in this field, fits the experimental results is no confirmation, taken alone, of the truth of the principles involved.

Further approximate or empirical relations will consequently be superfluous, so long as the fundamental theoretical principles of the subject remain indefinitely outlined. The rigorous mathematical development of the laws of molecular attraction—a field in which Mills has already performed valuable pioneer work—is the necessary prerequisite to any real progress.

## Summary.

The accuracy of the various equations proposed for representing heats of vaporization has been tested by comparison with the experimental data of Young. In three out of the four cases examined, the equations of the author and of Mills afford most satisfactory agreement. In the remaining case the experimental figures are shown to be inaccurate.

It has been pointed out that the heat of vaporization is a quantity so adapted to representation by different formulas that no conclusions can be drawn as to their relative theoretical merits. At present, the equations are useful only as checks upon the experimental data.

Nichols Laboratories of Inorganic Chemistry,
Columbia University, New York City.

---

# THE POTENTIAL OF SILVER IN NONAQUEOUS SOLUTIONS OF SILVER NITRATE.[1]

By Vernette L. Gibbons and F. H. Getman.

Received June 1, 1914.

1. Introduction: (*a*) Aim of the Investigation; (*b*) Preparation of Materials. 2. Measurements of Electrical Conductance. 3. Determination of Transport Numbers. 4. Determination of the Electromotive Force of Various Concentration' Cells. 5. Discussion of Results. 6. Summary. 7. Chronological Bibliography.

## 1. Introduction.

The study of the potentials of metals in nonaqueous solutions of their salts was begun by Campetti[2] about twenty years ago. Since, however, the drop electrode was employed in these experiments the results cannot be considered trustworthy.

A few months later, Jones[3] published results of measurements of the combinations

$$Ag \mid AgNO_3 \text{ in solvent I} \mid AgNO_3 \text{ in solvent II} \mid Ag.$$

The solvents used were water, ethyl alcohol, methyl alcohol and acetone.

---

[1] A Dissertation presented to the Faculty of Bryn Mawr College by Vernette L. Gibbons in part fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] *Atti accad. Torino*, **28,** 61 and 228 (1893).

[3] *Z. physik. Chem.*, 14, 346 (1894).

The concentrations of both solutions were identical for each individual experiment. Electromotive forces of considerable numerical value were obtained, but they varied with the combination employed. He concluded that the solution tension of silver depends upon the nature of the solvent in which the salt is dissolved.

Kahlenberg[1] carried out a long series of investigations of the behavior of ten different metals, in solutions of their salts in about thirty different solvents. He measured the potential of silver in 0.1 $N$ solutions of silver nitrate in twenty-four different solvents. The silver nitrate solution formed one part of the cell, and in each case the other part was either a normal or 0.1 $N$ calomel electrode. The metals dipped into solutions contained in test tubes or open beakers and the connection between the two vessels was made by means of a strip of filter paper folded to several thicknesses. Thus the solutions were liable to change in concentration because of evaporation or of absorption of moisture from the atmosphere. The difference of potential at the junction of the two liquids was neglected and no definite temperature was maintained. The change in electromotive force caused by the interaction of the ions of the two electrolytes at the junction was entirely overlooked.

The following year Kahlenberg[2] measured the electromotive force of concentration cells of silver nitrate in pyridine and acetonitrile. He compared the results with the values calculated by means of the Nernst equation

$$E = \frac{RT}{nF} \log_e \frac{m_1\Lambda_1}{m_2\Lambda_2}, \qquad (1)$$

assuming that the potential at the junction between the two solutions was negligible. Although a fair agreement between experimental and calculated values had been obtained when aqueous solutions were used, here an utter lack of agreement was found, and he was forced to the conclusion that the formula was not applicable to cells involving nonaqueous solutions.

In a later article, Kahlenberg[3] gave the results of measurements of the electromotive force of the system

Ag | 0.1 $N$ $AgNO_3$ in water | 0.1 $N$ $AgNO_3$ in pyridine and water | Ag.

He found that, by increasing the amount of water in the mixed solvent, the electromotive force of the cell diminished, and he concluded that the potential difference between silver and silver nitrate depended upon the composition of the solvent.

Carrara and D'Agostini,[4] from their investigation of concentration cells

---

[1] *J. Phys. Chem.*, **3**, 379 (1899).

[2] *J. Ibid.*, **4**, 709 (1900).

[3] *Z. Elektrochem.*, **11**, 385 (1905).

[4] *Atti R. Ist. Veneto*, **62**, 793 (1902).

in methyl alcohol, concluded that in this solvent the Nernst formula was applicable.

In 1905, Carrara[1] turned his attention to the influence of the solvent upon the solution pressure of the metals. He found that in methyl alcohol this pressure was less than in water and was, therefore, not independent of the nature of the solvent.

Sackur[2] criticized the work of Kahlenberg and also that of Carrara and D'Agostini. He maintained that neither had disproved the applicability of Nernst's law; that, in fact, in the case of the work of Carrara and D'Agostini the results with three out of the four metals investigated could be interpreted as in full accord with that law.

In the same year, Bjerrum[3] attempted to eliminate the diffusion potential at the junction of the two liquids by using a concentrated solution of potassium chloride as a "middle liquid" and obtained values more nearly constant for each experiment and with less variation in a series of experiments than when this "middle liquid" was not used.

The measurement of the electromotive force of concentration cells of silver nitrate in methyl- and ethylamine was undertaken by Bodländer and Eberlein[4] as a means of studying the complexes formed in these solvents. They considered that these ions are represented by the formulas, $Ag(CH_3NH_2)_2$ and $Ag(C_2H_5NH_2)_2$, thus showing the similarity of these solvents to ammonia.

The potential difference of concentration cells with liquid ammonia as a solvent was measured by Cady in 1905.[5] His conclusion was that the Nernst formula could be used to calculate the electromotive force when this solvent was used in the cells.

A large amount of experimental work was carried out by Neustadt and Abegg[6] for the purpose of determining the relation of the tension series of the metals to the solvent. $Ag \mid AgNO_3$ was always made one-half of the cell. In only a few cases is mention made of the use of a "middle liquid;" although, in several cases, the solution in the second half of the cell was a chloride. They concluded that the tension series was quite independent of the solvent. The liquid potentials in a given system were considered at some length but without reaching any definite conclusion.

The behavior of cadmium in alcoholic solutions of its salts was investigated by Getman.[7] He measured the electromotive force of the metal in different concentrations of its salts, the other half of the cell being in

---

[1] *Gazz. chim. ital.*, **35**, I, 132 (1905).

[2] *Z. Elektrochem.*, **11**, 385 (1905).

[3] *Z. physik. Chem.*, **53**, 428 (1905).

[4] *Ber.*, **36**, 3945 (1903).

[5] *J. Phys. Chem.*, **9**, 476 (1905).

[6] *Z. physik. Chem.*, **69**, 486 (1909).

[7] *Am. Chem. J.*, **46**, 117 (1911).

each case a normal calomel electrode. The changes in potential with concentration in the alcoholic solutions were found to be opposite to the change in aqueous solutions, *i. e.*, the potential of cadmium became more strongly negative with increasing concentration of the solutions of its salts. The electromotive force developed at the junction of the two solutions was assumed to be negligible. The possibility of the application of Nernst's equation to such nonaqueous solutions was considered doubtful.

In 1912 the potentials of zinc in alcoholic solutions of zinc chloride were measured by Getman and Gibbons,[1] one-half of the cell being in each case the normal calomel electrode. It was found that the potentials of zinc in solutions in ethyl alcohol became more strongly negative with increasing concentration of the solutions. This was the same effect observed by Getman in his study of solutions of cadmium salts. Solutions in methyl alcohol showed fluctuations of potential of more than ten millivolts, an effect which is to be studied further. Shortly after this, Dr. Laurie of Edinburgh, in a personal letter to one of us, called attention to the fact that the potential difference developed at the junction of the two liquids might sometimes have considerable influence.[2]

Roshdestwensky and Lewis[3] have studied concentration cells of silver nitrate in acetone. They not only measured the electromotive forces of various combinations of freshly prepared solutions, but they made similar measurements both with solutions which had stood for six weeks in the dark and with solutions which had stood one day exposed to the sunlight. The agreement of the results in all cases is within the limits of experimental error. The type of cell used was not described, but the two solutions were in direct contact, thus possibly developing a potential difference at the junction. In the following way, however, this potential difference was shown to be very slight. A solution of 0.01 $N$ silver nitrate was interposed as a "middle liquid" and the measurements repeated. The results agree with those for a similar cell without this "middle liquid." Therefore, assuming Nernst's law to be valid for these systems, Roshdestwensky and Lewis calculated the transport numbers for the ions and found that in solutions ranging in concentration between the limits of 0.02–0.007 $N$ the value for the anion lay between 0.60 and 0.58, and for more dilute solutions (0.007–0.0095 $N$) the value was 0.56. As a result of further attempts to eliminate the potential differences at the junction of the two liquids, they concluded that the validity of "middle" liquid methods for acetone solutions was doubtful since, in all cases, where an effect was observed there was an increase instead of a decrease of electromotive force.

---

[1] *Am. Chem. J.*, **48**, 124 (1912).

