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Isochoric Heat Capacity Measurements for Heavy Water Near the Critical Point

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Isochoric heat capacity measurements of D_2O are presented as a function of temperature at fixed densities of 319.60, 398.90, 431.09, and 506.95 $kg \cdot m^{-3}$. The measurements cover a range of temperatures from 551 to 671 K and pressures up to 32 MPa. The coverage includes one- and two-phase states and the coexistence curve near the critical point of D_2O. A high-temperature, high-pressure, adiabatic, and nearly constant-volume calorimeter was used for the measurements. Uncertainties of the heat capacity measurements are estimated to be 2 to 3%. Temperatures at saturation $T_S(\rho)$ were measured isochorically using a quasi-static thermogram method. The uncertainty of the phase transition temperature measurements is about ± 0.02 K. The measured C_V data for D_2O were compared with values predicted from a parametric crossover equation of state and six-term Landau expansion crossover model. The critical behavior of second temperature derivatives of the vapor pressure and chemical potential were studied using measured two-phase isochoric heat capacities. From measured isochoric heat capacities and saturated densities for heavy water, the values of asymptotic critical amplitudes were estimated. It is shown that the critical parameters (critical temperature and critical density) adopted by IAPWS are consistent with the T_S–ρ_S measurements for D_2O near the critical point.

KEY WORDS: adiabatic calorimeter; critical amplitudes; critical point; coexistence curve; crossover equation of state; density; isochoric heat capacity; light and heavy water.

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1. INTRODUCTION

Previously, isochoric heat capacities of heavy water were reported by Amirkhanov et al. [1, 2], Mursalov [3], Mursalov et al. [4], and Polikhronidi et al. [5]. Isochoric heat capacity measurements 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 %) along two isochores at densities of 370.37 and 400.00 $kg \cdot m^{-3}$. The measured data were presented only graphically. A comprehensive set of 23 liquid and vapor isochores was reported recently by Mursalov et al. [3, 4]. These measurements cover a temperature range from 294 to 746 K and densities between 52 and 1105 $kg \cdot m^{-3}$. The uncertainty of these measurements in the critical region is 4.5%. In the work by Mursalov et al. [4], the original experimental temperatures were adjusted downward by 0.45 K because the values of saturation temperatures for measured isochores were, on average, 0.45 K higher than saturation temperatures (including T_C) recommended by Levelt Sengers et al. [6] for the IAPWS formulation. Polikhronidi et al. [5] reported isochoric heat capacity measurements for heavy water at a very-near-critical density of 356.08 $kg \cdot m^{-3}$ for temperatures from 623.80 to 660.54 K in both the two- and one-phase regions. The same apparatus was used in this work to measure C_V of D_2O at four densities (319.60, 398.90, 431.09, and 506.95 $kg \cdot m^{-3}$) at temperatures between 551 and 671 K.

Crossover equations of state for D_2O have been independently developed by Kiselev et al. [7] and Wyczalkowska et al. [8]. The parametric crossover model developed by Kiselev et al. [7] is valid in the range of temperature $0.8T_C \leqslant T \leqslant 1.5T_C$ and density $0.35\rho_C \leqslant \rho \leqslant 1.5\rho_C$. This model incorporates scaling laws asymptotically close to the critical point and is transformed into a regular classical expansion far from the critical point. The parameters of the crossover equation were determined using *PVT* [9–11] and isochoric heat capacity data reported by Amirkhanov et al. [1] and corrected data by Mursalov et al. [4]. Wyczalkowska et al. [8] developed a six-term Landau expansion crossover model for D_2O in the critical region. This model also incorporates crossover from Ising-type to mean-field critical behavior of the Helmholtz-energy density. The system-dependent coefficients in this crossover equation of state for D_2O were determined from the following sets of available experimental data in the critical region: *PVT* [9, 11], vapor-pressure [9, 12], and isobaric heat capacity C_P [13, 14]. The range of validity of this equation of state is: $\rho > 165\ kg \cdot m^{-3}$, $T > 630\ K$, and reduced susceptibility $\bar{\chi}^{-1} = 2.0$.

It corresponds to ranges of temperature $630 < T < 820$ K at $\rho = \rho_C$ and density 165 $\text{kg} \cdot \text{m}^{-3} < \rho < 625$ $\text{kg} \cdot \text{m}^{-3}$ at $T = 630$ K. Wyczalkowska et al. [8] implied that the crossover parameters $(\bar{u}, \Lambda)$ and scaling-field parameters (c_t, c_ρ, c, d_1) are the same for both light and heavy water. They concluded that the thermodynamic properties of heavy water can be represented by the crossover model with the same crossover and scaling-field parameters as those for light water. Hill et al. [15] have developed a fundamental EOS for D_2O that is valid in the range up to 100 MPa and 873 K.

The chief purpose of this paper is to study the shape of the coexistence curve in the immediate vicinity of the critical point of D_2O, in order to exactly determine its critical temperature. Another aim of the paper is to estimate the values of asymptotic critical amplitudes of $C_V(A_0^{\pm})$ and the coexistence curve B_0 to check the universal ratio between asymptotic critical amplitudes predicted by scaling theory [22] and its comparison with values for light water. In our previous paper (Polikhronidi et al. [5]), we also measured C_V for light water along one near-critical isochore, 309.91 $\text{kg} \cdot \text{m}^{-3}$, using the present experimental apparatus in order to check its performance and verify calculation procedures.

1. EXPERIMENTAL

The calorimeter used for the present measurements has been described in detail in our previous work [5]. Since the apparatus, the construction of the calorimeter, and experimental procedure have been described in detail in several previous publications [5, 19–21, 25, 26], they will be only briefly reviewed here. The isochoric heat capacities were measured with a high-temperature, high-pressure, adiabatic, and nearly constant-volume calorimeter, which offers an uncertainty of 2 to 3%. The volume of the calorimeter, approximately 104.44 cm^3 (at atmospheric pressure and 297.15 K), is a function of temperature and pressure. The values of calorimeter volume was determined by using PVT data for pure water [27]. The pressure expansion $V(P)$ was determined by calculation using formula Love for spherical vessel [28–30]. The uncertainty in the determination of volume at any T and P in our experiment is about 0.05%. The mass of the sample was measured by using a weighing method with an uncertainty of 0.05 mg. Therefore, the uncertainty in the measurements of density $\rho = m/V(P, T)$ is about 0.06 to 0.10%. The heat capacity was obtained from the measured quantities $m, \Delta Q, \Delta T$, and C_0. The temperature of the sample was measured by a miniature standard 10 Ω PRT. Thermometer resistance at 0°C is $R_0 = 10.1230\ \Omega$ and the ration $R_{100}/R_0 = 1.3924$, where R_{100} is the thermometer resistance at 100 °C. The thermometer was calibrated by

(ITS-90 scale) the All-Russian Scientific Research Institute of Physical and Technical measurements (Moscow). The uncertainty of temperature measurements was less than 10 mK.

The heat capacity of the empty calorimeter C_0 was determined experimentally using a reference substance (helium-4) with well-known isobaric heat capacities [31], in the temperature range up to 1000 K at pressures up to 20 MPa. The uncertainty in the C_P data used for calibration of C_0 is 0.2%. The correction related to the non-isochoric behavior during heating was determined to an uncertainty of about 4.0 to 9.5% depending on the density. The standard deviation for this correction ΔC_V is 11%. The absolute uncertainty in C_V due to a break of the adiabatic condition is $0.013\ \mathrm{kJ \cdot K^{-1}}$. The uncertainty of C_V propagated from the uncertainties of the specific volume $\Delta V = 4 \times 10^{-4}\, V$ and the temperature $\Delta T = 0.01$ K is 0.16% near phase transition points (in the range lower than $T - T_S = 0.5$ K), and is 0.05% far from phase transition points. Thus, the combined standard uncertainty related to the indirect character of the measurements did not exceed 0.16%.

