

n_D^{25} of 1.49371 \pm 0.00001. Although this specific gravity is almost identical with that listed in the "International Critical Tables,"⁴ we have reason to believe that the value is a little too low for toluene of highest purity. A small portion of what we believe to be a more nearly pure toluene was used in part of the work. It had a specific gravity d_4^{25} of 0.86221 \pm 0.00003 and a refractive index of 1.49375 \pm 0.00003. We were not able to detect any difference in the solubility results obtained with the two grades of toluene.

Procedure.—The solubility curve was determined at 25.0 \pm 0.1° in a constant temperature bath by a titration method not greatly different from that previously described.¹ The refractive indices were measured with an Abbe refractometer at the same temperature. An immersion refractometer was used in obtaining the constants for the pure liquids. Large scale curves were plotted for the refractive indices *versus* concentration of each of the three components in the saturated solutions. These curves were used in determining the composition of the

conjugate solutions formed when alcohol in insufficient amounts to bring about homogeneity was added to two liquid phase mixtures of water and toluene. Samples were removed from each of the layers, after equilibrium had been reached, for the determination of refractive index. The results are given in Tables I and II. The values marked with a (*) were used in plotting the solubility curve with its tie lines as shown in Fig. 1. The conjugation curve (4) (p. 398), is also indicated. Its intersection with the solubility curve locates the plait point.

Summary

The solubility curve for the ternary system ethyl alcohol, toluene and water has been determined at 25.0°. The refractive indices of the saturated solutions have been recorded. The compositions of various conjugate solutions throughout a large range of concentrations have been measured.

(4) "International Critical Tables," Vol. III, p. 29.

LINCOLN, NEBRASKA

RECEIVED APRIL 26, 1939

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Molecular Freedom and Melting in Alkyl Halides

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In the course of an investigation relating the structure of organic molecules to their rotational mobility in the solid state, dielectric constant and apparent conductance measurements over a range of temperature and frequency were made on liquid and solid *i*-propyl and *n*-amyl bromides. The crystalline phases were also examined with the polarizing microscope. The *n*-amyl bromide molecule was chosen as less rod-like than long chain compounds,¹ but more anisotropic than the *i*-amyl, *i*-butyl and *i*-propyl derivatives. The latter was selected as intermediate in symmetry between the nearly spherical *t*-butyl halides² and the isobromides.³

The dielectric measurements with a capacity bridge involved the general procedure previously employed.⁴ The usual precautions of pumping off dissolved gases from the liquids, and of slow freezing to reduce void formation, were observed. Temperatures were determined with a platinum resistance thermometer. A small un-silvered dewar tube with a liquid air cooling device was mounted on the microscope stage for observations between crossed nicols.

Purifications of Materials

Final purification was fractionation through a packed jacketed 80 \times 2 cm. Pyrex column with still head equipped

for variable reflux ratio. Boiling points were measured with Anschütz type short range thermometers calibrated by the Bureau of Standards, and the surface for liquid-vapor equilibrium to give true boiling temperatures was increased by use of a mercury well in the column top. Refractive indices were determined with a Pulfrich refractometer.

***i*-Propyl Bromide.**—Material from the Eastman Kodak Co., dried over pure calcium bromide for several weeks, was twice fractionally distilled; b. p. 59.5°; f. p. -90.8°; n_D^{20} 1.42476. "International Critical Tables" values are: b. p. 59.6°; n_D^{20} 1.4251, while Skau and McCullough⁵ give b. p. 59.41° and f. p. -90.0°. As with the *i*-amyl bromide, the absence of Maxwell-Wagner interfacial polarization on freezing and the low apparent specific conductance values for the liquid assured purity.

***i*-Amyl Bromide.**—The Eastman product was dried over calcium bromide for two weeks and twice fractionated; b. p. 128.6°; m. p. -88.7°; n_D^{20} 1.44455; "International Critical Tables" values are: b. p. 127.9°; n_D^{20} 1.4444; whereas Skau and McCullough⁵ gave b. p. 129.6°, m. p. -87.9°, and Deese⁶ reports m. p. -88.0°.

Experimental Results

The dielectric constants, ϵ , and specific conductances k ($\text{ohm}^{-1} \text{cm.}^{-1}$) form Table I, in which, also, the temperatures are given in the first column, and the appropriate frequencies in kilocycles are indicated for the other data. Many measurements at intermediate temperatures have

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

(2) Forthcoming publication.

(3) Baker and Smyth, *THIS JOURNAL*, **61**, in press (1939).

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

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

(6) Deese, *ibid.*, **53**, 3673 (1931).

