J. Chem. Eng. Data 1982, 27, 1–11

Pressure–Volume–Temperature Relations of Propane[‡]

Raymond H. P. Thomas[†] **and Roland H. Harrison***

Bartlesville Energy Technology Center, U.S. Department of Energy, Bartlesville, Oklahoma 74003

A comprehensive experimental investigation of the isothermal and isochoric P–V–T properties of pure propane (99.998 mol %) covered the ranges 258.15–623.15 K, 0.8–12.5 mol dm^{-3}, and 0–400 bar. Measurements on the compressed single-phase fluid and the vapor–liquid, two-phase region were used to derive vapor pressures, critical constants (P_c = 42.4709 bar, ρ_c = 4.955 mol dm^{-3}, T_c = 369.85 K), P–V–T relations for the vapor and liquid branches of the coexistence envelope, and virial coefficients (B_0, C_0, D_0).

Introduction

The varied technologic role of propane as a cryogenic fluid, a hydrocarbon fuel, and a source hydrocarbon for petrochemical processing is sufficiently impressive, both in terms of its tonnage use and because of its mechanical fluid properties, that a more exact knowledge of its P–V–T surface is of great concern. Propane is not well characterized in thermodynamic terms, as compared to methane and ethane. A significant improvement in the data base can lead to substantially improved tables of properties and to significant savings in processing costs and energy. This work was initiated under the Bureau of Mines, Department of the Interior, and continued under the Energy Research and Development Administration for about 1 year. After being inactive for a period of about 2 years, the project was supported by the Department of Energy.

Experimental Section

The operation and the accuracy of the compressibility apparatus have been described (*1–4*), so only a brief summary is needed here. A sample of propane was sealed in a thin-walled pycnometer which formed a loosely fitting liner inside the compressibility bomb. The stainless-steel liner ended in a small capillary tube of known length and diameter. Before the assembly of the bomb and liner, the capillary was bent into a hook to complete a lock-and-key mechanism, in the assembled bomb, of which the bent capillary was the key. The pycnometer remained sealed and horizontal during assembly and the introduction of mercury into the evacuated space in the bomb and manifold of the compressibility apparatus. Mercury was metered into the void space of the assembled apparatus from a thermostated, quantitative-displacement compressor. A null-volume reading for the compressor was recorded when the pressure exerted by the mercury in the void space equaled the pressure of the sample (i.e., the vapor pressure of propane at 303.15 K). After the null setting was made, the bomb was set upright and the loosely fitting liner was forced to float upward, thereby breaking the capillary tube. Mercury under pressure then entered the liner and compressed the sample. The volume occupied by the sample was determined from the compressor setting, the volume of the pycnometer, and the null volume along with the predetermined variation of the volume of the entire system with temperature and pressure as determined in a run without sample. As usual, pressures were determined with a deadweight gauge calibrated against the vapor pressure of pure carbon dioxide at 273.15 K, 34.8501 bar, as determined by Sengers and Chen (*5*).

For the study of the coexistence envelope and vapor pressures, a piston of 0.5-in. diameter was used. The sensitivity of the deadweight gauge with this piston is $^1/_{200000}$. The highest pressure obtainable with the 0.5-in. piston is 100 bar. For the study of the supercritical temperature region and of pressure regions above 100 bar but below the critical temperature, a piston of 0.25-in. diameter was used. The sensitivity of the deadweight gauge with the latter piston is $^1/_{50000}$. Both gauges are of a new design by Douslin. The new feature of the design is that the vertical piston remains undisturbed while the cylinder surrounding the piston oscillates about its axis to reduce frictional effects at the piston–cylinder interface. Previous designs used a piston which oscillated in a fixed vertical cylinder. Here the problem of the frictional effects is solved while eliminating the movement of the piston. Corrections for the variation of the effective piston area for the 0.25-in. piston with pressure were based on values determined by Dadson (*6*). The 0.5-in. piston correction factor was determined by calibration against the 0.25-in. piston.

The temperature of the compressibility bomb, controlled to ±0.0005 K, was measured with a platinum resistance thermometer that was calibrated at the National Bureau of Standards in terms of IPTS-48 (*7*) and was corrected to IPTS-68 (*8, 9*). The ice point of the thermometer did not change significantly during the investigation. The mercury vapor in the sample was calculated as loss in volume of liquid mercury, assuming that the mercury vapor exhibited the same degree of nonideality as the compressed propane sample. A similar assumption was made in previous work (*4*).

Pressures are expressed in bars (1 bar = 10^5 Pa). The precision of the pressure and volume measurements was previously discussed (*2*). The maximum overall error in the measured compression factor, $Z = PV/RT$, varied from 0.03% at the lowest pressure and density to 0.3% at the highest temperature, pressure, and density.

Sample. The sample was purchased from Airco Industrial Gases with a reported purity of 99.993%. Propylene was the major impurity and was removed from the sample by passing the gas through a column of concentrated sulfuric acid on palladium sulfate treated Chromosorb W (40% concentrated H_2SO_4). The gas was passed through potassium hydroxide pellets to remove any sulfuric acid that might have been taken up and through magnesium perchlorate to remove any possible water. Removal of propylene was confirmed by gas chromatography. A column packed with F-20 alumina 100/120 mesh treated with hexamethyldisilazane was used. Nitrogen was found as another impurity. It was removed by alternatively cooling the sample to the temperature of liquid nitrogen, evacuating the space above the sample, and warming the sample to 60–70 °C. Seven cycles were necessary. The final purity of the sample using the F-20 alumina column was 99.998%.

The normal procedure in this kind of study is to complete the entire series of P–V–T measurements on one filling of the bomb using approximately 0.1 mol of sample. In this study, an accident occurred just after the critical temperature was reached. It was necessary to make a second filling to complete the measurements. The first filling used 4.466 61 g of sample while the second filling used 4.414 02 g of sample. The

---

[†] Present address: Allied Chemical Co., Buffalo, NY 14240.

[‡] Contribution No. 247 from the thermodynamics research branch at the Bartlesville Energy Technology Center.

Table I. *P-V-T* Relations for the Coexistence and Near-Critical Regions of Propane[a-c]

