Control of temperature should be maintained to prevent (1) distillation of solvent from the paper to the walls of the chamber, (2) disruption of the single phase solvent system; also because temperature has an effect on the constancy of the $R_F$ values.

The authors express thanks to Dr. John T. Edsall for the interest he has taken in this work.

## Summary

1. A study of partition chromatography with applied voltage has been presented.

2. $R_F$ values for ten amino acids obtained under the experimental conditions are given.

3. Paper buffered with phosphate at *p*H 6.2 has been used.

BEVERLY, MASSACHUSETTS RECEIVED MARCH 16, 1948

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[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

# The Electrical Conductance of Strontium Chloride and Strontium Bromide in Ethanol–Water Mixtures[1]

BY RICHARD LOUIS BATEMAN AND DWIGHT T. EWING

The earliest investigations of electrical conductance in mixed solvents were those of Lenz,[2] and Stephan.[3] This type of work was extended by other workers and particularly by Jones and coworkers.[4]

In general, these investigations showed that the conductance of electrolytes in mixed solvents decreased as the solvent viscosity and degree of solvation became greater but increased as the dielectric constant of the solvent and temperature became greater. A large part of these early investigations concerned the uni-univalent electrolytes with less attention given to those of higher valence types. No recorded data are given for the conductance behavior of strontium chloride and strontium bromide in ethanol–water mixtures.

The purpose of the present investigation was to determine the influence of concentration, solvent composition and temperature on the conductance behavior of strontium chloride in ethanol–water solutions and to note the influence of viscosity and dielectric constant of the solvent on the conductance of these solutions. For purposes of comparison, a limited amount of work was also done on the conductance of strontium bromide in ethanol–water solutions.

## Experimental

**Purification of Materials.**—J. T. Baker C. P. $SrCl_2 \cdot 6H_2O$ was recrystallized from conductance water once above and once below the transition temperature (61.34°) by the method of Richards and Yngve[5] and oven-dried to constant weight.

J. T. Baker C. P. KCl designated "special crystals" (low in Ca, Mg and $NH_4OH$ ppt.) were twice recrystallized from conductance water. The salt was then partially fused in a platinum crucible and transferred to a closed bottle while still hot.

Ethyl alcohol was purified by distilling 95% alcohol from concentrated sulfuric acid (20 ml. of acid per liter of alcohol) to remove amines. The distillate was then treated with alcoholic lead acetate[6] (3 g. of lead acetate in 5 ml. of water and then 5 g. of KOH in 25 ml. of alcohol) and distilled. Absolute alcohol was then prepared by treating each liter of distillate with fresh calcium oxide (200 g. per liter of alcohol), refluxing and distilling. In these distillations, the first and last portions of distillate were discarded. The water content was determined by density measurement and reference to standard density tables.[7] The alcohol thus obtained was 99.9% absolute and had a specific conductance of $2.0 \times 10^{-7}$ mho at 25°.

Conductance water was prepared by distilling water containing a little potassium permanganate through a block tin condenser. About 50% of the distillate was allowed to condense and only the middle fraction was retained. At 25° the specific conductance of this water was $1.00\text{-}1.04 \times 10^{-6}$ mho.

**Apparatus.**—A Leeds and Northrup Kohlrausch slide wire bridge with extension coils, tunable head phones, Curtis coil resistance boxes, adjustable air condensers and Leeds and Northup audiooscillator were used. All parts of the bridge assembly were protected by properly grounded shields. A thermostat bath filled with water was kept constant to within 0.01° during the series of measurements. Temperature measurements were made on a thermometer (No. 23044) that had been certified by the Bureau of Standards (certificate No. 49571). Temperature fluctuations were followed by a Beckmann thermometer. The conductance cells were of the Jones and Bollinger[8] type with the filling tubes widely separated. The electrodes were not platinized.[9] The primary standard solution for cell constants was the 0.01 demal KCl solution of Jones and Bradshaw.[10] Cells having low constants were calibrated using a more dilute solution which had been compared to the standard 0.01 demal KCl in another cell.

