

4. The precipitate is slightly soluble in alcohol and this necessitates washing with a saturated alcoholic solution of the precipitate.

5. Large amounts of foreign salts cause co-precipitation of the reagent and give high results.

**Advantages of the Method.**—1. It is particularly adapted to small amounts of fluorine due to the low conversion factor.

2. The precipitate is crystalline and is easily filtered and quickly washed.

3. The precipitate is stable and no ignitions have to be made.

4. Not counting the standing overnight, the time required for precipitation and further treatment of the precipitate to the final weighing is less than in any other gravimetric method for fluorine.

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### Summary

Fluorine may be quantitatively precipitated as triphenyltin fluoride as reported by Krause and Becker in 1920. The method is advantageous for small quantities of fluorine. The procedure for the precipitation and treatment of the fluoride is given.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

## DIPOLE ROTATION IN CRYSTALLINE SOLIDS

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Another paper<sup>1</sup> has presented the results of a preliminary investigation of the possibility of contribution to the dielectric constant of a crystalline solid through the rotation of a polar group in a molecule fixed in the crystal lattice or through the rotation of the entire molecule in the lattice. It was found that heptyl bromide, hydroquinone dimethyl ether, and anisole showed no such contribution, while the apparent small contribution in phenol and benzoyl chloride was attributed to the effect of impurities. As it is the purpose of the present paper to extend this investigation with an improved apparatus, it is desirable to give some consideration of the factors involved.

It is evident that, if freezing fixes the molecules in the space lattice, dipoles fixed in the molecules cannot orient in an externally applied field and their contribution to the dielectric constant becomes zero. Accord-

<sup>1</sup> Kamerling and Smyth, unpublished.

ingly, on solidification the dielectric constant of a polar substance ordinarily drops sharply to a value arising from induced polarization alone, this polarization being usually but slightly higher than and sometimes indistinguishable from the molar refraction for visible light.

Debye<sup>2</sup> has shown how the dielectric constant of a polar liquid may decrease with increasing viscosity, decreasing temperature, and increasing frequency of the alternating field used in the measurement because of the increasing difficulty of the molecules orienting in the externally applied field. He has even found that this theory of anomalous dispersion gives an adequate explanation of the results of Errera and other investigators upon ice.<sup>3</sup> Errera found a more or less similar anomalous dispersion in a number of polar organic substances in the solid state, which made it appear that the molecules of these substances could turn in the solid state as if in a viscous liquid.

Pauling<sup>4</sup> used the quantum mechanics and specific heat data to show the rotation of molecules with small moments of inertia in the space lattice. The hydrogen, oxygen, nitrogen, carbon monoxide, methane and hydrogen halide molecules were shown to rotate at temperatures between the freezing points and certain regions of transition, and it was predicted that the dielectric constants of the solid hydrogen halides at temperatures just below the melting points would be very high and dependent upon the temperature, the values being given by Debye's theory of the orientation of dipole molecules, while the low-temperature forms would have low dielectric constants nearly independent of the temperature. This prediction was strikingly confirmed for hydrogen chloride by the measurements of Cone, Denison and Kemp,<sup>5</sup> who, using the high frequency of 3000 kilocycles, found that the dielectric constant of the solid just below the melting point was actually higher than that of the liquid although the polarization was slightly lower. The dielectric constant-temperature curve does not conform to the simple Debye equation, but gives evidence of some anomalous dispersion before it finally drops sharply at a transition temperature to a low value for the dielectric constant. Pauling further concluded that heat capacity measurements on the ammonium halides showed transitions corresponding to the transition from oscillation to rotation of the ammonium ions and that the ammonia molecules in  $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ , the water molecules in alum, and the aliphatic carbon chains in mono-alkyl substituted ammonium halides showed symmetry, when examined with x-rays, arising from the rotation of the molecule or group in the space lattice.

<sup>2</sup> See Debye, "Polar Molecules," The Chemical Catalog Company, Inc., New York, 1929, Chap. V.

<sup>3</sup> Errera, *J. phys. radium*, [6] 5, 304 (1924); Granier, *Compt. rend.*, 179, 1314 (1924); "International Critical Tables," 1929, Vol. VI.

<sup>4</sup> Pauling, *Phys. Rev.*, 36, 430 (1930).

<sup>5</sup> Cone, Denison and Kemp, *THIS JOURNAL*, 53, 1278 (1931).

All of these rotations involve moments of inertia small in comparison with those involved in the possible rotations of the molecules of the organic substances investigated by Errera, for even a zig-zag carbon chain has a surprisingly low moment of inertia around its long axis. The rotation of the molecule or group depends not only upon its moment of inertia but also upon a potential function representing the averaged interaction of the molecule with surrounding molecules. This function may be calculated roughly from specific heat data, but, in the absence of such data for most of the substances to be considered and in view of the very approximate character of the theoretical treatment, the magnitude of the moment of inertia may be regarded as a rough criterion of the improbability of rotation. Evidently, only such molecular or group rotations should occur in a crystalline solid as involve small moments of inertia and internal fields and these may be studied by means of the dielectric constant when the molecule or group contains a dipole. Since the apparent conductance of a material may give quantitative evidence of anomalous dispersion, the conductance of the solids has been measured simultaneously with the dielectric constants at frequencies from 300 to 60,000 cycles.

**Apparatus.**—The capacity bridge used in the measurements was a slight modification of the instrument previously described.<sup>1,6</sup> The resistance in series with the condenser in each of the two capacity arms was replaced by a parallel resistance in the other capacity arm. Each of these resistances was a non-inductively wound 10,000-ohm General Radio Company Type 102-J decade box. The bridge could now be balanced much more accurately than formerly when a material of some conductance was in the measuring condenser. The resistance  $R$  of the condenser filled with the substance under investigation was calculated simply from the values of the two parallel resistances and the specific conductance  $k$  ( $\text{ohm}^{-1} \text{cm.}^{-1}$ ) of the material was calculated by means of the equation<sup>7</sup>

$$k = \frac{0.0885}{C_0 R}$$

in which  $C_0$  is the geometrical capacity in micromicrofarads of the condenser as obtained in the calibration for the calculation of the dielectric constant. The condensers used were the cylindrical type described previously,<sup>8</sup> a very small one being employed for ice and two large cells, one with gold cylinders, being used on the other substances. A platinum resistance thermometer was used to measure the temperature of the bath surrounding the cell and, in the measurements upon ethylene chloride, phenol and benzene, a second thermometer was placed in the center of the

<sup>6</sup> Smyth and Kamerling, *THIS JOURNAL*, **53**, 2988 (1931).