V dm^3 mol^{-1}	P bar
Sample #1	
T = 258.15 K	
1.249869	2.9178
1.082798	2.9181
0.915723	2.9179
0.748644	2.9179
0.414490	2.9180
0.080455	6.3633
0.080421	7.6568
0.080386	8.9537
0.080349	9.9440
0.080314	11.6045
Sample #1	
T = 263.15 K	
1.217901	3.4550
1.075823	3.4549
0.933743	3.4550
0.791670	3.4548
0.365451	3.4550
0.081451	5.1072
0.081415	6.3683
0.081374	7.4521
0.081341	8.8409
0.081308	10.1636
0.081238	12.8982
Sample #1	
T = 268.15 K	
1.246305	4.0622
1.052297	4.0623
0.931051	4.0623
0.809799	4.0622
0.324801	4.0626
0.224192	4.0628
0.104947	4.0631
0.082418	5.6743
0.082379	6.6885
0.082344	8.0353
0.082305	9.1602
0.082263	10.2027
0.082223	11.4643
0.082151	14.1049
Sample #1	
T = 273.15 K	
1.249522	4.7461
1.124571	4.7463
0.916331	4.7462
0.708078	4.7462
0.291594	4.7466
0.124990	4.7470
0.083408	6.0265
0.083331	8.3600
0.083250	10.5851
0.083216	12.0153
Sample #1--continued	
T = 273.15 K	
0.083213	11.9173
0.083177	13.3030
0.083137	14.4418
0.083101	15.8755
0.083066	17.0395
0.082995	19.8427
0.082988	19.5806
0.082664	31.8203
0.081994	56.7836
0.081308	84.5373
Sample #1	
T = 278.15 K	
1.269250	5.5122
1.161539	5.5124
0.982025	5.5127
0.802510	5.5123
0.263960	5.5128
0.120352	5.5134
0.084521	6.0833
0.084474	7.1627
0.084435	8.2392
0.084393	9.3781
0.084354	10.5791
0.084315	11.7641
0.084280	13.0267
Sample #1	
T = 283.15 K	
1.263052	6.3674
1.170101	6.3671
1.015192	6.3672
0.860287	6.3673
0.240660	6.3677
0.116722	6.3678
0.085655	7.0929
0.085612	8.0995
0.085568	9.1457
0.085527	10.1679
0.085483	11.2828
Sample #1	
T = 288.15 K	
1.273621	7.3158
1.165743	7.3160
1.030897	7.3159
0.896019	7.3160
0.761186	7.3160
0.626336	7.3161
0.491486	7.3159
0.356635	7.3161
0.221788	7.3164
0.113901	7.3165
0.086875	7.9194
0.086829	8.9012
0.086828	8.8347
0.086784	9.8265
0.086741	10.8510
0.086740	10.8734
0.086698	11.8656
Sample #1	
T = 293.15 K	
1.258924	8.3648
1.141858	8.3651
1.024784	8.3651
0.673570	8.3649
0.205287	8.3658
0.111630	8.3659
0.088159	9.1850
0.088121	10.2606
0.088074	11.2057
0.088027	12.2895
0.087985	13.2335
Sample #1	
T = 298.15 K	
1.213460	9.5201
1.108416	9.5202
1.006528	9.5202
0.599002	9.5203
0.191467	9.5211
0.109962	9.5213
0.089530	10.1770
0.089528	9.9579
0.089482	10.9750
0.089477	10.7420
0.089473	10.7285
0.089438	12.0354
0.089432	11.8514
0.089384	12.8233
0.089330	13.4937
0.089330	13.5456
0.088900	21.6794
0.088480	29.9220
0.087544	49.9699
0.086956	64.1832
0.086782	68.3990
0.086263	82.2069
0.085626	100.107
Sample #1	
T = 303.15 K	
1.247407	10.7891
0.980548	10.7891
0.535791	10.7891
0.179980	10.7902
0.108834	10.7904
0.091045	11.0109
0.090999	11.8319
0.090950	12.6305
0.090902	13.4664
0.090851	14.2477
0.090844	13.9081
0.090743	15.4884
0.090010	28.2543
0.088876	49.3643
0.088080	66.4663
0.087407	82.4078
0.086753	99.3319
Sample #2	
T = 303.15 K	
1.263944	10.7869
0.992788	10.7876
0.542529	10.7883
0.182361	10.7902
0.110399	10.7907
0.091048	11.3763
0.090997	12.2523
0.090946	13.0809
0.090848	14.6136
0.090786	15.4596
0.089793	32.3136
0.089448	38.5429
0.088812	51.2313
0.088481	58.3011
0.088010	68.2443
0.086675	101.807

[a] Brackets enclose results inside the vapor-liquid envelope.

[b] Dashed line brackets denote placement of phase boundary by calculation from equations 2 and 3.

[c] To retain precision, some values are reported to one more place than justified by absolute accuracy.

Table I (*Continued*)

V $dm^3\ mol^{-1}$	P bar
Sample #1	
T = 313.15 K	
1.253240	13.6918
1.116898	13.6917
0.776047	13.6917
0.435194	13.6923
0.162510	13.6917
0.094426	13.8827
0.094372	14.5334
0.094318	15.1488
0.094263	15.7756
0.094208	16.3494
0.094149	17.0151
0.094087	17.3471
0.094041	18.1578
Sample #1	
T = 323.15 K	
1.250000	16.1296
1.219512	16.4019
1.190476	16.6683
1.176471	16.7990
1.162791	16.9283
1.149425	17.0562
1.142857	17.1175
1.142204	17.1217
1.141550	17.1242
1.140251	17.1266
1.138952	17.1277
1.136364	17.1289
1.131226	17.1292
1.084045	17.1296
0.876516	17.1293
0.617116	17.1300
0.357704	17.1302
0.150171	17.1311
0.108728	17.1313
0.103506	17.1311
0.098245	17.6639

V $dm^3\ mol^{-1}$	P bar
Sample #1--continued	
T = 323.15 K	
0.098245	17.8074
0.098242	17.5748
0.098188	18.2878
0.098183	18.0462
0.098174	17.9697
0.098126	18.5701
0.098124	18.5441
0.098070	19.1327
0.098067	19.0827
0.098014	19.6595
0.098008	19.5245
0.097956	20.1714
0.097949	19.9523
0.097946	19.8670
0.097561	23.2532
0.095239	46.8562
0.093024	76.4665
Sample #2	
T = 323.15 K	
1.250000	16.1289
1.250000	16.1282
1.219512	16.4015
1.190476	16.6677
1.176471	16.7986
1.162791	16.9278
1.149425	17.0561
1.096986	17.1302
1.089652	17.1289
0.886963	17.1310
0.880948	17.1300
0.624473	17.1304
0.624469	17.1310
0.619873	17.1305
0.361963	17.1321
0.359186	17.1308
0.153641	17.1338
0.150485	17.1330

V $dm^3\ mol^{-1}$	P bar
Sample #2--continued	
T = 323.15 K	
0.098215	17.4819
0.098155	18.0554
0.098096	18.5967
0.098039	19.0998
0.097979	19.5866
0.095258	46.7880
0.090626	114.691
0.086927	212.865
0.083346	350.469
Sample #1	
T = 333.15 K	
1.250000	17.0035
1.111111	18.4486
1.000000	19.7554
0.952381	20.3575
0.943396	20.4746
0.930233	20.6455
0.909091	20.9251
0.892857	21.1420
0.891266	21.1581
0.848389	21.1629
0.691466	21.1632
0.495318	21.1638
0.299161	21.1635
0.142236	21.1643
0.103106	21.2775
0.103049	21.5953
0.102985	21.9548
0.102924	22.2882
0.102861	22.5774
0.102798	22.9609
0.102735	23.3012
0.102672	23.6250
0.102610	23.9657

V $dm^3\ mol^{-1}$	P bar
Sample #1	
T = 343.15 K	
1.250000	17.8590
1.000000	20.8904
0.833333	23.4083
0.769231	24.4840
0.740741	24.9774
0.714286	25.4418
0.701754	25.6631
0.690608	25.8558
0.661571	25.8611
0.545325	25.8617
0.400009	25.8618
0.254700	25.8618
0.138448	25.8624
0.109303	26.0538
0.109235	26.2474
0.109169	26.4450
0.109105	26.6510
0.109039	26.8680
0.108971	27.0772
0.108904	27.2900
0.108841	27.4786
0.108774	27.6796
Sample #2	
T = 343.15 K	
0.769231	24.4833
0.740741	24.9764
0.714286	25.4397
0.701754	25.6650
0.690608	25.8563
0.665967	25.8622
0.661570	25.8630
0.549010	25.8630
0.545292	25.8633
0.404773	25.8645
0.404773	25.8642
0.257737	25.8650

V $dm^3\ mol^{-1}$	P bar
Sample #2--continued	
T = 343.15 K	
0.257736	25.8652
0.140100	25.8667
0.140099	25.8668
0.109330	25.8796
0.109261	26.1083
0.109196	26.2944
0.109127	26.5038
0.109062	26.7317
0.108993	26.9138
Sample #1	
T = 348.15 K	
1.250000	18.2815
1.000000	21.4470
0.714286	26.3100
0.666667	27.2410
0.645161	27.6658
0.625000	28.0654
0.615385	28.2551
0.606061	28.4376
0.602405	28.4836
0.577962	28.4857
0.480130	28.4852
0.357765	28.4858
0.235520	28.4864
0.137673	28.4866
0.113263	28.6035
0.113196	28.7454
0.113126	28.9074
0.113067	29.0478
0.112997	29.2000
0.112933	29.3477
0.112865	29.4955
0.112797	29.6421
0.111111	33.7700
0.105264	56.8277

