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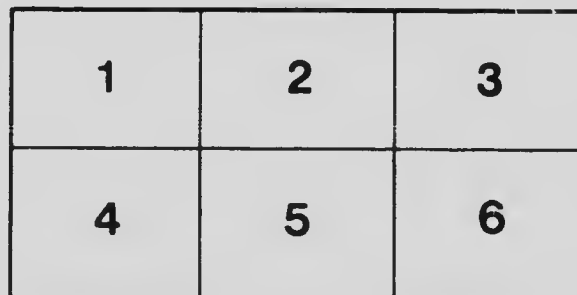
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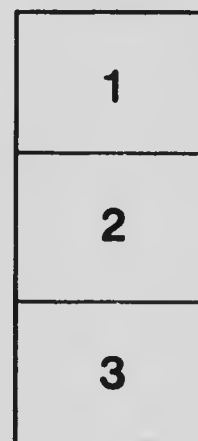
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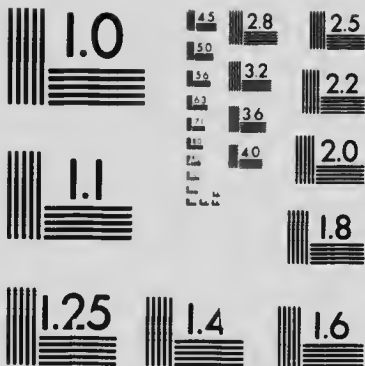
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DILUTE SOLUTIONS, BY J. A. GARDINER

(REPRINTED FROM THE BULLETIN OF THE ROYAL SOCIETY OF CANADA, 1908, No. 6.)

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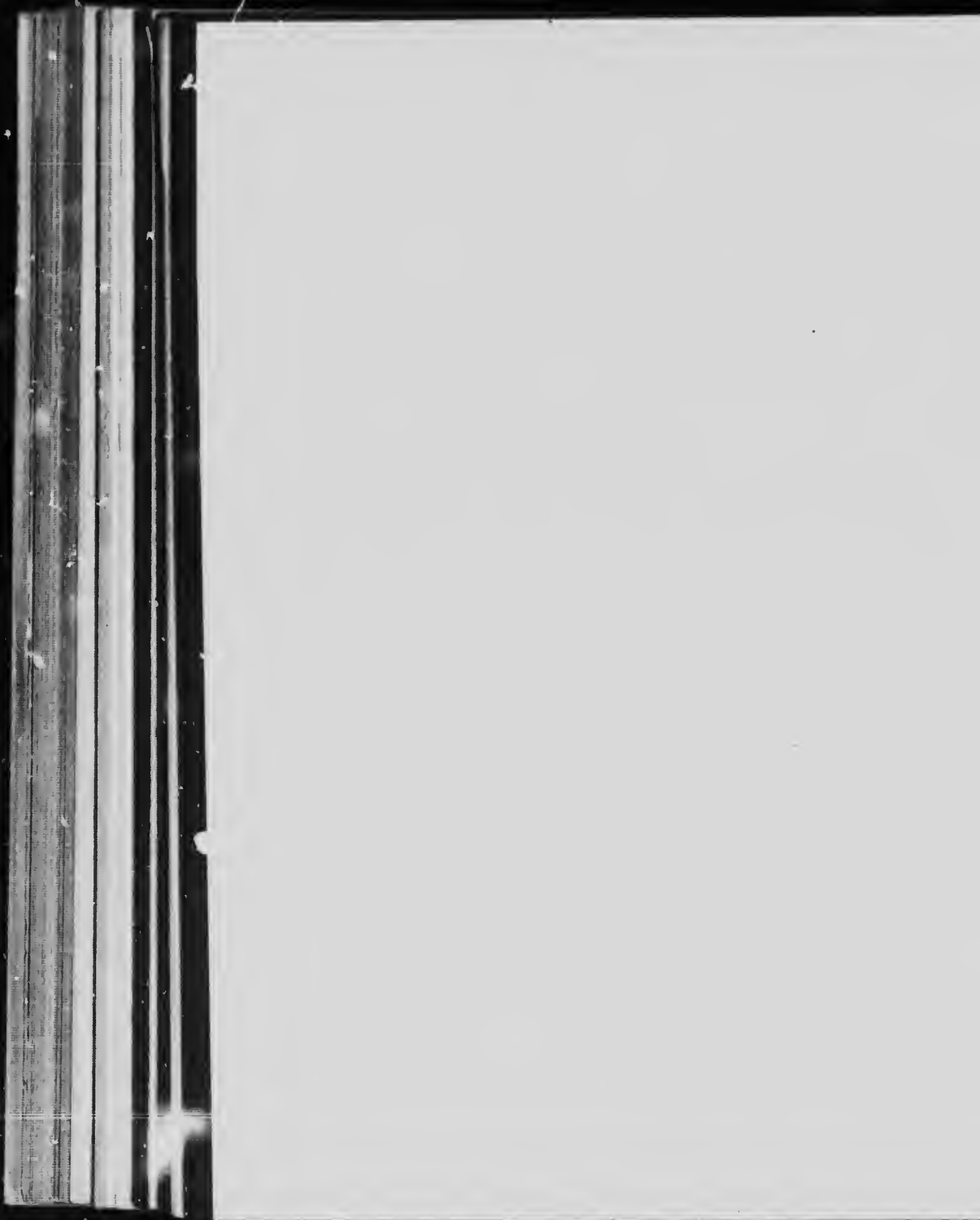
ON THE CONDUCTIVITY OF MIXTURES OF
DILUTE SOLUTIONS

By J. A. GARDINER, M.A.

