THE DIELECTRIC CONSTANTS OF SOLIDS AND MOLECULAR ROTATION

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INTRODUCTION

In recent years the dielectric constants of solids have received much less attention from scientific investigators than have those of liquids, which have given such valuable information concerning molecular structure. However, there is much of interest to be found in measurements of the dielectric constant of solids, particularly of solids with rotating molecules which will form the subject of a major part of the present discussion.

The dielectric constant of a substance was originally represented as arising from the induction of charges on the surfaces of the molecules (61, 10), the molar polarization P of the substance being given by the expression

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4\pi N}{3} \alpha_0$$

in which ϵ is the dielectric constant, M the molecular weight, d the density, N the number of molecules in a mole, and α_0 the dipole moment per molecule resulting from shift of charge induced by an electric field of unit intensity. The Maxwell relation (57) $\epsilon = n^2$, where n is the index of refraction, leads to identity between the molar polarization and the molar refraction. Substances for which the polarization is nearly equal to the molar refraction for visible light show an approximately constant polarization as required by the Clausius–Mosotti relation and, consequently, a dielectric constant which decreases slightly with rising temperature as the density decreases. Debye (19) accounted for the many substances which did not obey this relation by introducing the additional term

$$P_M = \frac{4\pi N}{3} \frac{\mu^2}{3kT}$$

in which μ is the permanent dipole moment of the molecule, k the Boltzmann gas constant, and T the absolute temperature. The entire expression may be written

$$P = a + b/T$$

Many determinations of the induced polarization a have shown it to be always larger, usually only slightly (76), than the molar refraction, which arises from the displacement of the electrons within each molecule and may, therefore, be represented as P_E. As this difference arises from the displacement of nuclei, atoms, or groups, which have too great inertia to be displaced in the rapidly alternating electric field of the light wave used in determining the electronic polarization P_E, it is called the atomic polarization P_A. $P_M = b/T$ may be much larger than $P_E + P_A = a$, but is, of course, zero when the molecules have no permanent dipole moments and will also be zero when the molecular dipoles are unable to orient in an externally applied field. The dielectric constant, therefore, gives us a means of examining not only the distribution and mobility of charge inside the molecule but also the freedom of the molecule in its environment.

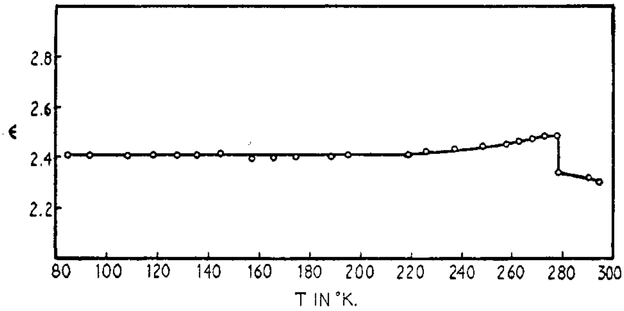

FIG. 1. Dielectric constant–temperature curve (at 50 kilocycles) of benzene

The experimental values for the dielectric constants of solids are less accurate than those for liquids, because of the difficulty of completely filling the space between the plates of the condenser with a homogeneous sample. The presence of impurities, particularly ionic impurities, even in extremely small quantities may introduce considerable errors in the neighborhood of the melting point. This latter effect necessitates caution in some cases in the interpretation of results near the melting point, but, in general, the validity of the conclusions to be drawn is not affected by the experimental errors.

NON-POLAR MOLECULES

For a solid consisting of non-polar molecules, that is, of molecules with no permanent dipole moment, the dielectric constant is very close to the square of the refractive index for visible light, and differs from the dielectric constant of the liquid only because of the difference in the number of molecules in unit volume. Thus, in the case of the non-polar substance benzene n_D^2 for the liquid at 20°C. is 2.25 and ϵ is 2.29 (84), while at 5°C. the dielectric constant of the supercooled liquid is 2.34 (78) and that of the solid 2.46. The failure of the dielectric constant–temperature curves for such solids (figure 1) to show any rise with increasing density at low temperatures is due to the fact that the material is usually frozen between the fixed plates of a condenser, so that increasing density does not alter the amount of material between the plates. The total polarization P is 27.01 for the vapor (58), 26.62 for the liquid at 10°C. (84), and 26.70 for the solid at 5°C. according to Errera (23), and 28.5 at 0°C. according to Morgan and Lowry (60). As P_E is 25.1, P_A may be taken as 1.9 (58). The difference in polarization between the solid and the liquid is evidently within the experimental error, as would be expected in view of the practically negligible effect which the environment of a group has upon its polarizability (75, 77). The case of benzene is typical of a large class of substances without dipole moment, such as the paraffins, whose dielectric constants depend upon the induced displacement of electrons and, to a very small extent, of atoms or groups in the molecules. These dielectric constants are almost independent of physical state and temperature, except in so far as these factors determine the number of molecules in unit volume, or, in other words, the number of charges present to undergo displacement. The slight rise of the curve for benzene near the melting point is the effect of minute traces of impurities.

NON-METALLIC IONIC SOLIDS

In non-metallic ionic solids, the dielectric constant still arises only from shift of charge as in the non-polar molecular solids, but the shift of ionic charge, which gives rise to P_A, may play a more important part than the electronic shift. Table 1 gives for the cubic latticed and, therefore, isotropic alkali metal halides except those of cesium the values of the dielectric constant ϵ and the squares of the refractive indices n_0 extrapolated from the visible region to infinite wave length by means of a classical dispersion formula, and table 2 gives the total and the atomic polarizations calculated from these values (24). The considerable differences between n_0^2 and ϵ are due to the displacements of the ions in the lattices. Both the total polarization P and the electronic P_E ($= P - P_A$) increase with increase in the size of either ion. The same trend is evident in the values of P_A, but it is only approximate. The larger one ion is, the smaller is the effect of the size of the other ion upon P_A. For ordinary field strengths, the actual ionic displacement is very small. For example, calculation shows that the average displacement of each ion in rubidium iodide produced by 300 volts per centimeter is only 10^{-6} A.U. As the displacement of the ions in the externally applied field depends upon the interionic forces, Errera

(24) has applied the Born theory of the lattice (6) to these dielectric constant values to calculate the infra-red wave lengths corresponding to the characteristic vibration frequencies in the lattices. From consideration of the fraction of the dielectric constant which is due to ionic displacement expressed as $(\epsilon - n_0^2)/(\epsilon - 1)$, Errera and Brasseur (26) conclude that, for solids of one family, the fraction of the total polarization dependent upon ionic displacement is greater, the smaller the ionic radius, the smaller the interionic distances, and the smaller the electronic polarizability. At first glance, this statement appears to be a direct contradiction of the evidence given by the P_A values in table 2 which tend to increase with ionic size.

TABLE 1

Dielectric constants and squares of refractive indices of alkali metal halides

	F		Cl		Br		I	
	ϵ	n_0^2	ϵ	n_0^2	ϵ	n_0^2	ϵ	n_0^2
Li	9.2	1.91	11.05	2.68	12.1	3.04	11.03	3.55
Na	4.9	1.74	5.77	2.32	5.99	2.60	6.60	2.96
K	6.05	1.83	4.76	2.17	4.78	2.35	4.94	2.64
Rb	5.91	1.93	5.20	2.18	4.70	2.34	4.81	2.58

TABLE 2

Total and atomic polarizations of alkali metal halides

	F		Cl		Br		I	
	P	P_A	P	P_A	P	P_A	P	P_A
Li	7.20	4.90	15.80	8.44	19.74	9.60	25.38	10.24
Na	8.45	5.48	16.58	8.30	20.05	8.90	26.60	10.44
K	14.63	9.57	20.83	10.29	25.10	11.65	30.18	11.45
Rb	17.32	10.73	25.21	13.02	27.25	12.06	33.41	12.82

Increasing ionic size and separation lessen the binding forces between ions of opposite charge and, therefore, cause increasing P_A. The conclusion of Errera and Brasseur is based upon the effect per cm.^{3} of substance, while the polarization values are based upon the number of molecules per mole. The greater number of ionic charges present per cm.^{3} in the substances formed of small ions more than compensates for the stronger binding forces and thus gives higher dielectric constants.