[2] *Proc. Roy. Soc. Edinb.*, **31**, 375 (1911).

[3] *J. Chem. Soc.*, **101**, 2094 (1912).

Measurements of the electromotive force of silver nitrate concentration cells with water and ethyl alcohol as solvents were carried out by Bell and Feild.[1] They used a closed apparatus of a U form, having an outlet tube in the middle, closed with a three-way stopcock, so that the two arms could be connected with each other or the solution drawn from either one without disturbing that in the other. In this way, the solutions could be brought to the same level in both sides of the tube without intermingling and could be kept separated except during the time of actual measurement. Apparently, the effect of gravity in causing interdiffusion was overlooked. Writing Nernst's law in the form

$$\frac{E}{\log_{10} C_1/C_2} = \frac{2v}{u+v} \cdot \frac{RT}{NF} \log_e 10 = K, \qquad (2)$$

they obtained from the data for concentration cells in water, values for $K$ that vary from 0.0560 to 0.0623. Taking the latter as the value of $K$ they calculated the value of $v$ in the above formula and found it to be 0.523 instead of 0.528 as given by Lehfeldt.[2] Since the values of $v$ are probably smaller in more concentrated solutions, $K$ will, of course, for such solutions, be proportionately smaller. In the same way, $K$ was calculated from the measurements of the electromotive forces of concentration cells in ethyl alcohol and, since $K$ varied, they assumed that the migration ratios were not constant. The value of $v$ calculated from the highest value of $K$ obtained was 0.62.

Bjerrum[3] sought to eliminate the potential at the junction by using, in one experiment, a saturated, and in another, a half-saturated solution of potassium chloride as a "middle liquid." By comparing the results of the two measurements and by extrapolating, he concluded that better results were obtained than when the potassium chloride solution was not present.

Cumming and Abegg[4] concluded that a saturated ammonium nitrate solution formed an exceptionally good "middle liquid" for eliminating the potential at the junction.

Thermodynamic principles were applied by Henderson[5] in the derivation of the following equation for calculating the potential developed between two aqueous solutions:

$$E = \frac{RT}{F} \frac{(u_1 - v_1)C_1 - (u_2 - v_2)C_2}{(u_1W_1 + v_1\overline{W}_1)C_1 - (u_2W_2 + v_2\overline{W}_2)C_2} \log_e \frac{(u_1W_1 + v_1\overline{W}_1)C_1}{(u_2W_2 + v_2\overline{W}_2)C_2} \qquad (3)$$

---

[1] THIS JOURNAL, **35**, 715 (1913).

[2] *Electrochemistry*, p. 256 (1904).

[3] *Z. physik. Chem.*, **53**, 49 (1905).

[4] *Z. Elektrochem.*, **13**, 17 (1907).

[5] *Z. physik. Chem.*, **59**, 118 (1907); **63**, 325 (1908).

$C_1$ and $C_2$ represent equivalent concentrations. $u_1$, $v_1$, $u_2$, $v_2$ represent absolute ionic velocities. $W_1$, $\overline{W}_1$, $W_2$, $\overline{W}_2$ represent the valences of the ions.

Subsequent investigations by Bjerrum[1] led him to conclude that, if the electromotive force remained constant for some minutes after contact between the liquids had been established, the effect of diffusion was negligible and Henderson's formula could be applied. He found, also, that if the connection between the two parts of the cell was made through a layer of sand much more constant results were obtained. In a second paper,[2] he showed that ammonium nitrate gave less satisfactory results than potassium chloride when used as a "middle liquid," but that it might be used in cases where the latter would give rise to chemical action. He also showed that the values obtained by extrapolation, when a solution of potassium chloride was used, agreed closely with those computed by means of Henderson's formula, and that, if the degree of dissociation was calculated by means of Nernst's equation, the result did not at all agree with the value obtained by calculation from conductance measurements.

The electrode and liquid potentials of nonaqueous solutions were studied by Isgarischew[3] who applied Henderson's formula to methyl alcohol solutions. He referred all his measurements to the normal hydrogen electrode as a standard. He prepared a calomel electrode in methyl alcohol, determined its electromotive force and, with the aid of this electrode calculated the electrode potential of several metals. Certain metals he found showed great tendency to become passive. The electrode potential of silver was obtained by using as one-half of the cell a Cd | $Cd(NO_3)_2$ electrode which had been measured against the calomel electrode. Since the potential of this cadmium electrode showed a tendency to increase quite rapidly at first, the two half cells were not placed in contact until a constant value had been obtained for the electromotive force of this electrode.

Isgarischew[4] made a further study of the passivity of metals and concluded that the phenomenon was caused by oxidation. In the case of copper, however, instead of an oxide, a complex compound of copper chloride and alcohol was formed on the surface of the metal. He measured the electromotive force of the combination

Ag | $AgNO_3$ in methyl alcohol | $AgNO_3$ in water | Ag,

and computed the liquid potential by means of Henderson's formula, obtaining an electrode potential much larger than when the cadmium electrode was used. He sought to measure similar combinations of ethyl

---

[1] *Z. Elektrochem.*, **17**, 58 (1911).

[2] *Ibid.*, **17**, 388 (1911).

[3] *Ibid.*, **18**, 568 (1912).

[4] *Ibid.*, **19**, 491 (1913).

alcohol and aqueous solutions, and stated that it was impossible to apply Henderson's formula to compute the liquid potential of such combinations, but gave no reasons for this conclusion.

The following simplification of Henderson's formula has recently been given by Cumming:[1]

$$E = \frac{RT}{F} \cdot \frac{K(2n-1)-K'(2n'-1)}{KW_1-K'W_2} \log_e \frac{KW_1}{K'W_2} \qquad (4)$$

$K$ and $K'$ are the specific conductances, $N$ and $N'$ the migration ratios and $W_1$ and $W_2$ the corresponding valences. This equation requires only data that can be determined experimentally; and, if it is assumed that the migration ratios in the two solutions are the same, the equation becomes identical with Nernst's equation. Cumming applied the equation to the results of Bjerrum and others on the potentials of various chloride solutions with calomel electrodes and obtained satisfactory values.

Since the experimental work to be described in the following pages was completed, Cumming and Gilchrist[2] have published a method for ascertaining the true values for the diffusion and electrode potentials from the observed potential of the cell. They conclude that a new boundary must be made shortly before the measurement is taken, and that capillary tubes must be avoided in the construction of an electromotive force cell.

Thus, as we have seen, considerable work has been done, especially within the last three years, upon the subject of the potentials of metals in aqueous and nonaqueous solutions of their salts. Many of these measurements have been made with open cells connected by capillary tubes, filter paper or sand, with "middle liquids" whose effect is more or less uncertain, or with closed cells, no attempt being made to calculate the potential at the junction between the solutions. It has, therefore, been considered advisable to carry out an investigation of the behavior of silver in nonaqueous solutions of silver nitrate. This combination was chosen because silver nitrate can be obtained and kept in a state of great purity. It is also soluble in a large variety of solvents. In some of these solvents it might be expected, from conductance measurements, that abnormal effects would be observed.

The development of the Cumming equation has made it possible to compute the potential at the junction of the two liquids from purely experimental data, and has thus removed one source of error.

The apparatus employed for the electromotive force measurements was free from the defects mentioned by Cumming and Gilchrist and embodied several improvements over the ordinary type of cell. The investigation divides itself into three parts as follows:

---

[1] *Trans. Faraday Soc.*, **8**, 86 (1913).

[2] *Ibid.*, **9**, 174 (1914).

I. The measurement of the conductance of the solutions employed.

II. The determination of the transport numbers in as many of these solutions as possible.

III. The measurement of the electromotive force of various concentration cells in each solvent, and the determination of the electromotive force of the following combinations:

Ag | 0.1 or 0.01 $N$ $AgNO_3$ in water | 0.1 or 0.01 $N$ $AgNO_3$ in solvent II | Ag

*Preparation of Materials.*—The silver nitrate used in making up the solutions was finely powdered and kept in a desiccator over phosphorus pentoxide.

The ethyl alcohol (high-grade commercial "Absolute" 99.6%) was dehydrated over lime ("aus Marmor") for several weeks. It was then distilled, using a fractionating column, and the distillate was collected in a receiver protected from the moisture and gases of the atmosphere by means of a tube filled with soda-lime. The boiling point was 78.8° at 757.4 mm. of mercury.

The methyl alcohol was subjected to the same treatment as the ethyl alcohol. The fraction boiling between 64.3° and 64.8° at 746 mm. of mercury was collected for use.

The acetone was dried over fused calcium chloride, distilled, allowed to stand over anhydrous copper sulfate several weeks, then redistilled and the fraction boiling between 56°–56.1° was collected. Its conductance was so slight it could not be measured.

Commercial aniline, was distilled, allowed to stand over fused potassium carbonate several days, then redistilled using a fractionating column. The distillation was repeated until a nearly colorless distillate was obtained which boiled between 181.5°–182° at 751.8 mm. of mercury. The conductance was too slight to be measured.

The pyridine, of the best grade obtainable, was treated with fused potassium hydroxide for several days, filtered and after repeated fractionations the portion boiling between 114°–116° at 742 mm. of mercury was collected.

