Summary

Equilibria and electrometric titrations involving iodine and bromine in hydrobromic acid have been experimentally investigated and mathematically analyzed with due reference to complex formation.

It is shown how to correct the molal potential of bromine in concentrated hydrobromic acids for complex formation. The corrected molal potential is constant over a wide range of concentration.

The true "replacement constant" for the reaction between iodine and bromide ion is evaluated, with correction for complex formation. It is 5×10^{-17} in 0.97 normal acid and 8×10^{-18} in 4.7 normal acid. This "constant" is plotted against the activity coefficient of the halide ion so that either can be interpolated or extrapolated.

The dissociation constant of iodine bromide (including complexes) is 2×10^{-8} in 0.97 normal, and 3×10^{-8} in 4.7 normal hydrobromic acid.

Electrometric titrations through the iodine point and iodine monobromide points were subjected to thorough experimental and mathematical treatment. The end-points are shown to coincide with the stoichiometrical end-points within 0.01%.

In solutions where $[\mathrm{Br}]_t = 3[\mathrm{I}]_t$, striking evidence of the presence of iodine tribromide or its complex ion IBr_4' was obtained. Its dissociation constant appears to be 0.3 ± 0.2.

CAMBRIDGE, MASSACHUSETTS

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Dipole Rotation and the Transitions in the Crystalline Hydrogen Halides

BY C. P. SMYTH AND C. S. HITCHCOCK

Previous work has shown the occurrence of dipole rotation in solid hydrogen chloride,[1] solid dimethyl sulfate and ice,[2] and the more obvious factors influencing rotation have been discussed in the paper which includes the latter substances. Measurements of the dielectric constants of crystalline hydrogen chloride, bromide and iodide down to liquid air temperatures and over a wide range of frequency are reported in the present paper in order to give further information on the problem of dipole rotation and to investigate from another point of view the peculiar transitions which have been observed in these hydrogen halides in the solid state.[3]

[1] Cone, Denison and Kemp, THIS JOURNAL, **53**, 1278 (1931).

[2] Smyth and Hitchcock, *ibid.*, **54**, 4631 (1932).

[3] Eucken and Karwat, *Z. physik. Chem.*, **112**, 467 (1924); Giauque and Wiebe, THIS JOURNAL, **50**, 101 (1928); **50**, 2193 (1928); **51**, 1441 (1929); Simon and Simson, *Z. Physik*, **21**, 168 (1924); Ruhemann and Simon, *Z. physik. Chem.*, **B15**, 389 (1932); Natta, *Mem. accad. Italia Chim.*, **2**, 15 (1931).

Apparatus

The dielectric constants and specific conductances were measured at frequencies from 300 to 60,000 cycles with the capacity bridge and the general procedure previously described.[2] The measuring cell which contained a platinum resistance thermometer immersed in the material inside the innermost cylinder was fitted closely into a hole drilled in a solid cylinder of brass, 20 cm. long and 6 cm. in diameter, which was suspended by four pieces of thin, strong string from a wooden cover fitted to a large Dewar tube. Liquid air was blown into the Dewar tube until a temperature close to −190° was obtained as the result of evaporation. As soon as the liquid had evaporated or had been withdrawn, the temperature started to rise at a rate of about 8° an hour, which decreased gradually to 3° an hour at −100°. Measurements were made at frequent intervals as the system warmed up, but readings were, at times, taken with falling temperature by blowing in a small quantity of liquid air and making the observation when the temperature in the cell had ceased to fall. The temperatures thus obtained are marked with x's in Table I.

When the cell was to be filled with material, it was immersed in a petroleum ether bath maintained by a liquid air cooling device[4] at a temperature which would condense the hydrogen halide vapor to a liquid without freezing it. When the cell had been filled with liquid by distillation, it was removed from the bath and gradually lowered into liquid air so that the material solidified as uniformly as possible from the bottom up. In spite of these precautions, the values obtained are presumably a little low because of the spaces between the crystals.

