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Experimental and Theoretical Studies of the Crossover Behavior of the Specific Heat $C_{v,x}$ of Ethane, Propane, and Their Mixture at Critical Isochores

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The specific heat at constant volume, C_v, of propane, and mixture with a concentration of $x = 0.0081$ mol fraction of propane was measured along the critical isochores at temperatures between 290 and 400 K. The measurements were performed with a high-temperature constant-volume adiabatic calorimeter. The uncertainty of most of the measurements is estimated to be less than 1.5%. Measurements have been carried out in both the one- and two-phase regions. The results for the pure components are compared with earlier measurements. Crossover equations for C_v obtained on the basis of the renormalization-group method and ε-expansion are applied to represent our experimental specific heat data for ethane, propane, and its mixture along the critical isochores.

KEY WORDS: critical phenomena; crossover equation; ethane; propane; specific heat.

1. INTRODUCTION

Ethane, propane, and their mixtures are important hydrocarbons and accurate information on their thermodynamic properties is desired for many applications. This binary system is of particular interest due to the

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abundance of ethane and propane in natural gas, an important commercial mixture. Modeling of $C_{v,x}$ of this mixture is also quite useful for the prediction of properties of other mixtures of hydrocarbons. The thermodynamic properties of ethane and propane mixtures in the critical region is important for technical applications (supercritical extractions and supercirtical technology).

The experimental and theoretical situation is not so clear for binary mixtures near the liquid–gas critical line. Theory has not been worked out in detail and experiments are scare. Theories are limited to the asymptotic ciritical region. As a general rule, the asymptotic behavior of criticial phenomena is much better knows than its crossover to regular behavior far from the critical point, and the behavior of one-component fluids is better understood than that of binary mixtures. There is no absolute pure substance in reality, and all experiments measure only, is a strict sense, some effective critical exponents. Therefore, it is important to understand how impurities may affect the critical exponents [1]. Consequently, there is a need for further experimental work in this field.

Previous specific heat C_{v} data for pure ethane and propane along the critical isochores have been reported in the literature [2–5]. However, sufficient information for the C_{v} of ethane + propane mixtures is lacking in the critical region.

2. EXPERIMENTS

The specific heat, C_{v}, of pure ethane, propane, and the mixture at critical isochores was obtained with a high-temperature constant-volume adiabatic calorimeter. The apparatus, technique, and computional procedures have been fully described previously [6–8]. In Refs. 7 and 8, for example, we have an account of the sources of uncertainty. In the present work, we have employed the same apparatus, methods, and computional procedures described in detail by Abdulagatov et al. [7, 8]. The basic idea of the adiabatic calorimeter consists of using a highly sensitive semiconducting material (Cu_2O) in the gap formed by two coaxial vessels. The thermocouple simultaneously performs the role of adiabetic protection, a thermal insulation layer, and a layer transmitting pressure to a stronger outer shell. The calorimeter was a multilayer system and basically consisted of an inner thin-walled vessel (60 mm in diameter and 0.5 mm in thickness) and an outer shell (7 mm in thickness). Stainless stell (1X18H9T) was used for making the vessel. The adiabatic conditions were controlled by a semiconductor layer of Cu_2O in the gap between the inner calorimeter vessel and the outer shell. The calorimeter had a volume of (400.58 ± 0.05) cm^3 at 293.15 K. The temperature difference between the calorimeter and the first thermal screen was maintained with an accuracy of 2.5×10^{-4} K, and that between the first and the second thermal screen, within 0.1 K. The temperature in the calorimeter was maintained accurately to 5×10^{-5} K. The temperature was measured with a platinum resistance thermometer (PRT-10) mounted in a tube on the inside of the sphere. The thermometer was calibrated by VNIIFTRI (Moscow). Pockets were used for placement of the inner heater and thermocouples. The temperatures are on the ITPS-68 scale. The uncertainty in temperature measured was less than ±10 mK.

