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Citation: *The Journal of Chemical Physics* **18**, 127 (1950); doi: 10.1063/1.1747429

View online: <http://dx.doi.org/10.1063/1.1747429>

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The Compressibility of, and an Equation of State for Gaseous Isobutane

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 (Received July 12, 1949)

The volumetric behavior of gaseous isobutane from 150° to 300°C and from 1.0 to 8.0 moles per liter has been studied. The constants of the Beattie-Bridgeman equation of state for gaseous isobutane are $R=0.08206$, $A_0=16.6037$, $a=0.11171$, $B_0=0.23540$, $b=0.07697$, $c=300 \times 10^4$ in units of normal atmospheres, liters per mole, degrees Kelvin.

THE determinations of the vapor pressures, orthobaric liquid densities, and critical constants of isobutane have been reported in an earlier paper.¹ The same loading of isobutane was used to study the

volumetric behavior in the region above the critical temperature by the method employed for other hydrocarbons.² The compressibility of isobutane (liquid and gas) from 21° to 121°C has been studied by Sage and Lacey,³ and from 38° to 238° by Morris, Sage, and Lacey.⁴

The isobutane used in the present investigation was furnished by the Linde Air Products Company through the courtesy of Dr. L. I. Dana. Its high degree of purity was indicated by the small change of vapor pressure with decrease in vapor volume. The mass of the sample of isobutane was 7.0074 g. After the completion of the 0.300° isotherm, we redetermined the pressure for densities 1.0, 2.0, and 3.0 moles per liter at 150°C. These checked with the pressures measured at the beginning of the investigation to better than 0.005 atmos., indicat-

TABLE I. Values of the constants of the Beattie-Bridgeman equation of state for gaseous isobutane.

$$\begin{aligned} p &= [RT(1-\epsilon)/V^2][V+B]-A/V^2 \\ A &= A_0(1-a/V) \\ B &= B_0(1-b/V) \\ \epsilon &= c/VT^3 \end{aligned}$$

Units: normal atmospheres, liters per mole, °K ($T^\circ\text{K} = t^\circ\text{C} + 273.13$)

$R = 0.08206$	$b = 0.07697$
$A_0 = 16.6037$	$c = 300 \times 10^4$
$a = 0.11171$	Mol. wt. = 58.077
$B_0 = 0.23540$	

TABLE II. Comparison of the pressures calculated from the equation of state with the observed pressures for gaseous isobutane (C_4H_{10}).

Density, moles/liter → Temp., °C (Int.) ↓	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	6.0	7.0	8.0
	Pressure, normal atmospheres											
150 obs	25.70	33.05	37.84	40.89	42.85	44.29	45.60	47.20	49.70	63.08	106.66	224.71
obs—calc	-0.14	-0.14	0.00	+0.30	+0.56	+0.46						
175 obs	28.45	37.63	44.49	49.75	54.04	57.92	61.95	66.77	73.34	98.41	160.44	303.79
obs—calc	-0.07	-0.04	+0.08	+0.22	+0.18	-0.34						
200 obs	31.13	42.06	50.93	58.36	65.02	71.51	78.52	86.85	97.67	134.54	214.22	
obs—calc	-0.04	-0.02	+0.08	+0.10	-0.09	-0.72						
225 obs	33.78	46.44	57.27	66.86	75.93	85.12	95.22	107.20	122.42	171.25	269.05	
obs—calc	-0.02	0.00	+0.08	+0.04	-0.17	-0.73						
250 obs	36.39	50.75	63.48	75.23	86.73	98.66	111.94	127.65	147.36	208.05		
obs—calc	-0.02	0.00	+0.03	-0.01	-0.15	-0.51						
275 obs	38.99	55.02	69.66	83.58	97.52	112.27	128.78	148.35	172.59	245.51		
obs—calc	-0.02	0.00	+0.03	+0.04	+0.03	+0.03						
300 obs	41.51	59.24	75.77	91.86	108.25	125.80	145.61	169.00	197.85			
obs—calc	-0.08	-0.03	+0.01	+0.10	+0.29	+0.68						
Average deviation, atmos.**	0.056	0.033	0.044	0.116	0.210	0.496						
Average % deviation**	0.181	0.090	0.083	0.224	0.353	0.656						

* For each temperature the first line gives the observed pressure and the second line gives the observed minus calculated pressure. The critical constants of isobutane are: $t_c = 134.98^\circ\text{C}$ (Int.), $p_c = 36.00$ normal atmos., $v_c = 0.263$ liters per mole, $d_c = 3.80$ moles per liter.

** Total average deviation, 0.159 atmos.; total average % deviation, 0.265%.

¹ J. A. Beattie, D. G. Edwards, and Stanley Marple, Jr., *J. Chem. Phys.* **17**, 576 (1949).

