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Compressibility of Isopentane with the Burnett Apparatus

I. HAROLD SILBERBERG,[1] JOHN J. McKETTA, and KENNETH A. KOBE[2]
University of Texas, Austin 12, Tex.

For the range in which modern compressibility data on isopentane at temperatures of interest are lacking, the Burnett method (*5*) is ideally suited. For complete and accurate establishment of the isotherms, the relatively low vapor pressures require an apparatus capable of accurate measurements at low as well as high pressures.

The Burnett apparatus constant, N, was determined by helium calibration to be 1.41507, and compressibility factor isotherms of gaseous isopentane, from 50° to 200° C. and at pressures up to 65 atm., were determined as described in the preceding article (*17*). Vapor pressures, saturated vapor densities, and second virial coefficients were also determined.

EXPERIMENTAL

Isopentane Purity. The research grade isopentane was obtained from the Phillips Petroleum Co. The purity of this isopentane, based on a determination of the melting point, was stated to be 100%. Dissolved air was removed from the hydrocarbon by two condensations under vacuum conditions at dry ice temperatures. The high purity of the isopentane was confirmed by a traverse of the two-phase region at 175° C. The vapor pressure from 90% vapor to 10% vapor (by volume) did not vary by more than 0.01 atm.

RESULTS

Vapor Pressures. Vapor pressures of isopentane were measured from 50° to 175° C. at 25° C. intervals, at least two measurements at each temperature. Separate charges of isopentane were used for each measurement. The observed vapor pressures were correlated and smoothed graphically by a residual technique and compared (Table I) with those values reported by Isaac, Li, and Canjar (*6*) and with values similarly smoothed from Young's data (*20*). The total maximum uncertainty in these vapor pressures including that portion corresponding to the temperature uncertainty, is estimated not to exceed 0.25%.

[1] Present address, Field Research Laboratory, Magnolia Petroleum Co., Dallas 21, Tex.
[2] Deceased.

Table I. Comparison of Vapor Pressure Data

Temp., °C.	Vapor Pressure, Atm. Isaac, others (*6*)	Young (*20*)	This Work
50	. . .	2.022	2.025
75	. . .	3.954	3.983
100	. . .	7.031	7.106
125	11.881	11.621	11.787
150	18.474	18.171	18.449
175	27.590	27.171	27.556

