which they have calculated.   This probably means that the degree of dissociation of picric acid in the presence of the acids is not merely dependent on the concentration of hydrogen ion.   Of the twelve different values obtained by the indicator method using different indicators and different comparison acids, only two lie outside the limits, and these are the only ones in which methyl green was used as an indicator.   The general conclusion may be drawn that a comparison of the results obtained with a number of different acids and different indicators will lead for simple solutions to values of the hydrogen ion concentration of reasonable reliability.

Using the same method, a determination of the hydroxide ion concentration in solutions of di-acid bases is now being carried out by one of the authors (L. H. G.).

The experimental work described in this article was done in the chemical laboratory of the University of Michigan.

CINCINNATI. OHIO. and ANN ARBOR, MICH.

THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF PLATINUM TETRAIODIDE AND OF IODINE IN ALCOHOL.

BY E. H. ARCHIBALD AND W. A. PATRICK.

It is evident that the study of non-aqueous solutions must be greatly extended before the mystery surrounding the phenomenon of solution can be satisfactorily explained.   Interesting examples of such solutions are those of the metallic iodides in ethyl alcohol.   The following pages contain an account of some measurements of the electrical conductivity of solutions of platinum tetraiodide and of iodine in ethyl alcohol.

Materials Used.

Iodine.—Kahlbaum's resublimed iodine was ground with a little potassium iodide and again sublimed.   This product, after being again carefully sublimed, gave the sample used in these experiments.

Platinum Tetraiodide.—Pure platinum was prepared by the repeated precipitation of ammonium chloroplatinate.   From the pure platinum a solution of chloroplatinic acid was prepared and the platinum thrown down as the iodide with iodine and sodium iodide.

Ethyl Alcohol.—Kahlbaum's absolute alcohol was boiled for several hours with a large excess of pure calcium oxide and distilled.   It was then allowed to stand for two days, with frequent shaking, over anhydrous copper sulfate.   It was then distilled, reserving for the experiment only the middle portion of the distillate.   This alcohol had a specific conductivity of 2.6×10^{-8} reciprocal ohms at $25°$.   If allowed to stand in contact with the air for only a few moments, its conductivity would *increase* tenfold.

Methyl Alcohol.—This alcohol was purified in the same way as the above, its specific conductivity was somewhat greater than that of the ethyl alcohol.

The conductivities of the above alcohols indicated that they were remarkably free from water. Every care was exercised to prevent the air of the laboratory from coming in contact with the pure solvents, or any of the solutions that would be appreciably affected thereby.

Apparatus Used.

The method of measuring conductivity was that of Kohlrausch. The bridge wire was carefully calibrated. Conductivity cells of the usual form were used, their constants being determined by means of 0.02 N potassium chloride. The temperature of the bath in which the electrolytic cells were kept was maintained at $25°. \pm 0.05$ by means of the usual regulator, the water in the bath being stirred by means of an electric motor. In the case of the measurements taken at $0°$, the cells were placed in large felt-wound vessels which were filled with crushed ice.

The results obtained for the conductivity of the platinum iodide solutions in ethyl alcohol are shown in the following table. Under the term dilution are given the number of liters containing one equivalent or onefourth of a gram-molecule of the iodide ($^1/_4PtI_4$). The conductivity values are expressed in reciprocal ohms and refer to a temperature of $25°$:

SOLUTIONS OF PLATINUM IODIDE IN ETHYL ALCOHOL.

Dilution.	Specific conductivity.	Equivalent conductivity.
10.0	0.00145	14.5
20.0	0.000815	16.3
40.0	0.000450	18.12
80.0	0.000250	20.00
160.0	0.000137	21.90
320.0	0.0000735	23.5
640.0	0.0000384	24.6
1280.0	0.0000192	24.6

The conductivity is here large, compared with the conductivity of most substances in organic solvents being for instance considerably greater than the conductivity of alcoholic solutions of cadmium iodide, as measured by Jones and Carroll.[1] The conductivity of the most concentrated solution is a little greater than that of 0.01 N potassium chloride, and this notwithstanding the fact that the particles which carry the current are probably ions with relatively low migration velocities.

