ON THE IONIZATION OF FUSED SALTS.[1]

By H. M. Goodwin and H. A. Wentworth.

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THE following investigation was undertaken in the spring and summer of 1905 in the hope of contributing something to our knowledge of the applicability of the well established laws of dilute solutions to fused mixtures, and possibly of throwing some light on the question of the constitution of salts in the state of fusion.

Investigations bearing upon the determination of the degree of dissociation of fused salts have already been published, but the results obtained are meagre and cannot be regarded as conclusive. This is chiefly due to the peculiar difficulties inherent in the problem which are not encountered in aqueous or other solutions at ordinary temperatures. Aside from the obvious experimental difficulties incident to working at high temperatures and with vessels unattacked by fused salts, are the difficulties arising from the fact that pure fused salts are in general such excellent electrolytic conductors; although their conductivities may now be determined with precision,[2] transference experiments in them are impossible, since no concentration changes occur at the electrodes during electrolysis, and data on the absolute velocity of migration of ions in such conductors are at present entirely wanting. Direct velocity experiments with fused electrolytes have been recently attempted in the electrochemical laboratory of the Institute, but the exceeding difficulty of the problem has prevented as yet the obtaining of any satisfactory results. With solutions of one salt in another the relations are far more difficult of analysis than in aqueous solutions where the conductivity of the solvent may practically be neglected. Here, to be sure, transference experiments are possible and Lorenz[3]

[1] This research was carried out under a grant from the Wm. E. Hale Research Fund, to the trustees of which grateful acknowledgment for the aid furnished by them is hereby made.

[2] An investigation on this subject is now being carried on by one of us, the results of which will be published shortly.

[3] Zeit. für Electrochemie, 10, 630, 1904.

has made a first attempt in this direction with solutions of lead chloride in potassium chloride, his results pointing to more complex relationships than had been supposed.

The most promising method of attacking the problem of the dissociation of one fused salt in another seems at present to lie in the application of some selective ion-phenomenon, *i. e.*, in measuring some quantity which depends, so far as we know, on the presence of a specific molecular or ionic complex. Of the quantities suitable for this purpose the electromotive force of certain voltaic cells composed of fused mixtures lends itself best for determining specific cation concentrations, provided that Nernst's theory of the voltaic cell is applicable to combinations of this type. It is upon the results of electrometric experiments that most previous work on this subject has been based and upon which the present investigation rests.

The first experimental work bearing upon the problem under consideration was carried out by Gordon[1] and consisted of the measurement of the electromotive force of concentration cells of the type

$$\mathrm{Ag}\left|\begin{array}{c}c_1,\ -\ \mathrm{AgNO_3}\\ \text{in}\\ \mathrm{KNO_3}+\mathrm{NaNO_3}\end{array}\right|\left|\begin{array}{c}c_2,\ -\ \mathrm{AgNO_3}\\ \text{in}\\ \mathrm{KNO_3}+\mathrm{NaNO_3}\end{array}\right|\mathrm{Ag},$$

equimolecular mixtures of sodium and potassium nitrates being used to give a solute of low melting point. The concentration of the silver nitrate was varied from 0.1 to 100 per cent. On the assumptions, first, that Nernst's formula applies to cells of this type, second, that the electrolytic solution pressure of silver is independent of the solutions in question, and third, that the dissociation of a 0.1 per cent. solution of silver nitrate may be regarded as complete, Gordon calculated that the dissociation of a 50 per cent. solution of silver nitrate was 69 per cent. at 236° C., and a 100 per cent. solution, *i. e.*, pure silver nitrate, was 58 per cent. dissociated. While the experimental results of this investigation which was carefully carried out may be accepted, certain of the above assumptions on which the computations rest render the conclusions open to question.

[1] Gordon, Zeit. f. Phys. Chem., **28**, 302, 1896.

