These observations are discussed and interpreted with the aid of the Chapman–Jouguet–v. Neumann treatment of detonation waves.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Heat Capacities and Dielectric Constants of Some Alkyl Halides in the Solid State[1]

BY LAWRENCE M. KUSHNER, ROBERT W. CROWE AND CHARLES P. SMYTH

For a number of years it has been recognized that certain molecules or polyatomic ionic groups in crystalline solids may rotate in the lattice below the freezing point. Two of the more important tools used in the investigation of this phenomenon have been measurements of dielectric constant and heat capacity. Since, in many cases, the effects studied are non-equilibrium in nature and therefore not very reproducible, it seemed advantageous to measure both of these properties simultaneously.

In this investigation, *t*-butyl chloride, *t*-butyl bromide, *i*-propyl bromide and *n*-amyl bromide were studied. The dielectric behavior of these compounds has been previously investigated. The molecules differ in shape, and therefore the ease of rotation in the solid state also varies considerably from compound to compound. The chief objects of the investigation were to correlate the thermal properties of these compounds with their dielectric behavior, and to determine the energy quantities involved in their transition from one phase to another.

Apparatus and Method of Measurement

The apparatus used for both heat capacity and dielectric constant measurements consisted of a combined heat conduction calorimeter and dielectric cell, constructed in such a way that the two quantities could be determined simultaneously. The principle of the measurement of heat capacity with such a calorimeter[1a] is the comparison of the time required to heat a known weight of sample through a definite temperature interval with that required, under identical conditions, to heat a known weight of a standard compound through that interval. The time required to heat the empty calorimeter through the same temperature interval must also be determined. Knowing these data, it is possible to calculate the average molar heat capacity C_{px} of the unknown substance in the temperature interval by means of the equation

$$C_{px} = \frac{W_s M_x C_{ps}}{M_s W_x} \cdot \frac{t_x - t_e}{t_s - t_e} \qquad (1)$$

In this equation, W, M and t are weight of sample in grams, molecular weight and time interval in seconds, respectively. The subscripts e, s and x refer to empty, standard substance and substance to be measured, respectively.

The calorimetric assembly was enclosed in a double wall glass jacket A (Fig. 1). It consisted of a calorimeter can C, a heating mantle B and a bakelite rod D. The mantle and enclosed calorimeter can were suspended on this rod which was supported by means of a bushing and pin Q. The copper heating mantle was in two parts threaded at point E, so that it could be easily opened in order to fill the enclosed can without disturbing the thermocouple wires. A removable

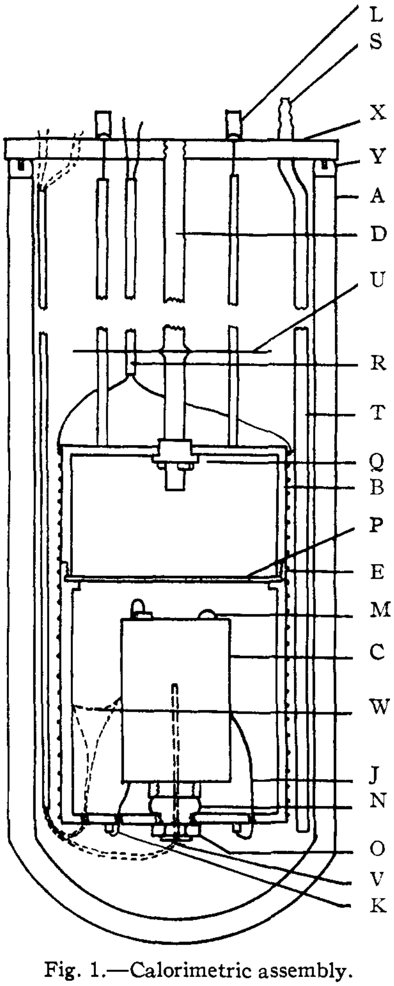

Fig. 1.—Calorimetric assembly.

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[1] This research was carried out with the support of the Office of Naval Research.

[1a] Ziegler and Messer, THIS JOURNAL, 63, 2694 (1941).

copper disc P was supported on a ledge running around the inside of the mantle, which served to make the upper part of the mantle an insulating chamber while the apparatus was in operation. The heating unit, consisting of about 30 ohms of nichrome wire, was wound around the mantle in a non-inductive manner and covered with glyptal lacquer. The leads to the heater R extended to the top of the assembly and then to two Variacs in series, with which the electrical input was controlled to maintain the desired temperature head between the mantle and calorimeter can.

