The paper spot method is sensitive to about 0.01 γ. In solutions of extremely low ionic strength, as little as 1 part of palladium in 300,000,000 parts of solution may be detected in 50-ml. Nessler tubes (220 mm.). Under the conditions in which the determinations are carried out, the concentration limit is 1:200,000,000, using either Nessler tubes or the roulette comparator. This corresponds to 0.25 γ of palladium with the former and 0.5 γ with the latter. The method may be made more sensitive by the use of smaller volumes. For instance, using 2 ml. of solution in small test-tubes which gave a column of liquid 50 mm. in height, 0.04 γ was detectable. With 10 ml. of solution and a column height of 80 mm., 0.1 γ was detectable.

The accuracy of the determination depends upon the concentration of palladium present, the volume of solution used, the method of matching, and the presence or absence of interfering substances. The accuracy reported below for the different amounts of palladium is based on a volume of 100 ml. using a roulette comparator (100 ml. tubes, 160 mm. to mark) with a Corning Filter no. 512 for amounts of palladium up to 20 γ and Filter no. 585 for larger amounts. The accuracy found under the most favorable conditions was as follows: 0.5–10 γ, 0.25 γ; 10.5–25 γ, 0.5 γ; 26–35 γ, 1 γ; 36–50 γ, 2.5 γ.

Acknowledgment.—The authors wish to express their appreciation to Charles J. Barton of this Laboratory for the data used in the relative absorption curves.

Summary

The reaction between p-nitrosodiphenylamine and palladous chloride has been described. This reaction is extremely sensitive and nearly specific for palladium. Studies have been made on the effect of salts, of hydrogen-ion concentration, of temperature, and of interfering substances on the color formation and stability of the compound.

The composition of the compound has been determined and found to correspond to the coordination compound $Pd[C_6H_5NHC_6H_4NO]_2Cl_2$. The compound has a purplish-brown color in the solid state but under the experimental conditions used in the colorimetric procedure it forms a red solution.

Relative absorption curves are given for solutions of the reagent and of the palladium compound.

Details are presented for a new colorimetric method permitting the determination of quantities of palladium of the order of a few γ, as well as results of its application. Procedures are also given for the determination of palladium when accompanied by gold and platinum.

The Vitrification and Crystallization of Organic Molecules and the Dielectric Behavior of i-Butyl and i-Amyl Bromides

BY WILLIAM O. BAKER AND CHARLES P. SMYTH

The relation of molecular structure to molecular interaction and rotational freedom in the solid state has been studied by means of dielectric constant and dispersion measurements on a series of molecules of differing shapes. In investigating the connection between the symmetry of the crystal lattice and the symmetry of the molecule, i-butyl and i-amyl bromides were examined as pear-shaped forms intermediate between the rod-like long[1] chain compounds, and the nearly spherical t-butyl halides.[2] Their ready vitrification permitted analysis of both crystalline and glassy behavior.

A capacity bridge coupled to a low-frequency, variable oscillator, and to a vacuum tube, six-stage amplifier was employed for the dielectric measurements in the same general fashion as that already described.[3] Temperatures were obtained from a platinum resistance thermometer. The crystals and glasses were examined over a wide temperature range with a polarizing microscope equipped with a transparent Dewar tube mounted on the stage. The cell containing the material to be measured was inserted in a brass block into which liquid air could be injected at any desired rate.[3] Further the block assembly was suspended in a large Dewar vessel, from the lower portion of which liquid air could be evaporated to provide a very slow rate of temperature change in the cell. The usual care was taken to reduce void formations between the condenser walls by pumping off dissolved gases from the liquid in the cell, by subsequent freezings and meltings, and by slow final freezing from the bottom of the cell upward.

(1) Baker and Smyth, THIS JOURNAL, **60**, 1229 (1938).

(2) Baker and Smyth, to be published.

(3) Smyth and Hitchcock, THIS JOURNAL, **54**, 4631 (1932); **55**, 1830 (1933).

Purification of Materials

The fractionation of these compounds was by a packed column of satisfactory efficiency, elsewhere described.[4]

i-Butyl Bromide.—The Eastman Kodak Co. product was dried over pure calcium bromide, and was fractionally distilled five times; the five fractions in the right boiling range were combined and refractionated. The final criteria for purity were the absence of Maxwell–Wagner polarization on melting, and a low specific conductance for the liquid: b. p. 91.9°; m. p. −118°; $n^{20.0}D$ 1.43440. A separately purified sample gave: b. p. 91.9°; $n^{20.0}D$ 1.43430. Skau and McCullough[5] report for a highly-purified sample, b. p. 91.72°; m. p. −118°. Kharasch and Potts[6] give $n^{20}D$ 1.4355. The tendency for rearrangement to *t*-butyl bromide of this compound was realized, but, under the conditions of distillation, very little should occur,[7] as indicated by the sensitive conductance measurements.

i-Amyl Bromide.—Material of the best Eastman Kodak Co. quality was dried over pure calcium bromide, and thrice fractionated: b. p. 120.5°; m. p. −112°; $n^{20.0}D$ 1.44154. The Landolt–Börnstein "Tabellen" (with $n^{20}D$ from "I. C. T.") give: b. p. 120.65°, m. p. −112.0°, $n^{20}D$ 1.4412.