Communicated by Professor J. C. McLENNAN.

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V.—On the Conductivity of Mixtures of Dilute Solutions.

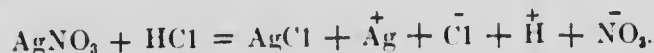
By J. A. CARDINER, M.A.

(Communicated by P. J. J. McLennan and read May 26, 1908).

INTRODUCTION.

In a recent paper by Mr. E. F. Burton¹ some numbers are given which shew that, when dilute hydrochloric acid was added to a colloidal solution of silver, a drop in the conductivity of the solution occurred. During the course of that investigation Mr. Burton also observed a similar effect when dilute hydrochloric acid was added to a dilute solution of silver nitrate.

Now, according to the ionic theory of electrolysis, silver nitrate in dilute solution is completely dissociated into silver and nitrate ions, i.e., AgNO_3 becomes $\text{Ag}^+ + \text{NO}_3^-$. The same is true of hydrochloric acid in dilute solution, HCl decomposing into the ions $\text{H}^+ + \text{Cl}^-$. Also when we add dilute HCl to dilute AgNO_3 , we should obtain the following:



Since the hydrogen ion possesses greater mobility than the silver ion which it displaces one would naturally expect the conductivity of the silver nitrate to increase on the addition of the hydrochloric acid. From the observation described above it seemed evident, however, that the conductivity under the circumstances stated, did not follow the ordinary laws of electrolysis, and in order to examine the effect more fully a series of experiments was made under a variety of conditions described below.

Description of the apparatus.—The resistance of the solution was measured by a method similar to that adopted by G. B. Bryan² in "The Conductivity of Liquids in Thin Layers." The arrangement is shewn in Fig. 1.

By means of the double commutator CC an alternating current was supplied to two corners of a Wheatstone Bridge, and since the connections to the galvanometer were reversed at the same time as the current, any current through the galvanometer was always in one direction. The commutator had two ebonite drums, each with two

¹ Phil. Mag., Nov. 1906, p. 472.

² Bryan, Phil. Mag. 45, pp. 253-270, 1906.

brass segments and four brushes. When driven at full speed it gave about 20 alternations per second.

In making the measurements the conductivity vessel was placed in a water bath, kept at a constant temperature by means of a thermostat. The thermostat was regulated so as to give a temperature of 25°C , and the conductivities of the solutions in the following

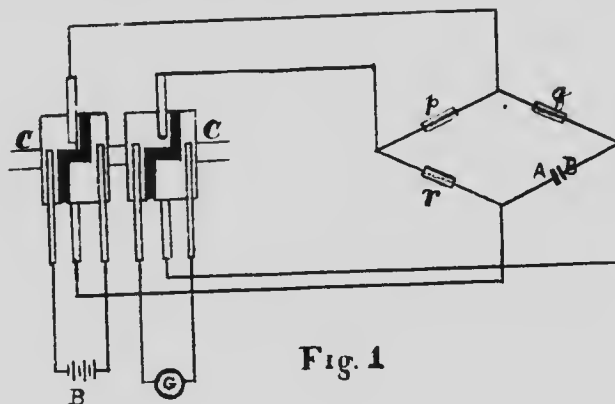


Fig. 1

experiments were found for that temperature. The electrodes, also, were coated with platinum black to prevent the absorption of liberated gases.

Experiment I.—To Prepare Standard Solutions of Silver Nitrate, Hydrochloric Acid, and Potassium Chloride.

The hydrochloric acid was standardised by means of sodium hydrate which was prepared by placing a piece of sodium freed from the petroleum and the crust of oxide, in the funnel F, made of nickel gauze. Fig. II. This funnel stood in a basin of distilled water, and over the whole a bell jar was placed as shewn in the diagram. Under the apex of the funnel was placed a platinum vessel D, which caught the sodium hydrate as it trickled down from the funnel above. The action was hastened by passing a current of steam through a tube placed in the water, so as to increase the evaporation. The sodium hydrate thus formed was made up to about the desired concentration, and the resulting solution was standardised by means of succinic acid, using phenolphthalein

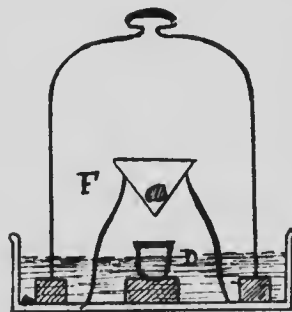


Fig. II.

as indicator. The sodium hydrate solution was then used to standardise the hydrochloric acid solution, using the same indicator as before.

