in Table V, where the amount of glucose adsorbed, when present alone in quantities of 2 to 3% would be much larger than 0.05%, since 0.09% is adsorbed at an initial concentration of 0.46%.

We wish to express our thanks to Mr. W. Leitch, of Joseph Bakers, Ltd., White Plains, N. Y., for his help in procuring the Norit. We also wish to thank Mr. Robert Whymper, Bermondsey, London, S. E., for his kind and valued advice.

MILWAUKEE, WISCONSIN.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF ILLINOIS.]

DETERMINATION OF THE ELECTROLYTIC POTENTIAL AND OVERVOLTAGE OF ARSENIC.

BY VINCENT B. MARQUIS.

Received May 18, 1920.

1. Electrolytic Potential.

The electrolytic potential of arsenic, or the potential between an arsenic electrode and a solution normal with respect to arsenious ions, has never been accurately determined because of the difficulty of determining the arsenious ion concentrations. In aqueous solution arsenious salts are strongly hydrolyzed and the metal ion concentration cannot be determined by conductivity measurements because of the presence of the acid which is formed by the hydrolysis. The conductivity of arsenious trichloride and hydrochloric acid solutions were measured by Zawidzki[1] with results as shown in the following table, in which *V* is the number of liters containing one mol and Λ the equivalent conductivity.

V.	Λ. $HCl + As(OH)_3$. 1/ohm.	Λ'. HCl. 1/ohm.	Λ' — Λ. 1/ohm.
16	366.3	368.5	+2.2
32	374.2	375.3	+1.0
64	379.6	379.2	—0.6

These results show clearly why conductivity measurements do not help in the determination of arsenious ion concentration. The ability of arsenious chloride to form arsenious cations has, however, been demonstrated by Kahlenberg and Lincoln[2] by measuring the conductivity of solutions of arsenious chloride in ethyl aceto-acetate and nitrobenzene.

The potential between an arsenic electrode and a normal solution of arsenious chloride was measured by B. Neumann[3] and found to be 0.550 volt. From this value it has been estimated by Abegg that the electrolytic potential of arsenic is +0.27 volt, using the scale in which hydro-

---

[1] Zawidzki, *Ber.*, **36**, 1434 (1903).

[2] Kahlenberg and Lincoln, *J. Phys. Chem.*, **3**, 28 (1899).

[3] Neumann, *Z. physik. Chem.*, **14**, 220 (1894).

gen is zero and potassium negative. From the same figures Wilsmore[1] estimates that the electrolytic potential is "less than —0.293 volt," taking potassium as positive.

In order to obviate the difficulty of finding the arsenious ion concentration it was decided to employ the method used by Roderburg for tungsten and also by Rideal for uranium. For the measurement of the electrolytic potential of uranium Rideal used a solution of uranium tetrachloride in ethyl alcohol. The salt is not rapidly hydrolyzed in cold solution and the metal ion concentration can be determined by conductivity measurements. The relation between the electrolytic potential in aqueous and alcoholic solutions is expressed by the following equation:

$$EP_w - EP_a = \frac{RT}{nF} \log \frac{P_w}{P_a}$$

in which EP_w and EP_a are the electrolytic potentials in water and alcohol, respectively, and P_w and P_a the solution pressures of the metal in each solution. According to Carrara and Agostini,[2] the value for the fraction P_w/P_a is the same for all metals and for copper and cadmium $EP_w - EP_a = 0.11$ volt. According to Roderburg the value for copper is 0.071 volt, and this value is also used by Rideal.

In the work described below dry arsenious chloride was dissolved in dry alcohol and the potential between this solution and an arsenic electrode was measured. The degree of ionization of the salt was determined by conductivity measurements and the electrolytic potential calculated by means of the Nernst equation.

In taking up this work the first thing to be determined was whether or not arsenious chloride is hydrolyzed by dry absolute alcohol. If such hydrolysis does take place, then it is clear that during the process the conductivity of the solution will gradually increase on account of the hydrochloric acid which is formed. The conductivity of a solution containing 0.0807 g. of arsenic trichloride in 50 cc. of alcohol was measured at different time intervals with results as shown in the following table. The temperature of the solution was 20°.

