

The long-ordered arrangement of 2-oleyl-1,3-distearin has been found to be different from the long-ordered arrangement of tristearin. From the X-ray diffraction data of 2-oleyl-1,3-distearin and related homologs, it was possible to propose an arrangement of glyceride molecules such that the lowered melting points of these compounds could be explained.

The crystallization of 2-oleyl-1,3-dimyristin

from solvent was found to yield the  $\beta'$  phase. This phase is apparently associated with the high-est melting form of this compound.

The fatty acid configuration of an oleyldistearin isolated from the seed fat of *Garcinia Indica* (Kokum butter) was definitely established by comparison of its X-ray diffraction data with the data obtained upon a synthetic 2-oleyl-1,3-distearin.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

## The Dipole Moment of Hydrogen Fluoride and the Ionic Character of Bonds

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In the discussion of the ionic character of the chemical bond, the dipole moments of the hydrogen halide molecules have played an important part.<sup>1a,2,3,4</sup> Of these, the moment of the hydrogen fluoride molecule was not determined experimentally because of the extreme reactivity of the substance. An early calculation by Kirkwood<sup>5</sup> gave a moment lower than that of hydrogen chloride, which led to an estimate of  $0.8 \times 10^{-18}$  e. s. u. for its value, while a more recent calculation by Dyatkina<sup>6</sup> gave a value of 3.09.

Since the predominantly ionic character attributed to the hydrogen-fluorine bond in contrast to the predominantly covalent character of the other hydrogen-halogen bonds involves a large difference in polarity and a correspondingly large uncertainty in quantitative conclusions based on the estimated polarity or moment of the hydrogen fluoride molecule, an experimental determination of the moment of the molecule has, for a long time, been highly desirable. It has now been possible to overcome the experimental difficulties caused by the extreme reactivity of hydrogen fluoride and measure the dielectric constant of the vapor.

### Apparatus and Method of Measurement

For the measurement of the dielectric constant of hydrogen fluoride vapor over a range of temperature and pressure, a measuring condenser and vacuum system were constructed of materials which, during a run, gave no measurable reaction with hydrogen fluoride at temperatures up to 100°. The cell was attached to the electrical measuring circuit previously used<sup>7</sup> in measuring the dielectric constants of gases and calibrated in the usual way, measurement of the dielectric constants of air and carbon dioxide being used as checks on the cali-

bration. It is hoped that a detailed description of the cell and vacuum system may be given in a future paper. The measurements at each temperature were carried out over a range of pressure, capacity readings being taken at four or five different pressures, and the dielectric constant at 760 mm. was calculated from the slope of the capacity-pressure curve as in earlier work.<sup>7</sup> The absence of any consistent drift in the readings during a period of time comparable to that required for the measurement showed the absence of error due to corrosion effects in the cell and the constancy of the moment values with temperature showed the absence of any error due to molecular association, which, even at atmospheric pressure, is negligible at the higher temperatures used. The accuracy of the measurements was somewhat less than that with the usual cell and vacuum system, but, in the moment values calculated from the results of 11 runs, the maximum deviation from the mean was only 2.1% and the average deviation only 0.9%.

### Experimental Results

In Table I are listed the values of the molar polarization,  $P$ , of hydrogen fluoride calculated from the dielectric constant measurement at each

TABLE I  
POLARIZATION AND DIPOLE MOMENT VALUES OF HYDROGEN FLUORIDE

$T$ , °K.	$P$ , cc.	$\mu \times 10^{18}$
305.1	76.1	1.92
324.1	70.1	1.91
332.3	67.8	1.90
	68.6	1.91
338.6	68.1	1.92
	65.5	1.88
351.8	66.3	1.93
	68.1	1.95
366.9	63.3	1.92
374.1	59.3	1.88
	59.3	1.88

Mean value 1.91

(1) Present address: Bell Telephone Laboratories, New York.

(1a) Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, Chap. II.

(2) Malone, *J. Chem. Phys.*, **1**, 197 (1933).

(3) Smyth, *J. Phys. Chem.*, **41**, 209 (1937); *THIS JOURNAL*, **60**, 183 (1938); **63**, 57 (1941).

(4) Wall, *ibid.*, **61**, 1051 (1939); **62**, 800 (1940).

(5) Kirkwood, *Physik. Z.*, **33**, 259 (1932).

(6) Dyatkina, *Acta Physicochim. U. R. S. S.*, **13**, 639 (1940).

(7) Wiswall and Smyth, *J. Chem. Phys.*, **9**, 352 (1941); Hurdis and Smyth, *THIS JOURNAL*, **64**, 2829 (1942).

absolute temperature,  $T$ . The third column gives the values of the moment,  $\mu$ , calculated from the difference between the polarization and the molar refraction, for which an approximate value,<sup>8</sup> 2.0, was used. The maximum uncertainty in this small molar refraction value can affect the dipole moment by no more than 1%.