Experimental Results

Table I contains the dielectric constants ϵ, the specific conductances k (ohm^{-1} cm.$^{-1}$), and the imaginary part of the dielectric constant ϵ'', which is related to the loss factor by tan $\delta = \epsilon''/\epsilon'$, where ϵ' is the normally recorded dielectric constant, ϵ. The columns of data are headed by the appropriate frequencies in kilocycles, and the temperatures are in °C.
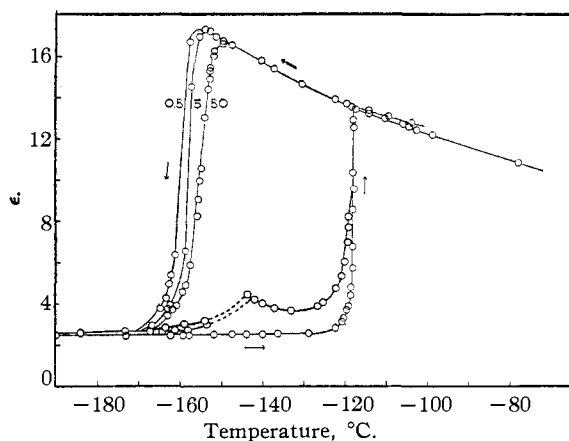

Fig. 1.—Variation with temperature and frequency of the dielectric constant of *i*-butyl bromide.

The data recorded were obtained from at least four separate runs, each of which reproduces the curves of Figs. 1 and 3 exactly. Exceptions, of

(4) Baker and Smyth, THIS JOURNAL, **61**, 1695 (1939).

(5) Skau and McCullough. *ibid.*, **57**, 2439 (1935).

(6) Kharasch and Potts, *ibid.*, **58**, 57 (1936).

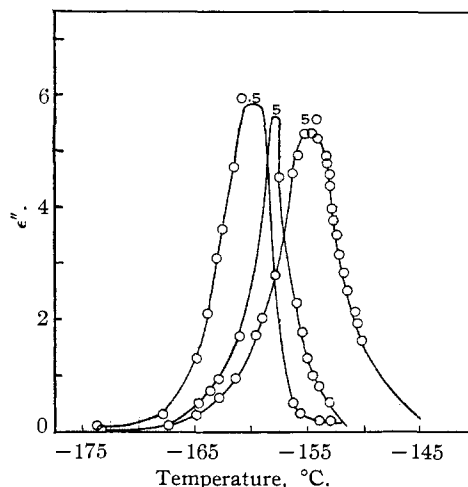(7) Michael, Scharf and Voigt. *ibid.*, **38**, 653 (1916).

Fig. 2.—Variation with temperature and frequency of ϵ'' for *i*-butyl bromide.

course, are the cases of those representing partial devitrification, which were dependent on previous treatment, and will be noted later. Values at intermediate temperatures have been omitted for the sake of brevity. The apparent values of ϵ'' for the liquid are too high because of a certain amount of direct current conductance.
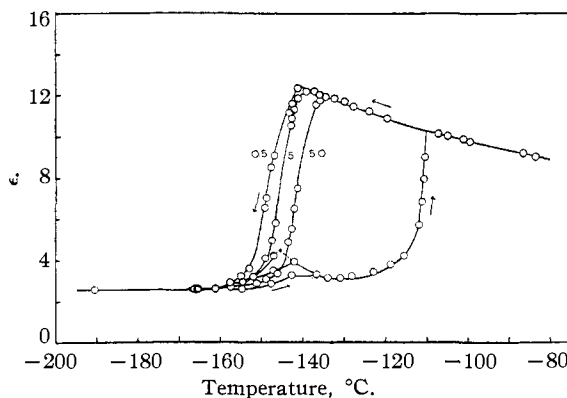
Fig. 3.—Variation with temperature and frequency of the dielectric constant of *i*-amyl bromide.

Discussion of Results

There is still uncertainty about the thermal and optical properties of glasses, about their mechanism of viscous flow, and about the question of their possessing definite vitrification and devitrification temperatures.[8] Commercial glasses, generally used as dielectrics, have been studied as to dielectric constant and loss, and breakdown potential, usually over short temperature ranges.[9]

(8) Richards, *J. Chem. Phys.*, **4**, 449 (1936).

(9) Morey, "The Properties of Glass." Reinhold Publishing Corp., New York, 1938. Chap. XX.

These, like ordinary organic glasses, such as sugars and glycerol, have strong intermolecular bonding, which complicates dielectric interpretations of structure. The simple bromides here investigated, although they have no hydrogen bonds linking the molecules, invariably form clear glasses on cooling.