The water used was distilled according to the method of Jones and Mackay. It was collected in a bottle well protected from the gases of the atmosphere.

## 2. Electrical Conductance.

All measurements were made at 25°. The thermostat consisted of two concentric galvanized iron tanks, the annular space between them being filled with sawdust. The water was well stirred and was heated by means of an incandescent lamp that had been coated with a ruby varnish to prevent the reducing action of light on the silver nitrate solutions. The temperature was maintained constant at 25 ± 0.05° by means of an electrically controlled Ostwald thermoregulator.

The mother solution in each solvent was made up by direct weighing, and the more dilute solutions were made from this by means of carefully calibrated burets and flasks.

The measurements of electrical conductance were made by means of the well-known Kohlrausch apparatus, a Leeds and Northrup cylindrical bridge being used. The cells were of two types. The ordinary Arrhenius form closed by a tight-fitting ebonite cover was used for most of the work, but the form described by Kreider and Jones[1] having a ground glass stopper and concentric cylindrical platinum electrodes, was used for the solutions in ethyl alcohol. The constants of these cells were determined by means of a potassium chloride solution containing one mol of the salt in 128 liters of water. Its equivalent conductance was taken as 142.4 at 25°. The cell constants were redetermined frequently during the investigation and were found to remain practically constant. The average value for the Arrhenius type of cell was 16.83 and for the Kreider and Jones type 2.63. The electrodes of the cell were platinized in the usual manner. After each measurement, the cell and electrodes were carefully cleansed, rinsed first with distilled water, then several times with absolute ethyl alcohol and dried in a current of pure dry air.

The cell was allowed to stand in the thermostat for twenty or thirty minutes and the contents were thoroughly stirred to insure a uniform temperature before a measurement was taken. From three to six readings were taken for each dilution. The cell was allowed to stand twenty minutes longer in the thermostat and the readings repeated. If the two sets of readings did not agree, the cell was freshly filled and another set of readings taken for comparison. Tables I to V give the results of these measurements.

TABLE I.—SILVER NITRATE IN ETHYL ALCOHOL.

| *m*. | *V*. | $\Lambda_{25^\circ}$. |
|---|---|---|
| 0.1 | 10.0 | 10.81 |
| 0.01 | 100.0 | 22.06 |
| 0.0078 | 128.4 | 23.72 |
| 0.003 | 333.3 | 28.14 |
| 0.001 | 1000.0 | 34.95 |
| 0.00056 | 1786.0 | 37.79 |
| 0.0003 | 3333.3 | 38.52 |
| 0.0001 | 10000.0 | 40.71 |

TABLE II.—SILVER NITRATE IN METHYL ALCOHOL.

| *m*. | *V*. | $\Lambda_{25^\circ}$. |
|---|---|---|
| 0.1 | 10.0 | 36.64 |
| 0.01 | 100.0 | 68.75 |
| 0.006 | 166.7 | 74.88 |
| 0.003 | 333.33 | 83.14 |
| 0.0012 | 833.3 | 87.30 |
| 0.001 | 1000.0 | 90.10 |
| 0.0003 | 3333.3 | 87.82 |
| 0.0001 | 10000.0 | 73.23 |

TABLE III.—SILVER NITRATE IN ACETONE.

| *m*. | *V*. | $\Lambda_{25^\circ}$. |
|---|---|---|
| 0.01 | 100.0 | 10.51 |
| 0.003 | 333.3 | 11.39 |
| 0.001 | 1000.0 | 15.43 |
| 0.0003 | 3333.3 | 20.78 |
| 0.00016 | 6250.0 | 25.60 |
| 0.0001 | 10000.0 | 28.06 |

TABLE IV.—SILVER NITRATE IN ANILINE.

| *m*. | *V*. | $\Lambda_{25^\circ}$. |
|---|---|---|
| 0.1 | 10.0 | 0.666 |
| 0.01 | 100.0 | 0.327 |
| 0.003 | 333.3 | 0.436 |
| 0.001 | 1000.0 | 0.678 |
| 0.0003 | 3333.3 | 1.082 |
| 0.0001 | 10000.0 | 1.651 |

---

[1] *Am. Chem. J.*, **45**, 295 (1911).

TABLE V.—SILVER NITRATE IN PYRIDINE.

| m. | V. | $\Lambda_{25°}$. |
|---|---|---|
| 0.1 | 10.0 | 24.80 |
| 0.01 | 100.0 | 33.85 |
| 0.003 | 333.3 | 43.68 |
| 0.001 | 1000.0 | 54.13 |
| 0.0003 | 3333.3 | 66.14 |
| 0.0001 | 10000.0 | 73.50 |
| 0.00006 | 16666.7 | 75.82 |

In Fig. 1 are plotted the values given in Tables I–IV. As a comparison, the results of other investigators are also given. The scale used in Fig. 1 being too small to show well the changes of conductance with dilution in solutions of silver nitrate in aniline, the results of Table V are plotted in Fig. 2 and compared with the results obtained by Sachanov[1] in more concentrated solutions. Curves similar to this conductance curve have been described by Franklin and Gibbs[2] for silver nitrate in solutions in methylamine, and by Shinn[3] for solutions of silver nitrate in ethylamine.

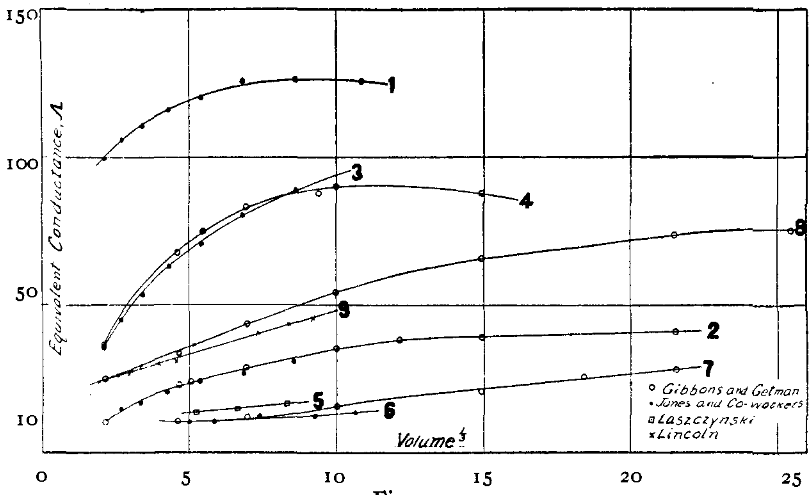

Fig. 1.

1, Conductance in Water. 2, Conductance in Ethyl Alcohol. 3 and 4, Conductance in Methyl Alcohol. 5, Conductance in Acetone at 18°. 6 and 7, Conductance in Acetone at 25°. 8 and 9, Conductance in Pyridine.

The conductance curve for silver nitrate in acetone at 18°, described by St. V. Laszizynski,[4] is also plotted in Fig. 1. As it lies above the curve obtained at 25° it indicates that the silver nitrate solutions in acetone have a negative temperature-coefficient. This phenomenon was observed

---

[1] *Z. physik. Chem.*, **83**, 129 (1913).

[2] THIS JOURNAL, **29**, 1389 (1907).

[3] *J. Phys. Chem.*, **11**, 537 (1907).

[4] *Z. Elektrochem.*, **2**, 55 (1895).

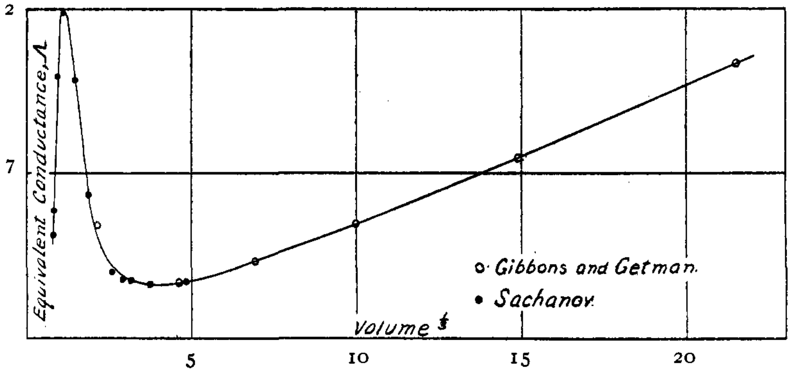

Fig. 2.—Conductance in Aniline.

by Cattaneo[1] for solutions of hydrochloric acid in ether, and by Getman and Gibbons[2] for solutions of zinc chloride in methyl alcohol.

## 3. Transport Numbers.

Since the data at hand, concerning the transport numbers of the ions of silver nitrate in nonaqueous solutions, were somewhat meager, it seemed best to carry out as full a series of such measurements as possible for the solutions under investigation.

Two forms of apparatus were employed for these determinations—the form designed by Mather and modified by Jones and Basset,[3] and a modified form of the Nernst-Loeb apparatus which has been designed in this laboratory and is illustrated in Fig. 3. The electrodes were in both cases made of pure silver wire fused to a stout piece of platinum wire which was in turn sealed into the glass tube and protected with fusion glass.

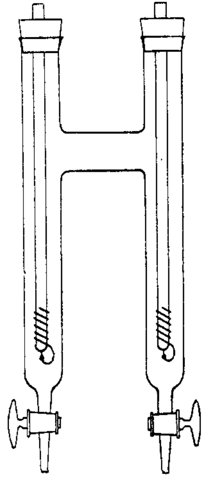

Fig. 3.

