

STUDIES ON THE IODINE COULOMETER

by

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INTRODUCTION

SUMMARY OF PREVIOUS INVESTIGATIONS ON THE IODINE COULOMETER.

The investigation of the iodine coulometer was begun by Herroun¹ in 1895. He electrolyzed zinc iodide between a platinum anode and a zinc cathode. The amount of iodine liberated at the anode was determined by titration with a standard solution of sodium thiosulphate. The sodium thiosulphate was standardized against a standard solution of iodine. Among the advantages of the iodine coulometer he pointed out the fact that dissolved oxygen, which diminished the yield at the cathode in other voltameters, will have no such action in a neutral solution of iodide; as the titration with standard solution of thiosulphate is a process of greater accuracy than the performance of the average balance, the exact determination of the amount of iodine liberated is both easy and rapid; the high electrochemical equivalent of iodine is also advantageous. Since he gave the results of only one electrolysis, the reproducibility of the method was not demonstrated.

As a part of another problem, Danneel² made a

comparison of Herroun's¹ zinc iodide coulometer and a silver coulometer. The amount of iodine liberated was determined by titration with standard thiosulphate. He does not state how the thiosulphate was standardized. The results of the four determinations which he reported show variations between \pm 0.3 to - 1.0 per cent. Danneel² regards the high electrochemical equivalent of silver and iodine as an advantage, so one would infer that he probably standardized the thiosulphate solutions against free iodine, by making up an appropriate iodine solution.

Kreider³ discredits Herroun's¹ remark by the following statement, "Herroun rather erroneously points to the high electrochemical equivalent of iodine as its chief advantage; this is obviously immaterial in a volumetric method". When thiosulphate solution is standardized against any substance except free iodine, Kreider's statement would be valid. But when thiosulphate solution is standardized against free iodine, as Herroun¹ did, then the high electrochemical equivalent of iodine is an advantage. Kreider³ used potassium iodide in place of zinc iodide since the former is commercially free from iodates and therefore can be acidified without

the liberation of iodine except for the action of atmospheric oxygen. Hydrochloric acid was used as the catholyte which prevented the accumulation of hydroxyl ions which upon migration to the anode region would produce a loss in iodine. The iodine was titrated with sodium thiosulphate which was standardized against arsenious oxide by means of an iodine solution. By means of a blank determination, he made a correction for the iodine liberated by atmospheric oxygen, in the acidified solution. He reports comparative tests with a filter-paper type silver coulometer. The iodine was from 0.06 per cent to 0.09 per cent high as calculated from the silver deposit. Kreider³ did not state the atomic weights used in his calculations but since his work was published early in 1905 he probably used the atomic weights of 1904. In 1904 the accepted atomic weight⁴ of arsenic was 75.0, that of silver was 107.93 and that of iodine was 126.85. Using these values along with the present (1934) atomic weights⁵ of arsenic (74.91), silver (107.880) and iodine (126.92) the iodine liberated was 0.10 per cent to 0.13 per cent high. This error may be due to the uncertainty of the correction made for the liberation of iodine by the atmospheric oxygen. Part of the error may

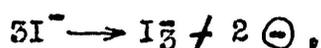
also be due to the use of arsenic trioxide in the standardization of the sodium thiosulphate solution. Baxter and Shaefer⁶ conclude that the composition of arsenic trioxide varies with the oxygen concentration prevailing during the sublimation and therefore is not suitable for use as an analytical standard of high precision. The error is probably not due to the use of the filter-paper type silver coulometer for the deposit in such a coulometer is abnormally high⁷, which would tend to make the equivalent amount of iodine liberated too low. The position of the platinum electrodes employed by Kreider³ probably caused the current density on the edges of the electrodes to be very high, thus accounting for the early liberation of gas at the anode.

Gallo⁸ used an iodine coulometer to determine the atomic weight of iodine. The platinum cathode, 4 square millimeters in area, was placed in the bottom of one limb of the apparatus and surrounded by solid iodine, which prevented the formation of the hydroxyl ion during the electrolysis. The platinum anode, 4 square millimeters in area, was placed half way up the other limb of the apparatus. The electrolyte was a solution of potassium iodide. Con-

tact between the two limbs was made by means of side arms which dipped into a wide mouth bottle. A current density of 0.1 ampere per square centimeter was used and the electrolysis was continued until 0.3 grams of iodine had been liberated. This was titrated by means of sodium thiosulphate solution. Gallo⁸ used porous-cup silver coulometers and made a correction of 0.018 per cent for inclusions in the silver deposit. Using the atomic weight of silver as 107.93, he found the atomic weight of iodine to be 126.89. The average deviation of 24 trials was 0.021 per cent and the maximum deviation was 0.075 per cent. Calculated on the basis of the accepted atomic weight of silver as 107.880 and making a correction of 0.004 per cent for inclusions in the silver deposit as recommended by Vinal and Bovard⁹, the atomic weight of iodine would be 126.81, a difference of 0.088 per cent from the accepted value 126.92.

Among the recent and more precise investigations of the iodine coulometer is that by Washburn and Bates¹⁰. Washburn and Bates used 10 per cent potassium iodide solution as electrolyte and surrounded the anode with a concentrated solution of potassium iodide and the cathode with a solution of iodine. They showed that

within the limit of error of the analysis, the same amount of iodine is formed from iodide at the anode as is converted into iodide ions at the cathode. Since identical amounts of iodine are involved in the reactions at both electrodes under varying conditions of concentration and current density, the only reaction involving electricity which occurs at the anode is represented by the following equation,



or a reaction or a set of reactions which are ultimately equivalent to this in the final analysis, which is, of course, just as satisfactory, for the value of the faraday does not depend upon the mechanism of the reaction but only upon the final result.

The reaction at the cathode would then be



or some reaction or set of reactions which are equivalent to this. Several iodine coulometers were used in series and the average deviation among the various coulometers and also the anode and cathode reactions was 0.002 per cent, thus indicating that the iodine coulometer is comparable to the silver coulometer in the determination of the fundamental constant, the faraday. They used a current density of 0.0015 am-

peres per square centimeter. The area of the anodes was 50 square centimeters. Hulett¹¹ calls attention to the high internal resistance of this iodine coulometer, which is obvious from the form of the coulometer.

