[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Dielectric Constants and Transitions of Solid Ammonia, Hydrogen Sulfide and Methyl Alcohol

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Previous investigations of dielectric constants have shown the occurrence of dipole rotation in a number of crystalline solids and the factors influencing this rotation have been discussed.[1,2] After the completion of the measurements to be described in this paper, a note by Kemp and Denison[3] summarized the results of similar measurements upon hydrogen sulfide. The present paper presents in detail the results of measurements of the dielectric constants of ammonia, hydrogen sulfide and methyl alcohol, which have been summarized in a letter to the Editor of this Journal.[4] The apparatus and technique employed was similar to that described in our earlier papers.[5,2]

Preparation of Materials

Ammonia.—The gas obtained by gently warming concentrated ammonium hydroxide solution was passed through two drying towers of freshly crushed calcium oxide and then through a tube containing sodium wire. It was condensed in the dielectric constant cell after a stream of it had passed through the train for half an hour; m. p. −77.7°.

Hydrogen Sulfide.—The first sample was prepared by treating stibnite crystals with concentrated hydrochloric acid and warming. The gas was passed through water to remove hydrogen chloride, dried with calcium chloride and phosphorus pentoxide, and condensed in the cell by means of a slush of solid carbon dioxide and ether; m. p. −85.5°. A second sample was prepared by the hydrolysis of aluminum sulfide, the gas being washed, dried and condensed as in the case of the first sample; m. p. −85.4°. This second sample was used to obtain the results given for hydrogen sulfide in Table I.

Experimental Results

The dielectric constants ϵ and the specific conductances k (ohm^{-1} cm.$^{-1}$) are given in Table I, the absolute temperatures being given in the first column and the frequency in kilocycles used in each measurement being designated as "k. c." Many determinations not needed for the accurate establishment of the behavior of the substances are omitted from Table I. The conductances of ammonia at 5 and at 1 kilocycles are omitted since they are practically the same as those at 0.3. The values for ammonia were obtained with rising temperature except for one set enclosed in parentheses. For solid hydrogen sulfide in the neighborhood of the transitions found, the dielectric constant and conductance were measured only at 5 kilocycles, the small increase in conductance in these regions showing that there could be little variation of the dielectric constant with frequency. Throughout the rest of the temperature range, the dielectric constants at 60 and at 0.3 were found to be identical with those at 5, while the conductances at 60 were very roughly ten times those at 5 and those at 0.3 were indistinguishable from those at 5, all varying too little with temperature to make the effect of the latter apparent. The results for hydrogen sulfide are, therefore, given for 5 kilocycles only but are given both for decreasing and for rising temperature. In Fig. 1 the values obtained with rising temperature are represented by hollow circles and those with decreasing temperature by filled-in circles, the two sets of values being in excellent agreement except in the transition regions. The molar polarization, $P = (\epsilon - 1)M/(\epsilon + 2)d$, in which M is the molecular weight and d the density, is given for hydrogen sulfide in Table II and the values are plotted against $1/T$ in Fig. 2. By use of the Grüneisen rule as in the earlier work on the hydrogen halides, the approximate density of the solid at the melting point was calculated from the value obtained by Natta[6] at 103°K. from the results of x-ray analysis and was used for d throughout. The density of the liquid was obtained from the measurements of Steele, McIntosh and Archibald.[7] Because of cavities in the solid, the absolute values of the dielectric constants and polarizations are probably

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(1) Cone, Denison and Kemp, THIS JOURNAL, **53**, 1278 (1931).

(2) Smyth and Hitchcock, *ibid.*, **54**, 4631 (1932); **55**, 1830 (1933).

(3) Kemp and Denison, *ibid.*, **55**, 251 (1933).

(4) Smyth and Hitchcock, *ibid.*, **55**, 1296 (1933).

(5) Smyth and Kamerling, *ibid.*, **55**, 462 (1933).

(6) Natta, *Atti accad. Lincei*, **11**, 749 (1930).

(7) Steele, McIntosh and Archibald, *Phil. Trans. Roy. Soc.* (London), **205**, 99 (1905).

low, but, relative to one another, small differences should be significant.

TABLE I

DIELECTRIC CONSTANTS AND SPECIFIC CONDUCTANCES

Ammonia (m. p. 195.4°K.)

