

## The Vapor Pressure, Orthobaric Liquid Density, and Critical Constants of Isobutane

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It should not be concluded from Eq. (17), in conjunction with Eq. (18), that Eq. (17) is a general law which applies to any mixture, irrespective of the form of  $G$ . For example, in a perfect solution of polymers, where

$$G/RT = \sum n_i \ln(n_i/\sum n_i), \quad (19)$$

one finds the following relation between turbidity

and osmotic pressure,

$$\tau_c/Kc - \partial c/\partial P = \phi_0^2(M_w - M_n)/RT.$$

This shows that it is essential, for Eq. (17) to be applicable, that the molar fractions in Eq. (19) are replaced by volume fractions. Conversely, Eq. (17) may be used to check the statistical theory of polymer solutions.

## The Vapor Pressure, Orthobaric Liquid Density, and Critical Constants of Isobutane

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The vapor pressures and orthobaric liquid densities of isobutane (propane-2-methyl) were measured from 30° to 125°C. The equation

$$\log_{10} p \text{ (normal atmos.)} = 4.31269 - 1126.71/T \quad (T = t^\circ\text{C (Int.)} + 273.13)$$

gives a fair representation of the vapor pressures.

The critical constants of isobutane are determined by the compressibility method. They are:  $t_c = 134.98 \pm 0.05^\circ\text{C}$  (Int.),  $p_c = 36.00 \pm 0.05$  normal atmos.,  $v_c = 0.263$  liters per mole (4.53 ml per g),  $d_c = 3.80$  moles per liter (0.221 g per ml). The uncertainty in the critical volume and density is 2 percent.

IN recent years the vapor pressure and critical constants of a number of hydrocarbons have been determined.<sup>1</sup> The vapor pressures and orthobaric densities of isobutane have been studied over various temperature ranges by several investigators<sup>2-6</sup> and the critical constants determined<sup>3,7</sup> by the disappearance of the meniscus method.

TABLE I. Vapor pressures and orthobaric liquid densities of isobutane.

Temp. °C (Int.)	Largest and smallest vapor volumes ml		Increase in vapor pressure atmos.	Vapor pressure normal atmos.	Orthobaric liquid density g/ml
30	77	41	0.005	3.941	0.549
50	96	4	0.002	6.701	0.518
75	98	2	0.004	11.932	0.480
100	103	0.01	0.004	19.573	0.428
125	46	20	0.008	30.440	0.353

<sup>1</sup> For the last report on this work see J. A. Beattie and D. G. Edwards, *J. Am. Chem. Soc.* **70**, 3382 (1948).

<sup>2</sup> G. A. Burrell and L. W. Robertson, *J. Am. Chem. Soc.* **37**, 2482 (1915).

<sup>3</sup> F. M. Sibert and G. A. Burrell, *J. Am. Chem. Soc.* **37**, 2683 (1915).

<sup>4</sup> Dana, Jenkins, Burdick, and Timm, *Refriger. Eng.* **12**, 387 (1926).

<sup>5</sup> B. H. Sage and W. N. Lacey, *Ind. Eng. Chem.* **30**, 673 (1938).

<sup>6</sup> W. M. Morris, B. H. Sage, and W. N. Lacey, *Am. Inst. Mining and Met. Eng., Tech. Pub.* 1128, *Petroleum* 2 (Nov. 1939).

<sup>7</sup> J. Harand, *Monats. F. Chem.* **65**, 153 (1935).

Recently several compilations of the vapor pressure and critical constants have been published.<sup>8,9</sup>

The isobutane used in the present investigation was furnished by the Linde Air Products Company through the courtesy of Dr. L. I. Dana.

The method of procedure for the determination of vapor pressure and compressibility has been described elsewhere.<sup>10</sup> The bomb with the glass liner was used. No attempt at further fractionation of the isobutane was made but it was distilled, frozen, and pumped several times in the process of loading the weighing bomb in order to remove any non-condensable gas.

The mass of the isobutane sample used was about 7 grams. In the determination of vapor pressure the volume of the sample was varied at each tem-

TABLE II. Comparison of calculated with observed vapor pressures of isobutane.  
 $\log_{10} p \text{ (calcd.)} = 4.31269 - 1126.71/T.$

Temp. °C (Int.)	Vapor pressure normal atmos.	Obs.-calc. atmos.
30	3.941	-0.001
50	6.701	+0.005
75	11.932	+0.013
100	19.573	-0.064
125	30.440	+0.073

<sup>8</sup> Anon., *Oil and Gas J.* **44**, No. 23, 115 (Oct. 1945).

<sup>9</sup> K. Hochmuth, G. H. Hanson, and M. L. Smith, *Trans. Am. Inst. Chem. Eng.* **42**, 975 (1946).

<sup>10</sup> J. A. Beattie, *Proc. Am. Acad.* **69**, 389 (1934).

TABLE III. Isotherms of isobutane in the critical region  
Molecular Weight, 58.077.