Vinal and Bates¹² continued the work of Washburn and Bates¹⁰ and determined the value of the faraday by the use of the coulometer. Birge¹³ used the value of the ratio I/Ag, as determined by Vinal and Bates¹², to compute a value for the atomic weight of iodine and obtained 126.892, a value differing considerably from 126.932 which Birge accepted as correct to within 2 in the last place. He commented upon the work of Vinal and Bates¹² by saying, "This appears to be a relatively inaccurate determination of I". However, this work was never intended to be a determination of the atomic weight of iodine. The work of Vinal and Bates¹² gave a direct determination of the ratio of the iodine and silver deposits, but the agreement of calculated values for the Faraday from the iodine and silver deposits will evidently depend very largely on the value ultimately adopted for the atomic weight of iodine. It now appears that at least part of the discrepancy pointed out by Birge¹³, in 1929, was due to the value which he accepted as the atomic weight of iodine, since the present (1934)

accepted value of the atomic weight of iodine⁵ is 126.92. Should additional chemical research show that the atomic weight of iodine is about .02 per cent lower than the present accepted value, the calculated values of the Faraday from the iodine and silver deposits would be thrown into very close agreement. The value of the Faraday (96,515) obtained by Vinal and Bates¹², by using the atomic weight of iodine as 126.92, is about 0.02 per cent higher than that found by using the silver coulometer (96,494) and calculated by using the atomic weight as 107.880. In other words, the amount of iodine liberated in the iodine coulometer was about 0.02 per cent lower than the iodine equivalent of the silver deposited in the silver coulometer.

In the discussion of their apparatus, Vinal and Bates¹² state, "The anodes consist of a platinum-iridium alloy, it having been found that iodine is without appreciable effect on such an electrode, though one of pure platinum is attacked". No experimental data are given to verify this statement. An electromotive force of 240 volts was used to pass a current on one-fourth of an ampere through the circuit consisting of 4 silver coulometers, 3 iodine coulometers and the bal-

last resistance of about 400 ohms. From this statement one can estimate the approximate resistance of the iodine coulometer by assuming a reasonable resistance of the silver coulometers. The total resistance of the coulometers was about 560 ohms. Assuming 20 ohms as the resistance of the 4 silver coulometers (it is probably much less than that¹⁴) would make the resistance of the 3 iodine coulometers about 540 ohms, or about 180 ohms each.

Cady¹⁵ designed a more practical iodine coulometer. The anode and anolyte were the same as those used by Washburn and Bates¹⁰. A 10 per cent solution of sodium chloride was used between the anode and the cathode regions in place of a dilute solution of potassium iodide. He introduced the use of a copper cathode in place of a platinum cathode and discontinued the use of iodine around the cathode to prevent the formation of hydroxyl ions. By changing the form of the apparatus the effect of the hydroxyl ions in causing a loss of iodine was minimized (if not entirely eliminated) and at the same time the resistance of the coulometer was reduced very materially. The author of this paper found the resistance of one of these coulometers to be about 37 ohms.

PURPOSE OF THIS INVESTIGATION.

Due to the convenience of use of a titration coulometer and the capability of precision of this instrument, more information concerning such a coulometer would be desirable. Rarely is it necessary to use a coulometer with the precision attained by Washburn and Bates¹⁰, but a more convenient and less expensive form of coulometer than the silver coulometer with a precision of 0.1 to 0.01 per cent would be a valuable instrument.

This investigation included a study of the following factors bearing on such a coulometer:

1. The anodic behavior of platinum and platinum-iridium alloys in iodide solutions. Vinal and Bates¹² pointed out that platinum dissolves anodically in potassium iodide solutions, but an alloy of platinum-iridium does not. Such factors as the effect of concentration of iodide, current density and temperature upon the loss of platinum were investigated.

2. Specifications of an iodine coulometer which will permit at least 0.05 faradays to pass. The size of the anode, the volume of the anolyte and the permissible current densities were investigated.

3. Variation of the form and size of coulometer

with respect to a reduction of the internal resistance, economy of electrode material and simplicity of operation.

4. A study of the analytical factors involved in obtaining the desired precision. Comparative experiments were made by using three iodine coulometers in series. The analytical procedure was varied until the desired precision was obtained.

5. Comparison of the re-designed iodine coulometer with the silver coulometer as specified by the Bureau of Standards¹⁶.

6. The temperature coefficient of the iodine coulometer.

7. Variation of the nature of the catholyte.

8. Use of so-called C. P. materials in place of specially purified substances.

9. Range of current densities permissible.

PURIFICATION OF MATERIALS

WATER.

Water from which the several salts were re-crystallized and which was used in making up all of the solutions used in this investigation was prepared and stored in the following manner:

Distilled water from the stock tap was first distilled from potassium permanganate solution which was acidified with sulphuric acid, and then from a solution of barium hydroxide. A block tin condenser was used. The distilled water was stored in pyrex flasks which had been used for that purpose for several years. These were fitted with tin foil covered cork stoppers. In no case was water used which had been stored longer than three days. The conductance of the water was about 4×10^{-6} mhos. The water used was in no case alkaline to phenolphthalein nor acid to methyl red.

POTASSIUM IODIDE.

The potassium iodide used was obtained by re-crystallizing Merck's C. P. crystals until it was no longer alkaline to phenolphthalein¹⁷ The re-

crystallized salt was dried in an electric oven at 150° C and then heated to slightly above 400° C for 4 hours. It was stored in glass stoppered bottles which were kept over calcium chloride in a desiccator which was placed in a dark desk. The above product was shown to be free from iodates and other interfering oxidizing agents and reducing agents by the tests which are discussed below. Some of the salt was kept over a year and still met the above mentioned specifications when the following tests were repeated. When protected from strong light a 50 per cent solution of the iodide remained colorless for at least twenty-four hours, thus showing the absence of oxidizing agents in the neutral solution. Enough iodine was added to a freshly prepared 50 per cent solution of the iodide to produce a faint coloration. This coloration persisted for at least twenty-four hours, thus showing the absence of interfering reducing agents. No iodine was liberated from an acidified solution that had stood in diffused light in an atmosphere of natural gas for two hours, thus showing the absence of iodates¹⁷. If iodates had been present, iodine would have been liberated according to the equation



The above mentioned natural gas was washed before being used by passing it, in succession, through pyrogallic acid, water, potassium permanganate and water.

If the test for iodates is attempted in air, iodine might be liberated by the oxygen of the air according to the equation¹⁷



The latter reaction was verified in the following manner. After iodates had been shown not to be present in a sample of potassium iodide solution, air was admitted to the apparatus and after a few minutes iodine began to be set free. Upon bubbling air through the solution, the rate of liberation of iodine was increased.

During the summer of 1934, Mallinckrodt's, analytical reagent, potassium iodide was used in place of the above mentioned sample. It was purified and tested in the above mentioned manner and gave just as satisfactory results.

SODIUM CHLORIDE.