TABLE I

Kc. <i>t</i> , °C.	<i>i</i> -C ₃ H ₇ Br								
	50			5			0.5		
	$k \times 10^{10}$			ϵ''			ϵ''		
Cooling									
- 85.6	16.07	16.07	16.08	60.2	47.3	46.2	0.22	1.71	16.7
- 90.6	16.52	16.58	16.59	58.7	41.0	40.2	.21	1.48	14.5
- 94.6	16.89	16.94	16.93	52.0	35.5	35.0	.19	1.29	12.7
- 97.2	17.09	17.16	17.17	50.3	35.3	34.3	.18	1.28	12.4
-100.9	17.47	17.53	17.50	45.2	30.2	29.5	.16	1.10	10.7
- 90.1	3.80	3.78	4.22	32.9	21.5	15.0	.12	0.78	5.5
- 90.4	3.52	3.63	4.09	33.5	19.6	13.8	.12	.71	5.0
- 91.8	3.39	3.53	3.85	31.8	17.7	12.0	.12	.64	4.4
-100.7	3.12	3.26	3.64	40.2	11.5	7.8	.15	.42	2.8
-103.5	3.06	3.20	3.55	43.5	10.0	6.3	.16	.36	2.3
-122.0	2.77	2.91	3.18	19.6	8.1	4.2	.07	.29	1.5
-127.2	2.72	2.77	2.97	7.1	4.2	2.2	.03	.15	0.8
-130.5	2.69	2.70	2.83	3.5	2.2	1.7	.01	.08	..
-132.7	2.68	2.68	2.74	..	1.9	1.4	..	.07	0.6
-156.8	2.61	2.61	2.60	3.5	0.5	0.6
-184.6	2.54	2.52	2.54
Warming									
-138.7	2.61	2.59	2.59	3.5	0.8	0.8	0.01	0.03	0.3
-128.3	2.62	2.65	2.80	3.5	1.2	1.5	.01	.04	.5
-125.7	2.63	2.69	2.88	8.9	3.8	1.5	.03	.14	.5
-119.3	2.66	2.87	3.03	17.7	6.2	2.0	.06	.22	.7
-115.2	2.71	2.98	3.14	35.2	6.7	2.9	.13	.24	1.1
-112.5	2.73	3.06	3.63	45.2	14.2	7.2	.16	.52	2.6
-108.7	2.81	3.13	3.79	55.4	14.9	7.2	.20	.54	2.6
-106.8	2.93	3.08	3.34

Kc. <i>t</i> , °C.	<i>i</i> -C ₃ H ₇ Br								
	50			5			0.5		
	$k \times 10^{10}$			ϵ''			ϵ''		
-101.5	2.98	3.28	4.02	53.6	17.7	8.0	0.19	0.64	2.9
- 94.7	3.21	3.58	4.49	45.2	21.7	9.5	.16	.79	3.4
- 92.4	3.53	4.01	5.07	46.8	25.7	13.2	.17	.94	4.8
- 91.3	4.13	4.58	5.93	52.0	35.2	19.6	.19	1.2	7.1
- 91.0	4.69	5.13	6.63	55.4	42.1	26.6	.20	1.5	9.7
- 90.8	5.10	5.60	7.64	52.0	46.3	34.8	.19	1.6	12.6
- 90.7	5.69	6.16	8.22	62.0	52.0	39.5	.22	1.9	14.3
- 90.7	6.28	6.74	8.29	65.3	57.0	48.6	.24	2.1	17.3
- 90.3	14.57	15.38	15.86	117.4	126.9	126.9	.42	4.6	45.7
- 85.9	16.16	16.17	16.05	106.0	101.7	102.0	.38	3.7	36.7
- 81.8	15.79	15.80	15.82	119.0	113.5	113.0	.43

Kc. <i>t</i> , °C.	<i>n</i> -C ₃ H ₇ Br								
	50			5			0.5		
	$k \times 10^{10}$			ϵ''			ϵ''		
Cooling (1)									
- 38.3	7.86	7.87	7.87	19.6	17.0	17.0
- 45.7	8.12	8.11	8.13	17.7	16.3	16.2
- 59.7	8.59	8.60	8.60	14.2	12.4	12.5
- 61.2	8.66	8.66	8.68	12.4	11.5	11.5
- 71.1	9.06	9.07	9.07	10.6	8.4	8.5
- 85.8	9.70	9.70	9.70	5.3	4.2	4.2
- 88.8	9.85	9.86	9.86	5.3	3.5	3.5
- 90.3	9.91	9.93	9.93	5.3	3.2	3.2
- 93.1	10.00	10.06	10.00	3.5	2.6	2.6
- 97.4	9.45	8.81	..	1.7	1.8
- 96.6	8.42	1.8
- 96.2	8.14	7.73	7.38	1.7	1.7	1.7
- 95.9	6.97	6.67	6.42	1.7	1.7	1.7
- 95.6	6.18	5.70	5.33	1.7	1.7	1.6
- 95.3	4.95	4.53	4.28	1.7	1.6	1.5
- 95.2	3.79	3.62	3.52	1.7	1.5	1.5
- 95.6	3.40	3.27	3.15	1.7	1.5	1.2
- 96.9	3.14	3.07	0.9
- 98.4	2.92	0.9
-105.0	2.68	2.68	2.678
-109.4	2.67	2.65	2.626
-111.6	2.62	2.62	2.605
-121.8	2.60	2.59	2.59
-128.2	2.58	2.58	2.58
-134.6	2.58	2.58	2.58
-173.0	2.47	2.47	2.45