The specific heat, C_v, is calculated from the measured quantities (ΔQ, ΔT, C_o, m) as follows:

$$C_v = \frac{1}{m}\left(\frac{\Delta Q}{\Delta T} - C_0\right) \tag{1}$$

where $\Delta Q = IU\Delta\tau$ is the energy released by the inner heater, $\Delta\tau$ is the heating time, ΔT is the temperature change resulting from addition of energy ΔQ, m is the mass of the substance, and C_o is the heat capacity of the empty calorimeter. The volume of the calorimeter was corrected for its variation with temperature and pressure. This correction was 5% of the total capacity. The heat losses through sections of the calorimeter not controlled by the semiconductor layer (Cu_2O) were 0.01%. The error in determining ΔT does not exceed ±3 mK. The heating time was fixed by means of a frequency meter with an accuracy of ±0.001 s. The heat capacity C_o of the empty calorimeter has been previously determined using various standard fluids (water, nitrobenzene, *n*-heptane) with a well-known heat capacity [9, 10]. The results of these measurements show that with a heat capacity of

$$C_0 = 161.2351 + 0.07871T \qquad (\mathrm{J \cdot K^{-1}}) \tag{2}$$

in the range from 280 to 500 K, which is not more than 15 to 20% of the total heat capacity of the system.

The power of the inner heater was determined with a relative error of 0.1%. The heat losses of the fluxes, as a result of inequality of the shell temperatures ($\Delta T_{12} \# 0$), can be calculated from the equation:

$$\Delta Q = \lambda(d_1 d_2/\Delta d_{12})\, \Delta T_{12}\, \Delta\tau \tag{3}$$

where λ is the thermal conductivity of Cu_2O; d_1 and d_2 are the inside and outside diameters of the shells; and $\Delta d_{12} = d_1 - d_2$ in the thickness of the Cu_20 layer. For our calorimetric system the amount of uncontrolled power $\Delta Q/\Delta\tau$ is estimated as 0.02 to 0.03 W. To check the reproducibility, the measurements at selected temperatures were repeated three or four times. The scatter of the experimental results did not exceed ±1.2%. At each experimental T and ρ_c, two or three measurements were performed with different values of ΔQ and ΔT. The measured specific heats are indeed independent of the applied temperature T difference and power Q difference. The relative error in determining the mass of the sample is ±0.01%. The average value of the working volume was determined with an error not exceeding ±0.02%. The density of the sample was determined as the ratio of the mass of sample m to the working volume V of the calorimetric bomb.

The estimated accuracy of the experimental C_v data at temperatures somewhat away from the critical point is of the order of 0.5%. However, within a few kelvins from the critical point the error increases to about 1.5%. All measurements were made with the samples vigorously stirred with a stirrer made of a thin perforated stell foil. This minimized the errors caused by gravity and assured homogenization of the sample investigated. The stirring was carried out by rotating the calorimeter around a vertical axis.

The purity of components ehtane and propane of the mixture was better than 99.95%.

3. RESULTS

The measurements of the specific heats were obtained along the critical isochores for the pure components and a mixture containing 0.0081 mol fraction of propane. The calorimeter was filled at room temperature, sealed off, and heated along the isochore. The specific-heat measurements commenced in the liquid–vapor region at room temperature and finished in the one-phase region.

The experimental values of C_v for pure ethane, propane, and the mixture are presented in Tables I–III and are shown graphically in Figs. 1–3. For the mixture (0.919 $C_2H_6 + 0.0081\ C_3H_8$), the measurements were made at the critical isochore in the temperatue range between 290 and 372 K. For ethane 93 measurements were made in both the one-phase and the two-phase regions; for propane, 159, and for the ethane + propane mixture, III. The specific heat C_v of pure ethane and propane along the critical isochore has been measured previously [2–5]. Detailed experimental studies of the behaviour of the C_v of pure ethane at critical isochore have been reported by Shmakov [3]. The measurements were performed in the temperature range from 295 to 315 K. Shmakov et al. [2, 4] obtained C_v

data for pure propane along the critical isochore ($\rho_c = 225\ \mathrm{kg \cdot m^{-3}}$) in the two-phase region at temperatures from 90 to 350 K. In 1982, Beketov [5] made measurements of C_v for pure propane in the two- and one-phase regions at the critical isochore at temperatures form 369.85 to 370.26 K. The C_v data of ehtane of Shmakov shows large systematic deviations from our experimental results, especially far away from the critical point to the two- and one-phase regions. Figure 2 shows that all sets of C_v data for propane are in satisfactory agreement. Figures 1 and 2 show the results for ethane and propane together with data from the literature [2–5]. From these figures we note that our experimental data for pure ethane are found to be lower by 10%, just as for propane [2, 4, 5], while those measured by Betekov [5] and Shmakov et al. [2, 4] are in good agreement (deviation within ±0.5%).