TABLE I

i-C$_4$H$_9$Br

t, °C.	Kc = 50 (ϵ)	5 (ϵ)	0.5 (ϵ)	50 ($k \times 10^{10}$)	5 ($k \times 10^{10}$)	0.5 ($k \times 10^{10}$)	50 (ϵ'')	5 (ϵ'')	0.5 (ϵ'')
				Cooling					
21.6	7.00	7.20	7.73	800	780	760	2.87	28.0	271.0
1.2	7.56	7.72	7.99	530	610	510	1.91	18.5	182.0
− 39.0	8.97	9.06	9.26	270	260	260	0.99	9.40	93.0
− 62.8	10.00	10.09	10.23	210	200	200	.77	7.40	73.0
− 78.3	10.81	10.88	11.00	170	170	160	.62	6.10	60.0
−103.1	12.40	12.47	12.52	108	107	105	.40	3.90	38.0
−106.0	12.63	12.66	12.68	104	100	99.4	.38	3.60	35.5
−107.6	12.75	12.81	12.80	94.7	90.5	89.7	.34	3.20	32.1
−118.3	13.63	13.64	13.64	45.2	43.5	43.5	.16	1.60	15.7
−120.2	13.78	13.82	13.83	40.2	36.7	35.9	.15	1.3	13.0
−122.5	14.01	14.02	14.02	33.5	29.5	29.5	.12	1.1	10.7
−130.8	14.68	14.67	14.67	15.9	10.5	10.6	.06	0.38	3.9
−137.6	15.47	15.52	15.55	14.2	2.3	2.3	.05	.08	0.80
−140.7	15.81	15.87	15.89	21.4	1.2	1.2	.08	.04	.40
−143.1	16.06	16.10	16.12	36.9	0.8	0.70	.13	.03	.30
−145.5	16.29	16.35	16.39	65.3	0.8	.50	.24	.03	.20
−148.1	16.55	16.66	16.65	161.5	1.3	.40	.58	.05	.10
−149.8	16.66	16.82	16.83	350	2.3	.20	1.25	.08	
−150.8	16.73			440			1.60		
−151.7	16.56	17.18	17.19	650	6.0	.40	2.34	.22	.10
−151.8	16.30			790			2.84		
−152.2	16.08			880			3.14		
−152.8	15.63			1050			3.76		
−153.1	15.37	17.28	17.32	1115	14.0	.50	4.02	.51	.20
−153.5	14.45			1287			4.64		
−153.8	14.31			1326			4.77		
−153.9	14.03	17.30	17.33	1350	21.0	.50	4.86	.80	.20
−154.1	13.78	17.28	17.33	1375	23.5	.40	4.95	.85	.20
−154.5	13.08	17.31	17.33	1443	27.3	.80	5.20	.99	.40
−155.0	12.27	17.30	17.31	1475	36.0	.60	5.31	1.30	.30
−155.4	10.63	17.17	17.32	1475	48.4	.80	5.31	1.75	.40
−155.7	10.01	17.17	17.31	1443	49.6	.90	5.20	1.79	.45
−156.3	9.11	16.91	17.31	1364	64.8	1.50	4.91	2.33	.60
−156.5	8.31			1272			4.50		
−158.1		14.61	16.71		126.0	7.80		4.54	2.8
−159.1	4.92			558			2.01		
−159.6	4.61			476			1.72		
^{a} −158.2	5.88			822			2.95		
−160.2		6.64			73.6				
−161.2	3.87			259			0.94		
−161.6		4.60	6.44		47.2	13.00		1.70	4.7
−161.8	3.71			238			.86		
−162.5		3.93	5.38		30.5	9.90		1.11	3.6
−162.7	3.51			164.0			.59		
−163.0		3.77	5.01		26.3	8.60		0.95	3.1
−163.2	3.38			133.2			.48		
−163.7		3.53	4.30		19.9	5.90		.72	2.1
−164.7	3.19	3.31	3.79	86.6	13.2	3.60	.31	.48	1.3
−167.7		2.92	3.04		3.3	1.00		.12	0.50
−173.5	2.62	2.66	2.67	7.1	0.7	0.40	.03	.02	.10
−190.3	2.52	2.57	2.58						

^{a} Shows complete reversibility at this point.

TABLE I   (*Continued*)