² For the last report on this work see Beattie, Ingersoll, and Stockmayer, *J. Am. Chem. Soc.* **64**, 546, 548 (1942). For a description of the apparatus and method see J. A. Beattie, *Proc. Am. Acad. Arts. and Sci.* **69**, 389 (1934).

³ B. H. Sage and W. N. Lacey, *Ind. Eng. Chem.* **30**, 673 (1938).

⁴ Morris, Sage, and Lacey, *Am. Inst. Mining and Met. Eng., Tech. Pub.* 1128, Petroleum 2, Nov. 1939.

ing that no decomposition had occurred throughout the entire series of measurements.

The measurements are reported in Table II. In Table I are given the constants of the Beattie-Bridgeman equation of state for isobutane determined from the isometrics below the critical density (3.80 moles per liter). The comparison of the pressures computed from this equation with the observed pressures is given in Table II. The total average percent deviation is 0.27 percent.

The pressures of Morris, Sage, and Lacey were at different temperatures and densities from our values. Their pressures were first interpolated to our densities

by suitable treatment of their isotherms, and then smoothed to our temperatures along isometrics. The agreement of the pressures so obtained with our observed pressures is excellent. From a density of 1 through 5 moles per liter and a temperature of 150 to 225°C the average percentage deviation (without regard to sign) is 0.23 percent, the largest positive deviation being 0.52 percent and the largest negative -0.57 percent. The algebraic average is 0.05 percent. For the ten points of densities 6, 7 and 8 moles per liter the average percentage deviation is 0.94 percent and the algebraic average +0.13 percent.

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 18, NUMBER 1

JANUARY, 1950

Hexacovalent Bond Orbitals II

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(Received July 11, 1949)

Further calculations are reported on the set of trigonal prism orbitals introduced in paper one of this series. The strongest orbitals found have a strength equal to 2.989. The results are used in discussing the difference in stability between these orbitals and the octahedral orbitals in structures of the following types: $\text{Fe}(\text{CN})_6^{\equiv}$, $\text{Fe}(\text{CN})_6^{\equiv}$, and SF_6 .

IN the first paper¹ of this series, s , p , and d orbitals were hybridized to give a set of trigonal prism orbitals more general than the set previously² obtained. Some calculations were reported on the new set.

In this paper further calculations are reported. In Table I m was³ set equal to one. Then θ_1 , the angle between the axis and the maximum in ψ_1 , and S , the maximum value of ψ_1 , were calculated. In Table II values were assigned m . Then n was chosen so as to obtain the strongest orbitals for each m , and the corresponding values of θ_1 and S were obtained. As in paper one¹ θ_1 and S are called the angle between the axis and bond one and the strength of the bond respectively.

The strongest bonds were found when m equals 0.5972 and n equals 0.8464. These bonds have a strength equal to 2.989. Thus these bonds are slightly stronger than cylindrical trigonal prism bonds, which were discussed by Hultgren.²

The configuration sp^3d^2 is of especial interest. This configuration in general yields the octahedral structure.⁴ The strength of an octahedral bond equals 2.923. The strength of the corresponding trigonal prism bond equals 2.737. However, trigonal prism bonds stronger than 2.923 may result if less of the p orbitals, the same amount or less of the s orbital, and more of the d orbitals are used in forming the bonds. In structures of

the $\text{Fe}(\text{CN})_6^{\equiv}$ and the $\text{Fe}(\text{CN})_6^{\equiv}$ types there are three unshared electron pairs, or two unshared electron pairs and one unshared electron, respectively, in the valence shells of the central atom. In structures of these types the energy obtainable in passing from the octahedral structure to a trigonal prism structure where the strength is greater than 2.923 apparently does not equal the energy needed for the excitation of the required number of unshared electrons. Some energy is required since the interaction energy of a shared electron is less than that of an unshared electron.

Consider the following rough estimates.⁵ Suppose the $d-p$ separation is 50 kcal./mole and the $d-s$ separation is 0 kcal./mole (i.e., a valence shell, unshared electron in a p orbital is 50 kcal./mole less stable than when it is in a d or s orbital). Assume that the bond energy equals 100 kcal./mole and that the bonds are 100 percent covalent.

TABLE I. Results of calculations on trigonal prism orbitals of type $s^n p^3 d^{3-n}$.

n	S , Strength of a bond	θ_1 , Angle between axis and bond 1
1.0000	2.737	47° 5'
0.9600	2.771	44° 20'
0.9000	2.789	42° 44'
0.8000	2.807	40° 57'
0.5070	2.825	37° 37'
0.3000	2.815	35° 57'
0.1000	2.771	34° 37'
0.0000	2.667	34° 1'

⁵ See H. Kuhn, *J. Chem. Phys.* **16**, 727 (1948).

¹ G. H. Duffey, *J. Chem. Phys.* **17**, 1328 (1949).

² R. Hultgren, *Phys. Rev.* **40**, 891 (1932).

³ The orbitals are of type $s^n p^{1+2m} d^{3-2m-n}$.

⁴ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1940).