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## The Compressibility of Gaseous Ethane in the High Density Region

BY JAMES A. BEATTIE, GOUQ-JEN SU AND GERALD L. SIMARD

The compressibility of gaseous ethane from 25 to 250° and from 0.5 to 5.0 moles per liter has been studied in this Laboratory; and the constants of an equation of state of gaseous ethane have been determined from these data.<sup>1</sup> Sage, Webster and Lacey<sup>2</sup> have determined the compressibility of the gas and liquid phases from 20 to 120° and to 240 atm. In order to extend the earlier data of this Laboratory to higher densities, we have determined the compressibility of the gas phase from 5 to 10 moles per liter over the temperature range 50 to 275°. The method of

composition having occurred. Thus the vapor pressure at 25° of ethane measured with a vapor volume of 40 cc. was 41.377 atm. before the compressibility runs, and 41.398 after the completion of all of the runs; the vapor pressure with a vapor volume of 0.7 cc. was 41.378 before the runs, and 41.453 after. In the earlier low density measurements the 275° isotherm had to be discarded due to the effects of decomposition of the ethane. It has been found that the slight film of tar remaining in the bomb after a series of measurements greatly increases the rate of decomposition. If

TABLE I

### COMPRESSIBILITY OF GASEOUS ETHANE (C<sub>2</sub>H<sub>6</sub>) IN THE DENSITY REGION 5 TO 10 MOLES PER LITER

The compressibility of gaseous ethane from 0.5 to 5 moles per liter and an equation of state for ethane are given in an earlier paper.<sup>1</sup> Molecular weight, 30.0462.

Density, moles/liter.....	5.0	5.5	6.0	6.5	7.0	7.5	8.0	9.0	10.0
Temp., °C. (Int.)	Pressure, normal atmospheres								
50	60.63	62.40	63.99	65.52	67.08	68.82	70.88	76.90	87.76
75	77.94	81.97	85.95	90.00	94.29	99.01	104.38	118.32	139.23
100	94.94	101.36	107.86	114.60	121.83	129.74	138.64	160.77	191.98
125	111.75	120.56	129.64	139.19	149.41	160.60	173.10	203.63	244.97
150	128.44	139.68	151.38	163.70	176.99	191.52	207.66	246.57	298.02
175	145.02	158.68	172.98	188.20	204.54	222.44	242.24	289.49	350.95
200	161.51	177.62	194.53	212.59	232.03	253.29	276.76	332.56	
225	177.89	196.44	215.98	236.88	259.42	284.02	311.09		
250	194.22	215.21	237.38	261.13	286.74	314.67	345.38		
275	210.47	233.90	258.69	285.28	314.00	345.30			

procedure has been described elsewhere,<sup>3</sup> the steel bomb being used for ethane.

The sample was from the same stock used in the earlier work and was obtained from the Buffalo Laboratory of The Linde Air Products Company, through the courtesy of Dr. L. I. Dana. Determination of the variation of vapor pressure with vapor volume<sup>4</sup> and the behavior of the ethane in the critical region<sup>4</sup> indicate that the sample was of exceptional purity. Ethane decomposes fairly rapidly when contained in steel vessels at temperatures above 250°. We were able, however, to complete the 275° isotherm without serious de-

this tar is removed the higher temperature isotherms can be studied without serious error due to decomposition.

### Results

The compressibility measurements are given in Table I. The 5 mole per liter isometric had also been studied in the earlier work<sup>1</sup> published from this Laboratory. The agreement is not all that could be desired: the pressures given in Table I for this isometric are higher than those of the earlier work by amounts increasing regularly with increasing temperature from 0.1% at 50° to 0.7% at 250°. Because of the larger volumes of gas at a density of 5 moles per liter in the present work, more confidence is placed in the values given in Table I.

### Summary

The compressibility of gaseous ethane (C<sub>2</sub>H<sub>6</sub>)

(1) J. A. Beattie, C. Hadlock and N. Poffenberger, *J. Chem. Phys.*, **3**, 93 (1935).

(2) B. H. Sage, D. C. Webster and W. N. Lacey, *Ind. Eng. Chem.*, **29**, 658 (1937).

(3) J. A. Beattie, *Proc. Am. Acad. Arts Sci.*, **69**, 389 (1934).

(4) J. A. Beattie, G.-J. Su and G. L. Simard, *THIS JOURNAL*, **61**, 924 (1939).

has been studied from 50 to 275° and from 5 to 10 moles per liter, thus extending to high den-

sities, the data previously obtained.