The equivalent conductivity increases with the dilution as is the case with almost all aqueous solutions, and it is particularly interesting to note that the equivalent conductivity becomes constant at great dilutions, which is the case with but few non-aqueous solutions. If we as-

[1] *Am. Chem. J.*, 32, 527 (1904).

sume that this constancy indicates that the dissociation is practically complete—a supposition we are continually making in the case of water solutions—and calculate the ionization coefficient for an 0.0125 N solution we find that at this concentration the platinum iodide is over 80% dissociated.

In connection with the above experiments we thought it would be of some interest to determin whether solutions of iodine in alcohol conducted the electric current; and if so, what the nature of this conduction is.

Few, if any, observations have been made of the conductivity of solutions of iodine in alcohols. Bruner[1] has measured the electrical conductivity of solutions of iodine in nitrobenzene and finds that the conductivity increases with time.

It is well known that when iodine is dissolved in organic solvents, the color of the solutions may be either violet or brown. In the case of the alcohols the color is brown. A great many investigators have concerned themselves with this variation in color. Paterno and Nasini,[2] from molecular weight determinations of iodine in benzene, concluded that in dilute solutions the iodine was present as I_2, while in concentrated solutions the molecule varied between I_2 and I_3. Loeb,[3] from vapor tension measurements, found in the case of solutions of iodine in carbon disulphide, where the color is violet, a molecule varying from I_2 to I_3 while the brown ether solutions gave I_4 as the formula.

Gauthier and Charpy[4] considered that the difference in color was due to the formation of complex molecules. They laid stress upon the fact that brown solutions become violet when heated, while the violet solutions turn brown when cooled.

Beckmann,[5] Hertz,[6] and Nernst[7] found experimental data that indicated I_2 as the formula for the iodine molecule in all solvents. Krüss and Thiele[8] studied this question very thoroughly from various points of view. They came to the conclusion that the behavior of the iodine could be best explained by the difference in size of the iodine molecule; that is, by assuming that it existed as $(I_2)n$ but behaved as I_2 as far as molecular weight determinations were concerned.

Lachman[9] has shown that those solvents which give brown solutions

[1] *Bull. Acad. Sci., Cracow* (1907).

[2] *Ber.*, **21**, 2153.

[3] *Z. physik. Chem.*, **2**, 606 (1888).

[4] *Compt. rend.*, **110**, 189.

[5] *Z. physik. Chem.*, **5**, 76 (1890).

[6] *Ibid.*, **6**, 385 (1890).

[7] *Ibid.*, **6**, 16 (1890).

[8] *Z. anorg. Chem.*, **7**, 52 (1894).

[9] THIS JOURNAL, **25**, 50 (1903).

of iodine are unsaturated, if the oxygen be regarded as tetravalent. On the other hand, the violet solutions are formed with such solvents as hydrocarbons which may be regarded as having their affinities satisfied.

Hillebrand and Glascock[1] have concluded from measurements of the lowering of the freezing point produced by iodine in various solvents, that in the case of the brown solutions there is a compound formed between the iodine and the solvent, while in the case of the violet solutions no such compound is formed.

If we assume, following Lachman, or Hillebrand and Glascock, that in the case of the brown solutions a compound is formed between the iodine and the solvent, we might expect from the behavior of solutions of alcohols in liquid hydrogen bromide that the compound would ionize to some extent and form a conducting solution. Again if, as suggested by Le Blanc, the iodine molecule breaks up into oppositely charged ions we would expect an appreciable conductivity.

Experimental.

Solutions of iodine in ethyl alcohol, 0.1 N and 0.01 N, were prepared and their conductivities measured. It was very soon apparent that the conductivity was increasing rapidly with the time. Accordingly, measurements were made at short intervals until the conductivity became constant. The time required for this to take place was about 25 hrs. at 25°. It was evident that a reaction was going on which involved the formation of a substance having a considerable conductivity in the alcohol.

