

## The Constancy of the Polarization of Non—Polar Molecules

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that the frequency  $1220\text{ cm}^{-1}$  is associated with the carbon-fluorine bond. This is not very likely to be correct, since all of the monohalides of benzene have frequencies in the neighborhood of  $1200\text{ cm}^{-1}$ .

From the existing data, it is not yet possible to draw definite conclusions with regard to the structure of benzene and its monohalides. When an assumption is made as to the symmetry of the fluorobenzene molecule, it is possible, by the methods developed by Brester<sup>8</sup> and Placzek,<sup>9</sup> to make certain statements about the normal vibrations of the molecule. If it be assumed, for example, that the fluorobenzene molecule is plane and has the symmetry  $C_{2v}$  (i.e., one two-fold symmetry axis and a symmetry plane passing through the axis) there will be 11 normal vibrations that are symmetrical with respect to both symmetry elements. The strongest and most highly polarized Raman lines will belong to this group. In addition, there will be 3 normal vibrations which are symmetrical with respect to a rotation of  $\pi$  about the axis and antisymmetrical with respect to a reflection in the symmetry plane. This group of frequencies is

forbidden in the infrared absorption but will occur in the Raman effect as lines with a depolarization of 6/7. Further, there are 6 normal vibrations that are antisymmetrical with respect to a rotation and symmetrical with respect to a reflection and, finally, 10 normal vibrations which are antisymmetrical with respect to both symmetry elements. Both of the last groups give Raman lines with a depolarization of 6/7.

If, on the other hand, the benzene molecule has a three-fold rather than a six-fold symmetry axis, as indicated by the Kekulé formula and by recent work of Weiler,<sup>10</sup> the fluorobenzene molecule would probably have at most just a single symmetry plane. The normal vibrations would then fall into two groups, 21 vibrations which are symmetrical with respect to a reflection in the symmetry plane and 9 that are antisymmetrical with respect to such a reflection. The symmetrical vibrations should, on the whole, be more intense in the Raman spectrum than the antisymmetrical vibrations.

The data on the Raman and infrared spectra of fluorobenzene and the other monohalides of benzene are not yet sufficiently complete to determine which, if either, of these models is the correct one.

<sup>8</sup> C. J. Brester, *Kristallsymmetrie und Reststrahlen*, Utrecht, 1923.

<sup>9</sup> Cf. G. Placzek, *Rayleigh-Streuung und Raman-Effekt*, Marx: Handbuch der Radiologie, 2nd ed., Vol. 6, Part II, Braunschweig, 1934.

<sup>10</sup> J. Weiler, *Zeits. f. Physik* **89**, 58 (1934).

## The Constancy of the Polarization of Non-Polar Molecules

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The dielectric constants of the vapors of *n*-hexane and *n*-heptane are measured over a range of temperature and used to show that the molecules of these substances have no detectable dipole moments. The constancy of the polarizations of non-polar vapors in contrast to the slight rise with

temperature of the polarizations of the same substances in the liquid state is attributed to the elimination of the intermolecular action which lowers slightly the polarizability of the molecules in the liquid state.

**B**ECAUSE of the general use of hexane and heptane as solvents in dipole moment measurements, it was deemed desirable to check the zero values assigned to their moments from measurements upon the liquids by examination of the vapors. At the same time, it has been possible to obtain further information upon the

more general question of the constancy of the polarization of non-polar molecules.

The dielectric constants of the vapors were measured as before.<sup>1</sup> The polarization  $P$  at each absolute temperature  $T$  was calculated from the

<sup>1</sup> K. B. McAlpine and C. P. Smyth, *J. Am. Chem. Soc.* **55**, 453 (1933); *J. Chem. Phys.* **2**, 499 (1934).

dielectric constant  $\epsilon$  and the molar volume  $V$  as  $P = [(\epsilon - 1)/(\epsilon + 2)]V$ . The extrapolation to zero pressure to eliminate the error in  $V$  caused by deviation of the vapor from ideal behavior was less satisfactory than usual because of the magnitude of the deviation due to the large size of the molecules. Consequently, in the case of heptane, the extrapolated values,  $P_0$ , are given only to one decimal place. For hexane, the values are more accurate and are taken from the polarization-pressure curve at 760 mm also, these being recorded as  $P_{760}$ .  $P_{760}$  contains, of course, the error caused by use of the ideal gas law to calculate  $V$ .

#### PURIFICATION OF MATERIALS

##### *n*-Hexane

A sample of a high degree of purity was lent by Dr. A. L. Henne and Dr. A. F. Shepard of the Midgley Foundation of the Ohio State University, to whom the writers wish to express their gratitude.

##### *n*-Heptane

Material from the Ethyl Gasoline Corporation was shaken with successive portions of concentrated sulfuric acid until the acid ceased to develop color. After removal of the acid layer, the heptane was washed with water, with potassium hydroxide solution and again with water. It was then shaken with mercury, filtered, dried over calcium chloride and distilled from sodium; b.p. 98.3°;  $n_D^{20}$ , 1.38763.

#### EXPERIMENTAL RESULTS

The experimental results are given in Table I.

