[Contribution from the Chemistry Department, Iowa State College]

CONDUCTANCE IN LIQUID HYDROGEN SULFIDE SOLUTIONS[1]

By G. N. Quam with J. A. Wilkinson

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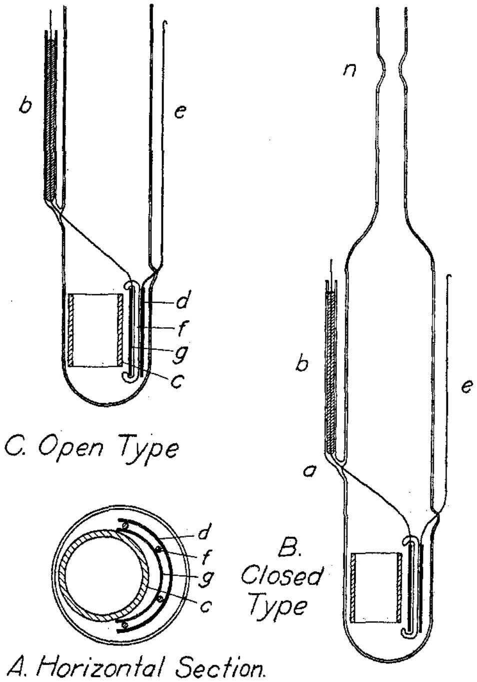
The results of other investigators have been referred to previously by one of the authors,[2] and the work which follows is an extension of previous measurements of conductivities in liquid hydrogen sulfide as a solvent.

Apparatus

A Wheatstone bridge arrangement with an induction coil and telephone receiver was used in determining the numerical values for the conductance. In order to obtain data for comparison with results obtained by others, some measurements were made using the conductivity cell in series with a milliammeter and a 110-volt direct current. In testing some solutions, which had been reported in the past as being conductors although one could obtain no evidence of any conductance with either of the above methods, a D'Arsonval wall galvanometer was used in series with the cell and the 110-volt direct current.

The wall galvanometer had a sensitivity of 1350 megohms per scale division and would therefore indicate as small a current as 0.741×10^{-9} amperes. Using this galvanometer in series with a cell and impressing an e.m.f. of 110 v. across them, the minimum conductance that could be detected would be 0.679×10^{-11} reciprocal ohms. Where the conductance is indicated as "nil" it means that the value is less than this, as the wall galvanometer set-up showed no current on closing the circuit.

The conductivity cells were made of thick-walled, soft glass tubing and those used for room temperature where the pressure was high were equipped with long necks that could be sealed at the constriction n, Fig. 1, B. The platinum electrodes were 18 mm. square and were held about 2 mm. apart by the tiny glass rods f, Fig. 1, A; the unit was held rigidly in place by the short glass tube c being forced in between the electrode and the outside wall of the cell.



C. Open Type

A. Horizontal Section.

Fig. 1.—Conductivity cells.

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[1] This paper is constructed from a portion of a thesis submitted by G. N. Quam to the Graduate School of Iowa State College in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Quam, This Journal, 47, 103 (1925).

In the calculation of cell constants the Kohlrausch value for specific conductivity for 0.02 *N* potassium chloride solution at 25° was used, namely, 2.768×10^{-3} reciprocal ohms. For the various cells used the constants varied from 0.04202 to 0.1055: for example, the constant of the cell for the solution of phosphorus trichloride was 0.05197; for that of methylamine hydrochloride, 0.1055; and for that of acetic acid, 0.04202. Conductivity values of the liquid hydrogen sulfide solutions were determined at temperatures varying between —80° and room temperature.

Although no corrections were made for contraction and expansion of the cells due to temperature changes, the data are comparable, for care was used to make all the cells from the same kind of glass tubing. The concentrations of the solutions were determined by calibrating the volumes of the cells in terms of the height of the column of liquid from the base of the cell to the bottom of the liquid meniscus.

Conductivity Measurements

Magri[3] reported the conductance of pure hydrogen sulfide as being "much less than 4×10^{-7} reciprocal ohms." From observations in this Laboratory using both high-frequency alternating current and 110-volt direct current, the conclusion was reached that the conductance is *very* much less than the above value and is less than 1×10^{-11} reciprocal ohms, which is about one-half the value for the conductance of pure water.

TABLE I

SPECIFIC CONDUCTANCE OF SATURATED SOLUTIONS IN LIQUID HYDROGEN SULFIDE

Solute	Sp. cond. (recip. ohms) $\times 10^7$	Solute	Sp. cond. (recip. ohms) $\times 10^7$
Hydrogen chloride	8.813	Stannic chloride	1.680
Chlorine	1.787	Thiocarbanilide	9.610
Bromine	1.614	Acetic acid (0.1 mole)	nil
Iodine	136.000	Acetic acid (0.1 mole, room temp.)	0.634
Iodine trichloride	13.420	Acetic anhydride	41.260
Sulfur monochloride	10.340	Thio-acetic acid	2.960
Phosphorus trichloride	0.4254	Acetyl chloride	18.800
Phosphorus tribromide	.5269	Aceto-amide	1.680
Arsenic trichloride	11.510		
Antimony trichloride	4244.000		

The specific conductivity was "nil" with the following solutes:

Potassium sulfhydrate
Ammonium sulfhydrate
Hydrogen sulfide hydrate
Bismuth trichloride
Carbon disulfide
n-Butyl sulfide
n-Butyl mercaptan
Thiophenol
p-Thiocresol
Thionaphthol
Chloroform
Bromoform
Iodoform
Trichloro-acetic acid
Benzoic acid
Dinitrobenzene
Stearic acid
Palmitic acid

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[3] Magri, *Atti. accad. Lincei,* **16,** 516 (1907).