<sup>7</sup> Debye, "Polar Molecules," The Chemical Catalog Co., Inc., New York, 1929, p. 99; Morgan and Lowry, *J. Phys. Chem.*, **34**, 2385 (1930).

<sup>8</sup> Smyth and Morgan, *THIS JOURNAL*, **50**, 1547 (1928).

cell. The general procedure and technique was similar to that previously outlined.<sup>1,6</sup>

### Purification of Materials

**Nitrobenzene.**—Merck "Pure" nitrobenzene was three times crystallized, twice dried with phosphorus pentoxide and fractionally distilled under reduced pressure; m. p. 5.67°;  $n_D^{20}$  1.55261.

**Aniline.**—Merck c. p. aniline was twice fractionally distilled and once recrystallized from its own melt; b. p. 183.7° (754.5 mm.); m. p. -6.15°;  $n_D^{20}$  1.58610.

**Phenol.**—The best sample was obtained by fractional distillation of Merck c. p. phenol and two recrystallizations of the material from its own melt; b. p. 181.9° (761 mm.); m. p. 40.7°.

**Ethylene Chloride.**—The same material used in earlier work;<sup>9</sup> b. p. 83.5-83.7°;  $n_D^{20}$  1.44476.

**Water.**—Conductivity water of specific conductance  $2 \times 10^{-8}$  ohm<sup>-1</sup> cm.<sup>-1</sup> was used.

**Benzene.**—Purified as in earlier work.<sup>10</sup>

**Dimethyl Sulfate.**—Eastman "Practical" dimethyl sulfate was fractionally distilled five times under reduced pressure, the last two times from over calcium oxide; b. p. 72.5-72.7° (13 mm.); m. p. -31.4°;  $n_D^{20}$  1.38738. A cooling curve showed that solidification occurred within a range of 0.3°.

**Diethyl Sulfate.**—Eastman "Practical" ethyl sulfate was fractionally distilled three times under reduced pressure, the third time from over calcium oxide; b. p. 93.0-93.2° (13 mm.); m. p. -25.2°;  $n_D^{20}$  1.40010. A cooling curve showed that solidification occurred within a range of 1°.

### Experimental Results

A large number of determinations have been made at frequencies from 300 to 60,000 cycles over a wide range of temperature upon substances in both the solid and the liquid state, in different stages of purification, and, in some cases, at different intervals of time after solidification. Only such determinations are included in this paper as are needed to show the dependence of the dielectric constant and, at times, the conductance upon the different variables. For example, the dielectric constant of nitrobenzene is so nearly independent of frequency in the range studied that the values are given at 60,000 and at 500 cycles only, and, similarly, the conductance is not followed throughout its entire course. As the dielectric constant is determined for a large aggregate of crystals, it represents a roughly weighted mean of the values for the different crystal axes. Also its value may be low because of the presence of pockets and interstices between the crystals, which, of course, cause errors in the conductance also. These errors do not, however, impair the value of the data for the purposes of the present investigation.

The dielectric constants  $\epsilon$  and the specific conductances  $k$  (ohm<sup>-1</sup> cm.<sup>-1</sup>) are given in Table I, the temperatures being given in the first column and the frequencies in kilocycles across the top of each group of data.

<sup>9</sup> Smyth, Dornet and Wilson, *THIS JOURNAL*, **53**, 4242 (1931).

<sup>10</sup> Smyth and Rogers, *ibid.*, **52**, 2227 (1930).