Kc	50	5	0.5	50	5	0.5	50	5	0.5
t, °C.		ϵ			$k \times 10^{10}$			ϵ''	
Warming									
−167.3	2.55	2.58	2.60	3.6	0.6	0.4			
−159.0	2.73	2.89	3.02	26.6	2.8	.6	0.10	1.00	0.20
−153.8	2.98	3.17	3.18	43.5	1.3	.2	.16	0.50	
−144.1	4.45	4.45	4.48	5.3	0.2	.2			
−141.8	4.15	4.15	4.19	3.6	.4	.4			
−139.9	4.00	3.99	4.00	2.2	.4	.5			
−137.0	3.77	3.77	3.79	2.2	.6	.6			
−133.1	3.66	3.66	3.66	2.2	1.1	1.1			
−126.1	3.82	3.84	3.97	3.6	4.3	4.1	.01	.16	1.5
−125.2	3.92	3.95	4.11	5.3	5.7	5.5	.02	.21	2.0
−123.9	4.07	4.10	4.34	7.1	7.6	7.0	.03	.28	2.5
−121.7	4.62	4.68	5.00	14.2	14.7	13.8	.05	.54	5.0
−120.6	5.18	5.26	5.77	19.6	19.6	19.0	.07	.71	6.9
−120.0	5.61	5.69	6.01	23.1	22.2	21.5	.08	.81	7.8
−119.3	6.46	6.59	6.90	26.6	26.7	26.2	.10	.97	9.5
−118.7	7.72	7.95	8.22	31.8	31.4	31.0	.12	1.14	11.2
−118.2	10.04	10.38	10.68	38.5	37.7	37.7	.14	1.36	13.6
−117.9	12.75	12.97	13.09	46.7	45.4	45.5	.17	1.64	16.4
−117.2	13.44	13.47	13.49	52.0	49.6	49.5	.19	1.79	17.8
−114.2	13.28	13.30	13.34	58.7	57.0	57.0	.21	2.05	20.5
− 95.0	11.85	11.91	11.98	141.4	138.3	137.2	.51	4.90	49.4
− 90.4	11.56	11.61	11.71	159.5	157.4	156.0	.57	5.67	56.2
−162.5	2.48	2.48	2.48	7.3					
−158.6	2.50	2.50	2.51	7.3	0.1				
−155.2	2.51	2.52	2.52	10.9					
−151.1	2.54	2.53	2.54	14.4					
−147.5	2.55	2.55	2.55	10.9					
−144.0	2.55	2.55	2.56	7.3					
−140.3	2.55	2.55	2.55	7.3					
−136.5	2.56	2.55	2.55	7.3					
−128.9	2.60	2.61	2.61	7.3	0.2	0.2			
−121.9	2.83	2.87	3.01	10.9	7.3	6.2			
−121.3	2.90	2.95	3.10	14.4	8.4	7.3			
−120.8	2.98	3.02	3.22	14.4	20.2	8.4			
−120.4	3.07	3.13	3.35	14.4	10.5	9.3			
−119.6	3.34	3.41	3.67	18.0	13.0	12.3			
−119.0	3.78	3.90	4.22	21.6	17.0	16.2			
−118.6	4.29	4.44	4.78	25.2	20.5	19.8			
−118.3	5.21	5.43	5.76	28.7	24.8	24.8			
−118.2	5.97	6.27	6.63	28.7	28.4	28.4			
−118.0	6.83	7.19	7.84	36.0	31.7	32.2			
−117.8	8.55	9.57	10.97	50.4	38.5	41.0			
−117.7	12.63	13.44	13.65	57.6	48.6	49.0			
−117.6	13.53	13.53	13.62	64.8	51.2	52.6			
−117.5	13.46	13.45		67.2	55.4				
−114.2			13.45			62.3			
−109.5	13.02	13.01	13.12	98.0	82.0	84.0			
−104.1	12.60	12.61	12.76	123.0	113.0	113.5			
− 98.6	12.19	12.22	12.38	151.3	150.2	150.0			

i-C₆H₁₁Br

Cooling

	50	5	0.5	50	5	0.5	50	5	0.5
23.2	5.98	6.01	5.98	35.2	18.3	18.2	0.127	0.67	6.6
5.5	6.36	6.38	6.38	31.8	15.9	15.7	.115	.58	5.7
2.0	6.49	6.52	6.51	28.1	15.5	15.0	.102	.57	5.5
− 18.3	6.92	6.95	6.94	28.3	8.6	8.2	.103	.31	3.0
− 55.7	8.04	8.02	8.05	25.2	2.8	2.8	.100	.10	1.0
− 62.8	8.24	8.25	8.26	24.9	2.2	2.2	.090	.08	0.80

TABLE I (*Continued*)

Kc	50	5	0.5	50	5	0.5	50	5	0.5
t, °C.		ϵ			$k \times 10^{10}$			ϵ''	
− 85.6	9.16	9.17	9.18	24.0	0.8	0.9	0.088	0.03	0.40
− 86.4	9.20	9.20	9.21	26.6	.8	.8	.097	.03	.30
− 99.5	9.80	9.81	9.81	35.2	.5	.5	.127	.02	.20
−107.3	10.22	10.24	10.24	17.7	.3	.3	.064	.01	.10
−119.5	10.94	10.97	10.98	9.2	.2	.3	.034	.01	.10
−121.1	11.04	11.06	11.07	23.1	.2	.2	.084	.01	.10
−122.8	11.15	11.19	11.19	24.8	.2	.2	.09	.01	.10
−124.4	11.25	11.29	11.29	30.0	.2	.2	.109	.01	.10
−125.3	11.32	11.35	11.35	30.0	.2	.2	.109	.01	.10
−128.0	11.50	11.56	11.54	43.5	.3	.2	.157	.01	.10
−129.3	11.60	11.65	11.65	55.3	.4	.2	.199	.01	.10
−130.9	11.69	11.76	11.74	73.7	.5	.2	.265	.02	.10
−132.5	11.80	11.87	11.87	111.0			.40		
−133.1	11.85			156.6			.564		
−133.7	11.90			148.9			.536		
−134.2	11.91	11.98	11.98	193.5	1.2	.3	.70	.04	.10
−136.6	11.75	12.08	12.05	410.0	3.2	.3	1.48	.12	.10
−137.5	11.61	12.17	12.13	508.9	4.6	.3	1.86	.17	.10
−138.2		12.18	12.18		7.1	.4		.26	.20
−139.4		12.15	12.16		12.9	.4		.47	.20
−141.5	7.49	12.31	12.31	1008	33.5	.4	3.63	1.21	.20
−141.2	7.58	12.16	12.19	1008	30.0	.4	3.63	1.09	.20
−141.2	7.74	12.09	12.09	1008	28.3	.4	3.63	1.03	.20
−141.6	7.24	11.91	11.90	975	35.2	.3	3.48	1.27	.10
−141.9	6.64	11.71	11.85	922	36.2	.9	3.30	1.31	.30
−142.1	6.47	11.60	11.75	910	38.5	.9	3.28	1.39	.30
−142.5	5.97	11.35	11.62	829	45.2	.9	2.98	1.63	.30
−142.7	5.54	10.92	11.35	739	50.3	1.2	2.72	1.81	.40
−143.3	5.14	10.54	11.24	683	60.4	1.5	2.45	2.17	.50
−143.5	4.86	10.35	11.17	622	62.0	1.5	2.24	2.23	.50
−146.8	3.36	5.81	9.09	258.0	73.4	8.6	0.940	2.64	3.1
−147.7	3.30	4.99	8.47	187.3	61.2	11.4	.680	2.20	4.1
−148.7	3.19	4.32	7.02	153.5	47.0	13.6	.553	1.70	5.0
−149.2	3.10	4.08	6.55	125.3	40.3	13.6	.452	1.46	5.0
−151.1	2.89			62.0			.223		
−152.8		3.18	3.64		13.2	3.8		0.48	1.4
−154.8	2.77	2.97	3.26	30.0	6.1	2.0	.109	.22	0.7
−155.2	2.77	2.92	3.18	30.0	4.8	1.8	.109	.18	.6
−157.5	2.69	2.79	2.90	17.7	2.2	0.8	.064	.08	.3
−164.0	2.60			3.6			.013		
−166.3		2.59	2.58		0.3	.3		.01	.10
−190.5	2.54	2.53	2.55						