The cylindrical calorimeter can, also of copper, is shown in Fig. 2. The hollow copper rod F served as a thermocouple well as well as a support for six thin copper conduction vanes G. Separated from the body of the can by teflon spacers I was a cylindrical copper tube H which served as the ungrounded plate of the condenser for dielectric constant measurements. The rest of the can was grounded by means of a copper wire J which terminated at the top in the mercury cup L. The ungrounded dielectric lead K terminated in another mercury cup. The threaded hole at the top of the can served as an opening for the introduction of samples to be measured. This hole was sealed during operation by a screw M fitted with a rubber washer. The can was supported in the mantle by a bakelite bushing N, which screwed into the bottom of the calorimeter can and was secured through the bottom of the mantle by a nut O. For purposes of neatness and insulation, all of the thermocouple, heater and dielectric leads were run through electrical spaghetti from the calorimeter and mantle to the top of the assembly. The top X was a disc of bakelite, through which holes were bored to accommodate all of the leads. At its center a threaded hole accommodated the bakelite supporting rod. Sealed to the top of the glass jacket A was the bakelite ring Y with a groove into which the top of the assembly fitted tightly. A brass nozzle-type fitting S and attached rubber tube T served as the entrance for a slow stream of dry nitrogen while the apparatus was in operation. Two thin steel discs U served as radiation shields. For cooling, and during a run, the entire unit was suspended in a large dewar filled with liquid nitrogen.

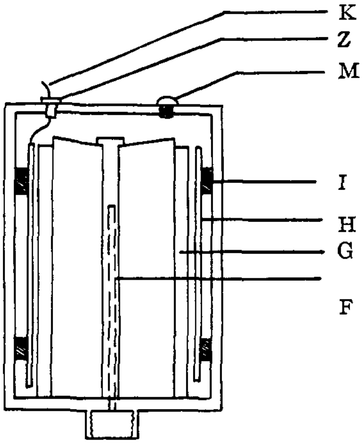

Fig. 2.—Combined calorimeter can and dielectric cell.

Two sets of copper–constantan thermocouples were used. One set W consisted of two junctions, one soldered to the inside of the heating mantle and the other to the outside of the calorimeter can. Its purpose was the measurement of the temperature head between the two. The thermocouple V, used for the measurement of the temperature of the sample, had one junction in the thermocouple well and the other in a dewar containing ice and distilled water. White potentiometers and Leeds and Northrop high sensitivity galvanometers were used to measure both the heating head and sample temperature. The measuring thermocouple was calibrated by obtaining e.m.f.'s for the boiling point of nitrogen, the boiling point of oxygen, the melting point of ice and the boiling point of water. Check points were obtained with the use of a calibrated platinum resistance thermometer in use in this Laboratory. The transition and melting points of carbon tetrachloride and benzene, measured in preliminary runs, were in good agreement with accepted literature values for these compounds.

For measurement of dielectric constants, the unit was connected to an impedance bridge previously described,[2] by means of heavy copper leads.

The apparatus was calibrated with carefully purified carbon tetrachloride. The empty calorimeter was first cooled to the temperature of liquid nitrogen, and then heated at a constant head continuously up to about 0°. This temperature range was divided into approximately three-degree intervals and the time lapse between each interval recorded. Exactly 22 ml. of carefully purified carbon tetrachloride was then weighed out and introduced into the can by means of a hypodermic syringe. The empty weighing bottle and syringe were then reweighed. The weight of sample, as determined in this manner, was reproducible to 0.1%. The measuring process was then repeated using the same temperature intervals. The rate of heating was approximately 0.5° per minute. The liquid nitrogen level was kept well above the top of the mantle during the entire run. A variation of this level of one or two inches did not affect the results. Heat capacity values for carbon tetrachloride were obtained from the literature[3] and the value at the middle of each temperature interval was assumed as the average heat capacity for that interval.

The same procedure was followed for the measurement of the compounds discussed, and

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

[3] Stull, *ibid.*, **59**, 2726 (1937); Hicks, Hooley and Stephenson, *ibid.*, **66**, 1064 (1944).

TABLE I

PHYSICAL CONSTANTS OF COMPOUNDS

Compound	This research B. p., °C.	M. p., °C.	n^{20}_D	Literature B. p., °C.	M. p., °C.	n^{20}_D
t-C_4H_9Cl	50.5	−25.0	1.3859	50.6^{4}	−24.6^{4}	1.3847^{4}
				51.0^{5}	−27.1^{5}	1.3853^{6}
						1.3839^{7}
t-C_4H_9Br	72.8–73.0	−17.0	1.4280	73.1–73.3^{4}	−17.7^{4}	1.4276^{4}
				73.25^{5}	−16.2^{5}	1.4275–1.4277^{8}
i-C_3H_7Br	59.5	−89.0	1.4250	59.5–59.6^{10}	−90.8^{10}	1.4248^{10}
				59.41^{9}	−90.0^{9}	1.4251^{11}
n-$C_5H_{11}Br$	128.7–128.9	−88.0	1.4448	129.6^{9}	−87.9^{9}	1.4444^{11}
				128.6–128.8^{10}	−88.0^{12}	1.44455^{10}
					−88.7^{10}	

equation (1). was used to calculate the average heat capacity at each interval. The following equation was used to estimate the heats of transition and heats of fusion for the compounds measured

$$\Delta H_x = \frac{W_s M_x \Delta H_s}{M_s W_x} \cdot \frac{\Sigma_x}{\Sigma_s} \qquad (2)$$

where Σ is the portion of the running time in excess of that required by the normal heat capacity of the material in the transition or melting range. This value was obtained by plotting the time in seconds against the corresponding temperature interval and determining the time in excess of the normal values for each interval affected.

