strength should approach $+4$, as the ionic strength approaches zero. That this is the case is seen from Figs. 1 and 3.

From the values of k, it is seen that in mixtures of methanol and water, containing a large amount of the latter component, the methoxytriphenyl-carbinols are largely present in the ROH form.

From the practical point of view, the values of the constant

$$k' = \frac{[ROH]}{[ROCH_3]c_{H_3O}}$$

are more interesting than the k values. For the pentamethoxy indicator, k' is equal to 0.48, and for the hexamethoxy indicator, 0.94.

Finally, it may be mentioned that pK_{ROH} increases more when going from water to methanol as a solvent than that of other cation acids. The pK of the latter increases by about one unit.[1] In water, the pK values of penta- and hexamethoxy red are 1.85 and 3.3,[8] respectively. In methanol, the pK values increase by 2.45 and 2.85, respectively.

Summary

1. The effect of salts upon the color of penta- and hexamethoxytriphenylcarbinols in methanol corresponds to that of a system of uncharged base-cation acid.

2. In pure methanol, the carbinols are present

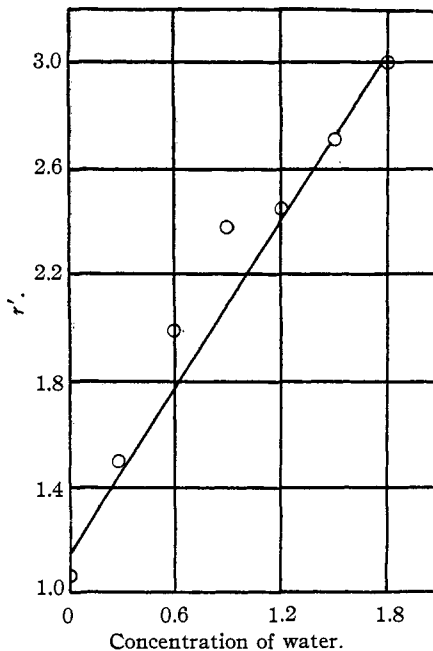(8) I. M. Kolthoff, THIS JOURNAL, 49, 1218 (1927).

Fig. 4.—Effect of water on the indicator ratio of hexamethoxy red in salicylate buffer.

mainly in the form of the methyl ether. The equilibrium constant of the reaction between the methyl ether and water has been evaluated.

3. The values of pK_{ROCH_3} and pK_{ROH} of the carbinols in methanol have been determined.

MINNEAPOLIS, MINN.   RECEIVED OCTOBER 3, 1938

The Molecular Structure of Hydrogen Fluoride[1]

BY S. H. BAUER, J. Y. BEACH[2] AND J. H. SIMONS

Structural studies of hydrogen fluoride may be traced back for more than half a century.[3] That the compound is polymerized in the vapor phase has been known since the early work of Mallet.[4] Simons and Hildebrand demonstrated that some of the polymers are of an order higher than tetramers,[5] for they obtained apparent molecular weights for the gas as large as 87.4. Further, they showed that *one* way of interpreting the available

(1) Part of these results were presented to the American Chemical Society at Milwaukee, September, 1938.

(2) National Research Fellow in Chemistry.

(3) Two reviews have appeared: J. H. Simons, *Chem. Rev.*, 8, 213 (1931); K. Fredenhagen, *Z. Elektrochem.*, 37, 684 (1931).

(4) Mallet, *Am. Chem. J.*, 3, 189 (1881).

(5) J. H. Simons and J. H. Hildebrand, THIS JOURNAL, 46, 2183 (1924).

vapor density data (over the pressure range 56 to 760 mm. and temperature range -39 to $88°$) rests on the assumption of the single equilibrium

$$n\, HF = (HF)_n$$
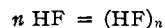
with $n = 6$ and

$$\log K_6 = \frac{+40,000}{4.597T} - 43.145$$

Although the data could be correlated with the existence of a larger number of species in equilibrium, the simpler hypothesis seemed reasonable in view of the fact that the molecular weight apparently approached 120 as the temperature was lowered and that within the experimental error agreement was found with the even whole number six for the degree of polymerization. Latimer

and Rodebush explained the association in terms of hydrogen bonds.[6]