### Discussion of Results

It has been found<sup>1a,2,3</sup> for the other three hydrogen halides that the electronegativity difference calculated from energy data and the dipole moments were very similar in value, which led to the belief<sup>3</sup> that the moment of hydrogen fluoride should be close to the electronegativity difference 1.9. The agreement is even closer in the case of hydrogen fluoride than in those of the other hydrogen halides, as shown in Table II, where  $x_A$  is the electronegativity of hydrogen and  $x_B$  that of the halogen as calculated by Pauling.<sup>1a</sup>

TABLE II  
ELECTRONEGATIVITY DIFFERENCE, DIPOLE MOMENT AND IONIC CHARACTER IN THE HYDROGEN-HALOGEN BONDS

	$(x_A - x_B)$	$\mu \times 10^{18}$	$er \times 10^{18}$	$\mu/er$ Obs.	$\mu/er$ Calcd. from equation		
					(1)	(2)	(3)
HF	1.9	1.91	4.44	0.430	0.60	0.43	0.43
HCl	0.9	1.03	6.07	.170	.19	.12	.17
HBr	.7	0.78	6.82	.114	.11	.07	.13
HI	.3	0.38	7.74	.049	.04	.01	.05

In Table II, the moment of the ionic structure for each molecule is calculated as  $er$ , the product of the ionic charge  $e$  and the internuclear distance  $r$ . As the most satisfactory approximation now available,  $\mu/er$  may be taken as a measure of the amount of ionic character possessed by a bond. The value of this quantity for hydrogen fluoride

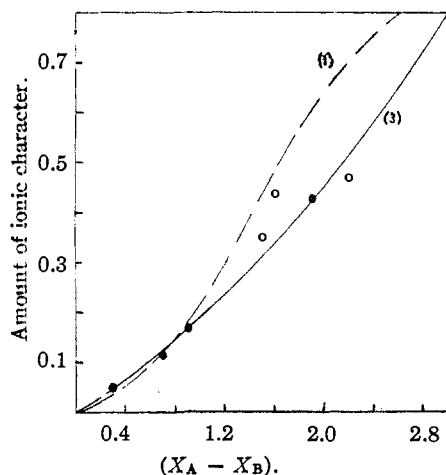


Fig. 1.—Relation of amount of ionic character of a bond A—B to the difference in the electronegativities ( $X_A - X_B$ ) of the atoms: ●, hydrogen halides; ○ alkali halides.

(8) Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., Inc., New York, N. Y., 1931, p. 149.

in Table II shows that, although the bond has two-and one-half times the amount of ionic character of the hydrogen-chlorine bond, it is still somewhat more covalent than ionic. Pauling's energy curves for hydrogen fluoride, of which the ionic curve cut below the covalent one, indicated<sup>1a</sup> an amount of ionic character just over one-half, which would require a dipole moment slightly greater than  $0.5 er$ , instead of the value  $0.43 er$  here observed.

In the absence of an experimental value for the dipole moment of hydrogen fluoride, Pauling estimated 60% as a reasonable value for the amount of ionic character in the bond and used<sup>1a</sup> it with the values calculated from the moments of the other three hydrogen halides repeated in Table II to construct a curve relating the amount of ionic character of a bond A—B to the difference in electronegativity ( $x_A - x_B$ ) of the atoms. This curve, which had a sigmoid form, was represented by an empirical equation

$$\text{Amount of ionic character} = 1 - e^{-0.25(x_A - x_B)^2} \quad (1)$$

which gave the fractions of ionic character for the hydrogen halides listed under (1) in Table II. Adjustment of the empirical constant  $C = 0.25$  to  $C = 0.156$  gives the similar equation

$$\text{Amount of ionic character} = 1 - e^{-0.156(x_A - x_B)^2} \quad (2)$$

which gives the correct value for the amount of ionic character of the hydrogen-fluorine bond but too low values for the other hydrogen-halogen bonds as shown under (2) in Table II. Although extreme irregularity has sometimes been observed<sup>3</sup> in such curves for bonds in polyatomic molecules, the experimental point for hydrogen fluoride falls on a curve through or very close to the origin and the points for the other hydrogen halides, which may be represented by the empirical equation

$$\text{Amount of ionic character} = 0.16(x_A - x_B) + 0.035(x_A - x_B)^2 \quad (3)$$

This gives the amounts of ionic character listed under (3) in Table II in very close agreement with the observed hydrogen halide values, as shown also by the calculated curve and the experimental points in Fig. 1. Although no great significance should be attached to so long an extrapolation, this equation gives the plausible value 91% for the ionic character of cesium fluoride, which has the greatest electronegativity difference, 3.3, of any possible pair of elements. It also gives better agreement than equation (1) with the ionic characters of the bonds in three salt molecules, calculated<sup>3</sup> from the approximate moments given by molecular beam measurements, as shown