Kc. <i>t</i> , °C.	<i>n</i> -C ₃ H ₇ Br								
	50			5			0.5		
	$k \times 10^{10}$			ϵ''			ϵ''		
Cooling (2)									
- 85.4	9.66	9.68	9.66	5.3	4.0	4.0
- 95.5	10.21	10.21	10.18	3.5	1.9	1.9
- 95.8	9.72	3.5
- 95.2	..	8.94	1.9
- 94.8	8.45	1.9
- 93.9	7.11	1.7
- 93.6	4.38	1.7
- 93.7	3.63	1.7
- 93.7	3.14	1.7
- 93.8	2.96	1.7
- 94.0	2.90	1.7
- 94.2	2.87	1.7
- 94.5	2.80	1.7
- 95.0	2.76	1.7
- 96.7	2.69
- 98.2	2.65	2.63	0.8
-101.3	2.55
-105.1	2.58
-108.7	2.56
-111.9	2.55
-115.2	2.54
Warming									
- 97.5	2.67	2.66	2.66	..	0.8	0.8
- 92.4	2.80	2.81	2.80	..	.9	.9
- 90.6	2.96	2.96	2.96	..	1.0	1.1
- 90.4	2.99	3.01	2.99	..	1.0	1.0
- 90.2	3.06	3.07	3.05	..	1.1	1.1
- 90.0	3.12	3.13	3.12	..	1.1	1.1
- 89.6	3.25	3.27	3.26	..	1.2	1.4
- 89.2	3.58	3.60	3.59	..	1.4	1.4
- 88.9	4.01	4.05	4.04	..	1.6	1.6
- 88.6	4.73	4.84	4.83	..	1.7	1.7
- 88.5	5.93	6.03	6.01	1.7	2.0	2.0
- 88.4	6.67	6.76	6.75	1.7	2.0	2.4
- 88.4	7.45	7.64	7.70	1.7	2.4	2.5
- 88.4	8.76	9.06	9.13	2.5	2.6	2.7
- 88.3	9.71	9.77	9.77	3.5	3.2	3.2
- 88.2	9.74	9.75	9.74	3.5	3.2	3.2
- 87.3	9.71	9.72	9.71	5.3	3.3	3.3
- 85.0	9.67	9.67	9.65	5.3	3.6	3.8
- 83.3	9.58	9.59	9.57	3.8	4.2	4.2

been omitted, but those given are often selected from different runs to demonstrate reproducibility. The imaginary part of the dielectric constant $\epsilon'' = 1.8 \times 10^9 k/f$, in which f , the frequency in kilocycles, is given for *i*-propyl bromide. The apparent values of ϵ'' just below the freezing point are too high because of a certain amount of direct current conductance. In the dielectric constant values for amyl bromide between 97.4 and 96.9°, the apparent decrease with decreasing frequency arises from the fact that the readings were taken in the order of decreasing frequency. Although the temperature changed by less than 0.01° during the readings at the three frequencies, the rapid crystallization with consequent setting of the dipoles caused a decrease in dielectric constant which was not influenced by the frequency.

Discussion of Results

Figure 1 represents the general immobilizing of the dipoles of *i*-propyl bromide upon freezing, after

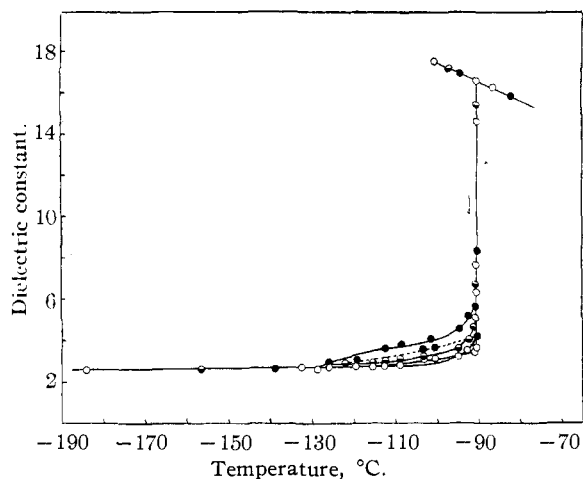


Fig. 1.—Temperature dependence of the dielectric constant of *i*-propyl bromide. (Filled circles represent values at 0.5 kc., half-filled circles values at 5 kc., and hollow circles values at 50 kc.)