Two commonly used and widely advertised samples of C. P. quality sodium chloride were recrystallized

in one case as often as four times, until solutions of the samples were no longer alkaline to phenolphthalein nor acid to methyl red. In each case the recrystallized samples were free from oxidizing material as shown by their failure to set iodine free from a neutral solution of pure potassium iodide. They were also free from reducing agents as shown by their failure to reduce the free iodine in a solution of iodine in potassium iodide. But when a few drops of a fifty per cent potassium iodide solution were added to the above samples a trace of a very finely divided yellow precipitate, which remained suspended, was obtained. This appeared to be an iodide of a heavy metal. For this reason the above samples of salt were rejected.

One of the five methods which Richards¹⁸ used to obtain pure sodium chloride was by fractional crystallization of selected transparent colorless crystals of Strasfurt halite. This suggested another source of sodium chloride. Transparent colorless natural crystals of sodium chloride were obtained from the Carey Salt Mine, Hutchinson, Kansas. After one recrystallization, this sample of salt gave a neutral solution free from oxidizing and reducing

agents. Solutions of this salt did not give a yellow precipitate when a few drops of a fifty per cent potassium iodide solution were added. For this reason, the natural crystals of Kansas salt were used as the source of sodium chloride. This was recrystallized until it gave a neutral solution free from oxidizing and reducing agents.

HYDROCHLORIC ACID.

Baker's analyzed, special arsenic free, concentrated hydrochloric acid was diluted down to about two normal. No acid was used which gave a test for oxidizing material¹⁷, that is, produced free iodine when it was mixed with a solution of potassium iodide in an atmosphere of natural gas.

This test was hardly necessary when one remembers that the acid never came in contact with the anode solution. However, pure acid was needed in the test for iodates in potassium iodide.

SODIUM THIOSULPHATE.

Merck's C. P. crystals (alkali free) were dissolved in conductivity water. The solution was alkaline to methyl red and acid to phenolphthalein. An approximately N/2 solution was made up and filtered through

a fritted glass filter and stored¹⁷ in a bottle which was painted black and had been used for that purpose for several years. Special precautions were taken to avoid a change in concentration of this solution due to vaporization. When necessary it was standardized against iodine as discussed below. Near the end point the titration was finished by using a dilute solution prepared by properly diluting the N/2 solution as is discussed below.

During the summer of 1934, Mallinckrodt's, analytical reagent, sodium thiosulphate was used in place of the above mentioned sample.

IODINE.

Mallinckrodt's, analytical reagent, iodine was ground with potassium iodide (purified as described above) and sublimed. The iodine and potassium iodide were mixed in the ratio of 6 grams of iodine to 2 grams of iodide¹⁹. Then the sublimation was twice¹⁷ repeated without the use of potassium iodide. The final product was placed in a glass stoppered bottle and kept over calcium chloride in a greaseless desiccator, although from the work of Foulk and Morris²⁰ this hardly seems necessary.

The apparatus recommended by Mellor¹⁹ was used in each of the sublimations. Immediately before sublimation was begun the entire sublimation vessel was heated to 150° C in an electric oven for at least 30 minutes to make sure that it was dry. After cooling the apparatus in a large dessicator, it was assembled and the sublimation was begun.

SILVER NITRATE.

A saturated solution of silver nitrate was prepared at about 100° C. The solution was made slightly acid with dilute nitric acid. The hot concentrated solution was decanted off of the excess crystals and filtered through a fritted glass filter. Then a clean pyrex test tube (6" x 1"), which was kept cool by a stream of water flowing continuously through it, was inserted into the hot filtered solution. Immediately the silver nitrate began to crystallize out upon the test tube. The crop of crystals thus obtained was washed by decantation and then it was recrystallized from conductivity water a second time. This time the solution was not acidified.

The recrystallized silver nitrate from the second recrystallization was fused in a platinum dish, which

was lifted out of the oven as soon as the last trace of solid salt had melted. The temperature of the electric oven was kept between 230° C and 300° C, as recommended by the Bureau of Standards¹⁶, this being high enough to drive off the moisture and the excess of acid. Under these conditions the salt retains from 0.001 to 0.003 per cent of nitric acid which is more suitable than neutral salt. After the dish of fused salt was placed in a desiccator and permitted to cool it was tested for reducing impurities²¹. The salt met the specifications of the Bureau of Standards¹⁶ since it failed to reduce N/1000 potassium permanganate solution under the conditions specified by Rosa, Vinal and McDaniel²¹, and it gave a crystalline deposit free from striations. The silver nitrate was stored in a ground glass stoppered bottle in a desiccator over calcium chloride. Black paper was wrapped around the glass bottle to avoid decomposition due to light, and the desiccator was placed in a darkened desk.

ANODIC BEHAVIOR OF PLATINUM AND PLATINUM-IRIDIUM ALLOYS IN POTASSIUM IODIDE SOLUTIONS.

DESIRABILITY OF INVESTIGATING THIS PHENOMENA.

Vinal and Bates¹² pointed out that platinum dissolved anodically in potassium iodide solutions, but an alloy of platinum-iridium did not. Since no data were presented on this point, it seemed desirable to investigate the effect of such factors as the concentration of iodide, current density and temperature upon the loss of platinum. It was thought that such a study might reveal the conditions under which pure platinum could be used without being attacked.

METHOD AND APPARATUS.

A full size diagram of the electrolytic cell which was used is given in figure 1. The container (M) was a test tube 15 centimeters in length and 4.5 centimeters in diameter. The anode (N) was a piece of thin sheet platinum or platinum-iridium alloy which was placed near the bottom of the container. Contact between the platinum anode and the external source of potential was made by means of a glass rod (O) which had a platinum wire (P) sealed into the lower closed end and was filled with mercury. This rod (O) dipped down into the