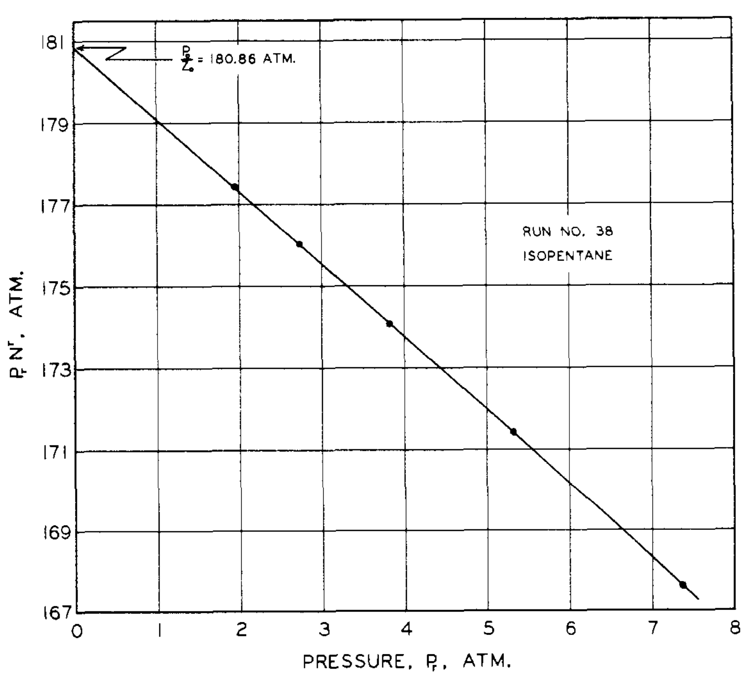

Figure 1. Graphical method to obtain p_0/z_0

Table II. Isopentane Experimental Compressibility Data

Temp., °C.	Run No.	r	p_r, Atm.	z_r	α_r, L./G. Mole
50	19	0	1.4710	0.9462	0.9698
		1	1.0557	0.9610	0.9796
50	20	0	1.9920	0.9275	1.0002
		1	1.3886	0.9482	0.9892
		2	0.9966	0.9630	0.9845
50	21	0	1.4569	0.9456	0.9901
		1	1.0465	0.9612	0.9831
75	22	0	3.9026	0.8842	0.8477
		1	2.8681	0.9195	0.8018
		2	2.0799	0.9436	0.7747
		3	1.4956	0.9601	0.7622
		4	1.0694	0.9715	0.7613
75	23	0	3.5131	0.8979	0.8302
		1	2.5638	0.9272	0.8112
		2	1.8527	0.9482	0.7988
		3	1.3296	0.9629	0.7971
75	24	0	3.1905	0.9090	0.8148
		1	2.3200	0.9353	0.7967
		2	1.6720	0.9539	0.7877
		3	1.1979	0.9671	0.7846
100	25	0	6.7037	0.8373	0.7431
		1	5.0032	0.8843	0.7081
		2	3.6705	0.9180	0.6840
		3	2.6609	0.9418	0.6697
		4	1.9142	0.9587	0.6606
		5	1.3693	0.9704	0.6619
		6	0.9761	0.9789	0.6619
100	26	0	5.8619	0.8614	0.7240
		1	4.3363	0.9017	0.6941
		2	3.1610	0.9301	0.6771
		3	2.2816	0.9500	0.6710
		4	1.6372	0.9647	0.6602
		5	1.1686	0.9744	0.6707
100	27	0	6.9790	0.8292	0.7493
		1	5.2320	0.8796	0.7046
		2	3.8440	0.9145	0.6810
		3	2.7904	0.9394	0.6650
		4	2.0095	0.9573	0.6507
		5	1.4378	0.9690	0.6602
		6	1.0256	0.9784	0.6449
125	28	0	11.5851	0.7557	0.6889
		1	8.9393	0.8251	0.6377
		2	6.6990	0.8750	0.6096
		3	4.9273	0.9107	0.5921
		4	3.5786	0.9360	0.5843
		5	2.5782	0.9542	0.5804
		6	1.8470	0.9673	0.5782
		7	1.3177	0.9766	0.5802
125	29	0	10.7907	0.7791	0.6688
		1	8.2412	0.8420	0.6264
		2	6.1383	0.8875	0.5988
		3	4.4948	0.9196	0.5844
		4	3.2556	0.9426	0.5760
		5	2.3414	0.9593	0.5679
		6	1.6752	0.9712	0.5617
		7	1.1936	0.9792	0.5693
125	30	0	10.0148	0.7992	0.6550
		1	7.5812	0.8561	0.6201
		2	5.6167	0.8975	0.5962
		3	4.0980	0.9266	0.5852
		4	2.9616	0.9476	0.5780
		5	2.1259	0.9626	0.5748
		6	1.5186	0.9730	0.5809
		7	1.0825	0.9814	0.5614
150	31	0	18.0699	0.6618	0.6499
		1	14.5502	0.7541	0.5868
		2	11.2212	0.8229	0.5480
		3	8.4143	0.8732	0.5233
		4	6.1944	0.9096	0.5067
		5	4.5045	0.9360	0.4933
		6	3.2442	0.9540	0.4923
		7	2.3237	0.9669	0.4946
		8	1.6585	0.9766	0.4899
150	32	0	16.6955	0.7014	0.6210
		1	13.1777	0.7834	0.5707
		2	10.0344	0.8442	0.5391
		3	7.4635	0.8885	0.5187
		4	5.4647	0.9206	0.5045
		5	3.9577	0.9434	0.4966
		6	2.8438	0.9593	0.4969
		7	2.0346	0.9712	0.4915
		8	1.4501	0.9795	0.4909
		9	1.0307	0.9852	0.4986
150	33	0	15.6042	0.7287	0.6037
		1	12.1613	0.8036	0.5607
		2	9.1842	0.8588	0.5345
		3	6.7941	0.8990	0.5162
		4	4.9541	0.9276	0.5074
		5	3.5775	0.9479	0.5057
		6	2.5676	0.9627	0.5044
		7	1.8348	0.9735	0.5015
		8	1.3062	0.9807	0.5130
175	34	0	27.2275	0.5160	0.6537
		1	23.6530	0.6344	0.5684
		2	19.2270	0.7297	0.5170
		3	14.9542	0.8031	0.4842
		4	11.2883	0.8579	0.4629
		5	8.3498	0.8979	0.4497
		6	6.0915	0.9270	0.4407
		7	4.4009	0.9477	0.4370
		8	3.1584	0.9624	0.4378
		9	2.2569	0.9732	0.4367
175	35	0	25.9482	0.5675	0.6129
		1	21.8641	0.6767	0.5438
		2	17.4135	0.7626	0.5013
		3	13.3594	0.8279	0.4737
		4	9.9905	0.8761	0.4561
		5	7.3413	0.9110	0.4485
		6	5.3317	0.9363	0.4393
		7	3.8415	0.9546	0.4365
		8	2.7512	0.9674	0.4357
		9	1.9631	0.9768	0.4346
		10	1.3970	0.9836	0.4317
		11	0.9914	0.9878	0.4525
175	36	0	27.4202	0.5059	0.6626
		1	23.9751	0.6260	0.5736
		2	19.5718	0.7231	0.5203
		3	15.2642	0.7980	0.4866
		4	11.5441	0.8541	0.4648
		5	8.5514	0.8952	0.4507
		6	6.2426	0.9248	0.4430
		7	4.5137	0.9462	0.4383
		8	3.2410	0.9614	0.4380
		9	2.3168	0.9725	0.4365
		10	1.6502	0.9803	0.4390
188.5	41	0	38.3129	0.2089	0.7822
		1	33.9477	0.2619	0.8236
		2	33.6009	0.3669	0.7138
		3	31.7303	0.4903	0.6085
		4	27.7948	0.6077	0.5347
		5	22.8396	0.7066	0.4866
		6	17.9163	0.7844	0.4558
		7	13.6144	0.8435	0.4354
		8	10.1210	0.8873	0.4218
		9	7.4096	0.9192	0.4131
		10	5.3654	0.9419	0.4101
		11	3.8570	0.9582	0.4105
		12	2.7600	0.9702	0.4090
		13	1.9676	0.9788	0.4081
188.5	42	0	36.2542	0.2073	0.8283
		1	33.9211	0.2744	0.8103
		2	33.4860	0.3834	0.6973
		3	31.3051	0.5072	0.5963
		4	27.1514	0.6224	0.5268
		5	22.1453	0.7184	0.4817
		6	17.2880	0.7936	0.4523
		7	13.0913	0.8504	0.4329
		8	9.7062	0.8922[a]	.....
188.5	43	0	34.5354	0.2156	0.8604
		1	33.8613	0.2991	0.7841
		2	33.1429	0.4142	0.6696
		3	30.4021	0.5377	0.5760
		4	25.9214	0.6487	0.5137
		5	20.8839	0.7396[b]	.....

