

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Molecular Rotation in Solid Arsine and Other Hydrides

BY C. P. SMYTH AND S. A. MCNEIGHT

This paper presents measurements of dielectric constant made in continuation of previous work^{1,2} on the rotation or non-rotation of molecules in solid hydrides and discusses the results in relation to the properties of the other hydrides and the factors affecting rotation. The apparatus and technique employed were essentially the same as that described in earlier papers^{1,3} from this Laboratory, the same bridge being used. However, because liquid hydrogen cyanide attacked the gold cylinders of the measuring cell normally used, a new condenser was made for this substance from tin tubes turned to such a size as to give a geometrical capacity of 10 micromicrofarads. When liquid hydrogen became available for the first time for the measurements on arsine, the brass block surrounding the glass cell containing the condenser was replaced by a similar block of lead in order to obtain greater heat capacity and slow down the rate of temperature change at very low temperature. For the measurement of these low temperatures the calibration of the platinum resistance thermometer used in the other measurements was extended by using the boiling point of hydrogen as an additional fixed point.

Preparation of Materials

Hydrogen Cyanide.—This material was prepared from potassium cyanide and sulfuric acid according to the directions given in "Organic Syntheses."⁴ It was condensed at 0° and the middle portion distilled into the condenser cell; m. p. 259.2°K.

Hydrogen Selenide.—Hydrogen selenide was prepared in an oxygen-free apparatus by dropping freshly boiled, dilute hydrochloric acid upon aluminum selenide, which had been prepared by the ignition of an intimate mixture of powdered aluminum and selenium containing a 50% excess of selenium over that required by the formula Al_2Se_3 . The gas was dried by passage over calcium chloride and phosphorus pentoxide and condensed by means of a slush of acetone and solid carbon dioxide, which froze it immediately to the solid, preventing possible decomposition in the liquid phase.

Arsine.—Arsine was generated in a system previously flushed out with oxygen-free hydrogen by dropping 30% sulfuric acid upon an alloy of 53% zinc and 47% arsenic

according to the method used by Cohen.⁵ It was dried by passage over calcium chloride and phosphorus pentoxide and condensed by a slush of acetone and solid carbon dioxide.

Experimental Results

The dielectric constants ϵ and the specific conductances k ($\text{ohm}^{-1} \text{cm.}^{-1}$) are given in Table I, the absolute temperatures being given in the first column and the frequencies in kilocycles across the top of each group of data. Many determinations at intermediate temperatures and frequencies are omitted for the sake of brevity, but more values than usual are included for arsine because of its peculiar behavior. All the values listed were obtained with rising temperature, but arsine was taken up and down several times between liquid air temperature and the melting point. The upper transition temperature and the melting point obtained were identical with those in Table I and the shape of the dielectric constant-temperature curve obtained for this region was the same as that in Fig. 3. As the liquid was refrozen each time, small differences naturally occurred in the absolute values of the dielectric constant. Consequently, none of these check values are given in Table I and most of the specific conductances, which did not change significantly above the lowest transition, are omitted. As the hydrogen selenide measurements, through an unfortunate chain of circumstances, are incomplete, only the dielectric constant values are given.

Discussion of Results

The first attempt to measure solid hydrogen cyanide by Dr. W. S. Walls in this Laboratory was unsuccessful because the interaction of the liquid cyanide with the gold condenser was sufficient to give high conductance on solidification. The first results obtained in the present investigation were uncertain for the same reason, but the results in Table I obtained with a tin condenser appear satisfactory. The melting point 259.2°K. obtained for this sample of hydrogen cyanide is in excellent agreement with the value 259.1°K. given by "International Critical Tables" and 259°K. found by Lewis and Schutz,⁶ but its lack

(1) Smyth and Hitchcock, *THIS JOURNAL*, **55**, 1830 (1933).

(2) Smyth and Hitchcock, *ibid.*, **56**, 1084 (1934).