Carbon tetrachloride was chosen as a standard because it is easily purified and has its transition and melting point at temperatures near to those of the compounds under investigation. It is estimated that the average error in measurement of the heat capacity was ±0.5 cal./deg. mole below −20°. Above that temperature the accuracy decreased because of the difficulty in holding the heating head constant.

Purification of Materials

All of the compounds investigated, except for the carbon tetrachloride used for calibration, were obtained from the Paragon Testing Laboratories in Orange, New Jersey. The products as obtained from the manufacturer were first washed with 6 N sodium carbonate solution and with several portions of distilled water. They were then dried over anhydrous calcium chloride for twenty-four hours and fractionally distilled at atmospheric pressure in a five-foot column packed with glass helices. The physical constants of the compounds are compared with the best corresponding literature values in Table I.

Experimental Results

The dielectric constants ϵ' and heat capacities for t-butyl chloride and t-butyl bromide with the temperatures of measurement are given in Table

TABLE II

DIELECTRIC CONSTANTS AND HEAT CAPACITIES

t, °C.	ϵ'(50 kc.)	C_p cal./deg. mole	t, °C.	ϵ'(50 kc.)	C_p cal./deg. mole
		t-C_4H_9Cl			
−151.0	2.05	19.1	−53.8	3.58	
−147.5		19.5	−53.7	5.17	
−143.0		19.9	−53.3	9.46	
−139.0		20.3	−53.0	10.68	
−135.0		20.6	−52.5	11.60	
−131.0		21.1	−50.5	12.95	
−126.5		21.2	−49.3	13.40	
−122.5		22.0	−45.0		28.5
−118.5		23.2	−43.3	13.47	
−115.5		23.8	−42.0		28.7
−111.5		24.9	−40.5	13.47	
−108.0	2.07	25.7	−39.0		29.2
−104.0		26.8	−37.5	13.42	
−100.5		27.6	−36.0		29.6
− 97.0	2.07	28.2	−33.0		30.2
− 93.5		29.5	−31.6	13.25	
− 90.2	2.14		−30.0		31.1
− 90.0	2.21		−28.6	13.11	
− 83.0	2.23	26.4	−27.5		[illegible]
− 80.0	2.23	26.4	−25.8	13.00	
− 76.5		26.4	−25.0	12.24	
− 73.0	2.25	26.5	−23.7	12.00	
− 70.0		26.5	−21.5		36.4
− 66.5	2.27	26.8	−20.2	11.76	
− 63.5		27.2	−18.5		36.2
− 61.7	2.30		−16.0		36.4
− 60.0		27.7	−14.7	11.45	
− 58.5	2.33		−13.5		36.5
− 57.0		28.2	−12.0	11.27	
− 54.2	2.40				
		t-C_4H_9Br			
−156.0		20.0	−131.0		22.1
−151.0	2.18	20.1	−126.5	2.23	23.0
−147.5		20.5	−122.5		23.4
−143.0		20.9	−118.5		24.6
−139.0	2.21	21.7	−115.5		25.4
−135.0		21.7	−111.5		26.2

(4) Baker and Smyth, THIS JOURNAL, **61**, 2798 (1939).

(5) Timmermans and Delcourt, *J. chim. phys.*, **31**, 85 (1934).

(6) Smyth and Dornte, THIS JOURNAL, **53**, 545 (1931).

(7) Kistiakowsky and Stauffer, *ibid.*, **59**, 165 (1937).

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

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

(10) Baker and Smyth, *ibid.*, **61**, 1695 (1939).

(11) "International Critical Tables."

(12) Deese, THIS JOURNAL, **53**, 3673 (1931).

TABLE II (*Continued*)

t, °C.	ϵ'(50 kc.)	C_p cal./deg. mole	t, °C.	ϵ'(50 kc.)	C_p cal./deg. mole
−108.0		27.2	−51.0		31.9
−104.0		28.1	−48.0		32.2
− 97.0		29.8	−45.0		32.8
− 93.5		30.4	−43.5	9.96	
− 91.5	2.36		−42.0	10.02	
− 90.0		31.2	−41.8	10.60	
− 86.5		32.1	−41.5	11.28	
− 85.0	2.40		−41.0	12.00	
− 83.0		33.0	−38.5	12.40	
− 80.0		33.5	−36.0		31.4
− 78.0	2.45		−33.0		31.6
− 76.5		34.0	−31.5	12.82	
− 73.0		35.1	−30.0		32.2
− 71.5	2.51		−27.5		32.8
− 70.0		35.9	−24.5		32.7
− 66.5		36.7	−21.5	12.91	33.0
− 65.0	2.80		−18.5	12.90	
− 64.7	3.35		−17.4	12.55	
− 64.5	4.90		−17.2	12.18	
− 64.3	6.72		−16.9	11.87	
− 64.0	7.73		−16.7	11.60	
− 63.5	8.05		−15.7	11.45	
− 62.2	8.60		−14.7	11.35	
− 61.2	8.96		−13.5		36.0
− 59.2	9.37		−10.5		36.0
− 57.0		31.7	− 9.2	11.10	
− 55.5	9.48		− 8.0		36.1
− 54.0		31.8			