0.1 N solution.		0.01 N solution.	
Time in hours.	Specific cond.	Time in hours.	Specific cond.
0	4.39 × 10⁻⁵	0	0.213 × 10⁻⁵
0.133	8.75 "	0.050	0.222 "
0.216	11.55 "	0.133	0.555 "
0.300	13.71 "	0.216	1.02 "
0.417	16.9 "	0.350	1.61 "
0.500	21.4 "	0.450	2.13 "
0.666	24.1 "	0.566	2.44 "
0.834	28.9 "	0.734	3.15 "
1.00	34.5 "	0.900	4.06 "
1.17	40.5 "	1.07	4.88 "
1.55	58.1 "	1.45	7.10 "
1.75	68.0 "	1.65	8.35 "
1.93	79.0 "	1.84	9.15 "
3.83	148.0 "	3.75	17.05 "
6.92	164.1 "	8.80	21.7 "
8.08	170.2 "	17.98	24.4 "
21.3	184.2 "	21.18	24.5 "
25.4	185.1 "	25.64	24.6 "

[1] THIS JOURNAL, 31, 26 (1909).

The values of the conductivity which show the rate at which the re-action was taking place in the case of the two solutions examined are given above. The conductivities are expressed in terms of reciprocal ohms.

The above values are shown graphically in Fig. 1, where the conductivities are plotted as ordinates, and time as abscissae. We notice that while in the case of the more concentrated solution the final value is much the greater, both attained their maximum value in about the same time.

Fig. I
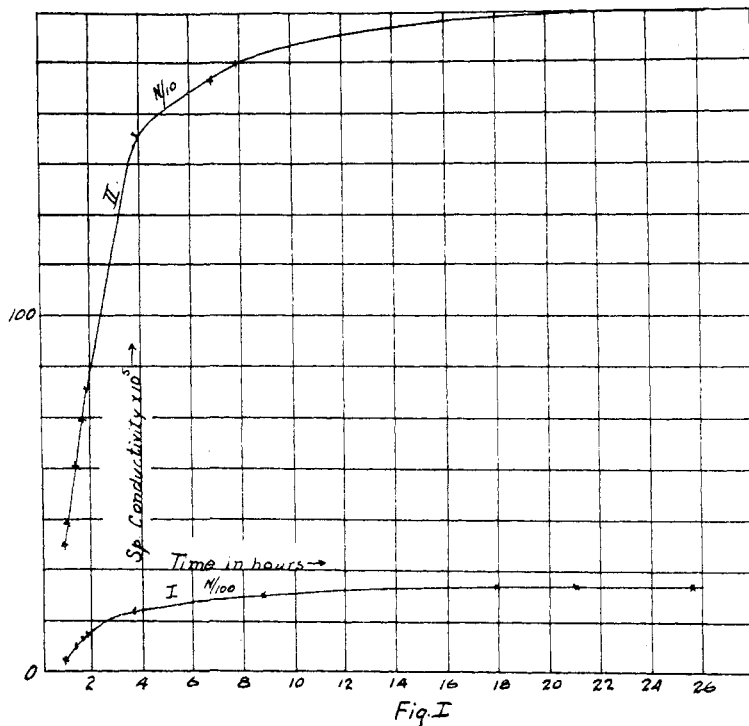
To ascertain whether this reaction was caused by the platinum black of the electrodes, two sets of solutions of the same concentration as those described above were made up. In one set a very small amount of platinum black was placed, but none in the other. After 25 hrs. the conductivities of all were measured, and those in which the platinum black had been had the same conductivity as the two solutions previously examined, while the set that had not been in contact with the platinum black had only very small conducting power, not much greater than what seems to be the initial conductivity of the iodine. Obviously the reaction had not taken place to any extent in the absence of the platinum black. Krüss and Thiele[1] have found that iodine reacts with alcohol at high tempera-

[1] *Loc. cit.*

tures. It may be that this is the same reaction, the velocity of which is increased enormously at low temperatures by the platinum black.

As might be expected as a result of this reaction, the color of the solution becomes much lighter.