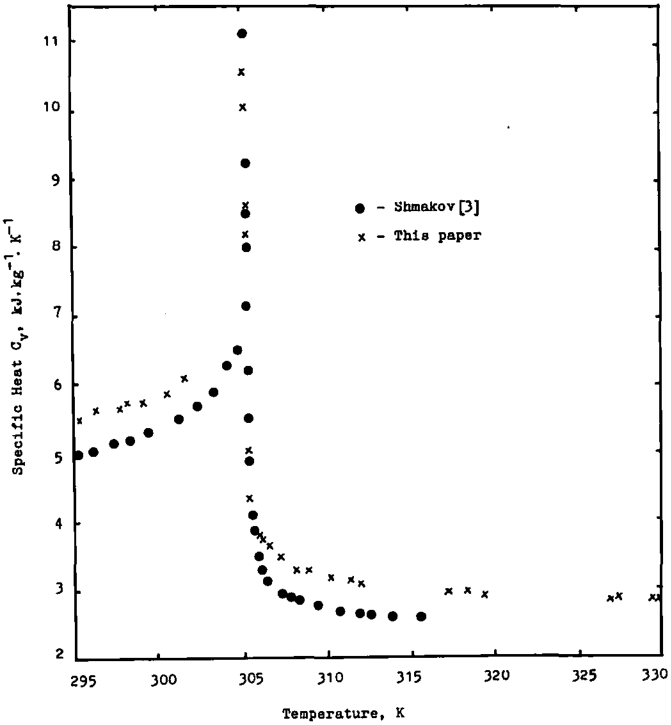

Fig. 1. Two- and one-phase specific heats C_v of ethane along the critical isochore as a function of temperature. (●) Shmakov [3] ($\rho_c = 205.00\ \mathrm{kg \cdot m^{-3}}$); (×) this paper ($\rho_c = 203.04\ \mathrm{kg \cdot m^{-3}}$).

Table I. Two- and One-Phase Specific Heats of Ethane at Critical Isochore: $\rho_c = 203.04\ \text{kg} \cdot \text{m}^{-3}$, $T_c = 305.323$ K

T (K)	C_V ($\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$)
Two phase	
292.388	4.925
292.644	4.980
292.900	4.933
293.156	4.882
293.412	4.935
293.668	4.979
293.924	4.983
295.200	5.095
295.455	5.041
295.710	5.097
295.965	5.084
296.220	5.105
296.475	5.079
297.796	5.163
298.000	5.230
298.254	5.235
298.508	5.219
298.762	5.255
299.016	5.248
299.270	5.298
299.523	5.266
300.530	5.392
300.782	5.558
301.034	5.584
301.286	5.699
301.538	5.674
305.211	7.741
305.236	8.049
305.261	7.975
305.286	8.442
305.311	9.525
One phase	
305.336	4.220
305.361	3.997
305.386	3.999
305.411	3.829
305.535	3.551
305.784	3.337
306.033	3.258
306.282	3.136
306.531	3.203
306.780	3.081

Table I. *(Continued)*

T (K)	C_v ($kJ \cdot kg^{-1} \cdot K^{-1}$)
One phase	
307.028	3.010
307.276	2.924
307.524	2.888
307.772	2.841
308.020	2.829
308.268	2.752
308.516	2.749
308.516	2.812
308.764	2.825
309.012	2.743
310.001	2.654
310.248	2.682
310.495	2.646
310.742	2.644
310.989	2.595
311.236	2.633
311.483	2.595
311.730	2.566
316.883	2.471
317.126	2.478
317.369	2.461
317.612	2.464
317.855	2.464
318.098	2.493
318.098	2.412
318.341	2.433
318.584	2.438
318.827	2.489
319.070	2.403
326.778	2.395
327.017	2.416
327.256	2.346
327.415	2.405
327.734	2.331
328.073	2.360
328.212	2.342
329.880	2.364
330.118	2.349
330.356	2.386
330.594	2.331
330.832	2.313
331.070	2.313
345.592	2.304
345.823	2.317
346.054	2.331

Table I. *(Continued)*

T (K)	C_v ($kJ \cdot kg^{-1} \cdot K^{-1}$)
One phase	
346.285	2.311
346.516	2.309
346.747	2.305
346.285	2.301
346.516	2.296
346.747	2.274
347.078	2.298
347.209	2.289
347.340	2.296
347.670	2.276
349.280	2.358
349.510	2.348
349.740	2.331
349.969	2.338
350.198	2.343
350.427	2.319
350.656	2.331
356.807	2.282
357.034	2.278
357.261	2.270
357.488	2.275
357.715	2.289
357.942	2.264
358.169	2.261
366.046	2.315
366.269	2.280
366.492	2.289
366.715	2.281
366.938	2.311
367.161	2.284
367.384	2.304
368.718	2.289
368.940	2.295
369.162	2.283
369.384	2.276
369.606	2.296
369.828	2.268
370.050	2.242
370.271	2.296
374.680	2.357
374.900	2.370
375.120	2.331
375.340	2.323
375.560	2.322
375.780	2.333