More recently the same problem has been taken up from a slightly different standpoint by Lorenz and his pupils at Zurich. Following an extended series of investigations[1] on decomposition potentials and on the electromotive force of cells composed of fused salts, Suchy[2] in 1901, from measurements of cells of the type computed

$$\mathrm{Pb} \left| \mathrm{PbCl_2} \right| \begin{matrix} \mathrm{AgCl} \\ \text{in} \\ \mathrm{LiCl + KCl} \end{matrix} \Big| \mathrm{Ag},$$

the dissociation of silver chloride in a lithium and potassium chloride mixture as follows:

Two cells of the above type differing only in the concentration of silver chloride were measured at temperatures varying from 500° to 650° C. The concentrations chosen were 1.858 n — AgCl and 0.035 n — AgCl respectively. If the observed electromotive force of these cells at corresponding temperatures be E_1 and E_2 respectively, and Nernst's formula be assumed to hold for each, then

$$E_1 - E_2 = \frac{RT}{2F} ln \frac{P_{Pb}}{p_{Pb}} - \frac{RT}{F} ln \frac{P_{Ag}}{p_1} - \frac{RT}{2F} ln \frac{P_{Pb}}{p_{Pb}} + \frac{RT}{F} ln \frac{P_{Ag}}{p_2}$$

or

$$E_1 - E_2 = \frac{RT}{F} ln \frac{p_1}{p_2},$$

$$= \frac{RT}{F} ln \frac{c_1}{c_2},$$

in which c_1 and c_2 are the *silver-ion* concentrations at the two electrodes respectively. If $E_1 - E_2$ be measured and the value of c_1 known or assumed, c_2 may be calculated. Suchy assumed that the 0.035-normal solution of silver chloride was completely dissociated, from which it followed that the computed dissociation of the 1.8-normal solution of silver chloride at 600° was 33 per cent. From measurements of a similar cell in which pure silver chloride replaced the silver chloride solution at one electrode, values for the dissociation of the pure salt at various temperatures were also computed. They varied from 17 per cent. at 520° to 60 per

[1] Czepinski, Zeit. für anorg. Ch., 19, 208, 1899. Lorenz, ibid., 19, 283, 1899. Weber, ibid., 21, 305, 1899. Lorenz, ibid., 22, 241, 1900.

[2] Suchy, Zeit. für anorg. Ch., 27, 152, 1901.

cent. at 730°. These results are regarded by the author as only first approximations. They rest on the following assumptions: (1) That a 0.035-normal solution of silver chloride in a chloride mixture is completely dissociated (questioned by Lorenz himself)[1]; (2) that the electrolytic solution pressure of silver may be regarded as independent of the solvent for solvents as widely different as fused pure silver chloride and a mixture of lithium and sodium chlorides (see discussion by Bodlander and Lorenz)[2]; (3) that the potential difference at the liquid junction is negligible — an assumption probably well founded; (4) that the effect of a common anion in the solvent on the dissociation of the solute may be neglected. This last assumption seems to have been entirely disregarded in all previous computations of the kind under discussion.

In concluding this resumé of previous work mention should be made of one other method of computation of the order of magnitude of the dissociation of a fused salt suggested by Abegg,[3] based on the assumption that the decomposition voltage of an ion is independent of the medium in which it is dissolved. Thus, if 0.7 volt be taken as the decomposition voltage of silver chloride, he computes that the silver ions in fused silver chloride must have a concentration of about 0.01 normal.

Beyond these investigations little has been accomplished in determining the degree of dissociation of fused electrolytes. It was with the hope of obtaining some further data which might contribute towards the elucidation of this problem that the following investigation was undertaken, particular attention being directed to the possible effect of the dissociation of the solvent on the dissociation of the solute.

APPARATUS AND METHOD.

Furnaces. — For carrying out the experiments described below, we required two furnaces, both of which were of the electrical resistance type. The principal furnace, in which the measurements were made, was constructed of four porcelain tiles forming the inside lining of a rectangular iron box. Through holes which extended from the top to the bottom edges of the tiles, were threaded

[1] Zeit. für Anorg. Chem., **32**, 246, 1902.

[2] Zeit. für Anorg. Chem., **31**, 389, 1902; **32**, 235, and 239, 1902.

[2] Zeit. für Chem., **5**, 353, 1899.

about twelve feet of No. 21 (B. & S.) platinum wire. The outside of the furnace was covered with asbestos to prevent radiation as far as possible.