Since so large a body of data could be fitted by the single equation, it was suggested that the concentration of polymers other than the hexamer is relatively low. If that is the case, it would be reasonable to suspect that a similar equilibrium exists in the liquid (shifted almost completely to the right) and this is indicated by its low surface tension (10.83 at $-7.6°$) and the independence of its Eötvös constant from temperature[7]; also by a group of approximate relationships which are generally used in the study of liquids.[8] However, upon analysis, a number of difficulties are apparent. Fundamentally, it is not clear how one would account for the predominant stability of the hexamer regardless what structure is assigned to it (both linear and ring configurations have been suggested).[9]
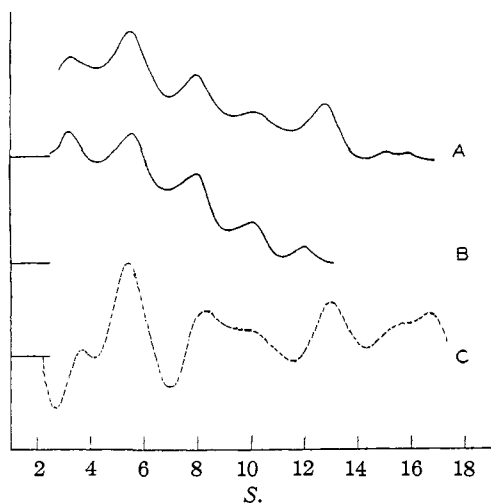

Fig. 1.—A, visual appearance of first set of photographs; B, visual appearance of final set, after volatile impurity had been removed by pumping; C, theoretical intensity curve for SiF_4. It is clear that the superposition of a small amount of C on B would give the intensity distribution initially observed (A).

Assuming that stabilization is due to resonance,[10] we cannot correlate a ring structure with the dielectric constant of hydrogen fluoride,

(6) W. M. Latimer and W. H. Rodebush, This Journal, 42, 1419 (1920).

(7) J. H. Simons and J. W. Bouknight, ibid., 54, 129 (1932).

(8) Collected in a master's dissertation, A. S. Russell, The Pennsylvania State College, June, 1937.

(9) J. D. Bernal and R. H. Fowler, J. Chem. Phys., 1, 515 (1933); W. H. Rodebush, Trans. Faraday Soc., 30, 776 (1934).

(10) Calculation for the case involving two protons (organic acid dimers) have been made by R. H. Gillett and A. Sherman, This Journal, 58, 1135 (1936).

which at $0°$ is 83.6, comparable to that of water.[11] Huggins[12] showed how the less symmetric complicated rings present in ice near its melting point may contribute appreciably to its dielectric properties. An explanation involving synchronized proton jumps in a planar hexagonal structure such as was suggested for H_6F_6 cannot possibly account for the rise in dielectric constant by a factor of 2.1 as kT is lowered to 0.73 of its original value even though the potential hump may be smaller for F–H—F than for O–H—O bonds. Furthermore, kinetic considerations will not permit the acceptance of a single equilibrium such as $6HF = H_6F_6$. Even if H_6F_6 is the polymer in largest concentration and the one of maximum molecular weight, lower polymers must be present.

If the concentration of polymers other than hexamers is truly relatively low, electron diffraction photographs of the vapor would show the pattern characteristic of the hexagonal configuration, provided, of course, the polymers do not dissociate when they enter the evacuated space; the monomer will only introduce a continuous background. The results of such an investigation are reported in this paper.

Experimental Details

The sample of hydrogen fluoride was obtained from a commercial tank of the liquid. This was received on a rush order for emergency use and was not of the highest purity. The gas was condensed into a copper vessel at $0°$, and the latter joined to the diffraction apparatus by means of a brass diaphragm valve (Hoke No. 322). The vapor pressure of the liquid at the temperature at which the investigation was conducted was approximately 350 mm. The initial photographs obtained from different samples showed clear sharp patterns of the form sketched in Fig. 1a; however, in each case, as pumping from the liquid was continued, the diffraction rings became fuzzy, the resulting patterns changed in appearance, and finally successive sets of photographs assumed the form indicated in Fig. 1b. Values of $s_0 \left(= 4\pi \dfrac{\sin \theta/2}{\lambda} \right)$ for the two sets of rings and the corresponding intensities of the maxima are tabulated in Table I, as are also the data for silicon tetrafluoride.[13]

(11) Fredenhagen and Dammlos, Z. anorg. allgem. Chem., 278, 272 (1928). A frequency of approximately a million cycles was used.

(12) M. L. Huggins, J. Phys. Chem., 40, 723 (1936).

(13) L. O. Brockway and F. T. Wall, This Journal, 56, 2373 (1934).