Preliminary observations of the conductivity values of liquid hydrogen sulfide solutions were made almost entirely with the open type of cell, C, Fig. 1, at the temperature of solid carbon dioxide. The specific conductivities of a number of saturated solutions were determined and the results are recorded in Table I.

The chloroform solution did not conduct although Antony and Magri[4] reported a value of 3 milliamperes with a similar set-up. The saturated solution of hydrogen chloride contained 43.2 mole per cent. of the acid. McIntosh and Steele[5] pronounced such a solution a non-conductor. Chlorine and bromine both reached a maximum conductivity value with increasing concentration, and then a lowering followed which seemed to be parallel to the oxidation of the sulfur of hydrogen sulfide. The value for iodine compares very well with that of Magri[6] who found it to be 1.34×10^{-5} reciprocal ohms. The phosphorus group halides present an interesting graduation. The conductivities of solutions of the chloride and bromide of phosphorus reached a maximum with increasing concentration; antimony trichloride solutions gave a very high value, comparatively, while those of bismuth trichloride were non-conductors. Antony and Magri,[4] however, reported a conductivity value of 3 milliamperes for a saturated solution of bismuth trichloride.

From the preliminary observations recorded above, it is evident that some solutions in which liquid hydrogen sulfide serves as a solvent do conduct the electric current to a considerable extent. In many instances conductivity might have resulted if the solutions had been raised to a higher temperature, as was the case with acetic acid.

It might be supposed that the conductivities of the halides of the phosphorus group were due to the liberation of the halogen acid by the reaction of the halide on the hydrogen sulfide. That, however, is probably not the case, since the values vary greatly from those for solutions of hydrogen chloride and, further, antimony trichloride gives conductivity values much greater than those for the solution saturated with hydrogen chloride.

It is rather difficult to account for the lack of conductance in a solution of bismuth trichloride. We know that the bismuth sulfurchloride, BiSCl, formed is insoluble, but the hydrogen chloride formed by this partial thiohydrolysis should show some conductivity. Since it does not, we must assume that the hydrogen chloride thus formed is held as a part of the bismuth sulfurchloride precipitate in the form of an addition product.

The conductances shown by the solutions of the halogens in liquid hydrogen sulfide were quite large especially in the case of iodine. In accounting

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[4] Antony and Magri, *Gazz. chim. ital.*, **35**, 206 (1905).

[5] McIntosh and Steele, *Proc. Roy. Soc.*, **73**, 450 (1904).

[6] Ref. 3, p. 518.

for this, Walden[7] postulated that the iodine formed both anions and cations, that is, the iodine molecule broke down into I^+ and I^- and these conduct the current. A dilute solution of iodine was placed in a specially constructed cell with the electrodes 2 cm. apart and arranged so that the anode and cathode solutions could be drawn off separately and analyzed after electrolysis. The solution was electrolyzed for ten hours using a 110-volt direct current. No change in color in the two compartments could be seen and no appreciable difference in the percentage of iodine could be found. This would indicate that Walden was correct in assuming that the iodine carried both positive and negative charges and would therefore not be concentrated at either electrode.

Conductance of Different Dilutions

Except where otherwise stated all of the measurements were made with the cell surrounded by solid carbon dioxide. Table II shows the conductance for solutions of the halides of the elements of the phosphorus family. With the same halogen the conductivity increases with the increase in the atomic weight of the other element. The noticeable thing is the extremely high values for antimony trichloride while bismuth trichloride does not conduct at all. Comparing phosphorus trichloride and tribromide, the conductance increases with the atomic weight of the halogen. Both indicated decomposition, however, with a subsequent lowering of the conductivity with increased concentration.

TABLE II

EQUIVALENT CONDUCTANCE OF HALIDES OF FIFTH GROUP ($\gamma \times 10^3$)

Mol. concn.	PCl_3	PBr_3	$AsCl_3$	$SbCl_3$	$BiCl_3$
0.01	....	....	1.2343	165.57	nil
.05	....	....	....	583.6	..
.0538	....	0.6643	....	.....	..
.069	0.2055	....	....	.....	..
.10	....	....	1.6387	14148.3	..
.1076	....	.365	....	.....	..
.162	....	.1679	....	.....	..
.20	....	....	1.918	.....	..
.2155	....	.0847	....	.....	..

Equivalent Conductivities of Acetic Acid Derivatives

Acetic acid did not conduct at low temperature but the data secured at room temperature are given in Table III along with values for acetic acid derivatives. If addition products form, as with thio-acetic acid, then the greater possibility of adding an H_2S group to the anhydride of acetic acid may be said to account for its higher conductivity value.

Considering the 0.1 *M* concentration the conductance of the solution was increased when the solute contained an amino sulfhydrate or chloride

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[7] Walden, *Z. physik. chem.*, **43**, 385 (1903).

TABLE III

EQUIVALENT CONDUCTIVITY OF ACETIC ACID AND ITS DERIVATIVES IN LIQUID HYDROGEN SULFIDE ($\gamma \times 10^3$)

The equivalent conductivity of trichloro-acetic acid and amino-acetic acid was nil

Mol. concn.	CH_3COOH	$(CH_3CO)_2O$	CH_3COSH	CH_3COCl	CH_3CONH_2
0.05	...	15.00	1.720	2.268	Concn. less than 0.01 mole 16.800 $\times 10^{-3}$ recip. ohms.
.10	0.541	17.595	2.050	2.964	
.15	...	13.75	1.620	4.170	
.20	...	....	1.282	5.750	
.25	...	....	1.184	4.750	

group in the place of the hydroxyl of the acetic acid molecule. But when a hydrogen of the methyl group was replaced by an amino group or all three by chloride radicals the conductivity was lowered to zero. In each case, where conductivity was apparent, a maximum value was reached with increase of concentration and reaction between the solute and liquid hydrogen sulfide was evident.

Equivalent Conductance of Ammonium Chloride Derivatives

The ammonium chloride solution did not conduct at all but the compounds having the hydrogen of the ammonium radical replaced by alkyl radicals furnished solutions having appreciable conductivity values. The conductivity increased with the number of alkyl radicals present and also with the increase of the molecular concentration, as shown in Table IV. The influence of the increase of alkyl radicals attached to the nitrogen nucleus is plainly shown.

TABLE IV

EQUIVALENT CONDUCTANCE OF AMMONIUM CHLORIDE DERIVATIVES IN LIQUID HYDROGEN SULFIDE ($\gamma \times 10^3$)

Mol. concn.	NH_4Cl	CH_3NH_3Cl	$(CH_3)_2NH_2Cl$	$(C_2H_5)_3NHCl$
0.0104	nil	....	.....	1532.700
.0113	..	....	641.500	.....
.0133	..	21.250	.....	.....
.0140	..	....	.....	8357.000
.034	..	....	15256.000	.....
.0448	..	....	.....	42969.000
.0468	..	78.420	.....	.....
.0508	..	....	.....	66004.000
.0544	..	132.600	.....	.....

In general, it appears from these data that the more positive the positive radical is and the more negative the negative radical, the higher the conductance value. This is in agreement with the statements made by Kraus[8] that compounds between strongly electronegative and electropositive constituents are electrolytes in solution or in the fused state, but when dis-

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[8] Kraus, "Properties of Electrically Conducting Solutions," Chemical Catalog Co., **1922**, p. 321.

tinctly electropositive and electronegative constituents are not present the compound is not an electrolyte.

Summary

1. Many substances dissolved in liquid hydrogen sulfide give solutions that conduct the electric current.

2. Solutions of the halides of the phosphorus family show increased conductivity with increase of atomic weight in the family with the exception of bismuth which forms an insoluble compound with liquid hydrogen sulfide.

3. The conductance of derivatives of acetic acid follows the rule that the greater the negativity and positivity of the groups joining the compound, the better the conductance.

4. Ammonium chloride is practically insoluble in liquid hydrogen sulfide, but the introduction of alkyl groups in the place of the hydrogen causes it to become soluble and also conducting in proportion to the number of alkyl groups introduced.

AMES, IOWA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 166]

THE MOVING-BOUNDARY METHOD FOR DETERMINING TRANSFERENCE NUMBERS. III. A NOVEL FORM OF APPARATUS

BY D. A. MACINNES AND T. B. BRIGHTON

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The purpose of this paper is to describe an apparatus for determining transference numbers by the method of moving boundaries, in which the solutions which join at the boundaries are initially brought together by a new method. The history and theory of the determination are sufficiently described in the first paper of this series.[1] The original apparatus of Denison and Steele[2] as modified by MacInnes and Smith[1] has been found to give results of high accuracy, but it requires delicate manipulation at certain stages in the determination of a transference number. The apparatus to be described requires no special skill to operate, and for that reason the authors hope that it will prove to be useful in elementary laboratories in physical chemistry. A determination with this apparatus is more easily carried out and is far more accurate than the Hittorf method as included in most laboratory courses. The moving-boundary method is, also, very much more effective than the Hittorf method as a demon-

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[1] MacInnes and Smith, THIS JOURNAL, **45**, 2246 (1923).

[2] Denison and Steele, *Phil. Trans.* **205A**, 449 (1906). *Z. physik. Chem.*, **57**, 110 (1906–7).