Summary

1. The use of methyl alcoholic solutions allows compounds of zirconium to be prepared without danger of hydrolysis.

2. The normal zirconium oxalate, $Zr(C_2O_4)_2$, was prepared and described.

3. Diphenyldinitrogen zirconium, $(C_6H_5N)_2Zr$, was prepared and described.

3950 WALNUT STREET
KANSAS CITY, MISSOURI

THE DIELECTRIC CONSTANT OF HYDROGEN CHLORIDE FROM 85 TO 165°K.

BY RICHARD M. CONE, GEORGE H. DENISON AND JACOB D. KEMP

A consideration of the motions of molecules in crystals has led Pauling[1] to conclude that in certain cases there is complete rotation of the molecules at temperatures below the melting point. He also points out that the transition from a condition in which most of the molecules undergo small oscillations about equilibrium orientations, to one in which they rotate completely, may take place over a very small increase of the oscillational quantum number.

Transitions in the solid hydrogen halides involving the absorption of considerable amounts of heat have been reported by Eucken and Karwat[2] and measured accurately by Giauque and Wiebe.[3] The transition in hydrogen chloride[3a] is perfectly isothermal at 98.36°K., and requires 284.3 calories per mole. Pauling associates such transitions with the taking up of rotational energy.

Whenever the molecules of highly polar substances, such as the hydrogen halides, are free to rotate, those substances must have a high dielectric constant. If the transition in hydrogen chloride at 98.36°K. has produced free rotation of the molecules, then the dielectric constant of the solid should increase considerably at that temperature, in accordance with Pauling's prediction. The purpose of this work was to determine whether or not such an increase occurs.

Apparatus and Experimental Procedure

Hydrogen chloride, prepared by allowing c. P. concentrated sulfuric acid to drop on c. P. sodium chloride, was condensed by liquid air. After

[1] L. Pauling, *Phys. Rev.*, 36, 430 (1930).

[2] Eucken and Karwat, *Z. physik. Chem.*, 112, 467 (1924); Karwat, *ibid.*, 112, 486 (1924).

[3] Giauque and Wiebe, (a) THIS JOURNAL, 50, 101 (1928); (b) *ibid.*, 50, 2193 (1928); (c) *ibid.*, 51, 1441 (1929).

boiling off the product at.atmospheric pressure and warming the container to room temperature, there was no evidence of moisture. From this result we concluded that the hydrogen chloride was sufficiently dry for our purpose.

The method of measuring the dielectric constants was similar to that employed by Zahn.[4] A Hartley oscillator, kept at a constant frequency of about 3000 kilocycles, was coupled capacitatively from the plate coil to the grid of a single circuit radio receiver which used two stages of audio frequency amplification. A second Hartley oscillator, tuned by a "Precision" standard condenser of the General Radio Company in parallel with the dielectric cell, was loosely coupled to the first; it was sufficient to have the oscillators a meter distant from one another without electrical connection. UX 201-A tubes were used throughout.

The dielectric cell consisted of two concentric copper cylinders, about 18 mm. in diameter and 90 mm. long, with a capacity in air of $42\mu\mu f$. The construction is apparent from Fig. 1, which is drawn to scale. At the conclusion of our experiments the cell showed no evidence of corrosion.

The solid hydrogen chloride obtained by condensation in liquid air was allowed to melt, and the dielectric cell was immersed in the liquid. The container was closed and the liquid frozen around the condenser. Since freezing began at the outside and at the bottom, and since there was a considerable depth of liquid above the condenser, any cracks formed in the process were probably filled by liquid flowing in from above.

A copper–constantan thermocouple made of wire calibrated in this Laboratory[5] was given us by Professor W. F. Giauque, and was used with a Leeds and Northrup Type K potentiometer for all temperature measurements.

Fig. 1.—A, glass spacers; B, thermocouple tube; C, condenser leads; D, thermocouple leads; E, filling tube.