TABLE I

Max.	Min.	First set s_0	First set $I_{app.}$	First set $I_{corr.}$	SiF$_4$ s_0	Second set s_0	Second set $I_{app.}$	Second set $I_{corr.}$	$s_{calcd.}/s_{obsd.}$ (2nd set) (HF)$_3$	zig-zag models (HF)$_5$
1		3.24	10	82	...	3.16	18	136	0.919	0.926
	2	4.27			...	4.28			1.031	1.019
2		5.48	20	420	5.41	5.53	20	428	0.999	0.985
	3	6.91			6.93	6.84			.950	.989
3		7.93	15	480	8.27	8.00	11	365	1.006	1.000
	4	9.26			...	9.08			1.000	1.010
4		10.17	7	244	...	10.03	4	130	1.044	1.045
	5	11.53			11.59	...			...	...
5		12.72	10	298	13.02	(12.00)	1	40	(1.097)	(1.097)
						Average			0.993	0.996
						Average deviation			.033	.025

Final values H—F$_{(bonded)}$ 1.00 ± 0.06 Å.

H—F$_{(H\ bonded)}$ 1.55 ± .06

FH—F$_{(H\ bonded)}$ 2.55 ± .03

Average FFF angle 140° ± 5°. Hydrogen approximately on line with fluorine atoms (±15°)

The following explanation for the phenomenon is suggested. A small amount of silicon tetrafluoride may have been carried over into the condensate; since its s_0 values approximate those of hydrogen fluoride in the region $5 \le s \le 12$, while the intensity distributions for the two substances are entirely different (Fig. 1c), a superposition of the SiF$_4$ and HF patterns results in the first type of photographs. Because of the relative insolubility of the silicon compound in the acid, pumping removes the impurity so that the subsequent patterns are due to relatively pure hydrogen fluoride. The silicon fluoride probably came from a reaction between the liquid and sand trapped in the iron of the container.

The modified radial distribution curves for the two sets of photographs (Fig. 2a, b) are very much alike, since neither the s_0 values nor the corrected intensities differ appreciably. The distances indicated are listed in Table II.

TABLE II

First set, Å.	Second set, Å.	Relative density	Corresponding to
1.12	1.10	2	HF directly bonded
1.59	1.56	3	H—F H bonded
2.58	2.56	4	FH—F
3.55	3.42	2	FH—F$_H$
4.03	3.95	2	H—F—H$_F$
5.00	4.84	3	FH—F—H$_F$

Distance between end atoms

Experience has shown that in a case such as this the first peak generally indicates a value higher than the one finally accepted.[14] Band

spectral data give 0.864 for the FH distance;[15] further, it is now well established that hydrogen bond formation elongates the HX separation only slightly.[16] Hence a reasonable value for the FH spacing in polymerized hydrogen fluoride is 1.00 Å. The FH—F distance indicated (2.56 Å.) is
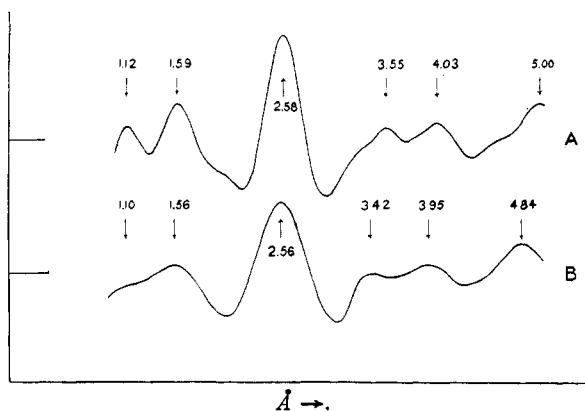

Fig. 2.—Modified radial distribution curves (method of Schomaker) for the first and final sets, respectively. The principal interatomic distances are indicated.

somewhat greater than the ones found in the alkali hydrogen fluorides.[17] Finally, to within the accuracy of the present method (±15°) one may place the H atoms on line with the fluorine atoms, so that the H—F separation is 1.56 Å.

for the hydrides of boron, S. H. Bauer, *ibid.*, **59**, 1096 (1937); **60**, 524, 805 (1938).

(15) H. Sponer, "Molekülspektren," Vol. I, Verlag von Julius Springer, Berlin, 1935.

(16) R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937). R. C. Herman and R. Hofstadter [*J. Chem. Phys.*, 6, 534 (1938)] suggest that the O–H distance is stretched from 0.97 Å. to approximately 1.07 Å. on hydrogen bond formation.