**Procedure.**—The ethanol-water solvents were prepared by the weight method. The electrolytic solutions were prepared in volumetric flasks after attaining thermal equilibrium in the thermostat bath. The conductance cells were rinsed several times with the appropriate solution, brought to thermal equilibrium and the conductance determined. All final readings were taken near the center of the bridge with the air condensers adjusted for the most satisfactory null-point. The cells were selected so that the resistance was ordinarily above 1000 ohms. Duplicate determinations were made from two independently prepared solutions. The conductance of the solvent was determined immediately before the preparation of the elec-

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(1) This paper represents part of a thesis submitted by Richard Louis Bateman to the Graduate Faculty of Michigan State College in partial fulfillment of the Ph.D. degree, June, 1944.

(2) R. Lenz, *Mem. de l'Acad. de St. Petersbourg*, **7**, 30 (1882).

(3) C. Stephan, *Wied. Ann.*, **17**, 673 (1882).

(4) H. C. Jones and co-workers, Carnegie Inst. Reports; No. 80 (1907), No. 180 (1913) and No. 210 (1915).

(5) Richards and Yngve, THIS JOURNAL, **40**, 91 (1918).

(6) S. Kiczales, *Ind. Eng. Chem.*, **20**, 493 (1928).

(7) "International Critical Tables," **3**, 118 (1928).

(8) Jones and Bollinger, THIS JOURNAL, **55**, 1780 (1933).

(9) J. R. Partington, *J. Chem. Soc.*, **99**, 1937 (1911).

(10) Jones and Bradshaw, THIS JOURNAL, **55**, 1780 (1933).

trolytic solution and the specific conductance of the solvent was subtracted from the specific conductance of the solution.

TABLE I

EQUIVALENT CONDUCTANCE OF STRONTIUM CHLORIDE IN ETHANOL–WATER MIXTURES AT 25°

| $C$[b] | | $\Lambda_c$[a] | | | | | | |
|---|---|---|---|---|---|---|---|---|
| % Ethanol | 0 | 5 | 20 | 40 | 60 | 80 | 90 | 99.89 |
| 0.1000 | 101.6 | 85.5 | 53.1 | 33.84 | 23.54 | 15.31 | ... | ... |
| ,0500 | 107.9 | 90.7 | 56.50 | 36.44 | 26.05 | 17.51 | 13.17 | ... |
| .0250 | 113.9 | 95.8 | 59.89 | 39.18 | 28.74 | 20.19 | 15.44 | ... |
| .0100 | 120.4 | 102.3 | 64,67 | 43.24 | 33.12 | 24.57 | 19.38 | 9.75 |
| .0050 | 124.2 | 105.2 | 66.33 | 45.45 | 35.62 | 27.51 | 22.23 | 11.80 |
| ,0025 | 127.2 | 108.4 | 68.23 | 46.54 | 37.87 | 30.96 | 25.76 | 14.27 |
| .0010 | 129.6 | ... | 69.38 | 48.53 | 40.96 | .... | 30.73 | 16.92 |
| .0000 | 134.5 | 115.0 | 71.7 | 50.8 | 44.2 | 41.4 | 37.4 | 22.1 |

[a] $\Lambda_c$ = ohm$^{-1}$ × cm.$^2$ × equivalent$^{-1}$. [b] $C$ = normality.

## Discussion

Figure 1 shows the influence of concentration on the equivalent conductance of strontium chloride in various ethanol–water mixtures at 25°. The absence of experimental transference data for the ions in these solutions made it unfeasible to evaluate $\Lambda_0$ with the aid of the Onsager equation.[11] Curves similar to those in Fig. 1 were drawn on a large scale and the values for $\Lambda_0$ were obtained by graphical extrapolation. As one might expect, the values of both $\Lambda_c$ and $\Lambda_0$ decrease as the percentage of ethanol becomes larger.