The effect of temperature on the reaction was next examined. At 0° the conductivity of a newly prepared solution increased only very slowly with time, so slowly that at this temperature it was possible to carry out the measurements of the initial conductivity of the iodine. At —78° the conductivity did not change appreciably upon standing in contact with the platinum black for 45 minutes.

The following values were obtained by measuring the conductivity of the iodine in ethyl alcohol at 0°. The solutions were made up and measured as quickly as possible, the alcohol being cooled to 0° before introducing the iodine. The alcohol used was as pure as we could prepare. Following the usual procedure in the case of aqueous solutions, we have subtracted the conductivity of the pure alcohol from that of the solution in order to arrive more nearly at the conductivity of the iodine. We recognize, of course, that in the case of either type of solution, this is a questionable method of procedure.

Concentration of solution.	Specific conductivity.	Equivalent conductivity.
0.1 N	2.36 × 10⁻⁶	0.0236
0.02 N	0.82 "	0.0413
0.01 N	0.67 "	0.0677

It is apparent from these measurements that the conductivity of the iodine in these solutions is very small. It may be asked if impurities present in either substance would not account for this observed increase in conductivity. In reply we can only say that each substance has been repeatedly treated in order to further purify it, and always gives the same conductivity.

It will be noted that the equivalent conductivity is increasing with the dilution, as is usually the case with aqueous solutions.

Measurements were also made of the conductivity of iodine in methyl alcohol. The measurements indicate a somewhat greater conductivity than in the case of the ethyl alcohol, with the same variation between the conductivity and the concentration, as shown above.

Bray has found the specific conductivity of aqueous solutions of iodine after they have stood for 15 minutes to be 3.8 × 10⁻⁶ which is of the same order, but a little greater than the above values.

A newly prepared solution of iodine in ethyl alcohol was tested as to its conductivity at 0°, then gradually cooled to —78°. Its conductivity continually decreased as the temperature fell, and no further indication could be found of a compound being formed even at this low temperature.

The conductivity of some very pure toluene was measured, and a solution of iodine prepared in this solvent, but not the slightest increase in conductivity due to the iodine present could be detected.

It seems not unlikely that the feeble conducting power of the alcoholic solutions of iodine, when first prepared, which are brown in color, is due to the dissociation of a compound formed between the alcohol and iodine. This compound is probably dissociated, however, only to a very small extent.

Summary.

(1) The conductivity of solutions of platinum tetraiodide in ethyl alcohol have been measured.

(2) The molecular conductivity of these solutions increases with the dilution and attains a constant value at dilutions of about 600 liters.

(3) The conductivity of solutions of iodine in alcohol increases with the time reaching a maximum value in about 25 hours.

(4) The velocity of the reaction which probably accounts for this increase in conductivity is greatly accelerated by the presence of platinum black.

(5) The initial specific conductivity of 0.1 N iodine in ethyl alcohol amounts to 2.4×10^{-6} reciprocal ohms.

(6) It is suggested that the brown color of the alcoholic solutions of iodine is due to the formation of a compound between the solvent and solute which is feebly ionized, giving the low initial conductivity observed.

SYRACUSE UNIVERSITY. SYRACUSE, N. Y.

CONTRIBUTIONS TO THE ELECTROCHEMISTRY OF HYDRONITRIC ACID AND ITS SALTS. II. THE REDUCTION OF HYDRO-NITRIC ACID BY CUPROUS OXIDE.

BY J. W. TURRENTINE AND RAYMOND L. MOORE.

In a previous communication[1] it was shown that corrosion efficiencies exceeding 100% were obtained when the metals magnesium, aluminium and zinc were made anode in a 2% sodium trinitride solution. In some instances the efficiencies approached 200%, the calculations being based on the cathode values obtained from a copper coulometer, and on the electrochemical equivalents of those metals computed from the valence normally displayed by them.

To account for the anomalously large values obtained under the conditions existing in these experiments, it was deemed plausible to hypothesize for those elements electrochemical equivalents twice as large as those ordinarily attributed to them. To do so it was necessary to consider them as dissolving electrochemically as metals of a lower valence. Thus,

---

[1] THIS JOURNAL, 33, 803 (1911).