A copper coulometer was used to measure the total current. Two copper plates, 2.2 by 5 cm. in dimensions, served as electrodes, one of which, the cathode, could be removed for cleaning and weighing. The solution in the coulometer was made up as follows: $CuSO_4.5H_2O$, 150 g.; $H_2SO_4$, 50 g.; $C_2H_5OH$, 50 g.; $H_2O$, 1000 g. During the passage of the current, a slow stream of carbon dioxide bubbled through the solution between the electrodes in the coulometer. The laboratory electrical circuit served as a source of current and it remained fairly constant during the time of each experiment.

The Jones and Bassett cell was carefully calibrated. To simplify the

---

[1] *Atti accad. Lincei,* [5] 2, 295.

[2] *Am. Chem. J.*, 48; 124 (1912).

[3] *Ibid.*, 32, 429 (1904).

method given by them, the apparatus was leveled and filled with distilled water to a suitable height. After marking each arm of the apparatus to indicate this level, it was emptied and thoroughly dried. The stopcock was closed and each arm filled with distilled water from a carefully calibrated buret. The volume required to fill each arm to the mark was noted. The stopcock was then opened and water added until it again stood at the same level. This operation was repeated three times with the following results:

|  | I.<br>Cc. | II.<br>Cc. | III.<br>Cc. |
|---|---|---|---|
|  | 55.56 | 55.83 | 112.21 |
|  | 55.54 | 55.80 | 112.23 |
|  | 55.45 | 55.76 | 112.24 |
|  | 55.45 | ..... | .... |
| Average, | 55.50 | 55.80 | 112.23 |

For each experiment 112.23 cc. of the solution were run into the apparatus from the buret and after inserting the electrodes it was placed in the thermostat. When sufficient time had elapsed for the temperature to become uniform, it was connected in series with the coulometer, a variable resistance and a milliammeter. The circuit was closed and the current allowed to pass through the solution several hours. When a sufficient amount of silver had separated at the cathode, the stopcock was closed, the cell was removed from the thermostat and the two solutions were filtered through glass wool into two 100 cc. flasks. Each arm was thoroughly rinsed several times and the wash water was added to the corresponding solution. After the solutions had acquired the temperature of the room they were diluted to 100 cc. and analyzed by Volhard's method. The ammonium thiocyanate solutions used were 0.1 and 0.025 *N* and were standardized against a corresponding aqueous solution of silver nitrate. The amount of silver in the solution was compared with the amount originally present.

This method was used for the measurement of the transport numbers of most of the solutions in methyl and ethyl alcohols. The analysis of the solution from the cathode chamber seldom gave the same value for the transport number as the analysis of the solution from the anode chamber. If any silver peroxide formed on the anode, the amount was very slight and the silver separated out in beautiful, shiny needles on the cathode. By taking the mean of the two values so obtained, the agreement of results was fairly good.

It seemed probable that the cause of the irregularity observed was that the unaltered portion of the solution did not lie midway between the electrodes. This would seem logical when the ions do not share equally in carrying the current. Schlundt[1] found that in the case of solutions of silver nitrate in pyridine and acetonitrile the unaltered portion or "middle layer" was much nearer the anode than the cathode.

This experience led to the designing of the form of apparatus illustrated in Fig, 3. It was used in a few of the experiments with solutions in the alcohols and with the solutions in pyridine. The apparatus was filled to a level above the horizontal connecting tube and the electrodes were inserted. The stoppers carrying the electrodes had a slight groove cut on one side to allow for the expansion of the contents of the cell, but in no case did the solution come in contact with these rubber stoppers. The outlet tubes of the two arms were protected by means of rubber caps sealed with glass rods. The apparatus was then placed in the thermostat and, after uniform temperature was acquired, connection with the circuit was made as in the previous experiments.

When sufficient silver had separated on the cathode, the following method was adopted to ascertain the exact position of the "middle layer." The solution was drawn from the anode arm into three or four tared glass stoppered weighing bottles, and the entire solution from the cathode arm was transferred to another weighing bottle. These portions were weighed and their content of silver determined by Volhard's method. These values were then compared with the amount of silver which would have been present if the solutions had maintained their original concentration. If there was a gain in silver, that portion was considered a part of the solution around the anode; if there was a loss in silver, that portion was considered a part of the solution around the cathode. If the change in the amount of silver present was less than 1%, that portion was considered the "middle layer." However, the amount of gain was added to the value for the solution around the anode or the amount of loss was added to the value for the solution around the cathode.

As an example, let us consider the measurements made with the 0.05 *N* solution of silver nitrate in ethyl alcohol.

| | Wt. of solution. | Orig. wt. of silver. | Final wt. of silver. | Change in silver. |
|---|---|---|---|---|
| I | 9.2174 | 0.06206 | 0.10147 | +0.03941 |
| II | 3.37880 | 0.02567 | 0.02533 | +0.00034 |
| III | 3.0431 | 0.02063 | 0.02045 | +0.00018 |
| IV | 9.1731 | 0.06229 | 0.05254 | —0.00975 |
| V | 19.8476 | 0.13486 | 0.10598 | —0.02888 |

| | | |
|---|---|---|
| Total solution in anode chamber | 16.048 g. | |
| Transport number of anion | | 0.613 |
| Total solution in cathode chamber | 29.021 g. | |
| Transport number of anion | | 0.593 |
| | Mean, | 0.603 |

---

[1] *J. Phys. Chem.*, **6**, 159 (1902).

In this case, it is quite evident that if the division had been made exactly in the middle of the solution, accurate values could not have been obtained.

Tables VI to VIII give the results of the values obtained for the various solutions:

$m$ = concentration of the solutions (made up accurately by weight).

$t$ = duration of the experiment in hours.

$E$ = reading of the milliammeter in milliamperes.

$A$ = the transport number of the anion (calculated from the analysis of the solution around the anode).

$C$ = the transport number of the anion (calculated from the analysis of the solution around the cathode).

TABLE VI.—SOLUTIONS IN ETHYL ALCOHOL.

| Apparatus. | *m.* | *t.* | *E.* | *A.* | *C.* | Mean. | Mean of series. |
|---|---|---|---|---|---|---|---|
| Jones and Bassett's......... | 0.1 | 4 | 3–4 | 0.626 | 0.707 | 0.667 | 0.673 |
|  | 0.1 | 5 | 3–4 | 0.668 | 0.683 | 0.675 |  |
|  | 0.1 | 5 | 3–4 | 0.632 | 0.718 | 0.676 |  |
| Jones and Bassett's......... | 0.05 | 8 | 2.5–3 | 0.751 | 0.752 | 0.7515 | 0.733 |
|  | 0.05 | 10 | 2.5–3 | 0.697 | 0.729 | 0.713 |  |
|  | 0.05 | 9 | 2.5–3 | 0.724 | 0.744 | 0.734 |  |
| Gibbons'.................. | 0.05 | $4^2/_3$ | 4 | 0.613 | 0.593 | 0.603 | 0.603 |
| Jones and Bassett's......... | 0.04 | 10 | 2.5–3 | 0.728 | 0.693 | 0.710 | 0.7105 |
|  | 0.04 | 10 | 2.5–3 | 0.705 | 0.717 | 0.711 |  |

TABLE VII.—SOLUTIONS IN METHYL ALCOHOL.

| Apparatus. | *m.* | *t.* | *E.* | *A.* | *C.* | Mean. | Mean of series. |
|---|---|---|---|---|---|---|---|
| Gibbons'.................. | 0.1 | 3 | 4–5 | 0.587 | 0.570 | 0.5785 | 0.578 |
|  | 0.1 | 3 | 4–5 | 0.584 | 0.572 | 0.578 |  |
| Jones and Bassett's......... | 0.1 | 3.5 | 5–8 | 0.765 | 0.571 | 0.668 | 0.617 |
| Jones and Bassett's......... | 0.07 | 3 | 5 | 0.637 | 0.607 | 0.617 | 0.650 |
|  | 0.07 | 3 | 5 | 0.767 | 0.600 | 0.684 |  |
| Gibbons'.................. | 0.07 | 4 | 4–5 | 0.5805 | 0.568 | 0.574 | 0.574 |
| Jones and Bassett's......... | 0.05 | 3 | 5–6 | 0.561 | 0.604 | 0.5825 | 0.581 |
|  | 0.05 | 3.5 | 5–6 | 0.572 | 0.587 | 0.5795 |  |
| Jones and Bassett's......... | 0.04 | 3 | 5–6 | 0.560 | 0.572 | 0.566 | 0.579 |
|  | 0.04 | 4 | 5.5 | 0.616 | 0.622 | 0.619 |  |
|  | 0.04 | 4 | 5.5 | 0.576 | 0.572 | 0.574 |  |
|  | 0.04 | 4 | 5.5 | 0.573 | 0.541 | 0.557 |  |

TABLE VIII.—SOLUTIONS IN PYRIDINE.

| Apparatus. | *m.* | *t.* | *E.* | *A.* | *C.* | Mean. | Mean of series. |
|---|---|---|---|---|---|---|---|
| Gibbons'.................. | 0.1 | 4 | 4–6 | 0.675 | 0.677 | 0.676 | 0.694 |
|  | 0.1 | 4 | 4–6 | 0.699 | 0.701 | 0.700 |  |
|  | 0.1 | 4 | 4–6 | 0.698 | 0.717 | 0.707 |  |
| Gibbons'.................. | 0.05 | 5 | 3–5 | 0.667 | 0.691 | 0.679 | 0.677 |
|  | 0.05 | 4 | 3–5 | 0.656 | 0.697 | 0.676 |  |

## Discussion of Above Tables.

*Ethyl Alcohol.*—Since the differences in the values obtained when Jones and Bassett's apparatus was used were so great, only the value obtained when Getman and Gibbons' apparatus was used will be compared with the values obtained by other investigators.