Figure 2 shows the influence of solvent composition on the equivalent conductance of 0.001, 0.005, 0.025 and 0.100 normal solutions of strontium chloride. Increasingly larger percentages of ethanol cause progressively smaller change in the equivalent conductance up to a point of inflection. Beyond this point, the change in equivalent

TABLE II

EQUIVALENT CONDUCTANCE OF STRONTIUM BROMIDE IN ETHANOL–WATER MIXTURES AT 25°

| $C$ | | $\Lambda_c$ | |
|---|---|---|---|
| % Ethanol | 0 | 40 | 60 |
| 0.1000 | ... | 36.02 | 26.92 |
| .0500 | 110.4 | 38.71 | 29.15 |
| .0250 | ... | 41.13 | 31.74 |
| .0100 | 122.9 | 44.31 | 35.14 |
| .0050 | ... | 45.83 | 37.54 |
| .0025 | 130.1 | 47.76 | 39.73 |
| .0010 | 134.0 | 49.45 | 42.13 |
| .0000 | 137.7 | 51.9 | 45.5 |

TABLE III

EQUIVALENT CONDUCTANCE OF 0.01 NORMAL STRONTIUM CHLORIDE IN ETHANOL–WATER MIXTURES AT 20, 25 AND 30°

| Temp., °C. | | $\Lambda_c$ | | |
|---|---|---|---|---|
| % Ethanol | 0 | 40 | 80 | 99.89 |
| 20 | 106.7 | 35.81 | 21.10 | 8.59 |
| 25 | 120.4 | 43.24 | 24.57 | 9.75 |
| 30 | 131.6 | 49.28 | 26.40 | 10.76 |

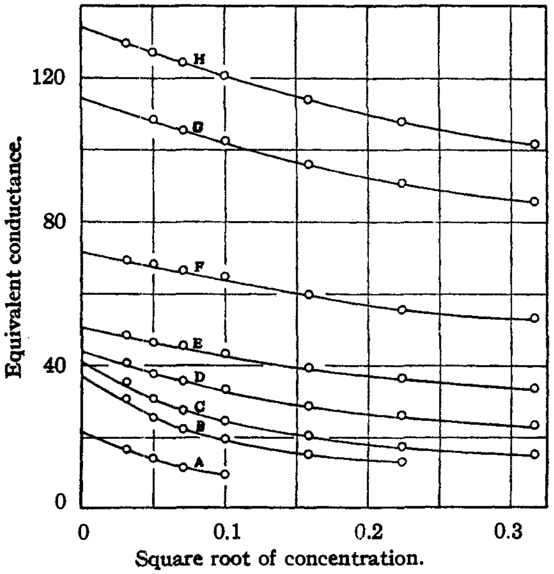

Fig. 1.—Equivalent conductance of strontium chloride in ethanol-water mixtures at 25°: A, 99.89%; B, 90%; C, 80%; D, 60%; E, 40%; F, 20%; G, 5% and H, 0% ethanol in solvent.

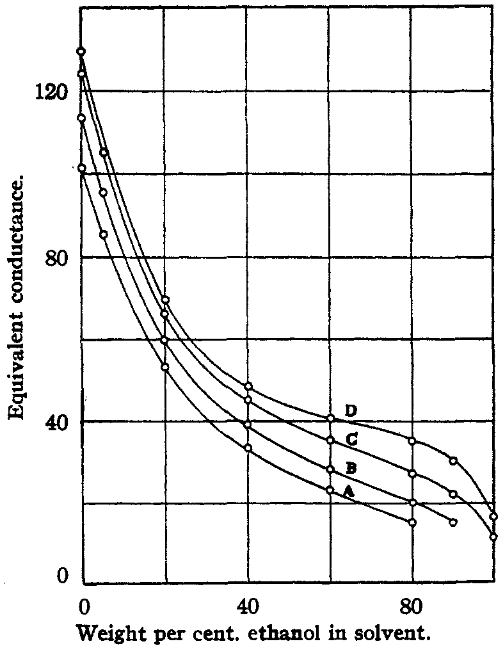

Fig. 2.—Equivalent conductance of strontium chloride in ethanol-water mixtures at 25°: A, 0.1 $N$; B, 0.025 $N$; C, 0.005 $N$ and D, 0.001 $N$.