Table II. Two- and One-Phase Specific Heats of Propane at Critical Isochore: $\rho = 222.4\ \mathrm{kg \cdot m^{-3}}$, $T_c = 369.96$ K

T (K)	C_v ($\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$)	T (K)	C_v ($\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$)
Two phase		One phase	
291.982	2.881	369.971	4.212
292.238	2.920	369.993	3.992
292.494	2.894	370.016	3.838
292.750	2.902	370.038	3.720
293.006	2.917	370.061	3.613
297.596	2.988	370.083	3.544
297.850	2.961	370.210	3.290
298.104	2.981	370.308	3.142
298.358	2.966	370.435	3.059
298.612	3.004	370.534	2.964
309.110	3.099	370.660	2.916
309.357	3.142	370.759	2.880
309.604	3.124	370.885	2.819
309.851	3.145	370.984	2.764
310.098	3.137	371.110	2.721
313.302	3.196	371.335	2.656
313.548	3.180	371.560	2.588
313.794	3.164	371.784	2.563
314.040	3.202	372.008	2.541
314.285	3.169	372.232	2.496
326.150	3.322	372.456	2.461
326.389	3.366	372.680	2.441
326.628	3.341	372.904	2.420
326.867	3.377	373.128	2.381
327.106	3.347	373.352	2.364
338.234	3.506	373.576	2.356
338.468	3.496	373.800	2.347
338.702	3.520	378.543	2.255
338.936	3.509	378.766	2.271
339.170	3.516	378.989	2.269
350.277	3.743	379.212	2.248
350.506	3.718	379.435	2.253
350.735	3.747	379.658	2.241
350.964	3.736	382.498	2.238
351.163	3.760	382.730	2.227
358.926	4.008	383.164	2.236
359.152	3.985	383.386	2.239
359.378	4.012	383.608	2.224
359.604	4.041	383.830	2.242
359.830	4.036	396.758	2.260
363.210	4.281	396.976	2.274
363.434	4.257	397.192	2.270
363.618	4.329	397.409	2.282

Table II. *(Continued)*

T (K)	C_v ($kJ \cdot kg^{-1} \cdot K^{-1}$)	T (K)	C_v ($kJ \cdot kg^{-1} \cdot K^{-1}$)
Two phase		One phase	
363.882	4.308	397.626	2.278
364.106	4.340	397.843	2.292
366.342	4.613	398.924	2.276
366.565	4.650	399.140	2.283
366.788	4.629	399.356	2.289
367.011	4.727	399.572	2.281
367.234	4.735	399.788	2.291
368.790	5.372	400.004	2.300
369.012	5.475	413.080	2.317
369.234	5.681	413.290	2.350
369.335	5.788	413.500	2.325
369.457	5.969	413.710	2.338
369.568	6.172	413.920	2.321
369.679	6.463	414.130	2.335
369.701	6.749	423.610	2.387
369.723	6.605	423.820	2.369
369.745	6.911	424.030	2.380
369.767	6.984	424.240	2.372
369.790	7.050	425.450	2.392
369.811	7.377	434.221	2.436
369.833	7.232	434.432	2.414
369.855	7.766	434.638	2.421
369.877	7.868	434.844	2.437
369.901	7.833	435.050	2.420
369.921	8.981	443.042	2.458
369.943	9.350	443.245	2.483
369.948	9.734	443.448	2.482
		443.651	2.459
		443.854	2.463
		455.090	2.505
		455.290	2.531
		455.490	2.517
		455.690	2.532
		455.890	2.525
		463.478	2.577
		463.676	2.553
		463.874	2.572
		464.072	2.550
		464.270	2.573
		464.467	2.561
		470.791	2.581
		470.988	2.609
		471.185	2.600
		471.382	2.594
		471.579	2.601

Table III. Two- and One-Phase Specific Heats of the Ethane + Propane Mixture at Critical Isochore [$x(C_3H_8) = 0.0081$ Mole Fraction]: $\rho_c = 207.5\ \mathrm{kg \cdot m^{-3}}$, $T_c = 306.96$ K