The apparatus shown in Fig. 1 was suspended within a cylindrical lead block of 10 kg. mass, and the whole placed in a Pyrex Dewar flask containing liquid air. A tight cover was fitted to the Dewar flask, and the temperature was lowered to 83°K. by boiling the air at reduced pressure. The liquid air was then sucked out and the apparatus allowed to warm slowly. As a consequence of the large heat capacity of the lead, the temperature rose only about three degrees an hour at 85°K.; accordingly, except from 95 to 107°K., dry air was blown in to warm the apparatus at the rate of about ten degrees an hour.
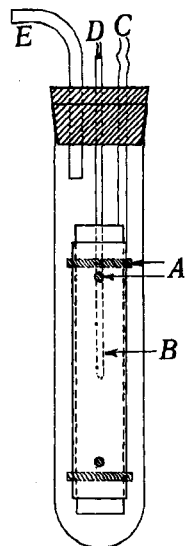
[4] Zahn, *Phys. Rev.*, **24**, 400 (1924).

[5] Giauque, Buffington and Schulze, THIS JOURNAL, **49**, 2343 (1927).

With one oscillator at constant frequency, the other, without the dielectric condenser, was tuned by the standard condenser until the beat note came to zero frequency. The dielectric cell was then switched in parallel with the standard condenser and the latter retuned until the beat note again became inaudible. The difference between the two settings of the standard gives the capacity of the dielectric cell; the ratio of the capacity of the dielectric cell in hydrogen chloride to its capacity in air is recorded as the dielectric constant of hydrogen chloride. Simultaneous readings were taken of temperature and capacity.
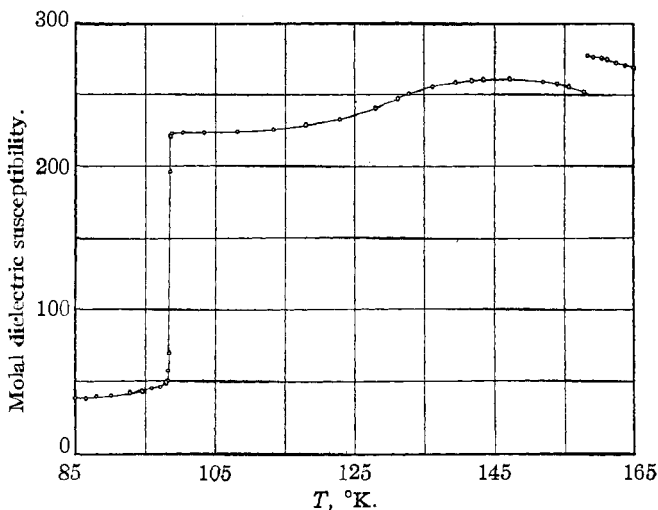

Fig. 2.—Molal dielectric susceptibility of hydrogen chloride.

The accuracy of the temperatures is $\pm 0.1°K.$, except above $150°K.$, where an accident to the thermocouple made the accuracy no greater than $\pm 0.4°K.$ The absolute accuracy of the dielectric constants is probably no better than $\pm 2\%$, as a consequence of the small capacity of the dielectric cell in air, but variations in the dielectric constant could be followed much more accurately. Of the 135 measurements made, the 40 given in Table I serve to establish the curve of Fig. 2; the deviation of the others from the curve is no greater than that of those shown in the figure.

Results

In Table I are listed for each value of the temperature: D, the dielectric constant; $D - 1$, which we may call the dielectric susceptibility; $(D - 1)M/d$, the molal dielectric susceptibility, where M is the molecular weight and d the density; and P, the polarizability, equal to $(D - 1)M/(D + 2)d$. In Fig. 2, molal dielectric susceptibility is plotted against T. Values for the density of the liquid are given by the formula $d = 1.270 -$

0.00276 T, according to Baumé and Perrot.[6]   The density of the solid is given by Simon and Simson[7] as 1.469 g./cc. at 107°K.   Though the use