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(11) L. Onsager, *Physik. Z.*, **27**, 388 (1926); **28**, 277 (1927).

conductance becomes progressively greater as the percentage ethanol increases. An explanation for this might be: in the less alcoholic solutions the change in viscosity is the most significant factor influencing conductance while in the more alcoholic solutions the change in dielectric constant is more significant. Between these two extremes, the two solvent properties are of about equal importance in influencing the conductance. Also, for an electrolytic solution of this type, the ionic "sizes" should vary with solvent composition giving a corresponding influence on conductance. From this, it would follow that Walden's rule[12] ($\Lambda_0\eta$ = constant) should not apply very accurately. The quantity $\Lambda_0\eta/D$ has been applied to electrolytes[13] and in the present case this quantity is more nearly a constant value than $\Lambda_0\eta$. Table IV gives $\Lambda_0$, $\Lambda_0\eta$ and $\Lambda_0\eta/D$ for strontium chloride in different ethanol–water mixtures at 25° in which $\eta$ is the viscosity and $D$ is the dielectric constant of the pure solvents.

TABLE IV

LIMITING CONDUCTANCES OF STRONTIUM CHLORIDE IN ETHANOL–WATER MIXTURES AT 25°

| % Ethanol in solvent | $\Lambda_0$ | $\eta^a$ poise | $D^b$ | $\Lambda_0\eta$ | $\Lambda_0\eta/D$ |
|---|---|---|---|---|---|
| 0 | 134.5 | 0.00895 | 78.5 | 1.204 | 0.0153 |
| 5 | 115.0 | .01087 | 75.6 | 1.250 | .0165 |
| 20 | 71.9 | .01808 | 67.0 | 1.300 | .0194 |
| 40 | 50.8 | .02374 | 55.0 | 1.206 | .0219 |
| 60 | 44.2 | .02232 | 43.4 | .986 | .0227 |
| 80 | 41.4 | .01738 | 32.8 | .719 | .0219 |
| 90 | 37.4 | .01422 | 28.1 | .532 | .0189 |
| 99.89 | 22.1 | .01104 | 24.2 | .244 | .0101 |

[a] "International Critical Tables," 5, 22 (1929). [b] G. Akerlof, THIS JOURNAL, 54, 4133 (1932).

From Table IV it may be observed that $\Lambda_0\eta/D$ is relatively constant for solutions containing between 20 and 90% ethanol in the solvent.

Figure 3 illustrates, at 25°, the dependence of $\Lambda_0$ and $\Lambda_0\eta$ on the composition of the solvent for strontium chloride solutions and gives the values for the viscosities and dielectric constants of the pure solvents.

Figure 4 shows the influence of temperature on the equivalent conductance of 0.01 normal solutions of strontium chloride in four different solvent compositions. In all cases the temperature coefficients are positive and become less as the temperature increases. From tangents to these curves at 25° the information in Table V was obtained.

TABLE V

TEMPERATURE COEFFICIENT OF CONDUCTANCE OF 0.01 NORMAL STRONTIUM CHLORIDE IN ETHANOL–WATER MIXTURES AT 25°

| % Ethanol in solvent | $\Lambda$ | $d\Lambda/dT$ | $(d\Lambda/dT)/\Lambda$ |
|---|---|---|---|
| 99.89 | 9.75 | 0.20 | 0.0232 |
| 80 | 24.57 | .51 | .0208 |
| 40 | 43.24 | 1.47 | .0340 |
| 0 | 120.3 | 2.55 | .0125 |