TABLE I. Polarization values.

| $T$ , °K | <i>n</i> -Hexane |         | $T$ , °K | <i>n</i> -Heptane |       |
|----------|------------------|---------|----------|-------------------|-------|
|          | $P_{760}$        | $P_0$   |          | $P_{760}$         | $P_0$ |
| 337.7    | 31.55            | 30.10   | 348.2    | 34.7              |       |
| 388.3    | 30.80            | 30.08   | 357.4    | 34.7              |       |
| 428.2    | 30.39            | 30.02   | 396.8    | 35.1              |       |
| 484.3    | 30.13            | 29.94   | 460.9    | 35.0              |       |
| 558.4    | (29.40)          | (29.40) | 501.3    | 34.9              |       |

#### DISCUSSION OF RESULTS

The polarization values for hexane show how the effect of deviation from ideal behavior

diminishes with rising temperature, the difference between  $P_{760}$  and  $P_0$  becoming small. The apparent small decrease in  $P_0$  with rising temperature becomes greater as the temperature is higher, while, as the function of the reciprocal of the absolute temperature given by the Debye equation, it should become smaller if the molecule possesses a dipole moment. Although the thermal decomposition of hexane at these temperatures should be negligibly small,<sup>2</sup> it seems probable that the large surface of the gold-palladium alloy of the cell in which the vapor is measured causes a slight decomposition into smaller molecules of lower polarization, the increased decomposition with rising temperature being so pronounced at 558.4° that the polarization value is enclosed in parentheses. It is probable, therefore, that the true polarization is approximately constant at 30.1. This is in contrast to the small linear rise with temperature shown by hexane and other hydrocarbons in the liquid state.<sup>3, 4</sup> Liquid *n*-hexane at 323°K has a polarization 29.92 and its polarization-temperature curve extrapolated to about 370°K would give a polarization equal to that of the vapor. It may be remarked here that the tendency previously observed in several cases for the points to fall below the slowly ascending straight line of the polarization-temperature curve when temperatures not far below the boiling point are reached may be attributed to the separation of gas which is in solution at low temperatures and to the consequent formation of bubbles between the condenser plates.

The variation with temperature of the polarization of heptane is no greater than the possible error in the values and shows no definite trend. The mean 34.9 would seem to be approximately correct. At room temperature the polarization of the liquid is 34.5 and extrapolation of its polarization-temperature curve gives 34.9 at about 410°K. For both hexane and heptane, the absence of any decrease in polarization with rising temperature, other than that presumably arising from slight decomposition, points to zero moment for both molecules in conformity with

<sup>2</sup> F. E. Frey and H. J. Hepp, Ind. and Eng. Chem. **25**, 441 (1933).

<sup>3</sup> C. P. Smyth and W. N. Stoops, J. Am. Chem. Soc. **50**, 1883 (1928).

<sup>4</sup> R. W. Dornte and C. P. Smyth, J. Am. Chem. Soc. **52**, 3546 (1930).

previous results on the substances in the liquid state and with the zero values found for gaseous methane,<sup>5</sup> ethane<sup>6</sup> and propane.<sup>1</sup>

In the liquid paraffins<sup>3, 4</sup> and in liquid carbon tetrachloride and carbon bisulfide, investigated recently in this laboratory by Professor A. E. Stearn, the polarization is an approximately linear function of temperature, increasing about 1 percent for each 100° rise in temperature. The measurements on the vapors cannot be as accurate as those on the liquids but the experimental errors in the vapor values are not so large as to obscure a tendency toward a 1 percent per 100° rise in the polarizations of the seven non-polar hydrocarbon vapors which have been accurately measured. Over temperature ranges of 150° to 260° the maximum difference between the lowest and the highest polarization value of each substance investigated was not more than 1.2 percent with the exception of the early values for ethane, which showed a difference of 1.7 percent. A variation like that in the liquid would give an increase of about 1.5 to 2.6 percent in the vapor over these temperature ranges, a change which would make itself readily apparent in the measurements. In liquid carbon bisulfide, the polarization increases from 20.96 at 203°K to 21.20 at 303°K, while Zahn<sup>7</sup> reported a mean value 22.36 for the vapor, the maximum difference between three values from 325.1° to 489.2°K being 0.4 percent.

It was suggested in earlier work<sup>3</sup> that the force fields of adjacent molecules in the liquid might slightly reduce the ease of displacement of the electrons in the molecules and hence the polariza-

tion, while, as the molecular separation and motion increased with rising temperature, the effect of the force fields would decrease and the polarization increase. As an argument against this hypothesis, it was pointed out later<sup>4</sup> that, in binary mixtures of heptane with substances having strongly polar molecules, the refractions of the components were practically independent of the composition of the mixtures,<sup>8</sup> although the internal field must have varied considerably with the concentration of the dipoles in the liquid. In recent work upon the effect of solvent upon the moment of ethylene chloride in solution,<sup>9</sup> it was found that the solvent raised the moment of the ethylene chloride molecule above that found for the vapor but that chloroform, which has a moment  $1.05 \times 10^{-18}$ , did not raise the moment more than did non-polar solvents. It was suggested, therefore, that the effect of the solvent was due to the electric field associated with the outer part of the molecule and falling off inversely as a high power of the distance. If the lowering of the polarizability of a molecule in the liquid is due to this field, it might well vary with concentration by an undetectable amount. It is possible, therefore, that the polarization of a liquid may be slightly lowered by these molecular force fields, the effect of which diminishes with rising temperature and disappears when the molecules are separated by vaporization of the liquid, leaving the very slightly higher and constant polarization observed for the vapor. Actually, it is only the condition of the molecule in the vapor state to which the Lorentz-Lorenz and the Debye equations should apply.

<sup>5</sup> R. Sänger, *Phys. Zeits.* **27**, 556 (1926).

<sup>6</sup> C. P. Smyth and C. T. Zahn, *J. Am. Chem. Soc.* **47**, 2501 (1925).

<sup>7</sup> C. T. Zahn, *Phys. Rev.* **35**, 848 (1930).

<sup>8</sup> C. P. Smyth, E. W. Engel and E. B. Wilson, Jr., *J. Am. Chem. Soc.* **51**, 1736 (1929).

<sup>9</sup> A. E. Stearn and C. P. Smyth, *J. Am. Chem. Soc.* **56** (1934).