Within the furnace was placed a box of thin cast iron, the approximate inside dimensions of which were 5.7 cm. × 3.2 cm. × 6.4 cm. deep. This formed the receptacle for a bath consisting of a mixture of fused sodium and potassium nitrates with a small amount of silver nitrate added. The composition of this bath was not determined exactly, a mixture of nitrates being used simply to obtain a low melting point. Gordon found in his experiments that the composition of the intermediate electrolyte, connecting the halves of a concentration cell, had no effect on the results. The bath was well stirred by a glass stirrer driven by a small electric motor, and was kept covered with several sheets of mica to prevent excessive radiation. The surface of the liquid seemed to be the greatest source of heat loss, but for temperatures below 500° C. this was not excessive, when the apparatus was well shielded from air currents. The temperature was regulated by an adjustable rheostat connected in series with the furnace, and could be maintained constant to within 2° C., as long as desired.

Another large platinum resistance furnace was used for melting the salts in the proper cells prior to plunging them into the above described nitrate bath for measurement. This was constructed by winding about three meters of No. 28 platinum wire on a clay cylinder, 25 cm. high by 8 cm. diameter, previously coated with pure magnesium oxide ; the cylinder was then heat insulated by packing it with a layer of magnesia ten centimeters thick. It was found convenient to first melt the salts in this furnace, as the glass vessels usually cracked if they were put directly into the fused salt bath. Both furnaces were run on the 110 volt D.C. circuit and the heating current adjusted by rheostats.

Temperature Measurements. — Temperatures were measured by a platinum-rhodium junction. The junction was inserted in the bath between the two parts of the vessel containing the fused salts to be measured. The stirring was, however, so effective that all parts of the bath were always practically at the same temperature.

The temperatures were deduced from deflections of a sensitive

d'Arsonval galvanometer of the Le Chatelier type. In order to prevent changes in the sensitiveness of the galvanometer due to temperature changes in the room from time to time, the galvanometer was enclosed in a small air thermostat built up of asbestos and magnesia board, the mirror being observed through a small window. As great precision in temperature regulation was unnecessary in this investigation, the sensitiveness of the galvanometer was so adjusted that one degree temperature change gave a deflection of about one scale division. The instrument could easily be read to one half of a division, hence temperatures could be measured to one half a degree without difficulty, a precision greater than the work really demanded. The junction was calibrated every few days throughout the work, and the calibration was found to remain very constant. The following points were taken for calibration : water, 100°, naphthalene 218°, benzophenone 306°, sulphur 445°. The cold junction was kept always at zero degrees in an ice mixture.

Potential Measurements. — Potentials were measured by the usual Poggendorf compensation method, by balancing them against a fall of potential along a calibrated slide wire bridge. The voltages were repeatedly checked by comparison with a standard Weston cell and a Clark cell standarized at the Reichsanstalt. A Lippmann electrometer sensitive to 0.0003 volt was used as indicating instrument. All circuits were carefully insulated, and to prevent any possible leakage from the 110 volt heating circuit, the latter was opened before each potential measurement.

Form of Cell. — The cells were made of Bohemian glass. As this does not begin to soften until about 800° C., it was sufficiently hard for all temperatures used in our experiments, which did not exceed 450°. For the first portion of the work, H-tubes, 9 cm. in length and 6.4 mm. diameter, having an inclined cross arm of small tubing were used. This cross arm was filled with a plug of prepared asbestos which was found to completely prevent diffusion of the solutions in the two sides. The liquid-liquid contact came well within the boundaries of the plug. The H-tubes were immersed to within 3 cm. of their top, in the fused nitrate bath, their contents being thus entirely insulated from the material of the bath. The greater portion of our work was carried out with cells of this kind.

Since, however, these were found to crack rather easily, the following modified form of cell was used in some of the later work. In this the two electrodes were contained in separate glass tubes drawn down at the end, as in the experiments of Suchy and others, electrolytic connection between them being made by means of the liquid constituting the bath. The potentials obtained in this way were found to check exactly those obtained with the closed tubes. The tubes were suspended in the bath so that the level of the liquid within and without was the same. To prevent convection and diffusion, the ends were closed with asbestos plugs.

The electrodes consisted of fine platinum wires heavily plated with pure silver. These electrodes were scraped and washed perfectly clean before using. Similarly prepared electrodes gave concordant results. The electrodes were carefully suspended in the molten salts and served also the purpose of stirring the latter.