In anisotropic solids, the different forces in different directions cause differences in the dielectric constants in these directions. Thus, in the orthorhombic sulfates of strontium, barium, and lead—celestite, barite, and anglesite (26)—the refractive index of each is about the same along its three crystal axes, but the dielectric constant along the *b*-axis is approximately double those along the *a*- and *c*-axes, which are nearly equal. ϵ_b for anglesite has the unusually high value 54.6, more than ten times that due to electronic displacement alone. In a group of six rhombohedral carbonates, the refractive index along the equal *a*- and *b*-axes is larger than that along the *c*-axis. The dielectric constant along the *a*- and *b*-axes is slightly larger than that along the *c*-axis except in magnesite, where it is 15 per cent smaller than that along the *c*-axis. A group of four orthorhombic carbonates has almost equal refractive indices along the *a*- and *b*-axes, with somewhat lower values along the *c*-axis. The same is approximately true of the dielectric constants except in aragonite, which has a value along the *a*-axis 60 per cent higher than that along the *b*-axis. Titanium dioxide (71, 56) in the form of brown rutile, which is tetragonal, is a particularly striking example of the effect of ionic displacement, having a dielectric constant 170 parallel to its optic axis and a value 86 perpendicular to this axis. The excess of the mean values over the mean dielectric constant 78 found for transparent rutile may be due to impurities.

Rising temperature tends to decrease the dielectric constant of a non-metallic ionic solid by decreasing the number of molecules per cm.^{3} as in the case of the non-polar molecular solids. At the same time, however, the greater separation of the ions produced by the increasing volume weakens the forces between them and thus increases their ease of displacement. In the cases of calcium fluoride and sodium chloride examined by Bretscher (7), the calculated increase of dielectric constant due to weakening of the interionic forces is nearly three times as large as the decrease caused by decreasing density. The expression for the total variation of dielectric constant with temperature obtained by Bretscher is

$$\frac{1}{\epsilon}\frac{d\epsilon}{dT} = \left\{\frac{(\epsilon - \epsilon_0)}{3\epsilon}(n + 2) - \frac{\epsilon - \epsilon_0}{\epsilon} - \frac{(\epsilon_0 - 1)(\epsilon_0 + 2)}{3\epsilon}\right\}\frac{1}{V}\frac{\partial V}{\partial T}$$

where V is the volume and ϵ_0 is the contribution to the dielectric constant of all oscillators except that due to residual rays. The values calculated by Bretscher for the temperature variation of ϵ are considerably smaller than the observed, but of the correct order of magnitude.

NON-ROTATING POLAR MOLECULES

Solids consisting of polar molecules, that is, molecules possessing permanent dipole moments, commonly behave like those consisting of non-polar molecules, because solidification usually fixes the molecules with such rigidity in the lattice that orientation of the dipoles in an externally applied field is impossible. P_M is therefore zero, and the dielectric constant depends simply upon the displacement of charges induced inside the molecule. The values of the electronic polarization P_E are unaffected by the presence of the dipole moments and the values of P_A are little, if any, larger than those of the non-polar molecules (76). The dielectric constant of the solid thus depends upon the same factors as in the non-polar molecular solid. The dielectric constant temperature curve shows a great difference at the melting point, for, in the case of the non-polar molecular solid, the small change produced by melting is usually a slight drop caused by decrease in the number of molecules per cm.^{3}, while the polar molecules acquire freedom of rotation on melting and P_M changes abruptly from zero to a value often many times that of $P_E + P_A$. Nitromethane (85), which has a large dipole moment and, consequently, a large value of P_M in the liquid, affords a particularly striking example of this change at the melting point (figure 2). An impure sample of a polar substance may show a considerable increase in dielectric constant and in apparent conductance as the melting point is approached, presumably because of the separation of a small amount of a liquid phase. A slight increase in carefully purified solids may be due to the acquisition by an occasional molecule of sufficient

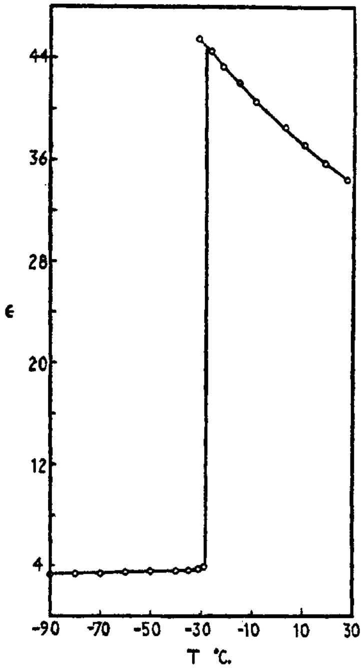

FIG. 2. Dielectric constant-temperature curve (at 70 kilocycles) of nitromethane

freedom to orient in an externally applied field or to the effect of increasing conductance upon the apparent value of the dielectric constant. A carefully purified solid nitrobenzene of melting point 5.67°C. showed an increase in dielectric constant from 3.25 at 0°C. to 3.62 at 5°C., while pure solid benzene of melting point 5.4°C. increased by only 0.009 from 0° to 5°C., and benzene saturated with water (0.01 to 0.05 per cent) before freezing increased by only 0.01 from 0° to 5°C. (78). These comparative figures would certainly be interpreted as giving evidence of some molecular rotation in the solid nitrobenzene were it not that a very minute amount of ionic impurity could conceivably have caused the rise in dielectric constant as the melting point was approached. It seems probable, however, that loosening of the molecular lattice as the melting point is approached gives sufficient freedom to an occasional molecule to permit its orientation in the externally applied field.

MOLECULAR ROTATION AND THERMAL ENERGY

In considering the possibility of molecular rotation in solids it is necessary to weigh also the evidence given by specific heats and x-ray analysis. The thermal energy of solids as evidenced by their specific heats is due mainly to the translational vibrations of the atoms, ions, or molecules about fixed points in the crystals or in the molecules, although rotational vibration or very occasionally, free rotation of a molecule or polyatomic ion may play a part. A molecule in which all the atoms lie in a straight line may rotate easily around this line as axis, but, as such rotation involves only the minute inertia of the electrons, it has a negligible effect on the ordinary properties of the substance and will not be considered here. Molecular rotation as discussed in the present paper means rotation in which an actual translation of atomic nuclei occurs. Recent work on the diffraction of x-rays by liquids (68) has indicated the existence of a rough approximation to a lattice-like arrangement of molecules, as in crystals. Instead of the perfectly random translational motion and complete freedom of rotation which was formerly attributed to the molecules of a liquid, Debye has recently suggested (21) that the molecules are vibrating about points which themselves move relatively slowly through the liquid. Each molecule is, of course, acted upon by strong electric forces due to the surrounding molecules. Unless the molecule has spherical symmetry, one or more of its orientations in the electric field of force surrounding it are more stable than any others. If the maximum difference of potential energy between the different orientations of the molecule is less than its thermal rotational energy, the molecule can rotate freely, but if this energy difference is greater than the thermal energy of the molecule, the latter will tend to oscillate rotationally about an orientation of minimum potential energy.

The problem of rotational oscillation, which has been treated theoretically by Pauling (66) and others (31, 32) for crystals, may be simply illustrated by considering the case of the hydrogen chloride molecule in its crystal. Since this molecule contains a dipole in the H—Cl line with its positive end toward the hydrogen, it will tend to orient with this H—Cl axis in the direction of the electric field in which the molecule lies, the positive hydrogen side of the molecule pointing toward the negative side of the field. Turning of the axis of the molecule through an angle θ from this position will increase the potential energy of the molecule by an amount V, which may be conveniently represented as a function of θ by the equation

$$V = V_0 (1 - \cos \theta)$$

$2V_0$ is evidently the increase in potential energy when the axis of the molecule is turned through an angle of 180°. The thermal energy of the molecule will cause it to rotate back and forth around the position $\theta = 0°$, unless this thermal energy is greater than $2V_0$, when it will turn over the potential energy hump and rotate freely. Pauling (66) gave an approximate theoretical treatment of the problem, showing that the commencement of molecular rotation with rising temperature accounted for a number of transitions which specific heat measurements had revealed in certain solids, and predicting that dielectric constant measurements would show freedom of rotation above these transitions. Fowler (31) recently used partition functions to represent the effect of molecular rotation upon the specific heats and dielectric constants of these substances which show transitions. The equations thus obtained show that the transitions should occur, but require the changes to be more gradual than those actually observed and are not successful in predicting where they should occur. Frenkel, Todes, and Ismailow (32) have based an approximate treatment on the assumption that the transition from non-rotation to rotation is very sharp, so that a rotating phase and a non-rotating phase are in equilibrium at a definite transition temperature. They are unable, however, to obtain much support of their treatment from the experimental facts. In view of the difficulty of fitting any quantitative theoretical treatment to the facts, it seems desirable to assemble a large body of experimental evidence and consider it qualitatively in the light of the fundamental principles which must guide any quantitative treatment.