The silver nitrate and potassium chloride solutions were made by dissolving known weights of each in distilled water, and afterwards making the solutions up to the desired concentration.

Experiment II.—To Determine the Cell Constant.

The constant K which, for a given cell, depends on the size and shape of the electrodes, and on their distance apart, is equal to the ratio $\frac{\text{specific conductivity}}{\text{measured conductivity}}$ or since the conductivity = $\frac{1}{\text{resistance}}$ we have $K = \text{specific conductivity} \times \text{measured resistance}$. In order to find the value of K a $\frac{N}{50}$ solution of KCl whose specific conductivity at $25^{\circ}C$ is known to be 2.768×10^{-3} , was taken and its resistance found at that temperature by the method described above. The mean of several readings obtained in this way gave a resistance of 29.265 ohms, so that $K = 2.768 \times 10^{-3} \times 29.265 = .08100552$, with this constant the specific conductivity of any other solution was therefore given directly by $\frac{K}{\text{resistance of the solution}}$

Experiment III.—To 75 c.c. of redistilled water there was added drop by drop $\left(\frac{1}{30} \text{ c.c.}\right)$ a $\frac{N}{10000}$ solution of HCl and the specific conductivities found for the different concentrations are given in the following tables I, II and III :

TABLE I.

Temp.	Concentration.	Spec. Conductivity.
$25^{\circ}C$	Water	2.70×10^{-6}
"	$4.4 \times 10^{-8} N$ HCl	2.70×10^{-6}
"	8.8×10^{-8} "	2.70×10^{-6}
"	22.2×10^{-8} "	2.793×10^{-6}
"	66.6×10^{-8} "	2.857×10^{-6}
"	133.3×10^{-8} "	3.240×10^{-6}
"	222.2×10^{-8} "	3.522×10^{-6}

TABLE II.

Temp.	Concentration.	Spec. Conductivity.
25°C	Water	2.314×10^{-6}
"	4.4×10^{-8} HCl	2.314×10^{-6}
"	8.8×10^{-8} "	2.314×10^{-6}
"	17.7×10^{-8} "	2.314×10^{-6}
"	44.4×10^{-8} "	2.250×10^{-6}
"	111.1×10^{-8} "	2.314×10^{-6}
"	244.4×10^{-8} "	2.70×10^{-6}

TABLE III.

Temp.	Concentration.	Spec. Conductivity.
25°C	Water	2.025×10^{-6}
"	4.4×10^{-8} HCl	2.076×10^{-6}
"	8.8×10^{-8} "	2.076×10^{-6}
"	13.3×10^{-8} "	2.104×10^{-6}
"	26.6×10^{-8} "	2.189×10^{-6}
"	71.1×10^{-8} "	2.70×10^{-6}
"	159.9×10^{-8} "	3.176×10^{-6}

The above tables and the curves plotted in Figs. III, IV and V, shew that on the addition of the first few drops of $\frac{N}{10000}$ HCl there was very little change in the conductivity of the solution, but as the HCl solution became more concentrated the conductivity gradually increased.

Experiment IV.—To 75 c.c. of redistilled water there was added a drop ($\frac{1}{27}$ c.c.) of $\frac{N}{1000}$ AgNO_3 , thus giving a 4.94×10^{-7} normal solution of silver nitrate. To this solution was added, drop by drop, a $\frac{N}{10000}$ solution of HCl. The variation in conductivity for different concentrations of the hydrochloric acid is shown by the numbers in tables IV, and the curve in Fig. VI.

TABLE IV.

Temp.	Concentration.	Spec. Conductivity.
25°C	Water	2.745×10^{-6}
"	$4.94 \times 10^{-7}n$ AgNO ₃	2.812×10^{-6}
"	AgNO ₃ sol. along with $4.4 \times 10^{-8}n$ HCl	2.745×10^{-6}
"	8.8×10^{-8} "	2.571×10^{-6}
"	13.3×10^{-8} "	2.612×10^{-6}
"	35.5×10^{-8} "	2.704×10^{-6}
"	66.6×10^{-8} "	2.745×10^{-6}
"	133.3×10^{-8} "	2.842×10^{-6}
"	122.2×10^{-8} "	3.115×10^{-6}

From these values it will be seen that on adding successive drops of a $\frac{N}{10000}$ solution of HCl to a 4.9×10^{-7} normal solution of AgNO₃, the conductivity at first rapidly decreased and after reaching a minimum, steadily increased with the amount of HCl added.

This experiment was repeated, using solutions of AgNO₃, gradually increasing in concentration each time.

The results are given in tables V, VI, VII, VIII, IX, X.