Preparation of Salts. — The following salts were used in our experiments: sodium, potassium, and silver nitrates and silver chlorate. The sodium and potassium nitrates were recrystallized until free from chlorides; "C.P." silver nitrate was recrystallized twice. Silver chlorate was made by precipitating barium sulphate from a hot saturated solution of silver sulphate, with barium chlorate, the latter being first freed from all traces of chloride by crystallization. The silver chlorate, was then separated from the slight excess of barium chlorate in the filtrate, by fractional crystallization. Silver chlorate separates out as beautiful, long, fine, shiny needles, which are easily dried.

Preparation of Mixtures. — All salts were first fused and cooled in a desiccator before the final weighing. The mixtures were then made up in the following manner: The pure fused salts were weighed out in the desired proportions. The sodium or potassium nitrate, as the case might be, was then fused, and while just above its melting point, the silver salt was added. This procedure was followed in order to prevent any reduction of the silver salt by over heating before or during the process of fusion. It was found that the salts of the silver, when once in solution, could be kept fused far above their decomposition points without any apparent reduction. For example, silver chlorate melts at about 230° and decomposes

at about 270°; but, if dissolved in 95 per cent. of sodium nitrate, it can be carried above 350° without any apparent decomposition. After adding the silver salt, the mixture was thoroughly stirred and allowed to cool, vigorous stirring being continued as long as possible. When cold the mixture was broken up and very finely ground in a mortar until different samples gave the same analysis. If the mixtures were allowed to cool without continual stirring, a hard crystalline mass was obtained, which varied in appearance as the composition changed. The mixtures of sodium and silver nitrates solidified in a coarsely crystalline mass which could be broken up easily. With the mixtures of potassium and silver nitrates, however, the texture was fine, and as the concentration of the silver nitrate approached 50 per cent. the mass became extremely hard, resembling marble in appearance. The same was true of silver chlorate, although the mass became very hard with only a small percentage of silver chlorate added.

With the higher concentrations of silver nitrate, the salts were analyzed both before and after the measurements, but with mixtures containing only a very small percentage of silver, this procedure was not practicable. For these mixtures the salts were dried carefully and the proportions made up by weight, the conditions tending to cause a reduction of the silver salt being eliminated so far as possible.

Procedure. — The general procedure for making a potential measurement was as follows: The two mixtures to be investigated were put into their containing vessels or cells and placed in the air-bath furnace to fuse, this bath being kept just above the melting point. As soon as the salts had melted, the vessels were quickly transferred to the nitrate bath of the main furnace, which had previously been brought to the desired temperature. The electrodes were then inserted, the mixtures well stirred, and the measurements begun. As a rule the electromotive force increased rapidly at first, reached a maximum, remained constant for a time and then decreased slowly. The time required for the electromotive force to reach a constant value varied somewhat with each type of cell. The mean of a series of readings taken over an interval of five to ten minutes after the electromotive force had become essentially constant was taken as the observed electromotive force of the cell.

Density Determinations. — In order to calculate the concentration of the various solutions used, in terms of their normality, the density of the salt mixtures had to be determined. The following method was used: a cylinder of Brazilian quartz was cut from a crystal parallel to the principal axis, and used as the sinker of a Westphal balance, a set of weights being adjusted so as to correspond to its volume. A correction for its expansion with the temperature could be made, as the coefficients of expansion along and at right angles to the principal axis of quartz are known. The sinker was suspended in the molten salt the density of which was desired. This was fused in a large platinum crucible placed in the larger electric furnace. In certain experiments where the highest precision attainable was desired the natural quartz sinker was replaced by a fused quartz cylinder, this material being preferable on account of its very small expansion coefficient.

The densities of mixtures of silver and sodium nitrates were all measured, as well as those of a few mixtures of silver and potassium nitrates. For solutions of silver chlorate in sodium nitrate the densities were not measured, but estimated, it being assumed that for a given concentration the same change in density from that of the pure solute (sodium nitrate) occurred, as in the case of silver nitrate solutions. This seemed justified, as the densities of pure silver nitrate and of pure silver chlorate were found to be very nearly the same, and the concentration of all solutions investigated was not greater than 5 per cent. This assumption does not introduce an appreciable error, compared with the precision of other factors of the work.

The data on the density of the fused salts used in this research are not inserted in this paper as they are to be published shortly in connection with the research before mentioned on the conductivity of fused salts.