V $dm^3\ mol^{-1}$	P bar
Sample #2	
T = 348.15 K	
1.250002	18.2808
0.358483	28.4897
0.236034	28.4910
0.111093	33.7170
0.105255	56.8612
0.100014	95.0962
0.095249	153.466
0.090913	238.349
0.086958	356.945
Sample #1	
T = 353.15 K	
1.250000	18.7008
1.000000	22.0001
0.666667	28.1774
0.588235	29.9036
0.555556	30.6205
0.540541	30.9448
0.526316	31.2460
0.521390	31.3084
0.501230	31.3085
0.420583	31.3098
0.319774	31.3091
0.218965	31.3086
0.138317	31.3077
0.118180	31.3646
0.118111	31.4617
0.118041	31.5614
0.117972	31.6670
0.117905	31.7596
0.117836	31.8649
0.117768	31.9642
0.117698	32.0558

Table I (*Continued*)

V dm^3 mol^{-1}	P bar
Sample #1	
T = 358.15 K	
1.250000	19.1171
1.000000	22.5466
0.666667	29.1010
0.526316	32.5253
0.500000	33.1615
0.476190	33.7166
0.454545	34.1957
0.449438	34.3044
0.428537	34.3511
0.364581	34.3515
0.284636	34.3516
0.204686	34.3523
0.140733	34.3526
0.124610	34.4076
0.124539	34.4605
0.124469	34.5214
0.124401	34.5737
0.124329	34.6271
0.124260	34.6819
0.124190	34.7379
Sample #1	
T = 363.15 K	
1.250000	19.5317
1.000000	23.0624
0.666667	30.0100
0.500000	34.5044
0.400000	37.0628
0.392157	37.2306
0.384615	37.3845
0.380228	37.4699
0.377358	37.5238
0.370366	37.6318
0.358561	37.6327
0.311345	37.6326
0.252300	37.6330
0.196022	37.6325
0.146014	37.6338
Sample #1--continued	
T = 363.15 K	
0.134213	37.6351
0.133918	37.7354
0.133766	37.7868
0.133628	37.8822
0.133342	37.9350
0.133203	37.9853
Sample #2	
T = 363.15 K	
0.500000	34.5036
0.400000	37.0640
0.392157	37.2318
0.384615	37.3860
0.380228	37.4717
0.377358	37.5271
0.370374	37.6342
0.359610	37.6350
0.312163	37.6348
0.252854	37.6365
0.193542	37.6371
0.146092	37.6379
0.134224	37.6393
0.134151	37.6401
0.134013	37.6764
0.133934	37.7069
0.133865	37.7264
Sample #1	
T = 365.15 K	
1.250000	19.6966
1.000000	23.3057
0.666667	30.2885
0.500000	35.0349
0.500000	35.0316
0.400000	37.7801
0.400000	37.7741
0.370370	38.4562
0.370370	38.4503
Sample #1--continued	
T = 365.15 K	
0.363636	38.5927
0.363636	38.5866
0.357143	38.7172
0.357143	38.7106
0.350877	38.8306
0.350877	38.8236
0.344828	38.9304
0.344828	38.9245
0.337544	39.0174
0.327750	39.0172
0.288563	39.0184
0.288558	39.0184
0.288554	39.0179
0.239582	39.0176
0.239582	39.0182
0.190595	39.0188
0.190595	39.0187
0.151432	39.0182
0.139965	39.0190
0.139824	39.0349
0.139751	39.0492
0.139750	39.0478
0.139678	39.0628
0.139608	39.0645
0.139535	39.0851
0.139468	39.0906
0.139467	39.0904
0.139197	39.1456
0.139194	39.1430
0.139040	39.1800
0.139036	39.1815
0.138898	39.2064
0.138897	39.2108
0.138758	39.2374
0.138756	39.2427
0.138613	39.2748
Sample #1	
T = 367.15 K	
0.400000	38.4975
0.333333	40.0241
0.322581	40.2009
0.312500	40.3433
0.307692	40.4025
0.305810	40.4235
0.303951	40.4443
0.301203	40.4497
0.291844	40.4498
0.261950	40.4495
0.224589	40.4498
0.187231	40.4506
0.157335	40.4511
0.149813	40.4500
0.148099	40.4514
0.147954	40.4552
0.147883	40.4612
0.147811	40.4697
0.147811	40.4684
0.147742	40.4734
0.147671	40.4799
0.147600	40.4868
0.147100	40.5287
Sample #1	
T = 368.15 K	
1.250000	19.9435
1.000000	23.6288
0.666667	30.9095
0.500000	35.8179
0.400000	38.8515
0.333333	40.4775
0.312500	40.8399
0.303030	40.9734
0.298507	41.0291
0.294118	41.0785
0.289855	41.1209
0.285714	41.1579
Sample #1--continued	
T = 368.15 K	
0.281199	41.1843
0.274869	41.1850
0.249548	41.1850
0.217909	41.1848
0.186267	41.1858
0.186267	41.1853
0.160952	41.1854
0.154020	41.1928
0.153949	41.1958
0.153881	41.1987
0.153807	41.2025
0.153734	41.2051
0.153665	41.2097
0.153594	41.2130
Sample #1	
T = 369.15 K	
0.400000	39.1992
0.400000	39.2036
0.333333	40.9284
0.285714	41.7132
0.270270	41.8569
0.266667	41.8772
0.263158	41.8979
0.259740	41.9150
0.256410	41.9285
0.255102	41.9335
0.253808	41.9345
0.253808	41.9346
0.247310	41.9347
0.227910	41.9342
0.203636	41.9346
0.179374	41.9346
0.166669	41.9342
0.163601	41.9473
0.163526	41.9476
0.163454	41.9493
Sample #1--continued	
T = 369.15 K	
0.163382	41.9497
0.163310	41.9511
0.163238	41.9526
0.163168	41.9527
0.163168	41.9528
0.163025	41.9556
0.162880	41.9578
0.162738	41.9601
0.161310	41.9877
0.159974	42.0186
0.153847	42.2770
Sample #1	
T = 369.65 K	
0.333333	41.1546
0.307692	41.6621
0.285714	41.9883
0.266667	42.1777
0.263158	42.2030
0.259740	42.2248
0.256410	42.2437
0.253165	42.2610
0.250000	42.2752
0.229026	42.3156
0.211407	42.3162
0.193778	42.3162
0.179699	42.3160
0.175925	42.3167
0.175711	42.3168
0.175496	42.3187
0.175344	42.3186
0.174421	42.3212
0.173707	42.3234
0.172995	42.3260
0.172993	42.3266
0.172638	42.3275
0.172279	42.3292
0.171567	42.3328

Table I (*Continued*)

