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Liquid Hydrogen Chloride. Electrical Conductance and Dielectric Constant

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Liquid hydrogen chloride has a specific electrical conductivity of 0.35×10^{-8} reciprocal ohms at $-85°C$. The temperature coefficient is negative: -0.65×10^{-10} in the range from $-84°C$ to $-64°C$. The molecular conductivity at infinite dilution is estimated to be 184 ($-85°C$) and 192 ($-53°C$). The ionization constant is 0.083×10^{-16} at $-78°C$ and 0.051×10^{-16} at $-68°C$. The change in heat content of the ionization reaction is:

$$(x+y+2)\mathrm{HCl} \rightarrow (\mathrm{H_2Cl \cdot HCl}_x)^+ + (\mathrm{Cl \cdot HCl}_y)^-, \qquad \Delta H_{195} \doteq -3500 \text{ cal.}$$
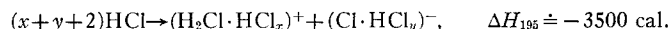
INTRODUCTION

LIQUID hydrogen chloride has been studied as an ionizing solvent by various investigators[2] and for this purpose its dielectric constant, electrical conductivity and viscosity must be known. These quantities have been determined earlier.[3] We wish to report here new values for the first two properties since they differ considerably from the figures given in the literature.

The conductivity cells. Since we wished to determine the electrical properties of liquid hydrogen chloride in the temperature range from $-90°$ to about $15°C$ it was necessary to construct cells which would withstand pressures from 1 to 50 atmospheres. We constructed five different types of cells but found the first four designs undesirable for various reasons.[1] The final design which satisfied all our requirements is shown in Fig. 1. These all-glass cells withstood the pressure involved satisfactorily and it can be seen that the platinum electrodes (nonplatinized) are not affected by the pressure changes involved when the cells are placed in various temperature baths. The tungsten inseals were covered with glass along their full length so that the platinum wires only were exposed to the hydrogen chloride. The cells were washed with dilute hydrochloric acid and conductivity water. The cell constants were determined with 0.0125N hydrochloric acid and were 0.00373, 0.00321,

0.00451 and 0.00400 for the four cells used. The cylindrical electrodes were 14.0 cm long; the inner cylinder had a radius of 0.60 cm and the outer one 0.80 cm. The distance between the two electrodes was 0.1 cm. The cells were baked out at $415°C$ for four days and hydrogen chloride was distilled into them. They were heated between each run, having been flushed with liquid hydrogen chloride.

The cell constants should have been determined with a standard liquid of much lower specific conductance than the hydrochloric acid used in order to avoid the Parker effect.[4] However the conductivities to be measured were such low order that this correction appeared to be unnecessary.

Preparation and drying of hydrogen chloride. The gas was generated by dropping concentrated sulphuric acid onto solid sodium chloride in a thoroughly evacuated and flamed out system. Two drying agents were employed: Phosphorus pentoxide and a combination of calcium chloride and magnesium perchlorate.

While Fairbrother[5] has shown that phosphorus pentoxide is a satisfactory drying agent for hydrogen chloride gas, if the latter is not very wet, we find that it is unsatisfactory when the gas is to be liquefied and then used for the determination of the electrical conductivity of the liquid. The second drying agent mentioned gave a much better product for the purpose of conductivity measurements.

It should be noted that the hydrogen chloride did not come in contact with mercury surfaces after it was dried and fractionally distilled. Mercury vapor also was excluded from the

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[1] This article is based upon a thesis presented to the faculty of the Graduate School of the University of Minnesota by R. E. Peck in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] P. Walden, *Ostwald-Drucker Handbuch der allgem. Chemie IV (1 and 2)*; Akad. Verlags G. m.b.H. (Leipzig, 1924).

[3] Reference 2 and I. C. Tables.

[4] Th. Shedlovsky, J. Am. Chem. Soc. **54**, 1411 (1932).