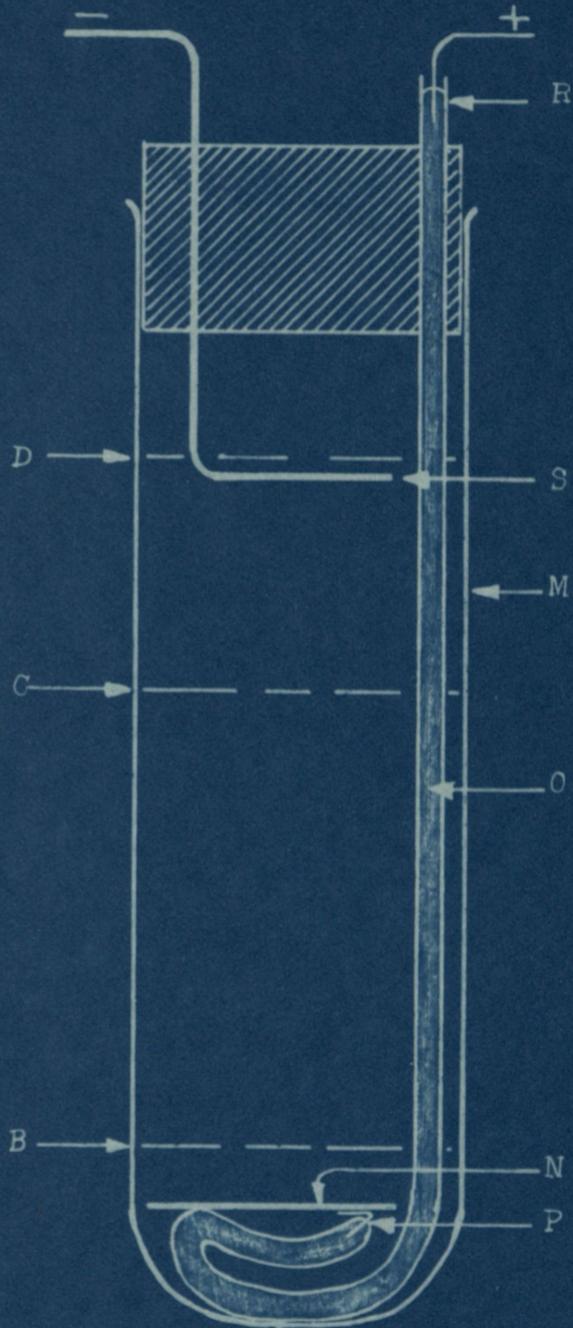


Figure 1. (Full size).

container in such a manner that the closed bent end of the rod was beneath the anode and the upper open end (R) extended above the top of the container. The anode (N) rested upon the wire (P) sealed into the lower closed end of the rod (O). This made it possible to remove and weigh the anode accurately and detect any change in weight with use. Anodes 1 and 2 were made of platinum which was obtained from Bishop and Company in May, 1930. Anodes 3 and 4 were of platinum-iridium alloy which was obtained from Bishop and Company in May, 1930. Anode O was made of platinum which was obtained from Bishop and Company in June, 1932. Anodes 5, 6, 7 and 8 were too small to make good contact by merely laying them upon the wire which made contact to the outside sources of potential so they were sealed to this wire. These anodes were of pure platinum, but since they could not be removed separately their weights could not be obtained. The cathode (S) was a piece of coiled copper wire which was placed near the top of the container and was held in place by inserting it through the rubber stopper which partially closed the container.

In assembling the cell, 100 cc of 10 per cent sodium chloride solution was introduced. Then the anode and

cathode were put in place, being held firmly by the rubber stopper through which they passed. A third hole in the stopper, formed by cutting away a sector equivalent to about one-fourth of the stopper, permitted the electrolyte to be introduced by means of a pipette. With care, a definite volume of potassium iodide solution (usually 25 cc of 50 per cent) was pipetted beneath the layer of the previously introduced sodium chloride solution. Since the iodide solution is the more dense it formed a distinct layer in the bottom of the container, and since it has a different index of refraction than that of the sodium chloride solution, a sharp meniscus (B) was formed between the layers of the solutions. Care was taken to have the anode entirely surrounded by the iodide solution. Above the top meniscus (C) of the chloride solution a layer (50 cc) of 2N hydrochloric acid was carefully pipetted. Lastly, the cathode was lowered so that it just touched the top (D) of the acid layer.

A diagram of the electrical circuit used in this part of the investigation is given in figure 2. B represents a number of storage cells placed in series. The current, indicated by the ammeter (A), could be varied by changing the value of the resistance (R) in

the circuit. A varying number of electrolytic cells (C) were used in the different runs.

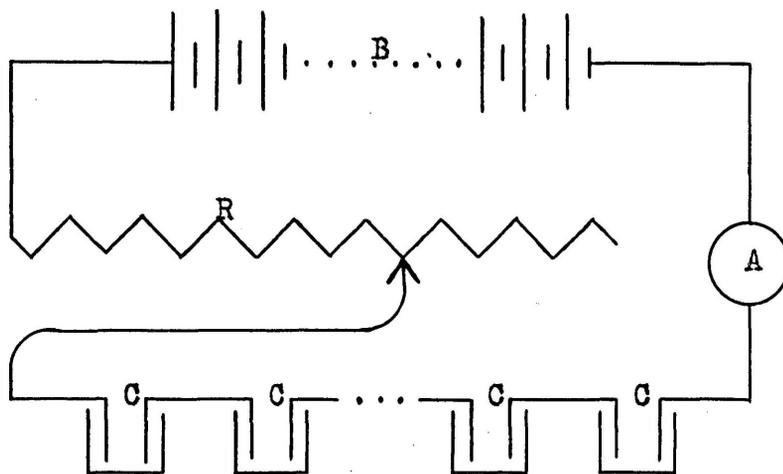


Figure 2.

The weighings of the anodes were made upon a Voland and Sons chemical balance. The beam was graduated to 0.1 mg. The sensitivity was such that weighings of the anodes could be estimated to about 0.05 mg. The set of weights used had been calibrated by the Bureau of Standards. In this part of the investigation, the weighings were not corrected to vacuum.

MANIPULATION.

The solutions used in this part of the investigation were always freshly prepared on the day they were to be used. Usually, at least four cells were connected in series and electrolysis was permitted to proceed either until 0.05 faradays had passed or until gas began to be liberated at the anode. As soon as a cell began to gas it was shorted out and the electrolysis was continued until the other cells in turn began to gas or until 0.05 faradays had passed.

As soon as the electrolysis was concluded the anodes were removed and any adhering iodine was removed from the anodes by dissolving it in potassium iodide solution. Then the anodes were washed with potassium dichromate cleaning solution and rinsed with conductivity water. The anodes were dried in an oven at 200° C for at least one and one half hours and then cooled in a dessicator over concentrated sulphuric acid for two hours before weighing.

During the entire washing, drying and cooling processes the anodes were kept in Gooch crucibles. Thus it was not necessary to touch the anodes with anything except the Gooch crucible, which itself went through the cleaning process, until the anode

touched the weight pan of the balance in weighing.

Washburn and Bates¹⁰ used current densities ranging from 0.0004 amperes per square centimeter to 0.005 amperes per square centimeter and permitted the current to flow until 0.05 faradays had passed. Vinal and Bates¹² used current densities of 0.005 amperes per square centimeter and 0.001 amperes per square centimeter and permitted the current to flow until 3600 coulombs had passed. Since higher current densities would be more effective in attacking the platinum anodes, it was decided to use much higher current densities and permit at least 0.05 faradays to pass in each trial. Washburn and Bates¹⁰ and Vinal and Bates¹² used 25 cc of 50 per cent potassium iodide solution as the anolyte. Table 2 will show that in most of the trials in this part of the investigation the amount and concentration of the anolyte was the same as that just mentioned.