TABLE V.

Temp.	Concentration.	Spec. Conductivity.
25°C	Water	2.596×10^{-6}
"	$9.8 \times 10^{-7}n$ AgNO ₃	2.700×10^{-6}
"	AgNO ₃ sol. along with $4.4 \times 10^{-8}n$ HCl	2.613×10^{-6}
"	8.8×10^{-8} "	2.764×10^{-6}
"	17.7×10^{-8} "	2.822×10^{-6}
"	39.9×10^{-8} "	3.022×10^{-6}
"	84.4×10^{-8} "	3.139×10^{-6}
"	173.3×10^{-8} "	3.375×10^{-6}

TABLE VI.

Temp.	Concentration.	Spec. Conductivity.
25°C	Water	2.454×10^{-6}
"	$24.6 \times 10^{-7} \text{ n AgNO}_3$	2.842×10^{-6}
"	AgNO ₃ sol. along with $4.4 \times 10^{-8} \text{ n HCl}$	2.802×10^{-6}
"	$8.8 \times 10^{-8} \text{ n}$ "	2.892×10^{-6}
"	$17.7 \times 10^{-8} \text{ n}$ "	3.000×10^{-6}
"	$26.6 \times 10^{-8} \text{ n}$ "	3.033×10^{-6}
"	$88.8 \times 10^{-8} \text{ n}$ "	3.039×10^{-6}
"	$155.5 \times 10^{-8} \text{ n}$ "	3.046×10^{-6}
"	$244.4 \times 10^{-8} \text{ n}$ "	3.315×10^{-6}

TABLE VII.

Temp.	Concentration.	Spec. Conductivity.
25°C	Water	2.613×10^{-6}
"	$29.6 \times 10^{-7} \text{ n AgNO}_3$	3.201×10^{-6}
"	AgNO ₃ sol. along with $4.4 \times 10^{-8} \text{ n HCl}$	3.182×10^{-6}
"	$8.8 \times 10^{-8} \text{ n}$ "	3.189×10^{-6}
"	$17.7 \times 10^{-8} \text{ n}$ "	3.306×10^{-6}
"	$44.4 \times 10^{-8} \text{ n}$ "	3.521×10^{-6}
"	$88.8 \times 10^{-8} \text{ n}$ "	3.600×10^{-6}
"	$155.5 \times 10^{-8} \text{ n}$ "	3.715×10^{-6}
"	$244.4 \times 10^{-8} \text{ n}$ "	2.050×10^{-6}

TABLE VIII.

Temp.	Concentration.	Spec. Conductivity.
25°C	Water	2.700×10^{-6}
"	$34.5 \times 10^{-7}n$ AgNO ₃	3.521×10^{-6}
"	AgNO ₃ sol. along with $4.4 \times 10^{-8}n$ HCl	3.377×10^{-6}
"	8.8×10^{-8} "	3.400×10^{-6}
"	13.3×10^{-8} "	3.447×10^{-6}
"	22.2×10^{-8} "	3.681×10^{-6}
"	66.6×10^{-8} "	3.951×10^{-6}
"	133.3×10^{-8} "	4.111×10^{-6}
"	222.2×10^{-8} "	4.162×10^{-6}

TABLE IX.

Temp.	Concentration.	Spec. Conductivity.
25°C	Water	2.700×10^{-6}
"	$39.5 \times 10^{-7}n$ AgNO ₃	3.632×10^{-6}
"	AgNO ₃ sol. along with $4.4 \times 10^{-8}n$ HCl	3.632×10^{-6}
"	8.8×10^{-8} "	3.655×10^{-6}
"	13.3×10^{-8} "	3.913×10^{-6}
"	22.2×10^{-8} "	4.500×10^{-6}
"	88.8×10^{-8} "	4.909×10^{-6}
"	177.7×10^{-8} "	5.031×10^{-6}
"	266.6×10^{-8} "	5.400×10^{-6}

TABLE X.

Temp.	Concentration.	Spec. Conductivity.
25°C	Water	3.000×10^{-6}
"	$44.4 \times 10^{-7} \text{N AgNO}_3$	3.733×10^{-6}
"	AgNO ₃ sol. along with $4.4 \times 10^{-8} \text{N HCl}$	3.932×10^{-6}
"	8.8×10^{-8} "	4.500×10^{-6}
"	17.7×10^{-8} "	4.879×10^{-6}
"	84.4×10^{-8} "	5.226×10^{-6}
"	173.3×10^{-8} "	5.364×10^{-6}

Tables V, IX and the corresponding curves given in Figs. VII, VIII, IX, X, and XI, shew that the same effect was noticeable throughout until a silver nitrate solution of normality 39.5×10^{-7} was reached after which it was not observed, i.e., with concentrations above this the conductivity steadily increased with the addition of $\frac{\text{N}}{10000}$ HCl as will be seen from the measurements which are recorded in table X and illustrated in Fig. XII.