*Methyl Alcohol.*—The values for 0.1 and 0.07 *N* solutions obtained with Jones and Bassett's apparatus are considered much less accurate than the other values given in the above tables.

*Acetone.*—Attempts were made to determine experimentally the transport numbers in acetone solutions, but the maximum concentration that could be obtained even by shaking silver nitrate with acetone for 24 hrs. was only 0.01 *N* and the resistance of this solution was so great that the measurements were not considered trustworthy. This was the conclusion arrived at by Jones and Rouiller[1] in their work. Roshdestwensky and Lewis, from their electromotive force measurements of concentration cells, calculated the transport number for the anion of silver nitrate in acetone as 0.60 to 0.58 for dilutions ranging between 0.02 and 0.007 *N*. Jones and Rouiller determined the transport numbers for silver nitrate in mixtures of acetone and water. By extrapolation from the curves obtained by plotting their results, it seems probable that the value for a 0.01 *N* solution in pure acetone might lie between 0.60 and 0.62.

*Pyridine.*—The pyridine solutions could not be analyzed in the same way as an aqueous or an alcoholic solution, because of the basic and solvent properties of the pyridine. Two methods of eliminating the pyridine were tried: (1) the pyridine was neutralized with concentrated nitric acid; or (2) the greater part of the pyridine was distilled off from the solution before neutralizing it. The mixture of silver and pyridine nitrates was diluted with water and titrated with ammonium thiocyanate solution. The first method was less troublesome and gave fully as satisfactory results.

*Aniline.*—The analysis of the aniline solutions proved to be an insurmountable obstacle to the determination of the transport numbers in that solvent. All known methods were found to be impracticable.

## Comparison of the Values as Given by Various Investigators.

TABLE IX.—SOLUTIONS IN ETHYL ALCOHOL.

| $t°$. | $m$. | $A$. | Investigator. |
|---|---|---|---|
| 20 | 0.108 | 0.594 | Mather |
| 25 | 0.076–0.101 | 0.5988 | Jones and Bassett |
| 25 | 0.02 | 0.616 | Rouiller |
| 25 | 0.05 | 0.603 | Gibbons |

[1] *Am. Chem. J.*, 36, 475 (1906).

TABLE X.—SOLUTIONS IN METHYL ALCOHOL.

| $t°$. | $m$. | $A$. | Investigator. |
|---|---|---|---|
| ? | ? | 0.533 | Campetti |
| 25 | 0.0093 | 0.523 | Carrara |
| 25 | 0.10 | 0.5797 | Jones and Bassett |
| 25 | 0.02 | 0.572 | Jones and Rouiller |
| 25 | 0.10 | 0.578 | Gibbons |
| 25 | 0.07 | 0.574 | Gibbons |
| 25 | 0.05 | 0.581 | Gibbons |
| 25 | 0.04 | 0.579 | Gibbons |
| 21 | 0.1 | 0.613 | Schlundt |
| 22 | 0.025 | 0.564 | Schlundt |
| 22 | 0.025 | 0.554 | Schlundt |
| 25 | 0.1 | 0.694 | Gibbons |
| 25 | 0.05 | 0.677 | Gibbons |

## 4. Electromotive Force.

The electromotive force of cells of the following types was studied:

(1) Ag | $AgNO_3$, Conc. I | $AgNO_3$, Conc. II | Ag,

the solvent in the two solutions being identical, and

(2) Ag | $AgNO_3$, Aqueous | $AgNO_3$, Nonaqueous | Ag,

the solvents being different but the concentrations being identical. The more concentrated solutions were all made up at room temperature by direct weighing. The dilutions were made from these by means of carefully calibrated burets and flasks. The solutions were kept in the dark, and in no case was there more than a very slight tendency to turn brown, even when left standing several weeks.

The compensation method of Poggendorff was employed, an enclosed type of Lippmann electrometer being used as a zero instrument. Measurements with this instrument were correct to one millivolt, except when the poor conductance of the solutions or other disturbing factors introduced a larger error. The experimental cell was balanced against a chloride accumulator as a source of potential. The electromotive force of this cell was determined by means of a certified Weston Standard Element, before and after each measurement of the experimental cell. The electromotive force of this Standard Element was 1.01948 volts at 25°.

The experimental cell, illustrated in Fig. 4, consisted of two parts connected by means of a tight-fitting piece of rubber tubing. During an experiment, the stopcock $S$, of fairly large bore, was kept closed,

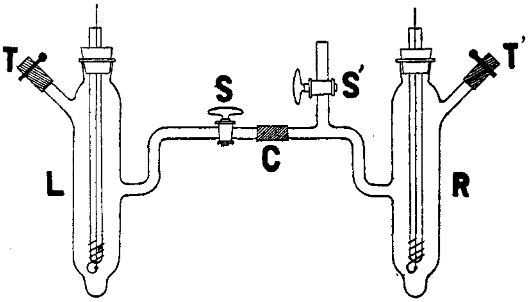

Fig. 4.

except while the measurements were actually being made. The electrodes were made of pure silver wire sealed to a stout piece of platinum wire, which, in turn, was sealed into a glass supporting tube and protected by fusion glass. The electrical connections were made through mercury placed in these glass tubes.

At first, some difficulty was experienced in obtaining constant values for the electromotive force of a given concentration cell, but by adopting the following method of procedure the electromotive force remained constant for at least 30 min. after contact between the two solutions had been made. The two half-cells were connected together at *C* and with the two stopcocks *S* and *S'* closed, the two solutions were poured into the cell until they were at the same level on each side, the denser solution being always put into the half-cell *R*. When the electrodes had been inserted and the clamps *T* and *T'* closed, the cell was supported in the thermostat and allowed to stand 25–30 min. in order to acquire a uniform temperature. Connection with the circuit was then established and the contact between the two solutions made as follows. The stopcock *S'* and clamp *T'* were opened and, by gently blowing into a pipet inserted at *T'*, the denser solution in *R* was forced up to the base of the tube carrying the stopcock *S'*. The clamp *T'* was then closed and the stopcock *S* and clamp *T* were opened. By blowing very gently into a pipet inserted at *T*, the solution in *L* was brought into contact with the first solution. The stopcocks *S* and *S'* and the clamp *T* were then closed. A measurement of the electromotive force was made at once. The stopcock *S* was opened just long enough to determine the point of balance on the bridge wire.

TABLE XII.

| $m_1$. | $m_2$. | *E*. | *K*. | $m_1$. | $m_2$. | *E*. | *K*. |
|---|---|---|---|---|---|---|---|
| Solutions in Ethyl Alcohol. | | | | Solutions in Acetone. | | | |
| 0.1 | 0.01 | 0.0408 | 0.0591 | 0.01 | 0.003 | 0.0293 | 0.0601 |
| 0.1 | 0.003 | 0.0650 | 0.0587 | 0.01 | 0.001 | 0.0537 | 0.0630 |
| 0.1 | 0.001 | 0.0922 | 0.0619 | 0.01 | 0.0003 | 0.0816 | 0.0665 |
| 0.1 | 0.0003 | 0.1297 | 0.0658 | 0.01 | 0.0001 | 0.1212 | 0.0771 |
| 0.1 | 0.0001 | 0.1648 | 0.0680 | Solutions in Aniline. | | | |
| 0.01 | 0.003 | 0.0276 | 0.0640 | 0.1 | 0.01 | 0.0373 | 0.0285 |
| 0.01 | 0.001 | 0.0538 | 0.0657 | 0.1 | 0.003 | 0.0548 | 0.0321 |
| 0.01 | 0.0003 | 0.0858 | 0.0670 | Solutions in Pyridine. | | | |
| 0.01 | 0.0001 | 0.1169 | 0.0674 | 0.1 | 0.01 | 0.0368 | 0.0425 |
| Solutions in Methyl Alcohol. | | | | 0.1 | 0.003 | 0.0592 | 0.0460 |
| 0.1 | 0.01 | 0.0462 | 0.0636 | 0.1 | 0.001 | 0.0831 | 0.0500 |
| 0.1 | 0.003 | 0.0746 | 0.0639 | 0.1 | 0.0003 | 0.1105 | 0.0577 |
| 0.1 | 0.001 | 0.1008 | 0.0626 | 0.1 | 0.0001 | 0.1375 | 0.0544 |
| 0.1 | 0.0003 | 0.1358 | 0.0634 | 0.1 | 0.00006 | 0.1532 | 0.0560 |
| 0.1 | 0.0001 | 0.1719 | 0.0637 | 0.01 | 0.003 | 0.0207 | 0.0502 |
| 0.01 | 0.003 | 0.0264 | 0.0600 | 0.01 | 0.001 | 0.0437 | 0.0549 |
| 0.01 | 0.001 | 0.0591 | 0.0670 | 0.01 | 0.0003 | 0.0723 | 0.0587 |
| 0.01 | 0.0003 | 0.0934 | 0.0675 | 0.01 | 0.0001 | 0.0978 | 0.0588 |
| 0.01 | 0.0001 | 0.1337 | 0.0677 | 0.01 | 0.00006 | 0.1179 | 0.0630 |

Two other readings were made at intervals of ten minutes. The electromotive forces calculated from these three bridge readings seldom varied from the mean value by more than one- or two-tenths of a millivolt.