Kc.	60	5	1	0.3	60	0.3
T, °K.	ϵ				$k \times 10^9$	
87.0	3.37	3.36	3.36	3.36	<1.0	<0.1
95.2	3.38	3.38	3.37	3.38	<1.0	<0.1
110.5	3.40	3.41	3.39	3.39	<1.0	<0.1
122.5	3.41	3.40	3.40	3.40	<1.0	<0.1
136.9	3.42	3.41	3.41	3.41	<1.0	<0.1
150.5	3.41	3.41	3.41	3.42	<1.0	<0.1
(172.1)	(3.46)	(3.51)	(3.61)	(3.75)	(1.7)	(0.5)
172.9	3.46	3.48	3.48	3.63	0.9	0.2
179.3	3.53	3.62	3.77	4.08	2.6	2.1
188.6	3.67	3.90	4.12	4.62	7.0	3.3
194.1	3.84	4.03	4.27	4.83	8.4	3.5

Liquid

Kc.	20	20
T, °K.	ϵ	k
195.5	25	5.5×10^{-6}

Hydrogen Sulfide (m. p. 187.7°K.)

Decreasing temperature		Rising temperature	
T, °K.	ϵ(5 kc.)	T, °K.	ϵ(5 kc.)
174.1	11.17	89.6	3.31
168.0	11.45	95.3	3.36
152.0	12.35	100.1	3.40
140.9	13.15	102.9	3.45
132.0	13.91	104.0	3.49
127.8	14.32	104.1	4.66
127.0	14.40	104.2	6.97
126.2	14.69	104.3	14.30
126.1	16.41	104.4	19.62
125.4	16.52	104.5	19.95
120.8	17.33	104.6	20.10
117.5	17.94	107.0	19.62
116.1	18.20	110.1	19.09
111.9	19.10	115.8	17.99
104.9	20.65	126.3	16.06
103.2	21.15	126.5	15.10
102.9	20.08	126.6	14.27
102.9	7.52	131.6	13.78
102.8	3.62	169.6	11.25
101.9	3.46	174.0	11.05
91.3	3.32	177.6	10.92
86.0	3.29	183.7	10.72
82 9	3.29	187.4	10.57
		187.7	10.53
		Liquid	
		187.7	9.26

$k \times 10^9$ (5 kc.)		$k \times 10^9$ (5 kc.)	
174.1–102.9	<0.02	89.6– 95.3	<0.02
102.9– 91.3	.05	100.1–102.9	.03
86.0– 82.9	< .02	104.0–104.3	.05
		104.4	.03
		104.5–183.7	< .02
		187.4	.05
		187.7	.2
		Liquid	
		187.7	1.6

The results of the measurements on the first sample of hydrogen sulfide are omitted from the tables, although the melting point of the material was identical with that found by Kemp and Denison[3] and only 0.1° lower than that of the second sample. The dielectric constant of the first sample was close to that of the second in the liquid state and in the solid just below the melting point, but, as the temperature fell, the dielectric constant of the first sample rose through a maximum and descended through a flat minimum before reaching the high temperature transition point. The flat S-shape of this section of the curve somewhat resembled that found by Cone, Denison and Kemp[1] for hydrogen chloride. A faint suggestion of a much-flattened S is given by our curves for the hydrogen halides between their melting points and their high temperature transitions.[2] Although the inflection in our hydrogen halide curves was too slight to interfere with the linearity of the P–$1/T$ curves, the polarizations of this first sample of hydrogen sulfide gave no approximation to linearity when plotted against $1/T$. Between the measurements of the two samples of hydrogen sulfide, the number of concentric cylinders in the measuring cell was reduced from three to two. It seems possible that the S-shape may be due to some effect of the macrostructure of the solid. In the absence of a satisfactory explanation, it is best to record the fact for possible future use and employ the seemingly more satisfactory data on the second sample, which gave considerably higher dielectric constant values at the lower temperatures.

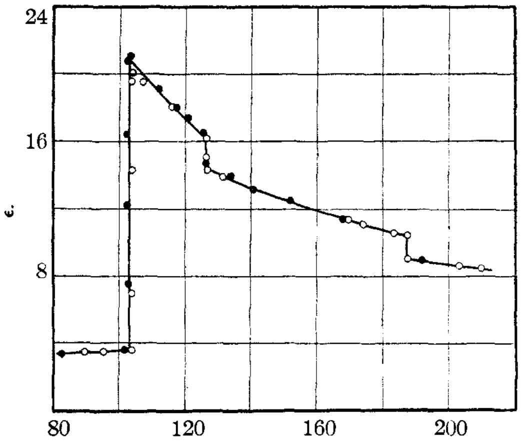

Fig. 1.—Temperature dependence of the dielectric constant (at 5 kc.) of hydrogen sulfide: ○, rising temperature; ●, decreasing temperature.