(3) Smyth and Hitchcock, *ibid.*, **54**, 4631 (1932); Smyth and Kamerling, *ibid.*, **55**, 462 (1933).

(4) "Organic Syntheses," John Wiley and Sons, Inc., New York, Coll. Vol. I, 1932, p. 307.

(5) Cohen, *Z. physik. Chem.*, **25**, 483 (1898).

(6) Lewis and Schutz, *THIS JOURNAL*, **56**, 1002 (1934).

TABLE I

DIELECTRIC CONSTANTS AND SPECIFIC CONDUCTANCES

Hydrogen Cyanide (m. p. 259.2°K.)

| Kc. T, °K. | 50 | 5 | 0.5 | 50 | 5 | 0.5 |
|---------------|-----------------|------|------|------|------|-------|
| | $k \times 10^9$ | | | | | |
| 86.7 | 2.35 | 2.39 | 2.33 | 0.40 | 0.07 | <0.05 |
| 102.2 | 2.38 | 2.41 | 2.36 | .40 | .07 | <.05 |
| 111.9 | 2.40 | 2.42 | 2.38 | .66 | .07 | <.05 |
| 122.0 | 2.42 | 2.42 | 2.41 | .73 | .07 | <.05 |
| 130.1 | 2.43 | 2.45 | 2.41 | .73 | .07 | <.05 |
| 137.2 | 2.44 | 2.46 | 2.43 | .86 | .07 | <.05 |
| 159.8 | 2.56 | 2.57 | 2.53 | 1.06 | .07 | <.05 |
| 167.6 | 2.58 | 2.60 | 2.56 | 1.06 | .07 | <.05 |
| 182.2 | 2.65 | 2.68 | 2.63 | 1.06 | .07 | <.05 |
| 193.5 | 2.70 | 2.73 | 2.72 | 1.06 | .13 | <.05 |
| 197.4 | 2.73 | 2.75 | 2.76 | 1.06 | .13 | <.05 |
| 211.2 | 2.81 | 2.86 | 2.97 | 1.25 | .26 | .07 |
| 223.7 | 2.91 | 3.01 | 3.22 | 2.11 | .33 | .07 |
| 226.5 | 2.95 | 3.03 | 3.33 | 2.24 | .46 | .13 |
| 246.8 | 3.61 | 4.70 | 8.17 | 17.4 | 6.89 | 4.92 |
| 250.9 | 5.2 | 7.9 | 19.4 | 109 | 95 | 119 |
| 252.1 | 5.6 | 9.1 | 26.0 | 125 | 151 | 163 |

Hydrogen Selenide

| Kc. T, °K. | 50 | 5 | 0.5 |
|---------------|------|------|------|
| 86.8 | 7.21 | 7.21 | 7.11 |
| 88.6 | 7.19 | 7.17 | 7.08 |
| 97.3 | 7.03 | 7.01 | 6.94 |
| 101.4 | 6.96 | 6.93 | 6.84 |
| 105.0 | 6.88 | 6.86 | 6.77 |
| 109.3 | 6.76 | 6.74 | 6.66 |
| 116.1 | 6.58 | 6.55 | 6.48 |
| 125.3 | 6.35 | 6.32 | 6.23 |
| 130.6 | 6.22 | | |
| 186.0 | 5.45 | 5.41 | 5.40 |
| 196.3 | 5.34 | 5.29 | 5.35 |
| 200.2 | 5.36 | 5.37 | 5.54 |
| 203.8 | 5.36 | 5.37 | 5.59 |
| 208.5 | 5.15 | 5.20 | |

Arsine (m. p. 156.4°K.)