Warming

−160.8	2.57	2.59	2.61	3.6	0.5	0.4	0.013	0.02	0.20
−154.9	2.62	2.72	2.83	12.5	2.2	.9	.046	.08	.30
−147.2	2.87	3.52	4.19	67.0	15.2	1.2	.241	.55	.40
−142.0	3.31	3.87	3.85	120.6	2.5	0.3	.434	.09	.10
−136.7	3.33	3.33	3.35	24.9	0.3	.2	.09		
−133.5	3.18	3.18	3.18	5.3	.2	.2	.020		
−130.6	3.22	3.23	3.22	2.2	.2	.2			
−129.5	3.28	3.28	3.28	2.2	.2	.2			
−121.3	3.52	3.52	3.54	0.9	.1	.2			
−120.2	3.62	3.62	3.63	.9	.1	.2			
−118.7	3.78	3.79	3.78	.9	.1	.2			
−116.9	4.03	4.04	4.04	.9	.1	.2			
−114.9	4.16	4.20	4.19	.9	.1	.3			
−112.0	5.69	5.76	5.75	.9	.2	.3			
−111.6	6.06	6.19	6.19	.9	.2	.3			
−111.3	6.59	6.67	6.67	.9	.2	.3			

TABLE I (*Concluded*)

Kc t, °C.	50	5	0.5	50	5	0.5	50	5	0.5
		ϵ'			$k \times 10^{10}$			ϵ''	
−111.0	7.14	7.20	7.28	0.9	0.2	0.3			
−110.8	7.78	7.92	7.94	.9	.3	.3			
−110.5	9.03	9.22		.9	.2				
−107.9			10.14			.4			
−106.2	10.19	10.18	10.20	2.2	.3	.4			
−105.0	10.12	10.10	10.13	2.2	.3	.4			
−103.9	10.04	10.02	10.04	0.5	.3	.4			
−100.5	9.90	9.87	9.96	3.5	.4	.5			
− 56.5	8.04	8.04	8.05	5.3	2.7	2.7	0.019	0.10	0.10
− 51.1	7.87	7.87	7.87	7.1	3.3	3.2	.026	.12	1.2
− 42.7	7.60	7.61	7.59	7.1	4.4	4.3	.026	.16	1.6
− 31.8	7.29	7.30	7.89	11.4	6.4	6.0	.041	.24	2.2
− 20.9	7.01	7.05	7.04	15.9	10.6	10.0	.058	.39	3.6

Previous dielectric studies on organic glasses over a temperature interval are reviewed in the Landolt–Börnstein "Tabellen."[10] The curves of Figs. 1 and 3 obtained with decreasing temperature resemble those found for liquid and glassy glucose by Thomas,[11] who used the frequency range 92 to 2600 kilocycles. Similar, more detailed studies on glucose,[12] glycerol and several monohydric alcohols[13] by Kobeko and co-workers produced the same sort of marked dispersion and decrease of dielectric constant over a short temperature range, the position of which was determined by the frequency of the applied field. Loss factors of commercial glasses have been measured at high frequencies by Hackel,[14] who used the immersion method of finding a polar liquid mixture with the same dielectric constant as the glass.