T (K)	C_v ($\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$)	T (K)	C_v ($\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$)
Two phase		One phase	
289.757	5.316	306.971	4.063
290.015	5.408	307.219	3.865
290.273	5.379	307.467	3.702
290.531	5.453	307.715	3.644
290.789	5.367	307.963	3.618
291.047	5.325	308.211	3.517
291.305	5.375	308.459	3.483
291.563	5.381	308.707	3.474
294.123	5.434	308.955	3.371
294.378	5.434	309.203	3.398
294.633	5.497	310.438	3.184
294.888	5.474	310.685	3.174
295.143	5.530	310.932	3.202
295.378	5.514	311.179	3.144
295.653	5.554	311.426	3.145
295.908	5.543	311.673	3.140
296.673	5.582	317.798	2.855
296.927	5.597	318.041	2.875
297.181	5.672	318.284	2.879
297.435	5.579	318.527	2.843
297.689	5.604	318.770	2.884
297.943	5.669	319.013	2.878
298.197	5.665	327.199	2.769
298.451	5.637	327.438	2.762
299.465	5.781	327.677	2.786
299.717	5.749	327.916	2.773
299.969	5.789	328.155	2.774
300.221	5.821	328.394	2.765
300.473	5.867	328.633	2.737
300.725	5.929	337.623	2.642
300.977	5.924	337.858	2.645
301.229	5.845	338.093	2.622
301.481	5.842	338.327	2.659
301.733	5.864	338.561	2.640
302.733	6.157	338.795	2.648
302.983	6.221	340.200	2.651
303.233	6.278	340.433	2.652
303.483	6.214	340.666	2.653
303.733	6.251	340.899	2.620
303.983	6.300	341.132	2.654
304.233	6.437	341.365	2.638

Table III. *(Continued)*

T (K)	C_v ($\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$)	T (K)	C_v ($\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$)
Two phase		One phase	
304.492	6.453	341.598	2.636
304.731	6.526	354.934	2.548
304.980	6.618	355.161	2.564
305.229	6.739	355.388	2.578
305.478	6.829	355.615	2.554
305.727	7.063	355.842	2.575
305.976	7.212	356.069	2.600
306.225	7.570	356.296	2.559
306.349	8.034	356.523	2.597
		364.199	2.532
		364.423	2.474
		364.647	2.521
		364.871	2.511
		365.095	2.477
		365.319	2.484
		365.543	2.522
		371.319	2.479
		371.540	2.436
		371.761	2.537
		371.982	2.454

4. DISCUSSION

To compare our experimental results with the crossover theory described elsewhere [11, 12], we fitted to a crossover equation for C_v

$$\begin{aligned} t &= (1 + kx^{-k_1})^{k_2}\,[x + (1 + kx^{-k_1})^{-1/k_1}] \\ \tilde{C}_v &= \tilde{C}_{vo} - 1 + (1 + kx^{-k_1})^{k_3} \end{aligned} \tag{4}$$

with $t = \tau(x)/\mathrm{Gi}$; $\tau = (T - T_c)/T_c$; Gi is a Ginzburg number; $\tilde{C}_v = C_v/B_{cr}$; $\tilde{C}_{vo} = C_{vo}/B_{cr}$; B_{cr} is a nonuniversal constant which represents a fluctuation-induced modification of the background specific heat when $\tau \ll \mathrm{Gi}$; C_{vo} is a background specific heat in the classical limit $\chi_T^{-1} \gg \mathrm{Gi}$; $k_1 = \Delta/\gamma$; $k_2 = (\gamma - 1)/\Delta$; $k_3 = \alpha/\Delta$; $k = 2.333$; and α, γ, and Δ are universal critical exponents. In the scaling regime ($t < < 1$) we obtain

$$\begin{aligned} x &= A_x^+ t^{\gamma}(1 + \alpha_x^+ t^{\Delta}) \\ \tilde{C}_v - \tilde{C}_{vo} &= A_c^+ t^{-\alpha}(1 + \alpha_c^+ t^{\Delta}) - 1 \end{aligned}$$

where A_x^+, A_c^+, a_x^+, and a_c^+ are universal critical amplitudes.