t, °C.	ϵ'			C_p cal./deg. mole
	50 kc.	5 kc.	0.5 kc.	
		i-C_3H_7Br		
−156.0				17.7
−151.0				18.0
−147.5	2.21	2.21	2.21	18.3
−143.0	2.21	2.21	2.21	18.7
−139.0				19.1
−135.0	2.22	2.22	2.28	19.4
−131.0	2.22	2.24	2.32	19.7
−126.5	2.22	2.28	2.39	20.1
−122.5	2.23	2.33	2.42	20.4
−118.5	2.25	2.39	2.46	20.9
−115.5	2.28	2.45	2.47	21.5
−111.5	2.32	2.47	2.49	22.2
−108.0	2.38	2.50	2.50	22.6
−104.0	2.46	2.51	2.51	23.3
−100.5	2.52	2.53	2.53	23.9
− 97.0	2.56	2.56	2.56	24.6
− 93.5	2.59	2.59	2.59	25.4
− 91.0	2.65			
− 89.5	3.17			
− 88.5	11.75			
− 87.5	13.43			
− 87.3	14.56			
− 86.9	14.60			
− 84.2	14.41			
− 83.0				30.0
80.0				29.9
77.5	14.05			
76.5				29.9
− 73.0				30.1
− 71.0	13.65			
− 70.0				30.2
− 66.5				30.3
− 63.5				30.3
− 57.5	12.87			
		n-$C_5H_{11}Br$ (unstable form)		
−163.0	2.41	2.41	2.41	
−156.0	2.41	2.41	2.41	23.5
−152.0	2.42	2.44	2.45	
−147.5	2.44	2.47	2.51	23.8
−143.0	2.45	2.54	2.61	24.1
−139.0	2.52	2.61	2.61	24.8
−135.0	2.61	2.62	2.62	24.9
−131.0	2.62	2.62	2.62	25.6
−126.5	2.62	2.62	2.62	26.4
−122.5	2.62	2.62	2.62	27.6
−118.5	2.64	2.64	2.64	29.2
−115.5	2.66	2.66	2.66	31.3
−111.5	2.70	2.70	2.70	33.8
−108.0				36.3
−104.0	2.74			9.2
−103.8	2.74			
−100.9	2.72			
		n-$C_5H_{11}Br$ (stable form)		
−151.0	2.37	2.37	2.37	23.2
−147.0	2.37	2.38	2.44	
−143.0	2.40	2.46	2.52	23.4
−139.0	2.47	2.50	2.52	23.9
−135.0	2.52	2.52	2.52	23.6
−131.0	2.52	2.52	2.52	24.1
−126.5	2.52	2.52	2.52	24.6
−122.5	2.52	2.52	2.52	25.1
−118.5	2.52	2.52	2.52	26.0
−115.5	2.52	2.52	2.52	27.2
−111.5	2.53	2.53	2.53	28.6
−108.0	2.55	2.55	2.55	29.9
−104.0				32.2
−101.6	2.60			
−100.5				34.8
− 97.0	2.68			43.8
− 93.5	2.77			
− 91.3	2.97			
− 90.2	3.11			
− 89.5	3.29			
− 88.8	3.63			
− 88.1	4.67			
− 87.8	5.75			
− 87.5	6.96			
− 87.3	7.70			
− 86.9	8.05			
− 85.5	8.95			
− 83.0				41.1
− 80.8	8.77			
− 80.0				40.9
− 77.5	8.66			
− 76.5				40.8
− 73.0				41.4
− 71.0	8.33			
− 70.0				41.4
− 66.5				41.8

II. Dielectric constants are reported only at 50 kc. for these compounds since no frequency dispersion was noticed throughout the entire range. Dielectric constants and heat capacities of *i*-propyl bromide and *n*-amyl bromide are also listed in Table II. In these compounds some dispersion was observed in the solid, and, therefore, dielectric constant values are reported at 0.5, 5 and 50 kc. Since the level of the liquid in the cell reaches but little above the top of the condenser plates at room temperature, the values of the dielectric constants in the solid state are somewhat low, especially at low temperatures, due to contraction as the substances were cooled. For the sake of brevity, only the more significant dielectric data have been recorded in Table II. The transition and fusion temperatures, heats of transition, heats of fusion and corresponding entropy changes, as observed here for the four compounds investigated, are listed in Table III.