Table 1.

Trial	Anode	% of iridium	C. D. in amps. per sq. cm.	Temp. at end of run	Time of run	Weight of anode before	Weight of anode after
1	#1	0.	0.02	30 ^o C	487 min.	1.7577 gm.	1.7577 gm.
5	"	"	0.2	40 "	80 "	1.7577 "	1.7577 "
9	"	"	0.2	40 "	87 "	1.7559 "	1.7559 "
12	"	"	0.2	40 "	83 "	1.7559 "	1.7559 "
16	"	"	0.3	60 "	40 "	1.7559 "	1.7559 "
25	"	"	0.3	80 "	60 "	1.7559 "	1.7559 "
2	#2	"	0.02	30 "	487 "	1.7724 "	1.7724 "
6	"	"	0.2	40 "	80 "	1.7724 "	1.7724 "
10	"	"	0.2	40 "	78 "	1.7711 ⁻ "	1.77105 ⁻ "
11	#0	"	0.2	40 "	81 "	1.8210 ^f "	1.8210 ^f "
15	"	"	0.3	60 "	33 "	1.8210 ^f "	1.8210 ⁻ "
24	"	"	0.3	80 "	70 "	1.8210 ⁻ "	1.8210 ^f "

Table 1 (continued).

Trial	Anode	% of iridium	C. D. in amps. per sq. cm.	Temp. at end of run	Time of run	Weight of anode before	Weight of anode after
3	#3	0.1	0.02	30° C	487 min.	1.8279 gm.	1.8279 gm.
7	"	"	0.2	40 "	87 "	1.8279 "	1.8279 "
13	"	"	0.2	40 "	86 "	1.8274"	1.8274 "
17	"	"	0.3	60 "	41 "	1.8274 "	1.8274"
23	"	"	0.4		6 "	1.8274 "	1.8274"
26	"	"	0.3	60 "	30 "	1.8274"	1.8274 "
4	#4	0.45	0.02	30 "	487 "	1.8167 "	1.8167 "
8	"	"	0.2	40 "	84 "	1.8167 "	1.8167 "
14	"	"	0.2	40 "	91 "	1.81595"	1.8159 ^f "
18	"	"	0.3	60 "	36 "	1.8159 ^f "	1.81595"
21	"	"	0.4		7 "	1.81595"	
22	"	"	0.4		10 "		1.81593"
27	"	"	0.3	60 "	33 "	1.81593"	1.81594"

The data in table 1 indicate that the loss in weight (if any) of the platinum of the platinum-iridium anodes would be negligible where accuracy not greater than 0.003 per cent is required.

In the case of the platinum anodes the highest current density used (0.3 amperes per square centimeter) was 60 times as high as the highest current density (0.005 amperes per square centimeter) used by Vinal and Bates¹². The lowest current density used was 4 times as high as the highest current density used by Vinal and Bates.¹²

Apparently ordinary temperatures have no effect on the phenomena, since at the beginning of each electrolysis the cell was at room temperature (about 30° C) and at the end of several trials the temperature of the cell had risen to 80° C.

In trials 24, 25, 26 and 27, 60 per cent potassium iodide solution was used. In the other trials 50 per cent potassium iodide solution was used as anolyte, this being the concentration employed by Vinal and Bates¹². As electrolysis proceeded the concentration of the anolyte steadily decreased. In nearly every trial listed in table 1 the electrolysis proceeded

until over half of the original potassium iodide in the anolyte was used up. This would mean that at the end of nearly every electrolysis, the concentration had fallen to about 25 per cent. Furthermore, the solution in immediate contact with the anode probably was much less concentrated than 25 per cent after the electrolysis had proceeded for a time. This would lead one to conclude that the concentration of anolyte would not effect the anodic behavior of platinum.

The change in weight of each of the electrodes between trials 5, 6, 7 and 8 and trials 9, 10, 13 and 14, respectively, was due to polishing of the electrodes and not due to any electrolytic action of any sort.

On July 1st the cells were run at a current density of 0.3 amperes per square centimeter. When the anodes were removed it was found that some of the iodine was adhering firmly to the anode. This could not be washed off with water, nor by dipping it in cleaning solution, so a gentle abrasive (bon ami) was used to loosen the iodine. Thereafter, the anodes were found to have lost weight to varying amounts. Since this was thought to be due to the polishing with bon ami, electrolysis at a current density of 0.3 amperes

per square centimeter was repeated, but this time the iodine was removed by dissolving it off with a saturated solution of potassium iodide. Trials number 15, 16, 17, 18, 24, 25, 26 and 27 show that there is no loss of platinum due to electrolysis at a current density of 0.3 amperes per square centimeter.

SOLE FACTORS INFLUENCING THE SPECIFICATIONS OF THE
IODINE COULOMETER.

In the comparison of the iodine coulometer and the silver coulometer about 3600 coulombs¹² should pass through the cells. This would cause a deposit of nearly 4 grams of silver which would be enough to permit a high degree of accuracy in weighing if the usual size of cathode is used in the silver coulometer. Ordinarily, less than this quantity of electricity passes during usual laboratory experiments. In the trials listed in table 2 an attempt was made to determine the specifications for a cell which would permit 0.05 faradays (about 4825 coulombs) to pass before gassing began at the anode. The cell was designed to permit at least 0.05 faradays to pass so that in the comparison of the iodine and silver coulometers it would not be necessary to stop the electrolysis at the exact moment that 3600 coulombs had passed.

The trials listed in table 2 are the same as those tabulated in table 1, with a few additions. The additional trials in table 2 are for anodes 5, 6, 7 and 8 which could not be weighed and therefore these trials have no essential place in table 1. Table 2 contains data that have a bearing on the specifications of an iodine coulometer.

Table 2.

Date	Trial	Anode	Size of anode in sq. cm.	C. D. in amps. per sq. cm.	Amount of KI soln.	% of KI soln.	Time for 0.05 F. to pass	Time for gassing to begin
8/25	1	#1	8.25	0.02	25 cc	50	487 min.	
"	2	#2	"	"	"	"	"	
"	3	#3	"	"	"	"	"	
"	4	#4	"	"	"	"	"	
6/27	5	#1	"	0.2	50 cc	"	48.7 min.	80 min.
"	6	#2	"	"	"	"	"	80 min.
"	7	#3	"	"	"	"	"	87 "
"	8	#4	"	"	"	"	"	84 "
7/2	9	#1	"	"	25 cc	"	"	87 "
"	10	#2	"	"	"	"	"	78 "
7/6	11	#0	"	"	"	"	"	81 "
"	12	#1	"	"	"	"	"	83 "

Table 2 (continued).