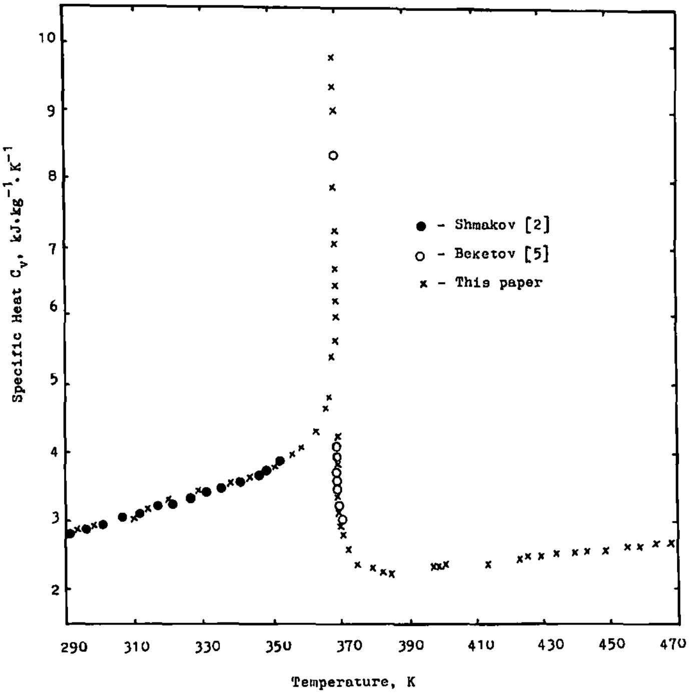

Fig. 2. Two- and one-phase specific heats C_v of propane along the critical isochore as a function of temperature. (●) Shmakov et al. [2] ($\rho_c = 225.00\ \mathrm{kg \cdot m^{-3}}$); (×) this paper ($\rho_c = 222.4\ \mathrm{kg \cdot m^{-3}}$); (○) Beketov [5] ($\rho_c = 224.00\ \mathrm{kg \cdot m^{-3}}$).

To fit the experimental data for the C_v of pure components one should use C_{vo}, B_{cr}, and Gi as nonuniversal adjustable parameters. The values of these constants for ethane and propane are listed in Table IV. The results are presented in Fig. 4. In Fig. 5. the percentage deviations of our C_v data from those calculated by the crossover equation, Eq. (4), are given for ehtane, propane, and the mixture. From Fig. 5 we conclude that our C_v measurements are consistent with Eq. (4) proposed by Belyakov and

Table IV. Parameters C_{vo}, B_{cr}, and Gi for Ethane, Propane, and Their Mixture

Parameter	Ethane	Propane	Ethane + propane
$C_{vo}\ (\mathrm{J \cdot g^{-1} \cdot K^{-1}})$	1.950 ± 0.025	2.068 ± 0.033	2.104 ± 0.024
$B_{cr}\ (\mathrm{J \cdot g^{-1} \cdot K^{-1}})$	2.840 ± 0.131	1.805 ± 0.085	3.852 ± 0.100
Gi	0.005	0.005	0.010

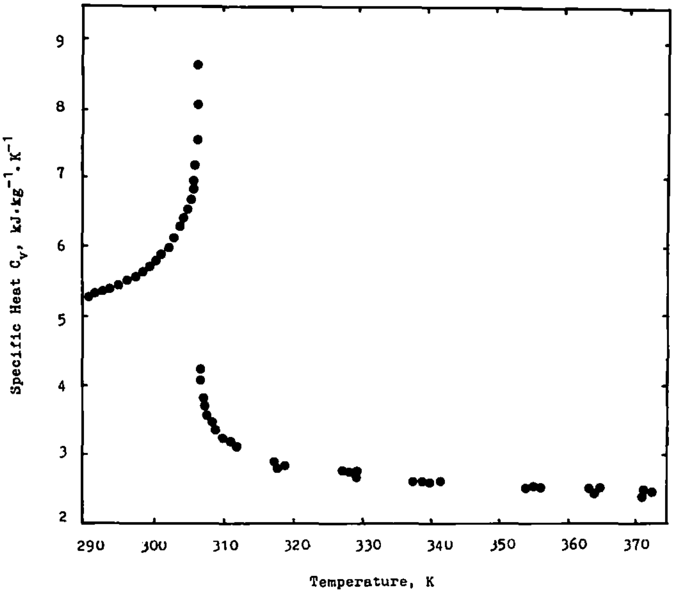

Fig. 3. Two- and one-phase specific heat $C_{v,x}$ of ethane + propane at the critical isochore ($\rho_c = 207.5$ kg $\cdot$ m^{-3}, $x = 0.0081$ C_3H_8) as a function of temperature.