V $dm^3\ mol^{-1}$	P bar
Sample #1	
T = 369.75 K	
0.253165	42.3244
0.250000	42.3404
0.246914	42.3507
0.243902	42.3625
0.240964	42.3712
0.238095	42.3768
0.232558	42.3899
0.225728	42.3928
0.225728	42.3923
0.210083	42.3917
0.210075	42.3923
0.206200	42.3931
0.202270	42.3941
0.194454	42.3944
0.194454	42.3940
0.187977	42.3946
0.187977	42.3945
0.181944	42.3958
0.179403	42.3952
0.178329	42.3970
0.177830	42.3967
0.177826	42.3967
0.177251	42.4008
0.176403	42.4025
0.175469	42.4051
0.173684	42.4100
Sample #2	
T = 369.75 K	
0.250000	42.3429
0.232558	42.3904
0.217489	42.3981
0.204940	42.3986
0.192381	42.3996
Sample #2--continued	
T = 369.75 K	
0.180046	42.4019
0.179684	42.4019
0.179322	42.4022
0.178960	42.4022
0.177512	42.4058
0.176065	42.4088
Sample #2	
T = 369.77 K	
0.250000	42.3563
0.240964	42.3881
0.238095	42.3949
0.235294	42.4004
0.232558	42.4049
0.229885	42.4079
0.225225	42.4124
0.215810	42.4144
0.204077	42.4143
0.192317	42.4148
0.182926	42.4159
0.180385	42.4168
0.179675	42.4183
0.178229	42.4206
0.176836	42.4242
0.175335	42.4282
Sample #2	
T = 369.79 K	
0.248733	42.3746
0.236896	42.4110
0.234098	42.4133
0.231375	42.4198
0.228719	42.4233
0.226115	42.4251
0.222904	42.4277
Sample #2--continued	
T = 369.79 K	
0.214150	42.4294
0.203211	42.4293
0.192268	42.4304
0.183513	42.4303
0.181186	42.4325
0.179751	42.4345
0.178298	42.4362
0.176854	42.4399
0.175408	42.4446
Sample #2	
T = 369.81 K	
0.250000	42.3821
0.238095	42.4212
0.232558	42.4322
0.229885	42.4355
0.227273	42.4386
0.224719	42.4409
0.220751	42.4444
0.212920	42.4450
0.203143	42.4445
0.193397	42.4457
0.185548	42.4461
0.182713	42.4480
0.181266	42.4486
0.179812	42.4509
0.177644	42.4551
0.175479	42.4615
Sample #2	
T = 369.83 K	
0.250000	42.3961
0.238095	42.4352
0.232558	42.4465
0.227273	42.4532
0.224719	42.4554
0.222222	42.4569
0.218723	42.4590
0.211674	42.4601
0.202798	42.4610
0.193946	42.4614
0.186864	42.4622
0.182731	42.4639
0.181284	42.4653
0.179839	42.4683
0.178389	42.4715
0.176223	42.4768
Sample #2	
T = 369.84 K	
0.250000	42.4015
0.238095	42.4429
0.227273	42.4608
0.224719	42.4626
0.222222	42.4640
0.219780	42.4662
0.217391	42.4671
0.210504	42.4682
0.202047	42.4693
0.202014	42.4674
0.194168	42.4686
0.188689	42.4701
0.187259	42.4709
0.185810	42.4705
0.183474	42.4716
0.181836	42.4739
0.178563	42.4793
Sample #1	
T = 369.85 K	
0.250000	42.4043
0.238095	42.4452
0.227273	42.4642
0.217391	42.4698
0.208333	42.4708
0.200000	42.4715
0.200000	42.4710
0.192308	42.4712
0.185185	42.4747
0.178571	42.4804
Sample #2	
T = 369.85 K	
0.250000	42.4082
0.238095	42.4493
0.227273	42.4677
0.224719	42.4700
0.222222	42.4717
0.219780	42.4726
0.217391	42.4742
0.210526	42.4753
0.204082	42.4755
0.200000	42.4763
0.196078	42.4765
0.194175	42.4771
0.194175	42.4767
0.188679	42.4779
0.186916	42.4777
0.185185	42.4781
0.181818	42.4819
0.178571	42.4869
Sample #2	
T = 369.86 K	
0.250000	42.4136
0.241138	42.4466
0.227273	42.4735
0.217391	42.4803
0.212766	42.4826
Sample #2--continued	
T = 369.86 K	
0.208333	42.4817
0.204082	42.4831
0.200000	42.4828
0.196078	42.4837
0.192308	42.4837
0.188679	42.4842
0.185185	42.4863
0.181818	42.4893
0.178571	42.4949
Sample #2	
T = 369.87 K	
0.250000	42.4201
0.238095	42.4616
0.227273	42.4814
0.217391	42.4883
0.212766	42.4895
0.208333	42.4907
0.204082	42.4911
0.200000	42.4917
0.196078	42.4919
0.192308	42.4921
0.188679	42.4929
0.185185	42.4941
0.181818	42.4979
0.178571	42.5039
Sample #2	
T = 369.88 K	
0.206186	42.4973
0.200000	42.4990
Sample #2	
T = 369.89 K	
0.206186	42.5056
0.200000	42.5067

Table I (*Continued*)

V, $dm^3\ mol^{-1}$	P, bar
Sample #1	
T = 369.90 K	
0.250000	42.4350
0.238095	42.4787
0.219298	42.5033
0.217391	42.5058
0.212766	42.5077
0.208333	42.5072
0.204082	42.5060
0.200000	42.5099
0.196078	42.5085
0.192308	42.5103
0.188679	42.5144
0.185185	42.5127
0.178571	42.5237
0.172414	42.5494
Sample #2	
T = 369.90 K	
0.206186	42.5130
0.200000	42.5148
Sample #2	
T = 369.91 K	
0.206186	42.5214
0.200000	42.5228
Sample #2	
T = 369.92	
0.206186	42.5291
0.200000	42.5299
Sample #2	
T = 369.93 K	
0.206186	42.5364
0.200000	42.5361
Sample #2	
T = 369.95 K	
0.206186	42.5517
0.200000	42.5516
Sample #2	
T = 370.05 K	
0.206186	42.6275
0.200000	42.6303
Sample #1	
T = 370.15 K	
0.400000	39.5533
0.333333	41.3761
0.285714	42.2615
0.250000	42.5958
0.222222	42.6830
0.210526	42.6958
0.200000	42.7020
0.190476	42.7100
0.181818	42.7249
0.166667	42.8449
Sample #2	
T = 370.15 K	
0.206186	42.7033
0.200000	42.7079
Sample #2	
T = 370.25 K	
0.206186	42.7803
0.200000	42.7858
Sample #2	
T = 370.35 K	
0.206186	42.8555
0.200000	42.8628
Sample #2	
T = 370.45 K	
0.206186	42.9326
0.200000	42.9409
Sample #2	
T = 370.55 K	
0.206186	43.0074
0.200000	43.0177
Sample #2	
T = 370.65 K	
0.206186	43.0840
0.200000	43.0961

molecular weight of propane was calculated by using the 1969 atomic weights of C, 12.011, and H, 1.008, and on the assumption that the samples were 100% propane. The values of density given in Table I are based on these values of molecular weight for both samples. The vapor-pressure values given in Table II are, of course, independent of density but dependent on purity of sample. Although in general the normal procedure for filling the pycnometer was used for both samples, the pycnometer was unfortunately not outgassed by heating prior to the transfer of propane sample 2 into it. Thus, a small impurity of air was introduced and led to the slightly higher vapor pressures for sample 2, as shown in Table I.

The $P-V-T$ values given in Tables III and IV for sample 2 have been corrected for the additional air impurity by using the difference in measured pressures at the critical point of 0.0051 bar. The amount of impurity was estimated to be 0.004 07%, and the moles of sample 2 are increased by 0.0014%. The corrections were made by assuming an ideal mixture and using the equation of state for air given by Yen (*10*). Corrected values for sample 2 and original values for sample 1 are both plotted in Figure 1.

Experimental Results

***Vapor–Liquid Coexistence Region*.** Vapor and liquid densities on the coexistence envelopes and the critical pressure, temperature, and density were derived from the original unsmoothed data for sample 1 which are recorded in Table I and Figure 1.