Date	Trial	Anode	Size of anode in sq. cm.	C. D. in amps. per sq. cm.	Amount of KI soln.	% of KI soln.	Time for 0.05 F. to pass	Time for gassing to begin
7/6	13	#3	8.25	0.2	25 cc	50	48.7 min.	86 min.
"	14	#4	"	"	"	"	"	91 "
7/7	15	#0	"	0.3	"	"	32.5 min.	33 "
"	16	#1	"	"	"	"	"	40 "
"	17	#3	"	"	"	"	"	41 "
"	18	#4	"	"	"	"	"	36 "
7/8	19	#5	4.125	0.2	"	"	97.4 min.	105 "
"	20	#6	"	"	"	"	"	110 "
"	21	#4	8.25	0.4	"	"	24.4 min.	7 "
"	22	#4	"	"	"	"	"	10 "
"	23	#3	"	"	"	"	"	6 "
7/9	24	#0	"	0.3	"	60	32.5 min.	50 "

Table 2 (continued).

Date	Trial	Anode	Size of anode in sq. cm.	C. D. in amps. per sq. cm.	Amount of KI soln.	% of KI soln.	Time for 0.05 F. to pass	Time for gassing to begin
7/9	25	#1	8.25	0.3	25 cc	60	32.5 min.	60 min.
"	26	#3	"	"	15 cc	"	"	30 "
"	27	#4	"	"	"	"	"	33 "
"	28	#5	4.125	0.2	25 cc	50	97.4 min.	116 "
"	29	#6	"	"	"	"	"	110 "
"	30	#7	1.74	"	"	"	231 min.	242 "
"	31	#8	"	"	"	"	"	234 "

The cells for trials 1, 2, 3 and 4 had the same anolyte as those used by Washburn and Bates¹⁰. In these trials gassing had not occurred at the time 0.05 faradays had passed. It would have been of interest to have known how long these would have continued before gassing occurred. This question did not occur to the author until after the anodes were weighed and it was found that the platinum had not been attacked. It was more important to investigate the effect of higher current densities so trials 1, 2, 3 and 4 were not repeated.

The cells for trials 9, 10, 11, 12, 13 and 14 differed from those for trials 5, 6, 7 and 8 only in the volume of anolyte used. It will be noticed that the time until gassing occurred was essentially the same even though cells for trials 5, 6, 7 and 8 had twice the volume of anolyte. 25 cc of 50 per cent potassium iodide solution contain an amount of iodine equivalent to about 11,000 coulombs. At the current density used in the above trials, in 48.7 minutes about 4825 coulombs (0.05 faradays) will have passed. At the time gassing occurred in all of the above trials, a quantity of potassium iodide was still present. Since the anolyte was not stirred local deple-

tion of potassium iodide around the anode probably occurred and diffusion of potassium iodide from the surrounding regions was probably too slow to replace the potassium iodide which was used up.

The cells for trials 15, 16, 17 and 18 and those for trials 21, 22 and 23 were made up exactly the same as the cells for trials 9, 10, 11, 12, 13 and 14. The trials differed though in that a current density of 0.3 amperes per square centimeter was used in trials 15, 16, 17 and 18 and a current density of 0.4 amperes per square centimeter was used in trials 21, 22 and 23. Thus when the current density was increased to 0.3 amperes per square centimeter the time until gassing occurred was essentially the same as the time until 0.05 faradays had passed. When the current density was 0.4 amperes per square centimeter 0.05 faradays had not been passed before gassing occurred. At the higher current density the depletion of the potassium iodide around the anode occurred more rapidly and it soon became impossible for diffusion of potassium iodide from the surrounding regions to replace the potassium iodide which was used up.

The cells for trials 24 and 25 were made up like the cells for trials 15, 16, 17 and 18 except that 25 cc of 60 per cent potassium iodide solution was substituted for 25 cc of 50 per cent potassium iodide. Notice that the same current density was used in these trials. Increasing the original concentration of anolyte increased the time until gassing occurred.

The cells for trials 26 and 27 were run at the same current density as those in trials 15, 16, 17 and 18. The time until gassing occurred was about the same when 15 cc of 60 per cent iodide solution was used as when 25 cc of 50 per cent iodide solution was used.

From the above facts, it would appear that for a cell of the physical dimensions specified, when 25 cc of 50 per cent anolyte is used, the upper limit of current density is near 0.3 amperes per square centimeter. Since the anode was 8.25 square centimeters in area, the total current was about 2.47 amperes. For the sake of comparison, let it be remembered that the specifications for a silver coulometer¹⁶ state that the current density at the cathode should not exceed 0.01 amperes per square centimeter, and that in the ordinary silver coulometer a current of not more than 1 ampere should be used.

Trials 19, 20, 28 and 29 are of interest since all of the conditions were exactly the same as in trials 9, 10, 11, 12, 13 and 14 except that the anodes were just half as large (4.125 square centimeters). In these trials the time until gassing began was much nearer the time until 0.05 faradays had passed. Also, in the cells of this design the upper limit of current density is somewhat above 0.2 amperes per square centimeter.

In trials 30 and 31 all of the conditions were exactly the same as in trials 19, 20, 28 and 29 except that the anodes were less than half as large (1.74 square centimeter). In these trials at a current density of 0.2 amperes per square centimeter, the time until gassing began barely exceeded the time for 0.05 faradays to pass. In order to be perfectly safe a current density slightly under 0.2 amperes per square centimeter should be used if 0.05 faradays are to be passed, although a current density of 0.2 amperes per square centimeter would be permissible in case smaller quantities of electricity are to be passed as will be the case in the comparison of the iodine and the silver coulometers.

VARIATION OF THE FORM OF THE COULOMETER.

FACTORS TO BE CONSIDERED.

A number of factors have tended to keep the iodine coulometer as designed by Washburn and Bates¹⁰ from being generally used. Chief among these probably is the high internal resistance as mentioned by Hulett¹¹. Another prohibitive factor is the cost of electrode material. A casual reading of the precise work by Washburn and Bates¹⁰ would lead one to believe that the form of the coulometer they used was too inconvenient for general use.

It is possible to vary the form and size of the iodine coulometer and cut down the internal resistance until it is comparable to that of the silver coulometer. The cost of the electrode material can be reduced until it no longer is a prohibitive factor. The form of the coulometer can be simplified so that it can be assembled in any ordinarily equipped laboratory. Rarely is it necessary to use a coulometer with the precision attained by the investigators mentioned above. Only with the utmost care could one attain such precision with the silver coulometer. By varying the form of the iodine coulometer it can be made more convenient and

easier to operate than the silver coulometer and yet have a precision of at least 0.02 per cent, which exceeds the precision necessary in most laboratory experiments. As used in the ordinary laboratory it is doubtful if greater precision is usually attained with the silver coulometer.