slight supercooling, with hindered rotational freedom extending to about -131° . Below this temperature, dispersion has disappeared, and the dielectric constant is nearly the square of the refractive index, as electron polarization alone would require. The polarizing microscope shows pronounced double refraction in the crystals, hence anisotropy, on solidification, so the rotation is probably not about all axes. The cubic, or, occasionally, the hexagonal, class is characteristic of molecular crystals in which rotational molecular freedom comparable to that in the liquid obtains.^{2,7} The sharp reduction of the dielectric constant at the freezing point suggests that rotation around any axis perpendicular to the C-Br line ceases at this temperature, while the gradual fall of the dielectric constant accompanied by anomalous dispersion from this temperature down to about -131° indicates the possibility of a decreasing hindered rotation about this axis or one nearly parallel to it, a behavior undetectable in many structures.

Although beginning at the same temperature as that at which it ends on cooling, the dispersion is more pronounced on warming, and a coöperative loosening, like rotational premelting, may occur.^{1,8,9} Inspection of Table I confirms the idea of hindered rotation with no transition in that the dielectric loss as indicated by ϵ'' shows only a steady decline after solidification.

The *i*-propyl bromide molecule is sufficiently

(7) Smyth, *Chem. Rev.*, **19**, 329 (1936).

(8) A. Ubbelohde, *Trans. Faraday Soc.*, **34**, 282, 292 (1938).

(9) A. Müller, *Proc. Roy. Soc. (London)*, **A158**, 403 (1937).

symmetrical to pack with an economy of free volume in the liquid, but its anisotropic lattice implies that the liquid arrangement is not of cubic-packed spheres. Hence, some supercooling is expected,³ but soon, on cooling, the thermodynamic potential, probably with the aid of short relaxation times, is able to effect crystallization with free energy diminution, unlike the cases of the more anisotropic *i*-butyl and *i*-amyl compounds. Further, standard theories that supercooling proceeds in the complete absence of nuclei are supported by the exact continuity of the supercooled ϵ curve with that for the liquid in Fig. 1. Minute crystallites would cause a sharp change in the dielectric constant.^{4,10}

Figure 2 shows the dielectric behavior of *n*-amyl bromide on cooling and warming. Like diethyl ether,^{11,12} it evidently possesses a monotropic transition resulting in a low temperature form which melts at -88.7° , about 5.9° higher than the phase which first appears on freezing. This transformation had appeared in thermal studies on *n*-amyl bromide⁶ for, about 25° below the melting point, the calorimeter was found suddenly to heat up 5° against a 10° shield gradient. Skau and McCullough⁵ confirmed the presence of two forms, an unstable one melting at -94.6° (a value close to -94.5° , our higher freezing point indicated on Fig. 2), and a stable one melting at -87.9° . They quote Simon¹³ as reporting a

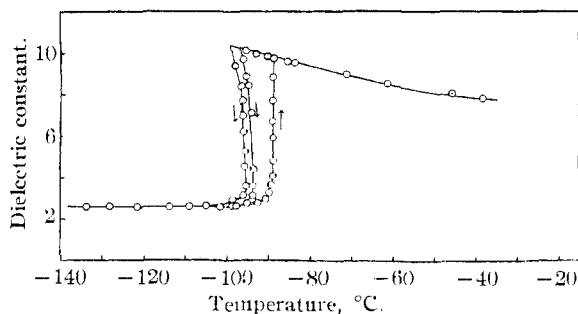


Fig. 2.—Temperature dependence of the dielectric constant of *n*-amyl bromide.

freezing point of -95.25° , a value close to the lower freezing temperature, -95.9° , on Fig. 2. The dielectric measurements, tracing the mechanical behavior of the polar molecules, reveal that, although their anisotropy prevents much supercooling, crystallization either does not pro-

(10) J. Errera, *Phys. Z. der Sowjetunion*, **3**, 443 (1933).

(11) Huettig and Smyth, *THIS JOURNAL*, **57**, 1523 (1935).

(12) McNeight and Smyth, *ibid.*, **58**, 1718 (1936).