TABLE III

HEATS AND ENTROPIES OF TRANSITION AND FUSION

	t, °C.	ΔH (kcal./mole)	ΔS (E. u./mole)
t-C_4H_9Cl			
Transition I	−90.0	0.41	2.3
Transition II	−53.5	1.39	6.4
Fusion	−25.0	0.48	1.9
t-C_4H_9Br			
Transition I	−64.5	1.35	6.5
Transition II	−41.6	0.25	1.1
Fusion	−17.0	0.47	1.8
i-C_3H_7Br			
Fusion	−89.0	1.56	8.5
n-$C_5H_{11}Br$			
Fusion	−88.0	2.74	14.8

Discussion of Results

Figure 3 shows the dielectric constant at 50 kc. and heat capacity of *t*-butyl chloride as functions of rising temperature. As mentioned before, no appreciable dispersion or conductance was observed throughout the entire temperature range. Here the two transitions in the solid and the melting point are clearly shown. Similar data for *t*-butyl bromide are shown in Fig. 4. Although these two molecules are very nearly the same shape, their dielectric and thermal properties in the solid state appear to differ somewhat. It is apparent from both dielectric and thermal data for these compounds that orientational freedom, comparable to that in the liquid, exists between transition II and the melting point. Practically all of the entropy necessary for a completely ordered crystal to become a liquid is obtained at the two transition points. This is clearly shown by the small entropy of fusion for the two compounds. These values are very close to the value of 2.0 e. u. obtained theoretically for the communal entropy of melting associated with the fusion of a crystal whose molecules gain only translational freedom during the melting process.[13]

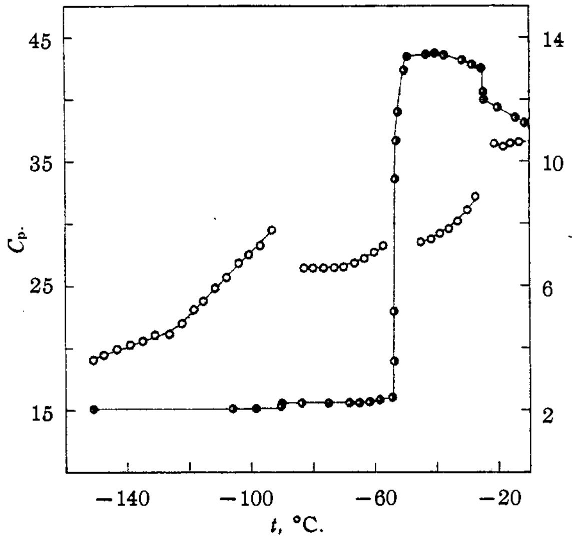

Fig. 3.—Heat capacities and dielectric constants of *t*-butyl chloride as functions of increasing temperature. (Hollow circles are for heat capacity and half-filled circles for dielectric constant at 50 kc.)

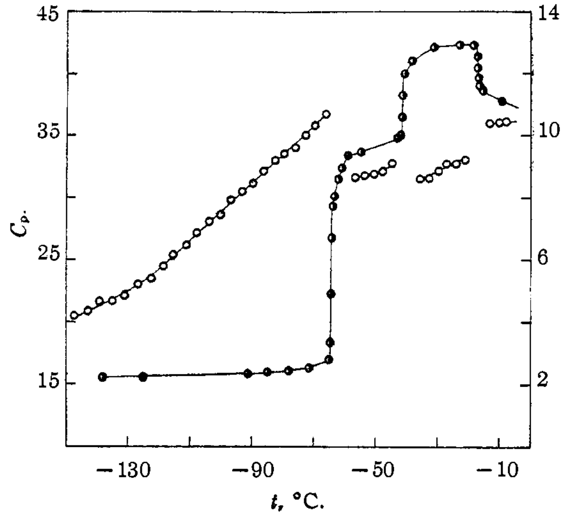

Fig. 4.—Heat capacities and dielectric constants of *t*-butyl bromide as functions of increasing temperature. (Hollow circles are for heat capacity and half-filled circles for dielectric constant at 50 kc.)

The heat of transition for transition I in the chloride is a great deal smaller than that for the bromide, as is also the change in dielectric constant. The sharp rise in dielectric constant clearly shows that this transition in the bromide is rotational. This is substantiated by the fact that examination of the crystals with a polarizing microscope showed the lattice to be anisotropic below the transition and isotropic above it.[4] A

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[13] Eyring and Hirschfelder, *J. Phys. Chem.*, **41**, 249 (1937).

similar examination of the chloride showed it to be strongly doubly refracting above transition I and isotropic between transition II and the melting point. Transition II in the chloride and transition I in the bromide were accompanied by a density change, indicating a considerable change in crystal structure in both cases. Transition I in the chloride probably alters the crystal structure only slightly, while transition II is undoubtedly rotational. Orientation of the dipoles is definitely possible above transition I in the bromide, but is somewhat restricted. At transition II, the lattice evidently expands enough to allow as much orientational freedom as that in the liquid. It may be that above this transition, the possible positions of orientation are more nearly of the same energy and more nearly symmetrical than they are before the transition takes place. The abnormal rise in C_p below transition I in both compounds may be due to an expansion of the lattice.