Experiment V.—A silver chloride solution was made by adding HCl to AgNO₃. This was passed through a filter paper, and the precipitate washed with distilled water in order to remove the hydrochloric and nitric acid. The precipitate was then transferred to a beaker containing a small quantity of distilled water. This solution was then added drop by drop to 76 cc. of distilled water until the conductivity of the resulting solution had increased by an amount corresponding to the increase in the previous case with AgNO₃. Then to this solution of AgCl there was added drop by drop a $\frac{\text{N}}{100}$ solution of HNO₃, and the conductivities taken as before. Tables XI, XII, XIII and the curves given in Figs. XIII, XIV and XV shew the variation in conductivity as obtained when a $\frac{\text{N}}{10000}$ nitric acid solution was added to different concentrations of the silver chloride solution.

TABLE XI

Temp.	Concentration.	Spec. Conductivity.
25°C	Water	2.189×10^{-6}
"	AgCl solution	2.304×10^{-6}
"	AgCl sol. along with $4.4 \times 10^{-8} \text{N HNO}_3$	2.219×10^{-6}
"	8.8×10^{-8} "	2.213×10^{-6}
"	13.2×10^{-8} "	2.282×10^{-6}
"	22.2×10^{-8} "	2.314×10^{-6}
"	66.6×10^{-8} "	2.348×10^{-6}
"	133.2×10^{-8} "	2.571×10^{-6}
"	222.2×10^{-8} "	2.842×10^{-6}

TABLE XII

Temp.	Concentration	Spec. Conductivity.
25°C	Water	2.120×10^{-6}
"	AgCl solution	2.439×10^{-6}
"	AgCl sol. along with $4.4 \times 10^{-8} \text{N HNO}_3$	2.299×10^{-6}
"	8.8×10^{-8} "	2.294×10^{-6}
"	13.3×10^{-8} "	2.256×10^{-6}
"	22.2×10^{-8} "	2.347×10^{-6}
"	66.6×10^{-8} "	2.454×10^{-6}
"	133.3×10^{-8} "	2.632×10^{-6}
"	222.2×10^{-8} "	2.934×10^{-6}

TABLE XIII.

Temp.	Concentration.	Spec. Conductivity.
25°C	Water	2.700×10^{-6}
"	AgCl solution	3.368×10^{-6}
"	AgCl sol. along with $4.4 \times 10^{-8} \text{ n HNO}_3$	3.361×10^{-6}
"	8.8×10^{-8} "	3.286×10^{-6}
"	17.7×10^{-8} "	3.375×10^{-6}
"	44.4×10^{-8} "	3.448×10^{-6}
"	88.8×10^{-8} "	3.529×10^{-6}
"	155.5×10^{-8} "	3.682×10^{-6}
"	244.4×10^{-8} "	4.01×10^{-6}

From the above tables it will be seen that as a $\frac{N}{10000}$ solution of nitric acid was added to a dilute solution of silver chloride a drop in the conductivity of the solution occurred at first, but as the nitric acid became more concentrated the conductivity steadily increased.

Experiment VI.—To 75 cc. of redistilled water there was added one drop $\frac{1}{30}$ cc. $\frac{N}{10000}$ HCl, thus giving a 4.4×10^{-8} normal solution of hydrochloric acid. To this solution there was added drop by drop a $\frac{N}{1000}$ solution of AgNO_3 , and the corresponding conductivities were determined. The variation in conductivity for different concentrations of the silver nitrate is shewn in table XIV, and illustrated by the curve in Fig. XVI.

TABLE XIV.

Temp.	Concentration.	Spec. Conductivity.
25°C	Water	2.418×10^{-6}
"	$4.4 \times 10^{-8} \text{ n HCl}$	2.454×10^{-6}
"	HCl sol. along with $4.9 \times 10^{-7} \text{ n AgNO}_3$	2.383×10^{-6}
"	9.8×10^{-7} "	2.382×10^{-6}
"	24.5×10^{-7} "	2.454×10^{-6}
"	73.5×10^{-7} "	3.115×10^{-6}
"	147.0×10^{-7} "	4.197×10^{-6}
"	245.0×10^{-7} "	5.625×10^{-6}

Here again a drop in conductivity was noticeable as a $\frac{N}{1000}$ of AgNO_3 solution was added to a 4.4×10^{-8} normal solution of HCl .

This experiment was repeated, beginning with an 8.8×10^{-8} normal solution of HCl , and the results which are given in table XV are shewn graphically by the curve in Fig. XVII.

TABLE XV.

Temp.	Concentration.	Spec. Conductivity.
25°C	Water	2.05×10^{-6}
"	$8.8 \times 10^{-8} \text{ n HCl}$	2.05×10^{-6}
"	$\text{HCl sol. along with}$ $4.9 \times 10^{-7} \text{ n AgNO}_3$	2.05×10^{-6}
"	9.8×10^{-7} "	2.131×10^{-6}
"	24.5×10^{-7} "	2.531×10^{-6}
"	73.5×10^{-7} "	3.375×10^{-6}
"	147.0×10^{-7} "	4.625×10^{-6}
"	245.0×10^{-7} "	6.231×10^{-6}

In this case the conductivity remained stationary at first and then gradually increased with the amount of AgNO_3 present in the solution.

