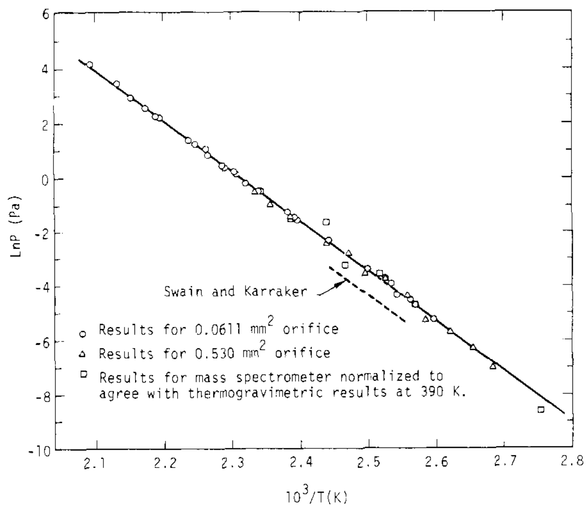

Figure 1. Vapor pressure vs. temperature for $U(thd)_4$.

times the values of Swain and Karraker at a given temperature. The corresponding temperature discrepancies would be about 7.2° at 392 K and 8.1° at 409 K, the lower and upper temperatures of their measurements or 6.5° and 13.8° at our temperature extremes. These differences are far beyond the combined estimated uncertainties for the two studies and we have no explanation for the discrepancy. One suspects a difference in composition because of the difference in melting points, but analyses of the materials were very similar and vapor composition from their material was identical with ours as shown by the mass spectra. It is surprising to find such a large effect on pressure with no detected change in vapor composition and no significant change in enthalpy of sublimation.

The reviewer suggested the discrepancy between our results and those of Swain and Karraker could result from temperature errors due to thermal gradients within the samples. This is possible, and our measurements were more susceptible to this type of error than Swain and Karraker's were because of the temperature gradients in our furnace; the gradients measured between the thermocouples in the furnace and inside the cell varied from about 0° at 100 °C to nearly 25° at 205 °C. Since calibrations were done with empty cells, errors could arise from differences, both conductive and radiative, in thermal transport. However, since the cells were in metal containers, within which the temperature gradient from bottom to top was only 8° at 205 °C, we think a temperature error large enough to explain the difference in results is unlikely.

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Received for review July 16, 1976. Accepted January 11, 1977. This work performed under the auspices of the U.S. Energy Research and Development Administration, Contract No. W-7405-Eng-48. Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Energy Research & Development Administration to the exclusion of others that may be suitable.

The P–V–T Behavior of Acetone in the Dense Gaseous Region

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Experimental PVT data were obtained for acetone in the dense gaseous region for temperatures between 233.7 and 265.3 °C and pressures between 92.4 and 363.8 atm. The experimental pressures and temperatures are presented for each constant mass run, and smoothed compressibility factors resulting from the data are tabulated. The experimental compressibility factors are in good agreement with values calculated from a generalized correlation of this property for polar fluids.

Experimental PVT data were obtained for acetone in the dense gaseous region with a constant volume apparatus. No previous PVT data were available for this substance for the conditions considered. Anderson, Kudchadker, and Eubank (*1*) determined the compressibility factor of acetone for temperatures from 25 to 150 °C and pressures to 7.15 atm. Bridgman (*3*) obtained liquid densities for this substance for elevated pressures and temperatures to 80 °C. Campbell and Chatterlee (*2*) determined saturated liquid and vapor densities for acetone for temperatures from 100 to 235 °C.

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Experimental Section

The experimental system was essentially the same as that described in detail previously (*4*, *5*). The constant volume cell was immersed in a molten salt bath controlled internally and externally. The temperature of the bath was measured with protected thermocouples which had been calibrated with a platinum resistance thermometer. The pressure was measured with a dead weight gauge by balancing the test gas with nitrogen by means of a high temperature differential pressure indicator. Modifications were made in the arrangement of the test system, insulation and heating of the bath, and fine pressure control.

The bath assembly was enclosed in a wooden structure 6 ft wide by 7 ft long. One side of the structure served as the control panel. After a vacuum had been obtained, acetone was injected into the system with a syringe. When thermal equilibrium had been reached the temperature and pressure were recorded.