In the single-phase region the pressure is referred to the vertical center of the sample, and in the two-phase region to the surface of the liquid. The way in which these reference points were used to calculate the fluid head corrections has been described (*2*). The maximum fluid head correction was 0.0003 bar in the vapor and 0.0004 bar in the liquid. Volumes or densities in Tables I and III are bulk values. Corrections for density gradients are not involved. In Table I, at 273.15, 288.15, 298.15, 303.15, and 323.15 K, some of the closely spaced points in the liquid region near the bubble point appear inverted, but the differences are due to a high dP/dV. The differences may be due to a volume error of no more than 0.002 mL, which is within the accuracy of the calibration of the volumetric mercury compressor.

***Vapor Pressure*.** Vapor-pressure measurements were made on sample 1 over the range 258.15 K and 2.9179 bar to the critical point at 369.85 K and 42.4709 bar. The vapor-pressure values from 258.15 to 358.15 K were previously available in periodic reports of work in progress at the Bartlesville Energy Technology Center and used in a correlation by Goodwin (*11*). The vapor pressures are listed in Table II and refer to sample 1. Vapor-pressure measurements were made with various fractions of the sample condensed from 0.010 to 0.999. The reported vapor pressure is usually the average of the pressure when 25%, 50%, and 75% of the sample is condensed. Some points at 5% and 95% were also considered. Duplicate vapor-pressure measurements on sample 2 were made at six temperatures to tie together the measurements on the two samples. The variation of the vapor pressure over the range of 5–95% of sample condensed is about 0.01% and 0.03% at lower temperatures and pressures for samples 1 and 2, respectively. At higher temperatures (333.15 K for sample 1, 348.15 K for sample 2) the variation is a few thousandths of a percent for sample 1 and less than 0.01% for sample 2. This small variation in pressure with percent of sample condensed is an indication of the high purity of the sample. The vapor pressures of the second sample are higher than those of the first by about 0.01% at all temperatures at which duplicate measurements were taken, except for 303.15 K, where the second sample has a somewhat lower vapor pressure.

The vapor-pressure values listed in Table II were fitted to the Goodwin equation (*11*):

$$\ln P(\text{bar}) = A + Bx + Cx^2 + Dx^3 + Ex(1 - x)^{\epsilon} \qquad (1)$$

where $x = (1 - T_b/T)/(1 - T_b/T_c)$ and ϵ is set equal to 1.47. T_b, the normal boiling temperature, was taken as 231.105 K as suggested by Das and Eubank (*12*). T_c, the critical temperature of 369.85 K, found in this work, was used. Values of the parameters were derived by using a weighted least-squares procedure (*13*) and are as follows: A = 0.023099, B =

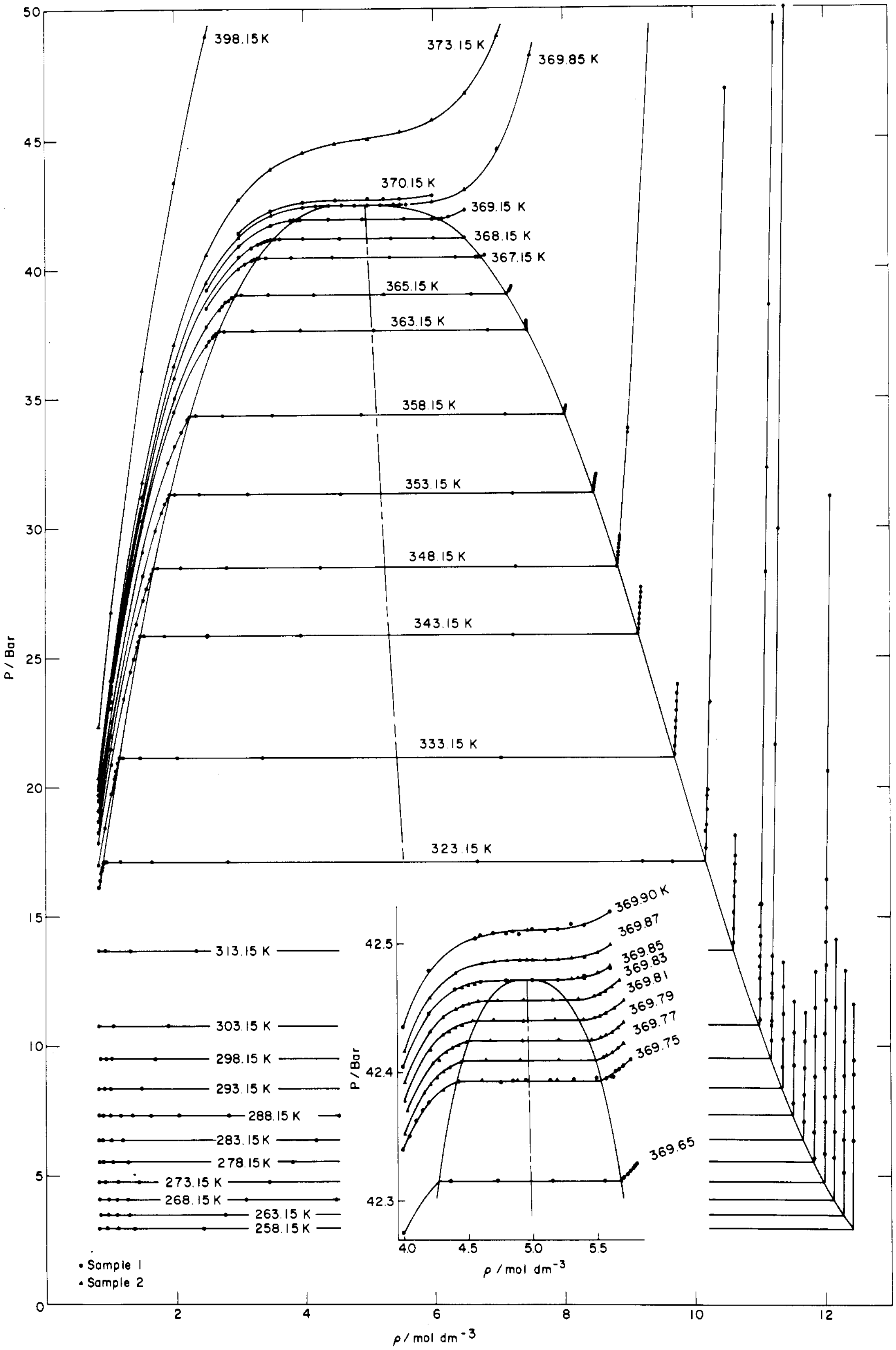

Figure 1. Vapor-liquid coexistence region of propane showing vapor pressure, coexistence envelope curve, critical point, and rectilinear diameter.

3.106110, $C = 0.899696$, $D = -0.280092$, and $E = 0.675616$. Table II lists the percent deviations from the experimental values of the values calculated by using eq 1.

In numerous investigations, the vapor pressure of propane has been reviewed (*11*, *12*, *14*). The most recently published investigation was done by Kratzke (*14*). Vapor pressures calculated by using eq 1 are higher than the experimental values obtained by Kratzke by an average of 0.06%, the disagreement increasing at higher temperatures. Kratzke's sample was reported to be 99.954% pure with no indication as to the impurity, and his pressure standard for the deadweight gauge was not documented.

Table II. Vapor Pressure of Propane Based on Sample 1

T/K	P/bar	$(\Delta P/P) \times 100^a$
258.15	2.9179	-0.033
263.15	3.4549	0.002
268.15	4.0623	0.009
273.15	4.7462	0.009
278.15	5.5125	0.007
283.15	6.3672	0.007
288.15	7.3159	0.003
293.15	8.3650	0.001
298.15	9.5202	-0.006
303.15	10.7891	-0.005
313.15	13.6918	-0.007
323.15	17.1300	0.000
333.15	21.1635	0.005
343.15	25.8618	0.004
348.15	28.4858	0.002
353.15	31.3087	-0.006
358.15	34.3518	-0.002
363.15	37.6327	0.001
365.15	39.0183	0.002
367.15	40.4500	0.001
368.15	41.1852	0.001
369.15	41.9345	-0.001
369.65	42.3160	-0.001
369.75	42.3931	0.000
369.85	42.4709	0.001

[a] $\Delta P/P = (P_{obs} - P_{calc})/P_{obs}$ where P_{calc} is the pressure calculated from equation 1.

