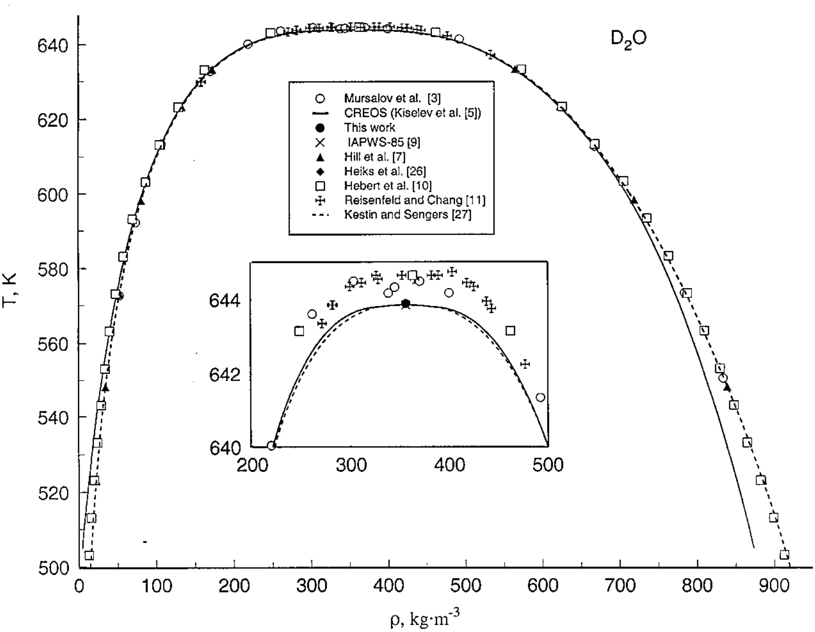

Fig. 3. Experimental liquid and vapor saturated densities of heavy water near the critical point derived by different authors together with values calculated from CREOS [5]. The inset shows the coexistence curve behavior in the immediate vicinity of the critical point.

+0.45 K. A major concern with the earlier measurements, already mentioned by Mursalov et al. [4], is the possibility of impurities in their D_2O sample. It is well established that the presence of either an H_2O impurity or, even more likely, a dissolved ionic species, could lead to a higher measured saturation temperature. However, to be certain, additional measurements of C_V along the near-critical densities (within $\pm 30\%$ of ρ_c), and near the phase transition temperatures in the one- and two-phase regions, are needed.

The measured value of the phase transition temperature $T_S = 647.02$ K (ITS-90) for light water at a density of 309.905 kg $\cdot$ m^{-3} is in good agreement with the literature value $T_S = 647.09$ K (ITS-90) [5, 18]. Excellent agreement, within 1.5 % was found between our measured value and that recommended by Levelt-Sengers et al. [9] for the first temperature derivative of the vapor-pressure curve at the critical point $(dP_S/dT)_C = 0.263$ MPa $\cdot$ K^{-1} for H_2O, while for D_2O our measured value of $(dP_S/dT)_C = 0.278$ MPa $\cdot$ K^{-1} deviates from a value estimated by Hill et al. [7] by about 6%, which is within the range of their uncertainty (5 to 8%).

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REFERENCES

1. Kh. I. Amirkhanov, G. V. Stepanov, B. A. Mursalov, and O. A. Bui, *Teploenergetika* **22**:68 (1973).
2. Kh. I. Amirkhanov, G. V. Stepanov, and B. A. Mursalov, *Dokl. Akad. Nauk SSSR* **163**:1189 (1965).
3. B. A. Mursalov, *Ph.D. thesis* (AZNEFTEXIM, Baku, 1975).
4. B. A. Mursalov, I. M. Abdulagatov, V. I. Dvoryanchikov, and S. B. Kiselev, *Int. J. Thermophys.* **20**:1497 (1999).
5. S. B. Kiselev, I. M. Abdulagatov, and A. H. Harvey, *Int. J. Thermophys.* **20**:563 (1999).
6. A. K. Wyczalkowska, Kh. S. Abdulkadirova, M. A. Anisimov, and J. V. Sengers, *J. Chem. Phys.* **113**:4985 (2000).
7. P. G. Hill, R. D. C. Macmillan, and V. Lee, *J. Phys. Chem. Ref. Data* **11**:1 (1982).
8. I. M. Abdulagatov, J. W. Magee, S. B. Kiselev, and D. J. Friend, *in Steam, Water, and Hydrothermal Systems: Physical and Chemical Meeting the Needs of Industry. Proc. 13th Int. Conf. Pro. Water Steam*, P. R. Tremaine, P. G. Hill, D. E. Irish, and P. V. Balakrishnan, eds. (NRC Press, Ottawa, 2000), p. 374.
9. J. M. H. Levelt Sengers, J. Straub, K. Watanabe, and P. G. Hill, *J. Phys. Chem. Ref. Data* **14**:103 (1985).
10. G. M. Hebert, H. F. McDuffie, and C. H. Secoy, *J. Phys. Chem.* **62**:431 (1958).
11. E. H. Riesenfeld and T. L. Chang, *Zeitschr. Phys. Chem.* **30**:61 (1935).
12. Kh. I. Amirkhanov, G. V. Stepanov, and B. G. Alibekov, *Isochoric Heat Capacity of Water and Steam* (Amerind, New Delhi, 1974).
13. I. M. Abdulagatov, N. G. Polikhronidi, and R. G. Batyrova, *J. Chem. Thermodyn.* **26**:1031 (1994).
14. I. M. Abdulagatov, N. G. Polikhronidi, and R. G. Batyrova, *Ber. Bunsenger. Phys. Chem.* **98**:1068 (1994).
15. N. G. Polikhronidi, R. G. Batyrova, and I. M. Abdulagatov, *Fluid Phase Equil.* **175**:153 (2000).
16. I. M. Abdulagatov, V. I. Dvoryanchikov, and L. G. Abramova, *J. Sol. Chem.* **28**:871 (1999).
17. N. B. Vargaftik, *Handbook of Physical Properties of Liquids and Gases*, 2nd ed. (Hemisphere, New York, 1983).
18. W. Wagner and A. Pruss, submitted for publication.
19. Kh. I. Amirkhanov, G. V. Stepanov, I. M. Abdulagatov, and O. A. Boi, *Isochoric Heat Capacity of Propan-1-ol and Propan-2-ol* (Dagestan Scientific Center of the Russian Academy of Science, Makhachkala, 1989).
20. G. Blank, *Warme Stoffubertragung* **2**:53 (1969).
21. W. L. Marshall and J. M. Simonson, *J. Chem. Thermodyn.* **23**:613 (1991).
22. S. L. Rivkin and T. S. Akhundov, *Teploenergetika* **9**:62 (1962).

23. S. L. Rivkin and T. S. Akhundov, *Atomnaya Energet*. **14**:581 (1963).
24. N. V. Tsederberg, A. A. Aleksandrov, T. S. Khasanshin, and D. K. Larkin, *Teploenergetika* **20**:13 (1973).
25. G. S. Kell, G. E. McLaurin, and E. Whalley, *Proc. Roy. Soc. Lond. A* **425**:49 (1989).
26. J. R. Heiks, M. K. Barnett, L. V. Jones, and E. Orban, *J. Phys. Chem.* **58**:488 (1954).
27. J. Kestin and J. V. Sengers, *J. Phys. Chem. Ref. Data* **15**:305 (1986).