The volume of the test vessel and associated tubing was

Table I. Experimental Data for Acetone

Mass (g)	Temp (°C)	Pressure (atm)	Density (g cm^{-3})
156.10	233.83	92.39	0.5018
	235.70	96.55	0.5018
	245.63	122.96	0.5015
	250.73	136.00	0.5014
	255.64	148.25	0.5013
	261.09	160.85	0.5012
	265.14	170.18	0.5011
159.67	233.70	105.67	0.5133
	235.70	112.82	0.5132
	241.14	124.46	0.5131
	245.64	136.51	0.5130
	250.74	149.82	0.5129
	255.53	162.14	0.5128
	265.26	187.06	0.5125
162.12	233.72	117.45	0.5211
	235.70	122.69	0.5211
	241.17	137.46	0.5209
	245.62	149.27	0.5208
	250.76	162.68	0.5207
	255.36	174.73	0.5206
	261.09	189.71	0.5205
	265.20	200.88	0.5204
167.09	233.65	138.45	0.5371
	235.70	144.51	0.5370
	241.18	160.57	0.5369
	248.97	183.11	0.5367
	250.75	188.01	0.5367
	255.48	201.53	0.5365
	261.09	217.45	0.5364
	265.16	228.82	0.5363
172.99	233.74	175.35	0.5560
	235.70	181.61	0.5559
	241.18	199.52	0.5558
	245.70	213.64	0.5557
	250.79	229.57	0.5555
	255.53	244.07	0.5554
	261.09	261.64	0.5553
	265.34	274.61	0.5552
177.08	233.68	203.40	0.5691
	235.70	210.65	0.5690
	241.15	229.16	0.5689
	245.72	244.55	0.5688
	250.75	261.57	0.5686
	255.60	278.15	0.5685
	261.09	295.58	0.5684
	265.20	308.17	0.5683
181.84	233.73	249.25	0.5843
	235.70	256.87	0.5843
	241.19	277.27	0.5841
	245.55	293.13	0.5840
	250.70	311.78	0.5839
	255.61	329.48	0.5837
	261.09	348.99	0.5836
	265.18	363.76	0.5835

calibrated for the temperature and pressure range of interest by the use of the ethyl alcohol data obtained previously (*4, 5*) and checked with PVT data for water. The effect of temperature and pressure on the volume can be represented as

$$V = V_0(1 + (2.366 \times 10^{-6})P) \quad (1)$$

where

$$V_0 = 304.932 + 0.012T \quad (2)$$

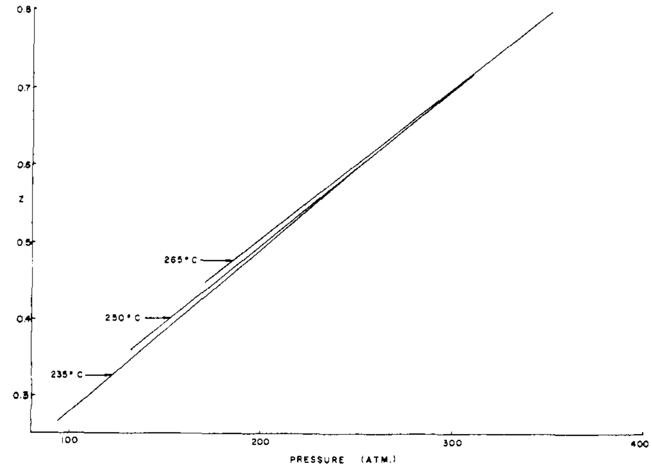

Figure 1. Experimental compressibility factors for acetone.

For the temperature range considered the volume of the test system was essentially constant, with an average value of approximately 311.3 cm^3. The acetone utilized was spectrophotometric grade, with a stated purity of better than 99.9%.

Results

Seven runs were conducted for sample weights between 156.1 and 181.8 g, temperatures between 233.7 and 265.3 °C, and pressures between 92.4 and 363.8 atm. Points were taken at approximately 5 °C intervals in temperatures. The experimental pressures and temperatures for each run are presented in Table I. The corresponding densities are also included for each point.

For each run the data were smoothed by relating pressure to temperature. Compressibility factors were then determined at constant temperature from the calculated pressure, calibrated volume, and the mass, and were related to pressure. The smoothed compressibility factors were then calculated at even pressures for each temperature and are presented in Table II. For most of the range considered the variation of z with pressure at constant temperature is essentially linear, as shown in Figure 1 for 235, 250, and 265 °C.

The combined error involved in weighing, pressure and temperature measurement, and volume calibration was estimated to be approximately 0.25%. Purity analyses with a gas chromatograph before and after the experimental runs indicated that some degradation of the acetone occurred during the measurements. It was found that the amount of reaction was very small at 235 °C, increasing slightly at 265 °C. At 285 °C a relatively large amount of reaction occurred. The amount of impurities created during an experimental run from 235 to 265 °C was estimated to be less than 0.4%.

Stipp, Bai, and Stiel (*6*) utilized experimental PVT data for ten polar fluids to develop a relationship for the compressibility factor in the gaseous and liquid regions of the form

$$z = z^{(0)} + \omega z^{(1)} + xz^{(2)} + \omega xz^{(3)} + x^2 z^{(4)} \quad (3)$$

The polar fluid correction terms $z^{(2)}$, $z^{(3)}$, and $z^{(4)}$ were tabulated for reduced temperatures from 0.8 to 1.15 and reduced pressures from 0.2 to 6.0. The third and fourth parameters ω and x account for the shape and polarity of the fluids.

