

to doubt that the outcome of the present investigation, 39.114, really represents the atomic weight of potassium.

It is needless to point out that this change in the atomic weight of potassium will affect many other atomic weights.

Summary.

This investigation upon the atomic weight of potassium presents, among other considerations, the following additions to the knowledge of the subject :

(1) The problem of preparing pure potassium bromide was solved in two ways.

(2) An unusually satisfactory method for preparing pure potassium hydroxide was developed. This method is applicable to other alkalies, and will be described elsewhere in greater detail.

(3) The ratio of silver to potassium bromide was redetermined, and found to be 100.000 : 110.319. The atomic weight of potassium was thus found to be 39.1143, if silver is 107.930 and bromine 79.953.

(4) The ratio of silver bromide to potassium bromide was found to be 100.000 : 63.373. This determination yielded an essentially equal value, $K = 39.1135$.

(5) These values confirm in a striking manner the simultaneously executed work upon potassium chloride, and unite with them in showing that the atomic weight of potassium is 39.114.

(6) By thus agreeing, these four values support the new value for the atomic weight of chlorine in relation to silver and bromine.

REACTIONS IN LIQUID AMMONIA.¹ (POTASSIUM AMMONOZINCATE, CUPROUS NITRIDE AND AN AMMONOBASIC MERCURIC BROMIDE)

BY F. F. FITZGERALD.

Received January 20, 1907.

Introduction.

The close relation between the properties of water and liquid ammonia has been pointed out by Prof. E. C. Franklin². Of all well known solvents ammonia resembles water most closely in its properties. As water is to be regarded as a compound of H and OH ions, so analogously ammonia is to be looked upon as a compound of H and NH₂ ions. Acid amides and metallic amides are related to ammonia as the ordinary acids and bases are related to water. Franklin and Stafford have shown³ that acid amides and metallic amides react with each other to form a class of compounds which are related to ammonia as the ordinary oxygen salts are

¹ From the author's thesis submitted to the Department of Chemistry of the Leland Stanford Junior University for the degree of Masters of Arts.

² Am. Ch. J., 21, 8.

³ Ibid., 28, 83.

related to water; and recently Franklin has shown that potassium amide reacts with certain heavy metal salts to form compounds which he calls ammonobases and ammonobasic salts in a manner analogous to the precipitation of insoluble bases and basic salts from aqueous solutions.

The hydroxides of some metals are soluble in an excess of a stronger base to form a class of salts of which potassium zincate is an example. In the same way certain metallic amides were found by Franklin¹ to be soluble in an excess of an amide of a more basic element to form presumably the analogous ammono salts.

This investigation was undertaken with the especial object in view of preparing representatives of this latter class of compounds. However, before proceeding with this work it seemed desirable in order to become familiar with the somewhat difficult manipulations involved in working with such a solvent as liquid ammonia, to begin with some preliminary work in the way of clearing up certain observations which had been made in this laboratory concerning the action of potassium amide on copper nitrate and on mercuric bromide.

Reaction between Copper Nitrate ($Cu(NO_3)_2 \cdot 4NH_3$) and Potassium Amide.—The preparation of the potassium amide used in these experiments and the general method of manipulation here followed are the same as described by Franklin².

Copper nitrate dissolves abundantly in liquid ammonia to a clear blue solution. When potassium amide is added to this solution until the blue color is almost destroyed, a permanent, olive-green precipitate is obtained. This is a dense precipitate, which settles quickly and is easily washed. An excess of potassium amide completely dissolves the precipitate, forming probably an ammono salt of potassium analogous to the hydro salt, potassium zincate. The precipitate retains its olive-green color after washing. When the tube containing the preparation is heated and evacuated, the precipitate turns nearly pure black. The solution of this substance in hydrochloric acid fails to develop the blue color of the cupric ion, showing that the copper has been reduced from the cupric to the cuprous condition. If the copper is thus reduced, nitrogen must be set free in the reaction and in some of the experiments this was collected over very dilute sulphuric acid, measured and reduced to standard conditions. As a basis for calculation, the original weight of the copper nitrate used was taken because all of the copper which is reduced does not appear in the final weighed preparation, as some is mechanically lost in transferring the supernatant liquid over the precipitate from one leg of the preparation tube to the other. A considerable number of analyses of different preparations were made. At first the tubes were evacuated at

¹ This Journal, 27, 820.