Basic postulates of the present report are supported by Hägg's[15] conclusion from X-ray data that organic glasses contain large groups of molecules linked together by strong associative forces. Glycerol glass has been found truly amorphous.[16] X-Ray patterns have been established as valid proofs of the non-crystalline nature of a glass.[17]

The curves of Figs. 1 and 3 obtained on cooling follow the Debye temperature dependence for a polar liquid down to the regions −150 to −165° for *i*-butyl bromide and −135 to −155° for *i*-amyl bromide. In these ranges, there is a gradual, frequency-dependent drop of the dielectric

constant to values approaching the square of the refractive index. This apparent rotational freezing differs from ordinary rotational immobilization on solidification in at least two ways. It does not occur sharply and shows no latent heat under the conditions of measurement. The gradual loss of rotational freedom suggests that the individual dipoles are orienting in a viscous medium, for, at a given temperature, it is seen that the molecules may be able to follow quite completely a field of frequency 500, and show little or no rotation in a field of 50,000 cycles.

Mechanically, it was found that *i*-butyl bromide became stiff at about −120°, and *i*-amyl bromide at about −115°. It would seem that, with decreasing temperature and increasing density, enhanced molecular field interaction removes librational freedom even in the absence of a phase change. An artificially increased interaction, such as that caused by high pressures, should then produce the same effect as lowering the temperature. This is confirmed by the experiments of Danforth,[18] who introduced pronounced dispersion at given frequencies in some ten compressible liquids like glycerol and isobutyl alcohol by measuring the dielectric constants under high pressures.

The range of temperature required for the setting of the dipoles with respect to a given frequency in liquids and glasses provides a contrast of the interaction of their molecules with the intermolecular action in crystals which have rotational transitions occurring within a very short or zero temperature interval.[2,3,19] In the latter, the sudden rearrangement of the crystal transition would seem to effect a critical interaction that blocks

(10) See also Tammann, "Der Glaszustand," Verlag L. Voss, Leipzig, 1933.

(11) Thomas, *J. Phys. Chem.*, **35**, 2103 (1931).

(12) Kobeko, *et al.*, *Physik. Z. Sowjetunion*, **4**, 83, 680 (1933).

(13) Kobeko, *et al.*, *J. Tech. Phys.* (*U. S. S. R.*), **8**, 715 (1938).

(14) Hackel, *Physik. Z.*, **37**, 160 (1936); *Ann. Physik*, **29**, 63 (1937).

(15) Hägg, *J. Chem. Phys.*, **3**, 42 (1935).

(16) Lark-Horovitz and Miller, *Phys. Rev.*, **47**, 813 (1935).

(17) Warren, *J. Applied Phys.*, **8**, 645 (1937).

(18) Danforth, *Phys. Rev.*, **38**, 1224 (1931).

(19) White and Morgan, *J. Chem. Phys.*, **5**, 655 (1937).

dipole orientation almost completely. However, the curves of Figs. 1 and 3 suggest that the glass slowly contracts with decreasing temperature so that there is a gradual immobilization of dipoles. This may be further evidence for a random molecular arrangement in glasses.

Even before the dipole theory, it was realized that the constituent particles of a dielectric did not all have necessarily the same relaxation time.[20] This concept has been applied to a variety of dielectrics by many workers, and recently Yager[21] has reviewed and extended the method of quantitatively estimating the distribution. The ordinary experimental values represent an average. A rough qualitative idea of the breadth of the distribution may be gained from a calculation of the ideal maximum value of ϵ'' for a given frequency as was done for several compounds by Morgan.[22] An observed maximum value obtained from Fig. 2 or Fig. 4 will deviate the more from the ideal value, which it would have if all the particles had a single relaxation time, the less uniform are the constituent units of the dielectric. The calculation of the ideal $\epsilon''_{\text{max.}}$ follows from the observation that the absorption is greatest when $x = 1$ in the Debye expression for ϵ.[23] That is, $\epsilon'' = x(\epsilon_1 - \epsilon_0)/(1 + x^2)$, where $x = \omega\tau(\epsilon_1 + 2)/(\epsilon_0 + 2)$, in which ϵ_1 = dielectric constant at zero frequency, obtained from graphical extrapolation of low frequency values; ϵ_0 = dielectric constant at infinite frequency, obtained from low temperature values of the crystalline solid; $\omega = 2\pi \times$ frequency in cycles; τ = relaxation time of particles. Then, $\epsilon''_{\text{max.}} = (\epsilon_1 - \epsilon_0)/2$.

TABLE II

	f, kc.	ϵ''max. Calcd.	ϵ''max. Obsd.
i-Butyl bromide	50	7.5	5.3
	5	6.7	5.6
	0.5	4.8	5.9
i-Amyl bromide	50	5.0	3.8
	5	3.9	4.5
	0.5	3.0	5.0

The most uniform relaxation times seemingly are characteristic of the temperature region in which ϵ'' is a maximum for a frequency of 5 kc. as the difference between observed and calculated values, which arises from variation in particle size, is smallest at this frequency for the values

(20) Von Schweidler, *Ann. Physik*, **24**, 711 (1907).
(21) Yager. *Physics*, **7**, 434 (1936).
(22) Morgan, *Ind. Eng. Chem.*, **30**, 273 (1938).
(23) Debye, "Polar Molecules," Chemical Catalog Company, Inc., New York, 1929, p. 94.