Time (after making the solution). Min.	Resistance. Ohms.
1	74.3
2	74.6
3	74.9
4	75.5
6	76.2
9	76.9
14	77.3
24	77.5
54	77.7

---

[1] Wilsmore, *Z. physik. Chem.*, 35, 318 (1900).

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

It will be seen from this table that the resistance instead of decreasing, as might be expected, slightly increased. This is explained by the fact that arsenious chloride forms an addition product with alcohol.[1] These results show that the change in arsenious ion concentration is slight and the solution quickly comes to equilibrium. The type of conductivity cell used permitted the exclusion of air so that no moisture was taken up by the solution during the experiment.

In order to determine the degree of ionization of arsenious chloride it was necessary to measure the conductivity of several solutions of increasing dilution so that the value of λ_∞, the molecular conductivity at infinite dilution, could be obtained by extrapolation. The conductivity measurements were made by the Kohlrausch method. The arsenic trichloride used was prepared by heating 40 parts of arsenious oxide with 100 parts of sulfuric acid to 100° and adding small pieces of fused sodium chloride. The arsenic trichloride was distilled off and redistilled from conc. sulfuric acid in order to make sure that it was dry. The absolute alcohol used was redistilled over calcium oxide. Its conductivity was 1.56×10^{-6}. The results are shown in the following table and are plotted in Fig. 1 according to the method suggested by Kohlrausch, where values of λ_1 are plotted as ordinates and $1/\sqrt[3]{\phi}$ (ϕ = volume in cc. in which one mol is dissolved) as abscissas. The values of λ shown below were corrected for the conductivity of the alcohol and give the average of several sets of readings in which both arsenious chloride prepared as described above and a sample furnished by E. H. Sargent Co. were used. There was good agreement between the readings obtained from these 2 samples of arsenious chloride.

Resistance. Ohms.	λ. 1/ohms.	$1/\sqrt[3]{\phi}$.
36.8	53.5	0.0303
61.0	64.6	0.0240
98.7	79.4	0.0191
113.9	87.0	0.0177
331.0	118.3	0.0110
606.0	127.2	0.0085

Original solution = 5.0340 g. of $AsCl_3$ per liter.
Temperature, 21°.
Conductivity of alcohol = 1.56×10^{-6}.
Cell constant = 0.05477.

The value for λ_∞ obtained by plotting these points and extending the curve to the axis is 155.0×1/ohms.

In order to measure the electrode potential of arsenic in an alcoholic solution it was necessary to prepare an alcoholic auxiliary electrode. The electrode used by Roderburg and Rideal consisted of mercury in

---

[1] Walden, *Z. physik. Chem.*, 43, 438 (1903).

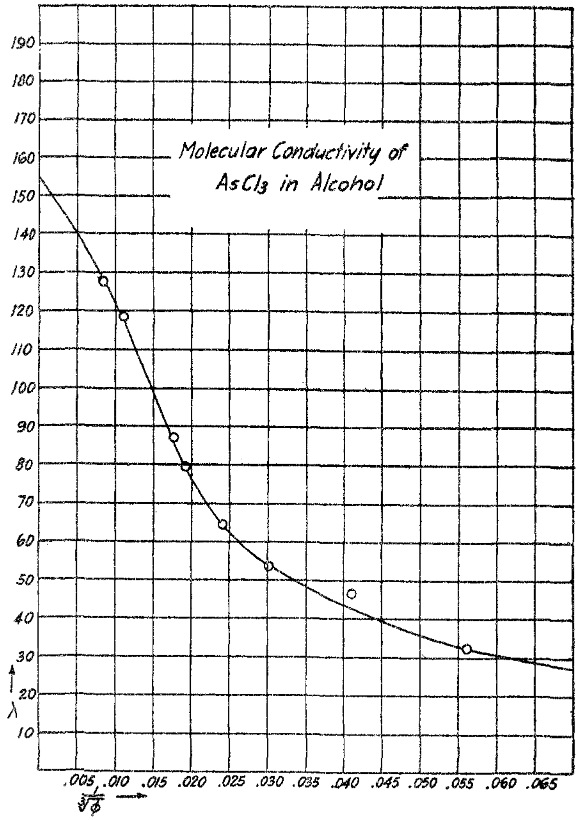

Fig. 1.