² Ibid.

ordinary temperature and these gave results which corresponded with no definite compound. Two analyses follow:

1. 0.1432 gram of substance gave 0.0114 gram of nitrogen and 0.1278 gram of copper.

2. 0.1516 gram of substance gave 0.1373 gram of copper and 0.0120 gram of nitrogen.

Calculated for Cu_3N	Found	
	I	II
Cu = 93.14	89.24	90.60
N = 6.86	8.00	7.90
100.00	97.24	98.50

Afterwards specimens were dried *in vacuo* at ordinary temperature and then the temperature was raised and the gas which was given off was collected and proved to be ammonia. The evacuation of the tube containing the preparation was continued at the higher temperature until no more gas was given off. The analysis was conducted in the same manner as the analyses of the earlier preparations. The substance was dissolved in dilute hydrochloric acid, the bulk of the copper precipitated by metallic aluminium and the last traces by hydrogen sulphide. The combined precipitate was then dissolved in nitric acid and the copper deposited electrolytically. The nitrogen was determined in the filtrate by distillation with potassium hydroxide and titration with standard solutions. The treatment and behavior of each preparation is as follows:

I. This preparation was heated to a maximum temperature of 160° . The weight of the sample was unfortunately not taken, but the following data were obtained. Weight of copper deposited, 0.1950 gram. Weight of nitrogen, 0.0149 gram. The atomic ratio of copper to nitrogen in the preparation was therefore 2.91 to 1.

II. When 0.8900 gram of $Cu(NO_3)_{2.4}NH_3$ was treated with potassium amide 0.0165 gram of nitrogen was set free, from which it follows that one atom of nitrogen was given off for every 2.95 atom of copper present in the original salt. The preparation was heated *in vacuo* to 160° . Of this 0.2143 gram gave 0.0154 gram nitrogen and 0.1997 gram copper.

III. From 0.8232 gram $Cu(NO_3)_{2.4}NH_3$, when treated with potassium amide, 0.0158 gram of free nitrogen was obtained from which the atomic ratio of the copper used to the nitrogen given off is calculated to be 2.89 to 1.

Of the final product heated *in vacuo* to 220° , 0.1693 gram¹ gave 0.0112 gram nitrogen and 0.1564 gram copper.

IV. Free nitrogen to the amount of 0.0167 gram was obtained by the

¹The weight of the sample as taken is probably too large, due perhaps to the introduction of spongy platinum or bits of glass in transferring the potassium amide solution into the salt solution. This chance of error had not been foreseen, and no provision for it had been made in the analysis.

action of potassium amide on 0.900 gram $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{NH}_3$, from which the ratio of the nitrogen given off to the copper used is calculated to be 1 to 2.97.

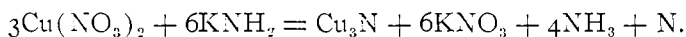
Unfortunately, the tube containing the final preparation exploded when the two legs of the apparatus were being sealed apart.

Preparation V. This preparation was heated to a maximum of 230° . 0.1328 gram of substance gave 0.0096 gram of nitrogen, and 0.1238 gram of copper.

Preparation VI. 0.1747 gram of substance freed of ammonia at 160° , gave 0.0120 gram of nitrogen and 0.1629 gram of copper.

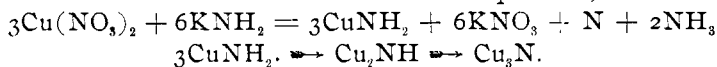
	Calculated for Cu_3N	II	III	Found	
				V	VI
N	6.86	7.2	6.6	7.2	6.87
Cu	93.14	93.2	92.4	93.2	93.20
	<u>100.00</u>	<u>100.4</u>	<u>99.0</u>	<u>100.4</u>	<u>100.07</u>

Cuprous nitride is therefore formed when the olive-green cuprous compound which is obtained by the reaction of potassium amide and copper nitrate is heated. It was obtained as a black amorphous mass. It is decomposed by water with the evolution of considerable heat. By sulphuric acid it is converted into equivalent quantities of cupric sulphate and metallic copper. It is completely soluble in hydrochloric acid. If heated in contact with the air, it is easily explosive but will stand considerable rise of temperature if heated *in vacuo*. The reaction is represented by the equation:



The fact that samples evacuated at ordinary temperature show a high content of nitrogen and a low content of copper makes it probable that the reaction takes place in at least two stages, and that the final reaction does not go to completion unless the substance be heated.