As the specific heat depends upon the energy associated with the various oscillations in the crystal, its variation with temperature may give evidence as to oscillation or free rotation of the molecule. The rotational oscillation of the molecules increases with rising temperature and may acquire sufficient energy in the solid to pass over the hump in the potential energy curve, which means free rotation. Although one would expect this attainment by the molecules of sufficient energy to rotate to be distributed over a considerable interval of temperature, it should be remembered that the setting-in of rotation of one molecule will weaken the forces which it exerts upon its neighbors and thereby facilitate their rotation. The setting-in of rotation may, therefore, be sharp like melting, and should commonly cause structural changes in the solid. The resulting transition is shown by a break in the specific heat–temperature curve, which rises sharply because of the heat of transition and sinks sharply again. However, such a break may also accompany a transition which can have nothing directly to do with molecular rotation.

As rotation makes the field of force exerted by a molecule symmetrical around the axis of rotation, it is apt to give symmetry to a lattice. If the rotating molecule is fairly symmetrical in form, the lattice is usually one which could be formed of close-packed spheres, commonly cubic or hexagonal. From the opposite point of view, if the crystal is isotropic, the potential energy of a molecule will tend to vary less with its orientation in the lattice, which means that the molecule is more apt to rotate freely. It is obviously desirable to correlate the lattice structure as revealed by x-ray analysis with the evidence of molecular rotation.

SUMMARY OF EXPERIMENTAL MATERIAL

Table 3 summarizes the information in regard to rotation or non-rotation in a large number of solids which either show rotation or might be expected to show it but do not. The table aims at completeness as far as concerns the information given by dielectric constant measurements, which provide the best means of examining the rotation of a molecule having a dipole moment, and lists most of the transitions more or less clearly indicated by specific heat measurements as due to the commencement or the cessation of rotation, but does not include all of the cases in which symmetry deduced from x-ray analysis is attributed to rotation. The first column gives the molecule or ion under consideration, and the third gives the temperatures of the rotational transitions and other transitions in the neighborhood or a statement of the absence of rotation. The second and fourth columns give, when possible, the forms of lattice below and above the transitions. Where no rotation occurs below a transition given in the third column, no statement of the fact is made in the second column.

TABLE 3

Lattice form and rotation or non-rotation of molecules in solids

MOLECULE OR ION	REFERENCES	LATTICE BELOW TRANSITION*	TEMPERATURE OF TRANSITION, °K.	LATTICE ABOVE TRANSITION*
H_2	(66)	Rotates at very low temperature		Hexagonal
Cl_2	(30)	No rotation		
Br_2	(55)	No rotation		
I_2	(66, 33)	Orthorhombic. No rotation		
O_2	(28, 35, 11, 69)	Orthorhombic	23.8	Orthorhombic
		Orthorhombic	43.5	Rotation. Hexagonal
N_2	(28, 11, 69, 47)	Cubic	35.4	Rotation. Hexagonal
CO	(28, 11)	Cubic	61.5	Rotation. Hexagonal
NO	(30, 45)	No rotation indicated		
N_2O	(14, 29)	Cubic. No rotation		
CO_2	(28, 29)	Cubic. No rotation		
CH_4	(11, 15)	Cubic	20.4	Rotation. Cubic
SiH_4	(12)		63.4	Rotation. Higher symmetry
NH_3	(30, 14, 79)	Cubic. No evidence of rotation		
PH_3	(13)		30	Rotation
		Rotation	89	Rotation. Cubic (103°)
AsH_3	(83)		20–32.1	Rotation. Cubic (103°)
		Rotation. Cubic	106.6	Rotation
NH_4^+ (in NH_4F)	(74)		242.4	No rotation indicated Hexagonal

NH_4^+ (in NH_4Cl)	(72, 74, 8)		242.7	Rotation. Cubic (CsCl type)
		Rotation. Cubic (CsCl type)	457.4	Rotation. Cubic (NaCl type)
NH_4^+ (in NH_4Br)	(74, 8)	Tetragonal	235.1	Rotation. Cubic (CsCl type)
		Rotation. Cubic (CsCl type)	410.9	Rotation. Cubic (NaCl type)
NH_4^+ (in NH_4I)	(74, 8)		230.6	Rotation. Cubic (CsCl type)
		Rotation. Cubic (CsCl type)	260.6	Rotation. Cubic (NaCl type)
$C_6H_{11}NH_3^+$ (in $NH_3C_6H_{11}Cl$)	(86)	Tetragonal	221.5	
			246.5	Limited rotation. Tetragonal, smaller unit cell
$C_{18}H_{37}NH_3Cl$	(2)	Orthorhombic. No rotation		
NH_4NO_3	(53, 41)	Hexagonal	213	NH_4^+ rotating. Hexagonal
		NH_4^+ rotating. Hexagonal	255	NH_4^+ rotating. Orthorhombic
		NH_4^+ rotating. Orthorhombic	305	NH_4^+ rotating. Orthorhombic
		NH_4^+ rotating. Orthorhombic	357	NH_4^+ rotating. NO_3^- probably rotating about the normal to the plane of the oxygens. Tetragonal
			398	Both ions rotating freely. Cubic
NO_3^- (in $NaNO_3$)	(51, 54, 5)	Hexagonal	548	Rotation of NO_3^- about the normal to the plane of the oxygens gradually attained. Hexagonal

* Unless otherwise indicated this information is taken from the compilations by R. W. G. Wyckoff, *The Structure of Crystals*, 2nd edition (The Chemical Catalog Co., Inc., New York, 1931) and *Supplement for 1930–1934 to the Second Edition* (The Chemical Catalog Co., Inc., New York, 1935).

TABLE 3—*Continued*

MOLECULE OR ION	REFERENCES	LATTICE BELOW TRANSITION*	TEMPERATURE OF TRANSITION, °K.	LATTICE ABOVE TRANSITION*
NO_3^- (in KNO_3)	(52)	Orthorhombic	400.8	NO_3^- rotating about the normal to the plane of the oxygens. Hexagonal
PH_4I	(17)	Tetragonal. No rotation		
H_2O	(78, 63)	Hexagonal. Rotation with difficulty		
H_2O (in $MgPt(CN)_4 \cdot 7H_2O$)	(26, 27)	Tetragonal. Rotation with some difficulty		
H_2O (in $CaPt(CN)_4 \cdot 5H_2O$)	(26)	Orthorhombic. Rotation not evidenced		
H_2O (in $SrPt(CN)_4 \cdot 5H_2O$)	(26)	Monoclinic. Rotation not evidenced		
H_2O (in $BaPt(CN)_4 \cdot 4H_2O$)	(26)	Monoclinic. Rotation not evidenced		
H_2O (in $Y_2Pt_3(CN)_{12} \cdot 21H_2O$)	(27)	Orthorhombic. Rotation with some difficulty		
H_2O (in $CuSO_4 \cdot 5H_2O$)	(26)	Triclinic. Rotation with some difficulty		
H_2O (in $Na_2S_2O_3 \cdot 5H_2O$)	(26)	Monoclinic. Rotation with some difficulty		
H_2O (in $NaKC_4H_4O_6 \cdot 4H_2O$)	(50, 25, 93)	Rotation. Orthorhombic		
H_2S	(79, 13, 49)	Rotation. Cubic	103.5	Rotation. Cubic
			126.3	Rotation
H_2Se	(83)		<89	Rotation. Cubic (103°)
HF	(14, 13)	No rotation		
HCl	(30, 16, 80, 37)	Orthorhombic	98.9	Cubic. Rotation