The data for these two compounds may be interpreted, at least partially, from symmetry considerations. The van der Waals radius for a methyl group is 2.0 Å., for Br, 1.95 Å. and for Cl, 1.80 Å.[14] From this, it is apparent that the bromide molecule is more nearly symmetrical than the chloride. This is probably the reason that the rotational transition appears at a lower temperature in the bromide than in the chloride.

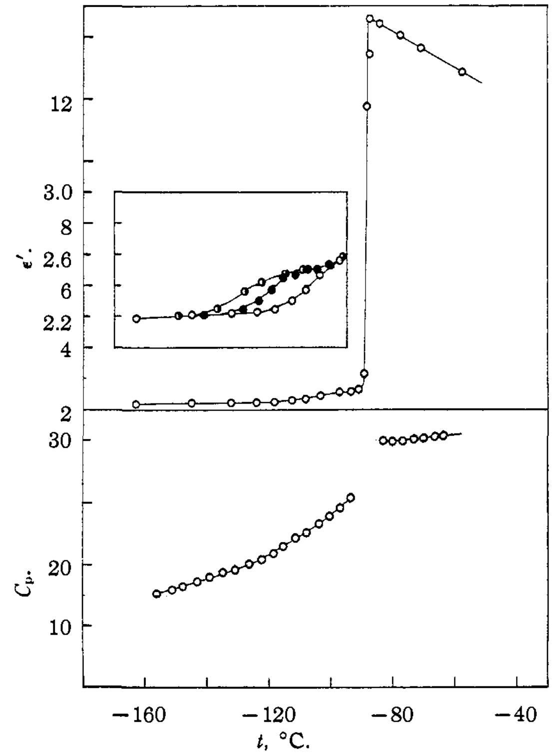

Fig. 5.—Heat capacities and dielectric constants of *i*-propyl bromide as functions of increasing temperature. (Lower curve represents heat capacity. Upper curve represents dielectric constant; hollow circles at 50 kc., filled circles at 5 kc. and half-filled circles at 0.5 kc.)

ΔH for the two transitions in the chloride is 1.80 kcal./mole, while for the bromide it is 1.60 kcal./mole. The lower value for the bromide is indicative of the ease with which rotation can commence in the crystals of symmetrical molecules. Emphasizing this point, it is to be noted that in completely symmetrical carbon tetrachloride, ΔH at the rotational transition is about 1.20[3] kcal./mole, and in neopentane 0.62 kcal./mole.[15] The value for neopentane is very low because of the completely non-polar nature of the crystal. ΔS for the two transitions in the chloride is 1.1 e. u. greater than the similar sum for the bromide. This is consonant with the concept that, although the chloride and bromide should achieve the same entropy increase from the onset of free rotation, the chloride should achieve an extra increment because of the additional volume, over that required by the bromide, that it must have to permit free rotation. ΔS for the two transitions in the chloride and bromide are 8.7 and 7.6 e. u., respectively. For completely symmetrical neopentane it is 4.39 e. u. and for carbon tetrachloride, 4.95 e. u. Here again the values are low because of the complete symmetry of the molecules.

The behavior of the dielectric constant and heat capacity of *i*-propyl bromide as a function of rising temperature is shown in Fig. 5. The dielectric constant–temperature curve is essentially the same as that previously reported[10] except that the rise in dielectric constant below the melting point is somewhat less pronounced, presumably, because of the greater purity of the material used in the present work. This is supported by the fact that the melting point, −89.0°, reported here, is nearly two degrees higher than the value, −90.8°,[10] previously reported from dielectric measurements. Another less carefully purified sample showed a very large rise in the dielectric constant below the melting point, giving the heat capacity–temperature curve a lambda-like character. The data recorded here were very reproducible and were obtained from a sample in which the dielectric constant showed a minimum increase in the region in question. The gradual rise in dielectric constant and frequency dispersion may be the result of the gradual onset of rotation as the melting point is approached. It should be noted that C_p also rises somewhat more rapidly with temperature in this region.

Previous dielectric and thermal investigations of *n*-amyl bromide[10,12] have shown that there is a marked hysteresis at the melting point. Furthermore, the melting and freezing points appear to be a function of the rate at which the sample

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(14) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1949, p. 189.

(15) Aston and Messerly, This Journal, 58, 2354 (1936).