TABLE I

DIELECTRIC CONSTANT, DIELECTRIC SUSCEPTIBILITY AND POLARIZABILITY OF HYDROGEN CHLORIDE

T, °K.	Dielectric constant, D	Dielectric susceptibility, D − 1	Molal dielectric susceptibility	Polarizability
84.8	2.595	1.595	39.65	8.629
86.7	2.602	1.602	39.83	8.655
88.0	2.655	1.655	41.13	8.837
90.1	2.676	1.676	41.65	8.910
92.8	2.757	1.757	43.67	9.181
94.6	2.798	1.798	44.68	9.314
96.0	2.869	1.869	46.46	9.542
97.2	2.940	1.940	48.23	9.763
98.0	3.036	2.036	50.60	10.048
98.2	3.083	2.083	51.78	10.187
98.3	3.369	2.369	58.89	10.968
98.4	3.893	2.893	71.91	12.203
98.5	8.893	7.893	196.19	18.011
98.6	9.893	8.893	221.05	18.587
98.8	9.964	8.964	222.83	18.624
100.4	9.988	8.988	223.42	18.637
104.4	9.995	8.995	223.59	18.640
108.2	10.012	9.012	224.01	18.649
113.4	10.083	9.083	225.78	18.686
118.0	10.202	9.202	228.74	18.746
122.9	10.369	9.369	232.88	18.828
128.0	10.679	9.679	240.58	18.975
131.2	10.941	9.941	247.10	19.094
132.9	11.083	10.083	250.64	19.157
136.2	11.274	10.274	255.38	19.239
139.5	11.393	10.393	258.34	19.289
141.8	11.441	10.441	259.52	19.309
143.5	11.464	10.464	260.11	19.319
147.2	11.499	10.499	260.97	19.333
152.0	11.417	10.417	258.93	19.299
154.0	11.345	10.345	257.15	19.269
155.7	11.274	10.274	255.38	19.239
157.9	11.131	10.131	241.82	19.178
158.3	10.845		(HCl is melting)	
158.5	10.643	9.643	277.09	21.917
159.2	10.583	9.583	275.82	21.919
160.4	10.536	9.536	275.31	21.962
161.2	10.488	9.488	274.32	21.966
162.5	10.393	9.393	272.04	21.952
163.8	10.298	9.298	270.37	21.985
165.2	10.202	9.202	268.45	22.000

[6] Baumé and Perrot, *J. chim. phys.*, **12**, 225 (1914).
[7] Simon and Simson, *Z. Physik*, **21**, 168 (1924).

of this value for the density at the freezing point is questionable, it is the only reliable one above the transition. A better value may alter the break in the curve at the melting point. This value was also used below the transition, as it is unlikely that the contraction of the solid drew more hydrogen chloride between the plates.

Discussion of Results

The isothermal nature of the change in dielectric constant at 98.4°K. (Table I shows that the change is practically complete over 0.2°K.) was to be expected from the isothermal nature of the transition reported by Giauque and Wiebe[3a] at the same temperature. The suggestion was made by Giauque and Wiebe in reference to hydrogen iodide[3c] that the excitation of only a few molecules may render the low temperature crystal lattice unstable, and that energy is absorbed at the transition to effect a change to a new crystalline form in which another degree of freedom is permitted. If the rotational energy in this new form is sufficiently small, a large fraction of the molecules may take up rotation during the transition. That the higher specific heat above the transition may be due in part to the taking up of this rotational degree of freedom is borne out by the gradual rise in the dielectric constant of the solid between 105 and 150°K. We may conclude from the small change in D on melting that in the solid near the melting point the molecules are rotating almost as freely as in the liquid.

The dielectric constant of the liquid decreases regularly with rising temperature; extrapolation of our curve to 183°K. confirms the value 8.85 found for that temperature by Schaefer and Schlundt.[8] Although our values for the liquid cover too short a range of temperatures to permit the application of Debye's equation, they seem to be in general accord with his theory of dipoles.[9]

We wish to acknowledge our indebtedness to Professor W. F. Giauque for his helpful suggestions in regard to this work.

Summary

The dielectric constant of solid hydrogen chloride has been measured from 85°K. to the melting point, and that of the liquid from the melting point to 165°K. The molal dielectric susceptibility and polarizability have been computed. At 98.4°K., the transition temperature, the dielectric constant changes isothermally from 3 to 10, a behavior which is in accord with Pauling's theory of the rotation of molecules in crystals.

BERKELEY, CALIFORNIA

[8] Schaefer and Schlundt, *J. Phys. Chem.*, 13, 669 (1909).

[9] P. Debye, *Physik. Z.*, 13, 97 (1912).