THE IODINE COULOMETER.

A full size diagram of the iodine coulometer, used in this investigation, is given in figure 5. The outer containing vessel (V) was a glass jar about 12 centimeters high and 8 centimeters in diameter. A bakelite ring (A) had an outside diameter greater than the outer vessel and an inside diameter just large enough to admit the glass jacketing cylinder (K). This was held in position by the flange (F) which rested upon the bakelite ring (A). The inner vessel (M), a large test tube (15 centimeters by 4.2 centimeters), was held in position by some rubber wedges (W). The anode (N) was a piece of thin sheet of platinum which was arranged exactly as the anode in the electrolytic cell in figure 1 except that in this case the anode (N) was sealed to the wire (p). (T) represents a layer of sealing wax which was put on the glass rod (R) before it was inserted through the

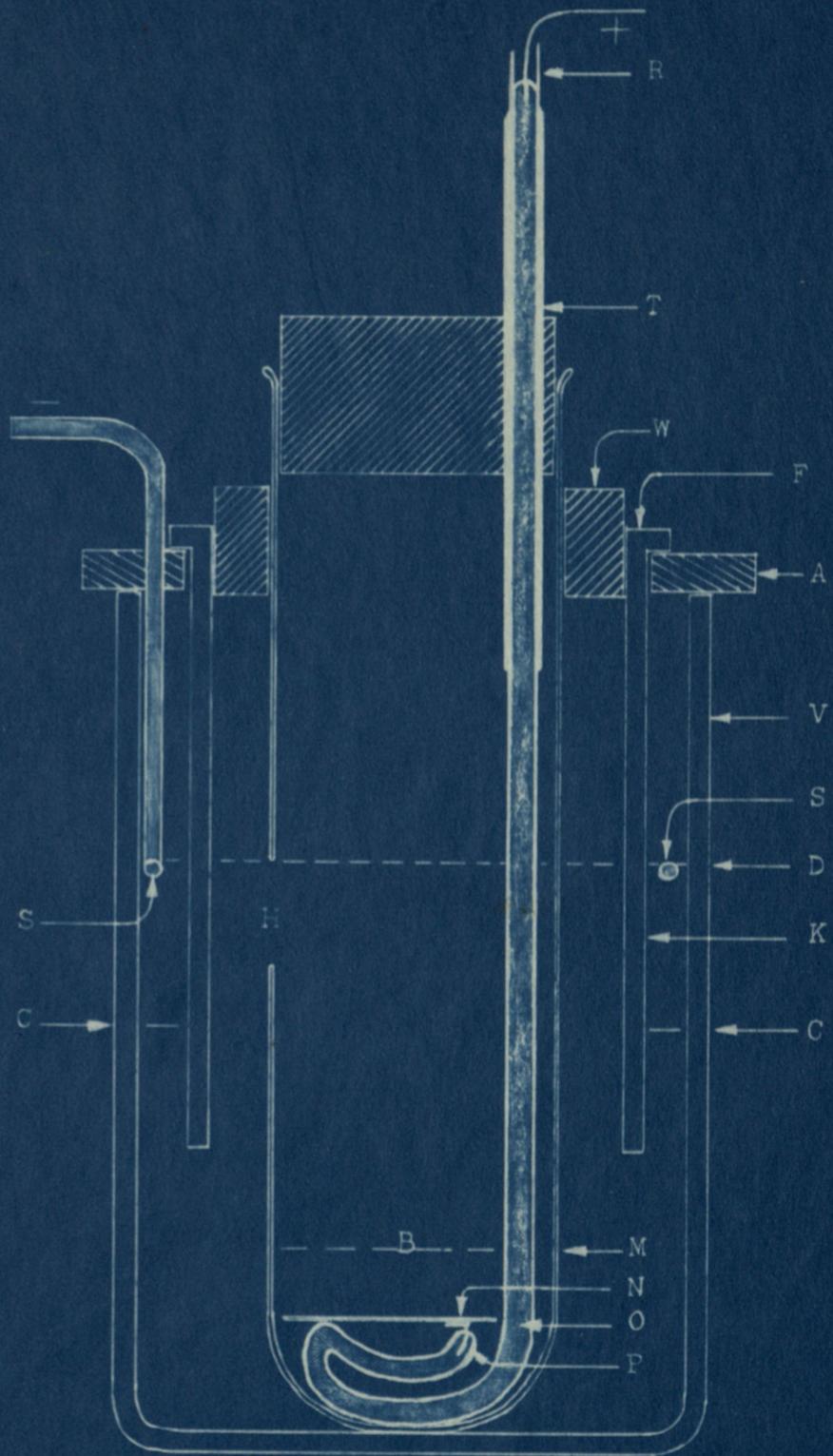


Figure 3. The Iodine Coulometer. (Full size).

stopper. This layer of wax passed through the stopper and extended about 3 centimeters above and about 2.5 centimeters below the stopper. During the comparison of the iodine coulometer with the silver coulometer it was found necessary to introduce the use of this layer of wax, as is discussed below, to prevent short-circuiting through the coulometer. The cathode (S) was a heavy piece of copper wire which was wrapped once around the jacketing cylinder and then extended up through the bakelite ring.

In assembling the coulometer, the jacketing cylinder and the inner vessel were placed in position. About 300 cc of 10 per cent sodium chloride solution was then introduced by way of the mouth of the inner vessel. Part of the sodium chloride solution passed from the inner vessel to the outer vessel by way of the holes (H) in the side of the inner vessel, and filled both vessels to the level of the lower edge of the holes (H). There were three holes (H) of about 1.5 centimeters diameter around the tube about 6.5 centimeters from the bottom. Then the anode was securely fastened in the inner vessel as is shown in figure 5. In case an air bubble happened to cling to the anode when

it was inserted, it was removed by shaking the anode, since it might have risen later and carried iodine with it, thereby causing a loss in iodine. With care, a definite volume of potassium iodide solution (usually 25 cc of 50 per cent) was pipetted beneath the layer of the sodium chloride solution in the inner vessel. The tip of the pipette was drawn to a small size so that the potassium iodide solution would run out slowly and thus avoid undue mixing. It required about 10 minutes for the potassium iodide solution to drain out of the pipette. A sharp meniscus was formed at the junction (B) of the iodide and chloride solutions. By inserting a pipette through a hole in the bakelite ring, 50 cc of 2 N hydrochloric acid was carefully pipetted above the sodium chloride solution, outside of the jacketing cylinder. The tip of each pipette used here (one for each coulometer) was drawn out to a small size and was turned at right angles to the stem of the pipette. It required about 25 minutes for 50 cc of the acid to drain out. The pipettes were supported above the coulometers, by means of ring stands and clamps, while the acid was being introduced. When this was carefully and slowly done a distinct meniscus (C) was formed between the acid and

sodium chloride solutions. If the proper amount of sodium chloride was used the cathode extended just beneath the top surface (D) of the acid layer.