Single-Phase Region. The procedures followed were similar to those previously described (*4*). Compressibility measurements were made on isotherms in the single-phase liquid and vapor regions up to the two-phase region. These were used to establish the coexistence envelope of sample 1. Such measurements were made up to the critical temperature of 369.85 K and slightly beyond to 370.15 K. Duplicate measurements on sample 2 were then made at the critical temperature and six subcritical temperatures so as to compare sample 1 and sample 2. For subcritical densities, the compressibilities were within an average of 0.005% of each other. The orthobaric liquid densities obtained at 303.15, 323.15, 343.15, and 363.15 K were an average of 0.0028 mol dm^{-3} higher for sample 2 than for sample 1. The orthobaric vapor densities for sample 2 at 323.15, 343.15, and 363.15 K were an average of 0.0004 mol dm^{-3} higher than those obtained for sample 1. After the duplicate measurements on sample 2 were complete, additional measurements were made just below the critical temperature and up to 373.15 K. At the critical temperature and at 373.15 K, measurements were taken starting at 0.8 and 1.0 mol dm^{-3} and increasing in density thereafter in steps of 0.5 mol dm^{-3} until a pressure of 100 bar was obtained. The 0.5-in. piston was then replaced by the 0.25-in. piston, and the same density incrementing procedure was followed at 369.85 and 373.15 K up to 400 bar. Measurements were also taken at the critical density, ρ = 4.955 mol dm^{-3}, at each isotherm above 369.85 K. Measurements in the high-pressure region up to 400 bar were then taken for 323.15 and 348.15 K. Isotherms from 398.15 to 623.15 K in steps of 25 K were then taken by using densities as described for the critical and 373.15 K isotherm with the difference that only the 0.25-in. piston was used. After each point at 400 bar was taken, a check measurement was taken at 0.8 mol dm^{-3} (last row in Table III) at the same temperature to ensure that the sample had not changed during the isotherm. The difference between the original and check measurements at 0.8 mol dm^{-3} was usually about 0.003%, except at 623.15 K, where the pressure appeared to be higher by 0.03% or 0.0121 bar. A final check made at 373.15 K and 0.8 mol dm^{-3} showed a pressure of 20.3521 bar which was only 0.01% above the original value. This change is well within the accuracy of the measurement and confirms that the sample had not decomposed.

The values of pressure given in Tables III and IV were adjusted for the air impurity by a minimum of 0.0016%, a maximum of 0.0171%, and an average of 0.0044%. The corrections decreased with increasing temperature and were highest at intermediate densities. In the temperature range from 323.15 to 370.15 K where duplicate points were taken, the corrected values for sample 2 differ from sample 1 values by an average of only 0.0035% and are plotted together in Figure 1.

Jepson, Richardson, and Rowlinson (*15*) studied the solubility of mercury in propane, but their data are too sparse to use for making corrections. However, Haar and Sengers (*16*) also studied the solubility of mercury in dense gases. They found the corrections to be important only at high temperature (400 °C) and actually to be very small in the region where the bulk of $P-V-T$ measurements using liquid mercury in the system exist.

Derived Results and Discussion

Coexistence Envelope and the Critical Point. Orthobaric liquid and vapor densities were determined from measurements of pressure, volume, and temperature made on sample 1 and listed in Table I. The method is the same as that used for ethane (*13*). Orthobaric liquid densities were obtained from 258.15 to 369.15 K, and orthobaric vapor densities were obtained from 323.15 to 369.15 K. The effect of precondensation of the vapor phase is most noticeable at 323.15 K. Orthobaric vapor densities were not obtained below 323.15 K because this required lower sample densities than could be obtained with the volume of the pycnometer and the number of moles of sample used. The values obtained for the first sample only are in Table V and Figure 1.

Equations 2 and 3 for the vapor and liquid arms of the

$$\rho_g/\rho_c = 1 + B_{1,g}|T - T_c|^{\beta} + B_{2,g}|T - T_c|^{\beta+\Delta} + B_{3,g}|T - T_c|^{\beta+2\Delta} \quad (2)$$

$$\rho_l/\rho_c = 1 + B_{1,l}|T - T_c|^{\beta} + B_{2,l}|T - T_c|^{\beta+\Delta} + B_{3,l}|T - T_c|^{\beta+2\Delta} \quad (3)$$

coexistence envelope, respectively, were used to represent the orthobaric densities. These equations are the same as those used by Douslin and Harrison (*4*). The value of β = 0.347 was derived from the slope of the straight line of log $(\rho_l - \rho_g)$ vs. log $|T - T_c|$. An iterative least-squares procedure was used to determine the remaining constants in the equations. The critical temperature was determined by an incremental least-squares adjustment. The critical density was determined iteratively from extrapolation of $(\rho_g + \rho_l)/2$ to T_c. The final least-squares fit gave a value of Δ = 0.71 and the coefficients listed as footnotes to Table V. The value of β = 0.347 is similar to the value of 0.350 found for ethane (*13*) and ethylene (*4*).

Table III. P-V-T Relations in the Supercritical Region for Sample 2[a]

T/K	369.85	373.15	398.15	423.15	448.15	473.15
ρ/mol dm^{-3}	P/bar					
0.8000	20.0795	20.3502	22.3694	24.3558	26.3144	28.2574
1.0000	23.8088	24.1616	26.7937	29.3715	31.9087	34.4194
1.5000	31.2108	31.7963	36.1326	40.3449	44.4707	48.5381
2.0000	36.2596	37.1124	43.3761	49.4228	55.3199	61.1218
2.5000	39.4460	40.5926	48.9559	56.9965	64.8442	72.5689
3.0000	41.2431	42.7041	53.2871	63.4633	73.4194	83.2293
3.5000	42.1003	43.8814	56.7427	69.1775	81.4072	93.5002
4.0000	42.4082	44.4922	59.6463	74.4742	89.1612	103.777
4.5000	42.4717	44.8193	62.2921	79.7018	97.0619	114.413
5.0000	42.4763	45.0450	64.9526	85.1946	105.556	125.962
5.5000	42.4819	45.3007	67.9654	91.3988	115.121	138.991
6.0000	42.5703	45.7557	71.7167	98.8374	126.427	154.247
6.5000	43.0530	46.7583	76.7903	108.239	140.326	172.689
7.0000	44.5802	48.9645	84.0207	120.605	157.914	195.556
7.5000	48.2295	53.4499	94.6332	137.347	180.603	224.410
8.0000	55.5597	61.8069	110.279	160.108	210.598	261.309
8.5000	68.6084	76.0935	133.332	191.300	249.625	308.836
9.0000	90.3646	99.1400	166.738	233.973	302.056	370.163
9.5000	124.373	135.040	212.987	291.857	370.443	
10.0000	174.372	186.266	278.103	369.870		
10.5000	246.086	260.348	366.591			
11.0000	345.621	362.073				
0.8000	20.0796	20.3500	22.3692	24.3549	26.3156	28.2586