[a]From smoothed curve through data of Runs 41.

[b]From smoothed curve through data of Runs 41 and 42.

[c]From smoothed curve through data of Runs 41, 42, and 43.

[d]Read from smoothed curve through data of Runs 37 and 38.

Table II. (Continued)

Temp., °C.	Run No.	r	p_r, Atm.	z_r	α_r, L./G. Mole
188.5	44	0	34.0915	0.2313	0.8542
		1	33.8175	0.3247	0.7565
		2	32.6845	0.4440	0.6444
		3	29.4211	0.5656[c]	.....
200	37	0	60.5676	0.2982	0.4499
		1	41.0822	0.2863	0.6744
		2	38.5548	0.3802	0.6241
		3	35.4938	0.4952	0.5522
		4	30.8015	0.6082	0.4939
		5	25.2360	0.7051	0.4537
		6	19.7978	0.7827	0.4261
		7	15.0493	0.8420	0.4076
		8	11.1952	0.8863	0.3943
		9	8.1971	0.9183	0.3870
		10	5.9394	0.9416	0.3817
		11	4.2724	0.9584	0.3780
		12	3.0572	0.9705	0.3746
		13	2.1788	0.9787	0.3795
		14	1.5495	0.9850	0.3758
200	38	0	47.7420	0.2640	0.5985
		1	40.0533	0.3134	0.6655
		2	37.7035	0.4174	0.5999
		3	34.0849	0.5340	0.5308
		4	28.9831	0.6426	0.4788
		5	23.3774	0.7334	0.4428
		6	18.1191	0.8044	0.4191
		7	13.6635	0.8584	0.4024
		8	10.1039	0.8982	0.3912
		9	7.3681	0.9269	0.3852
		10	5.3244	0.9478	0.3806
		11	3.8206	0.9624	0.3821
		12	2.7304	0.9732	0.3811
		13	1.9449	0.9810	0.3793
200	39	0	52.5919	0.2744	0.5356
		1	40.5076	0.2991	0.6717
		2	38.1470	0.3985	0.6122
		3	34.8027	0.5145	0.5416
		4	29.9010	0.6255	0.4862
		5	24.3044	0.7195[d]	.....
200	40	0	44.2136	0.2634	0.6468
		1	39.5416	0.3333	0.6546
		2	37.0562	0.4420	0.5846
		3	33.0871	0.5585	0.5181
		4	27.7843	0.6636	0.4701
		5	22.1913	0.7500	0.4374
		6	17.0863	0.8172[d]	

Compressibility. The compressibility factor z is defined by the equation, $z = pV/RT$ (Equation 1, *17*). Compressibility factor isotherms of isopentane were determined from 50° to 200° C. at 25° C. intervals. Also, a critical region isotherm was determined at 188.5° C., slightly above the accepted value for the critical temperature, t_c = 187.8° C. (*7, 12, 20*). The experimental data are presented in Table II.

The data of the complete runs were treated graphically (*17*). A large-scale plot of the values of $p_r N^r$ was used to determine the value of p_0/z_0 for each run. On these plots, of which Figure 1 is typical, readings of the ordinates as precise as 0.01% were easily made, and abscissa scales commensurate with this precision on the ordinate were used. The compressibility factor z_r was then calculated as follows:

$$z_r = \frac{p_r N^r}{p_0/z_0} \quad (2)$$

The data of the incomplete runs at 188.5° and 200° C. were treated with Equation 9 of the preceding article (*17*). The values of z_k for the incomplete runs were read from large-scale plots with a precision of 0.0001.

The experimental compressibility factor isotherms are shown in Figure 2. At the lower pressures, these isotherms are consistent with respect to temperature to within 0.03%. Smoothed molal volumes and compressibility factors for each experimental temperature are presented in Table III. The molal volumes V were calculated from the graphically smoothed values of z (Equation 1, *17*). The values for the saturated vapor in Table III were obtained by extrapolating the smoothed compressibility factor isotherms to the vapor pressures from this work shown in Table I.