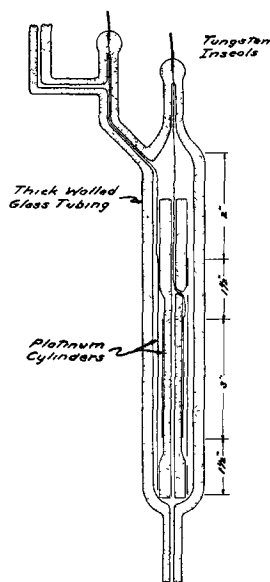[5] F. Fairbrother, J. Chem. Soc. 2, 1539 (1933).

FIG. 1. Conductivity cell for liquefied gases. Pressures up to 30 atmospheres.

system by appropriate means. The reason for these precautions was the fact that we could not obtain consistent results unless mercury was excluded. The results of the conductance measurements are shown in Table I. The measurements marked "fresh" were made as soon as the cell had been removed from the liquid-air bath, where the gas was condensed, and allowed to warm up to the temperature of the cryostat (−85°C). Agitation and standing would increase the conductivity several fold. Similar observations have been made by others, for example in the case of water by Noyes.[6]

The dielectric constant of liquid hydrogen chloride. The above-mentioned measurements were carried out with two different resistance bridges: one a slide wire bridge actuated by a homemade oscillator (500 and 2200 cycles) and a two-stage amplifier and a Jones conductivity bridge[7] No. 260418 at 500, 1000 and 2000 cycles. With the latter instrument it was possible to determine the dielectric constant from the reading of the balancing condensers. The results are given in Table II.

[6] A. A. Noyes, *The Electrical Conductivity of Aqueous Solutions* (Carnegie Institute, Washington, D. C., 1907), page 206.
[7] P. H. Dike, Rev. Sci. Inst. **2**, 379 (1931).

DISCUSSION OF RESULTS

The values of the specific conductivity of liquid hydrogen chloride reported here are lower than any found in the literature. It should be noted that the conductivity of freshly prepared hydrogen chloride is lower than that of the material after standing. In twenty-four hours the conductivity (at −85°C) changed from 0.7 to 5.4×10^{-8} mho (expt 10) and from 0.35 to 2.1×10^{-8} mho (expt 11). It seems that no better results can be obtained in glass-vessels and employing the usual methods of purification.

The temperature coefficient of the specific conductivity has been found to be negative (-0.065×10^{-9} mho/degree).

TABLE I. *The specific conductance of liquid hydrogen chloride (0.5, 1.0 and 2.0 kilocycles).*

Expt. No.	Drying Agent	Temp. Range $t°C$	L specific conductance at −85°C $\times 10^8$ (mhos)	$\frac{-\Delta L}{\Delta t} \times 10^9$	Remarks f. =fresh a.s. =after standing
1	P_2O_5	$-80 \to -20$	9.0	1.11	a s.
2	"	" $\to +10$	10 8	1.05	"
9	CaCl₂ and Mg(ClO₄)₂	$-10 \to$ "	6 8	0.47	"
10	"	$-60 \to$ "	5.4	0.48	"
11	"	$-85 \to 0$	2.1	0.07	"
9	"		1.0		f.
10	"		0.7		"
11	"	$-85 \to -60$	0.35	0 065	"

TABLE II. *Dielectric constant of liquid hydrogen chloride (1.0 kilocycle).*

temp. $t°C$	Dielectric Const.	density (grams/cc)	Molar Polarization P (cc)
−85.0	10.10	1.191	23.0
−80.5	9.80	1.179	23.1
−66.5	8.92	1.141	23.6
−34.8	7.33	1.046	23.7
−19.0	6.55	0.993	23.9
−15.0	6.32	0.980	23.7

Average P 23.5 cc.

TABLE III.

Solvent	$t°C$	$\eta\infty$	ϵ	x	$\lambda\infty$	Const.
H₂O	0	0.01780	88.1	3	264	0 160
"	18	.01060	80.8	"	379	.149
"	25	.00891	78.4	"	419	.143
C₂H₅OH	"	.01145	21.7	3 3	90	.157
CH₃OH	"	.00553	32 5	3.8	190	123
NH₃	−34	.00256	22.0	1 2	1001	.134
HCl	−89.8	.00474	10.45	1.7	(182)	(.144)
"	−84 8	.00458	10.10	"	(184)	"
"	−73.0	.00423	9 50	"	(186)	"
"	−53.0	.00364	8.40	"	(192)	"

Average const. .144

TABLE IV. $K_{i.p.}$ and K_i for the ionization of liquid hydrogen chloride.