Experiment VII.—To 75 cc. of redistilled water there was added drop by drop a $\frac{N}{1000}$ solution of AgNO_3 . The specific conductivities for the different concentrations of AgNO_3 are given in table XVI, and a curve representing them in Fig. XVIII.

TABLE XVI.

Temp.	Concentration.	Spec. Conductivity.
25°C	Water	2.077×10^{-6}
"	$4.9 \times 10^{-7} \text{ n AgNO}_3$	2.189×10^{-6}
"	9.8×10^{-7} "	2.314×10^{-6}
"	24.5×10^{-7} "	2.745×10^{-6}
"	73.5×10^{-7} "	3.521×10^{-6}
"	147.0×10^{-7} "	4.765×10^{-6}
"	245.0×10^{-7} "	6.231×10^{-6}

From these values it will be seen that the conductivity of a silver nitrate solution steadily increased with the concentration.

Summary.—1. Tables I-III shew that as a $\frac{N}{10000}$ solution of HCl was added to water there was, at first, very little change in the conductivity of the solution, but as the HCl solution became more concentrated the conductivity gradually increased.

2. Tables IV-IX shew that on the addition of HCl to AgNO_3 of various dilutions a drop in the conductivity was observed. When, however, a 39.5×10^{-7} normal silver nitrate solution was reached this effect disappeared.

3. A similar drop in the conductivity was observed when a dilute nitric acid solution was added to a dilute silver chloride solution. Also, when a dilute silver nitric solution was added to a dilute solution of hydrochloric acid.

4. In the case of the silver nitrate solution (Experiment VII) the conductivity steadily increased with the concentration.

Explanation.—Two explanations may be given of the above phenomenon (1) The fact that, in Experiment III, the conductivity remains steady at first, may be due to the absorption of hydrogen by the platinum electrodes, and (2) The drop in conductivity indicated in Experiments IV, V, VI may be due to the hydrogen ion attracting to itself the neutral AgCl , and becoming loaded. Its mobility might, thereby, be decreased so as to have a value below that of the silver ion which it displaced.

Up to the present the results obtained are not sufficient to discriminate between these two explanations, and it is hoped that with additional observations the problem raised may be cleared up. In conclusion I wish to thank Mr. E. F. Burton for his kind assistance in the course of these experiments.