Not improbably the precipitate first formed is cuprous amide or imide which then loses ammonia as indicated in the equations,



The formation of cuprous nitride by the action of ammonia gas on cupric oxide was discovered by Schötter¹ in 1841. He describes it as a green compound which turned black on heating, but on account of the method of formation he was unable to obtain a pure sample for analysis.

Reaction between Mercuric Bromide and Potassium Amide. Mercuric Brom-nitride, Hg : N-Hg-Br.—Franklin tried the action of potassium amide upon an excess of mercuric bromide and obtained results which seemed to show the formation of a compound of the preceding formula². The following experiments were carried on to verify his

¹ Ann., 37, 144.

² This Journal. 27. 829.

conclusions. Potassium amide was added to a large excess of mercuric bromide. This resulted in the formation of a yellow precipitate mixed at the juncture of the two liquids with small quantities of mercuric nitride. The contents of the tube were thoroughly mixed and the preparation was allowed to stand for twenty-four hours in contact with the mother liquor, when the precipitate appeared as a light yellow, homogeneous precipitate, which was easily washed. This preparation is with difficulty soluble in hydrochloric acid. Samples I and II were dissolved in hydrochloric acid, the mercury was precipitated as the sulphide and the nitrogen distilled as ammonia from the filtrate. Sample IV was suspended in dilute sulphuric acid and fine granulated metallic zinc was then added. The mercury was thus precipitated as metallic mercury, which was afterwards dissolved and deposited electrolytically. The filtrate was divided into two portions. In one half the bromine was determined by precipitation as silver bromide and in the other half the nitrogen by distillation. In effecting solution of sample III, it was boiled for such a length of time with sulphuric acid that it was thought useless to attempt a determination of the bromine. By continued boiling the greater part of the sample went into solution. Nevertheless, there was a small amount of precipitate left in suspension.¹ The mercury was precipitated as the sulphide with this residue in suspension, and both were weighed as mercuric sulphide. This probably accounts for the high percentage of mercury found in this sample.

I. 0.1689 gram of substance gave 0.1576 gram of HgS and 0.0048 gram of nitrogen.

II. 0.1189 gram of substance gave 0.1115 gram of HgS and 0.0036 gram of nitrogen.

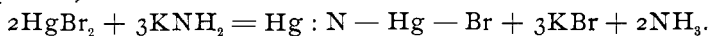
III. 0.1806 gram of substance gave 0.1709 gram of HgS.

IV. 0.2345 gram of substance gave 0.1895 gram of metallic mercury and $\frac{1}{2}$ of 0.2345 gram of substance gave 0.0036 gram of nitrogen and the other half gave 0.0452 gram of AgBr.

V. A fifth sample gave 3.25 per cent. nitrogen.

Calculated for Hg ₂ NBr		Found				
		I	II	III	IV	V
Hg	80.97	80.46	80.82	81.56	80.81
N	2.83	2.84	3.08	3.06	3.25
Br	16.20	16.38

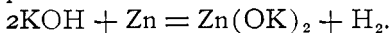
An ammonobasic bromide of mercury is therefore formed when potassium amide acts upon an excess of mercuric bromide in accordance with the equation,



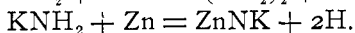
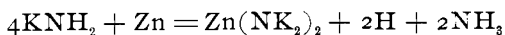
Action of Potassium Amide upon Metallic Zinc and upon Zinc Amide. Potassium Ammonozincate.—As indicated in the introduction to this paper, this investigation was undertaken to determine whether the analogy between the metallic derivatives of water and ammonia could be extended

¹ Probably mercurous bromide.

to the production of the ammonia analogues of that class of salts of which potassium zincate is an example. As is well known, potassium zincate is supposed to be formed¹ when potassium hydroxide acts upon metallic zinc. The "ideal" equation is as follows:



If the analogous reaction takes place when a liquid ammonia solution of potassium amide acts on metallic zinc, an ammonozincate of potassium should be formed in accordance with one of the following, or other obvious equations.