The results of the measurements are given in Table XII. The constant $K$ was calculated from the Nernst formula, written in the following form. The value of the transport number was assumed not to vary appreciably with the concentration:

$$K = \frac{E}{\log_{10} m_1\Lambda_1/m_2\Lambda_2} \tag{5}$$

When it was assumed that the observed values of the transport numbers were correct, and that they did not vary appreciably with the dilution, the values for $E$ calculated for the different cells showed, in no case, very close agreement with those observed.

In Table XIII the calculated and observed values for the transport number ($n$) of the anion of silver nitrate in the various solvents are given. ($n$) is calculated from the formula

$$n = \frac{v}{u + v} = \frac{E}{2 \times 0.0595 \log_{10} (m_2\Lambda_1/m_2\Lambda_2)} \tag{6}$$

and the observed value is in each case the mean of the value given in Tables IX–XI, excluding those found by Campetti and Carrara.

TABLE XIII.

| $m_1$. | $m_2$. | $n$ Calc. | $n$ Obs. | $m_1$. | $m_2$. | $n$ Calc. | $n$ Obs. |
|---|---|---|---|---|---|---|---|
| Solutions in Ethyl Alcohol. | | | | Solutions in Acetone. | | | |
| 0.1 | 0.01 | 0.496 | 0.603 | 0.01 | 0.003 | 0.505 | 0.62[1] |
| 0.1 | 0.003 | 0.493 | ..... | 0.01 | 0.001 | 0.541 | .... |
| 0.1 | 0.001 | 0.520 | ..... | 0.01 | 0.0003 | 0.559 | .... |
| 0.1 | 0.0003 | 0.553 | ..... | 0.01 | 0.0001 | 0.647 | .... |
| 0.1 | 0.0001 | 0.571 | ..... | Solutions in Aniline. | | | |
| 0.01 | 0.003 | 0.557 | ..... | 0.1 | 0.01 | 0.239 | .... |
| 0.01 | 0.001 | 0.565 | ..... | 0.1 | 0.003 | 0.490 | .... |
| 0.01 | 0.0003 | 0.567 | ..... | Solutions in Pyridine. | | | |
| 0.01 | 0.0001 | 0.566 | ..... | 0.1 | 0.01 | 0.357 | 0.620 |
| Solutions in Methyl Alcohol. | | | | 0.1 | 0.003 | 0.390 | ..... |
| 0.1 | 0.01 | 0.534 | 0.577 | 0.1 | 0.001 | 0.420 | ..... |
| 0.1 | 0.003 | 0.537 | ..... | 0.1 | 0.0003 | 0.443 | ..... |
| 0.1 | 0.001 | 0.526 | ..... | 0.1 | 0.0001 | 0.457 | ..... |
| 0.1 | 0.0003 | 0.533 | ..... | 0.1 | 0.00006 | 0.471 | ..... |
| 0.1 | 0.0001 | 0.535 | ..... | 0.01 | 0.003 | 0.422 | ..... |
| 0.01 | 0.003 | 0.504 | ..... | 0.01 | 0.001 | 0.461 | ..... |
| 0.01 | 0.001 | 0.563 | ..... | 0.01 | 0.0003 | 0.493 | ..... |
| 0.01 | 0.0003 | 0.554 | ..... | 0.01 | 0.0001 | 0.494 | ..... |
| 0.01 | 0.0001 | 0.569 | ..... | 0.01 | 0.00006 | 0.529 | ..... |

The electromotive forces of the combinations

Ag | 0.1 $N$ $AgNO_3$ in water | 0.1 $N$ $AgNO_3$ in solvent II | Ag

---

[1] This value is extrapolated.

were measured and the results are tabulated below. The first column designates the nature of the solvent II, $E$ the observed potential, $E_1$ the electrode potential in the aqueous solution, $E_2$ the potential at the junction between the two liquids which is calculated according to Cumming's formula given on page 1636, and $E_3$ is the electrode potential in solution II. The electrode potentials are referred to that of the hydrogen electrode as zero. The electrode potential $E_1$ in aqueous solution is calculated by means of the formula $E = E_p - 0.0595 \log m$, in which the value of $E_p$ is taken as 0.798 volt.

TABLE XIV.

| Solvent II. | $E$. | $E_1$. | $E_2$. | $E_3$. |
|---|---|---|---|---|
| Ethyl alcohol | +0.1004 | +0.7331 | +0.00217 | +0.8314 |
| Methyl alcohol | +0.0967 | +0.7331 | —0.00005 | +0.8298 |
| Acetone | +0.1712 | +0.7331 | +0.00202 | +0.9022 |
| Aniline | —0.2559 | +0.7331 | ..... | .... |
| Pyridine | —0.3618 | +0.7331 | —0.00017 | +0.3711 |

## 5. Discussion of Results.

An inspection of Figs. 1 and 2 brings to light certain differences between the conductance curves for nonaqueous solutions and the curve for aqueous solutions of silver nitrate. Considering the latter to represent a normal curve of conductance, the curves for nonaqueous solutions present certain abnormalities. This abnormality is most clearly shown in the curve for solutions in aniline and less clearly in the curves for solutions in acetone and pyridine. The curve for solutions in ethyl alcohol is quite similar to that for solutions in water, except that in the more concentrated region it appears somewhat flatter; while the curve for solutions in methyl alcohol shows a tendency to pass through a maximum in the more dilute regions.

In seeking a cause for these abnormalities it is important to consider the determination of the molecular weight of silver nitrate in these solvents. In certain cases, at the temperature of the boiling solvent, there is considerable interaction between the solvent and the salt, which renders the determination of the molecular weight extremely difficult. This is especially true when aniline is the solvent and true to a lesser degree in the other solvents. It is, however, a well known fact that these liquids show a great tendency to combine with the ions and that there are also present in such solutions polymerized molecules of the dissolved salt. Jones[1] showed that sodium iodide, cadmium iodide, and ammonium thiocyanate were polymerized to an appreciable extent when in solution in acetone. It has been shown by many investigators that in solutions in ethyl and methyl alcohol the solute frequently exists in a polymeric state.

[1] *Am. Chem. J.*, **27**, 16 (1902).

Getman and Gibbons[1] have shown this to be the case for zinc chloride. The molecular weight of silver nitrate in pyridine, as determined by Werner-Smujlow,[2] is 165.42 (mean value of series ranging from 160.02–169.82) but, as determined by Speransky and Goldberg,[3] it is 207.5 (mean value of series ranging from 199–210). This latter result was confirmed by Schroeder[4] who found the molecular weight to be 203.6 (mean value of series ranging from 186–214). By studying the equilibrium of the system, silver nitrate in pyridine from —65° to +110°, Kahlenberg and Brewer[5] discovered that these substances combine to form definite compounds at different temperatures and that, between —24° and +48.5°, the solid phase had the composition $AgNO_3.3C_5H_5N$, while above 79° there was no combination of the two substances, pure silver nitrate being in equilibrium with the solvent. This shows clearly that the molecular complexity of the solute at 25° would be even greater than at 115°, the boiling point of pyridine.

That there is a possibility of three different reactions taking place in solution where such complexes exist was discussed by Sachanov.[6] The complexes $C_m$ may decompose into simpler molecules, or they may ionize to form complex ions, or the simple molecules may ionize to form simple ions. These reactions can be represented as follows:

$$C_m \rightleftarrows mC,$$
$$C_m \rightleftarrows A' + K',$$
$$C \rightleftarrows \mathrm{A} + K,$$

where $A'$ and $K'$ denote the complex anion and cation, and $A$ and $K$ denote the simple anion and cation. The first two equations would hold true whether the complex was a polymerized molecule of the solute or a compound of solute and solvent. Walden[7] considers that ionization is caused and induced by the process of disaggregation of the polymerized salt molecules. In case the solvent has a high dielectric constant, this depolymerization into simple ions will be abrupt, and in a solvent with a low dielectric constant this change will be more gradual or the effect of the complexes will be more marked and prolonged. Arranging these solvents in the order of their dielectric constants, we see that the degree of the abnormality of the conductance curves follows practically the same order. This is shown in the following tabulation:

---

[1] *Am. Chem. J.*, **48**, 124 (1912).

[2] *Z. anorg. Chem.*, **15**, 18 (1897).

[3] *Z. physik. Chem.*, **39**, 369 (1902).

[4] *Z. anorg. Chem.*, **44**, 20 (1905).