The heat capacity was measured as a function of temperature at nearly constant density. The calorimeter was filled at room temperature, sealed off, and heated along a quasi-isochore. Each run for heat capacity was normally started in the two-phase region and completed in the one-phase region. The heat capacity rises to a maximum at the phase-transition temperature T_S for all measured densities, and then drops discontinuously to a value corresponding to the one-phase region. The abrupt changes of the isochoric heat capacity behavior near the phase transition temperature at constant density can be used to develop an accurate technique for measurements of saturation properties (T_S and ρ_S) of fluids (i.e., to determine the phase transition temperature T_S from the two-phase to a single-phase state). The techniques of determining parameters T_S and ρ_S at the coexistence curve and of measuring the heat capacity C_V at this curve are similar to the method of quasi-static thermograms as described in detail in our previous papers [5, 19–21, 25, 26].

The method of quasi-static thermograms makes it possible to obtain reliable data up to temperatures of $T_C \pm 0.01$ K with an uncertainty of 0.02 K. Near the phase transition points, the measurements were carried out in both the forward (heating) and backward directions (cooling) to extract phase transition temperatures for given densities, i.e., to determine the saturated properties (densities ρ_S and temperatures T_S). The reproducibility of the phase-transition temperature measurements is 0.02 to 0.03 K. All measurements were carried out with vigorous mixing using a stirrer made of a perforated thin foil of stainless steel. The commercial supplier of the D_2O provided a purity analysis of 99.9 mole%.

3. RESULTS AND DISCUSSION

Measurements of the isochoric heat capacity for D_2O were performed along four near-critical liquid and vapor isochores: 319.60, 398.90, 431.09, and 506.95 $kg \cdot m^{-3}$. The measurements cover a range in temperature from 551 to 671 K and pressures up to 32 MPa in the one- and two-phase regions. In total, 110 C_V measurements were made in the one-phase region and 159 measurements in the two-phase region. Values of phase transition temperatures T_S, one-phase C_{V1}, and two-phase C_{V2} isochoric heat capacities on the coexistence curve corresponding to the measured isochores were determined. The experimental values are given in Tables I and II and shown in Figs. 1a to 1e, and Figs. 2 to 6. Tightly spaced measurements were made near the phase transition points in order to precisely determine the phase-transition temperatures T_S.

Figures 1a to 1e show the experimental behavior of one- and two-phase C_V as a function of temperature for D_2O together with values calculated from the crossover models developed by both Kiselev et al. [7] and Wyszalkowska et al. [8]. Figure 1d shows the temperature dependence C_V for D_2O reported by Mursalov et al. [4], before and after a temperature shift along the isochore 398.90 $kg \cdot m^{-3}$, together with values measured in this work and calculated from crossover models [7, 8]. As one can see from Fig. 1d, the data by Mursalov et al. [4] after the shift show satisfactory agreement with both the new measurements and the calculated values. A deviation plot is given in Fig. 7. The deviation results for data reported in this work are: AAD = 5.57%, Bias = −4.5%, St. Dev = 5.12%, St. Err = 0.35%, and Max. Dev = 20.18% (N = 220) for the crossover equation by Kiselev et al. [7] and AAD = 6.76%, Bias = 0.21%, St. Dev = 7.65%, St. Err = 0.74%, and Max. Dev = 18.56% (N = 108) for the crossover equation by Wyszalkowska et al. [8]. Almost all of the measured C_V data (except for the critical isochore 356.08 $kg \cdot m^{-3}$) show systematically negative deviations from the crossover equation by Kiselev et al. [7], while the crossover equation by Wyszalkowska et al. [8] gives nonsystematic deviations. Maximum deviations up to 20% were found in the immediate vicinity of phase-transition temperatures.

Measured values of C_V for D_2O in the supercritical region, together with values calculated from crossover models [7, 8], are shown in Fig. 2. Figure 3 shows two-phase C_{V2} for D_2O as a function of specific volume along a number of near-critical isotherms. The experimental results of temperatures T_S and densities ρ_S along the coexistence curve, which were determined by using the method of quasi-static thermograms, and one- and two-phase isochoric heat capacities (C_{V1}, C_{V2}) on the coexistence curve are presented in Table II and Figs. 4 to 6 together with calculated and

Table I. Experimental Values of the One-Phase and Two-Phase Isochoric Heat Capacities of Heavy Water Along the Near-Critical Isochores

T (K)	C_V ($\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$)
$\rho = 319.60\ \mathrm{kg \cdot m^{-3}}$	
569.097	4.760
569.543	4.803
581.712	5.322
603.551	6.297
603.811	6.342
620.708	7.499
620.965	7.523
630.348	8.506
630.763	8.597
637.047	9.411
637.469	9.576
637.807	9.643
638.913	9.932
639.166	9.987
639.410	10.041
641.017	10.657
641.354	10.813
641.523	10.988
642.781	11.928
642.904	12.097
642.949	12.195
643.046	12.313
643.124	12.466
643.204	12.653
643.287	12.801
643.374	13.018
643.461	13.288
643.544	13.501
643.629	13.822
643.714	14.185
643.729	14.445
643.745	14.738
643.763	15.068
643.778[a]	**15.252**[a]
643.778[a]	**6.153**[a]
643.798	5.566
643.813	5.503
643.830	5.324
643.848	5.281
643.864	5.205
643.882	5.088
643.965	4.933
644.052	4.772
644.135	4.681
649.006	3.807
649.174	3.733
649.258	3.695
649.342	3.677
649.509	3.665
654.030	3.632
654.197	3.630
654.472	3.628
662.189	3.616
662.448	3.614
662.707	3.602
662.946	3.598
663.112	3.593
$\rho = 356.08\ \mathrm{kg \cdot m^{-3}}$	
623.80	7.489
623.88	7.409
623.97	7.482
624.05	7.473
624.15	7.499
624.24	7.495
624.53	7.508
628.13	7.976
628.30	7.894
628.49	7.942
628.67	7.955
628.85	8.070
629.74	7.893
629.92	7.885
630.01	7.843
630.18	7.899
639.15	9.479
639.32	9.273
639.59	9.348
641.91	10.160
641.99	10.340
642.09	10.410
642.17	10.380
642.36	10.721
642.45	10.876
642.54	11.039
642.63	11.114
642.72	11.165
642.80	11.255
642.90	11.345
642.98	11.636
643.08	11.600
643.16	11.944
643.24	12.185
643.34	12.493
643.42	12.694

Table I. *(Continued)*

T (K)	C_V $(\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}})$	T (K)	C_V $(\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}})$
643.52	12.879	636.962	8.098
643.61	13.424	637.131	8.118
643.70	13.660	638.484	8.436
643.79	14.250	638.658	8.497
643.88	16.365	638.827	8.572
643.88[a]	**21.239**[a]	639.075	8.645
643.88[a]	**8.347**[a]	639.244	8.675
644.05	7.027	639.406	8.679
644.15	6.383	642.868	10.623
644.24	6.138	642.985	10.634
644.33	5.969	643.122	10.735
644.42	5.747	643.208	10.899
644.49	5.796	643.292	11.051
644.59	5.574	643.377	11.288
644.67	5.524	643.473	11.473
644.77	5.400	643.548	11.574
644.86	5.313	643.630	11.774
651.55	4.400	643.713	12.332
651.64	4.321	643.730	12.826
651.73	4.394	643.747	13.072
651.82	4.313	643.764	13.260
651.91	4.277	643.769	13.412
651.99	4.235	643.771	13.585
652.09	4.216	**643.780**[a]	**14.257**[a]
652.30	4.255	**643.780**[a]	**6.078**[a]
652.43	4.318	643.788	6.003
652.53	4.363	643.796	5.942
652.61	4.350	643.808	5.663
652.71	4.335	643.850	5.528
652.80	4.300	643.872	5.426
660.01	3.940	643.960	5.139
660.10	3.946	644.050	4.938
660.18	3.891	644.135	4.723
660.28	3.917	644.213	4.671
660.36	3.867	647.328	3.809
660.46	3.844	647.495	3.756
660.54	3.810	647.664	3.652
		647.831	3.638
$\rho = 398.90\ \mathrm{kg \cdot m^{-3}}$		647.915	3.622
		654.123	3.368
551.136	3.817	654.280	3.351
586.498	5.309	654.521	3.347
587.500	5.493	662.116	3.313
623.957	6.850	662.448	3.299
624.043	6.852	662.698	3.280
624.469	6.877	670.489	3.165
628.646	7.193	670.737	3.160
629.157	7.277	671.067	3.157