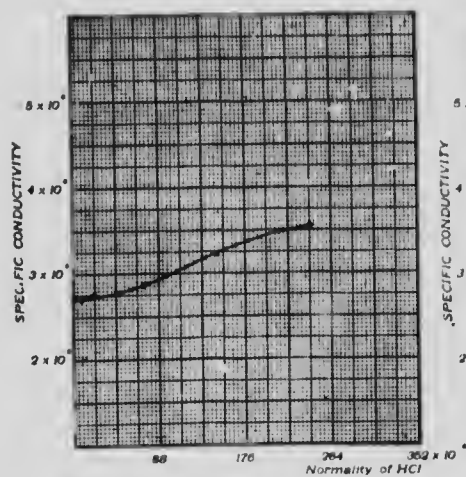


FIG. 3

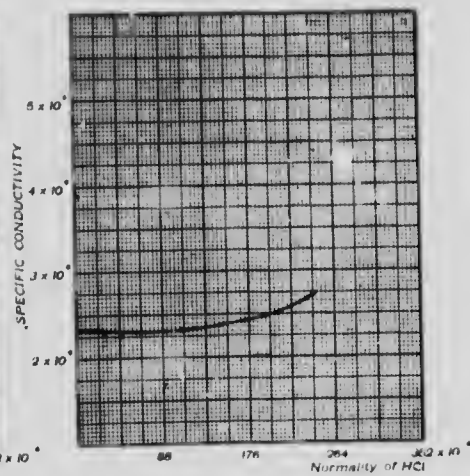


FIG. 4

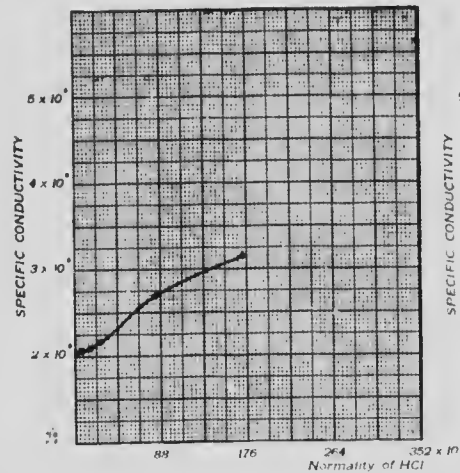


FIG. 5

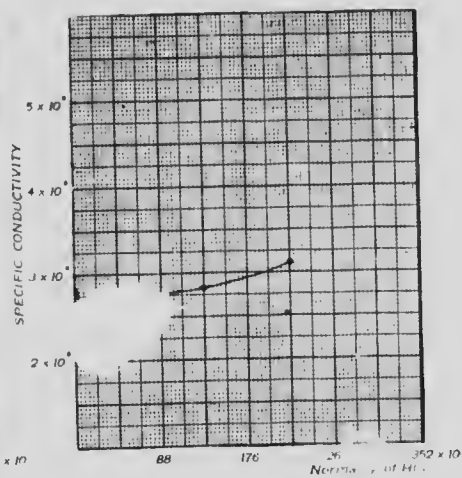


FIG. 6

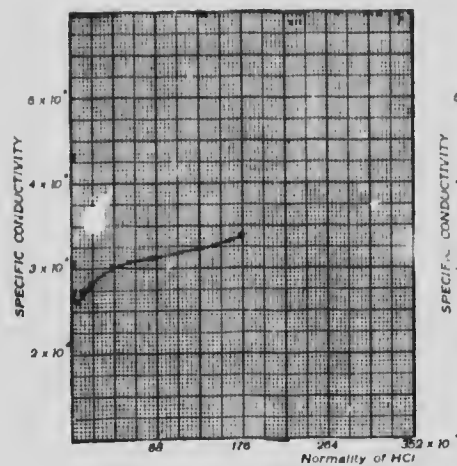


FIG. 7

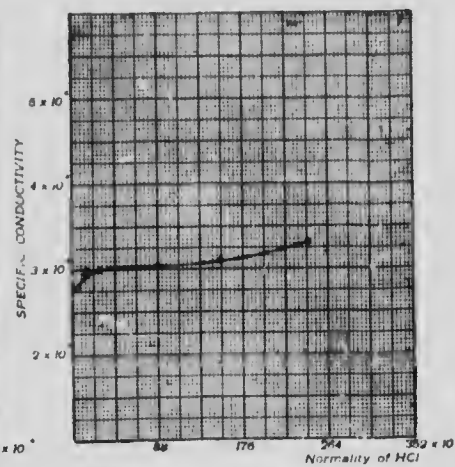


FIG. 8

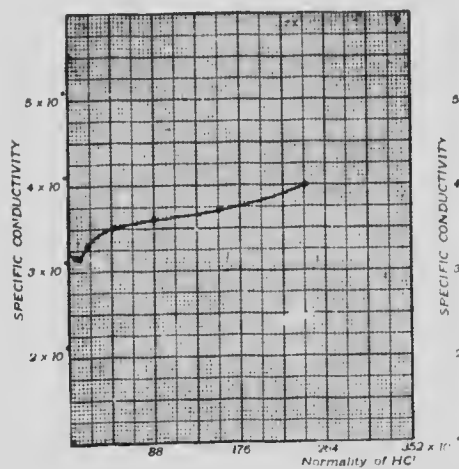


FIG. 9

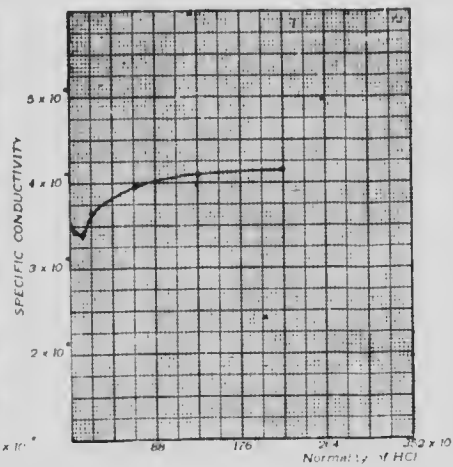


FIG. 10