| Kc. T, °K. | 50 | 20 | 5 | 1 | 0.5 |
|---------------|-----------------|------|------|------|------|
| | $k \times 10^8$ | | | | |
| 20.5 | 0.73 | 0.65 | 0.23 | 0.07 | 0.07 |
| 20.7 | .73 | 1.05 | .40 | .13 | .09 |
| 20.8 | 1.27 | 0.81 | .27 | .07 | .05 |
| 21.9 | 1.27 | .81 | .27 | .07 | .05 |
| 25.8 | 1.27 | .60 | .14 | .05 | .05 |
| 30.9 | 0.36 | .18 | .11 | .05 | .05 |
| 33.7 | .36 | .09 | .09 | .05 | .05 |
| 156.1 | .36 | .16 | .09 | .04 | .04 |

Liquid

| Kc. T, °K. | 50 | 20 | 5 | 1 | 0.5 |
|---------------|-----------------|------|------|------|------|
| | $k \times 10^8$ | | | | |
| 194.5 | .36 | .16 | .09 | .04 | .04 |
| 20.5 | 2.80 | 2.82 | 2.85 | 2.91 | 2.93 |
| 20.7 | 2.82 | 2.84 | 2.89 | 2.97 | 3.00 |
| 20.8 | 2.82 | 2.83 | 2.88 | 2.94 | 2.97 |
| 21.9 | 2.84 | 2.88 | 2.94 | 3.00 | 3.01 |
| 25.8 | 3.02 | 3.06 | 3.09 | 3.11 | 3.11 |
| 27.7 | 3.12 | | | | |
| 28.4 | 3.14 | | | | |

| | | | | | |
|-------|------|------|------|------|------|
| 30.9 | 3.17 | 3.17 | 3.15 | 3.16 | 3.18 |
| 31.5 | 3.19 | | | | |
| 31.8 | 3.21 | | | | |
| 32.1 | 3.39 | | | | |
| 32.1 | 3.46 | | | | |
| 32.2 | 3.46 | | | | |
| 32.4 | 3.45 | | | | |
| 32.8 | 3.44 | | | | |
| 33.7 | 3.42 | 3.41 | 3.38 | 3.38 | 3.38 |
| 34.6 | 3.39 | | | | |
| 40.2 | 3.27 | | | | |
| 44.1 | 3.22 | | | | |
| 45.8 | 3.19 | 3.17 | 3.14 | 3.14 | 3.13 |
| 47.8 | 3.17 | 3.15 | 3.14 | 3.14 | 3.14 |
| 54.9 | 3.10 | 3.09 | 3.08 | 3.09 | 3.12 |
| 58.0 | 3.08 | 3.06 | 3.06 | 3.08 | 3.07 |
| 71.9 | 2.96 | 2.95 | 2.94 | 2.97 | 2.98 |
| 76.2 | 2.92 | 2.90 | 2.90 | 2.92 | 2.93 |
| 79.5 | 2.85 | 2.84 | 2.84 | 2.86 | 2.85 |
| 82.5 | 2.78 | | | | 2.82 |
| 86.5 | 2.72 | | | | 2.77 |
| 88.5 | 2.70 | 2.72 | 2.71 | 2.74 | 2.75 |
| 93.4 | 2.69 | 2.69 | 2.68 | 2.71 | 2.72 |
| 98.0 | 2.68 | 2.67 | 2.66 | 2.70 | 2.71 |
| 103.9 | 2.67 | 2.66 | 2.66 | 2.68 | 2.70 |
| 106.4 | 2.66 | | | | |
| 106.6 | 2.66 | | | | |
| 106.6 | 2.71 | | | | |
| 107.0 | 2.71 | 2.70 | 2.70 | 2.72 | 2.75 |
| 113.6 | 2.70 | 2.68 | 2.67 | 2.68 | 2.70 |
| 116.7 | 2.69 | 2.68 | 2.66 | 2.67 | 2.69 |
| 121.8 | 2.68 | 2.67 | 2.65 | 2.67 | 2.68 |
| 127.3 | 2.68 | 2.67 | 2.65 | 2.66 | 2.68 |
| 134.0 | 2.68 | 2.66 | 2.64 | 2.66 | 2.67 |
| 140.1 | 2.67 | 2.66 | 2.64 | 2.66 | 2.67 |
| 143.5 | 2.67 | 2.66 | 2.64 | 2.66 | 2.69 |
| 151.2 | 2.67 | 2.66 | 2.64 | 2.66 | 2.69 |
| 156.1 | 2.64 | 2.62 | 2.62 | 2.63 | 2.64 |
| 156.3 | 2.51 | | | | |
| 156.4 | 2.52 | | | | |
| 156.4 | 2.58 | | | | |