That potassium amide does act upon metallic zinc was found to be the case. Under ordinary conditions the action is slow, but if a small amount

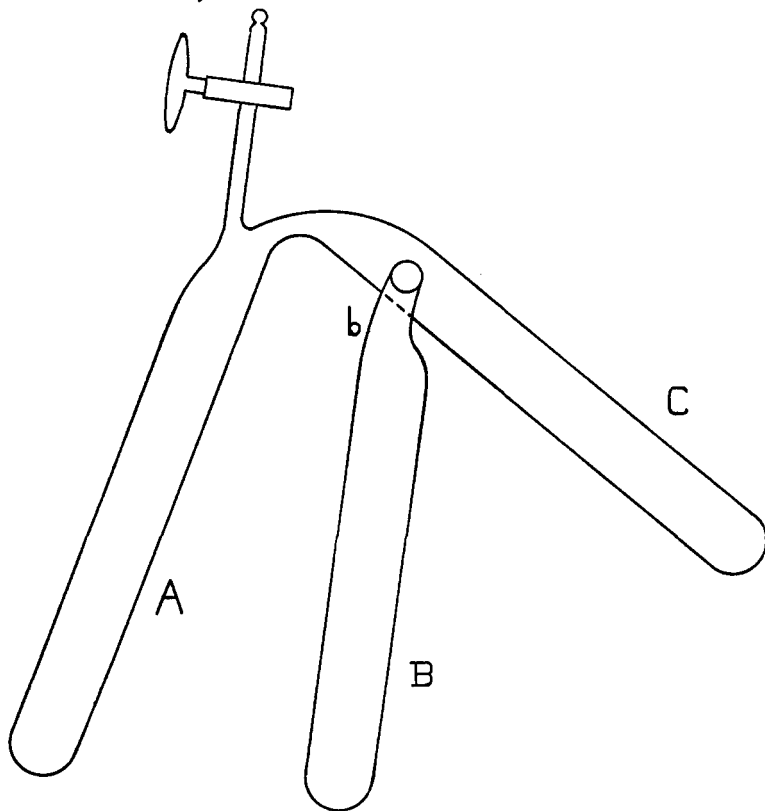


Figure I.

of platinum is alloyed with the zinc, the action is appreciably accelerated. In carrying out the experiment a three-legged tube was used as shown in figure I.

¹ Comey and Jackson : *Am. Ch. J.*, 11, 145.

The alloy in the form of finely divided turnings is placed in C and the potassium amide is prepared in B, in the same manner as in previous experiments. The potassium amide solution is then poured from leg B into leg C and allowed to stand in contact with the finely divided zinc. Hydrogen is given off, which would accumulate under great pressure were the stopcock not opened from time to time to permit its escape. At the end of a week the alloy which remains unacted upon is covered with a mass of beautiful, fine, colorless crystals. The excess of potassium amide is then washed back into B, the ammonia allowed to escape and the tube B sealed off at (b). Leg C is distilled three-fourths full of liquid ammonia and the salt transferred from the residue of zinc in leg C, to leg A by repeated solution and evaporation. The compound is not very soluble in liquid ammonia, but a fair specimen was obtained by 167 leachings continued through three days. The tube is sealed apart as before and the substance analyzed. For analysis the substance is dissolved in dilute hydrochloric acid and the solution divided into two parts. In one half the nitrogen is determined as before and in the other the zinc is precipitated by hydrogen sulphide, filtered, redissolved and reprecipitated as the carbonate. The potassium is determined in the filtrate as potassium chloride.

The treatment of two preparations follows:

Preparation I was heated to 160° , at which temperature it suffered no loss of weight. $\frac{1}{3}$ of 0.3909 gram of substance gave 0.0484 gram of nitrogen and the other half 0.0744 gram of zinc oxide and 0.1524 gram of potassium chloride.

Calculated for $Zn(NH_3)_2 \cdot 2KNH_2$		Found
Zn	31.5	30.6
K	37.7	40.9
N	27.0	24.8

Preparation II was heated to 160° with no loss of weight. On heating to 220° the sample lost ammonia and the analysis gave the following data. Weight of sample at 160° , 0.6127 gram; weight of sample at 220° , 0.5611 gram; difference, 0.0516 gram, was assumed to be ammonia, $\frac{1}{2}$ of 0.5611 gram of substance gave 0.1161 gram of zinc oxide and 0.2325 gram of potassium chloride, the other half gave 0.0559 gram of nitrogen.