contact with alcohol saturated with mercurous chloride and lithium chloride. According to Roderburg the potential of this electrode is +0.193 volt. The arsenic electrodes used were copper plated with arsenic. For their preparation a solution of 5 g. of arsenious oxide in 300 cc. of 33% hydrochloric acid was electrolyzed with a current density of 0.15 ampere per square decimeter. The deposit of arsenic was smooth, bright, and in good physical condition. The following system, Hg/HgCl and LiCl in alc./$AsCl_3$ in alc./As, had an e. m. f. of 0.153 volt. Therefore the electrode potential of the arsenic was +0.040 volt. The potential between an arsenic electrode and an aqueous solution of the same arsenious ion concentration is found by adding 0.071 to this value, which gives 0.111 volt. The solution contained 0.176 mol. of arsenious chloride per liter and it was found by conductivity measurement that $\lambda = 32.0$. Therefore, $\alpha = \lambda/\lambda_\infty = 32.0/155.0 = 0.206$ and the arsenious ion concentration was $0.176 \times 0.206 = 0.0363$. By substitution in the Nernst equation,

$$e = e_0 + \frac{RT}{nF} \log \frac{C}{C_0}$$

the value $e_0 = +0.138$ volt is obtained. Therefore, the electrolytic potential of arsenic is +0.138 volt, using the scale in which hydrogen is zero and potassium negative. The measurement was repeated with a different arsenic electrode and a solution which contained 0.0704 mol of arsenious chloride per liter. In this case λ was found to be 46.6 and α 0.301. The calculated value for e_0 was the same in this case as in the first determination, namely, +0.138 volt, thus placing arsenic between hydrogen and copper in the electromotive series.

2. Overvoltage.

The overvoltage of hydrogen on arsenic was determined by measuring the back e. m. f., or polarization, of a cell which consisted of a platinum anode, an arsenic cathode made as described above, and a *N* sulfuric acid electrolyte. The area of each electrode was one square centimeter. A gradually increasing e. m. f. was applied to these electrodes until a milliammeter indicated that current was just beginning to flow through the cell, showing that decomposition of the electrolyte had just begun. The polarization of the cell caused by this impressed e. m. f. was measured and by means of an auxiliary calomel electrode the anode and cathode polarizations, or overvoltages, were determined separately. Measurements were made by both the open and closed circuit methods. In the former the back e. m. f. is measured while the circuit furnishing the applied e. m. f. is open. It is necessary to make the readings very quickly because depolarization begins as soon as the circuit is broken. In the closed circuit method the arm of the auxiliary electrode vessel is drawn out at the end to a small tube which is bent up to a horizontal position and placed so that it almost touches the cathode. In this way the internal resistance of the electrolyte is largely eliminated and the potential between the cathode and the calomel electrode can be measured without breaking the main circuit. The value for the overvoltage of hydrogen on arsenic obtained by the open circuit method was 0.379 volt, while that by the closed circuit method was 0.478 volt.

This work was suggested by Dr. E. K. Rideal and carried out under his direction. The author wishes to take this opportunity to thank him for his many helpful suggestions and criticisms.

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS.]

THE LIQUID AMMONIA-SODIUM METHOD FOR THE DETERMINATION OF HALOGEN IN ORGANIC COMPOUNDS.

BY F. B. DAINS AND R. Q. BREWSTER.

Received May 27, 1920.

The liquid ammonia-sodium method for the determination of halogens in organic compounds was first published by Chablay.[1] This method had been independently developed in this laboratory, as the result of some observations by Dr. H. P. Cady, and was later published by Dains,[2] Vaughan and Janney. The process consists in dissolving 0.1 to 0.2 g. of substance, accurately weighed, in 30 to 50 cc. of liquid ammonia and

---

[1] *Ann. chim. phys.*, [9] 1, 469–519 (1914).

[2] THIS JOURNAL, 40, 936 (1918).