Kiselev [11] for the C_v. Equation (4) can be generalized to binary mixtures as follows:

$$\frac{\tau(\mu)}{\mathrm{Gi}} = (1+kx^{-k_1})^{k_2}\,[x+(1+kx^{-k_1})^{-1/k_1}]$$
$$\tau(\mu) = \left\{\left(\frac{\tau(x)}{x_A}\right)(1+\tau^{\alpha}(x)/x_A)^{-1}\right\}^{1/(1-\alpha)} \qquad (5)$$

where

$$x_A = \frac{A_{0x}}{R(1-\alpha)}\,x(1-x)\left(\frac{1}{T_c}\frac{dT_c}{dx}\right)^2, \qquad A_{0x} = (k^{\gamma/\Delta}+1)\,B_{cr} \qquad (6)$$

The values of constants C_{v0}, B_{cr}, and Gi for the mixture (0.9919 $C_2H_6 + 0.0081$ C_3H_8) are also listed in Table IV.

In accordance with the isomorphism hypothesis [13–16], all simple liquids and their mixtures belong to the same universality class. It is essantial that in solutions, the heat capasity $C_{v,\mu}$ at constant chemical potential is the value isorphous to the heat capacity C_v of a one-component liquid, rather than the heat capacity $C_{v,x}$ at constant molar concentration x. The

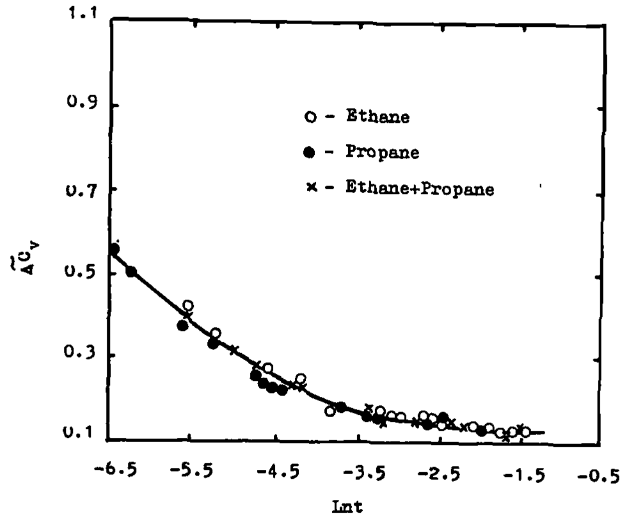

Fig. 4. The scaled specific heat at constant volume as a function of the scaled temperature for ethane (○), propane (●), and their mixture (×). The solid curve corresponds to the crossover Eq. (4).

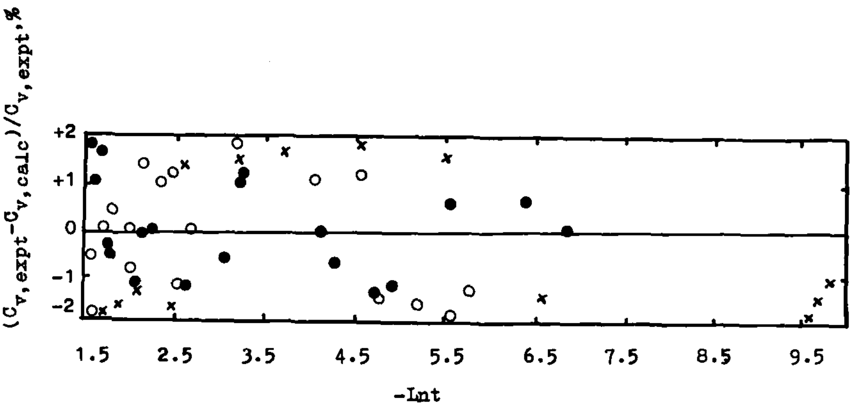

Fig. 5. Percentage differences between the experimental specific heats C_v obtained in this paper for ethane (○), propane (×), and ethane + propane (●) and the values calculated from the crossover Eq. (4).

character of critical behavior of the $C_{v,x}$ for mixtures is determined by a universal crossover function $\Phi(\varphi)$ [17]:

$$\Phi(\varphi)=\left(\frac{\varphi}{1+\varphi}\right)^{\alpha}\left[2-\left(\frac{\varphi}{1+\varphi}\right)^{\alpha/1-\alpha}\right] \tag{7}$$

where $\varphi = t(x)\xi^{1/\alpha}$ for $\rho=\rho_c(x)$, and $t(x)=(T-T_c(x))/T_c(x)$.