TABLE I  
DIELECTRIC CONSTANTS AND SPECIFIC CONDUCTANCES

Nitrobenzene (m. p. 5.67°)				Ethylene Chloride (m. p. -35.3°)								
k.c. = t, °C.	60	0.5	60 k (× 10 <sup>9</sup> )	t, °C.	60	5	1	0.5	60-0.5 k (× 10 <sup>9</sup> )			
-10	3.14	3.23	< 0.1	-60	2.56	2.56	2.57	2.58	< 0.1 throughout			
0	3.25	3.38		-50	2.57	2.57	2.59	2.61				
4	3.34	3.51		-40	2.63	2.63	2.65	2.66				
5	3.62	3.96	0.085	-38	2.85	2.85	2.88	2.90				
5 5	4.2	4.6	0 9	21	3.26	3.27	3.33	3.39				
Liquid												
5	36.0	36.2		8.3								
6	35.8	35.9		8.4								
8	35.5	35.6		8.6								
10	35.2	35.3		8.9								
20	33.3	33.4		10.8								
30	31.6	31.8		12.9								
Aniline (m. p. -6.15°)												
k.c. = t, °C.	60	5	1	0.5	0.3	60	5	1	0.5	0.3		
-70	3.32	3.32	3.33	3.33	3.33				< 0.1 throughout			
-50	3.44	3.44	3.45	3.46	3.46				< 0.1 throughout			
-30	3.60	3.63	3.66	3.68	3.69	0.34	0.09	0.025	0.02	0.02		
-20	3.69	3.70	3.72	3.74	3.76	.43	.15	.05	.03	.025		
-10	3.82	3.90	4.06	4.15	4.23	.68	.34	.17	.13	.10		
- 8	3.88	3.97	4.20	4.42	4.49	.85	.6	.29	.14	.10		
- 7	3.94	4.04	4.38	4.61	4.81	1.1	.68	.31	.21	.15		
Liquid												
- 5	7.51	7.51	7.60	7.66	7.76	4.75	4.9	4.9	4.85	4.85		
0	7.35	7.37	7.47	7.56	7.64	6.3	5.9	5.8	5.8	5.8		
20	6.78	6.80	6.97	7.07	7.17	10.5	10.2	10.0	9.95	9.95		
Phenol (m. p. 40.7°)												
k.c. = t, °C.	60	5	1	0.5	0.3	60	5	1	0.5	0.3		
-60	2.68	2.68	2.66	2.66	2.66							
-40	2.69	2.70	2.69	2.69	2.69	0.85						
-20	2.70	2.73	2.75	2.77	2.79	0.85	0.06	0.03	0.03			
-10	2.71	2.75	2.79	2.83	2.88	1	.15	.06	.03	0.03		
0	2.73	2.78	2.84	2.88	2.94	1.7	.21	.09	.06	.03		
10	2.74	2.80	2.90	2.96	3.01	2	.30	.15	.09	.09		
20	2.75	2.81	2.92	2.98	3.04	2.5	.32	.15	.09	.09		
30	2.79	2.84	3.00	3.09	3.16	2.5	.42	.21	.15	.15		
35	2.80	2.86	2.96	3.02	3.12	2.5	.36	.15	.12	.12		
38	2.84	2.92	3.05	3.13	3.20	3.4	.33	.15	.09	.09		
40	3.02	3.14	3.27	3.37	3.48	3.9	.45	.18	.15	.12		
40.5	3.23	3.52	3.82	3.99	4.13	6.5	.86	.38	.30	.27		
Liquid												
45	10.30	10.59	11.06	11.55	11.91	45.5	40.4	40.1	40.1	40.1		
Ice (m. p. 0°)												
k.c. = t, °C.	60	20	5	1	0.5	0.3	60	20	5	1	0.5	0.3
-70	2.98	2.97	2.99	3.33	3.59	4.00	1.1	0.11	0.11	0.069	0.052	0.052
-60	3.00	3.00	3.12	3.50	3.92	4.35	1.2	.24	.16	.11	.086	.086
-50	3.02	3.04	3.21	3.82	4.65	6.17	1.37	.43	.29	.24	.21	.21
-40	3.03	3.06	3.32	5.37	8.78	16.3	2.58	.89	.69	.58	.55	.48
-30	3.04	3.15	4.06	14.6	31.3	46.2	3.33	2.06	1.84	1.48	1.18	.62
-20	3.12	3.57	7.60	45.2	65.9	71.9	6.7	5.5	4.55	2.14	0.86	.31
-10	3.33	5.46	24.4	69.4	73.6	74.8	15.6	12.7	9.0	1.25	.40	.10
- 5	3.71	8.34	40.2	72.5	73.8	73.8	23.7	19.7	9.86	0.81	.20	.07
- 3	4.2	10.4	46.3	72.4	73.5	74.2	27.5	23.3	9.62	.65	.17	.052
- 1	4.3	12.3	51.6	72.5	73.6	73.7	29.9	25.6	8.85	.57	.17	.086

TABLE I (Continued)

0.0002 M KCl Solution (-0.0007°; eutectic point, -10.8°)												
k.c. = <i>t</i> , °C.	60	20	5	1	0.5	0.3	60	20	5	1	0.5	0.3
	ε (Falling temperature)						<i>k</i> (× 10 <sup>3</sup> )					
-70	3.04	3.24	4.32	9.06	11.5	15.6	2.6	1.29	0.86	0.51	0.41	0.33
-60	3.15	3.68	5.41	11.4	17.0	23.2	3.78	2.27	1.32	.74	.57	.43
-50	3.35	4.21	6.72	15.5	24.5	32.0	4.98	3.26	1.89	1.05	.74	.57
-40	3.64	4.80	8.12	22.2	37.4	50.1	7.12	4.36	2.74	1.57	1.13	.76
-30	3.93	5.32	10.4	39.0	63.4	75.7	9.35	6.35	4.46	2.32	1.34	.76
-20	4.08	6.13	17.3	62.5	84.4	93.2	14.2	10.5	7.4	2.4	1.24	.67
-10	4.20	8.27	34.5	90.8	112	121	23.7	19.2	12.0	2.74	1.49	.95
- 5	4.55	11.3	47.8	102	123	134	31.0	26.9	13.5	3.26	1.8	1.17
- 3	4.98	13.0	53.3	111	136	149	37.8	30.0	14.9	3.78	2.24	1.41
- 1	5.3	15.2	61.5	128	158	176	44.6	37.8	17.2	4.8	2.98	1.89
(Rising temperature)												
-40	3.64	4.78	8.11	22.4	37.1	51.5	6.7	4.3	2.7	1.5	1.1	0.69
-20	4.07	5.98	17.3	64.0	82.9	89.9	14.2	9.8	7.4	2.35	1.03	.55
-10	4.36	8.90	36.2	84.9	96.5	103	23.7	19.4	11.0	1.85	1.05	.62
- 3	5.53	15.2	55.6	91.1	102	107	36.0	29.2	11.2	1.9	1.03	.69
- 1	6.05	17.0	61.6	93.2	103	110	41.2	32.6	11.2	1.99	1.12	.79
Benzene saturated with water (0.01-5%)												
Benzene (m. p. 5.4°)												
k.c. = <i>t</i> , °C.	60	5	1	0.3								
0	2.307	2.307	2.309	2.306								
5	2.316	2.313	2.319	2.319								
Liquid												
5	2.341	2.344	2.347	2.344								
Benzene (f. p. 5.4°)												
<i>t</i> , °C.	60	5	1	0.3								
-50	2.318	2.322	2.321	2.327								
-30	2.335	2.340	2.346	2.354								
-10	2.352	2.362	2.381	2.404								
0	2.362	2.376	2.401	2.437								
5	2.372	2.389	2.418	2.455								
Liquid												
25	2.310	2.312	2.319	2.332								
Dimethyl Sulfate (m. p. -31.4°)												
k.c. = <i>t</i> , °C.	60	20	5	1	0.5	0.3	60	20	5	1	0.5	0.3
	ε						<i>k</i> (× 10 <sup>3</sup> )					
-90	2.98	2.99	3.03	3.06	3.09	3.14	< .01					
-80	3.02	3.02	3.10	3.16	3.21	3.26	< .01					
-75	3.06	3.06	3.12	3.21	3.25	3.28	< .01					
-72	3.07	3.09	3.13	3.21	3.28	3.35	< .01					
(Rising temp.)												
3.09	3.10	3.17	3.22	3.27	3.38	< .01						
(Falling temp.)												
8.25	8.22	8.17	8.32	8.50	8.57	0.089	0.053	0.018	0.018			
(1 hr. after transition)												
9.29	9.28	9.42	10.39	10.97	11.47	0.35	.35	.18	.09	.05	0.035	
(5 hrs. after transition)												
7.50	7.60	7.85	8.78	9.55	10.20	.71	.35	.27	.14	.12	.11	
-60	8.02	7.97	8.06	8.40	8.69	9.00	.36	.18	.089	.036	.036	.018
-50	7.88	7.90	8.09	8.76	9.29	9.87	.36	.36	.20	.089	.071	.053
-40	7.89	7.98	8.32	9.35	10.21	10.98	.89	.53	.34	.18	.14	.12
-35	8.01	8.13	8.60	10.03	11.04	11.90	.89	.71	.50	.32	.27	.25
-33	8.34	8.51	9.19	11.15	12.52	13.55	1.8	1.1	.71	.46	.41	.37
-32	8.62	8.86	9.70	11.95	13.45	14.70	1.8	1.4	.93	.62	.57	.53
Liquid												
-30	60.2	60.1	60.3	61.5	62.6	64.0	10					
-20	55.8	55.8	56.0	57.8	59.4	61.3	14					
0	48.3	48.3	48.9	51.4	53.5	55.9	25					
20	42.6	42.7	43.8	47.2	50.6	55.8	37					