The values in Table III for the unsaturated vapor are considered to have the following maximum errors: pressure, 0.04%; absolute temperature, 0.02%; compressibility factor

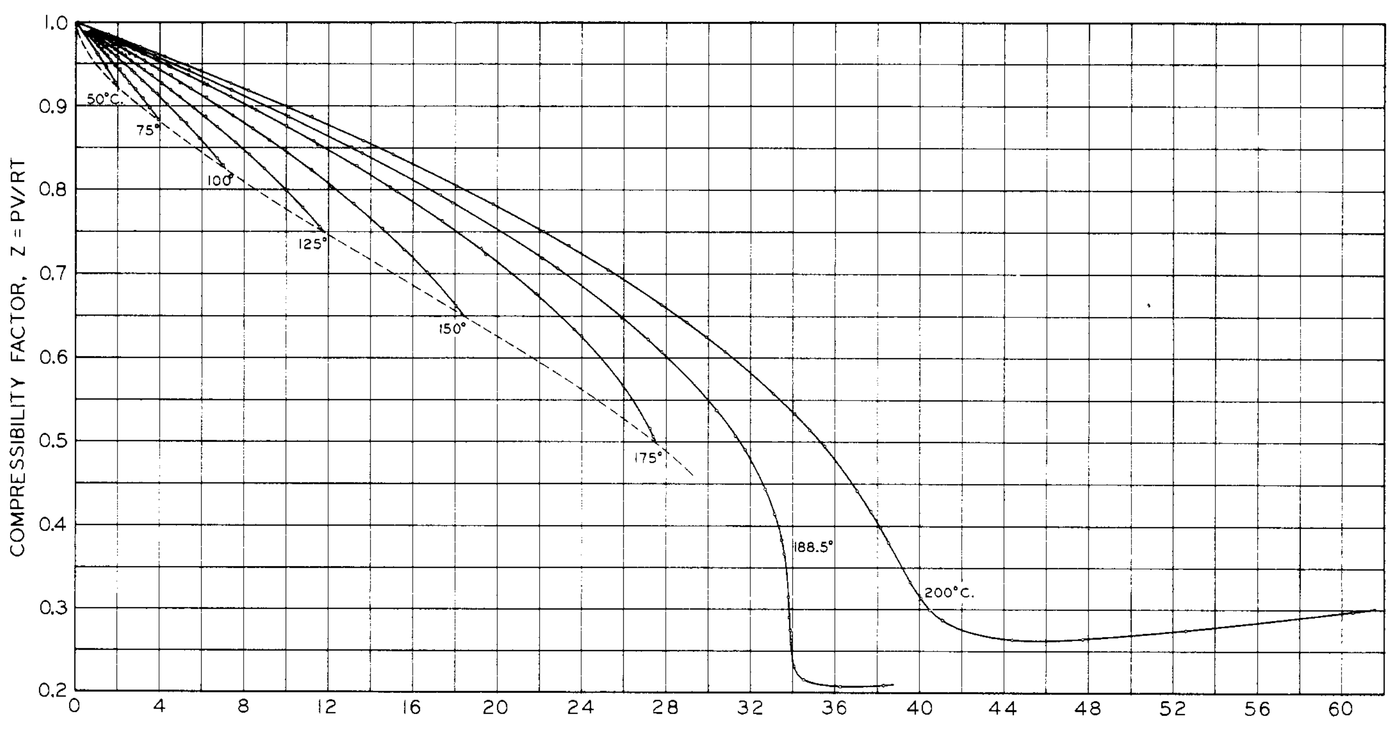

Figure 2. Experimental compressibility factor isotherms of Isopentane

Table III. Isopentane Smoothed Compressibility Isotherms

Temp., °C.	Pressure, Atm.	Volume, L./G. Mole	$z = \frac{pV}{RT}$
50	1	25.533	0.9629
	2	12.233	0.9227
	2.025[a]	12.067[b]	0.9216[b]
75	1	27.794	0.9729
	2	13.496	0.9448
	3	8.713	0.9150
	3.983[a]	6.324[b]	0.8816[b]
100	1	29.955	0.9783
	3	9.532	0.9339
	5	5.418	0.8847
	7	3.624	0.8285
	7.106[a]	3.556[b]	0.8252[b]
125	1	32.099	0.9825
	4	7.584	0.9286
	7	4.054	0.8687
	10	2.613	0.7997
	11	2.296	0.7730
	11.787[a]	2.077[b]	0.7494[b]
150	1	34.226	0.9857
	5	6.440	0.9273
	10	2.933	0.8448
	15	1.721	0.7436
	18	1.281	0.6641
	18.449[a]	1.222[b]	0.6495[b]
175	1	36.340	0.9882
	5	6.916	0.9403
	10	3.220	0.8757
	15	1.966	0.8020
	20	1.315	0.7150
	25	0.8789	0.5975
	27	0.7168	0.5263
	27.556[a]	0.6646[b]	0.4980[b]
188.5	1	37.472	0.9892
	5	7.166	0.9458
	10	3.366	0.8886
	15	2.083	0.8250
	20	1.427	0.7536
	25	1.011	0.6673
	30	0.6945	0.5500
	32	0.5668	0.4788
	33	0.4868	0.4241
	33.5	0.4325	0.3825
	33.6	0.4208	0.3732
	33.7	0.3934	0.3500
	33.8	0.3665	0.3270
	33.9	0.3157	0.2825
	34.0	0.2713	0.2435
	34.1	0.2566	0.2310
	34.2	0.2489	0.2247
	34.3	0.2439	0.2208
	34.4	0.2401	0.2180
	34.5	0.2374	0.2162
	35	0.2291	0.2117
	36	0.2187	0.2078
	37	0.2119	0.2070
	38	0.2075	0.2082
200	1	38.444	0.9902
	5	7.384	0.9509
	10	3.492	0.8993
	15	2.181	0.8426
	20	1.514	0.7799
	25	1.101	0.7090
	30	0.8072	0.6237
	35	0.5647	0.5091
	38	0.4133	0.4045
	39	0.3581	0.3597
	40	0.3061	0.3154
	41	0.2726	0.2879
	42	0.2532	0.2739
	45	0.2266	0.2626
	50	0.2084	0.2684
	55	0.1984	0.2810
	60	0.1917	0.2963

[a]Saturation pressure.
[b]Saturated vapor.

and molal volume, 0.20% each. The uncertainty in the latter two is somewhat larger because of the uncertainty in the vapor pressures.