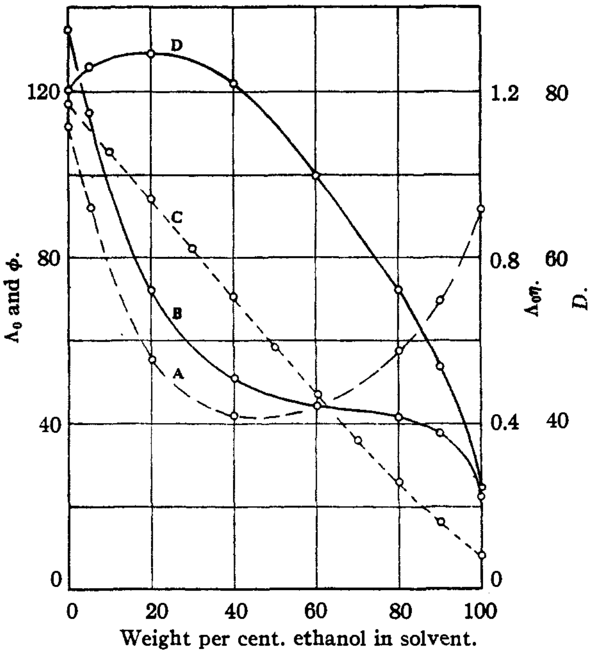

Fig. 3.—Curve A, the fluidity $\phi$ and curve C, the dielectric constant D of ethanol–water mixtures at 25°: Curve B, the limiting equivalent conductance $\Lambda_0$ and curve D, the conductance viscosity product $\Lambda_0\eta$ for strontium chloride at 25°.

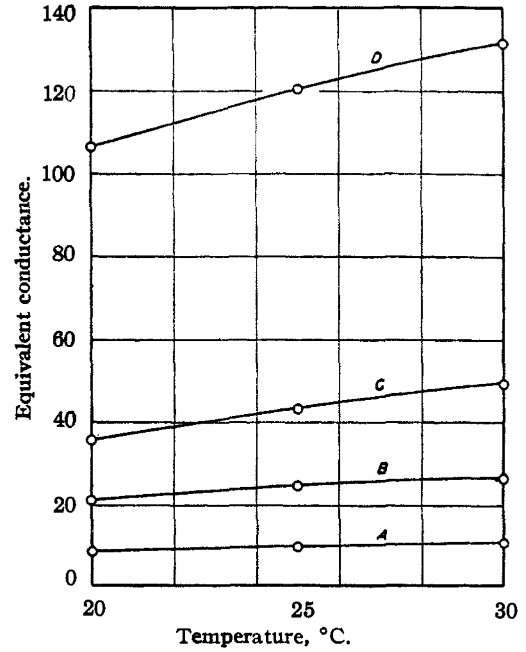

Fig. 4.—Equivalent conductance of 0.01 $N$ strontium chloride in ethanol-water mixtures as a function of temperature: A, 99.89%; B, 80%; C, 40% and D, 0% ethanol in solvent.

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[12] P. Walden, *Z. physik. Chem.*, 55, 207, 246 (1906).

[13] Van Rysselberghe and Fristom, THIS JOURNAL, 67, 680 (1945).

For the solvents used in Fig. 4, the temperature coefficients of the dielectric constants are negative and become smaller at the higher temperatures. This would tend to cause the conductance to be less at the higher temperatures and to influence the temperature coefficient of conductance less at the higher temperatures. For these same solvents the temperature coefficients of viscosity are negative and have smaller values at higher temperatures. This would cause an increase of conductance with increasing temperature but the rate of increase should be less at higher temperatures. Even though these two solvent properties work in opposition to each other, they both favor a smaller temperature coefficient at higher temperatures.

Preliminary work on the conductances of magnesium and barium chlorides gave curves of the same general form as those for strontium chloride.

## Summary

The conductances of strontium chloride and of strontium bromide in different ethanol–water mixtures have been measured at 25° and the significance of the results discussed.

The conductance of strontium chloride in different ethanol–water mixtures has been measured at 20, 25 and 30° and the temperature coefficients evaluated.

In strongly aqueous solutions the conductances are influenced mostly by the viscosity of the solvent and in the strongly alcoholic solutions mostly by the dielectric constant of the solvent.

EAST LANSING, MICHIGAN RECEIVED JANUARY 23, 1948

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

# Repulsive Forces in Relation to Bond Energies, Distances and Other Properties

BY KENNETH S. PITZER

While the concepts of quantum theory have given a qualitative understanding of most chemical bond phenomena, there are a number of less prominent features that remain puzzling. Many of the ideas in this paper have been held by the writer and very likely by others for some time. However, they were based on conflicting and uncertain data. The immediate reason for this paper is the recent developments in dissociation energy data which makes possible a greatly improved and considerably changed table of bond energies.