(17) For a summary of the data reported in the literature see M. L. Huggins, *J. Org. Chem.*, 1, 407 (1937). The following FHF distances have been determined: NaHF$_2$ 2.51 ± 2 Å.; KHF$_2$ 2.25 ± 0.2; NH$_4$HF$_2$ 2.37 ± 0.1 Å.

(14) See the radial distribution curves for the hydrocarbons. L. Pauling and L. O. Brockway, THIS JOURNAL, **59**, 1223 (1937);

Using these assignments and the three larger distances given by the final radial distribution, a set of independent values for the F–F–F angle are obtained

$$\overset{1}{F}\overset{2}{-H}\text{---}F^3$$
$$\diagdown H^4$$
$$\diagdown F^5$$

142° (4.84, 1–5)
142° (3.42, 1–4)
141° (3.95, 2–5)
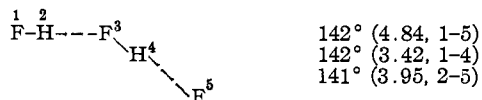
The possibility that the vapor of hydrogen fluoride (at the time the diffraction pattern is produced) consists predominantly of hexamers possessing a ring structure is thus definitely eliminated. Further evidence is presented by a com-
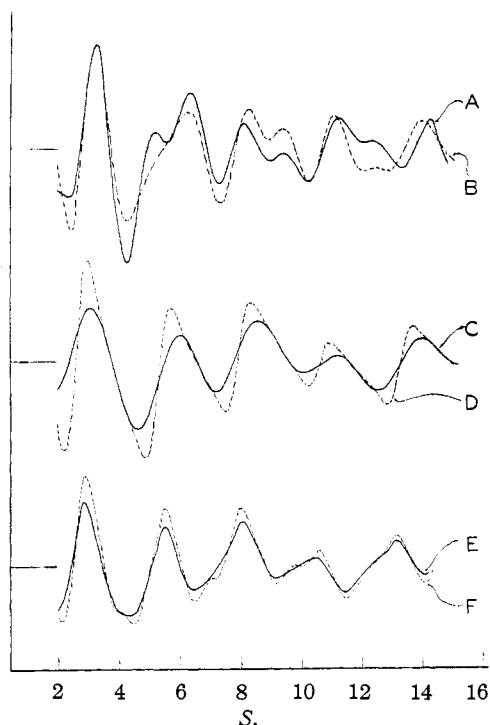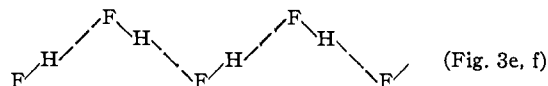

Fig. 3.—Theoretical intensity curves for the following models: A. Hexagonal; (HF)$_6$, F at corners, H midway between fluorine atoms; the F–F separation = 2.37 Å. B. Hexagonal; (HF)$_6$, F at corners, H nearer to one of the fluorine atoms; F–F = 2.37Å., H–F = 0.92 Å. C. Linear; FH—FH; F–F = 2.37 Å., H–F = 0.92 Å. D. Linear, as above; intensity for (HF)$_4$ divided by two so that this curve would be comparable to C. E. Zig-zag chain; (HF)$_3$; FFF angle 142°; F–F = 2.56 Å., HF = 1.00 Å. F. Zig-zag chain, as above; intensity for (HF)$_5$ divided by five-thirds so that this curve would be comparable to E.

parison of the calculated intensity distributions for two ring models (Fig. 3a, b) with the one observed. On the other hand, the forms of the

curves predicted on the basis either of the linear model

F–H---F–H---F–H---   (Fig. 3c, d)
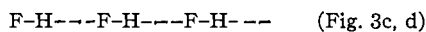
or of the zig-zag chain

$$\diagup F\diagdown_H\diagdown\diagup F\diagdown_H\diagdown$$
$$F\diagup^H\diagdown\diagup_F\diagup^H\diagdown\diagup_F$$ (Fig. 3e, f)

agree well with the observed pattern, the curve for the zig-zag model being somewhat more satisfactory. Also, the zig-zag model is favored by the radial distribution curve and is therefore proposed as being essentially the correct one. The fact that the peak at 4.9 Å. is of an intensity appreciably less than that at 2.6 Å. indicates that the polymers are mostly of low molecular weight; i. e., trimers, tetramers and pentamers. The fuzziness of the photographs is explained by the internal rotations which have little other effect on the pattern, apparently due to the large "valence" angles.