T/K	498.15	523.15	548.15	573.15	598.15	623.15
ρ/mol dm^{-3}	P/bar					
0.8000	30.1828	32.0969	33.9985	35.8941	37.7837	39.6677
1.0000	36.9040	39.3728	41.8299	44.2661	46.6957	49.1171
1.5000	52.5580	56.5390	60.4974	64.4177	68.3197	72.2236
2.0000	66.8615	72.5397	78.1688	83.7658	89.3120	94.8551
2.5000	80.2008	87.7522	95.2491	102.691	110.082	117.454
3.0000	92.9477	102.573	112.135	121.626	131.037	140.477
3.5000	105.484	117.393	129.242	141.006	152.716	164.415
4.0000	118.253	132.692	147.065	161.359	175.609	189.822
4.5000	131.704	148.940	166.151	183.270	200.350	217.378
5.0000	146.372	166.771	187.133	207.454	227.688	247.935
5.5000	162.921	186.866	210.807	234.696	258.515	282.336
6.0000	182.163	210.154	238.143	266.089	293.990	321.824
6.5000	205.158	237.773	270.317	303.005	335.439	367.852
7.0000	233.324	271.109	308.958	346.903	384.603	
7.5000	268.221	312.089	355.909	399.849		
8.0000	312.067	362.836				
8.5000	367.526					
0.8000	30.1835	32.0969	34.0012	35.8949	37.7848	39.6798

Table IV. Pressure on the Critical Isometric Line, $\rho = 4.955$ mol dm^{-3}, for Sample 2[a]

T/K	P/bar	T/K	P/bar
369.85	42.4709	370.55	43.0100
369.86	42.4779	370.65	43.0868
369.87	42.4863	371.15	43.4719
369.88	42.4936	372.15	44.2444
369.89	42.5012	373.15	45.0198
369.90	42.5093	398.15	64.7005
369.91	42.5170	423.15	84.6921
369.92	42.5246	448.15	104.784
369.93	42.5321	473.15	124.866
369.95	42.5474	498.15	144.973
370.00	42.5854	523.15	165.074
370.05	42.6246	548.15	185.118
370.15	42.7012	573.15	205.138
370.25	42.7789	598.15	225.083
370.35	42.8560	623.15	245.018
370.45	42.9329		

[a] These values have been adjusted for 0.004 07% air impurity.

Table V. Orthobaric Liquid and Vapor Densities of Propane

T/K	ρ_ℓ(obs) mol dm^{-3}	$\{\rho_\ell$(obs)$-\rho_\ell$(calc)$\}$[a] mol dm^{-3}	ρ_g(obs) mol dm^{-3}	$[\rho_g$(obs)$-\rho_g$(calc)$]$[b] mol dm^{-3}	W_i
258.15	12.415	0.000			500
263.15	12.270	-0.004			500
268.15	12.126	-0.003			500
273.15	11.983	0.003			500
278.15	11.829	0.003			500
283.15	11.671	0.003			500
288.15	11.507	0.002			500
293.15	11.338	0.001			500
298.15	11.165	0.002			500
303.15	10.982	-0.000			500
313.15	10.586	-0.011			500
323.15	10.173	-0.000	0.8758	-0.0012	500
333.15	9.697	0.000	1.1219	0.0021	500
343.15	9.144	0.001	1.4482	0.0014	500
348.15	8.825	0.003	1.6565	0.0000	500
353.15	8.459	0.003	1.9107	-0.0016	500
358.15	8.020	0.000	2.2362	-0.0022	499
363.15	7.451	-0.001	2.6920	-0.0011	496
365.15	7.146	-0.005	2.9492	0.0028	484
367.15	6.756	0.001	3.2941	0.0038	457
368.15	6.486	0.003	3.5273	-0.0064	300
369.15	6.083	0.010	3.9204	0.0130	50

[a] $\rho_\ell(\mathrm{calc})/\mathrm{mol\ dm^{-3}} = 4.955 + 1.2584|T-T_c|^{0.347} + 8.517 \times 10^{-3}|T-T_c|^{1.057} - 5.979 \times 10^{-5}|T-T_c|^{1.767}$ where $T_c = 369.85$.

[b] $\rho_g(\mathrm{calc})/\mathrm{mol\ dm^{-3}} = 4.955 - 1.1892|T-T_c|^{0.347} + 4.468 \times 10^{-3}|T-T_c|^{1.057} + 1.973 \times 10^{-4}|T-T_c|^{1.767}$ where $T_c = 369.85$.

Table VI. Critical Constants for Propane

ref	T_c/K	P_c/bar	ρ_c/(mol dm^{-3})
19	369.96	42.567	5.13
21	369.82	42.496	
22	369.81	42.486	4.92
20	369.74	42.537	4.85
11[a]	369.80	42.4204	4.96
this work	369.85	42.4709	4.955

[a] Data from this work up to 353.15 K was included in their correlation.

Table VII. Second Virial Coefficient for Propane

	$-B_0$/(dm^3 mol^{-1})			
T_{68}/K	this work	ref *24*	ref *26*	ref *25*
323.15	0.328		0.329 62	
333.15	0.3080			
343.15	0.2878			
348.15	0.2790			0.293
353.15	0.2710			
358.15	0.2631			
363.15	0.2555			
365.15	0.2525			
367.15	0.2502			
368.15	0.2483			
369.15	0.2468			
369.85	0.2462			
373.15	0.2413	0.247	0.240 15	0.256
398.15	0.2089	0.211	0.207 21	0.224
423.15	0.1814	0.183		0.197
448.15	0.1584	0.160		
473.15	0.1385	0.139		0.155
498.15	0.1213	0.121		
523.15	0.1064	0.109		
548.15	0.0931	0.096		
573.15	0.0813			
598.15	0.0707			
623.15	0.0610			

The critical point which we have determined in this paper from the experimental coexistence envelope satisfies the definition of the critical point. It is the point at which the first and second derivatives of pressure with respect to volume are zero, namely, $(\partial P/\partial V)_{T_c} = 0$ and $(\partial^2 P/\partial V^2)_{T_c} = 0$. The 369.85 K isotherm, plotted in Figure 1, satisfies this condition. The critical pressure, 42.4709 bar, is taken from the experimental data at $T_c = 369.85$ K and $\rho_c = 4.955$ mol dm^{-3}. These values and previous ones are given in Table VI. Previous values for the critical constants were reviewed by Kobe and Lynn (*17*) and later by Kudchadker, Alani, and Zwolinski (*18*). Lack of agreement may arise from varied purities of the samples. Several investigators reported having a pressure difference between the dew and bubble points of 0.04 bar, which is about 30 times larger than the values found in this work. Beattie et al. (*19*) had a sample with only 0.004-bar difference between the dew and bubble points at 75 °C but the critical values still differ from the present values. The most recent values reported by Mousa, Kay, and Kreglewski (*20*) were determined from a sample having a dew to bubble point pressure difference of less than 0.1 bar. For comparison, several other experimental values of the critical properties determined by Kay and Rambosek (*21*) and Clegg and Rowlinson (*22*) are also listed in Table VI along with a correlated value of Goodwin (*11*).

Thermal Pressure Coefficient**.** A definitive study of the variations of the isochoric derivative, $\gamma_V = (\partial P/\partial T)_V$, in the vicinity of the critical point was not made because of slight inconsistencies of the measurements using the two different samples of propane. The slope of the vapor-pressure curve at $T_c = 369.85$ K was found to be 0.778 bar K^{-1} for sample 1, and the slope of the critical isometric line above 369.85 K was found to be 0.765 bar K^{-1} from the corrected sample 2 data.