Table I. *(Continued)*

T (K)	C_V ($\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$)
$\rho = 431.69\ \mathrm{kg \cdot m^{-3}}$	
585.040	5.378
585.528	5.432
594.159	5.503
594.674	5.541
604.948	5.657
605.295	5.660
623.360	6.684
623.516	6.637
624.043	6.702
632.131	7.237
632.586	7.254
632.860	7.303
636.739	7.936
636.992	7.992
637.306	8.031
639.389	8.359
639.497	8.347
639.582	8.497
639.666	8.528
639.750	8.553
639.835	8.590
640.004	8.623
642.703	9.853
642.787	9.888
642.871	9.974
642.955	10.066
643.040	10.156
643.123	10.179
643.207	10.249
643.293	10.325
643.376	10.473
643.393	10.598
643.411	10.647
643.419[a]	**10.996**[a]
643.419[a]	**4.985**[a]
643.423	4.872
643.444	4.707
643.460	4.664
643.478	4.640
643.495	4.515
643.512	4.509
643.529	4.407
643.544	4.382
643.629	4.256
643.713	4.172
643.797	4.081
643.881	4.029
643.963	3.995
644.048	3.977
644.133	3.932
644.217	3.885
644.304	3.893
647.999	3.532
648.167	3.529
648.419	3.482
648.503	3.436
648.587	3.438
648.671	3.432
654.163	3.347
654.247	3.340
654.414	3.338
654.748	3.332
$\rho = 506.95\ \mathrm{kg \cdot m^{-3}}$	
601.739	5.273
602.013	5.303
617.141	5.717
617.893	5.736
628.504	6.272
629.249	6.319
629.573	6.341
634.001	6.698
634.612	6.723
636.202	6.888
636.445	6.937
636.710	6.977
638.569	7.129
638.653	7.153
638.882	7.178
638.991	7.196
639.160	7.203
639.328	7.214
639.346	7.220
639.380	7.226
639.413	7.278
639.434[a]	**7.305**[a]
639.434[a]	**3.420**[a]
639.447	3.350
639.464	3.339
639.481	3.285
639.498	3.228
639.582	3.193
639.751	3.147
639.920	3.108
640.089	3.092

[a] One- and two-phase saturation experimental points.

Table II. Experimental Values of the One- and Two-Phase Isochoric Heat Capacities (C_{V1}, C_{V2}), Temperatures (T_S), and Densities (ρ_S) of Heavy Water on the Coexistence Curve

T_S (K) Heating run	T_S (K) Cooling run	ρ_S ($\mathrm{kg \cdot m^{-3}}$)	C_{V1} ($\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$)	C_{V2} ($\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$)
639.434	639.432	506.95	3.420	7.305
643.419	643.362	431.09	4.640	10.996
643.394	–	431.09	–	–
643.780	643.732	398.90	5.942	14.257
643.883	–	356.08	8.347	21.239
643.778	643.690	319.60	6.153	15.252
643.701	–	319.60	–	–

experimental values from the literature. There are some differences between the IAPWS [6] accepted values of the critical parameters ($T_C = 643.847 \pm 0.2$ K, $\rho_C = 356 \pm 5\ \mathrm{kg \cdot m^{-3}}$) of D_2O and experimental saturated temperature and density data near the critical point reported in Refs. 3, 16, and 17. The IAPWS values of the critical parameters are consistent with

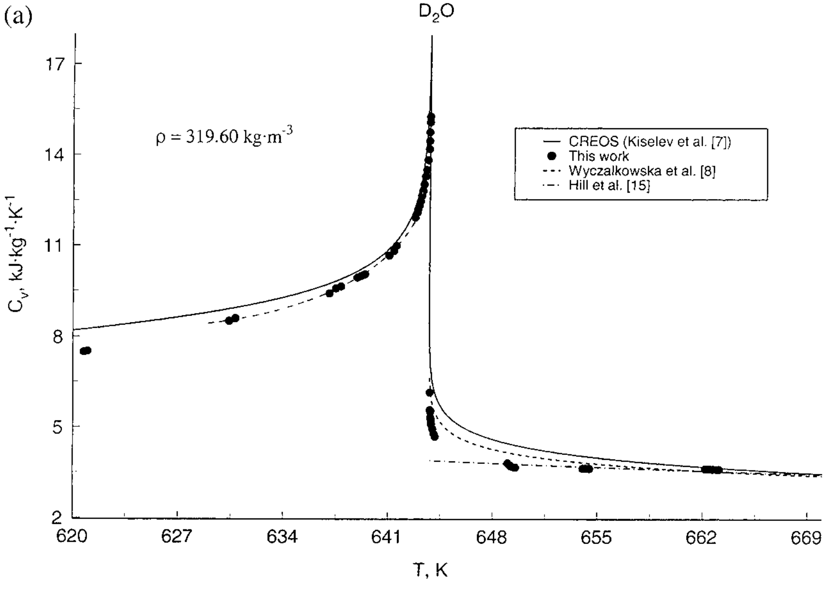
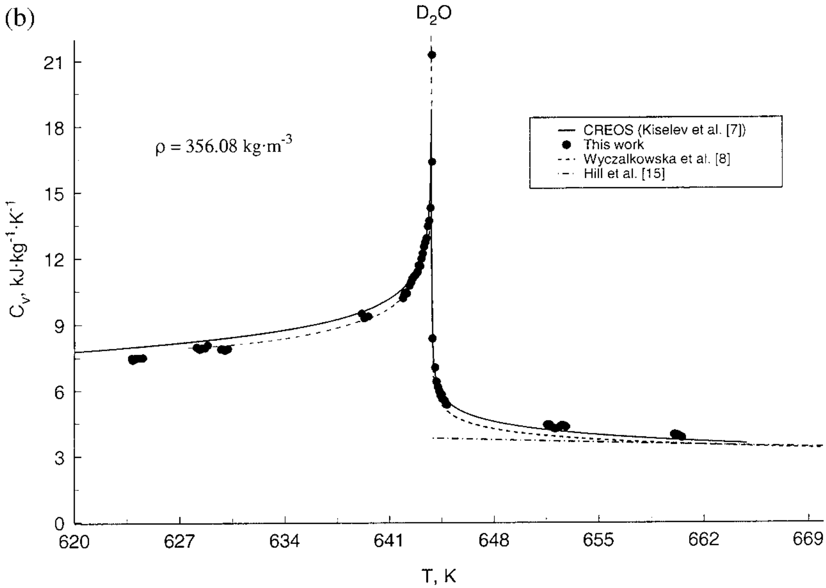


Fig. 1. (a)–(e) One- and two-phase experimental isochoric heat capacities of heavy water as a function of temperature along near-critical isochores together with values calculated from crossover equations of state.