Interpolated values of z for acetone resulting from the experimental data of this study at reduced temperatures of 1.0 and 1.05 and reduced pressures to 6.0 were compared with the compressibility factors determined from eq 3. The parameters utilized for acetone were T_c = 508.7 K, P_c = 46.6 atm, ω = 0.304, and x = 0.013. The average deviation between the calculated and experimental values was 0.39% for nine points.

Table II. Smoothed Compressibility Factors for Acetone

Pressure, atm	Temperature, °C						
	235.00	240.00	245.00	250.00	255.00	260.00	265.00
95.0	0.2643	0.2678	0.2721				
100.0	0.2758	0.2792	0.2832				
105.0	0.2872	0.2905	0.2944				
110.0	0.2985	0.3017	0.3054	0.3098			
115.0	0.3097	0.3128	0.3164	0.3206			
120.0	0.3209	0.3239	0.3273	0.3313	0.3360		
125.0	0.3320	0.3349	0.3382	0.3420	0.3465		
130.0	0.3431	0.3458	0.3490	0.3527	0.3569		
135.0	0.3540	0.3567	0.3598	0.3633	0.3673		
140.0	0.3650	0.3676	0.3705	0.3738	0.3777		
145.0	0.3758	0.3783	0.3811	0.3844	0.3881	0.3923	
150.0	0.3867	0.3891	0.3918	0.3948	0.3984	0.4024	
155.0	0.3974	0.3997	0.4023	0.4053	0.4087	0.4126	
160.0	0.4082	0.4104	0.4129	0.4157	0.4190	0.4227	0.4267
165.0	0.4188	0.4210	0.4234	0.4261	0.4292	0.4327	0.4366
170.0	0.4295	0.4315	0.4338	0.4364	0.4394	0.4428	0.4466
175.0	0.4401	0.4420	0.4442	0.4467	0.4496	0.4528	0.4565
180.0	0.4507	0.4525	0.4546	0.4570	0.4597	0.4628	0.4663
185.0	0.4612	0.4630	0.4650	0.4672	0.4698	0.4728	0.4762
190.0	0.4717	0.4734	0.4753	0.4774	0.4799	0.4828	0.4860
195.0	0.4822	0.4838	0.4856	0.4876	0.4900	0.4927	0.4958
200.0	0.4927	0.4941	0.4958	0.4978	0.5000	0.5026	0.5056
205.0	0.5032	0.5045	0.5061	0.5079	0.5100	0.5125	0.5154
210.0	0.5137	0.5148	0.5163	0.5180	0.5200	0.5224	0.5251
215.0	0.5241	0.5251	0.5265	0.5281	0.5300	0.5322	0.5349
220.0	0.5346	0.5354	0.5367	0.5382	0.5400	0.5421	0.5446
225.0	0.5450	0.5457	0.5469	0.5483	0.5499	0.5519	0.5543
230.0	0.5554	0.5560	0.5570	0.5583	0.5599	0.5617	0.5639
235.0	0.5659	0.5663	0.5671	0.5683	0.5698	0.5715	0.5736
240.0	0.5764	0.5766	0.5773	0.5783	0.5797	0.5813	0.5833
245.0	0.5868	0.5870	0.5874	0.5883	0.5896	0.5910	0.5929
250.0		0.5971	0.5975	0.5983	0.5994	0.6008	0.6025
255.0		0.6074	0.6076	0.6083	0.6093	0.6105	0.6121
260.0		0.6177	0.6179	0.6183	0.6191	0.6203	0.6217
265.0				0.6283	0.6290	0.6300	0.6313
270.0				0.6382	0.6388	0.6397	0.6409
275.0				0.6482	0.6486	0.6494	0.6504
280.0					0.6584	0.6591	0.6600
285.0					0.6683	0.6688	0.6696
290.0					0.6781	0.6784	0.6791
295.0						0.6881	0.6886
300.0							0.6982

Additional experimental compressibility factors were obtained for acetone in the liquid region for temperatures above 180 °C which were also in good agreement with the values calculated from eq 3.

Glossary

P	pressure, atm
P_c	critical pressure, atm
T	temperature, °K
T_c	critical temperature, °K
V	volume, cm^3
V_0	volume corrected to zero pressure, cm^3
x	fourth parameter for polar fluids
z	compressibility factor, PV/nRT
ω	acentric factor

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Received for review June 9, 1976. Accepted February 28, 1977. The authors are grateful to the National Science Foundation for the support of this work.