[5] *J. Phys. Chem.*, **12**, 283 (1908).

[6] *Z. physik. Chem.*, **83**, 129 (1913).

[7] THIS JOURNAL, **35**, 1649 (1913).

| Solvent. | D. C. |
|---|---|
| Water | 81.1 |
| Methyl alcohol | 31.2 |
| Ethyl alcohol | 25.8 |
| Acetone | 21.5 |
| Pyridine | 12.4 |
| Aniline | 6.85 |

Sachanov and Prscheborowsky[1] investigated the conductance of various electrolytes in six different solvents of very small dielectric constants. Many electrolytes showed maxima in very concentrated solutions, but in no case was a minimum observed. They concluded that this might be due to the very small dielectric constant of the solvent.

The diminution in conductance with increasing molar concentration, as shown by extremely concentrated solutions of silver nitrate in aniline, has been ascribed by Kraus[2] to the influence of the increasing viscosity of the solutions. Sachanov has shown[3] that, if the equivalent conductance $\Lambda$ is multiplied by the ratio of the viscosity of the solution to that of the solvent, $\eta'/\eta$, values are obtained which correspond to $\Lambda$ for solutions where the two viscosities are approximately equal.

As the temperature is increased the abnormalities in a conductance curve diminish. Jones and his co-workers[4] clearly stated the relations between the temperature and the conductance of an electrolyte in an aqueous solution. They showed that (1) the temperature coefficient of conductance of aqueous solutions of electrolytes is greater the greater the hydrating power of the electrolyte, that (2) the temperature coefficients of conductance for any given electrolyte increase with the dilution of the solution and this increase is greatest for those substances with large hydrating power. These two statements led to the conclusion that the decreasing complexity of the hydrates with rise of temperature is a very important factor in conditioning the large temperature coefficients of conductance shown by those substances which have a large hydrating power. It would seem that the abnormalities observed in nonaqueous solutions might also be explained in a similar way.

The values of the transport numbers calculated from the electromotive force measurements of concentration cells are quite different from those obtained experimentally. In all cases the experimental values are the larger. The direct measurement could only be carried out with solutions of fairly large concentrations (not less than 0.02 *N*). It can be seen that the values calculated for the extremely dilute solutions approach more nearly the experimental values. The transport numbers, in all the sol-

[1] *Z. Elektrochem.*, **20**, 39 (1914).

[2] THIS JOURNAL, **36**, 60 (1914).

[3] *Z. physik. Chem.*, **83**, 129 (1913).

[4] "Hydrates in Aqueous Solution," *Publ. Carnegie Inst.*, **60**, pp. 156–7 (1907).

vents for which experimental or calculated data could be obtained, show an increase in the value for the anion with increasing dilution, with the exception of the experimental values for solution in pyridine where the opposite effect is apparent. The values for solutions in methyl alcohol show a much greater degree of uniformity for calculated and observed values as well as much better agreement between the two series. In the determination of the transport numbers it was observed that the "middle layer" did not lie midway between the electrodes. If one examines the experimental data of Schlundt[1] for a solution of silver nitrate in pyridine, one notices this same fact. He found a "middle layer" less than one-third the distance from the anode. The middle layer for the alcoholic solutions was situated much nearer the median line of the cell. It has been proved by Kahlenberg and Brewer[2] that pyridine and silver nitrate combine at ordinary temperatures to form complex molecules, and Morgan and Kanolt[3] found that in a mixture of water and pyridine a large proportion of the pyridine traveled with the silver ions to the cathode. LeBlanc, in his "Textbook of Electrochemistry" (page 76), calls attention to Kohlrausch's discovery that, with monatomic univalent ions, the transport numbers of all solutes in aqueous solutions approach the value 0.50 with increasing temperature. He states that at the same time the difference in mobility of the two ions in each case actually increases.

The greatest shifting of the "middle layer" was observed when pyridine was used as the solvent for the silver nitrate and definite compounds of solvent and solute are known to exist in such solutions. If the cation carries with it a part of the solvent, the concentration of the silver in the cathode chamber will be abnormally low and a corresponding increase will be observed in the anode chamber. It seems probable that the movement of the solvent with the cation causes the shifting of the "middle layer" toward the anode. If the solvent moves with the anion, the "middle layer" should then shift toward the cathode. These ionic complexes break down more or less completely with increasing temperature and cause the transport numbers to approach a limiting value in aqueous solutions. Probably, when sufficient experimental data has been accumulated, it will be found that the transport numbers in nonaqueous solutions approach similar limiting values.

If the transport numbers do not increase with the dilution of the solution, $K$ as calculated in Table XII should have a constant value, but it is only in the case of solutions in methyl alcohol that $K$ has an even approximate constancy. In the four other solvents, $K$ increases steadily in value with the increasing difference in the concentration of the solutions

---

[1] *J. Phys. Chem.*, **6**, 159 (1902).

[2] *Ibid.*, **12**, 283 (1908).

[3] *Z. physik. Chem.*, **48**, 365 (1904); THIS JOURNAL, **28**, 572 (1906).

in the cell. Likewise, the values of the transport numbers calculated in Table XIII, show a steady increase with the changing difference of concentration in the cell. Both of these phenomena may be due to the same cause. The degree of the dissociation of the conducting complexes into simple ions will increase as the solution is diluted. In the more concentrated solutions the molar concentration is not correctly given by the weight of silver nitrate in a given volume of solution, hence $m\Lambda$ is the true value of the ionic concentration only in dilute solutions. The change in value of this factor would cause an increase in the computed value for both $n$ and $K$ (as is shown by Equations (5) and (6)). The fact that this abnormality is greatest in the case of aniline and pyridine, where the effect of the complexes is most clearly shown in the conductance curve, seems to substantiate this view. The Nernst equation, therefore, is not a true expression of all the factors which determine the difference of potential in these concentration cells.

In comparing the electromotive forces found when an aqueous solution was joined to a nonaqueous solution of the same concentration, it is at once noticed that, whereas the solutions in the alcohols and acetone are positive toward the aqueous solution, the solutions in aniline and pyridine are negative toward the aqueous solution. The value obtained by Isgarischew[1] for the electrode potential of silver in solutions of silver nitrate in methyl alcohol is slightly greater than the one given in Table XIV; but he used the Henderson formula for calculating the potential at the junction of the two liquids and this involved the use of $\Lambda_\infty$ which is by no means surely established. The value here given, therefore, seems more probable, since only experimental data were used in this calculation.

## 6. Summary.

The results obtained may be summarized as follows:

1. Conductance measurements of solutions of silver nitrate in ethyl alcohol, methyl alcohol, acetone, aniline and pyridine have been made for concentrations ranging between 0.1 and 0.0001 $N$. It has been shown that the conductance curve for solutions in aniline approaches a second maximum as the solutions become more dilute. It has also been shown that there is a relationship between the dielectric constant and the abnormalities of all the conductance curves.
2. The transport numbers of silver nitrate in ethyl alcohol, methyl alcohol and pyridine have been determined experimentally.
3. Measurements of the electromotive force have been made for a large number of concentration cells in the various solvents, an apparatus being used which is free from defects due to capillarity and constant communication of the two liquids.

---

[1] *Z. Elektrochem.*, 19, 491 (1913).

4. Values for the electrode potential of silver in the various solvents have been calculated.

5. The experimental data seem to prove that the abnormalities observed in nonaqueous solutions of silver nitrate are due to the combination of the solvent and the solute to form complex compounds which dissociate more or less gradually.

## 7. Chronological Bibliography.

### Difference of Potential.

1890. "Über die Potentialdifferenz zwischen zwei verdünnten Lösungen binärer Electrolyte," Planck, *Wiedemann's Ann.*, **40**, 561.

1893. "Über die Potentialdifferenz zwischen alkoholischen und wässerigen Lösungen eines und desselben Salzes," Campetti, *Atti accad. Torino*, **28**, 61 and 228.

1894. "Über die Lösungstension von Metallen," H. C. Jones, *Z. physik. Chem.*, **14**, 346.

1899. "The Electromotive Force of Concentration Cells," J. E. Trevor, *J. Phys. Chem.*, **3**, 95.

1899. "Difference of Potential between Metals and Nonaqueous Solutions of Their Salts," Kahlenberg, *J. Phys. Chem.*, **3**, 379.

1900. *Ibid.*, **4**, 709.

1900. "The Solution Tension of Zinc in Ethyl Alcohol," Jones and Smith, *Am. Chem. J.*, **23**, 379.

1902. "Über die elektromotorischen Kräfte zwischen einigen Metallen und den Lösungen ihrer Salze in Wasser und in Methyl alkohol," Carrara und D'Agostini, *Atti R. ist. Veneto*, **62**, 793.

1903. "Über die Zusammensetzung der in Lösungen existirenden Silber-verbindungen des Methyl- und Aethyl-amins," Bodländer und Eberlein, *Ber.*, **36**, 3945.

1905. "Über die elektromotorischen Kräfte zwischen einigen Metallen und den Lösungen ihrer Salze in Wasser und in Methylalkohol," Carrara und D'Agostini, *Gazz. chim. ital.*, **35**, I, 132.