In summary, when the saturated vapor of hydrogen fluoride is allowed to expand into an evacuated space through a very small opening, the electron diffraction patterns of the gas obtained immediately at the hole definitely exclude the possibility that the polymer present in the largest concentration has a hexagonal ring structure. The observed intensity distribution is compatible with the zig-zag chain model shown above and indicates the presence of several species of polymers. Best values for the interatomic distances are

F–H 1.00 ± 0.06 Å.
F---H   1.55 ± .06
F–H---F 2.55 ± .03

The FFF angle is approximately 140 ± 5°, and the hydrogen atoms are on line with the fluorine atoms (±15°). The data substantiate the original suggestion that polymerization is due to hydrogen bond formation.

Discussion

The assumption that only the single equilibrium 6HF = (HF)$_6$ is of importance is open to question. As was indicated in the introduction, no cause can be shown for the predominant stability of the hexamer relative to that possessed by polymers of higher and lower order. Further, to retain it the electron diffraction data would have to be discarded on the basis of the possibility that in the very short interval between opening the valve and making the exposure the rings break up into

pentamers, tetramers, etc., but that the latter take a much longer time to dissociate completely as would be demanded by the equation of Simons and Hildebrand.[18] Although not impossible this seems improbable. Let us then make the assumption, based on the electron diffraction data, that the vapor and liquid consists of a series of chain-like molecules in equilibrium; the following properties of the gas and liquid are considered from that point of view.

Vapor Density.—The available vapor density data can be accounted for equally well on the basis of a continued equilibrium. The fact that n is so close to six should be regarded as fortuitous.

Heat of Vaporization.—If the liquid consists of long chain polymers, the heat of vaporization per apparent molecular weight in the vapor phase is equal approximately to the energy of dissociation of one hydrogen bond. Upon artificially separating the energy of the liquid into E_{H-bond} (a primary valence force) and E_V (in which are lumped all van der Waals forces such as orientation, dispersion, etc.), one may write

$$\text{heat of vap.} = [(m - 1)E_H - mE_V]/m$$

where m is the average number of units of the apparent molecular weight which are associated in the liquid. Since E_H and E_V are of the same order of magnitude the observed calorimetric value of about 6.2 kcal. from the liquid at its boiling point to the saturated vapor[19] is, therefore, to be expected. A closer estimate of the ratio E_V/E_H, permits one to compute the ratio of broken to undissociated bonds in the liquid; various methods lead to an average polymerization ranging between six and ten.

Surface Energy.—Over the temperature range 0–20° the surface energy of hydrogen fluoride is only 34/116 that of water while the ratio of their heats of vaporization per apparent molecular weight in the vapor is 62/105. As a possible explanation we suggest that since the polymers may take on a nearly planar configuration, the process of transporting an $(HF)_x$ molecule from the body of the liquid entirely to the surface may involve the breaking of no hydrogen bonds. On the other hand, due to the tetrahedral coördination

of oxygen, water polymers must be considered three dimensional in structure; to bring a polymer to the surface and to permit the molecules to attain the lowest energy state through proper orientation at the interface involves the definite breaking of some hydrogen bonds.

In order to explain the fact that the Eötvös constant does not vary appreciably with temperature over a long temperature range, we shall have to assume that, as the equilibria are shifted to higher orders in the liquid, either the polymer composition remains constant with temperature or the characteristics of the different species are very similar.

Association in the Vapor Phase.—The association of hydrogen fluoride in the vapor is very high compared to that of water and the alcohols. This indicates that the FH—F bond is stronger than the OH—O bond provided the measured association is entirely due to hydrogen bond formation. The greater ionic character of the HF bond accounts largely for the difference in bond strengths.

Dielectric Constant.—For chain polymers of a highly polar substance one would expect a large dielectric constant. The model treated by Lars Onsager[20] would be approximated by ring, but not by chain, polymers. Hence the discrepancy between the moment expected[21] and that calculated from the equation quoted below points directly to chain polymerization. For fairly large ϵ, Onsager's formula reduces to

$$\frac{M}{d}\left[\frac{2\epsilon - n^2}{(n^2 - 2)^2}\right] = \frac{4\pi N}{9kT}\mu^2$$

where n is the index of refraction, and all the other symbols have their usual significance. If the index is approximately equal to 1.5, values of μ for the average polymer ranging from $2.9D$ at 0° to $3.3D$ at −73° are obtained. This variation may imply that there is a tendency for the chains to extend to their full length at the lower temperatures. The large increase in ϵ no longer appears anomalous. Parallel to the case of hydrogen fluoride, Onsager found that in liquid water a moment of the order of $3D$ must be assigned to the polymers.