The crossover function $\Phi(\varphi)$ takes into account the Fisher renormalization in mixtures. The parameter φ determines the renormalization of the specific heat critical exponent α. The parameter ξ is given by Kiselev et al. [17]:

$$\xi=\left(\frac{RT_c\rho_c}{P_c}\right)[2\alpha(1-\alpha)\,b^2T_c^2/ak\gamma(\gamma-1)\,x(1-x)]\left(\frac{dT_c}{dx}\right)^{-2} \tag{8}$$

At $\varphi \gg 1$, the function $\Phi(1)\approx 1$ and $C_{v,x}$ behave as that of a pure substance $C_{v,x} \sim t^{-\alpha}$. At $\varphi \ll 1$ the renormalization $\alpha \to -\alpha/(1-\alpha)$ takes place, and the singular part of the heat capacity tends to a finite value $C_{v,x}^{\text{sin.}} \simeq 2ak\xi$ which at $\xi \to 0$ also tends to zero.

For a theoretical interpretation of our $C_{v,x}$ experimental data we need the critical parameters as a function of the concentration. For this purpose we have made an assessment of the experimental information for the citical parameters of mixtures of C_2H_6 and C_3H_8. To represent the dependence of the critical parameters of the mixtures on the concentration x, we adopt analytic interpolation equations of the form [18]

$$T_c(x)=T_c^{(1)}(1-x)+T_c^{(2)}x+(T_1x+T_2x^2+T_3x^3+T_4x^4)(1-x) \tag{9}$$

$$P_c(x)=P_c^{(1)}(1-x)+P_c^{(2)}x+(P_1x+P_2x^2+P_3x^4)(1-x) \tag{10}$$

where x denotes the mole fraction of C_2H_6. The coefficients T_i and P_i have been determined by fitting Eqs. (6) and (7) to experimental data obtained in this work and by Matsche and Thodos [19]. The values obtained for the coefficients in Eqs. (9) and (10) are presented in Table V. From our

Table V. Critical-Line Parameters for the $C_2H_6+C_3H_8$ Mixture

Equation (9) for $T_c(x)$, K	Equation (10) for $P_c(x)$, bar
$T_c^{(1)}=369.80$	$P_c^{(1)}=42.4709$
$T_c^{(2)}=305.32$	$P_c^{(2)}=48.7180$
$T_1=35.8383$	$P_1=23.1713$
$T_2=-12.002$	$P_2=42.5957$
	$P_3=-148.0997$

Table VI. Parameter Values in the Crossover Function, Eqs. (7) and (8), for the $C_2H_6 + C_3H_8$ Mixture

T_c (K)	306.468
ρ_c ($\mathrm{mol \cdot L^{-1}}$)	6.2761
P_c (bar)	48.6
a	20.576
k	1.1554
dT_c/dx	−88.1222
φ	2.1×10^{20}
ξ	188.9165
α	0.112
β	0.325
γ	1.238
b^2	1.3563

experimental $C_{v,x}$ data we have deduced values for T_c and ρ_c at $x = 0.0081$. Our results $T_c = 306.468$ K and $\rho_c = 6.2761\ \mathrm{mol \cdot L^{-1}}$ are in agreement with the values implied by our correlating equations. The values of the parameter ξ was estimated from Eq. (8) with Eqs. (9) and (10) to evaluate the derivative (dT_c/dx). The values of the parameters ξ and φ for the $C_2H_6 + C_3H_8$ mixture are presented in Table VI. In a region where $t \gg \xi^{-1/\alpha}$, we have a pure fluid-like behavior, and where $t \ll \xi^{-1/\alpha}$ we have the renormalization of the critical exponent $\alpha \rightarrow -\alpha/(1-\alpha)$. From quantitative analysis of the shape of critical lines $T_c(x)$ and $P_c(x)$, using Eqs. (8)–(10), we find that for a $C_2H_6 + C_3H_8$ mixture the Fisher renormalization is observable in the range $0.4 \leqslant x \leqslant 0.9$ and at $0 \leqslant t \leqslant 0.075$ for critical isochores $\rho = \rho_c(x)$. In our case, the mixture ($x = 0.0081$) does not falls into this concentration range, therefore, the mixture ($0.9919\ C_2H_6 + 0.0081\ C_3H_8$) behaves as a pure substance in the entire range of the experiment. Our experimental results are in good agreement with these theoretically predictions.

5. CONCLUSIONS

We have presented new measurements of the specific heat C_v of pure ethane, propane, and their mixture in both the two- and the one-phase regions at critical isochores. We have demonstrated that the theoretically based crossover equations for C_v and $C_{v,x}$ are in good agreement with our experimental results.

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