Other Investigations. The physical properties of isopentane have been investigated for over 90 years. Its normal boiling point was measured as early as 1864 (*19*), and its critical constants were first reported in 1883 (*11*). Comprehensive studies of the volumetric behavior of isopentane have been reported by Young (*19*, *20*), Young and Thomas (*21*), Bridgman (*4*), and Isaac, Li, and Canjar (*6*). A study of the 200° C. isotherm by Kobe and Vohra appears in the following article (*8*). The work by Bridgman, at 0°, 50°, and 95° C. and pressures of 500 to 9000 kg. per sq. cm., was exclusively a study of the liquid phase, so no comparison with the present work is possible.

Young investigated isopentane at temperatures from −30° to 280° C. and at pressures from near atmospheric to 72.5 atm. (*19*). Critical constants were determined as well as vapor pressures from −30° C. to the critical temperature and orthobaric volumes from 10° C. to the critical temperature. Measurements on the gas phase were reported from 30° to 280° C. at intervals of 10° C. except in the critical region where the isotherms were spaced much more closely.

Young's data were smoothed as residual volumes and are compared in Table IV as molal volumes at selected pressures

Table IV. Comparison with Molal Volumes of Young

Temp., °C.	Pressure, Atm.	Molal Volume, Liters/G. Mole: Young (*19*)	Molal Volume, Liters/G. Mole: This Work	Dev., %
50	1	25.532	25.533	0.00
	2	12.224	12.233	-0.07
75	1	27.716	27.794	-0.28
	2	13.430	13.496	-0.49
	3	8.660	8.713	-0.61
100	1	29.885	29.955	-0.23
	3	9.480	9.532	-0.54
	5	5.382	5.418	-0.66
	7	3.590	3.624	-0.94
125	1	32.030	32.099	-0.21
	4	7.540	7.584	-0.58
	7	4.019	4.054	-0.86
	10	2.577	2.613	-1.38
	11	2.262	2.296	-1.48
150	1	34.158	34.226	-0.20
	5	6.395	6.440	-0.70
	10	2.896	2.933	-1.26
	15	1.692	1.721	-1.68
	18	1.254	1.281	-2.11
175	1	36.258	36.340	-0.23
	5	6.864	6.916	-0.75
	10	3.185	3.220	-1.09
	15	1.938	1.966	-1.42
	20	1.292	1.315	-1.75
	25	0.8564	0.8789	-2.56
	27	0.6880	0.7168	-4.02
200	1	38.354	38.444	-0.23
	5	7.324	7.384	-0.81
	10	3.444	3.492	-1.37
	20	1.488	1.514	-1.72
	30	0.7847	0.8072	-2.79
	35	0.5382	0.5647	-4.69
	40	0.2767	0.3061	-9.60
	45	0.2209	0.2266	-2.52
	50	0.2052	0.2084	-1.54
	60	0.1900	0.1917	-0.89

Table V. Comparison of Compressibility Factors at 1 Atm.

Temp., °C.	$z = pV/RT$: Young, Thomas (*21*)	$z = pV/RT$: This Work	Deviation, %
50	0.9628	0.9629	− 0.01
100	0.9756	0.9783	− 0.28
150	0.9870	0.9857	+ 0.13

with the results of the present work. The deviation between the two sets of volumes is consistent in its direction and increases very rapidly with pressure both at 175° and 200° C. This behavior suggests a systematic deviation in the pressure scales of the two investigations, a possibility which is also supported by the deviation in vapor pressures shown in Table I. In addition, Young's vapor pressures of normal pentane (*20*) are consistently lower than the values reported by Beattie, Levine, and Douslin (*2*), Li and Canjar (*10*), and Sage and Lacey (*13, 14, 15*). In fact, it appears to be generally true that the vapor pressures determined by Young in his numerous studies are consistently lower than those reported in more modern investigations.

In contrast, the saturated vapor volumes reported by Young (*19, 20*) at 50°, 100°, and 150° C. are higher by 0.35%, 0.43%, and 1.22%, respectively, than the values found in the present work. As the saturated vapor state is a univariant one, Young's saturated vapor volumes would be independent of any error in pressure measurement. Consequently, the possibility is suggested that Young's volume measurements may also have contained considerable error.

The low-pressure investigation of Young and Thomas (*21*) extended from 10.75° to 150° C. and from 60 to 825 mm. of mercury. The data reported at 50°, 100°, 150° C. were graphically smoothed as compressibility factor isotherms to compare them with the results of the present work (Table V).

Isaac, Li, and Canjar studied the compressibility of isopentane from 100° to 300° C. and from 100 to 200 atm. (*6*). The only gas-phase measurements made below the critical temperature were made in the vicinity of saturation. The comparison between the data at 175° and 200° C. and those of the present work is shown in Table VI. A detailed comparison made of the data of Isaac, Li, and Canjar (*6*) and of Young (*19*) revealed that above 100° C. the molal volumes of Isaac, Li, and Canjar are lower than those reported by Young except from about 36 to 43 atm. at 200° C. Young's molal volumes are, in turn, consistently lower than those of the present work.

Using a sample of the same isopentane as in the present work, Kobe and Vohra (*8*) determined the 200° C. compressibility factor isotherm in a conventional variable-volume type apparatus. Pressures ranged up to approximately 65 atm. At no pressure did the discrepancy between the compressibility factors so obtained and those of the present work exceed 0.20% and at most pressures agreement was to within 0.10%.

Second Virial Coefficients. Three types of expansions are commonly employed for the representation of volumetric behavior of a gas.

$$z = 1 + Bp + Cp^2 + \ldots \quad (4)$$

$$z = 1 + \frac{B'}{V} + \frac{C'}{V^2} + \ldots \quad (5)$$

$$pV = RT + B''p + C''p^2 + \ldots \quad (6)$$

Table VI. Comparison with Molal Volumes of Isaac and Others

Temp., °C.	Pressure, atm.	Volume, Liters/G. Mole: Isaac, others (*6*)	Volume, Liters/G. Mole: This Work	Deviation, %
175	26.600	0.7091	0.7511	-5.59
	26.807	0.6935	0.7335	-5.45
	26.988	0.6779	0.7181	-5.60
	27.201	0.6622	0.6991	-5.28
	27.382	0.6466	0.6824	-5.25
200	31.004	0.7096	0.7566	-6.21
	33.070	0.6156	0.6566	-6.24
	34.894	0.5372	0.5700	-5.75
	36.643	0.4587	0.4847	-5.36
	38.255	0.3797	0.3995	-4.96
	39.757	0.3016	0.3170	-4.86
	40.919	0.2623	0.2748	-4.55
	44.096	0.2231	0.2324	-4.00

Table VII. Second Virial Coefficients of Isopentane

Temp., °C.	$-B$, Liters/G. Mole: Experimental	$-B$, Liters/G. Mole: Smoothed
0	...	1.367
25	...	1.150
50	0.960	0.946
75	0.763	0.772
100	0.645	0.648
125	0.570	0.567
150	0.494	0.496
175	0.434	0.435
188.5	0.407	0.403
200	0.376	0.377