1905. "Über die Elimination des Diffusionspotentials zwischen zwei verdünnten wässerigen Lösungen durch Einschalten einer konzentrierten Chlorkaliumlösung," Bjerrum, *Z. physik. Chem.*, **53**, 428.

1905. "Elektrochemie der nichtwässerigen Lösungen," Carrara, *Gazz. chim. ital.*, **37**, I, 525.

1905. "Concentration Cells in Liquid Ammonia," Cady, *J. Phys. Chem.*, **9**, 476.

1905. "Zur Theorie der elektrolytischen Lösungstension," Brunner, *Z. Elektrochem.*, **11**, 915.

1905. "Die Spannungsreihe der Metalle," Kahlenberg. "Elektromotorische Kräfte zwischen Metallen und Lösungen ihrer Salze in Wasser und Methylalkohol," Carrara und D'Agostini. "Criticism of Above Articles," Sackur, *Z. Electrochem.*, **11**, 385.

1907. "Zur Eliminierung der Flüssigkeitspotentiale," Cumming und Abegg, *Z. Elektrochem.*, **13**, 17.

1907. "Zur Thermodynamik der Flüssigkeitsketten," Henderson, *Z. physik. Chem.*, **59**, 118.

1908. *Ibid.*, **63**, 325.

1908. "Elektrochemie der nichtwässerigen Lösungen," Carrara.

1909. "Uber elektrochemische Potentiale in nichtwässerigen Lösungemitteln," Neustadt und Abegg, *Z. physik. Chem.*, **69**, 486.

1911. "Differences of Potential between Cadmium and Alcoholic Solutions of Some of its Salts," Getman, *Am. Chem. J.*, **46**, 117.

1911. "On the Temperature Coefficient of Concentration Cells, in which the Same Salt is Dissolved in two Different Solvents," Laurie, *Proc. Roy. Soc. Edinb.*, **31**, 375.

1911. "Über die Gültigkeit der Planckschen Formel für das Diffusionspotential," Bjerrum, *Z. Elektrochem.*, **17**, 58.

1911. "Ueber die Elimination des Flüssigkeitspotentials bei Messungen von Elektrodenpotentialen," Bjerrum, *Z. Elektrochem.*, **17**, 389.

1912. "The Potentials of Zinc in Alcoholic Solutions of Zinc Chloride," Getman and Gibbons, *Am. Chem. J.*, **48**, 124.

1912. "The Electrochemistry of Solutions in Acetone. Part II. The Silver Nitrate Concentration cell," Roshdestwensky and Lewis, *J. Chem. Soc.*, **101**, 2094.

1912. "Über die Normalen und Flüssigkeitspotentiale nichtwässeriger Lösungen," Isgarischew, *Z. Elektrochem.*, **18**, 568.

1913. "Berichtigung zu der Abhandlung- Über die Normalen und Flüssigspotentiale nichtwässeriger Lösungen," Isgarischew, *Z. Elektrochem.*, **19**, 491.

1913. "Über die Passivierung der Metalle und ihre Abhängigkeit vom Lösungsmittel," Isgarischew, *Z. Elektrochem.*, **19**, 491.

1913. "The Electromotive Force of Silver Nitrate Concentration Cells," Bell and Feild, THIS JOURNAL, **35**, 715.

1913. "Elimination of Potential due to Liquid Contact," Cumming, *Trans. Faraday Soc.*, **8**, 86.

1914. "The Potential Due to Liquid Contact," Cumming and Gilchrist, *Trans. Faraday Soc.*, **9**, 174.

### Conductance.

1894. "Die electrische Leitfähigkeit von einigen Salzen in Aethyl- und Methylalkohol," Völlmer, *Wiedemann's Ann.*, **52**, 166.

1895. Über die Leitfähigkeit der Lösungen einiger Salze in Aceton," St. v. Laszczynski, *Z. Elektrochem.*, **2**, 55.

1899. "The Electrical Conductivity of Nonaqueous Solutions," Lincoln, *J. Phys. Chem.*, **3**, 457.

1903. "Über organische Lösungs- und Ionisierungsmittel," Walden, *Z. physik. Chem.*, **46**, 126.

1904. "Conductance of Silver Nitrate in Water, Ethyl and Methyl Alcohols," Jones and Bassett, *Am. Chem. J.*, **32**, 420.

1906. "The Relative Migration Velocities of the Ions of Silver Nitrate in Water, Methyl Alcohol, Ethyl Alcohol and Acetone, and in Binary Mixtures of these Solvents," Jones and Rouiller, *Am. Chem. J.*, **36**, 427.

1907. "The Electrical Conductivity of Methylamine Solutions," Franklin and Gibbs, THIS JOURNAL, **29**, 1389.

1907. "The Electrical Conductivity of Solutions in Ethylamine," Shinn, *J. Phys. Chem.*, **11**, 537.

1907. "Hydrates in Aqueous Solution," H. C. Jones, *Publ. Carnegie Inst.*, No. 60.

1908. "Elektrochemie der nichtwässerigen Lösungen," Carrara.

1909. "Limiting Conductivities of Some Electrolytes in Ethyl Alcohol," Dutoit and Rappeport, *C. A.*, **3**, 269.

1911. "The Conductivity of Certain Salts in Methyl and Ethyl Alcohols at High Dilution," Kreider and Jones, *Am. Chem. J.*, **45**, 282.

1912. "Lösungsmittel mit kleinen Dielektrizitätskonstanten," Sachanov, *Z. physik. Chem.*, **80**, 13.

1913. "Die anomalen Veränderungen der Leitfähigkeit," Sachanov, *Z. physik. Chem.*, **83**, 129.

1913. "Studies of the Electrical Conductance of Nonaqueous Solutions," Shaw, *J. Phys. Chem.*, **17**, 162.

1913. "The Dielectric Constants of Dissolved Salts," Walden, THIS JOURNAL, **35**, 1649.

1914. "Conductance and Viscosity of Electrolytic Solutions," Kraus, *Ibid.*, **36**, 35.

1914. "Einige Lösungsmittel mit kleinen Dielektrizitätskonstanten," Sachanov and Prscheborowsky, *Z. Elektrochem.*, **20**, 39.

1914. "Verbindung des gelösten Körpers und des Lösungsmittels in der Lösung," Dhar, *Z. Elektrochem.*, **20**, 57.

### Ionic Velocities.

1888. "Ueberführungszahlen und Leitvermögen einiger Silbersalze," Loeb and Nernst, *Z. physik. Chem.*, **2**, 948.

1894. "Der Einfluss der Lösungsmittel auf die Beweglichkeit der Ionen," Campetti, *Nuovo Cimento*, [3] **35**, 225.

1901. "A New Apparatus for Determining the Relative Velocity of Ions; with Some Results for Silver Ions," Mather, *Am. Chem. J.*, **26**, 473.

1902. "On the Relative Velocities of the Ions in Solutions of Silver Nitrate in Pyridine and Acetonitrile," Schlundt, *J. Phys. Chem.*, **6**, 159.

1904. "Determination of the Relative Velocities of Ions of Silver Nitrate in Mixtures of Alcohol and Water," Jones and Bassett, *Am. Chem. J.*, **32**, 409.

1904. "Über die Verbindung der Lösungsmittel mit den Ionen," Morgan und Kanolt, *Z. physik. Chem.*, **48**, 365.

1906. "The Compounds of a Solvent with the Ions," Morgan and Kanolt, *J. Chem. Soc.*, **28**, 572.

1906. "The Relative Migration Velocities of the Ions of Silver Nitrate in Water, Methyl Alcohol, Ethyl Alcohol, and Acetone, together with the Conductivity of Such Solutions," Jones and Rouiller, *Am. Chem. J.*, **36**, 427.

1912. "Calculation of Ionic Velocities of Silver Nitrate in Acetone Solutions," Roshdestwensky and Lewis, *J. Chem. Soc.*, **101**, 2097.

### Molecular Weight.

1897. "Molekulargewichtsbestimmungen in Pyridin," Werner und Schmujlow, *Z. anorg. Chem.*, **15**, 18.

1902. "The Molecular Weights of Certain Salts in Acetone," H. C. Jones, *Am. Chem. J.*, **27**, 16.

1902. "Elektrolyse einiger anorganischen Salze in organischen Lösungsmitteln," Speransky und Goldberg, *Z. physik. Chem.*, **39**, 369.

1905. "Verhalten von Silbersalzen in Pyridin," Schroeder, *Z. anorg. Chem.*, **44**, 20.

1908. "Equilibrium in the System Silver Nitrate and Pyridine," Kahlenberg and Brewer, *J. Phys. Chem.*, **12**, 283.

---

# A THEORY OF VALENCY AND MOLECULAR STRUCTURE.

BY WILLIAM C. ARSEM.

Received May 28, 1914.

Introduction. Historical. Outline of Theory: (*a*) Structure of Molecules; (*b*) Multiple Valency; (*c*) Valency Relations in the Periodic System. Applications of the Theory: (*a*) Mechanism of Reactions; (*b*) Tautomerism; (*c*) Conduction in Metals; (*d*) Association; (*e*) Dissociation and Conduction in Electrolytes; (*f*) Dissociation and Conduction in Gases; (*g*) The Charge and Apparent Mass of an Electron.

## Introduction.

The purpose of this paper is to advance a theory of molecular structure