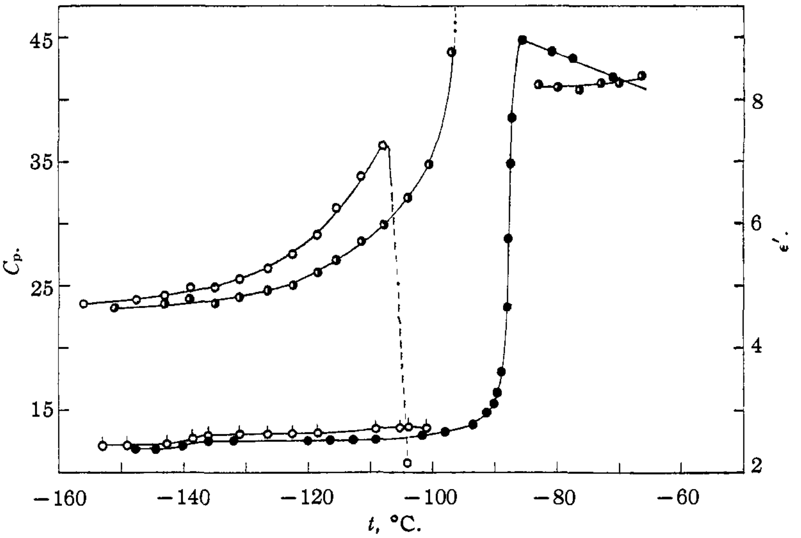

Fig. 6.—Heat capacities and dielectric constants of *n*-amyl bromide as functions of increasing temperature. (Hollow circles and circles with tails are for heat capacity and dielectric constant of unstable form. Half-filled circles and filled circles are for heat capacity and dielectric constant of stable form.)

is cooled or warmed. The hysteresis phenomenon has been ascribed to the existence of two phases, an unstable one formed on solidification undergoing a monotropic transition into another more stable form having a distinctly higher melting point. The nature of the two solid phases has not been discussed. The dielectric and thermal data, shown in Fig. 6, clearly substantiate the existence of two solid forms. The experimental procedure in the measurement of this compound consisted in cooling it first to the temperature of liquid nitrogen. The rate of this cooling, about 1.5° per minute, is evidently fast enough to prevent the stable crystals from growing. Heat capacity and dielectric measurements were then made on the unstable form. These data are represented in the upper C_p curve in Fig. 6. About 40° below the melting point, a rather abrupt rise in C_p began to appear, as though some type of transition were beginning to take place. At about 20° below the melting point, this form underwent a spontaneous change to the stable form with the evolution of heat. This resulted in apparent negative values of the heat capacity, indicated by the dotted line. The dielectric constant of the unstable form is slightly higher than that of the stable form, but not enough higher to indicate any considerable free rotation. The data on the stable crystals were obtained by holding the temperature of the sample about 10° below the melting point for two hours after the spontaneous change mentioned above had taken place and then allowing the sample to cool again to liquid nitrogen temperature. The heat capacity of this form is seen to be slightly lower and the apparent transition does not appear. However, the curve does begin to bend upward several degrees below the melting point, which may be due to small amounts of impurity, since the dielectric constant also begins to rise in this region. The small rise in the dielectric constant and the dispersion observed in both forms at about −140°, although not observed thermally, supports this idea. Another presumably less pure sample treated in the same manner showed a much more pronounced rise in dielectric constant at this point, and a correspondingly sharper rise in C_p below the melting point. The data shown here are for the purest sample obtained.

From the results obtained for *n*-amyl bromide it is evident that, by relatively rapid cooling, the unstable form can be "frozen-in." Not until the temperature is again elevated does this form change over to the more stable form. This phenomenon can be compared, in a sense, to that occurring in glasses, wherein a low temperature is required for crystal nuclei formation. *i*-Butyl bromide[16] gives a well defined example of this. On cooling, *i*-butyl bromide forms a glass which is relatively stable at very low temperatures. On warming, the usual glass transformation[17] begins to take place, but a temperature is soon reached where crystallization is spontaneous. Crystal nuclei, although unable to grow, can continue forming at very low temperatures. The difference in the dielectric constant of the two forms of *n*-amyl bromide indicates only slightly more orientational freedom in the unstable form. Due to the spontaneous change in crystal structure, it was impossible to estimate the ΔH of transition which appeared to be taking place in this form. Complete interpretation of the data must surely be speculative in the absence of X-ray studies of the compound. The ΔH of fusion found here, 2.74 kcal./mole, which includes the small amount of heat involved in the premelting, differs from that reported by Deese,[12] 3.44 kcal./mole, by an amount considerably greater than the probable error of our measurements.

Simultaneous measurements of dielectric constant and heat capacity were attempted for *i*-butyl bromide, but, because of the instability of the compound and the difficulty in obtaining reproducible results, none of the data have been reported here.

Summary

Simultaneous measurements of the dielectric constant and heat capacity of *t*-butyl chloride, *t*-butyl bromide, *i*-propyl bromide and *n*-amyl

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(16) Baker and Smyth, THIS JOURNAL, **61**, 2063 (1939).