HBr	30, 80, 38, 70, 64)	Orthorhombic	89	Cubic. Rotation
		Cubic. Rotation	113	Cubic. Rotation
		Cubic. Rotation	117	Cubic. Rotation
HI	(30, 80, 39)	Tetragonal (face-centered)	70	Tetragonal (face-centered). Rotation
		Rotation. Tetragonal (face-centered)	126	Tetragonal (face-centered). Rotation
HCN	(83)	No rotation		
CN^- (in KCN)	(90)	Probably rotating. Cubic		
CH_3Cl		No rotation around axis perpendicular to axis of symmetry		
CH_3Br		No rotation around axis perpendicular to axis of symmetry		
CH_3I		No rotation around axis perpendicular to axis of symmetry		
CH_2Cl_2		No rotation around axis perpendicular to axis of symmetry		
$CHCl_3$		No rotation around axis perpendicular to axis of symmetry		
CH_3NO_2	(85)	No rotation around axis perpendicular to axis of symmetry		
$CH_2Cl \cdot CH_2Cl$	(79)	No rotation		
n-$C_7H_{15}Br$	(46)	No rotation		

TABLE 3—*Concluded*

MOLECULE OR ION	REFERENCES	LATTICE BELOW TRANSITION*	TEMPERATURE OF TRANSITION, °K.	LATTICE ABOVE TRANSITION*
CH_3OH	(65, 48, 79, 82)		159	Limited rotation
$(CH_3)_3COH$	(82)	No rotation		
n-$C_8H_{17}OH$	(82)	No rotation		
n-$C_{12}H_{25}OH$	(2)	No rotation. Monoclinic	289	Rotation around chain axis. Hexagonal
$C_{21}H_{43}CO_2C_2H_5$	(9)		316	Limited rotation
$(CH_3)_2SO_4$	(78)	No rotation	203	Partial rotation
$(C_2H_5)_2SO_4$	(78)	No rotation		
d-Camphor	(92, 88)	Hexagonal (rhombohedral)	233–236	Rotation. Hexagonal (rhombohedral)
		Rotation. Hexagonal (rhombohedral)	370	Rotation. Cubic
dl-Camphor	(92, 88)		125–208	Rotation
Borneol	(92, 88)		173–223	Partial rotation
		Partial rotation	343–348	Rotation
Isoborneol	(92, 88)		173–223	Partial rotation
		Partial rotation	285–319	Rotation
Bornyl chloride	(92)		130–165	Rotation
d-Camphoric anhydride	(92)		408	Rotation
$C_6H_{11}OH$	(88)		205–250	Rotation
C_6H_5OH	(46)	No rotation		
$(C_2H_5)_2O$	(59)	No rotation		

$C_6H_5OCH_3$	(46)	No rotation		
$CH_3OC_6H_4OCH_3$	(46)	No rotation		
$(CH_3)_2CO$	(59)	No rotation		
$C_6H_5COC_6H_5$	(59)	No rotation		
$C_6H_5NO_2$	(78)	No rotation		
$C_6H_5NH_2$	(78)	No rotation		
CH_3NH_2	(59)	No rotation		
$(CH_2)_2(COOH)_2$	(88)	No rotation		

DISCUSSION OF EXPERIMENTAL MATERIAL

In solid hydrogen, which crystallizes in the hexagonal system corresponding to the closest possible packing of spheres, the H_2 molecule rotates (66). The forces between the hydrogen molecules are so weak that there is little variation in the energy of their orientation, and they rotate even with the low energies which they possess a few degrees above the absolute zero. On the other hand, the equally symmetrical diatomic molecule of iodine shows no rotation in its orthorhombic lattice, because the spacing of the molecules is so close in this lattice that they have no room to turn over. The specific heat curves for solid chlorine and bromine, the crystal structures of which are unlisted, also give no evidence of rotation. The upper of the two transitions listed for oxygen is indicated by the specific heat curve as due to the setting in of rotation or, at least, to a great increase in any freedom of rotation possibly existing below it and above the lower transition. The rotation of the nitrogen molecule sets in at a slightly lower temperature, while that of the less symmetrical carbon monoxide molecule, which has a small dipole moment, 0.11×10^{-18}, requires an appreciably higher temperature. One would expect to find rotation setting in for nitric oxide at a temperature not far from that of the rotational transition in carbon monoxide, but specific heat measurements give no positive evidence of any transition. If the molecules form the complex N_2O_2 at low temperatures, of which there is indication (45), the absence of rotation is explained. The linear triatomic molecules of nitrous oxide and carbon dioxide show no rotation in their cubic lattices because there is not sufficient space for end-over-end rotation.

Methane crystallizes in a cubic lattice and undergoes a sharp transition at 20.4°K., as shown by the specific heat–temperature curve, without any apparent change in the lattice structure. The molecule has the form of a regular tetrahedron with rounded corners and an indentation in the middle of each edge. Its symmetry is such that there should be little variation in the energy of its orientation. Rotation can thus set in at the low temperature found for its transition. The corresponding silicon compound SiH_4 undergoes a less sharp transition at 63.4°K. with a change to a more symmetrical lattice above the transition (12); data on the crystal structure are lacking. Although this monosilane molecule should be similar in form to that of methane, the larger silicon atom, which has a bond radius 50 per cent larger than that of carbon, gives a longer edge to the tetrahedron and a greater variation in the energy of molecular orientation, requiring a higher temperature to produce rotation.

The ammonia molecule, a flattened tetrahedron with a dipole moment of 1.46×10^{-18} (18), crystallizes in the cubic system. Neither specific heat nor dielectric constant measurements show molecular rotation in the crystal. The considerable dipole moment of the molecule as well as the lower symmetry of its form causes a much greater variation in the potential energy of its orientation than that found in methane and monosilane, the energy differences being apparently greater than the thermal energy of rotational oscillation which the molecules acquire before melting. It would seem that rotation might occur fairly easily around the axis of the dipole moment, which is the perpendicular drawn from the nitrogen nucleus at the apex of the molecular pyramid to the triangular base at the three corners of which lie the hydrogen nuclei. This rotation would not be revealed by the dielectric constant measurements, as it involves no motion of the molecular dipole, but it has not been evidenced in the specific heat measurements.

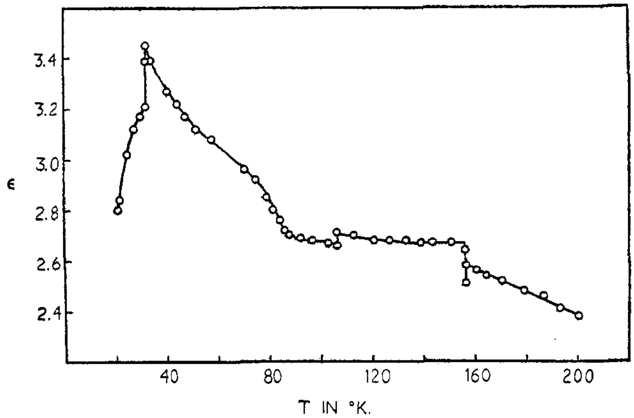

FIG. 3. Temperature dependence of the dielectric constant (at 50 kilocycles) of arsine

Phosphine, which should resemble ammonia in molecular shape as monosilane does methane, has a dipole moment of 0.55×10^{-18} and exists in a cubic lattice at 103°K. Below this temperature, two or more transitions are shown by the specific heats (13), which are indicative of molecular rotation above them. The small size of the dipole moment as compared to that of ammonia tends to reduce its contribution to the potential hump to slightly more than a third of that given by the ammonia dipole; the larger size of the molecule reduces the internal field and thus further reduces the potential hump which tends to prevent molecular rotation. However, the specific heat measurements show that the situation in phosphine is very involved, requiring further investigation. The dielectric constant of arsine (83) (figure 3) is higher at 20.5°K. than that of the liquid, but rises rapidly with temperature up to 32.1°K., where the rotational transition is complete. From this point up, the dielectric constant behaves like that of a liquid, the lattice being reported cubic at 103°K. The second transition at 106.6°K. produces a very slight rise in the dielectric constant, which then falls off much more slowly than before. This is similar to the effect of the upper transition in hydrogen bromide, hydrogen iodide, and hydrogen sulfide, indicating, probably, a change in lattice dimensions with consequent change in internal field but no fundamental alteration in lattice structure.