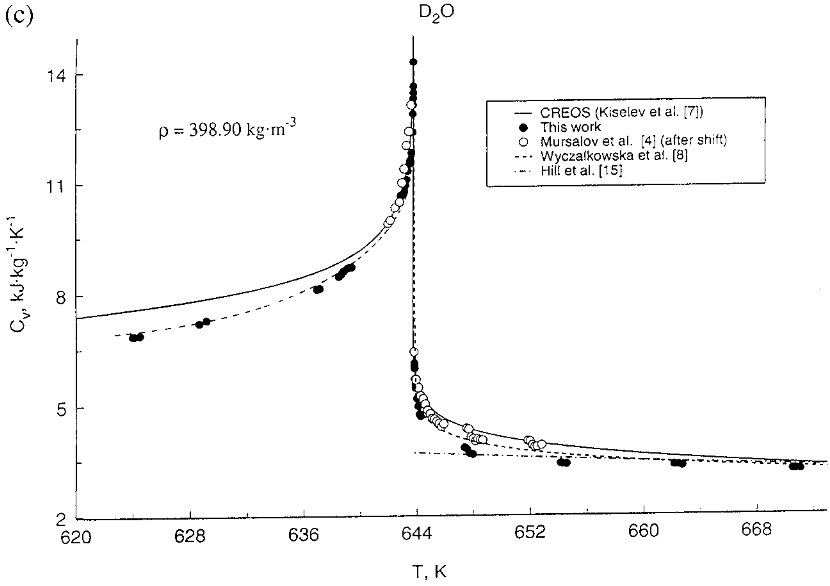
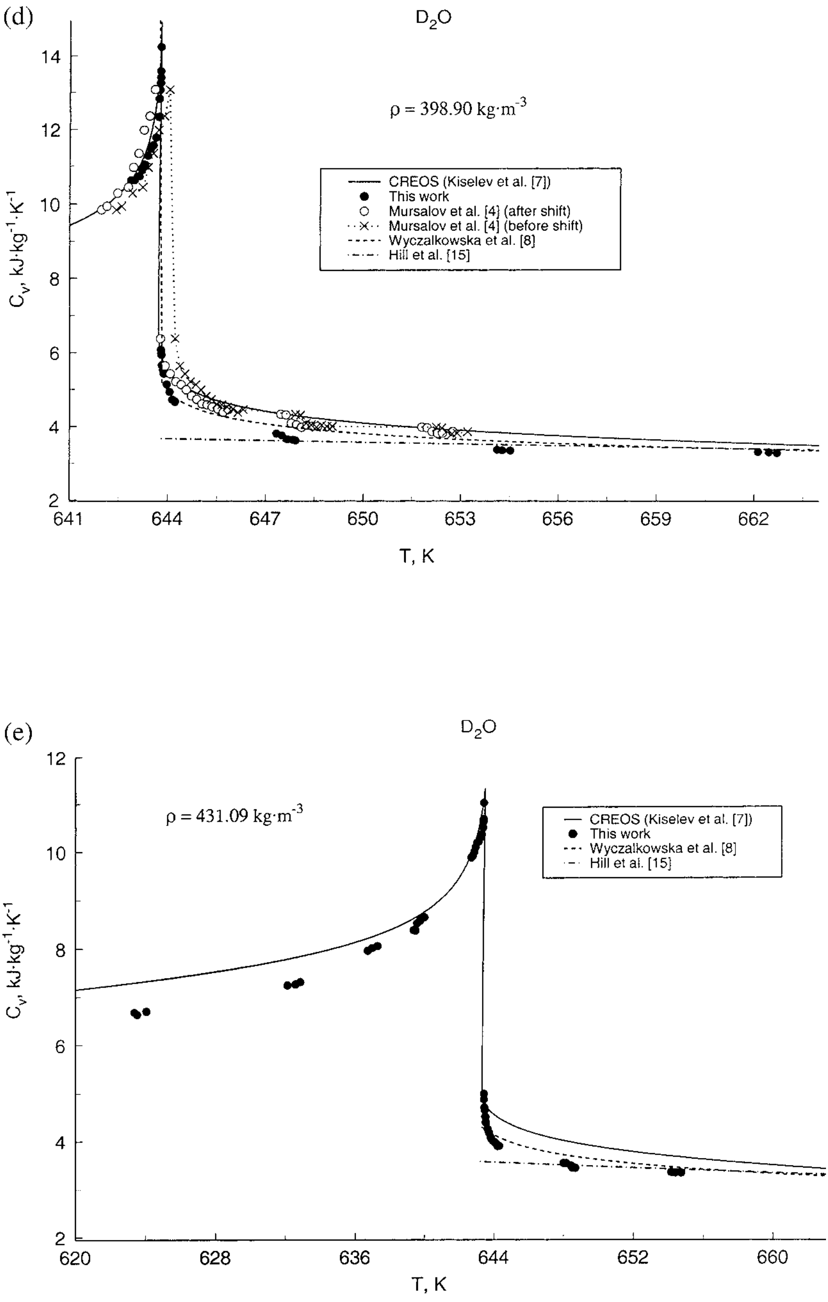


Fig. 1. *(Continued)*



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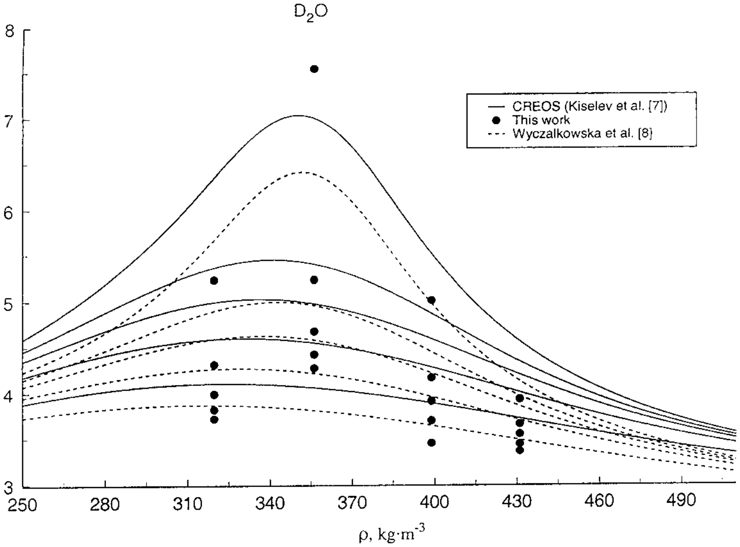

Fig. 2. One-phase experimental isochoric heat capacities of heavy water as a function of density along near-critical and supercritical isotherms together with values calculated from crossover equations of state.

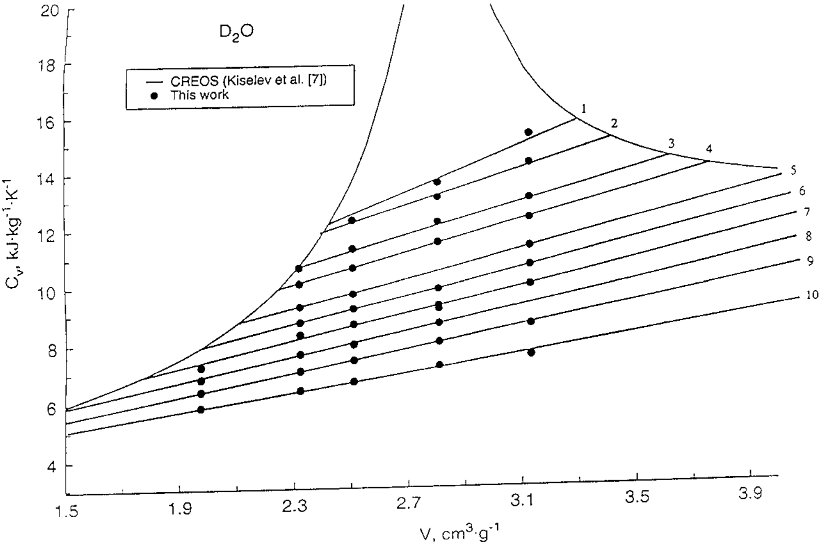

Fig. 3. Two-phase experimental isochoric heat capacities C_{V2} of heavy water as a function of specific volume V along near-critical isotherms. 1 – 643.778 K; 2 – 643.7 K; 3 – 643.4 K; 4 – 643.0 K; 5 – 642.0 K; 6 – 641.0 K; 7 – 639.0 K; 8 – 635.0 K; 9 – 630.0 K; 10 – 620.0 K.

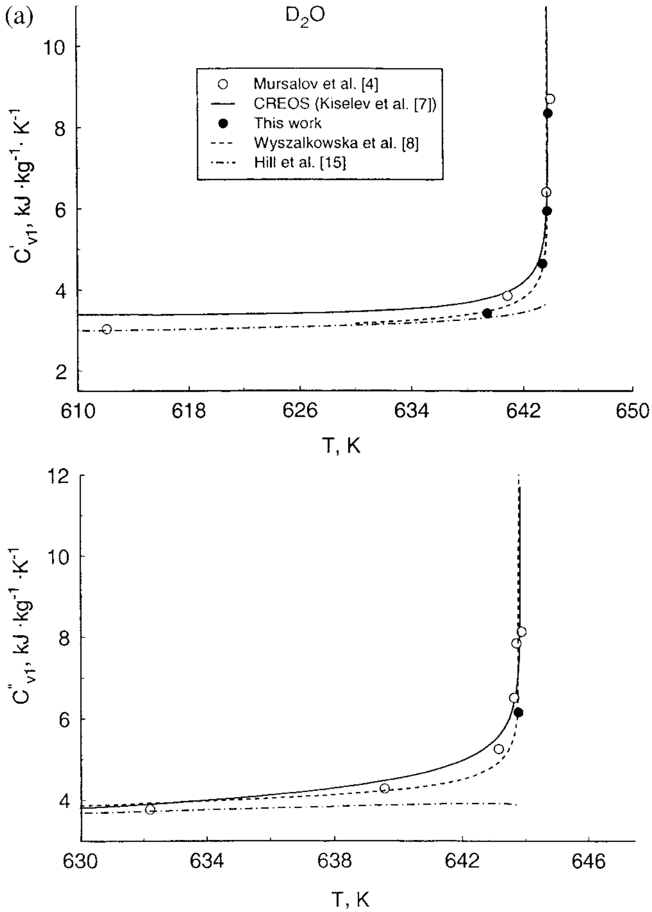

Fig. 4. (a) One-phase (liquid C'_{V1} and vapor C''_{V1}) and (b) two-phase (liquid C'_{V2} and vapor C''_{V2}) experimental isochoric heat capacities of heavy water at saturation as a function of temperature near the critical point together with values calculated from crossover equations [7, 8].

the high-accuracy experimental *PVT* data [9–11] for D_2O and the measurements by Marshall and Simonson [18]. Isochoric heat capacity measurements in the two- and one-phase regions are very sensitive measurements for locating the phase transition boundaries, especially near the critical point [5, 19–21]. C_V measurements near the phase-transition points (including two- and one-phase regions) provide extremely precise T_S–ρ_S data on the coexistence curve near the critical point. These data can be used to accurately estimate values of the critical parameters (T_C, ρ_C).

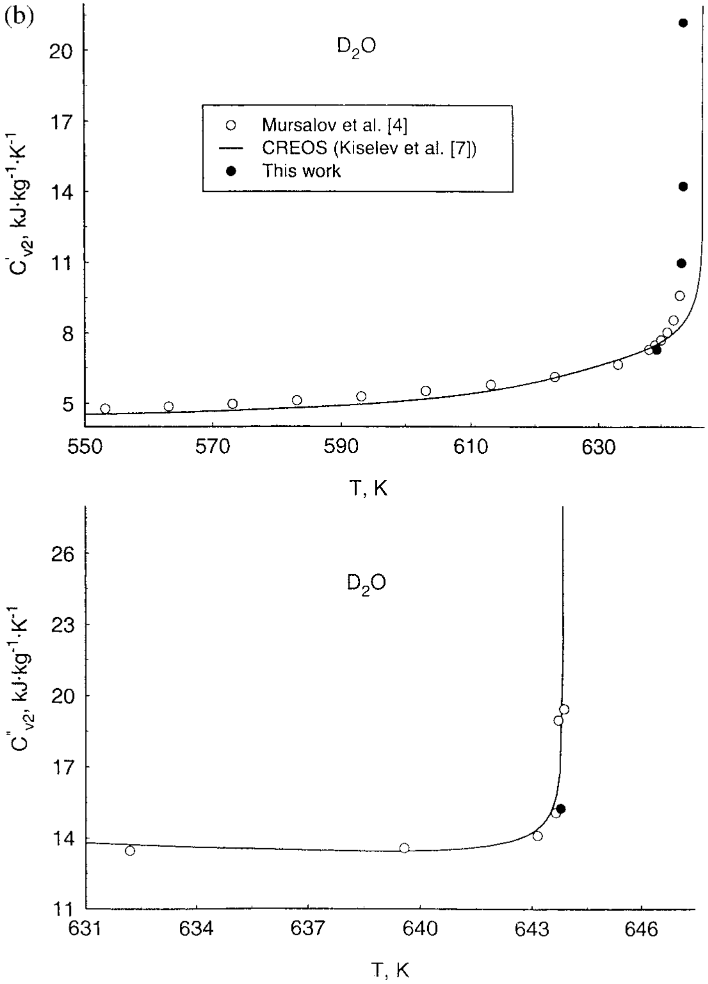

Fig. 4. *(Continued)*

As one can see from Table II and Fig. 6, our new experimental results agree with the IAPWS recommendation [6] for the critical temperature $T_C = 643.847$ K. This is consistent with the avaliable experimental *PVT* data for heavy water [9–11, 32] and with a direct visual observation by Blank [33] that was supported by measurements of Marshall and Simonson [18]. The critical temperature derived from previous C_V measurements by Mursalov et al. [4], Hebert et al. [16], and Riesenfeld and Chang [17] show a deviation from present results of about 0.45 K. As

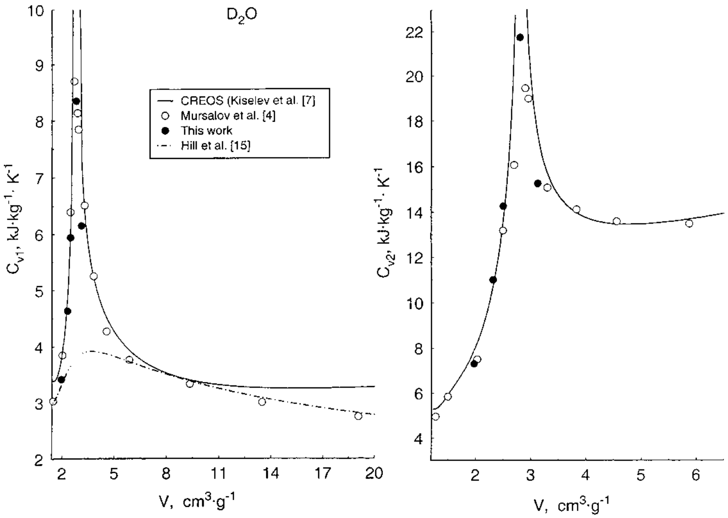

Fig. 5. Experimental liquid and vapor saturated densities of heavy water in the asymptotic critical region reported by different authors together with values calculated from crossover equations [7, 8] and IAPWS formulation [6].

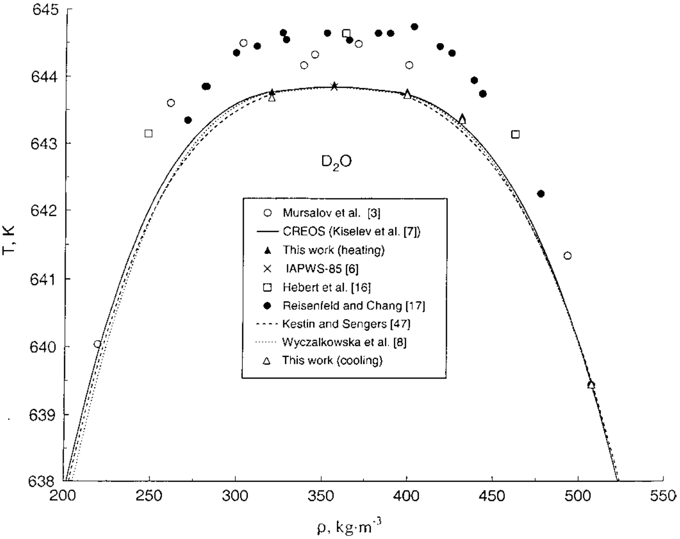

Fig. 6. One-phase (liquid C'_{V1} and vapor C''_{V1}) and two-phase (liquid C'_{V2} and vapor C''_{V2}) experimental isochoric heat capacities of heavy water at saturation as a function of specific volume near the critical point together with values calculated from crossover equation [7].

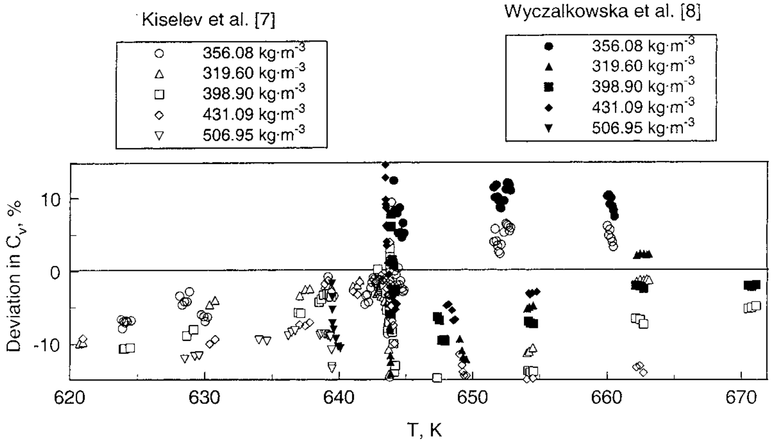

Fig. 7. Percent deviations of measured isochoric heat capacities of heavy water with the values calculated from crossover equations [7, 8].

explained by Mursalov et al. [4], there was a problem with the purity of the sample used for their measurements. Our new measurement of densities ρ_S and temperatures T_S at saturation agree with the shape of the coexistence curve for heavy water near the critical point adopted by IAPWS [6]. For example, the phase transition temperature of 643.83 K for a density of 356.08 $\text{kg}\cdot\text{m}^{-3}$ (the IAPWS accepted value of the critical density is 356.0 $\text{kg}\cdot\text{m}^{-3}$) differs from the critical temperature (the IAPWS accepted value is $T_C = 643.847$ K) by only 17 mK. Therefore, the new measurements support the previous temperature shift that was applied to the original measurements and reported by Mursalov et al. [4]. Figures 8 and 9 shows selected data for experimental isochoric heat capacity along the critical isochore (318.00 $\text{kg}\cdot\text{m}^{-3}$) for H_2O and T_S–ρ_S data at saturation near the critical point recommended by Abdulagatov et al. [34, 35].

Anisimov et al. [23] studied the asymptotic critical amplitudes A_0^+ and A_0^- of the isochoric heat capacity for light and heavy water. They reported updated values of the critical amplitudes and concluded that the critical amplitudes for D_2O and H_2O are very close. Kiselev et al. [7, 24] obtained values from the crossover equation of state for the critical amplitudes $A_0^+ = 34.1$ and $A_0^- = 64.8$ for D_2O ($A_0^+/A_0^- = 0.526$) and $A_0^+ = 32.04$ and $A_0^- = 60.89$ for H_2O ($A_0^+/A_0^- = 0.526$). These values of A_0^+ and A_0^- for D_2O differ by about 6.5% from the values for light water recommended by Anisimov et al. [23] ($A_0^+ = 32 \pm 1$ and $A_0^- = 61 \pm 2$). Therefore, as Anisimov et al. [23] concluded, additional experimental information is needed in the

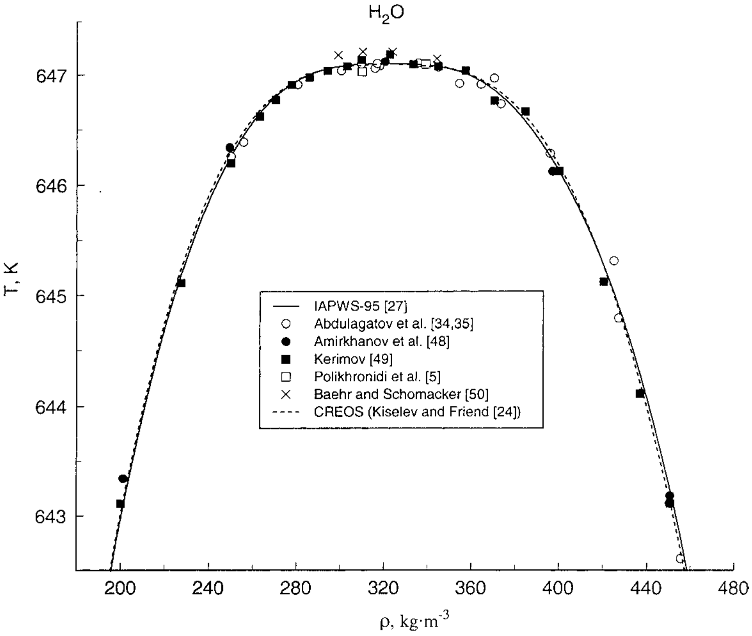

Fig. 8. Selected experimental liquid and vapor saturated densities of light water from the literature in the asymptotic critical region together with values calculated from a crossover equation [24] and IAPWS-95 formulation [27].

critical region of pure D_2O in order to resolve the discrepancies between various models. New experimental values of C_V and T_S–ρ_S for D_2O are reported in this work in the immediate vicinity of the critical point, for which the values should help to resolve these discrepancies. The asymptotic critical power laws for one- and two-phase isochoric heat capacities along the critical isochore and for saturated densities along the coexistence curve are [36, 37]

$$\frac{C_V T_C}{V P_C} = A_0^{\pm} t^{-\alpha}(1 + A_1^{\pm} t^{\Delta}) \quad \text{for} \quad \rho = \rho_C,\ T \geqslant T_C \quad \text{and} \quad \rho = \rho_C,\ T \leqslant T_C \tag{4}$$

$$\Delta\rho_{cxc} = B_0 t^{-\alpha}(1 + B_1 t^{\Delta}) \qquad \text{for} \quad T \leqslant T_C \tag{5}$$

where A_0^+ and B_0 are the asymptotical critical amplitudes for isochoric heat capacities and saturated density, respectively; A_1^+ and B_1 are the non-asymptotic critical amplitudes; $\alpha = 0.11$, $\beta = 0.325$, and $\Delta = 0.51$ are the