Preparation of Materials

Hydrogen Chloride.—C. P. concentrated sulfuric acid was allowed to drop upon C. P. sodium chloride. The resulting gas was washed with concentrated sulfuric acid and then condensed in a trap by liquid air. On evaporation at −85° no residue was apparent in the trap, showing the absence of an appreciable amount of water or other readily condensable impurities; m. p. −114.2°; transition point −174.2°.

Hydrogen Bromide.—Tank hydrogen, passed over heated platinized asbestos and then through calcium chloride and phosphorus pentoxide tubes to remove the moisture was allowed to mix with bromine vapor in a flask containing liquid bromine kept by a water-bath at about 35°. The gaseous mixture was passed through a piece of 18-mm. Pyrex glass tubing packed for about 25 cm. with platinized asbestos. The first portion of this tube was kept as hot as possible without causing the glass to soften in order to hasten the reaction, but the rest of the tube was kept considerably cooler so as to keep down the thermal dissociation. The gas was next passed through a trap cooled with a carbon dioxide–ether bath to condense out any excess bromine or water and finally was condensed in another trap with liquid air. The middle portion of this product was distilled into the measuring condenser; m. p. −86.8°.

Hydrogen Iodide.—Hydrogen iodide was synthesized from the elements by the method described above for hydrogen bromide. It was necessary to heat the mixing flask much more strongly in this case in order to ensure an adequate vapor pressure of iodine. The hydrogen iodide gas, after being formed in the heated platinized asbestos tube, was passed through a trap cooled by a salt–ice mixture to condense out the excess iodine and then condensed in another trap with liquid air. The middle portion was distilled into the measuring condenser; m. p. −50.7°.

Experimental Results

The dielectric constants ϵ and the specific conductances k (ohm^{-1} cm.$^{-1}$) are given in Table I, the temperatures being given in the first column and

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(4) Smyth and Morgan, THIS JOURNAL, **50**, 1547 (1928)

the frequencies in kilocycles across the top of each group of data. The temperatures could be measured precisely to hundredths of a degree, but as a change sometimes as large as several tenths occurred while the dielectric constant was being measured at the several frequencies, the values were averaged to the nearest tenth and slight corrections were made in the dielectric constant values to make them correspond to this temperature. Many determinations not needed for the accurate establishment of the behavior of the substances are omitted from Table I. The melting points determined for the three substances and given in Table I differ by less than 0.1° from those found by Giauque and Wiebe while the transition point found for hydrogen chloride is 0.5° higher, a difference which may arise from the use in the present measurements of a thermometer less accurately calibrated at the lowest temperatures. The dielectric constants measured at 60 kilocycles are plotted against temperature in Figs. 1, 2 and 3. In the regions of the hydrogen chloride transition and the two upper hydrogen bromide transitions, where the rapidity of change of the dielectric constant with temperature left no time for accurate measurements at more than one frequency, the small dependence of dielectric constant upon frequency justifies, in the absence of values at 60, the plotting of the values obtained at the intermediate frequencies of 20 and 5 kilocycles.

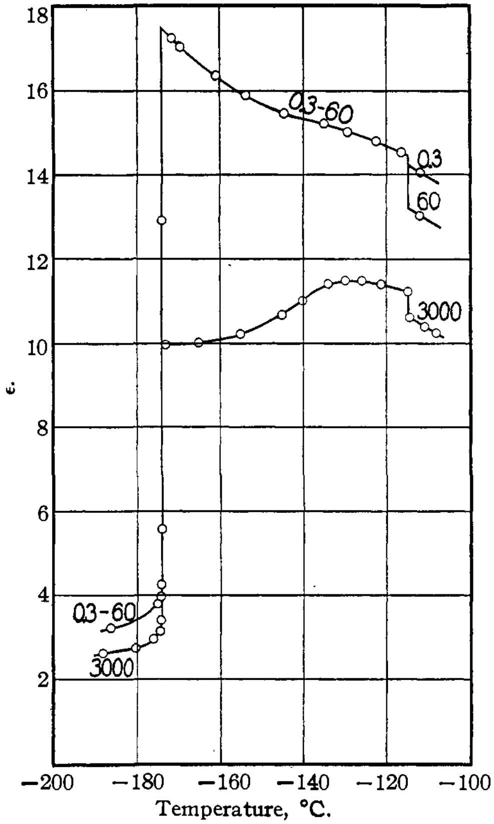

Fig. 1.—Temperature dependence of the dielectric constant (at indicated k. c.) of hydrogen chloride.

By the use of the Grüneisen rule, according to which a solid contracts about 9% in cooling from its melting point to the absolute zero, densities with a probable error of 2–3% have been calculated for solid hydrogen chloride at the melting point from the measurements of Simon and Simson[3] and for solid hydrogen iodide from those of Ruhemann and Simon.[3]

The value for hydrogen bromide similarly obtained from the measurement of Natta[3] at −170° was corrected by comparison with the density of the liquid at the freezing point and the differences between the liquid and the solid densities for hydrogen chloride and hydrogen iodide and should be in

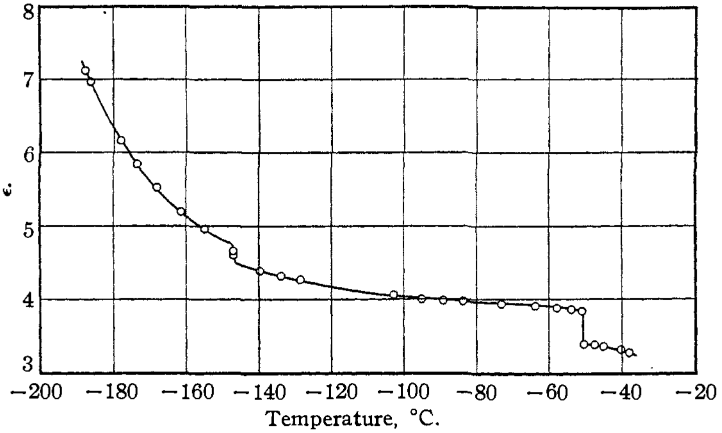

Fig. 2.—Temperature dependence of the dielectric constant (at 60 k. c.) of hydrogen iodide.

TABLE I

DIELECTRIC CONSTANTS AND SPECIFIC CONDUCTANCES

Hydrogen chloride (m. p. −114.2°)

K. c.	60	20	0.3	60	20	0.3
t, °C.		ϵ			$k \times 10^9$	
−186.1	3.21	3.22	3.26	<0.3	0.13	<0.01
−179.7	3.47	3.49	3.56	.43	.25	.017
−175.0	3.78	3.81	3.91	.85	.34	.017
−174.3		3.96			.42	
−174.2		4.25			.51	
−174.15		5.50			.68	
−174.1		12.9			1.3	
−171.2	17.24	17.25	17.25	<0.3	<0.1	<0.01
−169.3	17.04	17.03	17.05	< .3	< .1	< .01
−160.8	16.37	16.36	16.38	< .3	< .1	< .01
−153.6	15.89	15.88	15.90	< .3	< .1	< .01
−144.6	15.42	15.42	15.42	< .3	< .1	< .01
−134.9	15.21	15.21	15.25	< .3	< .1	.025
−129.3	15.04	15.04	15.11	< .3	.08	.05
−122.3	14.80	14.80	14.93	< .3	.17	.095
−116.6	14.52	14.53	14.64	< .3	.25	.10
		Liquid				
−112	13.08	13.15	14.05	76	76	76

Hydrogen iodide (m. p. −50.7°)

K. c.	60	0.3	60	0.3
t, °C.		ϵ	$k \times 10^9$	
−187.5	7.12	7.17	0.68	<0.01
−186.3	6.97	7.03	.68	< .01
−178.1	6.16	6.21	.25	< .01
−173.4	5.85	5.88	.17	< .01
−167.9	5.52	5.56	.25	< .01
−161.1	5.19	5.24	.17	< .01
−154.7	4.96	5.00	.17	< .01
−146.9	4.66		<0.1	< .01
−146.8	4.60	4.63	< .1	< .01
−139.8	4.38	4.40	< .1	< .01
−133.9	4.32	4.33	< .1	< .01
−128.3	4.26	4.28	< .1	< .01
−102.6	4.05	4.06	< .1	< .01
− 95.1	4.00	4.02	< .1	< .01
− 89.2	3.97	3.99	< .1	< .01
− 83.8	3.96	3.99	< .1	< .01
− 73.0	3.93	3.98	< .1	< .01
− 63.6	3.91	3.97	.34	< .01
− 57.9	3.88	3.98	.42	.02
− 53.9	3.87	3.98	.42	.04
− 51.7	3.85	3.96	.51	.03
− 50.8	3.83	3.98	.42	.06
		Liquid		
− 50.6	3.39	3.55	0.42	0.10
− 45.0	3.36	3.57	.85	.19
− 40.2	3.31	3.55	1.1	.27
− 36.9	3.27	3.53	1.3	.34

TABLE I (*Concluded*)

Hydrogen bromide (m. p. −86.8°)

K. c.	60	20	5	1	0.3	60	20	5	1	0.3
t, °C.			ϵ					$k \times 10^9$		
−189.0	12.3	16.2	21.5	24.2	25.0	142	59.6	11.9	0.85	0.56
−187.5	14.1	18.1	21.7	23.2	24.4	147	50	6.6	.85	.13
−186.0	17.2	20.8	23.4	24.8	26.1	153	43.7	5.95	1.02	.085
−185.0	18.7	24.4	31.1	33.9	36.2	211	81.7	15.3	1.2	.085
−184.5	21.6					252				
−184.0	24.4	30.5				276	92			
−183.8	25.4	31.7				283	100			
−183.6	27.3	33.6				289	101			
−183.4	29.5	35.7				287	95			
−183.3	31.7	36.8				252	85			
−183.2	33.5	35.9				164	32			
−183.0[a]	30.6	30.4	31.0	31.3	31.5	17	1.7	0.34	0.085	0.025
−182.0	24.95	24.94	24.98	25.03	25.01					
−181.3[a]	21.70	21.72	21.72	21.72	21.74			<0.1		
− 91.7								<0.1		

K. c.	20	5	0.3
t, °C.		ϵ	
−180.6[a]	20.6		
−179.5[a]	19.5		
−176.8	16.13	16.12	16.10
−175.0[a]	15.5		
−170.0[a]	13.09	13.10	13.13
−165.5	11.84	11.83	11.86
−165.2[a]	11.80		
−164.3[a]	11.75		
−163.2[a]	11.6		
−162.9[a]	11.4		
−162.7[a]	10.9		
−162.4[a]	9.71		
−161.7[a]	9.33	9.34	9.36

t, °C.	20	5
	ϵ	
−161.6		10.96
−161.3[a]	8.39	
−160.1[a]	8.38	
−158.1		10.27
−157.9		10.05
−157.8		9.77
−157.7		9.50
−157.6		9.22
−157.4		8.85
−157.3		8.68
−157.1		8.42
−156.6		8.27
−156.5[a]	8.30	
−156.0[a]	8.34	
−156.0		8.25
−155.9[a]	8.68	
−155.85		8.42
−155.82		8.65
−155.8		8.76
−155.7[a]	8.79	
−154.7		8.74
−152.6		8.68

t, °C.	60	5	0.3
		ϵ	
−151.4[a]	8.68	8.69	8.71
−151.0	8.64	8.65	8.66
−140.5	8.43	8.44	8.45
−140.2[a]	8.42	8.43	8.44
−130.6[a]	8.28	8.28	8.30
−126.8	8.32	8.33	8.33
−124.8	8.30	8.30	8.30
−113.7	8.25	8.25	8.26
−108.3	8.31	8.31	8.32
−104.0	8.36	8.36	8.37
− 97.5	8.25	8.26	8.27
− 91.7	8.07	8.08	8.09

K. c.	60	20	5	1	0.3	60	20	5	1	0.3
t, °C.			ϵ				$k \times 10^9$			
−87.5	7.83	[illegible]	7.86	8.14	8.48	0.85	0.51	0.41	0.19	0.08
					Liquid					
−85.0	7.00	7.00	7.02	7.13	7.33	4.2	4.1	3.95	3.8	3.7
−79.6	6.77	6.77	6.79	6.90	7.14	4.1	4.1	4.0	3.95	3.9
−74.6	6.57	6.58	6.60	6.73	6.93	4.5	4.5	4.4	4.3	4.3
−69.8	6.40	6.40	6.42	6.56	6.79	5.1	5.1	5.1	5.0	4.9

[a] Cooled down to this temperature.

error by no more than 5%. Since, once the material is frozen, no further change occurs in the number of molecules between the plates of the condenser, the density of the solid at the melting point as given in Table II has been used in calculating all the values of the polarization $(\epsilon - 1)/(\epsilon + 2)Md$ for the solid. As in the construction of the curves, the dielectric

TABLE II

MOLAR POLARIZATIONS (60 K. C.) AND REFRACTIONS

	HCl	HBr	HI	t, °C.	HCl	HBr	HI
MR_D (gas)	6.68[a]	9.14[a]	13.75[a]		Liquid		
$d_{m.p.}$ (solid)	1.4_3	2.4_5	3.0_5	−112	23.1		
t, °C.						Liquid	
−186	10.82	27.87	27.83	−85		24.28	20.83
−183	11.08	29.91	27.31	−70		24.06	20.70
−178	11.73	27.92	26.49	−53			20.48
−173	21.60	26.92	25.76				Liquid
−143	21.11	23.54	22.28	−50			19.84
−117	20.90	23.38	21.51	−37			19.64

[a] Smyth, *Phil. Mag.*, **50**, 361 (1925).

constant values at 60 k. c. have been used as far as possible. The few polarizations calculated for the liquids are obtained by using the densities determined by Steele, McIntosh and Archibald.[5] As the absolute values of the polarizations are necessarily rather approximate, only a few are given in Table II, the rest being shown in Fig. 4, where they are plotted against the reciprocals of the absolute temperatures.

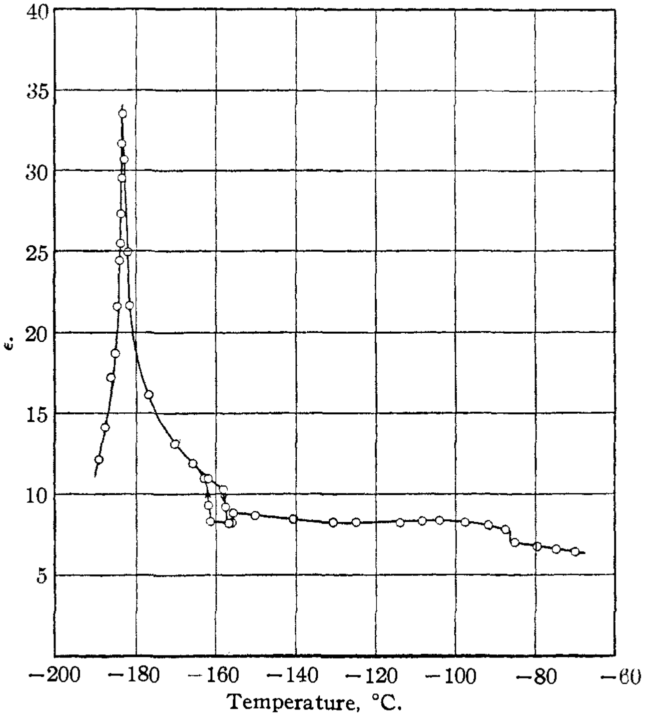

Fig. 3.—Temperature dependence of the dielectric constant (at 60 k. c.) of hydrogen bromide.

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(5) Steele, McIntosh and Archibald, *Z. physik. Chem.*, **55**, 129 (1906).

Discussion of Results

The heat capacity curve of Giauque and Wiebe for hydrogen chloride[3] shows a sharp drop at −174.64° corresponding to a diminished freedom of the molecule and, below this temperature, Ruhemann and Simon have found a much lower symmetry than that of the face-centered cube which exists above this transition point.[3] The slight change in the dielectric constant of hydrogen chloride on solidification and the rise of the low frequency values for the solid with falling temperatures (Fig. 1) show that dipole orientation occurs in the solid much as in the liquid. The linear variation of the polarization P with the reciprocal of the absolute temperature $1/T$ (Fig. 4) as required by the Debye equation, $P = a + b/T$, gives further evidence of the dipole orientation. At −174.2° the dielectric constant drops sharply to a value so low as to evidence little dipole orientation. Below this point there is a slight anomalous dispersion, as shown by the increased conductance (Table I) and the small variation of dielectric constant with frequency, the difference between 0.3 and 60 kilocycles being too small to show in Fig. 1. The small amount of dipole orientation remaining below this temperature diminishes rapidly with increasing frequency and decreasing temperature. The values of Cone, Denison and Kemp for 3000 kilocycles plotted in Fig. 1 are so low below −180° as to show practically no dipole orientation. The fact that these values between the freezing point and the transition point are much lower than those at the low frequencies and their passage through a maximum are evidence of a certain amount of anomalous dispersion like that occurring in a viscous liquid. In ice, the stronger internal field causes this dispersion to occur at

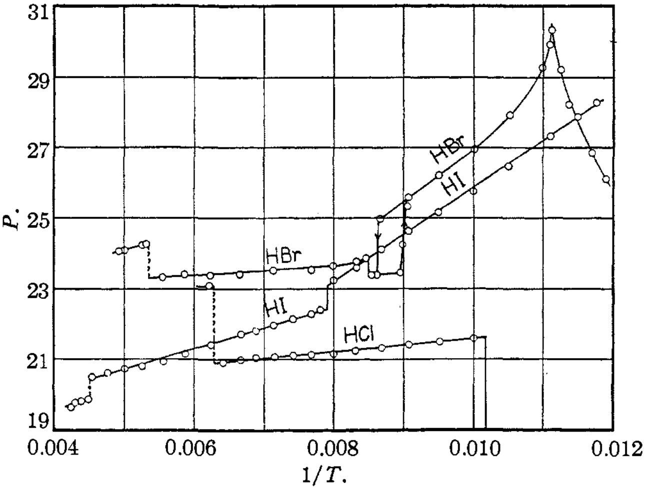

Fig. 4.—P–$1/T$ curves for the hydrogen halides.

lower frequencies and higher temperatures.[2] Part of the difference between the values of the present investigation and those of Cone, Denison and Kemp may arise from differences in calibration and filling of the cell. It is believed, however, that our values for the solid are a little low rather than high because of spaces between the crystals, while the values for the liquid are slightly high because of the error caused by conductance in low frequency measurements.

Ruhemann and Simon found a face-centered tetragonal lattice above, below, and between the two transition regions found for hydrogen iodide. Unfortunately, in the present investigation it was impossible to obtain temperatures low enough to reach the lower transition. The heat capacity curve of Giauque and Wiebe for hydrogen iodide shows an abrupt rise at about −148° followed, as the temperature decreases, by a descent of decreasing rapidity, the values being sufficiently high to indicate considerable molecular freedom. The dielectric constant rises slowly with decreasing temperature (Fig. 2), jumps slightly between −146 and −147.5°, and then increases with increasing rapidity. The P–$1/T$ curve (Fig. 4) consists of two straight lines with a break at the transition. The value of b calculated from the slope of the low temperature line gives a dipole moment 0.46×10^{-18} for the molecule, while that from the other line gives 0.32×10^{-18}, the mean 0.39×10^{-18} being practically identical with the value, 0.38×10^{-18}, found for the gas.[6] The very different effect of this transition upon the dielectric constant and polarization as compared to that in the case of hydrogen chloride may arise from the reduction of a certain amount of molecular rotation occurring above the transition to oscillation. As molecules executing complete rotation do not contribute to the dielectric constant through dipole orientation,[7] the reduction of complete rotation of some of the molecules to rotatory oscillation increases the number of molecules orienting in an externally applied field and so increases the dielectric constant. The reduction from rotation to oscillation apparently occurs at an increased rate in the region below −146°. In hydrogen chloride, which, with its smaller molecule and larger dipole moment, has a stronger internal field, the rotation is apparently reduced, within a very narrow temperature region, to such slight oscillation that dipole orientation becomes negligible.

The x-ray analysis by Ruhemann and Simon of hydrogen bromide at −191, −181 and −153° gave some indication of the probability of a rhombic face-centered lattice with no fundamental crystallographic changes accompanying the transitions, while Natta reported[3] a face-centered cubic lattice at −170° and one of lower symmetry below −175°. All three transitions found by Giauque and Wiebe occur with heat capacity values

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(6) Zahn, *Phys. Rev.*, **24**, 400 (1924).

(7) Debye, "Polar Molecules," The Chemical Catalog Co., Inc., New York, 1929, p. 153.

high enough to indicate considerable molecular freedom. The heating curve shown in Fig. 5 and checked by repetition has been run in order to obtain more information concerning these curious transitions. The upper transition is shown by the practically horizontal portion of the curve at −155.8° to be abrupt, while the middle transition indicated by the less steep portion from −157.1 to −158.0° appears to be gradual. In spite of the not inconsiderable energy change found by Giauque and Wiebe to accompany this upper transition, the abrupt drop in dielectric constant (Fig. 3) which it produces at −155.8° is very small. From −161.5 to −163.0° the curve rises sharply for the second transition and, for lower temperatures, ascends in a rapid curve. When the curve is taken with rising temperature, the break for this second transition does not commence

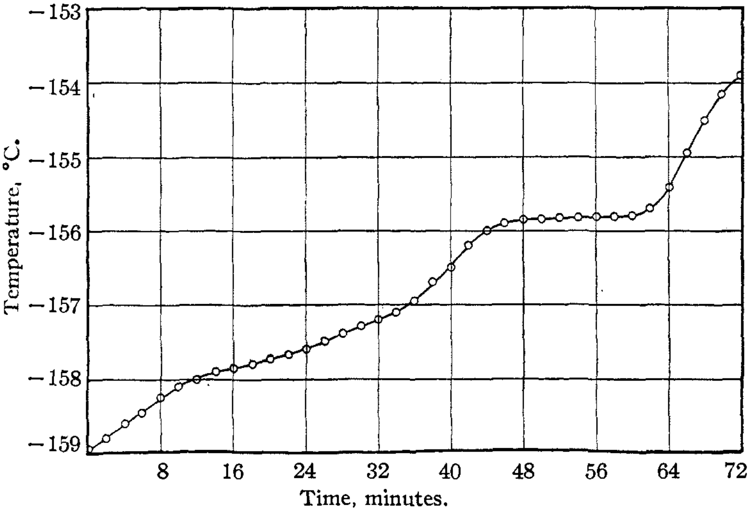

Fig. 5.—Heating curve for hydrogen bromide.

until −158.0° is reached and is completed at −157.1°, in exact agreement with the figures given by the heating curve. A rough cooling curve indicated −161.5° as the beginning of the second transition. Below the middle transition, in a region of rapidly falling heat capacity, the dielectric constant rises with surprising rapidity, the polarization being almost a linear function of $1/T$ (Fig. 4) down to about −173°, then rising more rapidly to the lowest transition. At approximately −183.0°, the heat capacity curve breaks sharply upward, strong anomalous dispersion sets in with a high apparent conductance and the position of a sharp maximum in the dielectric constant depends upon the frequency. Between −183 and −185° the maximum value was too high to measure at frequencies below 20 k. c. with the cell used. Evidently, the orientation of the molecules in the externally applied field is increasingly hampered by the internal field below −183° and the dielectric constant decreases rapidly much as in the case of ice as the temperature falls below its melting point.

It is interesting that only in the case of hydrogen bromide within 10° of its lowest observed transition and at the transitions themselves, does the polarization fail by much of being a linear function of the reciprocal of the absolute temperature as required by the Debye equation, which is strictly applicable only to gases. Except in the case of hydrogen iodide, which has been previously mentioned, the slopes of these straight lines give much too low values for the moment. The behavior is analogous in this way to that of pure polar liquids, which may give straight lines for the P–$1/T$ curves.[8] The rise in the dielectric constants on solidification is due to the increase in density of the materials. The polarizations, on the other hand, show a considerable drop on solidification in the case of hydrogen chloride, a small drop in hydrogen bromide, and a slight rise in hydrogen iodide. The extent of these changes is somewhat uncertain since the polarization values for the solids tend to be low because of the possibility of cavities in the material between the plates, and the apparent value of the dielectric constant of liquid hydrogen chloride is somewhat high because of conductance. However, it may be significant that the change decreases with decreasing molecular field from hydrogen chloride to hydrogen bromide to hydrogen iodide.

Although Ruhemann and Simon conclude that molecular rotation cannot be the cause of all transitions of this character, the hydrogen halide transitions seem to conform roughly to Pauling's theory[9] that they are due to the setting in of rotation about one or more crystal axes. If, however, the upper transition in hydrogen bromide is due to the setting in of rotation around one crystal axis, it is curious that the change in the dielectric constant curve is so small. Merely a small change in volume, which would involve a change in internal field, would account for the dielectric constant change. Moreover, Ruhemann and Simon[3] found no change in the ratio of the lattice constants for hydrogen iodide in the range 21–125°K., which is surprising if rotation around one or more axes begins in this region. What has been termed the reduction of a certain amount of molecular rotation to oscillation on passing through a transition with decreasing temperature may be the cessation of rotation around one crystal axis. Evidently, an externally applied field can cause these small molecules to rotate in the space lattice to almost the same extent as in the liquid, as predicted by the theory of Pauling. Transitions which reduce the thermal rotation may increase the orientation of the molecules in an externally applied field or may gradually or abruptly set the molecules in what appears to be an increased internal field, which permits little or no orientation in the externally applied field.

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(8) Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Company, Inc., New York, 1931, p. 31.

(9) Pauling, *Phys. Rev.*, **36**, 430 (1930).

Summary

The dielectric constants of hydrogen chloride, hydrogen bromide and hydrogen iodide have been measured from the liquid state near the freezing points down to −189° at frequencies from 300 to 60,000 cycles with special attention to the regions of transition. The transition temperatures shown by heat capacity measurements in the literature are closely checked by those shown by the dielectric constant curves. For some distance below the melting points the molecules in the crystalline solids orient in the externally applied field to almost the same extent as in the liquid, the polarizations usually varying between the transitions inversely as the absolute temperature. Change in molecular rotation at the transitions may result in an increase or a decrease in the dipole orientation in an externally applied field.

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Indicator Studies of Acids and Bases in Benzene[1,2]

BY VICTOR K. LA MER AND HAROLD C. DOWNES

1. Introduction

Although the quantitative study of acidity has been investigated exhaustively for the amphiprotic solvent water, and at present is being actively investigated for various acid and basic solvents, the subject has been virtually neglected for aprotic solvents like benzene. This has been due in no small part to the persistent view that the concept of acidity is without meaning in non-dissociating solvents. In a recent paper,[3] we have demonstrated that this view is erroneous since electrometric titrations of acids by bases can be carried out in benzene. In this present paper we shall give a quantitative measure of the acidity for a series of weak acids in benzene, by the use of indicator methods.

According to Brönsted[4] an acid HA is a substance which can dissociate a proton, leaving a conjugate base A, according to the scheme

$$\underset{\text{acid}}{\text{HA}} = \underset{\text{proton}}{\text{H}^+} + \underset{\text{base}}{\text{A}} \qquad (1)$$

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(1) This paper is from a dissertation presented by Harold C. Downes to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) A part of the material was presented at the Syracuse (June, 1932) meeting of the American Association for the Advancement of Science.

(3) La Mer and Downes, THIS JOURNAL, **53**, 888 (1931).

(4) Brönsted, (a) *Z. physik. Chem.*, **108**, 217 (1924), with Kai Pederson; (b) *Rec. trav. chim.*, **42**, 718 (1923), (definition of acid and base); (c) *J. Phys. Chem.*, **30**, 777 (1926); (d) THIS JOURNAL, **49**, 2554 (1927), with E. A. Guggenheim (catalysis by undissociated molecules); (e) *Ber.*, **61**, 2049 (1928), (indicators in benzene); (f) *Z. physik. Chem.*, **143**, 301 (1929), (acidity and ion potential); (g) *Chem. Rev.*, **5**, 284 (1928), (review of subject); (h) THIS JOURNAL, **53**, 2478 (1931), with Bell (reaction velocity in benzene); (i) Meeting of British Association 39, 1932 (medium effect).