**Bond Energies.**—Gaydon[1] has recently published a very fine compilation of dissociation energies. Furthermore his recommended value of *ca.* 170 kcal. for the heat of sublimation of carbon (to normal $^3P$ atoms) has been fully confirmed by new thermodynamic measurements of Brewer and Gilles[2] in this Laboratory. The heat of vaporization values of Kelley[3] together with some revisions of these values by Brewer[4] have been employed. These new data supplement the older values of Bichowsky and Rossini[5] upon which Pauling[6] based most of his bond energies. The conventions followed in Tables I and II follow Pauling's system except that the dissociation energies of the nomal $^3\Sigma$ states rather than excited singlet states are taken for O=O, S=S, etc. The energy of dissociation of a molecule completely into atoms is taken as the sum of the energies of all bonds. Thus the C–H bond energy is not the energy change of the reaction of $CH_4 = CH_3 + H$ but rather one fourth of the energy for $CH_4 = C + 4H$. The values are for 0°K. Heat capacities from 0 to 300°K. were estimated where necessary.

In Table I there are listed values for single bonds in elements and for single bonds to hydro-

TABLE I

SINGLE BOND ENERGIES (KCAL./MOLE AT 0°K.)

| Elements | | Hydrides | | Chlorides | |
|---|---|---|---|---|---|
| H–H | 103.2 | H–H | 103.2 | H–Cl | 102.1 |
| Li–Li | 26 | Li–H | 58 | Li–Cl | 118.5 |
| C–C | 80 (85) | C–H | 98.2 | C–Cl | 78 |
| N–N | 37 | N–H | 92.2 | N–Cl | 46 (?) |
| O–O | 34 | O–H | 109.4 | O–Cl | 49 |
| F–F | 50 (?) | F–H | 141 (?) | F–Cl | 60.3 |
| Na–Na | 17.8 | Na–H | 47 | Na–Cl | 97.7 |
| Si–Si | (45) | Si–H | 76 (?) | Si–Cl | 87 |
| P–P | (53) | P–H | 77 | P–Cl | 77 |
| S–S | 63 (?) | S–H | 87 (?) | S–Cl | 65 (?) |
| Cl–Cl | 57.1 | Cl–H | 102.1 | Cl–Cl | 57.1 |
| K–K | 11.8 | K–H | 42.9 | K–Cl | 101.4 |
| Cu–Cu | | Cu–H | 62 | Cu–Cl | 83 |
| Ge–Ge | (39.2) | Ge–H | ... | Ge–Cl | ... |
| As–As | (39) | As–H | 56 | As–Cl | 69 |
| Se–Se | (50) | Se–H | 67 | Se–Cl | 59 |
| Br–Br | 45.4 (53) | Br–H | 86.7 | Br–Cl | 52.1 |
| Rb–Rb | 11.1 | Rb–H | 39 | Rb–Cl | 101.0 |
| Ag–Ag | ... | Ag–H | 53 | Ag–Cl | 71 |
| Sn–Sn | (35) | Sn–H | ... | Sn–Cl | 76 |
| Sb–Sb | (42) | Sb–H | ... | Sb–Cl | 75 |
| Te–Te | (49) | Te–H | 59 | Te–Cl | ... |
| I–I | 35.6 (51) | I–H | 70.6 | I–Cl | 49.6 |
| Cs–Cs | 10.4 | Cs–H | 41 | Cs–Cl | 103 |

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(1) A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, London, 1947.

(2) L. Brewer and P. Gilles, unpublished data.

(3) K. K. Kelley, U. S. Bureau of Mines, Bulletin 383, 1935.

(4) L. Brewer, "The Thermodynamic and Physical Properties of the Elements," Declassified Atomic Energy Report CC 2058, 1945.

(5) F. R. Bichowsky and F. D. Rossini, "Thermochemistry of Chemical Substances," Reinhold Pub. Co., New York, N. Y., 1936.

(6) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.