Liquid

| | | | | | |
|-------|------|------|------|------|------|
| 157.1 | 2.57 | 2.56 | 2.54 | 2.58 | 2.60 |
| 165.5 | 2.54 | 2.54 | 2.52 | 2.53 | 2.54 |
| 171.4 | 2.52 | 2.51 | 2.50 | 2.54 | 2.53 |
| 181.1 | 2.48 | 2.46 | 2.45 | 2.45 | 2.48 |
| 187.6 | 2.46 | 2.44 | 2.44 | 2.45 | 2.48 |
| 194.5 | 2.41 | 2.40 | 2.40 | 2.40 | 2.41 |
| 200.9 | 2.38 | 2.38 | 2.38 | 2.39 | 2.41 |

of sharpness is indicative of the presence of impurities, which are presumably responsible for the rapid increase in the dielectric constant and conductance of the solid as the melting point is approached. The conductance becomes so high near the melting point that the dielectric constant can no longer be measured with any accuracy but a temperature-time curve shows the absence of any transition in this region. The dielectric constant-temperature curve in Fig. 1 shows no transition

and gives no positive evidence of molecular rotation. The gradual rise with temperature below the region of the melting point is probably due to the effect of increasing conductance and the rapid rise in the region of the melting point together with increasing dependence upon frequency is due both to the rapid increase in conductance resulting from the formation of liquid and the presence of ions and to the direct effect of liquid of high dielectric constant and ions in raising the dielectric constant. The value⁷ for liquid hydrogen cyanide 194.4 at 259.7°K., the highest found for any pure liquid, shows that the presence of appreciable quantities of liquid in the solid would raise the dielectric constant markedly and also shows that freedom of rotation in the solid would give a dielectric constant over 200 instead of between 2 and 3. Use of a density value 0.925 at 233°K.⁸ and of the Grüneisen rule together with a dielectric constant value from Table I gives a molar polarization 9.2 for the solid at 100°K. Subtraction of the electronic polarization 6.3⁹ gives 2.9 for the atomic polarization as compared to the zero value found in the more accurate measurements on the gas.⁹ The rough value 2.9, as far as it is significant at all, probably indicates that the dielectric constant values even at 100°K. are a little high because of conductance. However, the results certainly do not preclude the possibility of the rotation of an occasional molecule in the lattice of the solid, particularly as the region of the melting point is approached, but make it apparent that it is at most only a very occasional molecule that might have the freedom necessary for rotation.

In view of the freedom of molecular rotation in solid hydrogen chloride, bromide and iodide,¹ one might anticipate rotation in solid hydrogen cyanide. However, the factors which tend to prevent rotation are obviously stronger in the latter substance. The linear triatomic molecule of hydrogen cyanide must depart farther from a spherical shape than do the molecules of hydrogen chloride, bromide and iodide, as the minimum value for the distance of the hydrogen from the nitrogen nucleus would seem to be about 1.34 Å.¹⁰ as compared to an internuclear distance 1.28 Å. in hydrogen chloride and the maximum molecular diameter perpendicular to this axis in which the nuclei lie

must be considerably smaller in the hydrogen cyanide molecule. The hydrogen cyanide lattice, which has not yet been subjected to x-ray analysis, would seem, therefore, to offer the possibility of a molecular arrangement such that any considerable turning of the molecules would cause them to overlap and prevent further turning and, consequently, give no chance for free rotation. This appears to be the case in the cubic lattice of the linear carbon dioxide molecule.¹¹ If molecular rotation is not prevented by overlapping, the potential energy barrier which the molecule has to pass in order to rotate through an angle of 360° should be high because of the large dipole moment⁹ 2.93×10^{-18} , which is nearly three times as large as that of the hydrogen chloride molecule,¹² 1.03×10^{-18} . This potential energy barrier may well be so large that the thermal rotational energy of

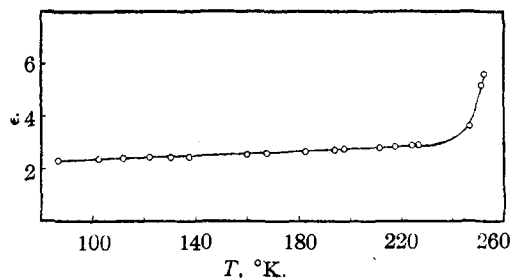


Fig. 1.—Temperature dependence of the dielectric constant (at 50 kc.) of hydrogen cyanide.

the molecules is too small below the melting point to make it possible for the molecules to pass, that is, to rotate. A possible third factor is the formation of a hydrogen bond between molecules, which gives abnormal properties to ammonia, water and hydrogen fluoride and hinders or prevents molecular rotation in the lattices of their solid forms. The first two factors, however, are quite sufficient to account for the non-rotation of the hydrogen cyanide molecule in the lattice of its solid form and Lewis and Schutz⁶ conclude that the great abnormality of the liquid form is due not to hydrogen bond formation but to the high dipole moment of the molecule.

The x-ray photographs of potassium cyanide, which crystallizes in a cubic lattice, give no evidence of separate carbon and nitrogen positions, which is probably indicative of rotation of the cyanide ion in the lattice¹¹ (p. 364). The potential barrier to rotation of this ion should be much

(7) Fredenhagen, *Trans. Am. Electrochem. Soc.*, **60**, 153 (1931).

(8) Werner, *Z. physik. Chem.*, **B4**, 371 (1929).

(9) Smyth and McAlpine, *This Journal*, **56**, 1697 (1934).

(10) Cf. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932).

(11) Wyckoff, "The Structure of Crystals," The Chemical Catalog Company, Inc., New York, 1931, p. 235.

(12) Zahn, *Phys. Rev.*, **24**, 400 (1924).

smaller than that for the hydrogen cyanide molecule for the departure of the ion from sphericity must be less than that of the molecule, its dipole moment should be much smaller, and the factor of the possible hydrogen bond is absent. There is, therefore, no conflict between the interpretation of the x-ray photographs as showing rotation of the cyanide ion in the potassium cyanide lattice and the non-rotation here found for the hydrogen cyanide molecule in its lattice.

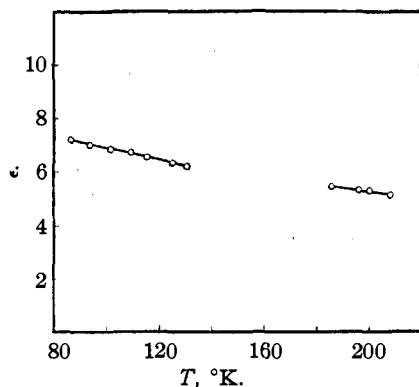


Fig. 2.—Temperature dependence of the dielectric constant (at 50 kc.) of hydrogen selenide.

The incomplete measurements on solid hydrogen selenide in Table I and Fig. 2 show by the high values of the dielectric constant and their increase with decreasing temperature as required by the Debye equation for polar molecules in the liquid and gaseous states that the molecules are able to rotate, probably with much the same freedom as in the liquid. The dielectric constant-temperature curve below 130.6°K. is sufficiently different from that above 186.0°K. to suggest a probable discontinuity somewhere between these two temperatures resulting from a transition like the upper transition found in hydrogen sulfide² and in hydrogen iodide.¹ Use of Natta's density value 2.456 for the cubic lattice at 103°K.¹³ and the Grüneisen rule gives a density value of 2.33 at the melting point, which, combined with the dielectric constant value at 86.8°K., gives a molar polarization value 23.4. As the molar refraction for the H_α line is 11.95¹⁴ and the atomic polarization must be small, this gives a value of about 12 for P_M , the polarization due to the dipole moment of the molecule. From this the apparent moment of the molecule is calculated to be 0.4×10^{-18} ,

(13) Natta, *Nature*, **127**, 129 (1931); *Atti accad. Lincei*, **11**, 749 (1930).

(14) Frivold, Hassel and Skjulstad, *Physik. Z.*, **37**, 134 (1936).

little lower than the rough value $0.5-0.6 \times 10^{-18}$ which one would estimate from consideration of the moments of other hydrides. Naturally, this is not to be taken as a determination of the dipole moment of hydrogen selenide, but is to be regarded as evidence that the molecule has much the same freedom of rotation in its lattice down to liquid air temperature that it has in the liquid.

Although the melting point of the arsine used was 3.2° below that given in "International Critical Tables," melting occurred sharply, but because of some tendency toward decomposition, the sample was probably not of a high degree of purity. In considering the data for arsine in Table I and Fig. 3, it should be borne in mind that, because of its small dipole moment¹⁵ 0.16×10^{-18} , the dielectric constant is small and increases but slowly with falling temperature. On this account, the scale used in Fig. 3 for the dielectric constant is

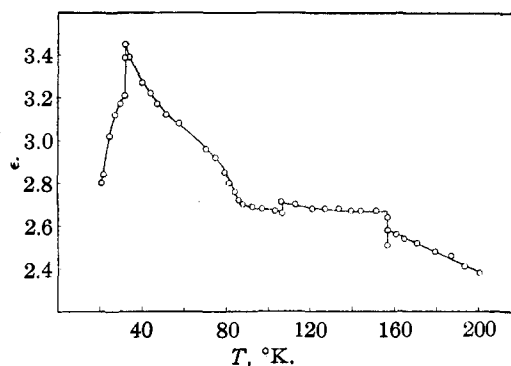


Fig. 3.—Temperature dependence of the dielectric constant (at 50 kc.) of arsine.

much larger than that usually employed so that secondary effects having nothing to do with the fundamental factors involved may affect the shape of the curve. The drop of the dielectric constant during melting below the value for either the solid or the liquid has not been previously observed as far as the authors know, although a sharp rise above the value for either the solid or the liquid has been observed in some cases where two phases presumably existed below the melting point because of considerable quantities of impurity.¹⁶ This drop and rise which occurs within a temperature range of only 0.3° is clearly shown by numerous values determined during the rising temperature run represented in Table I, but does not appear in either the cooling or the heating curve previously run through the melting point with the

(15) Watson, *Proc. Roy. Soc. (London)*, **117A**, 43 (1927).

(16) Cf. Yager and Morgan, *THIS JOURNAL*, **57**, 2071 (1935).

same sample. The upper transition point evident at 106.6°K. was checked accurately by a temperature-time curve. This transition appears similar to the slight upper transitions occurring in hydrogen bromide,¹ iodide,¹ sulfide² and, probably, in the selenide. As in these substances, the rate of change of the dielectric constant with temperature is much more rapid below it than above it. The two points of inflection between the two transitions probably arise from secondary effects of which we are unaware. A single unexplained point of inflection was found in the curves for hydrogen chloride, bromide and iodide, and in an unpublished curve for a sample of hydrogen sulfide slightly less pure than that for which a curve without inflection was published.

As incomplete cancellation of the effects of the inductance of the circuit causes small errors in the dielectric constant values, differences of 0.01 or 0.02 between values at different frequencies are meaningless. However, a pronounced anomalous dispersion is evident during the lower part of the transition which is incomplete at the lowest temperature reached. Although the material was maintained within 0.3° of this temperature for three hours, the rising temperature values in Table I agree well with those obtained during the relatively rapid initial cooling, showing that stable equilibrium existed throughout. The variation of the dielectric constant with frequency is greatest at 20.7°K., where the apparent conductance actually shows a maximum at 20 kc. Evidently at least some of the arsine molecules can rotate at 20.5°K. with a difficulty which decreases rapidly with rising temperature, the variation of the dielectric constant with frequency having disappeared at 30.9°K., where the transition is still incomplete. Above 31.8°K. the acquisition of rotational freedom occurs almost as sharply as does the entire process in hydrogen chloride at its one transition. Although the thermodynamic behavior of solid hydrogen¹⁷ requires molecular rotation and the specific heat-heat temperature curve for methane¹⁸ shows the setting in of rotation at 20.4°K., no molecule other than these has been found to rotate at so low a temperature as that here found for arsine.

Application of the Grüneisen rule to the density value¹⁹ 1.96 found for arsine at 103°K. gives the density at the melting point, which is used with

(17) Pauling, *Phys. Rev.*, **36**, 430 (1930).

(18) Clusius and Perlick, *Z. physik. Chem.*, **B24**, 313 (1934).

(19) Natta, *Gazz. chim. ital.*, **60**, 851 (1930).

the values in Table I to calculate a molar polarization 16.0 at 20.5°K., 19.1 at 33.7° and 15.3 at 151.2°. The apparent dipole moment calculated for the molecule from the variation of polarization with temperature in the region between 33.7 and 80°K. is 0.15×10^{-18} , indistinguishable from the value 0.16×10^{-18} obtained for the gas,¹⁵ which would seem to indicate freedom of molecular rotation in this region comparable to that in the liquid state.

In the three groups of hydrides of which ammonia, water and hydrogen fluoride are the first members, the smallest molecule does not rotate in the cases of solid ammonia² and hydrogen fluoride²⁰ and rotates only with great difficulty in ice, probably because of hydrogen bonds between the molecules or, possibly, merely because the smallest molecules with their large dipole moments are surrounded by the strongest fields of force. The larger molecules of these three groups of hydrides show rotation which extends to lower temperature the smaller the dipole moment, arsine being the molecule of smallest moment. In the next group of hydrides, methane, the first member, having zero dipole moment and no possibility of hydrogen bond formation, rotates down to very low temperature.¹⁸ It is evident that the moment of inertia of the molecule does not have the dominant effect in determining rotation or non-rotation that has been attributed to it at times. Monosilane²¹ requires a temperature 43° higher to bring about molecular rotation than does methane, but this may be due to stronger intermolecular forces rather than to the larger moment of inertia of the molecule.

Of these hydrides which have been considered, all have cubic lattices in the regions of free molecular rotation except hydrogen iodide, which is tetragonal, its *a*- and *c*-axes differing by only 8%, and possibly monosilane which has not been determined. Since free rotation gives spherical symmetry to a molecule, it is natural that molecules possessing it form lattices corresponding to an arrangement of close-packed spheres, which is roughly approximated by the molecular arrangement in a liquid. It is not surprising, therefore, that the dielectric behavior of solid arsine above its lower transition could be roughly approximated by extrapolation of the curve for the liquid. Indeed, from a molecular point of view these solid

(20) Clusius, Hiller and Vaughen, *Z. physik. Chem.*, **B8**, 427 (1930); Clusius, *Z. Elektrochem.*, **39**, 598 (1933).

(21) Clusius, *Z. physik. Chem.*, **23**, 213 (1933).

hydrides with rotating molecules differ little from liquids.