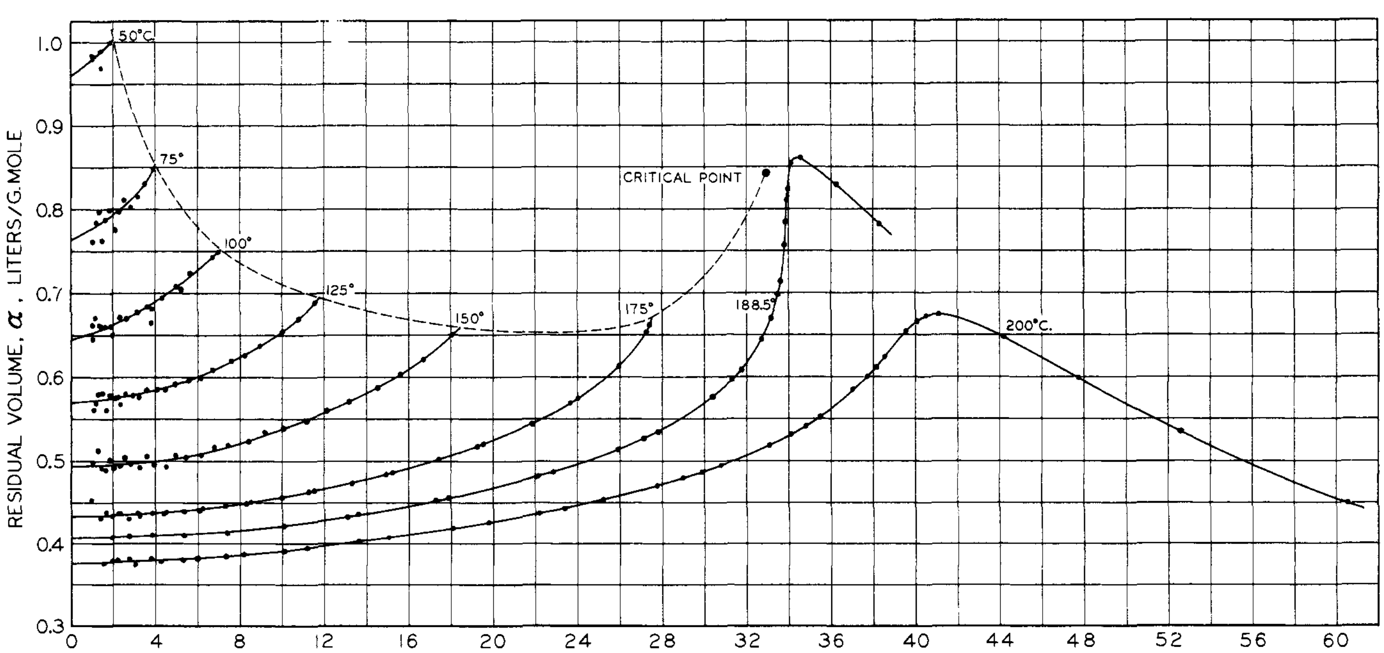

Figure 3. Reduced volume isotherms of isopentane

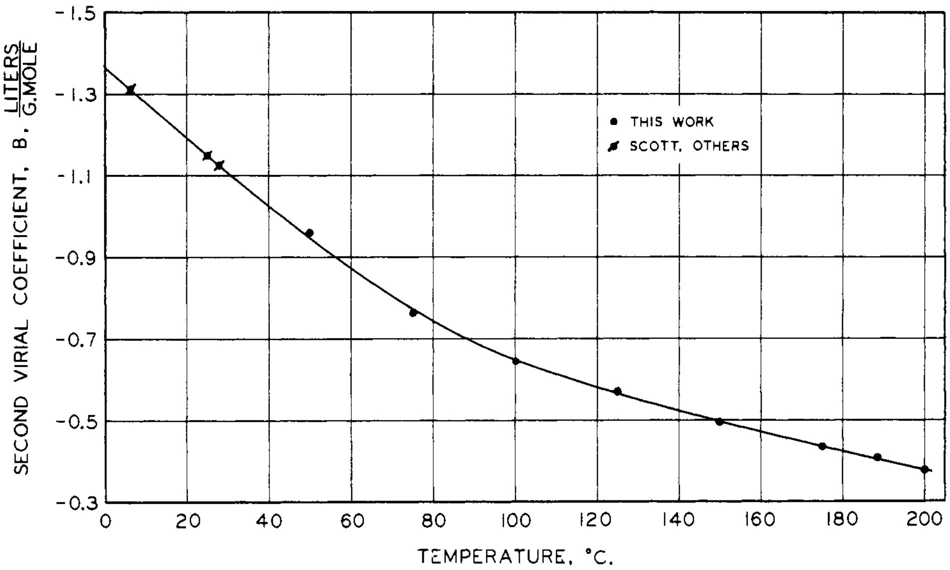

Figure 4. Experimental second virial coefficients of isopentane

For the case in which all three series are infinite,

$$B' = B'' = BRT \tag{7}$$

Because the second virial coefficient is a property of the gas and not of the particular equation selected to describe the behavior of that gas, symbol B is assigned to the second virial coefficient. In such a case, the units of the coefficient indicate with which equation it may be employed.

The residual volume α is defined by the following relation:

$$\alpha = \frac{RT}{p} - V = \frac{RT}{p}(1 - z) \tag{8}$$

Residual volumes of isopentane were calculated from each experimental compressibility measurement (Figure 3). Equations 4, 5, and 6 show that

$$\underset{p \to 0}{\text{Limit}}\ \alpha = -BRT = -B' = -B'' \tag{9}$$

The second virial coefficients of isopentane were therefore determined from the zero-pressure intercepts of the isotherms of Figure 3.

The experimental second virial coefficients are presented in Table VII and are correlated graphically in Figure 4 with the values reported by Scott and others (*16*). Also included in Table VII are the smoothed values read from the curve of Figure 4. It is believed that the errors in these smoothed values do not exceed 0.030 liters per gram mole at 50° C. decreasing to 0.015 liters per gram mole at 200° C.

The experimental second virial coefficients of isopentane were also correlated on a reduced basis with the coefficients of normal pentane and neopentane reported by Beattie and coworkers (*1*, *3*). The critical constants employed were those selected by Rossini and others (*12*). The correlation is shown in Figure 5.

According to the Berthelot equation of state, the second virial coefficient may be expressed as

$$B = \frac{9}{128}\,\frac{RT_c}{p_c}\left(1 - \frac{6}{T_R^2}\right) \tag{10}$$

Lambert and others (*9*) compared experimental second virial coefficients of many organic vapors, including hydrocarbons, with values calculated from Equation 10 and found that, for the nonpolar compounds, the equation represented the data within their experimental accuracy. For the purposes of correlation as B/V_c, Equation 10 may be written as

$$\frac{B}{V_c} = \frac{9}{128}\,\frac{1}{z_c}\left(1 - \frac{6}{T_R^2}\right) \tag{11}$$

Table VIII. Comparison of Experimental and Calculated Reduced Second Virial Coefficients

T_R	$-B/V_c$ Smoothed Experimental	Berthelot Equation
0.6	4.37	4.10
0.7	3.08	2.94
0.8	2.16	2.19
0.9	1.68	1.68
1.0	1.31	1.30
1.1	1.02	1.04
1.2	0.82	0.83
1.3	0.65	0.66