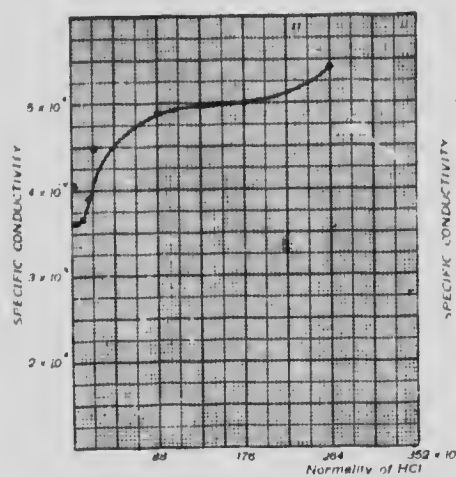


FIG 11

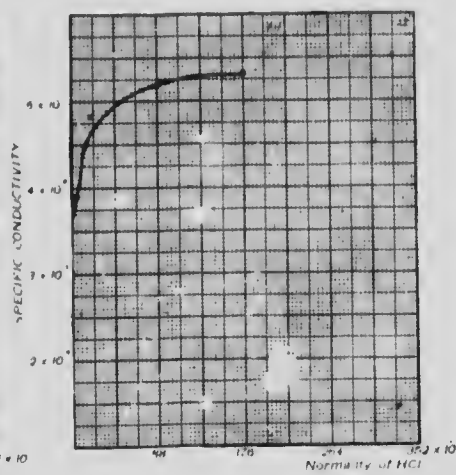


FIG 12

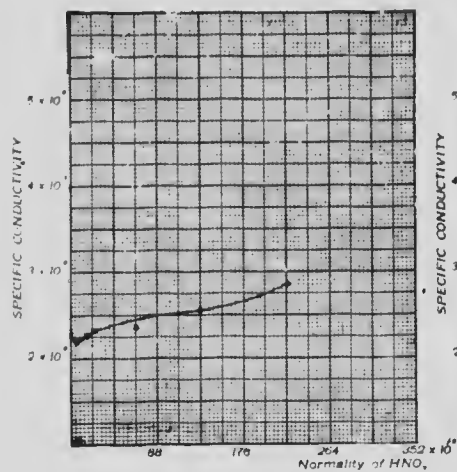


FIG 13

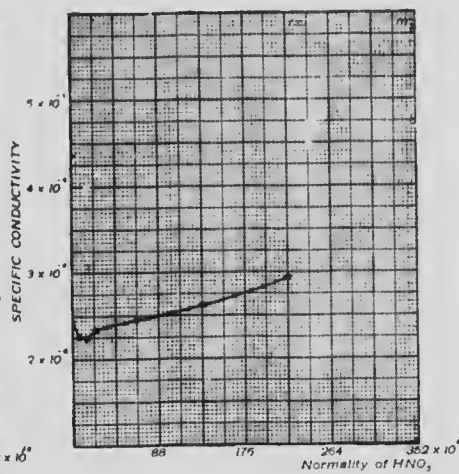


FIG 14

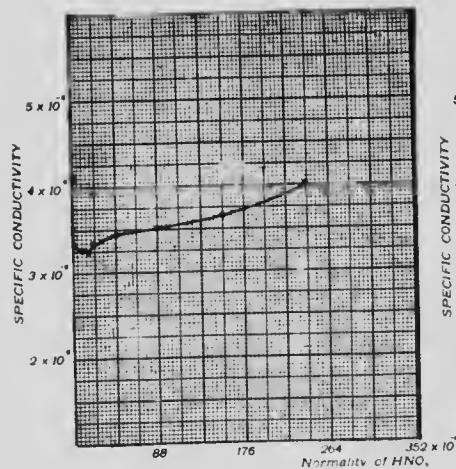


FIG 15

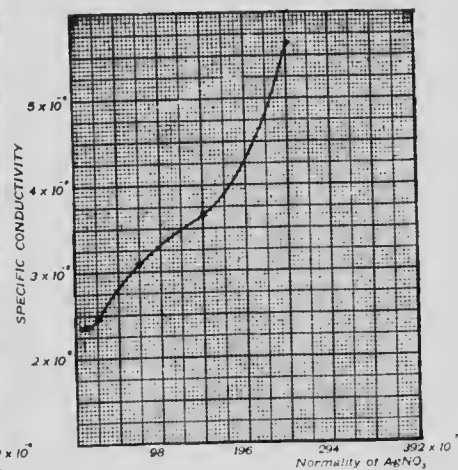


FIG 16

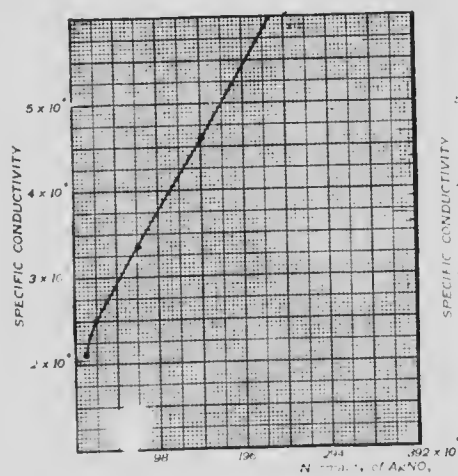


FIG 17

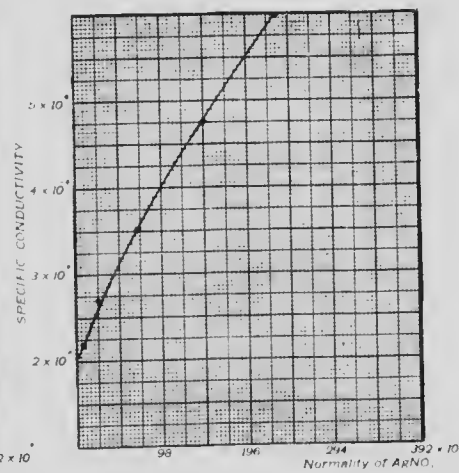


FIG 18