TABLE I (Concluded)

k.c. = $t, ^\circ\text{C.}$	Diethyl Sulfate (m. p. $-25.2^\circ$ )									
	60	5	1	0.5	0.3	60	5	1	0.5	0.3
	$\epsilon$									
-70	2.91	2.91	2.96	3.15	3.24		0.035	0.018	0.018	
-50	3.24	3.30	3.60	3.98	4.24		.089	.058	.035	0.035
-40	3.44	3.54	4.01	4.47	4.87		.14	.071	.053	.053
-30	4.06	4.18	4.93	5.63	6.33	0.18	.18	.12	.09	.09
-28	4.65	4.79	5.63	6.54	7.24	.35	.25	.18	.14	.12
	Liquid									
-25	37.5	37.5	37.6	38.1	38.6			2.3		
-20	36.4	36.4	36.7	37.4	37.8			2.7		
0	32.7	32.7	33.2	33.8	34.4			3.6		
20	29.2	29.4	31.0	32.4	33.6			7.4		

### Discussion of Results

The behavior of nitrobenzene, which has a moment  $3.9 \times 10^{-18}$ , is typical of the normal pure polar substance, the difference between the values at 60 and at 0.5 kilocycles being too small to be evident in Fig. 1.

The dielectric constant rises with falling temperature as required by the Debye equation until solidification occurs, when it drops sharply. There is no abnormality in the curve for the liquid just above the freezing point or supercooled a little below it, which argues strongly against any suddenly increased formation of aggregates in this region, as such formation would almost certainly alter greatly the effect of the large dipoles in the molecules and change the course of the curve. The considerable decrease in the dielectric constant and in the conductance of the solid as the temperature falls just below the freezing point is probably due to the disappearance of a trace of liquid arising from the presence of minute quantities of impurities.

The continued slow decrease as the temperature decreases further is a phenomenon observed in all of the solids in Table I. It may be due to the displacement of a very small number of ions, which becomes less as decreasing temperature renders the structure more rigid and becomes greater

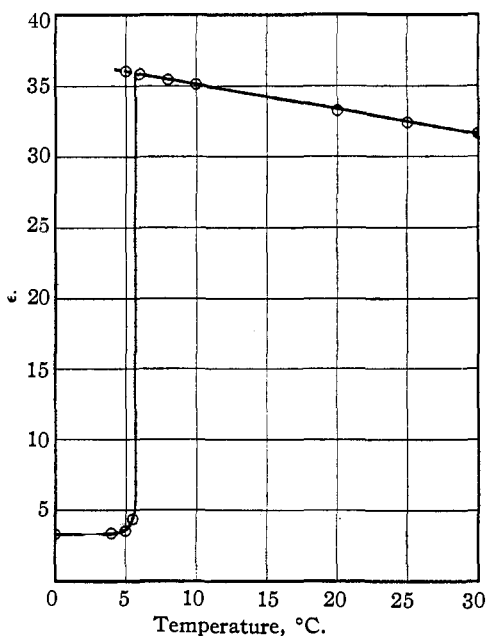


Fig. 1.—Variation of the dielectric constant of nitrobenzene with temperature (500–60,000 cycles).

as decreasing frequency of the applied field gives more time for the process of displacement to continue, thus causing a slight increase in dielectric constant with decreasing frequency as generally observed in Table I. This latter effect is just distinguishable in liquid nitrobenzene, but is very strong in liquid dimethyl sulfate, which has a much higher conductance, and to a lesser extent in diethyl sulfate. It was also very apparent in unreported measurements made upon an impure sample of acetic acid, which had a considerable conductance. It is not impossible that an occasional molecule in the solid may possess sufficient freedom of motion to orient in the field, an orientation which, of course, would be more difficult the lower the temperature and the higher the frequency. Although no great accuracy is claimed for these conductance measurements, it is interesting to note that those for the liquid lie within the range of the values given in "International Critical Tables,"  $2 \times 10^{-7} - < 2 \times 10^{-10}$ .