The ammonium ion has a higher symmetry than the NH_3 molecule, presumably, resembling the methane molecule in form and size. However, because of its charge and that of the anion occurring with it in the solid ammonium halides, a much stronger internal field should exist in the crystal, and the differences in the energy of orientation should be greater than in the methane crystal. Accordingly, the rotational transition shown by specific heat measurements in ammonium chloride occurs at a temperature 222°C. above that in methane. The same transition is found in ammonium bromide and iodide, but the transition temperature becomes lower with increase in size of the halide ion, which weakens the internal field of the crystal, thus lowering the potential energy humps that tend to prevent rotation. Ammonium bromide has a tetragonal lattice below the transition and a cubic above, where rotation causes greater symmetry. The chloride and iodide have apparently not been investigated with x-rays below this transition. All three show a second transition, which seems to be a mere lattice change. Although the lattices are cubic both above and below these upper transition temperatures, they are of the sodium chloride type above and of the cesium chloride type below. In the ammonium fluoride crystal, which is hexagonal, the small fluoride ion gives so strong an internal field that molecular rotation is not indicated by the specific heat–temperature curve, although a slight hump occurs in it at about the temperature of the transition in ammonium chloride. Possibly a hydrogen bond between the ammonium and the fluoride ion may fix the former and prevent rotation.

n-Amylammonium chloride forms a lattice like that of the high temperature form of ammonium chloride, except that the extended zig-zag carbon chain extends the lattice in the direction of its axis, causing the form to be tetragonal. The separation of the chains is sufficient to permit rotation of the $C_5H_{11}NH_3^+$ ions around their axes, the rotation presumably setting in at the temperature of the lower transition. Molecular rotation accounts for the fact that ammonia is often found by x-ray analysis on axes of symmetry too high for its intrinsic symmetry, as in $Co(NH_3)_6Cl_2$ (4). Bernal (2) by x-ray analysis has found $C_{18}H_{37}NH_3Cl$ to be orthorhombic without any rotation, but Müller (62) finds, with rising temperature, a gradual setting-in of rotation around the axis of the chain in the paraffins $C_{21}H_{44}$

and $C_{23}H_{48}$. The paraffins from $C_{24}H_{50}$ to $C_{34}H_{70}$ which he has investigated show transitions 5° to 10°C. below their melting points with an apparent gradual setting-in of rotation in the narrow temperature ranges between the transition and the melting points.

Ammonium nitrate offers one of the most interesting examples of ionic rotation, although some doubt exists in regard to certain of the statements concerning it in table 3. A gradual transition at about 213°K. suggests the setting-in of rotation of the ammonium ion, which is apparently occurring at 240°K. The nitrate ion begins to rotate about the axis normal to the plane of its three oxygens when the transition from orthorhombic to tetragonal occurs at 357°K., and the cubic lattice results when this rotation becomes free in all directions at 398°K. giving the nitrate as well as the ammonium ion spherical symmetry. Sodium nitrate shows a gradual transition at 548.5°K. without change of crystal form, resembling the 357°K. transition of ammonium nitrate in that the NO_3^- ion begins to rotate in the plane of its three oxygens, the number of rotating nitrate ions increasing rapidly as 548.5°K. is approached. Austin and Pierce (1) have shown that, as the rotation increases, the crystal expands rapidly in the direction of the axes of rotation, indicating a weakening of the forces between the planes in which the ions lie. This type of rotation of the nitrate ion sets in at a considerably lower temperature in potassium nitrate, a lattice change within the orthorhombic system occurring. Kracek, Hendricks, and Posnjak (53) state the probability that the nitrate ion has spherical symmetry, owing to rotation, in calcium, barium, strontium, and lead nitrates and nickel nitrate hexammoniate. Many thermal transitions found in other inorganic solids containing small or symmetrical ions are doubtless caused by the setting-in of rotation, but the information concerning them is not sufficient to warrant their discussion here.

Phosphonium iodide, which has tetragonal symmetry, shows no transition between liquid air and room temperature (12), although one might look for molecular rotation. The lower symmetry of the lattice may make the potential humps high enough to prevent rotation. The transition in monosilane is 43°C. higher than in methane, and in the strong field of the ionic lattice the difference between ammonium and phosphonium may be much greater.

For ice, which has a hexagonal lattice, the specific heat–temperature curve shows no transition at atmospheric pressure (73, 36) and gives no direct evidence of molecular rotation. The dielectric constant measurements (22, 40, 44, 63, 78, 89) show the possibility of rotation with a difficulty which increases rapidly but continuously with falling temperature. Under some conditions, the dielectric constant is distinctly higher than that of liquid water, 88.0 at 0°C. (91), and its general behavior is like that of a very viscous polar liquid, in which molecules with large dipole moments orient in an externally applied field but do so with great difficulty. For frequencies of 1/3 to 1/270 per second, Murphy (63) finds a value about 150 at −90°C., falling off gradually with rising temperature and rapidly with falling temperature. His values, about 99 for 1000 cycles at 0°C., for example, are higher than those of Smyth and Hitchcock (78), which are reproduced in figure 4 because they cover such a range as to show well the decrease in dielectric constant with rising temperature at low frequencies like that in a polar liquid. The higher values found by Murphy may be due to better filling of his condenser with the solid or to ionic impurities, which are sufficient even in distilled water to raise the value appreciably (78).

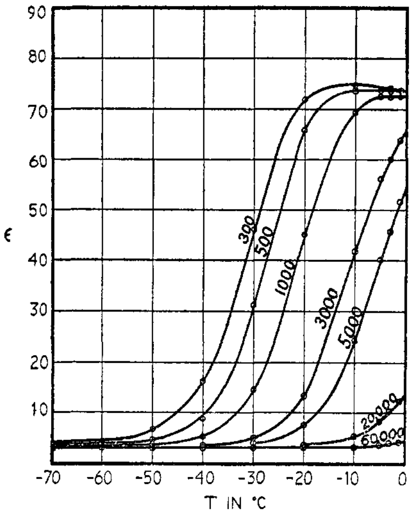

FIG. 4

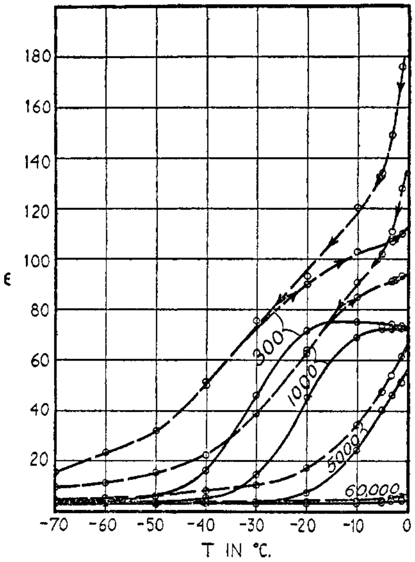

FIG. 5

FIG. 4. Variation of the dielectric constant of ice with temperature and frequency (in cycles).

FIG. 5. Variation of the dielectric constant of frozen 0.0002 *M* potassium chloride solution with temperature and frequency (in cycles).

Pauling (67) accounts for the entropy of ice by supposing that a crystal can exist in any one of a large number of configurations, each corresponding to certain orientations of the water molecules and change from one configuration to another resulting from rotation of some of the molecules or movement of some of the hydrogen nuclei to other equilibrium positions in the lattice. The very recent discussion of the specific heat and entropy of ice by Giauque and Stout (36) adopts this point of view in contrast to the earlier view of Giauque and Ashley (34), which supposed rotation of the H_2O molecule even at very low temperature around the line bisecting the H—O—H angle, a view difficult to reconcile with the strong internal field of the crystal and the consequent variation of potential energy with the orientation around this axis. Huggins (43) has given a qualitative explanation of the dielectric constant of ice, in terms only of the displacement of the hydrogen nuclei from one equilibrium position to another between the oxygens in the lattice. Stearn and Eyring (87) have calculated from the observed dielectric constant values that such displacements involve reasonable energy changes, as would molecular rotation also. Although the behavior of the dielectric constant of ice is explicable in terms of other types of polarization than that depending upon the orientation of its polar molecules, the turning of the molecule with difficulty in the externally applied field seems to be consistent with all the facts (cf. 20, 3). The fact that a similar dependence of dielectric constant upon frequency and temperature has been observed in four salts with water of hydration (26, 27), in two of them along one crystal axis only, supports the supposition that it is a question of molecular orientation or rotation in ice.