(13) Simon, *Bull. soc. chim. Belg.*, **38**, 47 (1929).

ceed rapidly enough, or does not release sufficient latent heat, completely to return the system to a "true" freezing point. This would seem to explain the divergent data of previous investigators, for the freezing point will appear to vary with the bath gradient.

Many polymorphic transitions involving only anisotropic lattices, as the polarizing microscope showed both forms of *n*-amyl bromide to be, are found to involve rotational freedom about at least one molecular axis.¹ However, Fig. 2 resembles similar data for diethyl ether¹² in indicating, after occasional orientation just below the freezing point has ceased, that only electronic and atomic polarizations are contributing to the dielectric constant. An X-ray analysis of the transformation would seem desirable, as discovery of a mode of motion not involving librations in the rearrangement of a molecular lattice might result.

Optical examination gave direct evidence of the transition. The initial crystals were strongly anisotropic, but the double refraction increased when a given sample was held at a low temperature. When the sample was frozen, cooled briefly about 30° below the melting point, and then allowed to warm up quite rapidly, sharp melting of the unstable form was first observed. However, distributed through the liquid were tabular, strongly doubly-refracting crystals which did not themselves melt until a distinctly higher temperature. The latter were the so-called stable form. On prolonged standing at low temperature, the transformation was complete, and only one melting process was observed under the microscope.

The observation that *i*-propyl bromide melted at nearly the same temperature as *n*-amyl bromide, and about 20° higher than *n*-propyl bromide, coupled with data from other work,^{2,3} led to examination of the melting properties of simple alkyl halides. The mono-halides, and especially the bromides, were chiefly considered, because they have closely similar polarizabilities and permanent moments, obey Trouton's rule well as shown by available data,¹⁴ and exhibit no extensive liquid association. They should thus have comparable behavior in condensed phases. Also, the dimensions of the molecules should be little altered by interchanges of methyl and bromo groups, since the same method of measurement

yields 2.0 and 1.9 Å., respectively, for their radii.¹⁵ Even a chlorine atom with radius of 1.65 Å. approximates the methyl group in size. Hence, it is not surprising that the relationships noted below apply to the isomeric hydrocarbons as well as to the isomeric halides.

Writers on the theories of fusion and of liquids have considered the thermodynamic and statistical changes accompanying melting.¹⁶⁻¹⁸ Hirschfelder, Stevenson and Eyring explained the low entropies of fusion of substances which gained non-translational degrees of freedom in the solid state (as by rotational transitions) as arising from the communal sharing of free volume possible on liquefaction. They have shown that if complete communal sharing immediately occurs,¹⁹ the entropy of fusion, ΔS_f , should be 2 e. u. for a substance already possessed of rotational freedom, as found for *t*-butyl chloride.

Relationships among the entropies of fusion of structurally similar compounds also have been sought,²⁰⁻²² but without definite reference to structure. Melting points are often regarded as constitutive properties of organic compounds²³ and an empirical equation connecting them with molecular weights has been suggested.²⁴ The linear relation between number of C atoms and melting points for odd or even members, respectively, of an homologous series, has been long known,²³ and it has been observed without explanation that isomers often deviate from such straight lines.

Thermal and viscosity data are listed in Table II, under the headings m. p., melting point; ΔS_f , entropy of fusion; t. p., transition point; ΔS_t , entropy of transition; $\Delta t_{liq.}^{\circ}$, liquid interval under normal conditions, in degrees; $\Delta E_{vis.}$, the activation energy for viscous flow, in calories per mole; and $\Delta E_{vap.}$, the energy of vaporization in calories per mole.

Figure 3 demonstrates, as shown by the data of Table II, that nearly spherical molecules, which have rotational transitions in the solid, melt far

(15) Stuart, "Molekülstruktur," Verlag von Julius Springer, Berlin, 1934, p. 48.

(16) Herzfeld and Mayer, *Phys. Rev.*, **46**, 995 (1934).

(17) Frenkel, Todes and Ismailow, *Acta Phys.-Chim. U. R. S. S.*, **1**, 97 (1934); Frenkel, *ibid.*, **4**, 341 (1936).

(18) Hirschfelder, Stevenson and Eyring, *J. Chem. Phys.*, **5**, 896 (1937).

(19) For other cases see Gurney and Mott, *Trans. Faraday Soc.*, **35**, 364 (1939).

(20) Walden, *Z. Elektrochem.*, **14**, 713 (1908).

(21) Kordes, *Z. anorg. allgem. Chem.*, **160**, 67 (1927).

(22) Clusius, *Z. Elektrochem.*, **39**, 598 (1933).

(23) Gilman, "Treatise on Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1938, Chap. 20.