Summary

The dielectric constants and specific conductances of solid hydrogen cyanide and hydrogen selenide have been measured from liquid air temperature to the regions of the melting point and those of arsine have been measured from liquid hydrogen temperature to the region of the boiling point over a frequency range from 0.5 to 50 kilo-

cycles. No molecular rotation is found in solid hydrogen cyanide while the molecule rotates freely in the selenide even at liquid air temperature. The arsine molecule rotates freely down to 32.1°K. where a transition sets in, which is not complete at 20.5°K. and is accompanied by some anomalous dispersion. The molecules of the hydrides tend to rotate more readily the smaller their dipole moments.

PRINCETON, NEW JERSEY

RECEIVED JUNE 29, 1936

[CONTRIBUTION FROM THE WILLIAM G. KERCKHOFF LABORATORIES OF THE BIOLOGICAL SCIENCES, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Thermal Data. VI. The Heats of Combustion and Free Energies of Seven Organic Compounds Containing Nitrogen

BY HUGH M. HUFFMAN, EMORY L. ELLIS AND SIDNEY W. FOX

In the first paper¹ of this series we presented heat capacity data for the following seven compounds, *d*-alanine, *l*-asparagine (anhydrous), *l*-asparagine monohydrate, *l*-aspartic acid, *d*-glutamic acid, creatine and creatinine. These data were used to calculate the entropies of the compounds, which were further utilized in conjunction with the heats of combustion and certain other auxiliary data to calculate the standard free energies of formation of these compounds.

Due to the general unreliability of the older combustion data appearing in the literature, we have redetermined this quantity for each of the seven compounds mentioned above. In so doing we have kept constantly before us the necessity of establishing the purity and the physical state of the compounds as well as the need for calorimetry of high precision and accuracy.

These new combustion data have been used in conjunction with the entropies obtained by Huffman and Borsook¹ and certain other auxiliary data to calculate new and more reliable free energy data for these compounds.

Calorimetric Method

The method and apparatus used have been described in previous communications.² No essential changes in method or apparatus have been made. All of the combustions were made in a Parr bomb having a volume of 0.380 liter with an initial oxygen pressure of 30 atm. and with 1 ml. of water in the bomb. The platinum wire technique^{2a} was used exclusively. During the course of this investi-

gation our resistance thermometer developed a short circuit. After repair the thermometer characteristics were found to have changed but upon recalibration identical results for the energy equivalent of the calorimeter were found. Numerous calibrations of the calorimeter have been made, at irregular intervals throughout the course of this investigation, with Bureau of Standards benzoic acid, samples 39d and 39e, having for its isothermal heat of combustion at 25.0° the value 26,419 international joules per gram true mass. We have used oxygen from several cylinders supplied by the "Linde Air Products Company" and at cylinder pressures varying from 1950 to 450 pounds. The precision of our calibration data has remained the same as that previously reported, namely, an extreme deviation from the mean of slightly more than 0.01%. The precision error calculated from the formula recommended by Rossini³ was 0.005%.

In several cases we have found it necessary to use oil as an auxiliary substance. The combustion value of this oil has been controlled by occasional combustions and the value found was 10,830 ± 3 cal. per gram weighed in air. When the mass of the oil is determined by difference after adding it directly to the sample in the crucible an additional uncertainty is introduced when the material is hygroscopic. To avoid this uncertainty as well as to permit the addition of small quantities, the following method was adopted. The oil was kept in a small hypodermic syringe and the amount added was determined from the mass difference in this syringe.

Units and Corrections

The unit of energy used throughout this paper is the defined conventional calorie which is derived from the international joule by multiplying by the factor 1.0004/4.185. The method of calculation, the corrections and the symbols used are the same as those given by Stiehler and Huffman.^{2b} The molecular weights are based on the 1935 table of atomic weights. In applying the correction for true mass

(1) Huffman and Borsook, *THIS JOURNAL*, **54**, 4297 (1932).

(2) (a) Huffman and Ellis, *ibid.*, **57**, 41 (1935); (b) Stiehler and Huffman, *ibid.*, **57**, 1734 (1935).

(3) Rossini, *Chem. Rev.*, **18**, 233 (1936).