The great effect of ionic impurities upon the dielectric constant of ice is shown by figure 5, in which the solid lines represent the dielectric constants of frozen conductivity water and the broken lines the values for a frozen 0.0002 M solution of potassium chloride which contained 278,000 water molecules for each potassium ion and chloride ion (78). The curves for each frequency are connected by a bracket, which is marked with the frequency in cycles. At low frequencies the dielectric constants of the frozen solution were much higher on first cooling down slowly from the freezing point than on warming up. Arrows pointing downward and upward distinguish the curves for falling and rising temperatures. With increasing frequency, the difference between the falling temperature and the rising temperature curves becomes small and actually reverses, and the difference between the pure ice and the frozen solution almost disappears.

Errera and his coworkers (26, 27) have found that the dielectric behavior of a number of salt hydrates is very similar along at least one crystal axis to that of ice. Single crystals of $MgPt(CN)_4 \cdot 7H_2O$ and $Y_2Pt_3(CN)_{12} \cdot 21H_2O$ show dielectric constants along the a- and b-axes almost independent of temperature and frequency, while along the c-axis the dielectric constant is much higher and dependent upon temperature and frequency, indicating the rotation with some difficulty of one or more of the molecules of water of hydration. Rotation appears possible in the corresponding calcium and strontium compounds and in $BaPt(CN)_4 \cdot 4H_2O$, which has a dielectric constant of 9.5 along the c-axis. Rotation is also evident in the pentahydrates of copper sulfate and sodium thiosulfate.

The extraordinary behavior (50, 25, 93) of Rochelle salt, $NaKC_4H_4O_6 \cdot$

$4H_2O$, must be attributed to orientation of the H_2O dipoles. Dielectric constant values as high as 20,000 and as low as −381 have been observed, the values depending not only upon frequency and temperature but also upon field strength. The dielectric constant shows an anomalous dispersion curve similar in form to that given by a refractive index in a region of absorption. Orientation of the dipoles in the external field is accompanied by further orientation in the internal field, analogous to that occurring in ferromagnetism, the result being a dielectric analogy of the Curie point. As the rotating unit is only one of several factors in the lattice of these hydrates, the crystal form may have a lower symmetry than in the cases of those substances in which the entire molecule is rotating.

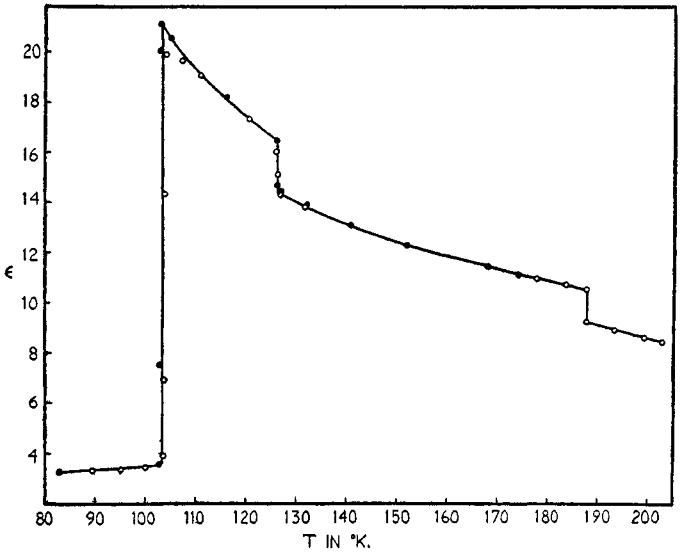

FIG. 6. Dielectric constant–temperature curve (at 5 kilocycles) of hydrogen sulfide: circles, rising temperature; dots, falling temperature.

Hydrogen sulfide is shown by its specific heat–temperature curve (13) to undergo two transitions in the crystal, which are checked within 0.1°C. by breaks in the dielectric constant–temperature curve (figure 6) (79, 49). This latter shows that freedom of molecular rotation occurs below the melting point and is practically unaffected by the higher transition, which is evidently only a minor lattice change; the rotation ceases abruptly below the lower transition, 103.5°K. At about this temperature x-ray analysis shows a cubic lattice, which presumably persists up to the melting point but is not necessarily the structure below the lower transition. Preliminary dielectric constant measurements (83) show that hydrogen selenide, which has a cubic lattice at about 103°K., possesses freedom of molecular rotation in the crystal even at liquid air temperature.

Hydrogen fluoride resembles water and ammonia in that its specific heat–temperature curve shows no transition in the solid above liquid air temperature (14). X-ray and dielectric constant data are not available. Increase in the size of the halogen brings about molecular rotation in the crystal. Hydrogen chloride solidifies with a cubic lattice which has a dielectric constant (figure 7) (16, 80) higher than that of the liquid, increasing in accordance with the Debye equation as the temperature falls and dropping sharply to a low value as molecular rotation ceases at 98.9°K., where specific heats (30, 37) indicate a rotational transition. Below this transition x-ray analysis shows orthorhombic symmetry and, for some degrees below it, the slowly diminishing dielectric constant and conductance, which latter rises sharply at the transition, indicate a very slight or

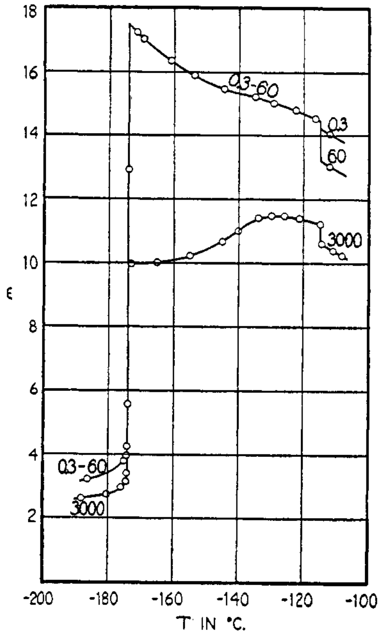

FIG. 7

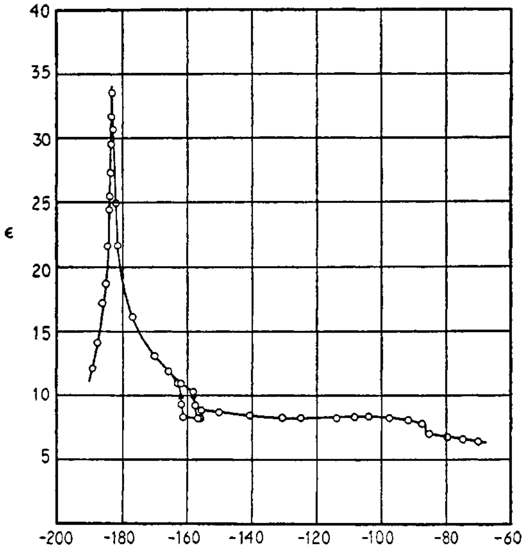

FIG. 8

FIG. 7. Temperature dependence of the dielectric constant (at indicated kilocycles) of hydrogen chloride.