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## The Electron Diffraction Investigation of Methylacetylene, Dimethylacetylene, Dimethyldiacetylene, Methyl Cyanide, Diacetylene, and Cyanogen

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### Introduction

In consequence of the apparent constancy and additivity of interatomic distances for covalently-bonded atoms<sup>1</sup> and of the dependence of interatomic distance on bond type, it has been found<sup>2</sup> that the determination of values of interatomic distances in molecules can be used in the study of the types of bonds represented in the molecules. This procedure is especially valuable in the study of conjugation and other resonance phenomena.<sup>3</sup> In order to test the postulate that the internuclear distance of two bonded atoms is determined essentially by the nature of the bond between the two atoms and is not at all or is only slightly influenced by the other bonds in the molecule an electron-diffraction investigation of isobutene, tetramethylethylene, mesitylene, and hexamethylbenzene was carried out<sup>4</sup>; this led to the conclusion that in these four molecules, in which there are methyl groups substituted in ethylene or benzene, the carbon-carbon single-bond distance has the same value,  $1.54 \pm 0.02$  Å. (to within the estimated experimental error) as in other hydrocarbon molecules. Further support for this conclusion is provided by the recent X-ray investigation of crystalline hexamethylbenzene by Robertson and Brockway,<sup>5</sup> who have found 1.53 Å. for the bond distance for the methyl groups attached to the benzene ring, in place of the value 1.48 Å. reported some years ago.<sup>6</sup>

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(1) M. L. Huggins, *Phys. Rev.*, **28**, 1086 (1926); V. M. Goldschmidt, *Skrifter Norske Videnskaps-Akad. Oslo* (1926); N. V. Sidgwick, *Ann. Repts. Chem. Soc.*, **28**, 384 (1931); L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

(2) L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932); L. Pauling, L. O. Brockway and J. Y. Beach, *THIS JOURNAL*, **57**, 2705 (1935).

(3) See, for example, a forthcoming paper by V. Schomaker and L. Pauling, to be published in *THIS JOURNAL*.

(4) L. Pauling and L. O. Brockway, *ibid.*, **59**, 1223 (1937).

(5) J. M. Robertson and L. O. Brockway, private communication.

(6) K. Lonsdale, *Proc. Roy. Soc. (London)*, **A123**, 494 (1929).

It is accordingly of great interest that the value found spectroscopically for the large moment of inertia of methylacetylene by Herzberg, Patat, and Verleger<sup>7</sup> and verified by Badger and Bauer<sup>8</sup> should lead, on the assumption that the other interatomic distances in the molecule have their normal values, to the value  $1.462 \pm 0.005$  Å. for the carbon-carbon single-bond distance in this molecule, in which the single bond is adjacent to a triple bond. In order to evaluate this distance independently we have investigated methylacetylene by the electron-diffraction method, and have also investigated the related substances dimethylacetylene, dimethyldiacetylene, methyl cyanide, diacetylene, and cyanogen. The results of this work are described and discussed below.

### Experimental Methods and Results

**Preparation of Methylacetylene.**—The attempt was first made to prepare methylacetylene by the method of Lebeau and Picon,<sup>9</sup> involving the action of methyl iodide on the sodium compound of acetylene in liquid ammonia solution. The yields were very small, however, and the method was abandoned. The substance was finally prepared by a modification of the method of Johnson and McEwen.<sup>10</sup> 1,2-Dibromopropane (55 g., b. p. 141° at 760 mm.), which was prepared for us by Professor H. J. Lucas, was run slowly into a solution of potassium hydroxide (56 g.) in 95% ethanol (56 ml.), heated in a reflux by an oil-bath at 160°. The gas evolved during the vigorous reaction was passed into a solution of cuprous chloride (prepared by the method of "Organic Syntheses," Coll. Vol. I, p. 163) in ammonium hydroxide (sp. gr. 0.880). The precipitated yellow copper derivative of methylacetylene was filtered off and suspended in water, an excess of concentrated hydrochloric acid was added, and the mixture was boiled under reflux. The evolved gas was dried in calcium chloride U-tubes at 0° and then collected as liquid in a tube cooled with solid carbon dioxide and isopropyl alcohol. The contamination of acetylene was removed by

(7) G. Herzberg, F. Patat and H. Verleger, *J. Phys. Chem.*, **41**, 123 (1937).

(8) R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 599 (1937).

(9) P. Lebeau and M. Picon, *Compt. rend.*, **156**, 1077 (1913).

(10) J. R. Johnson and W. L. McEwen, *THIS JOURNAL*, **48**, 469 (1926).