(24) Austin, *THIS JOURNAL*, **52**, 1049 (1930).

(14) Landolt-Börnstein, "Tabellen."

TABLE II

Substance	M. p., °K.	ΔS_f	T. p., °K.	ΔS_f	$\Delta t^{\circ}\text{liq.}$	$\frac{\Delta E_{\text{vis.}}}{\text{cal./mole}}$	$\frac{\Delta E_{\text{vap.}}}{\Delta E_{\text{vis.}}}$
CH ₃ Br	180.1					96.2	
C ₂ H ₅ Br	155.1	9.03				156.0	
<i>n</i> -C ₃ H ₇ Br	163.1	9.56				181.0	1770
<i>i</i> -C ₃ H ₇ Br	184.1					148.4	1770 3.5
<i>n</i> -C ₄ H ₉ Br	160.4	13.5				214.3	
<i>i</i> -C ₄ H ₉ Br	155.1	(3.87) ^a				209.6	1990 3.5
<i>t</i> -C ₄ H ₉ Br	255.4	low				90.9	2680 2.4
<i>n</i> -C ₅ H ₁₁ Br	185.1	18.6				216.7	
<i>i</i> -C ₅ H ₁₁ Br	161.1					232.6	1760 4.3
<i>n</i> -C ₆ H ₁₃ Br	188.1	23.0				241.0	
CCl ₄	250.3	2.30	255.5	4.79		99.9	2500 2.7
<i>t</i> -C ₄ H ₉ Cl	248.5	2.0	219.3 ^b			75.2	2490 2.4
CBr ₄	366.7	0.79	319.4	1.68		95.9	
C ₂ Cl ₆ ^c	459.9	4.3	344.2	7.3		0	
C(CH ₃) ₄	253.1					29.5	
C ₆ (CH ₃) ₆	377.1	4.51	148.1	3.24		2.8	
(CH ₃) ₃ CCH:CH ₂ ^d	158.4	1.65	124.9	8.32		155.9	
(CH ₃) ₂ CH(CH ₂) ₂ CH ₃	154.0	13.8				209.1	
CH ₃ CH ₂ CH(C ₂ H ₅)CH ₂ CH ₃	154.3	14.7				212.1	
CH ₃ C(CH ₃) ₂ (CH ₂) ₂ CH ₃	148.1	9.5				204.5	
(CH ₃) ₂ CHCH ₂ CH(CH ₃) ₂	152.5	10.5				204.2	
CH ₃ CH ₂ C(CH ₃) ₂ CH ₂ CH ₃	138.2	12.2				221.0	
(CH ₃) ₃ CHC(CH ₃) ₃	247.7	2.14	121.0	4.69		106.3	

^a Value probably low because of glass formation; Timmermans, *Bull. soc. chim. Belg.*, **44**, 17 (1935). ^b Baker and Smyth, to be published. ^c Parijs, *Z. anorg. allgem. Chem.*, **226**, 424 (1936). ^d Kennedy, Shomate and Parks, *This Journal*, **60**, 1507 (1938); b. p.'s from Edgar, Calingaert and Marker, *ibid.*, **51**, 1483 (1929); Huffman, Parks and Thomas, *ibid.*, **52**, 3241 (1930).

above the "normal" temperature, as *t*-butyl bromide melts at 255.4°K., 95° above *n*-butyl bromide. Further, those molecules of somewhat lower symmetry, which can still acquire some rotational freedom before melting, like that found above for *i*-propyl bromide, will still melt significantly higher and with correspondingly lower entropies of fusion than their non-rotating isomers. This agrees with the position of *i*-propyl bromide on Fig. 3, and, conversely, the normal location of the *n*-amyl bromide point confirms the dielectric results in deciding against rotational freedom in the solid.

The abnormal positions of methyl chloride and bromide probably do not mean exceptional librational freedom, although rotation about the C-X axis would not be detected by dielectric measurements, which, for methyl bromide, yield a solid state polarization only slightly higher than the molecular refraction.²⁵ However, the methyl halide lattices contain a high concentration of dipoles, and might be expected to have greater lattice energies than the higher homologs, in which the dipoles are diluted by the hydrocarbon residues.

(25) Morgan and Lowry, *J. Phys. Chem.*, **34**, 2385 (1930).