Temp. °C	(Int.)	134.60	134.70	134.80	134.85	134.88	134.90	134.95	134.97	134.98	134.99	135.00	135.05	135.15
density moles/liter	volume liters/mole	Pressure, normal atmospheres												
3.108	0.3218	35.705	35.769	35.823	35.847	35.861	35.870	35.895	35.907			35.923	35.946	35.997
3.227	0.3099	35.733	35.801	35.852	35.882	35.899	35.908	35.931	35.939			35.961	35.986	36.038
3.291	0.3039	35.753	35.809	35.868										
3.356	0.2980	35.773	35.816	35.874	35.904	35.919	35.928	35.955	35.966	35.970	35.977	35.981	36.010	36.065
3.423	0.2921	35.770	35.823	35.882	35.910	35.926	35.934							
3.495	0.2861	35.771	35.828	35.886	35.915	35.932	35.940	35.973	35.978	35.988	35.993	35.998	36.024	36.084
3.569	0.2802	35.769	35.829	35.889	35.922	35.939	35.946	35.974	35.983	35.993	35.998	36.004	36.007	36.092
3.647	0.2742		35.828	35.887	35.922		35.952	35.979	35.990	35.994	36.004			
3.686	0.2713							35.982	35.990					
3.727	0.2683	35.773	35.831	35.890	35.921	35.946	35.953	35.983	35.992	36.000	36.005	36.009		
3.768	0.2654							35.983	35.994	35.997				
3.811	0.2624		35.825	35.889	35.922	35.944	35.953	35.983	35.994	35.999	36.008	36.012	36.042	36.100
3.855	0.2594							35.983	35.996					
3.899	0.2565	35.770	35.832	35.892		35.944	35.954	35.984	35.996	36.002	36.008	36.013		
3.992	0.2505	35.769	35.826	35.894	35.925	35.945	35.956	35.988	36.000	36.003	36.011	36.018	36.048	36.110
4.088	0.2446	35.769	35.833	35.893		35.945		35.990	36.002			36.020		
4.189	0.2387	35.770	35.832	35.895	35.927	35.947	35.960	35.995	36.005	36.013	36.019	36.026	36.054	36.117
4.297	0.2327		35.838											
4.409	0.2268	35.776		35.907	35.943	35.965	35.978	36.015	36.024			36.046	36.080	36.144
4.653	0.2149	35.799	35.890	35.967	36.010	36.028	36.045	36.084	36.092			36.119	36.153	36.226

perature from about 90 ml to a value less than the orthobaric liquid volume. The change of vapor pressure with vapor volume gives an indication of the purity of the sample. The orthobaric liquid density was determined at each temperature from the break in the curve of pressure *versus* volume.

The measured vapor pressures are listed in Table I. The small increase in pressure with decrease in vapor volume indicates that the sample was of exceptional purity. The vapor pressures were represented by the equation:

$$\log_{10} p \text{ (normal atmos.)} = 4.31269 - (1126.71/T), \\ (T = t^\circ\text{C (Int.)} + 273.13),$$

and the representation of the measurements by this equation is given in Table II. Our vapor pressures are in fair agreement with those of Dana and co-workers<sup>4</sup> and of Sage and Lacey,<sup>5</sup> and are in even better agreement with the two values published by Morris, Sage, and Lacey.<sup>6</sup>

Our measured orthobaric liquid densities are listed in Table I. The estimated uncertainty is 0.001 g per ml. Our measured densities are on the average 0.002 g per ml higher than those of Sage and Lacey,<sup>5,6</sup> and are higher than the values of Dana and co-workers<sup>4</sup> at 30° by 0.003 g per ml and lower at 50° by 0.001.

The measurements of the compressibility of iso-

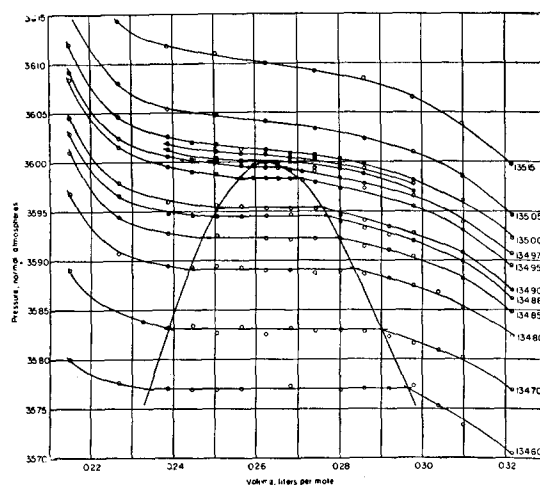


FIG. 1. Isotherms of isobutane in the critical region. The isotherms immediately above 134.97 are 134.98 and 134.99.

butane in the critical region are given in Table III and plotted in Fig. 1. From the plot we find for the critical point:  $t_c = 134.98 \pm 0.05^\circ\text{C}$  (Int.),  $p_c = 36.00 \pm 0.05$  normal atmospheres,  $v_c = 0.263$  liter per mole (4.53 ml per g),  $d_c = 3.80$  moles per liter (0.221 g per ml). The uncertainty in the critical volume and density is 2 percent. Sibert and Burrell<sup>3</sup> give  $t_c = 133.7^\circ\text{C}$ ,  $p_c = 36.54$  atmos., and Harand<sup>7</sup> gives  $t_c = 133.8^\circ\text{C}$ .