in Table II. Figures 2 and 4 confirm this conclusion in showing the 5 kc. dispersion curves to be narrowest, with the sharpest peaks, for, as Yager[21] notes, the narrower the ϵ'' vs. temperature peak, the narrower the distribution of relaxation times, and hence of constituent units.
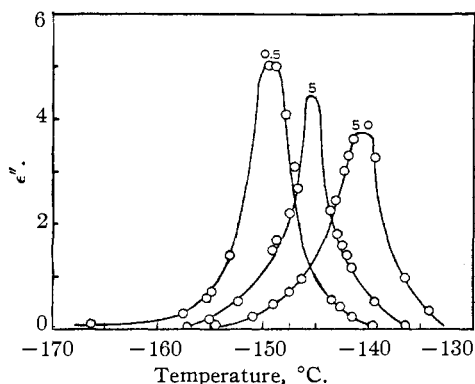

Fig. 4.—Variation with temperature and frequency of ϵ'' for *i*-amyl bromide.

Isobutyl bromide glass appears to be most homogeneous at about $-158°$, and isoamyl bromide at about $-145.5°$, whereas a greater variety of agglomerates exists above and below these temperatures. A glass probably contains molecular aggregates[9,15] which must dissociate before molecules can orient to form a crystal lattice. The ordered crystalline state has a lower free energy than the glass, and hence the latter is forced toward the former by a thermodynamic potential that increases with decreasing temperature. It would seem that at just about the temperature of the maximum absorption for 5 kc. in the two glasses, dissociation of the vitreous aggregates has resulted in a maximum homogeneity of particle size. Because of the generally similar behavior of the molecules of the two substances, like relations should obtain for each between the temperature T_i at which the re-ordering enters and the lower temperature T_f of apparent rotational freezing, if temperature difference may be considered as measuring thermodynamic potential. As will be noted below, some devitrification was found to enter at the temperatures of rotational freezing, T_f. The relations found are

i-butyl bromide $T_i(-158°) - T_f(-170°) = 12°$
i-amyl bromide $T_i(-145.5°) - T_f(-160.0°) = 14.5°$

These temperature intervals are, as would be expected, approximately the same, with the larger molecule showing the larger interval.

The portions of Figs. 1 and 3 indicated as ob-

tained with rising temperature are next noted. The physical states of i-butyl bromide at $-175°$, and of i-amyl bromide at $-165°$, are those of undercooled liquids (glasses) far below their normal freezing points. Their instability as non-crystalline forms increases with decreasing temperature, but the fruition of this crystallizing tendency is opposed by the increase with lowered temperature of the relaxation times of the molecules. However, around $-170°$ for i-butyl and $-160°$ for i-amyl bromide, a certain amount of devitrification has occurred, because the dielectric constant–temperature curve from measurements at 0.5 kc. on Fig. 1, was completely reversible with temperature anywhere down to about $-167°$, while if the glass was cooled below about $-167°$, and then warmed, the dielectric constant values did not return to those required by the reversible curve. Similar results at a higher temperature were found for i-amyl bromide. Moreover, the isotropic glasses began to show scattered areas of double refraction when examined with the polarizing microscope. Because of relaxation effects, the amount of crystal formation observed at $-170°$ for i-butyl and $-160°$ for i-amyl bromides should depend on the length of time the sample is held at the given temperature after the liquid is cooled. The upper of the two rising temperature curves on Fig. 1 was obtained when the specimen was held near $-180°$ for upwards of thirty minutes. Similar treatment produced the heating curve on Fig. 3. Evidently there was not time for complete crystallization. Presumably, crystallization had proceeded from many nuclei scattered throughout the glass, but there were still vitreous regions when the measurements with rising temperature were begun. Molecules in the crystal lattice of i-butyl bromide cannot rotate in the applied field, as the lower curve with rising temperature on Fig. 1 shows, for the dielectric constant is there produced only by atomic and electronic polarization, except in the region of some rotational pre-melting as often observed.[1,24,25] However, molecules still in the glass distributed among the crystal groups should be able to orient as soon as a sufficiently high temperature is reached. For n-amyl bromide, as seen in Fig. 3, an increase in dielectric constant is found in about the same temperature region in which it declined on the cooling of the pure glass.

For i-butyl bromide, the region of increase is shifted to somewhat higher temperatures. A speculation on the reason for this is that, in the sample of i-butyl bromide for which the data are graphed, crystallization has progressed so far that the large crystalline groups in a predominantly crystalline lattice inhibit, by their locally oriented force fields, the rotation of the glass molecules dispersed among them. This is consistent with the fact that the maximum dielectric constant on the warming curve of i-amyl bromide, although occurring at a lower temperature, is a larger percentage of the true glass value than that for the i-butyl bromide. In the curves for both compounds, the dispersion characteristic of the glass is found. Further, the dielectric loss data in Table I for both compounds show a maximum with rising temperature in the region of the temperature of the dielectric constant maximum. This also demonstrates the regaining of partial rotational freedom by those molecules still in the vitreous condition.