(17) Kauzmann, *Chem. Revs.*, **43**, 219 (1948).

bromide have been made from liquid nitrogen temperatures to temperatures well above their melting points in a heat conduction type calorimeter, so constructed that the calorimeter can serve also as a dielectric cell. *t*-Butyl chloride and *t*-butyl bromide, because of their spherical shape, have marked rotational transitions above which their molecules can orient freely in the lattice. *i*-Propyl bromide showed less rise in dielectric constant below the melting point than had previously been observed. *n*-Amyl bromide showed the existence of two solid forms, one of which is unstable. By rapid cooling, the unstable or lower melting form could be obtained at liquid nitrogen temperatures. Subsequent warming indicated an optimum temperature at which this form changed spontaneously into the higher melting more stable form. The heat capacity of both forms has been measured.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Thermal and Dielectric Evidence of Polymorphism in Some Long-Chain *n*-Alkyl Bromides[1]

BY ROBERT W. CROWE AND CHARLES P. SMYTH

It has been realized for some time that many straight-chain organic compounds are capable of existing in more than one form in the solid state, the particular modification assumed being dependent not only upon the substance itself but upon its previous history and to a large extent upon its present environment. This phenomenon has been studied in long-chain acids,[2,3,4,5] esters,[4,6] alcohols,[4,6,7,8] halides,[5,9] hydrocarbons[10] and other compounds by cooling curves, X-ray studies and dielectric constant measurements. In many cases the transitions from one form to another are monotropic and appear only on cooling, especially in the shorter members of the series. These changes are usually attributed to changes in the angle of tilt of the hydrocarbon chain with respect to the terminal plane in the crystal. Dielectric constant studies have shown the possibility of molecular rotation about the long axis in some forms. Polymorphism, however, is not common in members of an homologous series until the number of carbon atoms in the chain exceeds thirteen or fourteen with the result that very few studies have been made on the lower members. Thermal measurements by Deese,[11] dielectric studies by Baker and Smyth,[12] and more recent thermal and dielectric measurements in this Laboratory[13] on *n*-amyl bromide have shown, however, that this compound exists in two solid modifications with different melting points, the lower melting form being the less stable. Mair[14] has also been able to isolate two forms of *n*-nonyl bromide with melting points −29.06 and −30.71°. It has seemed desirable to investigate dielectrically and thermally a number of the lower bromides in an effort to determine whether polymorphism is a characteristic only of the odd members and whether rotational freedom about the long axis exists in any of the forms.

In this investigation, simultaneous dielectric constant and heat capacity measurements were made on *n*-heptyl, *n*-octyl, *n*-nonyl and *n*-undecyl bromides from liquid nitrogen temperatures to temperatures above their respective melting points. In addition, dielectric constant measurements were made on these compounds as well as on *n*-decyl, *n*-tridecyl and *n*-pentadecyl bromides in the vicinity of their melting points with a much lower rate of change of temperature.

Purification of Materials

n-Heptyl bromide from the Paragon Testing

TABLE I

MELTING POINTS AND REFRACTIVE INDICES OF BROMIDES

No. of C atoms	This research M. p., °C.	This research n^{20}_D	Literature M. p., °C.	Literature n^{20}_D
7	−58.8 and −56.1	1.45057	−58.86,[15] −58.25[16]	1.4505[17]
8	−55.0	1.45267	−55.0[18]	1.45267[17], 1.4527[19]
9	−30.8 and −29.0	1.45467	−30.8[4] −30.71 and −29.06[14]	1.45417[17]
10	−29.2	1.45607	−29.62[4]	1.45527[17], 1.4558[19]
11	− 9.9	1.45777	−13.15[4]	1.45697[17]
13	5.9		5.94[4]	
15	18.5		18.63[4]	

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(1) This research was carried out with the support of the Office of Naval Research.

(2) Garner and King, *J. Chem. Soc.*, 1849 (1929).

(3) Francis, Piper and Malkin, *Proc. Roy. Soc. (London)*, **A128**, 214 (1930).

(4) Meyer and Reid, THIS JOURNAL, **55**, 1574 (1933).

(5) Francis, Collins and Piper, *Proc. Roy. Soc. (London)*, **A158**, 691 (1937).

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

(7) Hoffman and Smyth, *ibid.*, **71**, 431 (1949).

(8) Ott, *Z. physik. Chem.*, **193**, 218 (1944).

(9) Hoffman and Smyth, to be published.

(10) Muller, *Proc. Roy. Soc. (London)*, **A138**, 514 (1932).

(11) Deese, THIS JOURNAL, **53**, 3673 (1931).

(12) Baker and Smyth, *ibid.*, **61**, 1695 (1939).

(13) Kushner, Crowe and Smyth, *ibid.*, **72**, 1091 (1950).

(14) Mair, *Bur. Standards J. Research*, **9**, 457 (1932).

(15) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1947.

(16) Sherrill, THIS JOURNAL, **52**, 1982 (1930).

(17) Vogel, *J. Chem. Soc.*, 636 (1943).

(18) Deffet, *Bull. soc. chim. Belg.*, **40**, 385 (1931).

(19) Whitmore, Sutherland and Cosby, THIS JOURNAL, **64**, 1360 (1942).