

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) ($^{\circ}\text{K}.$)
 T = Absolute temperature ($T_{0^{\circ}\text{C.}} = 273.16^{\circ}\text{K}.$)
 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

LITERATURE CITED

- (1) Beattie, J. A., Douslin, D. R., Levine, S. W., *J. Chem. Phys.* **20**, 1619-20 (1952).
- (2) Beattie, J. A., Levine, S. W., Douslin, D. R., *J. Am. Chem. Soc.* **73**, 4431-2 (1951).
- (3) *Ibid.*, **74**, 4778-9 (1952).

- (4) Bridgman, P. W., *Proc. Am. Acad. Arts Sci.* **66**, 185-233 (1930-1).
- (5) Burnett, E. S., *J. Appl. Mechanics* **58**, A136-40 (1936).
- (6) Isaac, R., Li, K., Canjar, L. N., *Ind. Eng. Chem.* **46**, 199-201 (1954).
- (7) Kobe, K. A., Lynn, R. E., Jr., *Chem. Revs.* **52**, 117-236 (1953).
- (8) Kobe, K. A., Vohra, S. P., *J. CHEM. ENG. DATA* **4**, 329 (1959).
- (9) Lambert, J. D., others, *Proc. Roy. Soc. (London)* **A196**, 113-25 (1949).
- (10) Li, K., Canjar, L. N., *Chem. Eng. Progr. Symposium Ser.* **49**, No. 7, 147-9 (1953).
- (11) Pawlewski, B., *Ber.* **16**, 2633-6 (1883).
- (12) Rossini, F. D., others, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," p. 327, Carnegie Press, Pittsburgh, 1953.
- (13) Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.* **34**, 730-7 (1942).
- (14) Sage, B. H., Lacey, W. N., "Thermodynamic Properties of Hydrocarbons," pp. 70-82, Am. Petroleum Inst., New York, 1950.
- (15) Sage, B. H., California Institute of Technology, personal communication Dec. 21, 1956.
- (16) Scott, D. W., others, *J. Am. Chem. Soc.* **73**, 1707-12 (1951).
- (17) Silberberg, I. H., Kobe, K. A., McKetta, J. J., *J. CHEM. ENG. DATA* **4**, 314 (1959).
- (18) Warren, C. M., *Mem. Am. Acad. Arts Sci.* **9**, 156-176 (1867-73).
- (19) Young, S., *Proc. Phys. Soc. (London)* **13**, 602-57 (1894).
- (20) Young, S., *Sci. Proc. Roy. Dublin Soc.* **12**, 374-443 (1909-10).
- (21) Young, S., Thomas, G. L., *Proc. Phys. Soc. (London)* **13**, 658-65 (1895).

RECEIVED for review February 3, 1958. Accepted July 30, 1959.

Volumetric Behavior and Critical Constants of Isopentane

SURINDER PAL VOHRA and KENNETH A. KOBE¹
 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 re-

sistance 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-

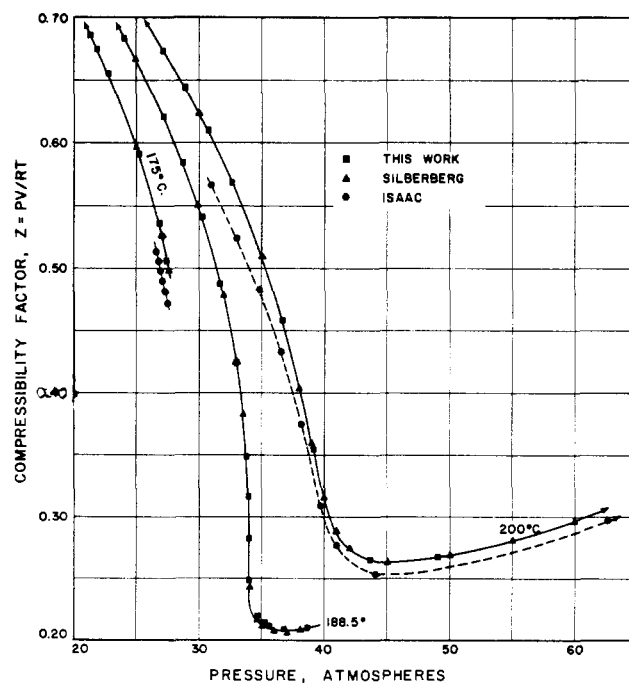


Figure 1. Compressibility of isopentane

¹Deceased.