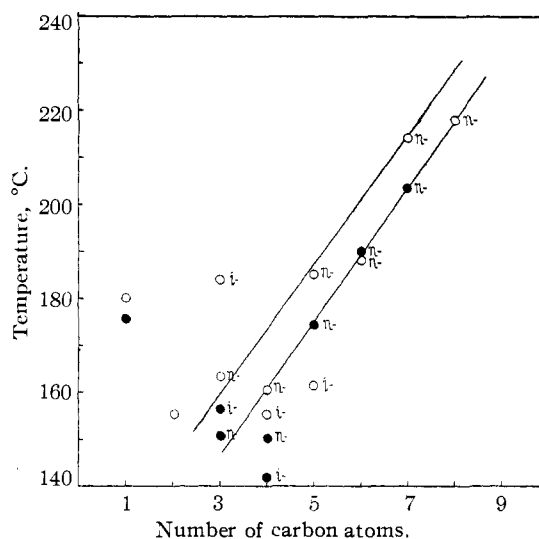


Fig. 3.—Graph of melting point against number of carbon atoms in alkyl chlorides and bromides. (Filled circles ● represent chlorides, hollow circles ○ bromides.)

The following proposals indicate agreement between the thermodynamic and mechanical interpretations of melting properties. The trend toward equilibrium in a system under given conditions involves an increase in entropy while maintaining the minimum free energy feasible.

At a given temperature, a solid can acquire entropy with small change of free energy by going over into the liquid, so melting occurs, and, at a still higher temperature, the boiling point, complete transition to the gas, the most disordered and hence highest entropy state of all, takes place. If, however, the symmetry of a molecule is such that its interaction with neighbors in a lattice does not vary much with its orientation, thermal agitation may give it sufficient kinetic energy to acquire, by means of a polymorphic transition, or simply a gradual loosening, a degree of rotational freedom approaching that in the liquid. A satisfying degree of disorder or increase in entropy has been introduced, and the actual melting can be economically postponed to a higher temperature, when the tendency to increase the entropy still further, by gaining translational freedom, finally causes liquefaction. That a lattice whose molecules possess orientational freedom should have a reduced entropy of fusion is shown in another way by

$$\Delta S_f = R \ln (W_l/W_s)$$

where W_l = number of ways of realizing the liquid state, W_s = number of ways of realizing the solid state; the order of magnitude is given by a W_l/W_s ratio of 2 in which $R \ln 2 = \sim 1.4$ cal./mole/°,²⁶ for example.

From their approximate obedience to Trouton's rule, most normal liquids are found to have the same entropy of vaporization at their boiling points. Hence, from the above argument, one would expect those molecules which gain extra entropy in the solid, and thus melt higher than is normal, to have liquid ranges much shorter than similar but less symmetrical molecules behaving normally in the solid. This is borne out in Table II, where *n*-butyl bromide has a liquid range of 214° and *t*-butyl bromide is a liquid for only 91°. Striking examples of very symmetrical molecules with solid transitions, that gain so little entropy on melting that they go over into the vapor almost immediately, are hexamethylethane, with 2.8° of liquid interval, and hexachloroethane, which, like iodine, forms no liquid under normal conditions. X-Ray studies have shown the onset of rotational freedom in these two molecules,^{27,28} as their non-polarity precludes dielectric investigation. The recorded ΔS_f of hexachloroethane,

(26) Oldham and Ubbelohde, *Trans. Faraday Soc.*, **35**, 328 (1939).

(27) West, *Z. Krist.*, **A88**, 195 (1934).

(28) Finbak, *C. A.*, **32**, 1996 (1938); *Tids. Kjem. Bergvesen*, **17**, No. 9 (1937).

which would be the entropy change on sublimation less that of vaporization, is little more than half the entropy of transition, so a vanishingly small liquid range is suggested.

i-Butyl and *i*-amyl bromides, which vitrified readily, appear on Fig. 3 to melt too low, possibly because of the efficiency of their packing in the liquid as indicated by glass formation. However, since the dielectric studies showed that the molecules could not rotate in the crystalline solids,³ it would appear that the conditions of a small change in internal energy accompanied by a large, desirable entropy increase would lower the melting temperature.

The *t*-butylethylene data are included to provide another example besides carbon tetrabromide of an entropy of fusion less than the 2 units to be expected from communal volume sharing. Although its liquid range 160° is greater than those of the alkyl halides which have transitions, it is still a bit shorter than that of the unbranched butylethylene.

Data for six of the isomeric heptanes, at the bottom of Table II, further illustrate the generalizations. As the symmetry of the molecule finally reaches the maximum possible in 2,2,3-trimethylbutane, the melting point rises from a normal one around 150 to 247.7°K., and, correspondingly, the liquid interval drops from an average of over 200 to 106.3°. Parks and Huffman²⁹ observed that increased branching in a paraffin hydrocarbon leads to a marked decrease in ΔS_f . This behavior is understandable in the light of the present results, where the additional symmetry to be derived from branching may produce librational freedom in the solid.