FIG. 8. Temperature dependence of the dielectric constant (at 60 kilocycles) of hydrogen bromide.

occasional but decreasing freedom of rotation. Hydrogen bromide (figure 8) resembles the chloride in showing rotation, but differs from it in possessing two additional transitions above that at which the lattice probably changes from orthorhombic to cubic with the setting-in of rotation. Because of disagreement between investigators (64, 70) the crystal structure is not certain, but the orthorhombic modification reported by Natta (64) in the neighborhood of the lowest transition probably corresponds to the lattice of non-rotating molecules, and the cubic lattice reported by him in the vicinity of the two upper transitions presumably consists of rotating molecules. Ruhemann and Simon (70), however, believe that the lattice is face-centered rhombic throughout. The two additional transitions are so close together that it can only be said that the dielectric constant (80) is slightly lower between them, but above them the dielectric constant–temperature curve is much flatter, showing a marked change in the internal field of the crystal. The lowest of the three transitions differs from all the others which are here discussed in that the dielectric constant rises very high and depends upon the frequency of the field in the immediate neighborhood of the transition. It appears that this may be a dielectric Curie point, a phenomenon previously observed only in Rochelle salt (25, 50, 93). Hydrogen iodide resembles the chloride and bromide in behavior, but differs from all the other simple molecules which rotate in the crystal in that it has a face-centered tetragonal lattice. The dielectric constant measurements have not been extended to the low temperature at which the specific heat indicates the commencement of rotation (39), but the one transition which occurs above this temperature causes a very slight drop in dielectric constant, followed by a much smaller rate of decrease in the dielectric constant with rising temperature. This transition evidently involves a change in the internal field, as in the case of the highest hydrogen bromide transition, but here also x-ray analysis shows no molecular rearrangement. Indeed, except for an abnormally large decrease in volume, presumably caused by the transitions, the lattice remains unchanged down to 21°K. (70), a temperature below the lowest transition. The temperature necessary to produce rotation decreases with increasing size of the halogen in this group of compounds, as it does in the ammonium halides. Increasing molecular size also facilitates rotation in the groups consisting of water, hydrogen sulfide and hydrogen selenide and ammonia, phosphine and arsine. The reverse is true in the case of methane and monosilane, where also the first member of the group rotates in contrast to the other three groups, in which the first member shows no rotational transition. All of these rotators except the ammonium ion, methane, and monosilane have dipoles, which decrease in size with increasing size of the molecule and are, at the same time, farther separated from one another the larger the molecule. In both of these ways, therefore, increasing size of the molecule should facilitate rotation by decreasing the height of the potential energy hump which tends to prevent molecular rotation. In the ammonium halides the field due to the negative charge of the halide ion decreases with increasing ionic size, and the potential hump is thereby reduced. In all of these solids van der Waals forces are tending to draw the molecules or ions together, but the potential energies due to these forces should not vary greatly with orientation of the ions or molecules. The van der Waals forces must be greater in monosilane than in methane, because of the greater polarizability of the molecule (75). The variation in the resulting potential energies with molecular orientation may be sufficient to account for the higher rotational transition temperature of monosilane.

The energy changes (13) accompanying these rotational transitions seem not to show any very general relationships. The heats of fusion of the hydrides in which rotation occurs are much lower than those of ammonia, water, and hydrogen fluoride, since they have already acquired considerable amounts of energy before reaching the melting point.

The small molecule of hydrogen cyanide shows no molecular rotation in the solid according to recent dielectric constant measurements (83). It may be that the HCN molecules, which are linear, are so located in the lattice as to block one another's rotation, as do the I_2 molecules in their crystal. The large dipole moment, 2.93×10^{-18} (81), in the small molecule would give a strong internal field and a large variation in potential energy with orientation of the molecule, which would tend to prevent rotation. The x-ray photographs of potassium cyanide give no evidence of separate carbon and nitrogen positions, which would be expected if the cyanide ion were rotating in the lattice (90). It seems probable that the potential barrier to rotation of this ion is lower than that for the hydrogen cyanide molecule, so that rotation may occur.

In view of the ease of rotation of methane and of hydrogen chloride, bromide, and iodide, it is interesting to conclude from the low dielectric constant values found (60) for solid methyl chloride, bromide, and iodide that there is no molecular rotation around any axis perpendicular to the carbon–halogen line. The dielectric constant, of course, gives no information as to rotation around the carbon–halogen line, in which the molecular dipole lies. Low dielectric constants found (60) for solid methylene chloride and chloroform also give no evidence of molecular rotation. The dielectric constants of solid ethylene chloride (79), examined for intramolecular rotation as well as that of the molecule as a whole, and of solid nitromethane (85) show no rotation. It is probable that all of these molecules are so located in their lattices as to block one another's rotations around axes perpendicular to the axes of symmetry in which the dipole moments lie. The dielectric constant of heptyl bromide shows no rotation, perhaps because of the low temperature at which it melts.

In methyl alcohol specific heat measurements show a transition a short distance below the melting point, and dielectric constant measurements show some freedom of rotation above this transition (79, 82). A new factor enters into the consideration of this rotation, for it might be a rotation of the entire molecule, as in the previous cases examined, or it might be merely a rotation of the hydroxyl group around the single carbon–oxygen bond, with which the dipole in the H—O makes an angle not far from 110°. If it is rotation of the hydroxyl group within the molecule, similar rotation should occur at least as easily and probably more easily in the higher aliphatic alcohols. As the specific heats which have been determined for higher aliphatic alcohols show no rotational transition, and as dielectric constant measurements (82) upon tertiary-butyl alcohol and *n*-octyl alcohol show that there is no dipole rotation in these solids, it must be the entire molecule which rotates in solid methyl alcohol. However, the dielectric constant is so much lower in the solid than in the liquid that the freedom of rotation is evidently much more reduced by the internal field of the solid than by that of the liquid. Possibly rotation occurs only about the C–O axis. Bernal (2) has found by x-ray analysis that dodecyl alcohol shows a transition from monoclinic to hexagonal at 289°K. with molecular rotation setting in around the axis of the carbon chain. It is probable that the higher temperature attainable before melting gives the necessary energy which was lacking in the case of the lower melting octyl alcohol.

Ethyl behenate, with its very long carbon chain and considerable dipole not far from one end of the chain, shows by its dielectric constant (9) that it possesses some freedom of rotation above a transition at 316°K., which is only 4.8° below its melting point. The situation is complicated by the existence of two α-forms above this transition and two β-forms below it, with the possibility of metastable equilibrium. However, the polarizations of the α-forms are somewhat less than half way from those of the β-forms, which show no rotation, up to that for the liquid. Presumably, there is in the α-form some rotation about the axis of the long carbon chain like that in dodecyl alcohol and the long chain hydrocarbons previously mentioned.

Methyl sulfate (figure 9) shows a tremendous drop of 52 units in its dielectric constant on solidification at 241.7°K., but the value 8 of the solid shows the persistence of some freedom of dipole orientation (78). The tendency of this value to increase slightly with falling temperature indicates sufficient freedom to permit of a partial conformation to the Debye equation for the dielectric constant. This freedom disappears abruptly when the dielectric constant drops to 3 at about 203°K., which is to be regarded as a rotational transition. If the two CH_3—O groups attached to the central sulfur atom were free to rotate around their sulfur-oxygen bonds, the dipoles associated with the C—O bonds might possibly account for the value of the dielectric constant between the melting point and the transition. However, it appears probable that the two methyl groups would collide frequently and interfere with one another's motion, and that their freedom of rotation might be hindered by the forces exerted upon them by the rest of the molecule. It seems more probable that, between the transition point and the melting point, the molecule is free to turn around an axis which makes an angle quite different from 90° with the axis of the effective dipole of the molecule as a whole. This means that only the component of the moment perpendicular to the axis of rotation, that is, $\mu \sin \theta$, where θ is the angle between the dipole axis and the axis of rotation, contributes to the dielectric constant in this region. The fact that ethyl sulfate (78) shows no molecular rotation indicates that the greater bulk of the ethoxyl group prevents either its rotation or that of the whole molecule, as the case may be.

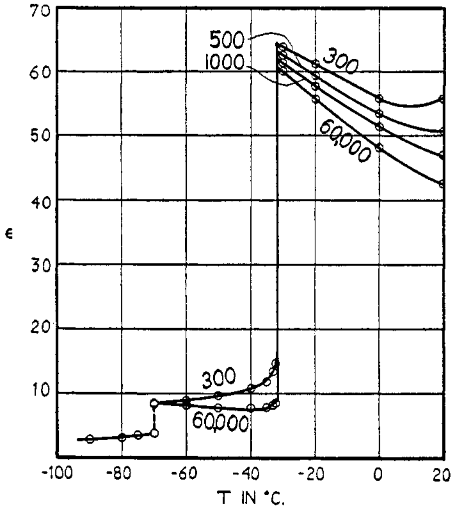

FIG. 9. Variation of the dielectric constant of dimethyl sulfate with temperature and frequency (in cycles).

The recent work of Morgan and his coworkers (88, 92) has shown that molecules bulkier than methyl sulfate may rotate in the solid. The dielectric constant of *d*-camphor hardly changes on solidification to a cubic crystal at 450.7°K., and rises with decreasing temperature in the manner usual with a polar liquid. It is practically unaffected by a change from the cubic to a rhombohedral crystal at 370°K., but shows the disappearance of rotation from 236° to 233°K. when the crystals are transformed into very birefringent crystals, also rhombohedral. Molecular rotation persists in *dl*-camphor to a lower temperature, falling off rapidly below 208°K. and gradually for nearly 90° more. Borneol and isoborneol, which differ from camphor in possessing a CHOH group instead of a carbonyl group and, therefore, have a considerably smaller dipole moment, show rotation which ceases at a much higher temperature than in camphor. It is interesting to note that the mere interchange of the hydrogen and hydroxyl in the CHOH group changes the transition temperature 40° and causes a great difference in sharpness, isoborneol requiring about 35° and borneol about 5° for the major part of the change. Bornyl chloride, which has a chlorine instead of the hydroxyl of borneol, shows molecular rotation down to about 165°K. and *d*-camphoric anhydride shows it between freezing at 495°K., which lowers the dielectric constant but slightly, and a sharp transition at 408°K., where it ceases. The dielectric constant of cyclohexanol does not change on freezing, but falls off between 250°K. and 205°K., depending upon the frequency of the field, which shows that free rotation becomes difficult in this region and ceases below it. Other cyclohexyl compounds also are mentioned (88) as showing molecular rotation in the solid. The freedom of rotation of these large molecules is attributed by White and Morgan (88) to a loosening of the structure by great atomic vibration within the molecules, evidence of which is given by the large atomic polarization found for *d*-camphor. However, as the three dimensions of the camphor and related molecules do not differ greatly from one another, it is probable that the energies of many and, possibly in some cases, of all of the orientations of the molecule in the lattice differ from one another mainly in the energies of the molecular dipole in the field surrounding it. As the large hydrocarbon residues of the molecules presumably separate the dipoles widely, as compared to their spacing in a lattice of small molecules, they should lie in a comparatively weak field. It would appear, therefore, that molecular rotation should be possible without loosening by great intramolecular vibration. In the cyclohexane derivatives, it is easy to picture rotation occurring, at least around an axis perpendicular to the ring.

One might attribute the rotation in the borneols merely to the hydroxyl group in a molecule rigidly held in the lattice, but, as the other large molecules must rotate in order to account for their dielectric constants, there is no reason to suppose that the entire molecule does not rotate in the case of these hydroxyl compounds. Phenol, anisole, and hydroquinone dimethyl ether, which were investigated by the dielectric constant method for possible rotation of the hydroxyl or methoxyl groups, show no molecular or group rotation in the solid. Dielectric constant measurements show no rotation in nitrobenzene and benzophenone; the latter was investigated because of its existence in different forms. As an entire benzene ring with attached group would have to rotate to be apparent in these measurements, it is natural to obtain a negative result. Aniline and methylamine also show no rotation of the molecule as a whole or of the NH_2 group around its carbon link. Ethyl ether, investigated because of the difference between its freezing and melting points (42), and acetone and succinic acid, which show small humps in their specific heat curves, give no evidence in their dielectric constant values of either molecular or group rotation (59). Indeed, dielectric constants have failed to establish definitely the existence of the free rotation of any group within a molecule in the solid state unless water of hydration is regarded as an intramolecular group. Specific heats are, however, sometimes interpreted as indicating group rotation within a molecule (66).

CONCLUSIONS

Of the eighteen substances of known crystal form in table 3 which show unrestricted ionic or molecular rotation, twelve, if potassium cyanide is included, are cubic when this rotation is occurring, four hexagonal, one, *d*-camphor, rotates freely both in its cubic and its higher temperature hexagonal form, and one, hydrogen iodide, is tetragonal, its *a*- and *c*-axes differing by only 8 per cent. The four which are only hexagonal are diatomic molecules rotating and melting at low temperature. Since free rotation gives spherical symmetry to a molecule, it is natural to find that molecules possessing it form lattices corresponding to the arrangements of close-packed spheres. When the axes of a molecule or ion are markedly different in length, rotation about only one of them, although tending to increase the symmetry, does not necessarily give rise to a cubic or hexagonal lattice.

It is evident that the moment of inertia of the molecule does not have the dominant effect in determining rotation that has been attributed to it in some discussions. The setting-in of rotation occurs at a higher temperature in monosilane than in methane, but this may be due to stronger intermolecular forces rather than to the larger moment of inertia of the molecule. The non-rotation of hydrogen fluoride and the very limited rotation in ice are due to hydrogen bonds between the molecules, or, possibly, merely to the strong internal fields in the crystals and the considerable dipole moments of the molecules as in ammonia. The heavier hydrides analogous to each of these three show rotation at lower temperatures with increasing weights and, hence moments of inertia, probably because of the decrease in dipole moments with increase in size. The ease of rotation of the camphor and similar molecules with very large moments of inertia shows that large moment of inertia in itself is not sufficient to prevent rotation. Actually, examination of Pauling's theory (66) shows that the moment of inertia is a factor in determining the oscillational or rotational energy levels of the molecule and, hence, the distribution of energy among the molecules, but does not directly affect the potential energy barrier which the molecule has to pass in order to rotate, except through its small effect in determining the zero energy level. It is this barrier which is all-important in determining rotation or non-rotation. If the molecule has a much larger moment of inertia around one axis than around the others, its rotation around this axis is more apt to be blocked by its shape. Increasing molecular size, incidentally involving increasing moments of inertia, gives greater potential energies between the molecules and, consequently, in most cases greater variation of potential energy with orientation of the molecule in the lattice or, in other words, greater potential barriers to prevent rotation. The shape of the molecule is one of the most important factors in determining these barriers, since upon it will depend largely their distance of approach in a rotational oscillation, and upon this distance primarily depends the intermolecular force. If the molecules do not actually block one another's rotation in the lattice, then the differences in the van der Waals forces exerted by different kinds of atoms and the size of the molecular dipole moment become important factors.

The setting-in of rotation may occur gradually because of the unequal distribution of energy among the molecules, as in borneol or in arsine, in which latter substance the transition, after a gradual start, ends with a sharp increase in rotation. Commonly, however, the transition accompanying the setting-in of rotation occurs almost as sharply as melting, because of the weakening of the intermolecular forces in the neighborhood of a molecule which has begun to rotate. In a number of cases a second transition occurs with little or no lattice change after rotation has set in with rising temperature, its only considerable effect upon the dielectric constant being a change in its variation with temperature, presumably as the result of change in the internal field. It is probable that, in some cases, rotation sets in at the lowest transition about one axis only, and that the higher transition involves the setting-in of rotation around another axis, as in the case of the nitrate ion in ammonium nitrate.

It has been previously mentioned that the energy changes accompanying the transitions of the hydrides seem to show no general relationships, although the heats of fusion of the hydrides with rotating molecules are much lower than those of the hydrides with non-rotating molecules. The energy absorbed by a solid when molecular rotation sets in lies between 3 per cent and nearly 100 per cent of the heat of fusion. Commonly, the energy content of a solid with rotating molecules just below the melting point differs from that of the liquid just above the melting point by little, if any, more than it differs from that of the solid below the temperature where rotation sets in. From a molecular point of view, the essential difference between a solid with rotating molecules and a liquid is that the molecules of the solid are vibrating about points fixed in a lattice, while molecules of the liquid are vibrating about points which migrate slowly and irregularly through the liquid.

No attempt is made in the present discussion to consider solids containing more than one substance, except insofar as the effect of impurities is concerned. It is evident that non-polar molecular solids and most polar molecular solids have low dielectric constants arising principally from electronic displacements, while ionic solid dielectrics have higher, sometimes much higher, dielectric constants because of ionic displacements in addition to the electronic. A few polar molecular solids have molecules which are able to rotate within a considerable range of temperature, giving high dielectric constants over this range, and a few essentially ionic solids contain polar groups which can rotate and greatly increase the dielectric constant under certain conditions of temperature and frequency.

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