TABLE II

MOLAR POLARIZATION (5 kc.) OF HYDROGEN SULFIDE

MR_D(gas) = 9.57; $\mu = 0.95 \times 10^{-18}$; $d_{m.p.} = 1.12$

T, °K.	P	T, °K.	P	T, °K.	P
85	13.16	115	25.85	160	23.79
90	13.24	120	25.65	170	23.51
95	13.39	125	25.44	180	23.26
100	13.50	130	24.71	185	23.18
103	13.55 26.41	140	24.35	Liquid	
		150	24.03		
110	26.06			187.7	24.80

Although two samples of methyl alcohol were purified with some care, and were found to have the correct boiling point, their melting points were about 1° below that given in "International Critical Tables" and lacked sharpness. The account of the purification is therefore omitted and only a qualitative account is given of the results on this substance.

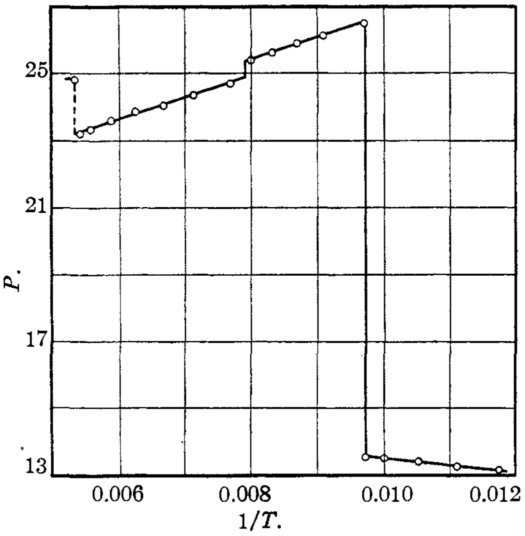

Fig. 2.—P–$1/T$ curve for hydrogen sulfide.

Discussion of Results

The melting point found for ammonia, 195.4°K., is identical with that given in "International Critical Tables," but the conductance of the liquid, 5.5×10^{-6}, just above the melting point as compared to a value less than 1×10^{-8} at $-33°$ given by "International Critical Tables" is sufficient to show the presence of traces of ionic impurities. In view of the great effect produced by very small quantities of ionic impurities in the case of ice,[2] it is safe to attribute to the effect of these impurities the increase in conductance and dielectric constant of the solid and the apparent slight anomalous dispersion as the melting point is approached. It may be concluded, therefore, that there is practically no dipole rotation in solid ammonia. This accords with the fact that Eucken and Karwat,[8] in specific heat measurements, have found no transitions in solid ammonia between 25°K. and the melting point.

The melting point found for hydrogen sulfide, 187.7°K., is in excellent agreement with the value 187.6°K. found by us for the first sample of the material and by Kemp and Denison and with the value 188° given by Clusius.[9] It is believed that these values are more accurate than the older values, 189.5°K. found by Maass and McIntosh[10] and 190.2°K. found by Steele, McIntosh and Archibald[7] and given in "International Critical Tables." The latter investigators found 1×10^{-7} for the conductance of liquid hydrogen sulfide, a value nearly 100 times those in Table I, which, in turn, are much higher than the value, less than 10^{-11}, found by Quam and Wilkinson,[11] which is presumably correct.

The dielectric constant curve in Fig. 1 shows a transition at 103.0°K. with falling temperature and at 104.1°K. with rising temperature. Temperature–time curves check these values well, the cooling curve giving 102.9°K. and the heating curve 104.1°K. Although a lag in transitions in the solid state is a familiar phenomenon,[12] this definite difference of 1.1° is surprising in view of the slow rate of temperature change to which the material was subjected. With rising temperature, the temperature of the solid rose only 0.1° during the first forty minutes of this transition and 0.4° during the entire transition, which lasted seventy minutes. The mean value for the temperature of transition, 103.5°, is identical with that found by Kemp and Denison and only 0.1° lower than that found by Clusius in specific heat measurements. Another transition at higher temperature is shown by the dielectric constant curve at 126.1°K. with falling temperature and 126.4°K. with rising temperature. The temperature–time curves give 126.3 and 126.6°. The smaller difference between the transition temperatures obtained on heating and on cooling seems to correspond to the smaller heat of transition observed by Clusius, 108.4 cal./mole, as compared to 361.2 cal./mole for the lower transi-

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[8] Eucken and Karwat, *Z. physik. Chem.*, **112**, 467 (1924).