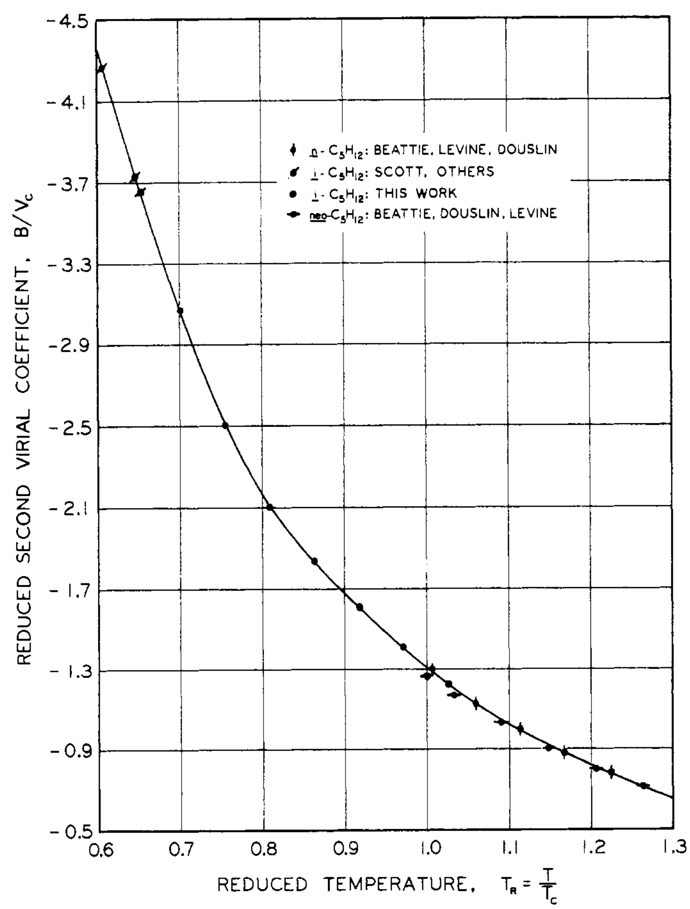

Figure 5. Experimental second virial coefficients vs. reduced temperature

Using a value of z_c of 0.269 (*12*), reduced second virial coefficients were calculated from Equation 11 and compared with values read from the curve of Figure 5. The comparison is made in Table VIII. Above T_R = 0.7, the agreement is within the experimental accuracy of the virial coefficients.

NOMENCLATURE

B = Second virial coefficient
N = Apparatus constant
p = Absolute pressure
R = Gas constant, 0.0820544 (liter) (atm.) / (g. mole) (°K.)
T = Absolute temperature ($T_{0°C.}$ = 273.16°K.)
T_R = Reduced temperature, T/T_c
V = Molal volume
z = Compressibility factor, pV/RT
α = Residual volume, $\frac{RT}{p} - V$

Subscripts:

r,k = Number of the expansion
c = Critical state
0 = Initial state of a run

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Volumetric Behavior and Critical Constants of Isopentane

SURINDER PAL VOHRA and KENNETH A. KOBE[1]
University of Texas, Austin, Tex.

Serious disagreement in the volumetric properties of isopentane arose between the results of Isaac, Li, and Canjar (*4*) and those of Silberberg, McKetta, and Kobe (*7*). Deviations in the regions covered by both investigators ranged from 4.0 to 6.2%. Values obtained by both groups differ from the work of Young (*8*) in 1894. The work of Isaac, Li, and Canjar was done in a variable-volume apparatus while that of Silberberg, McKetta, and Kobe (*7*) done in a Burnett apparatus. It was considered desirable to repeat the work in a variable volume apparatus. Because the critical constants have not been checked since the work of Young (*9*) in 1910, they were determined also.

EXPERIMENTAL

Isopentane. The sample was taken from the cylinder used by Silberberg. Because the isopentane left in the Burnett apparatus at the conclusion of that work was transferred back to the cylinder, it is probable that some air leaked in during the process. The isopentane was frozen with liquid nitrogen and the permanent gases were evacuated. The sample was melted and the first 10% was evacuated; the sample was distilled into a second receiver, leaving the last 10% in the original flask. This operation was repeated several times. However, the behavior of the sample indicated that the isopentane was not as pure as desired. The vapor pressure of the liquid increased with decreasing vapor volume, and the isotherms in the critical region showed a slope instead of being flat. At 173°C. the vapor pressure increased by 0.093 atm. when the vapor volume was reduced from 90% to 10%. Silberberg (*6*) has observed about a 0.05-atm. increase under these same conditions.

Method and Apparatus. The apparatus used in this investigation is essentially that described by Beattie (*2*). Thermostat temperatures were controlled to 0.005°C. by a platinum resistance thermometer in conjunction with a photoelectric cell relay and a Mueller bridge. The actual thermostat temperatures were measured by the same platinum resistance thermometer. A known amount (2.8139 grams) of isopentane was charged to the *P-V-T* bomb using a weighing bomb and charging union techniques described elsewhere (*3*).

In the determination of the critical constants, the usual pro-

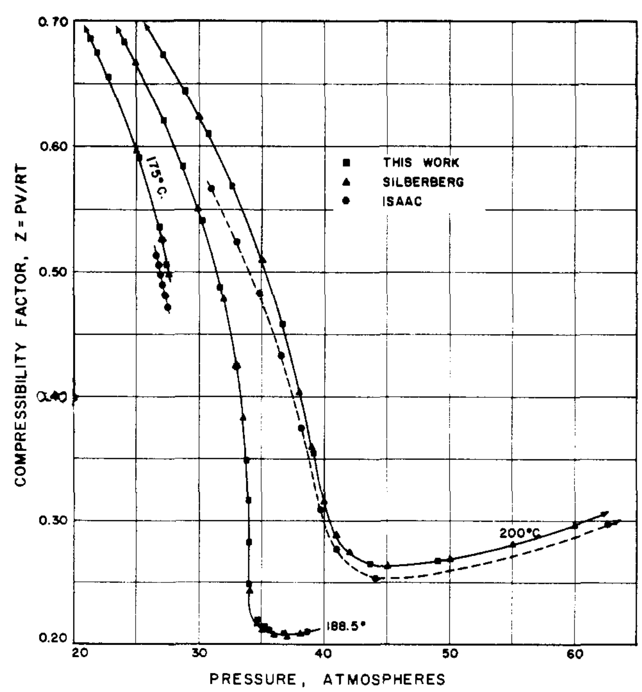

Figure 1. Compressibility of isopentane

[1] Deceased.