Calculated for $Zn(NHK)_2 \cdot 2NH_3$		Found
Zn	34.2	33.2
K	41.1	43.5
N	22.1	19.93

If the original substance had been $Zn(NHK)_2 \cdot 2NH_3$ and it had lost one molecule of ammonia, the calculated loss would have been 8.2 per cent. The loss as found was 8.4 per cent. Assuming the loss in weight as ammonia and adding its nitrogen thus lost to the nitrogen later found in the substance, and taking the weight of the sample at 160° as a basis, the analysis calculates as follows:

Calculated for $Zn(NHK)_2 \cdot 2NH_3$		Found
Zn	31.5	30.41
K	37.7	39.82
N	27.0	25.2

Failing to obtain a good analysis from a compound prepared in this way, a second method was tried. From an aqueous solution of a zinc salt the hydroxide of zinc is precipitated by potassium hydroxide. On addition of an excess of potassium hydroxide, this precipitate goes into solution as potassium zincate. If the analogy between the behavior of the hydroxides and the amides holds in this case, potassium amide should dissolve zinc anide, or at least react with it to form a potassium ammono-zincate. The experiment was conducted as follows:

A tube is blown as shown in Figure 2. The leg B, which has the stopcock *c* attached to it, is drawn out and thickened at D so that the tube E may be sealed off at D while the apparatus is partially evacuated. The tube E is blown with a glass spiral spring so that it may be handled with little danger of breaking at D and has a stopcock F at its lower end. Potassium amide is prepared in leg A as before and the ammonia is al-

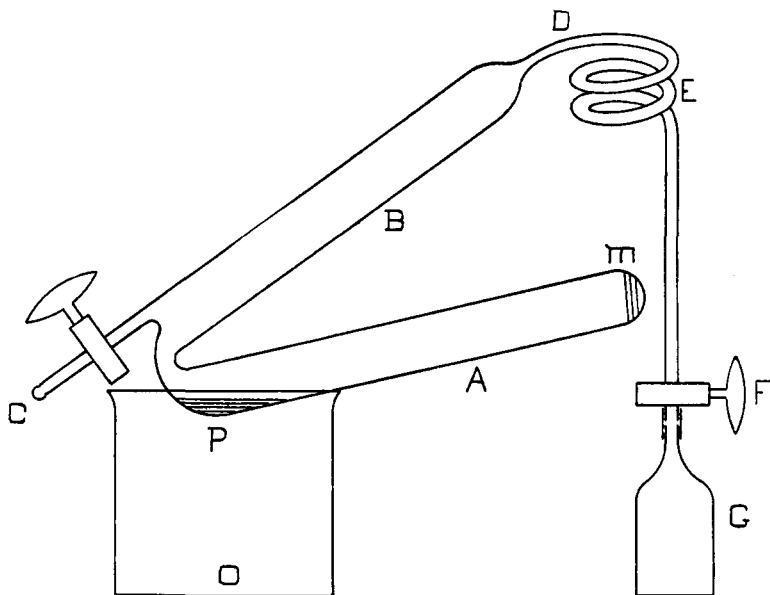


Figure II.

lowed to escape, leaving the solid potassium amide in the lower part of the leg at *m*. The apparatus at *C* is then attached to a water pump and the tube evacuated. The stopcock, *C*, is then closed and a bottle containing zinc ethyl, *G*, is attached to the tube, *E*, as shown in the figure and stopcock, *F*, opened. The bottle, *G*, is then placed in warm water and the

tube is cooled at *p* by the beaker *o*, of ice water. In this way zinc ethyl is distilled from *G* to *p*. When a sufficient quantity has been distilled over, *F* and *C* are closed and *E* sealed off at *D*. The zinc ethyl is then carefully poured into leg *B*. The tube *c* is connected with the cylinder containing the stock of ammonia and the gas allowed to react with the zinc ethyl, which it does in accordance with the equation of Frankland, $\text{Zn}(\text{C}_2\text{H}_5)_2 + 2\text{NH}_3 = \text{Zn}(\text{NH}_2)_2 + 2\text{C}_2\text{H}_6$. The accumulating ethane is permitted to escape by temporarily opening stopcock, *C*, as desired. When the reaction is complete, the zinc amide appears as a solid white mass. Liquid ammonia is then distilled into the tube and the potassium amide solution poured into leg *B*. The potassium amide solution changes the zinc amide immediately to a flocculent precipitate, which if left to stand overnight is converted into a mass of colorless crystals. The analysis of the substance was conducted as before.