[9] Clusius, *Z. Elektrochem.*, **39**, 598 (1933).

[10] Maass and McIntosh, *Trans. Roy. Soc. Canada*, [3] **8**, 65 (1914).

[11] Quam and Wilkinson, THIS JOURNAL, **47**, 989 (1925).

[12] *Cf.* Tammann, "States of Aggregation," D. Van Nostrand Company, New York, 1925, p. 125.

tion. The mean transition temperature, 126.3°K., is identical with that found by Kemp and Denison and only 0.1° higher than that found by Clusius from the specific heat curve.

The low temperature transition corresponds to a change from rotation to non-rotation of the dipoles like that in hydrogen chloride, for, below the transition, the polarization is less than 4 cm.^{3} greater than the refraction for the sodium D line and, above it, the much larger polarization varies linearly with $1/T$ as required by the Debye equation, $P = a + b/T$. As in the case of hydrogen chloride, the apparent dipole moment calculated from b is much smaller than that observed for the gas, about one-third as large in this case. Only a slight change in b, the slope of the curve, is brought about by the upper transition, thus indicating little change in the dipole rotation, and only a slight change in polarization is caused by fusion.

These results on ammonia and hydrogen sulfide and the earlier measurements on hydrogen chloride are in complete accord with the specific heat results of Clusius,[9] who found no transitions in solid hydrogen fluoride, ice and ammonia, while the corresponding larger molecules, hydrogen chloride, hydrogen sulfide and phosphine, showed rotational transitions. Clusius attributed the difference in behavior to larger dipole moments in the smaller molecules, bringing about a completely fixed molecular orientation on solidification. Actually, hydrogen fluoride may have a smaller dipole moment than the chloride. As the mutual potential energies of the dipoles vary inversely as the cubes of the distances between them, the smaller molecular sizes may also contribute to fixing the orientation, although the smaller moments of inertia reduce the energy required for molecular rotation. The apparent molecular rotation indicated by the dielectric constant of ice,[2,13] which decreases with falling temperature and rising frequency of the measuring field without any sharp transition, may be due to the possession of freedom of rotation by a small fraction of the molecules in the complex solid structure.[14]

The dielectric constant of methyl alcohol just below the freezing point is much lower than that of the liquid, but high enough to indicate some freedom of dipole rotation. Its rapid decrease with increasing frequency and decreasing temperature in this region may be due, to a considerable extent, at least, to impurities. A sharp drop at 159.1°K. to a value so low as evidently to arise almost wholly from the molecular polarizability indicates the practical cessation of dipole rotation. This transition is close to the average of those found from specific heat measurements, 157.4°K. by Kelley[15] and 161.1°K. by Parks.[16] Although this is a transition between two different crystalline forms, the dielectric constant of the higher temperature form is sufficiently large to indicate some dipole rotation. As the specific heat measurements of Parks show no transitions in ethyl and propyl alcohol, where larger size would tend to prevent rotation of the molecule as a whole but should not directly affect rotation of the hydroxyl group within the molecule, it appears probable that the dipole rotation in solid methyl alcohol is a rotation of the entire molecule rather than of the hydroxyl group within the molecule. For the present, however, this conclusion must be regarded as speculative.

Summary

The dielectric constants of ammonia, hydrogen sulfide and methyl alcohol have been measured from 83°K. to the melting points at frequencies from 0.3 to 60 kilocycles. In agreement with the results of specific heat measurements,no molecular rotation and no transitions are found in ammonia, while two transitions are found in hydrogen sulfide and one in methyl alcohol. For some distance below the melting point the molecules of hydrogen sulfide appear to possess almost the same freedom of rotation as in the liquid, while, in methyl alcohol, some freedom of molecular rotation apparently exists in the narrow region between the melting point and the transition point.

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(13) Wintsch, *Helv. Phys. Acta*, **5**, 126 (1932).

(14) *Cf.* Bernal and Fowler, *J. chim. phys.*, **1**, 515 (1933).

(15) Kelley, THIS JOURNAL, **51**, 180 (1929).

(16) Parks, *ibid.*, **47**, 338 (1925).