Virial Coefficients**.** The virial equation of state is given in eq 4.

$$PV/RT = 1 + B_0/V + C_0/V^2 + D_0/V^3 + \ldots \qquad (4)$$

The temperature-dependent coefficients B_0, C_0, and D_0 are defined in the equations

$$B(V) = \{(PV/RT) - 1\}V \qquad B_0 = \lim_{1/V \to 0} \{B(V)\} \qquad (5)$$

$$C(V) = \{B(V) - B_0\}V \qquad C_0 = \lim_{1/V \to 0} \{C(V)\} \qquad (6)$$

$$D(V) = \{C(V) - C_0\}V \qquad D_0 = \lim_{1/V \to 0} \{D(V)\} \qquad (7)$$

and were evaluated by using the graphical procedure described in ref *4*. Second virial coefficients were derived from 323.15 to 623.15 K, third virial coefficients from 343.15 to 623.15 K, and fourth virial coefficients from 373.15 to 623.15 K.

Table VII lists the values for the second virial coefficients found in this work and those derived from the analysis (*23*) of

Table VIII. Third and Fourth Virial Coefficients for Propane

T/K	$10^2 C_0$/ (dm^6 mol^{-2})	$10^4 D_0$/ (dm^9 mol^{-3})
343.15	1.916	
348.15	1.909	
353.15	1.978	
358.15	1.991	
363.15	2.000	
365.15	1.982	
368.15	2.035	
369.85	2.035	
373.15	1.995	+1.10
398.15	1.825	−0.10
423.15	1.627	0
448.15	1.480	+0.10
473.15	1.345	0
498.15	1.243	−0.10
523.15	1.155	+0.20
548.15	1.083	+0.25
573.15	1.010	+0.90
598.15	0.941	+1.85
623.15	0.878	+2.58

the data of Beattie, Kay, and Kaminsky (*24*). The values based on the data of Beattie, Kay, and Kaminsky are more negative by 1.5% than those found in this work. The agreement is better if the two highest temperatures reported by Beattie et al. are omitted. A possible reason for the greater disagreement at higher temperatures is the decomposition of the sample used by Beattie et al., as noted in their paper. Deschner and Brown's (*25*) values for the second virial coefficient are in poor agreement with values of this work. Second virial coefficients based on the data of Cherney, Marchman, and York (*26*) and calculated by Pompe and Spurling (*27*) are 0.6% less negative than the values of this work. Third and fourth virial coefficients are listed in Table VIII. Graphs of the second and third virial coefficients would be relatively smooth and have the usual shape, including the hump in the third virial at lower temperatures.

Acknowledgment

The initial direction of this project by D. R. Douslin and his design of the new deadweight gauges are especially recognized. The assistance of S. E. Knipmeyer in servicing the equipment and machining the 0.25-in. deadweight gauge piston and cylinder and J. F. Messerly for the analysis and purification of the sample is deeply appreciated.

Glossary

A, B, C, D, E	constants in Goodwin vapor-pressure equation
$B_{1,g}$, $B_{2,g}$, $B_{3,g}$	constants in equation of saturated vapor densities
$B_{1,l}$, $B_{2,l}$, $B_{3,l}$	constants in equation of saturated liquid densities
B_0	second virial coefficient, dm^3 mol^{-1}
C_0	third virial coefficient, dm^6 mol^{-2}
D_0	fourth virial coefficient, dm^9 mol^{-3}
P	pressure, bar
R	gas constant, dm^3 bar K^{-1} mol^{-1}
T	temperature, K
V	molal volume, dm^3 mol^{-1}
x	$(1 - T_b/T)/(1 - T_b/T_c)$
Z	compressibility factor = PV/RT

Greek Letters

β, Δ	exponential constants in equations of saturated gas and liquid densities
γ	$(\partial P/\partial T)_V$
ϵ	exponential constant in Goodwin equation
ρ	molal density, mol dm^{-3}

Subscripts

b	denotes property at normal boiling point
c	denotes property at critical point
g	denotes property of gas phase
l	denotes property of liquid phase

Literature Cited

(1) Beattie, J. A. *Proc. Am. Acad. Arts Sci.* **1934**, *69*, 389.
(2) Douslin, D. R.; Moore, R. T.; Dawson, J. P.; Waddington, G. *J. Am. Chem. Soc.* **1958**, *80*, 2031.
(3) Douslin, D. R.; Harrison, R. H.; Moore, R. T. *J. Chem. Thermodyn.* **1969**, *1*, 305.
(4) Douslin, D. R.; Harrison, R. H. *J. Chem. Thermodyn.* **1976**, *8*, 301.
(5) Sengers, J. M. H. Levelt; Chen, W. T. *J. Chem. Phys.* **1972**, *56*, 595.
(6) Dadson, R. S. "The Accurate Measurement of High Pressures and the Precise Calibration of Pressure Balances"; The Institution of Mechanical Engineers and the International Union of Pure and Applied Chemistry, Joint Conference on Thermodynamics and Transport Properties of Fluids, July 10–12, 1957; The Institution of Mechanical Engineers: London, 1958.
(7) Stimson, H. F. *J. Res. Natl. Bur. Stand., Sect. A* **1961**, *65*, 139.
(8) Comité International des Poids et Mesures. *Metrologia* **1969**, *5*, 35.
(9) Douglas, T. B. *J. Res. Natl. Bur. Stand., Sect. A* **1969**, *73*, 451.
(10) Yen, Ming-Shih. Masters Thesis, University of Idaho, Moscow, ID, 1975. Private communication from Richard T. Jacobsen, Chairman of the Mechanical Engineering Department.
(11) Goodwin, R. D. "Provisional Thermodynamic Functions of Propane from 85 to 700 K at Pressures to 700 Bar"; NBS IR 77-860, July 1977; prepared for the American Gas Association, 1515 Wilson Boulevard, Arlington, VA 22209.
(12) Das, T. R.; Eubank, P. T. "Advances in Cryogenic Engineering"; Plenum Press: New York, 1973; Vol. 18, p 208.
(13) Douslin, D. R.; Harrison, R. H. *J. Chem. Thermodyn.* **1973**, *5*, 491.
(14) Kratzke, H. *J. Chem. Thermodyn.* **1980**, *12*, 305.
(15) Jepson, W. B.; Richardson, M. J.; Rowlinson, J. S. *Trans. Faraday Soc.* **1957**, *53*, 1586.
(16) Haar, L.; Sengers, J. M. H. Levelt. *J. Chem. Phys.* **1970**, *52*, 5069.
(17) Kobe, K. A.; Lynn, R. E., Jr. *Chem. Rev.* **1953**, *52*, 117.
(18) Kudchadker, A. P.; Alani, G. H.; Zwolinski, B. J. *Chem. Rev.* **1968**, *68*, 659.
(19) Beattie, J. A.; Poffenberger, N.; Hadlock, C. *J. Chem. Phys.* **1935**, *3*, 96.
(20) Mousa, A. H. N.; Kay, W. B.; Kreglewski, A. *J. Chem. Thermodyn.* **1972**, *4*, 301.
(21) Kay, W. B.; Rambosek, G. M. *Ind. Eng. Chem.* **1953**, *45*, 221.
(22) Clegg, H. P.; Rowlinson, J. S. *Trans. Faraday Soc.* **1955**, *51*, 1333.
(23) Hirshfelder, J. O.; McClure, F. T.; Weeks, I. F. *J. Chem. Phys.* **1942**, *10*, 201.
(24) Beattie, J. A.; Kay, W. C.; Kaminsky, J. *J. Am. Chem. Soc.* **1937**, *59*, 1589.
(25) Deschner, W. W.; Brown, G. G. *Ind. Eng. Chem.* **1940**, *32*, 836.
(26) Cherney, B. J.; Marchman, H.; York, R. *Ind. Eng. Chem.* **1949**, *41*, 2653.
(27) Pompe, A.; Spurling, T. H. "Virial Coefficients for Gaseous Hydrocarbons", Division of Applied Organic Chemistry Technical Paper No. 1; Commonwealth Scientific and Industrial Research Organization: Melbourne, Australia, 1974.

Received for review February 25, 1981. Accepted September 8, 1981.