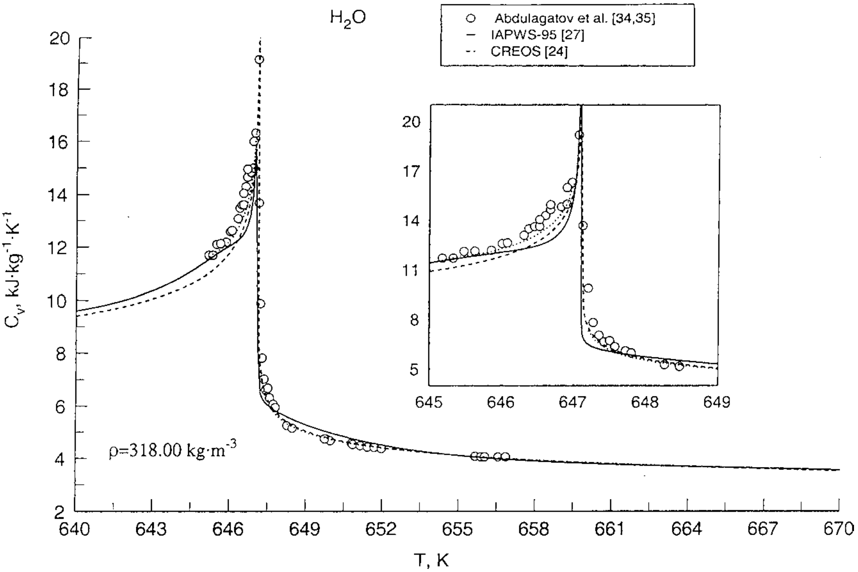

Fig. 9. Selected one- and two-phase experimental isochoric heat capacities of light water as a function of temperature along the critical isochore (318.0 kg·m^{-3}) together with values calculated from crossover equations of states [8, 24] and the IAPWS-95 formulation [27].

universal critical exponents [38–40]; $t=(T-T_C)/T_C$; and $\Delta\rho_{cxc}=(\rho-\rho_C)/\rho_C$. An important question is whether the asymptotic critical amplitudes for D_2O and H_2O are identical [23]. The values of the asymptotical critical amplitudes for D_2O derived from the present experimental data and for H_2O derived from selected experimental data [34, 35] are given in Tables III–V. As Table III shows, the values of asymptotic critical amplitudes depend on the fitting range of the experimental data. Due to the dependence of asymptotic critical amplitudes on the fitted temperature range, it is difficult, and sometimes not possible, to conclude that the values of A_0^+ for D_2O and H_2O may coincide. But some results from Tables III and IV showed that the values of asymptotic critical amplitudes A_0^+ for D_2O and H_2O agree to within their statistical uncertainties.

The parameters of the singular terms of the crossover equations of state developed by Kiselev et al. [7] and Wyczalkowska et al. [8] were determined using various data sets and various temperature and density ranges. Therefore, it is no surprise that the asymptotic critical amplitudes for D_2O and H_2O are different. Table V shows a comparison of our recommended experimental values of the asymptotical critical amplitudes (A_0^+, B_0) for light and heavy water with values estimated from crossover

Table III. Experimental Values of the Asymptotic Critical Amplitudes of Isochoric Heat Capacities for Heavy Water

$\rho_C = 356.08\ \mathrm{kg \cdot m^{-3}},\ T > T_C$

Critical Amplitude	Fitting range $\Delta T = T - T_C$	χ_ν^2
$A_0^+ = 32.826 \pm 0.238$	16 K	1.10
$A_0^+ = 32.648 \pm 0.263$	9 K	1.24
$A_0^+ = 34.973 \pm 0.476$	1 K	1.07

$\rho_C = 356.08\ \mathrm{kg \cdot m^{-3}},\ T < T_C$

Critical Amplitude	Fitting range $\Delta T = T_C - T$	χ_ν^2
$A_0^- = 67.240 \pm 0.351$	21 K	1.18
$A_0^- = 67.050 \pm 0.373$	16 K	1.12
$A_0^- = 66.519 \pm 0.602$	5 K	0.96
$A_0^- = 65.945 \pm 0.772$	1.8 K	0.99

Table IV. Experimental Values of the Asymptotic Critical Amplitudes of Isochoric Heat Capacities for Light Water

$\rho_C = 318.00\ \mathrm{kg \cdot m^{-3}},\ T > T_C$

Critical Amplitude	Fitting range $\Delta T = T - T_C$	χ_ν^2
$A_0^+ = 33.325 \pm 0.645$	10 K	1.05
$A_0^+ = 34.781 \pm 0.765$	4 K	1.02
$A_0^+ = 35.939 \pm 0.921$	3 K	1.02
$A_0^+ = 37.091 \pm 1.127$	1 K	1.05

$\rho_C = 318.00\ \mathrm{kg \cdot m^{-3}},\ T < T_C$

Critical Amplitude	Fitting range $\Delta T = T_C - T$	χ_ν^2
$A_0^- = 70.921 \pm 0.597$	2.0 K	1.20
$A_0^- = 69.572 \pm 0.691$	1.1 K	1.12
$A_0^- = 63.476 \pm 0.916$	0.5 K	1.03

Table V. Experimental Values of the Asymptotic Critical Amplitudes of Isochoric Heat Capacity and Coexistence Curve for Light and Heavy Water

Critical Amplitude	Experiment (this work)	Kiselev et al. [7, 24]	Anisimov et al. [23]	Levelt Sengers et al. [41]	Kiselev and Kostukova [42]
$B_0(H_2O)$	1.952 ± 0.030	1.972	1.952 (1.956)	1.980	1.980
$B_0(D_2O)$	2.018 ± 0.090	2.050	–	–	–
$A_0^+(H_2O)$	33.325 ± 0.645	32.04	31.95 (32.09)	33.72	32.93
$A_0^+(D_2O)$	34.973 ± 0.476	34.10	–	–	–
$A_0^-(H_2O)$	63.476 ± 0.916	60.89	60.88 (61.15)	63.42	62.58
$A_0^-(D_2O)$	65.945 ± 0.772	64.79	–	–	–

models [7, 23, 24, 41, 42]. A comparison between experimental values of universal amplitude ratio A_0^+/A_0^- derived in the present work from isochoric heat capacity measurements along the critical isochore with values predicted by theory [22] and crossover equations [7, 23, 24, 41, 42] is given in Table VI.

At coexistence, the relation of Yang and Yang [43] is

$$\frac{C_{V2}}{T} = -\frac{d^2\mu}{dT^2} + V\frac{d^2P_S}{dT^2} \tag{6}$$

where C_{V2} is the two-phase isochoric heat capacity and V is the specific volume. According to this relation, the two-phase isochoric heat capacity C_{V2} is a linear function of the specific volume V along each isotherm (see Fig. 3), the slopes of which equal $T(d^2P_S/dT^2)$, while the intercepts for $V=0$ are related to $-T(d^2\mu/dT^2)$. Measured values of two-phase isochoric heat capacities were fitted with Eq. (6) to calculate the values of the second temperature derivatives (d^2P_S/dT^2) and $(d^2\mu/dT^2)$. The results are given in Table VII and in Figs. 10 and 11. Figure 10 also contains the (d^2P_S/dT^2) data calculated from the vapor-pressure equation by Hill et al.