The dielectric constant of the solid is much lower and shows much less variation with frequency than the values found by Errera,<sup>8</sup> a difference attributable to the presence of impurities in the material used in the latter's measurements. There is nothing to suggest the extraordinary behavior reported by Wolfke and Mazur,<sup>11</sup> whose values for the dielectric constant of liquid nitrobenzene are in excellent agreement with those in Table I above  $9.5^\circ$ . Below this temperature, however, their values drop rapidly to 10.973 at  $6.01^\circ$ , show a slight rise on solidification, 11.365 at  $5.50^\circ$ , and decrease only to 9.709 at  $-75^\circ$ . It is very difficult to picture the large nitrobenzene molecules as possessing sufficient freedom of motion in the solid state to give so large a dielectric constant. Wolfke and Mazur determined an energy change of 0.14 cal. per gram as accompanying a transformation from one liquid phase to another at  $9.5^\circ$ . Calculation from this heat of transformation shows that only 0.00043 mole fraction of impurity would be required to lower this transition down to the freezing point, below which it would not occur. A similar calculation shows that this same amount of impurity would lower the freezing point only  $0.024^\circ$ . The observed melting point of our material  $5.67^\circ$  is in satisfactory agreement with that given in "International Critical Tables,"  $5.72 \pm 0.10^\circ$ , and higher than the value  $5.5^\circ$  reported by Mazur.<sup>12</sup> Although it is evident that there may be enough impurity in our material to prevent the occurrence of a transition, the melting point found by Mazur would seem to indicate the presence of a greater amount of impurity in his material. Other investigators<sup>13</sup> have failed to find discontinuities in other physical properties of liquid nitrobenzene as found by Wolfke and Mazur.

<sup>11</sup> Wolfke and Mazur, *Z. Physik*, **74**, 110 (1932); Mazur, *Nature*, **126**, 993 (1930).

<sup>12</sup> Mazur, *ibid.*, **127**, 893 (1931).

<sup>13</sup> Masson, *ibid.*, **128**, 726 (1931); Massy, Warren and Wolfenden, *J. Chem. Soc.*, 91 (1932); Friend, *Nature*, **129**, 471 (1932).



If the dielectric constant of solid nitrobenzene is taken as 3.1 and the density of the solid at 0° given by "International Critical Tables" as 1.2229 is used, the polarization,  $P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d}$ , is calculated as 42.1, while the molar refraction of the liquid extrapolated to infinite wave length is 31.6. The atomic polarization  $P_A$ , calculated as the difference 10.5, is slightly higher than the value 8 previously reported,<sup>14</sup> and is probably too high because of the effect which produces increase of dielectric constant with rising temperature and decreasing frequency. These results tell nothing as to the possible rotation of the nitro group about its bond to the ring because the moment of the group lies in the axis of possible rotation,<sup>15</sup> but they do show that the molecules are firmly fixed in the space lattice with certainly little and, probably, no opportunity of rotation.

Solid ethylene chloride resembles nitrobenzene in behavior. The effect of temperature and frequency upon the dielectric constant is less at temperatures well removed from the melting point. A value of 1.44 was determined for the density of the solid at the melting point, which made possible the calculation of the polarization as 23.8, and of  $P_A$  as 3.0. This shows clearly that the externally applied field does not produce rotation of the molecule as a whole or, to any extent, of the two halves of the molecule relatively to one another. The latter point is interesting in view of the fact that the temperature variation of the moment of the molecule in solution and in the gaseous state has shown that here the two halves of the molecule oscillate about the C-C line as axis.<sup>16</sup>

The aniline molecule has a moment,  $1.56 \times 10^{-18}$ , and, as the two N-H bonds lie in a different plane from the C-N, rotation around the latter bond as axis would alter the orientation of the resultant dipole. Aniline resembles nitrobenzene in behavior, showing no abnormality just above the melting point, the same sharp drop in dielectric constant and conductance on freezing and the same slowing up of the decrease in the values as the temperature is lowered. However, at  $-70^\circ$ , the decrease of dielectric constant with falling temperature is still pronounced, although the variation with frequency has almost disappeared, and the values are high for so low a temperature. This suggests that there may be some turning of the  $\text{NH}_2$  group to effect a partial dipole orientation in the field, which would, of course, contribute to the dielectric constant. The small moment of inertia of the  $\text{NH}_2$  group about the C-N line should make this easy, unless the internal field is strong. However, if decreasing temperature is decreasing the contribution of this dipole orientation to the dielectric con-

<sup>14</sup> See Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., Inc., New York, 1931, p. 164.

<sup>15</sup> Ref. 14, p. 121.

<sup>16</sup> Smyth, Dornte and Wilson, *THIS JOURNAL*, **53**, 4242 (1931); Zahn, *Phys. Rev.*, **38**, 521 (1931).

stant, increasing frequency should also cause it to decrease. As it does not do so to an appreciable extent at the low temperature, it appears improbable that the dielectric constant receives any contribution from dipole orientation through rotation.

The general course of the values for phenol in Table I is similar to those for aniline and nitrobenzene. The apparent anomalous dispersion just below the melting point is presumably due to water, which is very difficult to remove and is certainly present in small amount. The presence of water is also probably responsible for slight humps in the curves at low frequencies between 20 and 30° and for the fact that the curves at low frequencies obtained with rising temperature, the data for which are not given in Table I, lie slightly above those obtained with falling temperature. A difference between the curves obtained with falling and with rising temperature is commonly observed when impurities are present because of delay in the attainment of equilibrium in the solid. A difference was hardly detectable in the case of the other substances which have been discussed.

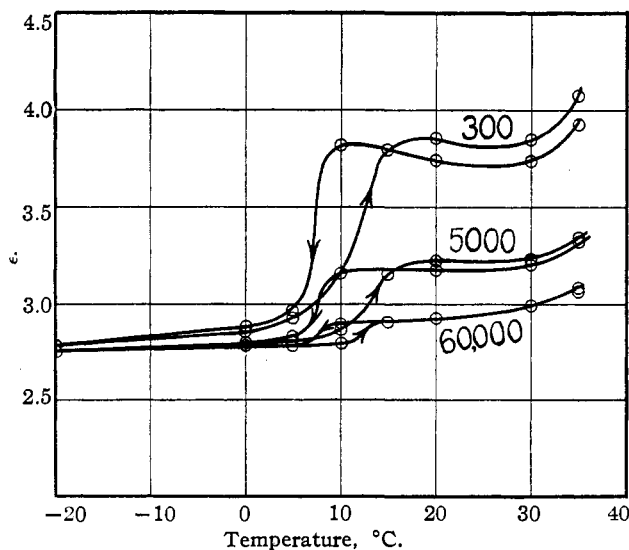


Fig. 2.—Variation with temperature and frequency of the dielectric constant of phenol containing a small quantity of water.

Another more thoroughly dried sample had the same freezing point and gave values close to those in Table I. A less pure sample of freezing point 40.5° gave the curious curves shown in Fig. 2, which are similar to those obtained for another sample of about the same purity. The curves marked with arrows pointing down along them represent values obtained with falling temperature and those with arrows pointing up values obtained with rising

temperature. The curves at each frequency form a sort of hysteresis loop starting at  $15^\circ$  and ending at about  $5^\circ$ . The conductance curves not shown have somewhat similar loops closing at  $5^\circ$  but clearly defined at the upper end only in the case of the higher frequencies. Rhodes and Markley,<sup>17</sup> investigating the system phenol-water, obtained a melting point  $40.8^\circ$  for carefully purified phenol and found that on adding water to phenol a eutectic point was reached at  $15.9^\circ$ . Below this point, however, the curve could be extended to represent a metastable equilibrium so that, in an area extending down to  $-1.2^\circ$ , solid phenol could exist in metastable equilibrium with a solution of water in phenol. The curves in Fig. 2 indicate that the material contains liquid, a solution of water in phenol, which, as the temperature is lowered, begins to solidify rapidly at  $10^\circ$  and has practically all solidified at  $5^\circ$ . With rising temperature liquid begins to form just below  $10^\circ$  causing the sharp rise in dielectric constant and conductance up to the eutectic point for stable equilibrium, above which no sharp change occurs until the melting point is approached. If  $40.8^\circ$  is the freezing point of pure phenol, the curve obtained by Rhodes and Markley shows that our material of freezing point  $40.7^\circ$  contains about 0.026% water and the less pure material of f. p.  $40.5^\circ$  about 0.078%, all the impurity present being assumed to be water. In spite of the low moment of inertia of the O-H group about the C-O line, there is no definite evidence in Table I of a contribution to the dielectric constant through rotation of the O-H dipole, although the possibility of orientation of an occasional group or molecule in the field is not excluded.

Ice was first prepared from distilled water, then from conductivity water, which gave somewhat lower values of the dielectric constant, and finally from conductivity water after long soaking and rinsing of the cell. This last ice had a slightly lower dielectric constant than that made from

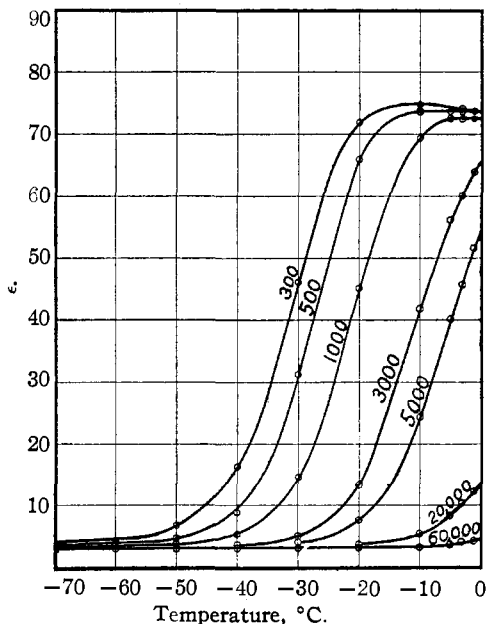


Fig. 3.—Variation of the dielectric constant of ice with temperature and frequency.

<sup>17</sup> Rhodes and Markley, *J. Phys. Chem.*, 25, 527 (1921).

the first conductivity water and no change was effected by further soaking and rinsing of the cell. The values in Table I and Fig. 3 are for a very pure ice.

The curves for ice are like those for a very viscous liquid. At the lowest frequencies, the dielectric constant is close to that of liquid water, and, for the first few degrees of temperature decrease, actually rises as the lessened thermal motion interferes less with the orientation of the polar molecules in the external field. As the temperature is further lowered, the increasing rigidity of the structure reduces molecular orientation until,

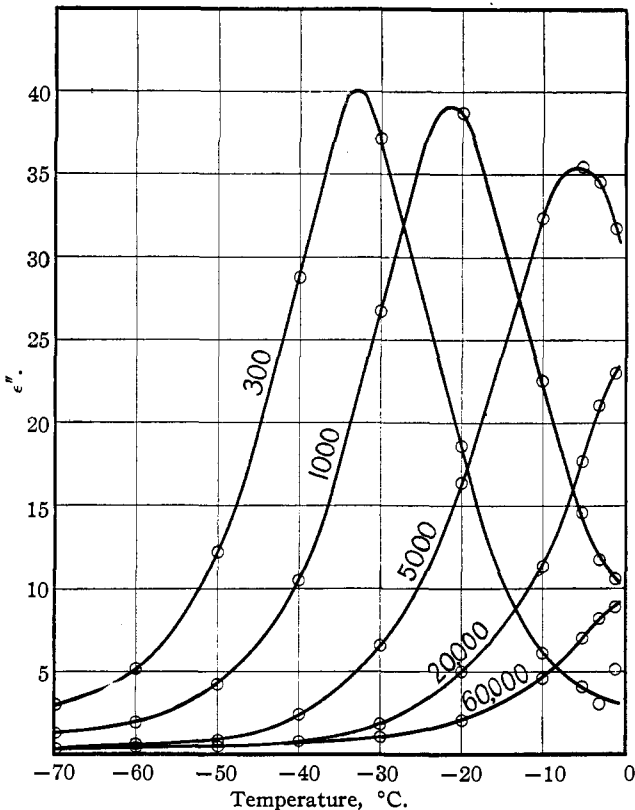


Fig. 4.—Variation of  $\epsilon''$  for ice with temperature and frequency.

at  $-70^{\circ}$ , the dipole of moment  $1.85 \times 10^{-18}$  contributes little to the dielectric constant even at low frequency. At 60,000 cycles even just below the melting point, so little time is given the molecule to turn that the dipole contributes little more to the dielectric constant than at  $-70^{\circ}$  and 300 cycles. The anomalous dispersion is best shown by plotting the values of  $\epsilon''$  for each frequency against temperature (Fig. 4).  $\epsilon''$  is shown in the

equation  $\epsilon = \epsilon' - i\epsilon''$ , in which the first term on the right is the real part and the second the imaginary part of the dielectric constant.<sup>18</sup> It is calculated by means of the equation<sup>19</sup>  $\epsilon'' = 9 \times 10^{11}(2k/f)$ , in which  $k$  is the conductance and  $f$  the frequency in cycles. These curves make clear the fact that we are dealing with a typical anomalous dispersion, the maximum moving to lower temperature as the frequency decreases. Evidently the molecules possess a certain freedom of rotation which diminishes gradually as the temperature is lowered. There is no abrupt disappearance of this freedom of rotation as in the case of hydrogen chloride. The existence of rotation at these temperatures is consistent with the small moment of inertia of the molecule.

In view of the evident influence of small quantities of impurities upon the results, it seemed desirable to investigate ice with a known quantity of impurity. A 0.0002 *M* solution of potassium chloride in some of the same conductivity water, containing one potassium chloride to every 278,000 water molecules, was, therefore, frozen in the cell. The calculated freezing point,  $-0.0007^\circ$ , was indistinguishable in these measurements from that of pure water. The rather high eutectic point,

$-10.8^\circ$ , assured the absence of liquid throughout most of the range of the measurements. The dielectric constant curves obtained at four frequencies are plotted in Fig. 5 as broken lines, arrows pointing down along the curves indicating measurements taken with falling temperature. The solid lines are similar curves for pure ice given for comparison, the values obtained with falling and with rising temperature being approximately the same. The minute amount of potassium chloride increases the dielectric constant to a surprising extent at the low frequencies, but has relatively little effect at 60,000 cycles. No alteration in the trend of the curves is apparent at the

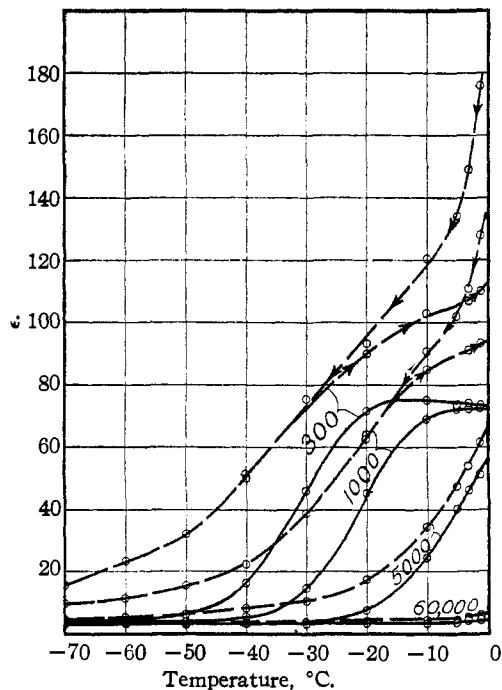


Fig. 5.—Variation of the dielectric constant of frozen 0.0002 *M* KCl solution.

<sup>18</sup> Ref. 2, p. 94.

<sup>19</sup> Cf. Ref. 2, p. 99.

eutectic point and the lower curves obtained with rising temperature at the low frequencies show that a long time is required for the attainment of equilibrium in the solid. At frequencies of 5000 and more the rising and falling curves are too close together to be distinguishable from each other. It appears that the increase in dielectric constant is due to the displacement of the ionic charges by the field, which is greater the longer the time in which the field acts in one direction. The conductance is increased by the potassium chloride ten-fold in the liquid to  $2.2 \times 10^{-5}$  and to a smaller extent in the solid.

When water saturated with benzene (0.15%) at  $0^\circ$  was frozen and measured, the dielectric constant and conductance values obtained were the same as those of pure ice and the conductance of the liquid was also indistinguishable from that of pure water. This is to be expected as the amount of benzene present is insufficient to dilute the water enough to alter these properties by a detectable amount and as no ions or dipoles are introduced by it. The effect of saturating benzene with water is shown by the data in Table I. As the benzene, saturated with water at room temperature, was slightly cloudy with separated water at the freezing point, the total water content was probably about 0.05%, although the solubility at  $5.4^\circ$  obtained by extrapolation is 0.008%.<sup>20</sup> Pure benzene shows practically no change of dielectric constant with frequency either in the solid or in the liquid and a conductance too small to measure, but the benzene saturated with water shows a markedly higher dielectric constant,<sup>21</sup> a conductance of the order of  $2 \times 10^{-10}$ , and variation with frequency particularly just below the freezing point, as would be expected. It is easy to see, therefore, how a substance containing a small amount of water as impurity, particularly, a substance which may hydrolyze to give ionic impurities, may show a considerable apparent anomalous dispersion when the pure substance would show none.

Four different samples of methyl sulfate were studied, the third and fourth of which were moderately pure as indicated by the freezing point curve. The results for the third sample, which were in good agreement with those for the fourth, are given in Table I with values for the second sample at the lowest temperatures, where impurities caused but little error. The two sets of values at  $-65^\circ$  were determined for the fourth sample during five hours' standing at  $-65^\circ$  and are not directly comparable with the other values. Although, as previously remarked, the high dielectric constant curves for the liquid (moment =  $3.3 \times 10^{-18}$ ) at different frequencies (Fig. 6) are somewhat separated from one another, probably because of the displacement of ionic impurities, they rise with falling temperature in accordance with the Debye equation. The sharp drop on

<sup>20</sup> See Seidell, "Solubilities," New York, D. Van Nostrand Company, Inc., 1928.

<sup>21</sup> Cf. Williams, *Physik. Z.*, 29, 204 (1928).

solidification does not extend as low as with the other polar substances and the dielectric constant is obviously too large to arise from an ordinary induced polarization, which suggests the occurrence of some dipole orientation. The values are much lower than those found by Errera for the solid, which must have contained considerable quantities of impurities. The separation of the curves and downward slope of those for low frequencies below the freezing point is probably due to displacement of ionic impurities

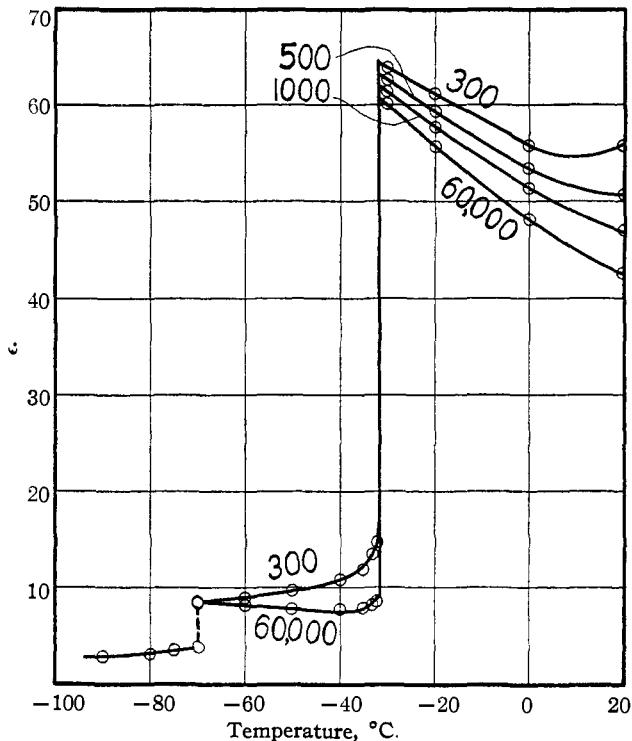
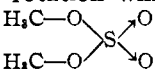


Fig. 6.—Variation of the dielectric constant of dimethyl sulfate with temperature and frequency.

as in cases previously discussed. At frequencies of 60,000 and 20,000 (not shown) cycles, where the effect of ions has been shown to be small, the curves rise with falling temperature in such a way as to support the indication of dipole orientation given by the high values of the dielectric constant. At  $-70^{\circ}$  the curves drop sharply to values like those obtained for the other solids at low temperatures and, below  $-70^{\circ}$ , resemble these other curves. Cooling curves run on two samples of the solid show a transition beginning at  $-71.0^{\circ}$  and heating curves on the same samples a transition at  $-68.0^{\circ}$ . This explains the high value of the dielectric constant found at  $-70^{\circ}$  with falling temperature while a low value is found with rising temperature.

The transition from the state of lower dielectric constant to that of higher brings about an abnormally high initial value of the constant which decreases somewhat on standing as shown by the values at  $-65^\circ$  one hour and five hours after the substance had been brought to the transition temperature. Possibly the transition brings about a temporary loosening of the structure which facilitates the dipole orientation apparently occurring above the transition point.

The transition appears to resemble that predicted by Pauling and found by Cone, Denison and Kemp for hydrogen chloride. However, the sharp drop on solidification and the subsequent absence of marked anomalous dispersion show that dipole orientation in the solid cannot come from turning of the molecule freely in the alternating field unless such turning is limited to certain axes. It is more natural, however, in view of the large moment of inertia of the molecule, to seek rotation in a group of small inertia within the molecule. The only rotation which can give rise to

dipole orientation within the molecule  is that of the two methoxy groups around the S-O bonds as axes. Although no evidence has been obtained of rotation of the methoxy group in solid anisole and hydroquinone dimethyl ether,<sup>1</sup> it is quite possible that the different molecular spacing and internal field in dimethyl sulfate should permit the rotation of the polar CH<sub>3</sub>-O group, the moment of inertia of which about the line of the S-O bond is not large.

The remote possibility had been considered that the sharp drop in dielectric constant and conductance at  $-70^\circ$  might be due to the solidification here of a small quantity of a liquid phase containing sulfuric acid, but the complete absence of any such effect in the less pure diethyl sulfate eliminated this possibility. The curves for the latter substance drop sharply on solidification to values like those usually found for solids and, presumably, containing no contribution from dipole orientation. This is not surprising as the rotation of the ethoxy group is less probable than that of the methoxy because of its greater moment of inertia and the greater possibility of the larger groups' interfering with one another's rotation.

The results of this investigation show that there is no suddenly increased formation of molecular aggregates in the liquids here studied as the freezing point is approached. They show the tremendous effect that very small quantities of impurities may have upon the dielectric constant of a solid measured at low frequencies and thus give warning of the care which must be used in interpreting the results of such measurements. They also suggest the dielectric constant as a very sensitive instrument for the investigation of some equilibria and transitions in solids. No evidence has been found of the free rotation of large polar molecules in solids, although it is not impossible that the methyl sulfate molecules should rotate around



certain axes. The high dielectric constants found by Errera for such solids must be attributed to the presence of impurities. However, the occasional rotation of a large molecule in a solid, particularly just below the melting point, cannot be positively excluded by the results. The rotation found for the molecule in ice and presumably for the small polar group in solid dimethyl sulfate and the absence of rotation of the large molecules give further confirmation of Pauling's conclusions as to the rotation in the solid of molecules and groups having small moments of inertia.

### Summary

Dielectric constants and specific conductances have been measured over a wide range of temperature and frequency for nitrobenzene, ethylene chloride, aniline, phenol, ice, benzene, dimethyl sulfate and diethyl sulfate in the solid state, and for certain of them as liquids near the melting point.

It is shown that no suddenly increased formation of molecular aggregates occurs in the liquids as the freezing point is approached. No evidence has been obtained of the second liquid phase in nitrobenzene reported by Wolfke and Mazur.

It is found that a very small quantity of impurity may have a very large effect upon the dielectric constant of a solid measured at low frequencies and the dielectric constant is suggested as a means for the investigation of some equilibria and transitions in solids. No evidence has been found of the rotation of large polar molecules in solids, although the possibility of an occasional rotation of a large molecule, particularly just below the melting point, is not excluded and it is not impossible that the methyl sulfate molecules should rotate around certain axes. As indicated by the results of previous investigators, molecules rotate in ice, which, in this respect, behaves like a very viscous liquid. No rotation of small polar groups in the molecules was found except in dimethyl sulfate, where, apparently, the methoxy group gives dipole orientation down to a transition point at  $-70^{\circ}$ .

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