TABLE III  
IONIC CHARACTER IN DIATOMIC ALKALI HALIDE MOLECULES

	Obs.	Calcd. (1)	Calcd. (3)
NaI	0.35	0.43	0.32
KI	.44	.47	.35
KCl	.47	.70	.52

The average difference between the values under "Obs." calculated from the rough moment values and plotted as circles in Fig. 1 and those calculated from the electronegativity equation (3) is only half as great as that between "Obs." and "Calcd. (1)," obtained from the electronegativity equation (1). It thus seems worth while to use equation (3) for the construction of a table which may be employed to estimate the approximate amount of ionic character of a bond from the electronegativity difference of the two bonded atoms. In Table IV, the amounts of ionic character calculated from equation (3) are multiplied by 100 to give the percentage of ionic character. The values in the latter part of the table are even more approximate than the others since they are the result of an extrapolation. Although equation (3) gives a reasonable enough value for the ionic character of cesium fluoride, it would give more than 100% ionic character for hypothetical electronegativity differences greater than 3.5 and is obviously not to be applied at the extreme limits of the electronegativity difference, where, in any event, the approximate character of the underlying theory renders meaningless the calculation of a very small amount of covalent character or a very small amount of ionic character.

TABLE IV  
RELATION OF AMOUNT OF IONIC CHARACTER OF A BOND A-B TO THE DIFFERENCE IN THE ELECTRONEGATIVITIES ( $x_A - x_B$ ) OF THE ATOMS

$(x_A - x_B)$	% Ionic	$(x_A - x_B)$	% Ionic
0.2	3	1.8	40
.4	7	2.0	46
.6	11	2.2	52
.8	15	2.4	58.5
1.0	19.5	2.6	65
1.2	24	2.8	72
1.4	29	3.0	79.5
1.6	34.5	3.2	87

#### Summary

The dipole moment of hydrogen fluoride has been measured in the vapor state.

The moment value, which is numerically identical with the electronegativity difference between hydrogen and fluorine calculated from energy data, shows the hydrogen-fluorine bond to have 43% ionic character.

A new table is constructed for the estimation of the approximate amount of ionic character in a bond from the difference in the electronegativities of the two bonded atoms.

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## The Heat Capacities, Heats of Transition, Heats of Fusion and Entropies of Cyclopentane, Methylcyclopentane and Methylcyclohexane<sup>1</sup>

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The Bureau of Mines has begun recently a research program to obtain precise and accurate values of the thermodynamic constants of hydrocarbons and related compounds. In this paper we present the results of our low temperature investigation of three naphthenes. All of these compounds have been investigated by other workers. Cyclopentane was studied by Jacobs and Parks<sup>4</sup> from 90° K. to room temperature and also by Aston, Fink and Schuman<sup>5</sup> over the temperature range 12 to 291° K. We have thought it desirable to repeat the measurements because of the importance of the experimental value of the entropy in helping to decide on the configuration of this molecule and also as a further check on the agreement of thermal data from this Laboratory and Penn State. Methylcyclopentane<sup>6</sup> and methylcyclohexane<sup>7</sup> were also studied by the Stanford workers from about 90° K. to room temperature.

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(4) Jacobs and Parks, *THIS JOURNAL*, **58**, 2354 (1936).

(5) Aston, Fink and Schuman, *ibid.*, **65**, 341 (1943).

(6) Huffman, Parks and Barmore, *ibid.*, **53**, 3876 (1931).

(7) Parks and Huffman, *ibid.*, **52**, 4381 (1930).

#### Description of Materials

The samples of API-NBS hydrocarbons have been made available by the American Petroleum Institute and the National Bureau of Standards through the A. P. I. Research Project 44. The samples were purified at the National Bureau of Standards by A. P. I. Research Project 6 under the supervision of F. D. Rossini, from material supplied by several laboratories.

**Cyclopentane**, by the A. P. I. Research Project 45 on the "Synthesis and Properties of Hydrocarbons of Low Molecular Weight" at the Ohio State University, under the supervision of Cecil E. Board.

**Methylcyclopentane**, by the Houdry Process Corporation, through the courtesy of E. A. Smith.

**Methylcyclohexane**, by the A. P. I. Research Project 45 at the Ohio State University, and the Barrett Division of the Allied Chemical and Dye Corporation.

In the course of our calorimetric investigation, we have also studied the melting points of these compounds, under equilibrium conditions in the usual manner. The experimental and certain derived data for these compounds are summarized in Table I. Since the measurements were made on the compounds in a sealed calorimeter under their own vapor pressure, the observed temperatures are triple points. In determining the temperatures corresponding to a given fraction in the liquid form, the calorimeter and environment were kept at the same temperature (as indicated by a copper-constantan difference couple) and