Investigations of Cells of the Type

$$\mathrm{Ag}\left|\begin{matrix}\mathrm{AgNO_3\ in\ N\ \ O_3}\\ c_1\end{matrix}\right|\left|\begin{matrix}\mathrm{AgNO_3\ in\ NaNO_3}\\ c_2\end{matrix}\right|\mathrm{Ag}.$$

The first series of experiments were carried out on cells of the above type which are identical with those investigated by Gordon,

except that in his cells a mixture of sodium and potassium nitrate was used as solvent. While Gordon in his experiments chose his solutions of concentrations from 0.1 to 100 per cent. silver nitrate, we have extended the experiments to diluter solutions to which the assumptions underlying the application of Nernst's formula may with more probability be assumed to hold. Experiments have also been repeated with concentrated solutions in order to determine the limits within which Nernst's formula applies.

For dilute solutions the electromotive force of the above cell may be written

$$E = \frac{RT}{F} ln \frac{(Ag)_1}{(Ag)_2}, \qquad (1)$$

where $(Ag)_1$ and $(Ag)_2$ are the concentrations of the silver ions in the two solutions respectively. Now from conductivity measurements of pure fused nitrates, it is certain that both the sodium and silver nitrate must be more or less dissociated. If we assume that dissociation in a fused salt takes place as in aqueous solutions, *i. e.*, in the case of sodium nitrate according to the equation

$$NaNO_3 = \overset{+}{Na} + \overset{-}{NO_3},$$

and if the mass action law applies to the equilibrium of this reaction, then at any given temperature

$$\frac{(Na) \times (NO_3)}{(NaNO_3)} = \text{constant},$$

where the symbols in parenthesis represent the concentrations of the respective ions and undissociated molecules. If to this nitrate as solvent, silver nitrate be added in such quantities that the resulting solutions are so dilute with respect to silver nitrate that the number of NO_3 ions per unit volume arising from its dissociation may be neglected compared with the number of NO_3 ions resulting from the dissociation of the solvent, then, over the range of concentrations to which this assumption applies, the total number of NO_3 ions present may be regarded as practically constant, *i. e.*, we may assume $(NO_3) = \text{const.}$, and hence also $(Na) = \text{const.}$ If further the silver nitrate dissolved in sodium nitrate dissociates according to the equation

$$AgNO_3 = \overset{+}{Ag} + \overset{-}{NO_3}$$

we have for a given temperature

$$\frac{(Ag) \times (NO)_3}{(AgNO_3)} = \text{constant.}$$

Since by supposition (NO_3) = constant it follows that

$$\frac{(Ag)}{(AgNO_3)} = \text{constant,}$$

from which by proportion we obtain

$$\frac{(Ag)}{(Ag) + (AgNO_3)} = \text{constant.}$$

But $(Ag) + (AgNO_3) = c$ the total concentration of silver nitrate dissolved in the sodium nitrate; hence for solution (1) we have

$$\frac{(Ag)_1}{c_1} = \text{constant,}$$

and for solution (2)

$$\frac{(Ag)_2}{c_2} = \text{constant,}$$

therefore,

$$\frac{(Ag)_1}{(Ag)_2} = \frac{c_1}{c_2},$$

or in other words as long as the solutions of silver nitrate in a nitrate are dilute, the ratio of the silver ion concentration at the two electrodes is equal to the ratio of the total silver nitrate concentration of the solution. The formula for the electromotive force may therefore be written

$$E = \frac{RT}{F} ln \frac{c_1}{c_2} \qquad (2)$$

and hence values of E computed on the basis of Nernst's theory and *total* concentrations of silver nitrate should agree with experimental results if the mass action law applies to cases like the above, and this will be true whether the dissociation of the silver nitrate is great or small. To assume complete dissociation for the solute at any given concentration because of a close agreement between observed values and values computed by the above formula, as was done by Gordon in his investigation is, therefore, open to question.

We have tested formula (2) over a range of concentrations with the results given below.

TABLE I.

$AgNO_3$ in $NaNO_3$.