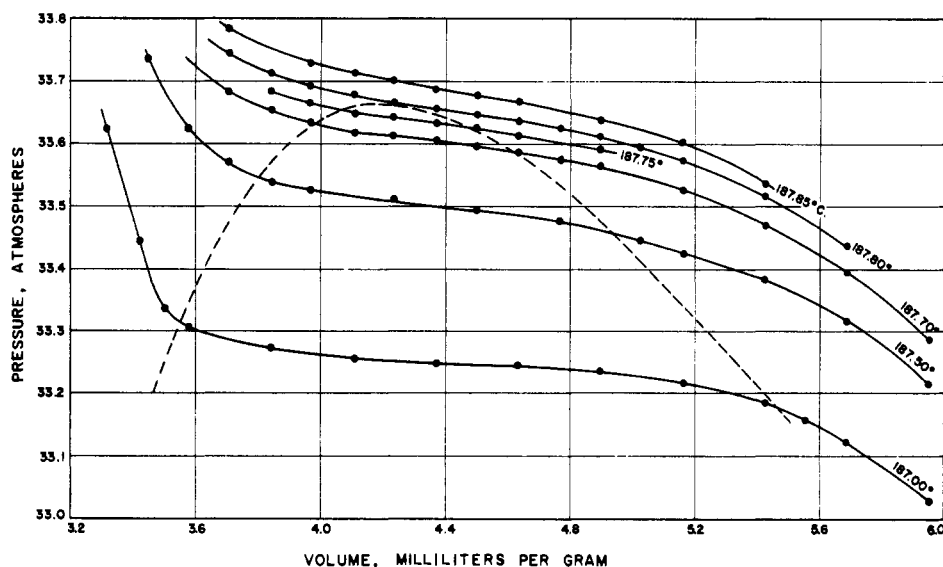


Figure 2. Isotherms of isopentane in the critical region

cedures for the determination of compressibility isotherms were followed. Such isotherms were determined below and above the critical temperature. Because of the impurities in the sample, the behavior of the piston gage was watched very carefully,

Table I. Compressibility of Isopentane
(175°, 188.5°, and 200° C. Isotherms)

Sp. Vol., Ml./G.	Pressure, Atm.	Sp. Vol., Ml./G.	Pressure, Atm.	Sp. Vol., Ml./G.	Pressure, Atm.
175° C.		188.5° C.		200° C.	
17.042	20.850	15.714	23.303	13.345	27.168
16.386	21.377	14.921	24.069	12.019	28.860
15.726	21.896	14.918	24.077	10.694	30.696
14.671	22.783	12.015	27.176	9.3708	32.663
12.036	25.143	10.695	28.731	6.7256	36.716
10.188	26.816	9.3753	30.328	4.8744	39.186
9.9238	27.039	8.0563	31.833	3.6866	41.407
9.3991	27.451	6.7369	33.076	3.2724	43.707
8.8693	27.583 ^a	5.4177	33.804	2.9253	49.042
		4.8901	33.932	2.7611	54.708
		4.3627	34.009	2.6899	59.460
		3.8353	34.100	2.5696	68.688
		3.3082	34.694	2.4883	75.753
		3.1762	35.168	2.3368	101.584
		3.1060	35.559	2.2373	129.180
		2.9752	36.774	2.1703	154.774
		2.8666	38.557	2.1182	181.981

^aVapor pressure.
Data above 65 atm. are not shown in Figure 1.