Table VI. Experimental Values of the Universal Amplitude Ratios Together with Theoretically Predicted Values

Critical Amplitude Ratio	Experiment (this work)	Levelt Sengers et al. [41]	Anisimov et al. [23]	Kiselev et al. [7, 24, 42]	Ising model [22]
A_0^+/A_0^- (H_2O)	0.525 ± 0.008	0.532	0.525	0.526	0.523 ± 0.009
A_0^+/A_0^- (D_2O)	0.530 ± 0.004	–	0.525	0.526	0.523 ± 0.009

Table VII. Second Temperature Derivatives (d^2P_S/dT^2) and $(d^2\mu/dT^2)$ from Two-Phase Isochoric Heat Capacities Measurements of Heavy Water

T_S (K)	d^2P_S/dT^2 $(\mathrm{kPa \cdot K^{-2}})$	$d^2\mu/dT^2$ $(\mathrm{J \cdot kg^{-1} \cdot K^{-2}})$
605.0	1.527	−5.65
610.0	1.900	−5.30
615.0	1.924	−5.25
620.0	2.291	−4.93
621.0	2.337	−4.90
622.0	2.370	−4.88
623.0	2.374	−4.89
624.0	2.381	−4.89
625.0	2.422	−4.79
626.0	2.436	−4.79
627.0	2.478	−4.78
628.0	2.490	−4.70
630.0	2.656	−4.69
632.0	2.744	−4.63
634.0	2.857	−4.62
636.0	2.961	−4.61
638.0	3.275	−4.65
638.5	3.359	−4.68
639.0	3.414	−4.70
639.4	3.455	−4.75
640.0	3.600	−4.80
641.0	3.751	−4.90
642.0	3.700	−5.70
642.5	4.103	−5.50
643.0	4.201	−5.90
643.2	4.400	−6.00
643.4	4.500	−6.10
643.6	4.504	−7.03
643.7	4.901	−7.11
643.8	8.102	−7.52

[15] and the crossover equation of state by Kiselev et al. [7]. The uncertainties of the derived values of second temperature derivatives (d^2P_S/dT^2) and $(d^2\mu/dT^2)$ are within 5 to 8%. As one can see from Fig. 11, the second temperature derivatives of the chemical potential derived from the present two-phase C_{V2} measurements show a negative singularity $(d^2\mu/dT^2) \to -\infty$, like that seen for propane [44, 45]. The opposite sign of divergence

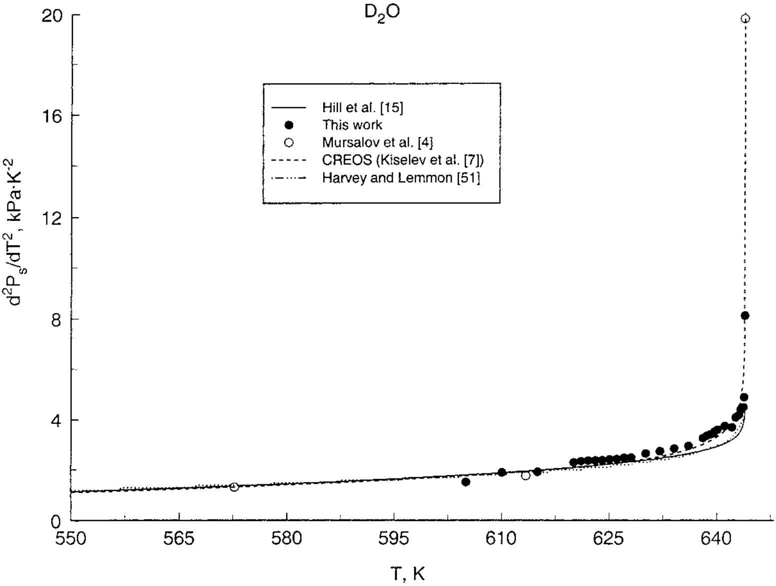

Fig. 10. Second temperature derivatives of the vapor-pressure curve for heavy water derived from isochoric heat capacity measurements as a function of temperature near the critical point together with values calculated from a crossover model [7] and a vapor-pressure equation of Hill et al. [15].

$(d^2\mu/dT^2) \rightarrow +\infty$ was found for carbon dioxide [25, 46]. The negative divergence $(d^2\mu/dT^2) \rightarrow -\infty$ for heavy water at the critical point is consistent with recent theoretical suggestions [44, 45].

Fisher and Orkoulas [44] showed that previous scaling descriptions must be extended by introducing the pressure into the ordering field. They estimated the strength of the Yang–Yang anomaly as measured by the ration $R_\mu = A_\mu/(A_P + A_\mu)$, where A_μ and A_P are the asymptotic critical amplitudes for second temperature derivatives of chemical potential $d^2\mu/dT^2 \approx A_\mu \tau^{-\alpha}$ and vapor pressure $d^2P_S/dT^2 \approx A_P \tau^{-\alpha}$, respectively. At $R_\mu = 0$, therefore $A_\mu = 0$, the divergence of two-phase isochoric heat capacity caused by divergence of the d^2P_S/dT^2 while $d^2\mu/dT^2$ remains finite. If $R_\mu \neq 0$, i.e., $A_\mu \neq 0$, the divergence of the two-phase isochoric heat capacity is caused by divergence of both d^2P_S/dT^2 and $d^2\mu/dT^2$. Fisher and Orkoulas [44] showed that the strength of the Yang–Yang anomaly is $R_\mu = -j_2/(1-j_2)$, where $j_2 \neq 0$, therefore, $R_\mu \neq 0$ for fluids. For previous scaling models, $j_2 = 0$. For propane the scaled strength of the anomaly is $R_\mu = 0.56$ [44].

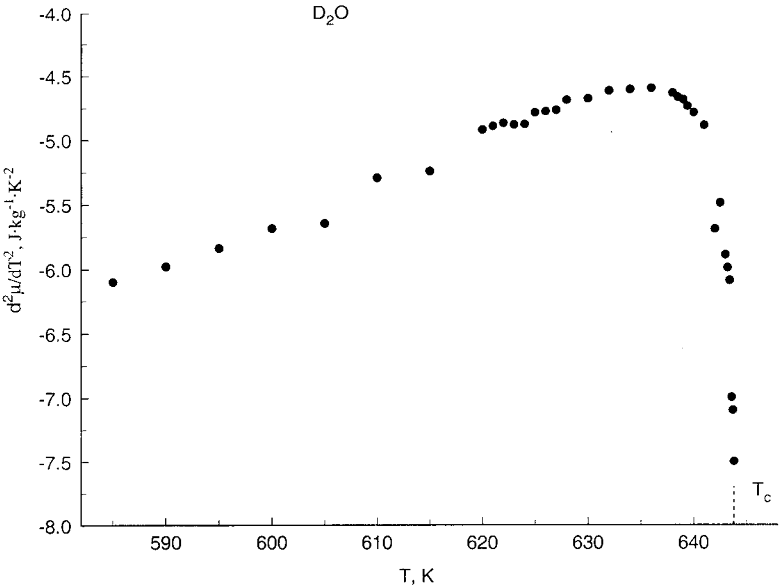

Fig. 11. Second temperature derivatives of the chemical potential for heavy water derived from isochoric heat capacity measurements as a function of temperature near the critical point.

4. CONCLUSIONS

Measurements are presented for the isochoric heat capacity of heavy water for near-critical isochores of 319.60, 398.90, 431.09, and 506.95 $\text{kg} \cdot \text{m}^{-3}$ in a temperature range from 551 to 671 K and pressures up to 32 MPa in the one- and two-phase regions, including the coexistence curve. Uncertainties of the measured values of heat capacity are estimated to be 2 to 3%. For each measured density, a phase transition temperature was determined. The uncertainty in a phase transition temperature measurement is not more than ± 0.02 K. The measured saturated densities and temperatures show good agreement with the critical properties of D_2O adopted by IAPWS. The results of the isochoric heat capacity and saturated density measurements are in good agreement (AAD = 5.57% for the parametric crossover equation [7] and AAD = 6.67% for the six-term Landau expansion crossover model [8]) with values calculated with crossover models. Measured values of heat capacities and saturated densities were used to estimate asymptotical critical amplitudes for D_2O. Good agreement among experiment, calculations from crossover equations, and predictions from theory was found for asymptotical critical amplitudes and their universal ratios. The asymptotical critical amplitudes of the heat capacity and the coexistence curve were also calculated for light water from selected experimental data. The derived values of asymptotical critical amplitudes for light and heavy water were close to each other, but it is difficult to conclude if they are identical because the values depend on the fitting range. From measured values of two-phase isochoric heat capacities for D_2O, the values of second temperature derivatives of vapor pressure and chemical potential were derived. The new experimental results justify the temperature shift in the previous work by Mursalov et al. [4].

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