Equivalent Concentration of $AgNO_3$ at 400° C.		Temperature.	E (Observed).	$E=\frac{RT}{F}\ln\frac{c_1}{c_2}$. (Calculated).	Δ Difference.
c_1	c_2				
0.00986	0.06206	350	−0.1014	−0.0986	+0.0028
0.00986	0.06206	350	−0.0996	−0.0986	+0.0010
0.00986	0.1220	337	−0.1335	−0.1320	+0.0015
0.06206	0.1220	349	−0.0370	−0.0362	+0.0008
0.5565	0.1220	340	+0.0781	+0.0800	−0.0019
0.5565	0.00986	340	+0.2094	+0.2130	−0.0036
0.5250	0.04999	329	+0.1230	+0.1220	+0.0010

In Table I. are given the results of experiments made with the diluter solutions. In the first and second columns are given the concentrations of the silver nitrate solutions expressed (throughout) in equivalents per liter and calculated from measurements of their density and percentage composition ; in the third column is given the temperature of the cell at the time of the measurement ; in the fourth column the observed electromotive force (taken plus from solution (1) to (2)) ; in the fifth column, the electromotive force calculated by formula (2), and in the last column the difference between the observed and calculated *numerical* values.

It will be seen that up to half normal solutions the agreement is practically complete, the experimental error in cells of this type being from 0.001 to 0.002 volt.

Replacing the sodium nitrate by potassium nitrate as a solute we obtained an equally good agreement between calculated and observed values of the electromotive force. Thus for a cell in which $c_1 = 0.3205$, $c_2 = 0.0480$, $t = 347°$ C., the observed value of $E =$ 0.1003 volt while the computed value was 0.1008 volt. Over this range of concentrations therefore, formula (2) holds valid.

When, however, the concentration of the silver nitrate exceeded about 0.5 normal the deviations between observed and calculated values became increasingly greater and always in the same direction. This will be seen from Table II. These measurements were all carried out at approximately 350°. The concentrations (first and

TABLE II.

$AgNO_3$ in $NaNO_3$. Temperature = 350° C.

Equivalent Concentration of $AgNO_3$.		E (Observed).	$E = \frac{RT}{F} ln \frac{c_2}{0.01}$ (Calculated).	$E = \frac{RT}{F} ln \frac{c_1}{0.01}$ Reduced.	$\frac{c_1}{0.01}$	$\frac{(Ag)_1}{(Ag)_{.01}}$
c_1	c_2					
0.531	0.0507	0.1230	0.0875	0.2105	53	55
0.531	0.0572	0.1160	0.0908	0.2068	53	53
1.065	0.0421	0.1660	0.0752	0.2412	107	100
1.780	0.1094	0.1412	0.1258	0.2670	178	159
2.345	0.0643	0.1812	0.1000	0.2810	235	199
4.63	0.0418	0.2313	0.0758	0.3071	463	331
7.38	0.684	0.1066	0.2213	0.3279	738	528
13.20	0.0668	0.2502	0.1003	0.3505	1320	764
22.48[1]	0.273	0.1963	0.1957	0.3720	2250	1100

second columns), were as before computed from density determinations of the solutions in question. The third column contains the mean value of the observed electromotive force. In the fourth column are given the computed values of the electromotive force of similar cells, the diluter solutions of which are always 0.01 normal, and the more concentrated solutions of which are c_2 respectively. As c_2 is in every case (except one, 0.68) less than 0.5 normal, these values may be accepted as correct as just shown by the above results in Table I. If therefore these electromotive forces be added to the corresponding observed value of E for cells in which c_2 is the diluter concentration, we obtain the electromotive force of cells in each of which the diluter solution is 0.01 normal and the more concentrated solution c_1 respectively. This assumes that the liquid junction potentials are negligible. All cells may thus be referred to a common concentration, namely 0.01 normal. The computed value of the ratio of the concentration $c_1/0.01$ for each of the cells is given in column six, while the ratio of the silver ion concentration $(Ag)_1/(Ag)_{0.01}$ as computed from formula (1) is given in the last column. It is seen that in passing from solutions 0.5 normal those of greater concentration the computed and observed ratios begin to deviate with increasing rapidity, the ratio of the silver ions being less than the ratio of the total silver nitrate concentrations. This is what theory would lead us to expect as soon as the concentration of the NO_3 ions coming from

[1] Pure silver nitrate.