Further studies of the dielectric properties of the pure liquid, particularly their variation with the frequency used, would be of great interest.

(18) We found that when a very narrow and short lead-in tube was used to join the valve with the nozzle, the photographs were the same as with a wide long tube. From the density of the pattern one may estimate that the pressure of polymers at the point of diffraction was greater than 100 mm.

(19) The calorimetric value varies with temperature. Simons and Bouknight, THIS JOURNAL, **55**, 1458 (1933); Fredenhagen and Willmann, Z. anorg. allgem. Chem., **210**, 217 (1933).

(20) L. Onsager, THIS JOURNAL, **58**, 1486 (1936).

(21) C. H. D. Clark estimated the moment to be 1.6D [Physik. Z., **35**, 622 (1934)], while Smallwood thought it nearer to 2.0D [Z. physik. Chem., **B19**, 242 (1932)].

Water–hydrogen fluoride mixtures also present unusual properties for study through this means.

The assumption of an equilibrium of a series of chain-like polymers has not yet given us an adequate explanation of the apparent approach of the molecular weight of the gas to the value 120 as the temperature is lowered. The viscous behavior of the liquid is also difficult to understand. On the one hand, since the experimental heat of activation for viscous flow for many normal liquids is in the neighborhood of a third or fourth of the heat of vaporization,[22] one would expect hydrogen fluoride to have a considerably greater fluidity than does water. On the other hand, the chain lengths are estimated to be much longer in the former than in the latter substance and hence the viscosity should be correspondingly greater for hydrogen fluoride. Although no measurements have been made, qualitative observations indicate that the viscosity must be low.

The structure of hydrogen fluoride is of considerable interest; infrared and Raman spectra might be used to test the correctness of the model suggested in this paper.

Summary

An electron diffraction study of gaseous hydrogen fluoride resulted in patterns which are incom-

(22) J. Hirschfelder, D. Stevenson and H. Eyring, *J. Chem. Phys.*, **5**, 896 (1937).

patible with a hexagonal structure wherein the fluorine atoms are at the corners and the hydrogen atoms at any position along the sides; agreement between observed and calculated intensity curves was found, however, when a zig-zag chain configuration was assumed. The fuzziness of the rings strongly supports the view that a number of different polymers are present.

Best values for the interatomic distances are:

$$\text{F–H} \quad 1.00 \pm 0.06 \text{ Å.}$$
$$\text{F---H} \quad 1.55 \pm .06 \text{ Å.}$$
$$\text{F–H---F} \quad 2.55 \pm .03 \text{ Å.}$$

The average FFF angle is $140 \pm 5°$, and the hydrogen atoms are on line with the fluorine atoms ($\pm 15°$).

The possibility that the saturated vapor consists of the monomer and a chain or ring hexamer which dissociates into various chain-like fragments before the photographs are taken, when the vapor suddenly is allowed to expand into the evacuated chamber, has not been eliminated definitely; but this appears unlikely for there are a sufficient number of collisions in the gas nozzle for the gas to reach its equilibrium composition. Several of the properties of liquid hydrogen fluoride have been correlated on the basis of a continued equilibrium between chain polymers, and the difficulties of this assumption are also indicated.

The Vapor Pressure and Critical Constants of Normal Butane

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

In the course of a study of the compressibility of normal butane, we measured the vapor pressure of butane at several temperatures and investigated several isotherms in the critical region thereby locating the critical point. The method of procedure has been described elsewhere[1] and is the same as that used to locate the critical points of propane[2] and normal heptane,[3] the bomb with the glass liner being used for normal butane.

The *n*-butane was obtained from the Buffalo Laboratory of The Linde Air Products Company

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

(2) J. A. Beattie, N. Poffenberger and C. Hadlock, *J. Chem. Phys.*, **3**, 96 (1935).

(3) J. A. Beattie and W. C. Kay, THIS JOURNAL, **59**, 1586 (1937).

through the courtesy of Dr. L. I. Dana. It was fractionated by us five times, mainly for the purpose of removing permanent gases. Two separate loadings of the compressibility bomb were made: the vapor pressure at 75, 100, 125 and 150° and the isotherms in the critical region were investigated before the compressibility runs were made with the first loading; and the vapor pressure at 150° and the critical isotherm were measured with the second loading.

Results

Vapor Pressure.—The vapor pressures of normal butane are given in Table I. At each