The applicability of the explanation of the melting point variation among isomers may be further examined in the camphor compounds. Camphor has a rotational transition in the solid state,^{30,31} and is a symmetrical molecule, as may be seen from kinetic theory models. If it is made unsymmetrical and the solid transition thus eliminated by moving the two methyl groups from the inner bridge to the outer ring, fenchone results, which should, by the above concept, have a lower melting point and a longer liquid interval than camphor. This is well confirmed by the comparison: α -camphor, m. p. 451.8°K., liquid interval, 30.4°; fenchone, m. p. 278.1°K., liquid in-

(29) Parks and Huffman, *Ind. Eng. Chem.*, **23**, 1138 (1931).

(30) Yager and Morgan, *THIS JOURNAL*, **67**, 2071 (1935).

(31) White and Morgan, *ibid.*, **67**, 2078 (1935).

terval, 188°. Similar considerations may be extended through the camphor series, where other rotational transitions are known.^{30,31} Hence, the size of the molecules involved would not seem to limit the validity of the principle.

An independent index of the symmetry a molecule is likely to exhibit in condensed phases, and hence of its properties arising therefrom, comes from an examination of the activation energy of viscous flow, interpreted by the modern theory of viscosity.^{32,33} Eyring has shown that to make a hole the size of a molecule in a liquid requires the same energy as to vaporize the molecule. Further, the mechanism of viscous flow involves an activation process which, apparently, requires extra volume, on the part of the flowing molecules, perhaps that swept out by a rotating couple. For nearly spherical molecules, this needed free volume is about one-third the size of a molecule, that is, the ratio $\Delta E_{\text{vap.}}/\Delta E_{\text{vis.}}$ is 2.5 to 3.³³ For rod-like molecules, however, the flow process seemingly goes in the most economical way, say by the couple's rotation about an axis parallel to the chain axes. Then, the $\Delta E_{\text{vap.}}/\Delta E_{\text{vis.}}$ ratio is about 4,³² as rods rotating by each other require relatively less extra volume than spheres. This idea agrees with the independent calculations of the activation energies for orientation of *i*-butyl and *i*-amyl bromides.³ The activation energies for viscous flow listed in Table II were calculated from the data in the Landolt-Börnstein "Tabellen." Perfectly straight lines for the plots of $\log \eta$ against $1/T$ were obtained. The $\Delta E_{\text{vap.}}$ values are from $\Delta H_{\text{vap.}} - (pV)_{\text{vap.}}$. The ratios are very approximate, but are consistent with the rest of the scheme in showing that a molecule which requires a large fraction of the energy of vaporization for the process of viscous flow will, in general, have a sufficiently symmetrical force field to gain vibrational degrees of freedom in the solid, and hence exhibit a reduced ΔS_f . An alternative method of statement is that molecules whose force fields interact nearly equally in all

orientations with those of surrounding molecules in condensed phases will have no preferred arrangements in the flow process, and $\Delta E_{\text{vap.}}/\Delta E_{\text{vis.}}$ will be 2.5 to 3. However, molecules whose interaction potentials vary greatly with orientation will possess $\Delta E_{\text{vap.}}/\Delta E_{\text{vis.}}$ ratios of 4 or more indicating definite relative positions during flow, and, further, will be unlikely to show rotational freedom in the solid. Exceptions to this latter class are certain of the long chain compounds,¹ but, here, the mode of motion in the solid, about one axis only, is very like that found to be easiest in the flow process.

It may thus be concluded from fusion data, coupled with dielectric and crystallographic results, that members of a homologous aliphatic series (including isomers) melting above the normal temperatures indicated by the graph of melting point against number of carbon atoms have gained entropy by rotational freedom in the solid. Hence, since fewer than the normal degrees of freedom are gained on fusion, these compounds will have abnormally short liquid intervals. Viscosity results agree with the other structural data in assigning this behavior to symmetrical molecules.

Summary

Dielectric constant and dipole loss measurements over a range of temperature and frequency on liquid and solid *i*-propyl bromide reveal a small hindered rotational freedom of the molecules in the anisotropic molecular lattice over a 40° interval below the freezing point. Similar studies on *n*-amyl bromide show that its already-known monotropic transition, which results in a melting point (-88.7°) 5.9° higher than the freezing point, does not involve detectable rotational freedom. These results, together with measurements on *t*-butyl halides as well as other data in the literature, lead to a correlation of the melting points, heats and entropies of fusion, and liquid intervals of alkyl halides with the shapes and mobilities of their molecules in the crystals.

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RECEIVED APRIL 3, 1939

(32) Eyring, *J. Chem. Phys.*, **4**, 283 (1936).

(33) Ewell and Eyring, *ibid.*, **5**, 726 (1937).