Table II. Isotherms in the Critical Region of Isopentane

Density, G./Ml.	Vol- ume, Ml./G.	Temperature, °C.					
		187	187.5	187.7	187.75	187.8	187.85
		Pressure, Normal Atm.					
0.1680	5.953	33.029	33.216	33.289			
0.1758	5.689	33.122	33.317	33.396		33.439	
0.1799	5.558	33.158					
0.1843	5.425	33.186	33.383	33.470		33.518	33.538
0.1937	5.162	33.218	33.426	33.526		33.574	33.602
0.1989	5.028		33.457			33.594	
0.2042	4.898	33.237	33.471	33.566	33.592	33.612	33.639
0.2099	4.764		33.478	33.575		33.627	
0.2158	4.634	33.245		33.588	33.614	33.636	33.669
0.2222	4.500		33.495	33.597	33.626	33.648	33.679
0.2288	4.370	33.249		33.607	33.633	33.658	33.688
0.2361	4.235		33.512	33.614	33.643	33.668	33.701
0.2435	4.106	33.257		33.618	33.649	33.680	33.715
0.2518	3.972		33.527	33.635	33.667	33.691	33.730
0.2603	3.842	33.273	33.540	33.653	33.685	33.712	
0.2697	3.708		33.571	33.684		33.745	33.783
0.2794	3.579	33.307	33.623				
0.2857	3.500	33.367					
0.2904	3.444		33.737				
0.2924	3.420	33.443					
0.3016	3.315	33.624					

Table III. Comparison of the Critical Constants of Isopentane

Source	t_c , °C.	p_c , Atm.	d_c , G./Ml.
This work	187.8 ± 0.05	33.66 ± 0.05	0.236 ± 0.005
Pawlewski (5)	194.8		
Altschul (7)	187.1	33.3	
Young (9)	187.8	32.9	0.2343

particularly near the saturated vapor and liquid states. Entrance into the two phase region was marked by a slow fall of the piston caused by addition of a 1-gram weight to the pan.

Experimental Data. Table I presents compressibility data for 175°, 188.5°, and 200° C. isotherms. These data are compared with those of others (4, 7) in Figure 1.

The results of the measurements of the compressibility of isopentane in the critical region are given in Table II. These isotherms are plotted in Figure 2, and the critical constants derived from the plot are compared with the results of other workers in Table III. The agreement of the authors' values of critical temperature and critical volume with those of Young (9) is striking.

DISCUSSION

Compressibility data obtained at 175°, 188.5°, and 200° C. agree with those of Silberberg and coworkers (7) within 0.2%, which is claimed to be the experimental accuracy, except in high density region of 188.5° C. where the effect of impurities is pronounced. Even in this region maximum deviation is less than 1.0%.

Because of an additional source of error in the critical region, introduced by the impurities, it is hard to estimate the magnitude of uncertainties in the critical constants. Nevertheless, the values presented in Table III were chosen after a realistic evaluation of these uncertainties.

LITERATURE CITED

- Altschul, M., *Z. physik. Chem.* **11**, 577 (1893).
- Beattie, J. A., *Proc. Am. Acad. Arts Sci.* **69**, 389 (1934).
- Couch, E. J., "Thermodynamic Properties of Nitrous Oxide," Ph.D. dissertation in Chemical Engineering. The University of Texas, Austin, Tex., 1956.
- Isaac, R., Li, K., Canjar, L. N., *Ind. Eng. Chem.* **46**, 199 (1954).
- Pawlewski, B., *Ber.*, **15**, 2143 (1882).
- Silberberg, I. H., University of Texas, personal communication, 1958.
- Silberberg, I. H., McKetta, J. J., Kobe, K. A., *J. Chem. Eng. Data* **4**, 323 (1959).
- Young, S., *Proc. Phys. Soc. (London)* **13**, 602 (1894-5).
- Young, S., *Sci. Proc. Roy. Dublin Soc.* **12**, 374 (1909-10).

RECEIVED for review July 21, 1958. Accepted July 30, 1959. Work done as part of investigations supported by the Office of Ordnance Research under contract number DA-23-072-ORD-685.