Temperature: °C	−88	−83	−78	−73	−68	Remarks
$L \times 10^9$ (mho)	3.70	3.36	3.05	2.72	2.38	Run 11(f)
C (moles/liter)	32.90	32.55	32.15	31.80	31.42	
$(\lambda = 1000L/C) \times 10^7$	1.123	1.032	0.948	0.855	0.757	
λ_∞	182	184	186	187	188	Table III
$(\alpha = \lambda/\lambda_\infty) \times 10^9$	0.617	0.562	0.508	0.456	0.402	
$(K_{i.p.} = (H^+)(Cl^-)) \times 10^{16}$	4.20	3.30	2.67	2.03	1.59	
$(K_i = (H^+)(Cl^-)/(HCl)) \times 10^{16}$	0.125	0.103	0.083	0.066	0.051	

The dielectric constant decreases with increasing temperature (Table II). If we assume that the usual expression for molar polarization[8] holds for liquids then we find the molecular polarization for liquid hydrogen chloride to be 23.5 cc. Smyth and Hitchcock[9] report 23.1 cc at −112°C.

The equivalent conductance. It is possible to calculate the equivalent conductance of liquid hydrogen chloride from the specific conductance and density. The latter has been obtained by Maass and Wright.[10] If we could obtain the equivalent conductance of hydrogen and chloride ions at infinite dilution, we could calculate the ionization constant and the ion product constant for the ionization of liquid hydrogen chloride. It is possible to obtain a very reasonable estimate for the equivalent conductance (λ_∞) of hydrogen chloride at infinite dilution in liquid hydrogen chloride by the use of a relation established by Walden[2]

$$\lambda_\infty \cdot \eta_\infty \cdot x = \epsilon \cdot \text{const.},$$

where η_∞ = the absolute viscosity of the solvent in poises, x = the association factor obtained from the temperature variation of the molar surface energy and ϵ = the dielectric constant of the solvent (see Tables III and IV).

The values of the ionization constant at various temperatures enable us to calculate the temperature coefficient of its logarithm (−0.02)
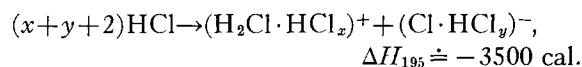
and by means of the well-known relation

$$(d \log K_i)/(dT) = \Delta H/2.3RT^2$$

we find

$$\Delta H_{195} = -4.6 \times 0.02 \times (195)^2 = -3500 \text{ cal.}$$

This value is the heat absorbed for the ionization act of HCl in liquid hydrogen chloride

$$(x+y+2)HCl \rightarrow (H_2Cl \cdot HCl_x)^+ + (Cl \cdot HCl_y)^-,$$
$$\Delta H_{195} \doteq -3500 \text{ cal.}$$

Several weak acids have been shown by Harned and Embree[11] to have negative heats of ionization especially at higher temperatures. These calculations are based on the lowest values of the conductivity of freshly prepared liquid hydrogen chloride and since these conductivities are very low and hence difficult to measure, it must be realized that the ionization constant, the ion product constant and the heat of ionization are not determined to a high degree of accuracy. It is clear that the calculation just given has significance only in the case that the measured conductance is really due to the conductivity of liquid hydrogen chloride and not due to some impurity. The three following facts cause us to believe that we have measured the conductivity of liquid hydrogen chloride: (1) The method of purification involved several (three to seven) fractional distillations; (2) The fresh material used for the measurements was kept at low temperatures (−180° to −60°C), where solubility rates of impurities are slow; (3) The conductivity rose on agitation and standing.

[8] C. P. Smyth, *Dielectric Constant and Molecular Structure.* (Chem. Catalog Co. N. Y., 1931.)

[9] C. P. Smyth and C. S. Hitchcock, J. Am. Chem. Soc. **55**, 1830 (1933).

[10] O. Maass and C. H. Wright, J. Am. Chem. Soc. **43**, 1098 (1921).

[11] H. S. Harned and N. D. Embree, J. Am. Chem. Soc. **55**, 1050 (1934).