$\frac{1}{2}$ of 0.3072 gram of substance gave 0.0399 gram of nitrogen and the other half 0.0603 gram of zinc oxide and 0.1155 gram of potassium chloride.

Calculated for	$\text{Zn}(\text{NHK})_2 \cdot 2\text{NH}_3$	Found
N	27.0	26.0
Zn	31.5	31.5
K	37.7	39.4
	<hr/> 96.2	<hr/> 96.9

Unfortunately, the analytical results do not point to any simple definite compound. The specimens were beautiful, were apparently pure and were well crystallized. It does not seem probable that the analytical results were vitiated by an impurity of the substance. However, the work shows two things. First, that metallic zinc is acted upon by potassium amide with the evolution of hydrogen and the formation of an ammonio potassium zincate; and second, that potassium amide acts on zinc amide to form the same compound. This potassium ammonio zincate appears as a colorless crystalline substance. It is but slightly soluble in ammonia, is decomposed by water with the evolution of heat into zinc hydroxide, ammonia and potassium hydroxide and is easily soluble in hydrochloric acid. It remains unchanged at a temperature of 160° but at about 220° loses ammonia to about 8.5 per cent. of its original weight.

The preparation of hydro-alkaline zincates has been attempted by a number of investigators who have reported compounds of widely different composition¹. As examples of the calculated formulas, the following may be given: $\text{Zn}_3\text{O}_6 \cdot \text{Na}_4 \cdot \text{H}_2 \cdot 17\text{H}_2\text{O}$, $2\text{Zn}(\text{OH})(\text{ONa}) \cdot 7\text{H}_2\text{O}$, $\text{ZnO}_2 \cdot \text{K}_2 \cdot \text{ZnO}$ and $\text{Zn}(\text{OK})_2$.

SUMMARY.

The experiments described in this paper show that in liquid ammonia solutions—

¹ Comey and Jackson, *Am. Ch. J.*, 11, 145.

1. Cuprous nitride is formed by the action of potassium amide on a liquid ammonia solution of cupric nitrate.
2. The ammono basic mercuric bromide, $\text{Hg} : \text{N} - \text{Hg} - \text{Br}$, is formed by the action of potassium amide on an excess of mercuric bromide.
3. Metallic zinc is acted upon by a liquid ammonia solution of potassium amide in a manner analogous to the action of an aqueous solution of potassium hydroxide, to form a well crystallized ammono-zincate of potassium.
4. The same compound is formed by the action of a solution of potassium amide on zinc amide.

This work was carried on in the laboratory of Stanford University at the suggestion and under the direction of Prof. E. C. Franklin. The earthquake of April 18th unfortunately interfered with further investigation upon the formation of the ammono-zincate of potassium.

THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF THE ALCOHOLS IN LIQUID HYDROGEN BROMIDE.

BY E. H. ARCHIBALD.
Received January 18, 1907.

Introduction.

It has been shown by Steele, McIntosh and Archibald¹, that a large number of organic substances dissolve in the liquid halogen hydrides to give solutions which conduct the electric current. In the case of all the substances examined it was found that, as distinguished from aqueous solutions of inorganic substances, the molecular conductivity decreased rapidly as the dilution increased. The results given in the above paper included observations on a typical member of several classes of organic substances, but no attempt was made to study any one class as a whole.

The interesting variation of molecular conductivity with dilution, alluded to above, seemed to warrant a more detailed and somewhat more accurate study of solutions of several classes of these substances, particularly as regards the conductivity of the more dilute solutions. Accordingly a more or less complete study has been made of solutions of the alcohols in liquid hydrogen bromide and the results obtained are described in the following pages.

Apparatus.—In order that the conductivity of a dilute solution which had a high resistance might be measured with some degree of accuracy, it was necessary that the electrodes of the conductivity cell should be comparatively large and that the distance between them should be relatively short.

These conditions are secured in the form of cell shown in Figure 1, which is of the ordinary "dip" variety. One electrode is sealed to the out-

¹ Phil. Trans., A. 205, 99 (1905).