Finally, the reason for decrease of the dielectric constant with further temperature rise, as seen on the lower curves of Figs. 1 and 3, is probably that, at the temperature of the maximum, the molecules still in the vitreous state have again acquired sufficiently short relaxation times to crystallize, especially under the orienting influence of numerous crystalline groups. That these latter do predominate is confirmed by the maximum dielectric constant, in the case of i-butyl bromide 4.5, instead of the 17.3 of the true glass. As crystallization in the solid state proceeds, the dielectric constant falls to the true crystal value, and then rises again on melting.

The above explanation may be applied to a recent report on the first production of boron trioxide crystals by McCulloch.[26] An ordinary boron trioxide glass held at 250° for three days, after it had stood at room temperature for a much longer period, showed a considerable amount of crystallization as indicated by X-ray analysis. The melting point of a nearly glass-free mass of boron trioxide crystals (99.6%) was found to be 460–470°. The glass at room temperature, 450° below the normal freezing point, may now be regarded as under a large thermodynamic potential tending toward crystallization. Some few very minute crystal nuclei are actually formed, as, indeed, such are found in laboratory glass at

(24) Ubbelohde, Trans. Faraday Soc., **34**, 282, 292 (1938).
(25) Müller, Proc. Roy. Soc. (London), **A158**, 403 (1937).
(26) McCulloch, THIS JOURNAL, **59**, 2650 (1937).

ordinary temperatures.[27] However, precisely as here indicated for *i*-butyl and *i*-amyl bromides on Figs. 1 and 3, an increase in temperature to shorten the relaxation time of the molecules facilitates widespread devitrification and is actually essential for a substance with intermolecular bonding like that in boron trioxide. It is suggested that efforts to crystallize organic glasses and sirups might be facilitated by cooling the substance to low temperatures, and then re-warming to a point near, but well below, the melting point of the crystals sought. The dielectric results show mechanically the reorientation that must accompany the crystallization.

The present results, together with those of other work involving a variety of molecular structures,[1,2,4] indicate relations of the structure of the liquid state to the tendency toward glass formation as follows:

a. Moderately unsymmetrical, say pear-shaped, molecules, like *i*-butyl and *i*-amyl bromide, can pack randomly in the liquid with an economical use of volume. Hence, although the molecules are on the whole disordered, their efficient packing permits them to remain in the liquid arrangement far below the normal crystallization temperature. Such substances should vitrify.

b. Long-chain compounds, although they often form viscous liquids, do not generally supercool, as dielectric studies, a sensitive test for supercooling, have shown for several examples including the associated cetyl alcohol. Here, it is probable that the rod-like molecules are already locally, at least, quite well aligned in crystal-like array in the liquid. Random scattering would waste a relatively large volume, and hence would be energetically unfavorable. Indeed, X-ray data indicate alignment along the long axis even in *n*-heptane.[28,29] Hence, when long-chain compounds are cooled to the freezing point, they simply set into the crystal lattice and do not form glasses.

c. Very symmetrical, nearly spherical molecules which form cubic lattices, and especially those which are known to exhibit a rotational freedom in the crystal comparable to that in the liquid,[2,30] in agreement with the above postulates, commonly do not supercool. They may be considered to compose a liquid structure of close-packed spheres, which set into the cubic lattice with little rearrangement and probably no reorientation, and thus have no tendency toward glass formation.

d. As expected, and noted elsewhere,[4] molecules of symmetry intermediate between the pear-shaped and rod-like structures show degrees of supercooling varying with their particular shapes, and very rarely leading to true glass formation.

Extensive inter-molecular bonding in a liquid may so effectively alter the shape of the constituent particles as to require modification of the above conclusions from molecular data alone.

In addition to the data already cited in support of these conclusions, the evidence given by recent work[31] on some pure hydrocarbons may be noted. It was reported that the normal paraffins crystallized readily without supercooling, whereas certain branch-chained paraffins, conforming with the conditions of paragraph above, solidified to glasses. Also, it has been reported[32] that two of the branched heptanes, unlike their other isomers, failed to crystallize even when cooled to 70°K. An efficient but random packing should, therefore, be assigned to their liquid structures.

Summary

The dielectric constants and conductances of isobutyl and isoamyl bromides have been measured with a capacity bridge at frequencies of 0.5, 5 and 50 kilocycles at temperatures from −190 to 30° above their melting points. The substances have also been examined with a polarizing microscope over these wide temperature ranges.

It is found that, when the substances in the liquid state are cooled, they form glasses, which crystallize at low temperatures, their properties depending upon the degree of crystallization brought about by thermal treatment. Examination of these and other, previously studied molecules leads to generalizations as to glass formation. It is concluded that molecules which pack efficiently in the liquid, but which do not form isotropic lattices, should tend to vitrify. The temperature of narrowest distribution of relaxation times may indicate the point at which the vitreous aggregates begin to dissociate.

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(27) Warren and Biscoe. *J. Am. Ceram. Soc.*, **21**, 259 (1938).
(28) Katzoff, *J. Chem. Phys.*, **2**, 841 (1934).
(29) Pierce. *ibid.*, **3**, 252 (1935).
(30) Smyth, *Chem. Rev.*, **19**, 329 (1936).

(31) Smittenberg, Hoog and Henkes, THIS JOURNAL. **60**, 17 (1938).
(32) Huffman, Parks and Thomas. *ibid.*, **52**, 3241 (1930).