the silver nitrate itself is no longer negligible compared with the concentration of NO_3 in the solute. Until however, we have further data on the degree of dissociation of the latter and are thereby in a position to compute its effect on the dissociation of an added nitrate, dissociation values computed from the last two columns of Table II., can have but little significance.[1]

CELLS OF THE TYPE

$$\mathrm{Ag}\left|\begin{matrix}\mathrm{AgClO_3\ in\ NaNO_3}\\ c_1\end{matrix}\right|\left|\begin{matrix}\mathrm{AgClO_3\ in\ NaNO_3}\\ c_2\end{matrix}\right|\mathrm{Ag}.$$

We next investigated a concentration cell in which the solute and solvent had no ion in common. Silver chlorate was chosen as solute and sodium nitrate as solvent. For this cell, the conclusion arrived at in the discussion of the preceding cells, namely that for dilute solutions the ratio of Ag-ion concentration and total concentration at the two electrodes is the same, no longer holds; for an interchange of ions between solvent and solute probably takes place according to the reaction

$$\mathrm{AgClO_3 + NaNO_3 = AgNO_3 + NaClO_3}$$

some undissociated silver nitrate and sodium chlorate being formed. If the amount of undissociated silver nitrate thus formed is appreciable, the concentration of silver ions will not be equal simply to the concentration of $AgClO_3$ multiplied by its percentage dissociation, but, depending upon the quantity of undissociated silver nitrate formed will be less than this. We should expect, therefore, that the computed ratio of the silver ion concentration in a concentration cell of this type would not be equal to the concentration ratio of the dissolved salt even in dilute solutions, but would be less. This was in fact found to be the case as the results in table III. clearly show. Here it will be seen that all values of the electromotive force calculated on the basis of the formula $E = \frac{RT}{F} ln \frac{c_1}{c_2}$, where c_1 and c_2 are the total concentrations of the solutions, are in every case *greater* than the ob-

[1] Since this paper went to press, the third part of Professor Lorenz's work on the "Elektrolsye Geschmolzener Salze" has reached me and I note that he has come to this same conclusion.

TABLE III.

$AgClO_3$ in $NaNO_3$.

Equivalent of Concentration of $AgClO_3$.		Temperature.	E (Observed).	$E=\frac{RT}{F} ln \frac{c_1}{c_2}$. (Calculated).	Δ Difference.
c_1	c_2				
0.0756	0.0358	349	0.037	0.040	−0.003
0.0756	0.0235	332	0.053	0.060	−0.007
0.0756	0.0235	345	0.053	0.061	−0.008
0.294	0.0235	345	0.116	0.136	−0.020
0.294	0.0235	357	0.116	0.136	−0.020
0.493	0.0756	356	0.095	0.101	−0.006

served values, by amounts considerably in excess of the experimental error. Over this same range of concentration, with silver nitrate as solute, the agreement between observed and calculated values was complete. The difference between observed and computed values indicates either that the dissociations of silver chlorate changes (diminishes) rapidly with increasing concentration, or that the effect of the reaction between solvent and solute results in the formation of a very considerable amount of undissociated silver salt. In either case it seems reasonable to conclude that the dissociation of the chlorate is by no means complete or even approaching 100 per cent. at the concentrations investigated.

In view of the present state of our ignorance of the absolute value of the dissociation of any fused salt in even dilute solutions, it seems to us premature to attempt to conclude more from the above experiments than that Nernst's theory of the cell and the laws underlying the mutual effect of one ionized salt on another hold for salts in the molten state as well as in aqueous solution. These conclusions seem, however, well established by the above experiments, and hence the great importance which must be attached to the effect of the ionized portion of the solvent on the ionization of the solute in cases of fused inorganic mixtures. The analogue in aqueous solutions is to be found in hydrolytic phenomena at very high temperatures when water itself becomes much dissociated. As soon as the degree of dissociation of fused silver nitrate or chlorate has been once independently established, the above measurements will afford data for the computation of their dissociation at various other concentrations.

An attempt is being made at the present time to obtain from electrometric measurements on another type of cell the value of the dissociation constant of one of the salts used in the preceding experiments and it is hoped that shortly we may be able to state more definitely than at present whether the high conductivity of fused electrolytes is due to a great migration velocity of their ions resulting from the high temperatures to which they are subjected, or to a high degree of dissociation as has been usually assumed.

RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY.