

**Results.**—As an example, the data obtained in an investigation of brom cresol green in benzoate buffer are shown by the solid curve in Fig. 1. From the graph, a value of  $pK' = 0.4$  is obtained. Knowing that, for benzoic acid,  $pK_A = 10.25^2$ , we find  $pK_I$  of brom cresol green to be 10.65.

In Table I is given a summary of  $pK$  values of indicator-buffer systems at various ionic strengths, as well as the values at infinite dilution. The behavior of indicator-buffer systems is more clearly seen in Fig. 2, where it is found that the systems studied fall into a few well-defined groups.

### Discussion

The behavior of acid-base indicators in ethanol is much the same as in methanol. At infinite dilutions, the curves approach the slope of 5.8, required by the Debye-Hückel limiting law. At higher salt concentrations, the ionic diameter and individual molecular characteristics bring about variations that can be expected.

The behavior of sulfonephthaleins in ethanol is in agreement with the extension of the concept of Bjerrum<sup>4</sup> as discussed in a previous paper.<sup>1</sup> This is indicated in Fig. 1, in which the system of brom cresol green in benzoate is compared in methanol and ethanol. Although the general shapes of the curves are the same, the ethanol curve is compressed toward the zero-concentration axis. In other words, the individual effects of the separate charges on a zwitterion become apparent at much lower salt concentrations than in methanol. As a result, although the limiting slope is greater in ethanol, the limiting value

(4) N. Bjerrum, *Z. physik. Chem.*, **104**, 147 (1923).

of  $pK$  above the horizontal portion of the curve is about the same in the two solvents.

The same comparison seems applicable in cases of the other zwitterion indicators, *i. e.*, thymolbenzein, thymol blue in trichloroacetate and methyl orange. The behaviors of the basic indicators, methyl yellow and neutral red, are in accord with present concepts. Methyl red behaves as if the intermediate form (Red II) is a true amino acid and not a zwitterion, in agreement with results found in methanol. In trichloroacetate, it behaves as a cation acid; in benzoate as an uncharged acid.

In Table II is given a summary of the true ionization constants of the indicators studied. These are calculated from the  $pK'$  values obtained in this study and accepted values of  $pK_A$  found in the literature. The  $pK_A$  of veronal was found to be 13.1, from a study of the brom cresol purple-veronalate system. For comparison, the values in methanol and water are also listed. The value for tropeoline 00 was determined in dilute hydrogen chloride.

### Summary

1. A study has been made of the dissociation of acid-base indicators in ethanol, especial attention being paid to the effect of ionic strength.
2. Values of thermodynamic ionization constants of these indicators have been measured.

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## The Conductance of Solutions of Organosubstituted Ammonium Chlorides in Liquid Hydrogen Sulfide

BY E. E. LINEKEN<sup>1,2</sup> AND J. A. WILKINSON

### I. Introduction

Organic ammonium salts were found to form conducting solutions in the liquid hydrides of phosphorus, sulfur, and the halogens by McIntosh and Steele,<sup>3</sup> and in the liquid hydrides of the halogens and sulfur by Steele, McIntosh and

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(3) D. McIntosh and B. D. Steele, *Proc. Roy. Soc. (London)*, **A73**, 450-463 (1904).

Archibald.<sup>4</sup> Antony and Magri<sup>5</sup> have reported that solutions of tetramethylammonium iodide, in liquid hydrogen sulfide, conduct. Quam and Wilkinson<sup>6</sup> have reported the conductances of solutions of methylammonium, dimethylammonium, and triethylammonium chlorides at a number of different concentrations in liquid hydrogen sulfide. Their work shows distinctly the

(4) B. D. Steele, D. McIntosh and E. H. Archibald, *Phil. Trans. Roy. Soc. (London)*, **A205**, 99-167 (1906).

(5) U. Antony and G. Magri, *Gazz. chim. ital.*, **35**, 206-226 (1905).

(6) G. N. Quam and J. A. Wilkinson, *THIS JOURNAL*, **47**, 989-994 (1925).

increased conductance of solutions of substituted ammonium chlorides as the number of substituents increases. Their report indicates also an increased molecular conductance with increasing concentration. The present investigation was undertaken to repeat earlier measurements using modern bridge technique, to extend the concentration range for these solutions and to make measurements on solutions of other organosubstituted ammonium chlorides in order to be able to compare the conductances of several series of compounds. The compounds selected were mono-, di-, tri-, and tetramethylammonium chlorides and the corresponding ethyl and *n*-propyl compounds.

The conductances of all solutions in liquid hydrogen sulfide are much lower than those of similar solutions in water. This might be expected on comparison of their viscosities and dielectric constants at somewhat similar temperatures. The conductances of the hydrogen sulfide solutions were determined at  $-78.5^\circ$ , which is the equilibrium temperature of the mixture of solid carbon dioxide and ether. At this temperature the dielectric constant of liquid hydrogen sulfide is 9.05 compared to 81.5 for water at  $16.3^\circ$ . The viscosity for hydrogen sulfide at the same temperature is 4.12 millipoises compared to 17.94 for water at  $0^\circ$ .

## II. Apparatus, Chemicals and Method

### 1. Shielded, Alternating Current Wheatstone Bridge.—

The shielded bridge was constructed in general according to that described by Shedlovsky.<sup>7</sup> The twin (double) variable air condenser which Shedlovsky used was replaced in this work by two 500 mmf. variable air condensers, one shunting the conductance cell and the other shunting the measuring resistance. The ratio arms were of 5000 ohms each and were a unit from a General Radio Company Type 216 capacitance bridge. No provision was made for reversing the ratio arms. The earthing circuit was made of two 5000-ohm coils similar to those described above, a 20-ohm variable rheostat, and two 500 mmf. variable air condensers. Each instrument comprising the bridge was mounted in a separate covered compartment of a galvanized iron box. The box served for a shield and every precaution was taken to ensure symmetrical shielding. While making a measurement, covers were removed from those compartments containing the balancing

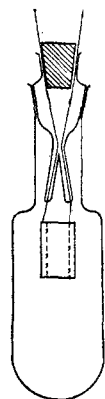


Fig. 1.

resistance, the condenser shunting the balancing resistance, and the detector switch. The conductance cell was not shielded. Terminals leading to the oscillator, the

amplifier, and the conductance cell were mounted on the side of the box with adequate bakelite insulation. Wires leading to the oscillator and amplifier were shielded. All connections between shields were soldered and grounded at one point. Connections between parts of the bridge were made through rather large holes cut in the walls of the various compartments of the galvanized iron box.

The balancing resistance consisted of a Leeds and Northrup decade box, 1–9,999 ohms, and calibrated International Resistance Company Type WW-1 precision wire resistors totaling  $1.49 \times 10^6$  ohms. Resistances larger than  $1.5 \times 10^6$  ohms were determined by shunting the conductance cell with a  $5 \times 10^6$ -ohm resistor, measuring the combined parallel resistance, and calculating that of the solution in the cell. During the latter part of the investigation a  $1.5 \times 10^6$ -ohm Shallcross resistor was added, permitting a direct balance up to  $3 \times 10^6$  ohms. The use of Shallcross wire wound resistors has been described by Cox, Kraus and Fuoss.<sup>8</sup> When measuring resistances lower than  $5 \times 10^3$  ohms, the 5000 ohm ratio arms were replaced with a Leeds and Northrup Kohlrausch slide wire. The slide wire was used at its midpoint, or at a point not more than five of its one thousand divisions from the midpoint, when measuring resistances between 115 and 500 ohms. Only when measuring resistances less than 115 ohms was it not used at the midpoint. This includes but seven determinations, the highest four of the tetrapropyl, the highest of tetraethyl, and the highest two of the tetramethyl compounds.

2. **The Oscillator and Amplifier.**—The oscillator was designed according to that described by Jones and Josephs.<sup>9</sup> The two-stage amplifier was constructed according to the design described by Bickford.<sup>10</sup>

3. **Conductance Cells.**—The cell used for all measurements excepting those for the monosubstituted ammonium chlorides contained electrodes in the form of two concentric cylinders of platinum separated at a distance of about one millimeter by glass bead-like separators. The leads of platinum wire were sealed into glass tubes which protruded downward from the ground-glass stopper of the electrode vessel. The leads were brought out through the top of the cell stopper and were held apart by a rubber stopper. This arrangement is shown in Fig. 1. The rubber stopper served also to prevent moisture from condensing in the tubes supporting the electrodes, thereby short-circuiting the electrodes. The electrode vessel had a volume of approximately 100 ml. The constant of the cell was approximately 0.01. Because of its removable electrodes, this cell had to be restandardized at frequent intervals. No more than four runs were made without restandardizing the cell, and usually less than this. Only twice were four runs made based on one standardization.

The cell used in measuring the monosubstituted compounds contained three concentric platinum cylinders 80 mm. long and 17, 19 and 21 mm. in diameter.<sup>8</sup> The electrodes were separated by glass beads as before. The leads were of heavy platinum wire and were brought out

(8) N. L. Cox, C. A. Kraus and R. M. Fuoss, *Trans. Faraday Soc.*, **31**, 749–761 (1935).

(9) G. Jones and R. C. Josephs, *THIS JOURNAL*, **50**, 1049–1092 (1928).

(10) W. G. Bickford, *Thesis, Library, Iowa State College, Ames, Iowa*, 1935.

(7) Shedlovsky, *THIS JOURNAL*, **52**, 1793–1805 (1930).

through the cell walls on opposite sides of the cell where the constriction takes place. The leads then passed into glass tubes which extended far enough above the stopper so that they would be at about room temperature to minimize condensation of moisture. The glass tubes were sealed into small mercury cups. The stopper was of glass ground into the electrode vessel. The heavy platinum leads supported the electrodes and the possibility of more than a very slight movement of the electrodes as a unit was obviated by a number of tips of glass projecting inward from the walls of the vessel. The constant of this cell was 0.001.

The cell having the higher cell constant was standardized directly against a 0.01 normal solution of potassium chloride at 25.0° according to the data of Parker and Parker.<sup>11</sup> The cell having the lower constant was standardized by comparing the resistance of conductivity water in it and in the first cell.

**4. Preparation of Liquid Hydrogen Sulfide.**—Figure 2 shows the arrangement of apparatus for the preparation, purification, and liquefaction of hydrogen sulfide. Concentrated hydrochloric acid was added from the dropping funnel B to powdered calcium sulfide in the three-liter distilling flask A. Accumulations of calcium chloride solution could be removed by applying suction to the bottle C and opening the cock D to the atmosphere. The hydrogen sulfide was washed with water in bottles E and F which removed most of the hydrogen chloride. Bottle G was charged with a saturated solution of barium hydroxide and this after being converted to barium hydrosulfide would react with any hydrogen chloride remaining in the gas stream. Towers H and I contained calcium chloride for drying. J contained aluminum sulfide which further dried the gas, liberating at the same time an equivalent amount of hydrogen sulfide, and reacting with any small amount of hydrogen chloride set free from the calcium chloride.<sup>12</sup> K and L contained phosphorus pentoxide. Much of the liquefaction took place in M and was completed in the electrode vessel in N. M and N were cooled with a mixture of solid carbon dioxide and ether. O contained phosphorus pentoxide to prevent condensation in the electrode vessel of water vapor from the air in the form of ice. O was used only infrequently as sufficient hydrogen sulfide escaped liquefaction to prevent the entrance of air into the exit tube.

The average specific conductance of twenty-three samples of liquid hydrogen sulfide prepared as described above was  $3.08 \times 10^{-10}$  mho. This agrees well with the value reported by Bickford,<sup>13</sup>  $3.1 \times 10^{-10}$ . The conductances of these twenty-three samples range from  $0.9 \times 10^{-10}$  to  $8.7 \times 10^{-10}$  mho.

Four other samples, prepared with a smaller and older sample of aluminum sulfide in bottle J showed specific conductances ranging from  $9 \times 10^{-10}$  to  $44.41 \times 10^{-10}$  mho. These values are cited as evidence that aluminum sulfide plays an important part in purifying the gas.

**5. The Substituted Ammonium Chlorides.**—These were prepared or purified carefully. The final drying of each compound was accomplished (after careful washing

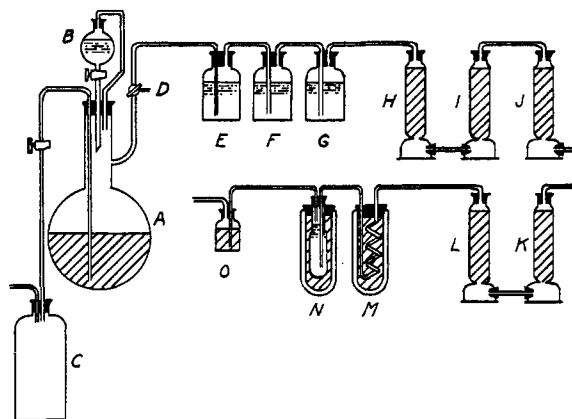


Fig. 2.

with absolute ether) by drawing dry air at reduced pressure slowly through the finely ground salt for a number of days. Immediately before use, the compound was transferred to a dry weighing bottle. These salts are hygroscopic but, providing the compounds were very dry to start with and were transferred to the weighing bottle and to the liquid hydrogen sulfide rapidly and only on days when the absolute humidity of the air was low, no detectable absorption of water occurred. The analyses of the compounds are shown in Table I.

TABLE I  
ANALYSES OF THE SUBSTITUTED AMMONIUM  
CHLORIDES

Compound, chloride	Chlorine, %	
	Calcd. from formulas	Found by anal.
Methylammonium <sup>a</sup>	52.52	53.14 53.11 <sup>c</sup>
Dimethylammonium <sup>a</sup>	43.49	43.42 43.50
Trimethylammonium <sup>a</sup>	37.10	37.06 37.04
Tetramethylammonium <sup>b</sup>	32.35	32.34 32.20
Ethylammonium <sup>a</sup>	43.49	43.48 43.66
Diethylammonium <sup>a</sup>	32.35	32.28 32.34 32.39
Triethylammonium <sup>b</sup>	25.76	25.89 25.69
Tetraethylammonium <sup>b</sup>	21.36	21.53 21.18
Propylammonium <sup>b</sup>	37.10	37.10 37.13
Dipropylammonium <sup>b</sup>	25.76	25.74 25.76
Tripropylammonium <sup>b</sup>	19.72	19.94 19.80
Tetrapropylammonium <sup>b</sup>	15.99	16.08 16.19

<sup>a</sup> Eastman Kodak Co. products, purified in this Laboratory. <sup>b</sup> Prepared and purified in this Laboratory. <sup>c</sup> Methylammonium chloride proved to be non-conducting in liquid hydrogen sulfide and was not further purified.

**6. Procedure.**—After measuring the resistance of the liquid hydrogen sulfide at the temperature of the cooling bath of solid carbon dioxide and ether ( $-78.5^\circ$ ),<sup>14</sup> a sample of the finely powdered, dry organosubstituted ammonium chloride was added from a weighing tube. After solution was complete, the resistance of the solution was measured, and the cell was lifted out of its freezing mixture only far enough to permit measuring the distance between a selected point at the top of the cell and the meniscus. The volume of solution in the cell was determined from a calibration

(11) H. C. and E. W. Parker, *THIS JOURNAL*, **46**, 312-335 (1924).(12) J. A. Wilkinson, *Chem. Reviews*, **8**, 237-250 (1931).(13) W. G. Bickford, *Iowa State Coll. J. Sci.*, **11**, 35-38 (1936).(14) A. Theil and E. Schulte, *Z. physik. Chem.*, **96**, 312 (1920).

curve comparing distances from the top of the cell to the menisci for known volumes of water at room temperature. The contraction of the glass in cooling from room temperature to that of the freezing mixture is small and was neglected. After completing these measurements for one solution, another weight of salt was added, and the measurements were continued. Sorption effects at the electrodes were assumed to be negligible. They have been shown to be negligible at concentrations above  $10^{-5}$  normal for solutions in several non-aqueous solvents at  $25^\circ$ .<sup>8</sup>

### III. Results

The results are shown in Table II where  $C$  is the concentration in moles per liter and  $\Lambda$  is the molecular conductance.  $K_s$  indicates the conductance of solvent and  $K$  that of the solute.

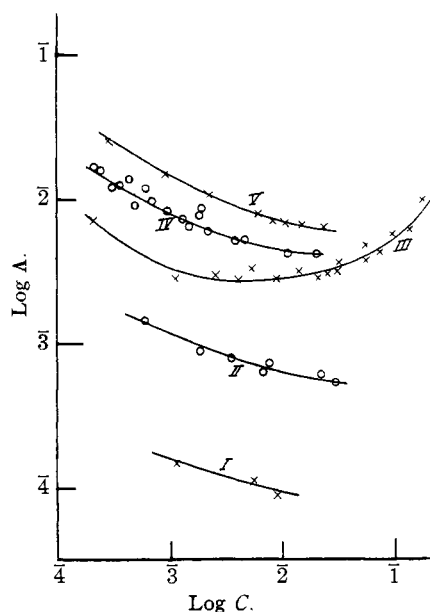


Fig. 3.—Conductance curves for substituted ammonium chlorides in hydrogen sulfide at  $-78.5^\circ$ : I,  $C_2H_5NH_3Cl$ ; II,  $C_3H_7NH_3Cl$ ; III,  $(CH_3)_2NH_2Cl$ ; IV,  $(C_2H_5)_2NH_2Cl$ ; V,  $(C_3H_7)_2NH_2Cl$ .

The specific conductances of the monomethyl and monoethyl compounds are not much greater than that of pure liquid hydrogen sulfide, and those for the propyl compound are about twice that of the pure solvent. With corrections as large as these, the results are not accurate and are given merely to indicate their order of magnitude.

The conductance of the solvent was significant (at greatest, 11% of that of the solution) in measuring the more dilute solutions of the di- and trisubstituted salts. For the tetrasubstituted compounds, the correction was never

greater than one part in one thousand, and for most solutions it was negligible.

Figures 3 and 4 show the plots for the data of Table II.

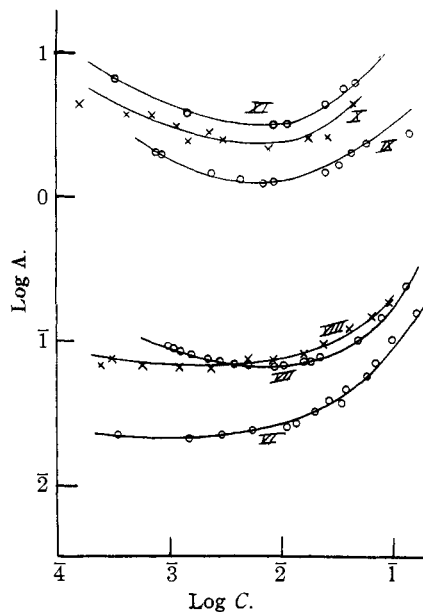


Fig. 4.—Conductance curves for substituted ammonium chlorides in hydrogen sulfide at  $-78.5^\circ$ : VI,  $(CH_3)_3NHCl$ ; VII,  $(C_2H_5)_3NHCl$ ; VIII,  $(C_3H_7)_3NHCl$ ; IX,  $(CH_3)_4NCl$ ; X,  $(C_2H_5)_4NCl$ ; XI,  $(C_3H_7)_4NCl$ .

### IV. Discussion of Results

The greater the number of groups substituted in the ammonium radical the greater the conductance becomes. The mono substituted compounds are poor conductors and very little evidence of conductance with the monomethyl compound was observed. This may be due to the fact that the solubility of the compound in liquid hydrogen sulfide is almost nil.

In general the higher the molecular weight of the substituted group, the higher is the value of the conductance. The only exception to this is that the triethyl compound shows higher conductance than the tripropyl ammonium chloride at low concentrations.

The conductance is not greatly altered by changing the substituent from methyl to ethyl to propyl groups. Changing the number of the substituted groups has a greater effect on the magnitude of the conductance, the greatest increase occurring when going from the tri- to the tetrasubstituted compounds.

The compounds in general show an increasing



which do not show this, the monosubstituted salts and dipropyl- and diethylammonium chlorides, would be expected to have increasing conductance in more concentrated solutions. Additional measurements were made extending concentrations to higher values than those reported for dipropyl and diethylammonium chlorides but no increase in conductance with increasing molecular concentration was noticed with these two salts.

**Acknowledgments.**—The authors are indebted to Dr. W. G. Bickford for help and suggestions while constructing the conductance bridge and its auxiliaries. A substantial part of the experi-

mental work was done in the Chemistry Laboratories of the University of Vermont.

### V. Summary

The conductances of solutions of mono-, di-, tri- and tetrasubstituted methyl-, ethyl- and *n*-propylammonium chlorides in liquid hydrogen sulfide have been measured. These show that the molecular conductance increases both with the number and the size of the substituted groups, the number having a greater effect than the size.

The conductance concentration curves show a minimum which is characteristic of solutions of electrolytes in solvents of low dielectric constant.

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[CONTRIBUTION FROM THE LABORATORY OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

## Chemical Activation by Isomeric Radioactive Transition; the Reaction of Br<sup>80</sup> (18 min. half-life) with Carbon Tetrachloride

BY JOHN E. WILLARD

Investigations in this Laboratory utilizing radioactive bromine have shown that it undergoes a reaction with carbon tetrachloride. This reaction is not activated by either heat or light but must be accounted for on the basis of chemical activation resulting from the radioactive transition of Br<sup>80</sup> (4.4 hr. half-life) to Br<sup>80</sup> (18 min. half-life).

Freshly prepared radioactive bromine contains a mixture of Br<sup>80</sup> (4.4 hr. half-life), Br<sup>80</sup> (18 min. half-life) and Br<sup>82</sup> (34 hr. half-life), all of which may be formed from the common isotopes Br<sup>79</sup> and Br<sup>81</sup> by neutron capture. Br<sup>80</sup> (4.4 hr.) and Br<sup>80</sup> (18 min.) are radioactive isomers<sup>1,2,3,4</sup> the first of which changes into the second as a result of a loss in nuclear energy. In somewhat less than 70% of the transitions<sup>5</sup> this energy appears as a gamma ray while in the remaining transitions it serves to eject a conversion electron from one of the electron shells of the atom.

It has been shown that the change from Br<sup>80</sup> (4.4 hr.) to Br<sup>80</sup> (18 min.) is capable of activating the hydrolysis of *t*-butyl bromide,<sup>2</sup> the rupture of bromate ion,<sup>3</sup> and the decomposition of ethylene dibromide.<sup>6</sup> These reactions result in the preferential splitting out of Br<sup>80</sup> (18 min.) atoms from

the parent molecule. The activation of these processes has been attributed to the recoil energy imparted to the Br<sup>80</sup> (18 min.) by the ejection of a gamma ray or conversion electron, but in view of a subsequent determination<sup>7</sup> of the energy of the conversion electrons involved, this explanation is not tenable.

In agreement with the work cited above, it has been found that Br<sup>80</sup> (18 min.) is the reactive bromine species in mixtures of bromine isotopes with carbon tetrachloride. Calculations discussed below indicate that only those transitions of Br<sup>80</sup> (4.4 hr.) to Br<sup>80</sup> (18 min.) which occur with the emission of a conversion electron result in reaction with the carbon tetrachloride. The electronic rearrangements which follow such emission afford ample energy to account for the activation.

The results which have been obtained emphasize the fact that special precautions must be exercised in the use of certain radioactive elements as isotopic tracers if erroneous conclusions are to be avoided. It is to be noted, however, that Br<sup>82</sup> (34 hr.) may be used as an isotopic tracer without danger of ambiguity. This isotope may be obtained by allowing mixtures of isotopes to stand until the relatively short-lived Br<sup>80</sup> isomers have decayed.

(7) (a) Valley and McCreary, *Phys. Rev.*, **55**, 666 (1939); (b) **55**, 863 (1939).

(1) Snell, *Phys. Rev.*, **52**, 1007 (1937).

(2) Segre, Halford and Seaborg, *ibid.*, **55**, 321 (1939).

(3) DeVault and Libby, *ibid.*, **55**, 322 (1939).

(4) Roussinov and Yusephovich, *ibid.*, **55**, 979 (1939).

(5) Siday, *Nature*, **143**, 681 (1939).

(6) Le Roux, Lu and Sugden, *ibid.*, **143**, 518 (1939).