REDUCTION OF THE INTERNAL RESISTANCE.

The form of the coulometer eventually used is about the same as that designed by Cady¹⁵, but the size has been changed in order to cut down the internal resistance. The internal resistance of this cell would be approximately that due to the sum of the lengths of the columns of liquids extending from the cathode down under the jacketing cylinder, thence up to the holes (H) and then down to the anode (N). By increasing the cross sectional area of any or all of these and by decreasing the lengths of these columns the internal resistance should be decreased. The jacketing cylinder should not be entirely removed as the acid must be kept in the region of the cathode.

The above mentioned columns of liquids were longer and of less cross section in the coulometer designed by Cady¹⁵ than in the one diagramed in figure 3. The internal resistance of the Cady coulometer was found to be 37 ohms which is certainly an improvement over the one used by Wash-

burn and Bates¹⁰ which had a resistance of about 180 ohms. The resistance of the coulometer diagramed in figure 3, was 5.9 ohms and remained practically constant during the passage of 3600 coulombs.

A jacketing cylinder which was long enough to reach the bottom of the outer containing vessel was put in the coulometer in figure 3. The resistance of the coulometer was measured when the jacketing cylinder was at different distances from the bottom. As is obvious from the results in table 3, the resistance decreased noticeably when the cylinder was raised so that the distance between the cathode and the anode was shortened.

Table 3.

Height of cylinder above bottom.	Resistance of coulometer.
0.1 cm.	9.4 ohms.
1.5 "	8.2 "
3.5 "	6.5 "
4.2 "	5.9 "
5.3 "	5.0 "
Cylinder removed	3.7 "

ECONOMY OF ELECTRODE MATERIAL.

Washburn and Bates¹⁰ used a platinum cathode which was surrounded by iodine to prevent the formation of hydroxyl ions. In order to economize on material, a copper cathode surrounded by 2 N hydrochloric acid was used. By increasing the current density at the anode it is possible to use a much smaller anode. Washburn and Bates¹⁰ used a platinum anode of 50 square centimeters and a maximum current density of 0.005 amperes per square centimeter, which corresponds to a maximum current of 0.25 amperes. In the comparative experiments on the iodine coulometer discussed below, an anode of 4.125 square centimeters was used at a current density of 0.2 amperes per square centimeter, which corresponds to a current of 0.825 amperes. Thus it is possible to economize on electrode material and yet pass a larger current than was used by Washburn and Bates¹⁰.

COMPARATIVE EXPERIMENTS ON THE IODINE COULOMETER.

PURPOSE.

Before comparing the iodine coulometer to the silver coulometer, it was decided to run several of the iodine coulometers in series and compare them with each other. Such comparative experiments indicated the precision of the instrument and also helped develop the technique in manipulating the cell after the electrolysis was finished. The procedure of carrying out the titration was changed slightly during the several experiments. The procedure described below seemed to be the most satisfactory.

MANIPULATION OF THE COULOMETERS.

Three iodine coulometers, such as the one diagramed in figure 3, except that the wax layer (T) was omitted here, were assembled in the manner discussed above, 25 cc of 50 per cent potassium iodide solution being used as the anolyte. The anodes were 4.125 square centimeters in area and a current density of 0.2 amperes per square centimeter was used. According to table 2, this arrangement should be permissible, especially

since the electrolysis was continued until only 3600 coulombs had passed.

The coulometers were connected in series, inserted in the electrical circuit diagramed in figure 2 and the current was adjusted to 0.825 amperes. The current remained practically constant during the course of the experiment which lasted 72 minutes and 43 seconds. No attempt was made to control the temperature of the coulometers. At the beginning of each run their temperature was that of the room (about 30° C). At the end of the experiment their temperature had risen about 5 degrees above room temperature. The manipulation of the coulometers was the same in each of the three series listed in table 4.

ANALYSIS OF THE ANODE PRODUCT.

When 3600 coulombs had passed through the coulometers the current was interrupted and the analysis of the anode product was begun. In turn, the inner vessel of each of the three coulometers was removed, a portion of the clear sodium chloride solution was carefully poured out of the hole (H) and it was then placed aside (preferably in the dark) to await analysis. The analysis of one of the anode solutions was immediately begun. This required about one and one-half

hours. Then the anode solution of the second cell was titrated in about the same time. Thus the anode solution in the third cell stood at least three hours before it was titrated. The anode solutions were titrated with a solution of sodium thiosulphate, in the following manner.

A liter of approximately normal sodium thiosulphate was made up and kept in a dark bottle. A portion of this solution was diluted to exactly one-hundredth the concentration of the approximately normal solution. This was done by weighing 3.82595 grams of the concentrated solution from a weight burette and diluting it with 378.770 grams of water. The weight burette was weighed on a Christian Becker chainomatic balance. The water was weighed on a Sartorius balance of large capacity. The set of weights was calibrated by the Bureau of Standards and weighings were corrected to vacuum. The specific gravity of the dilute solution was determined by means of a Parker and Parker²² pyknometer and found to be 1.0009 at 30⁰ C.

The titration was carried out by using a definite amount of the concentrated solution, and then finishing the titration with the dilute solution.

The concentrated solution was added from a weight burette and the dilute solution was added from a volume burette which had been calibrated by the Bureau of Standards. Since the specific gravity of the dilute solution was known, the amount of sodium thiosulphate in grams of concentrated solution could be determined by multiplying the volume by the specific gravity and dividing the product by 100. These are the amounts tabulated in table 4.

Since 3600 coulombs were passed through the solution, an amount of iodine equivalent to about 37.3 cc of normal thiosulphate should have been liberated. Approximately 30 cc of thiosulphate was introduced into the titration vessel (a 500 cc Erlenmeyer flask) from a previously weighed weight burette. This was diluted with about 30 cc of conductivity water. Then the iodine solution was slowly siphoned from the inner vessel of the coulometer under the layer of thiosulphate solution in the titration vessel, by means of the arrangement diagrammed in figure 4.

The end of the capillary tube (D) was drawn to a fine tip and was bent so that it fitted snugly against the bottom of the inner vessel (A). The

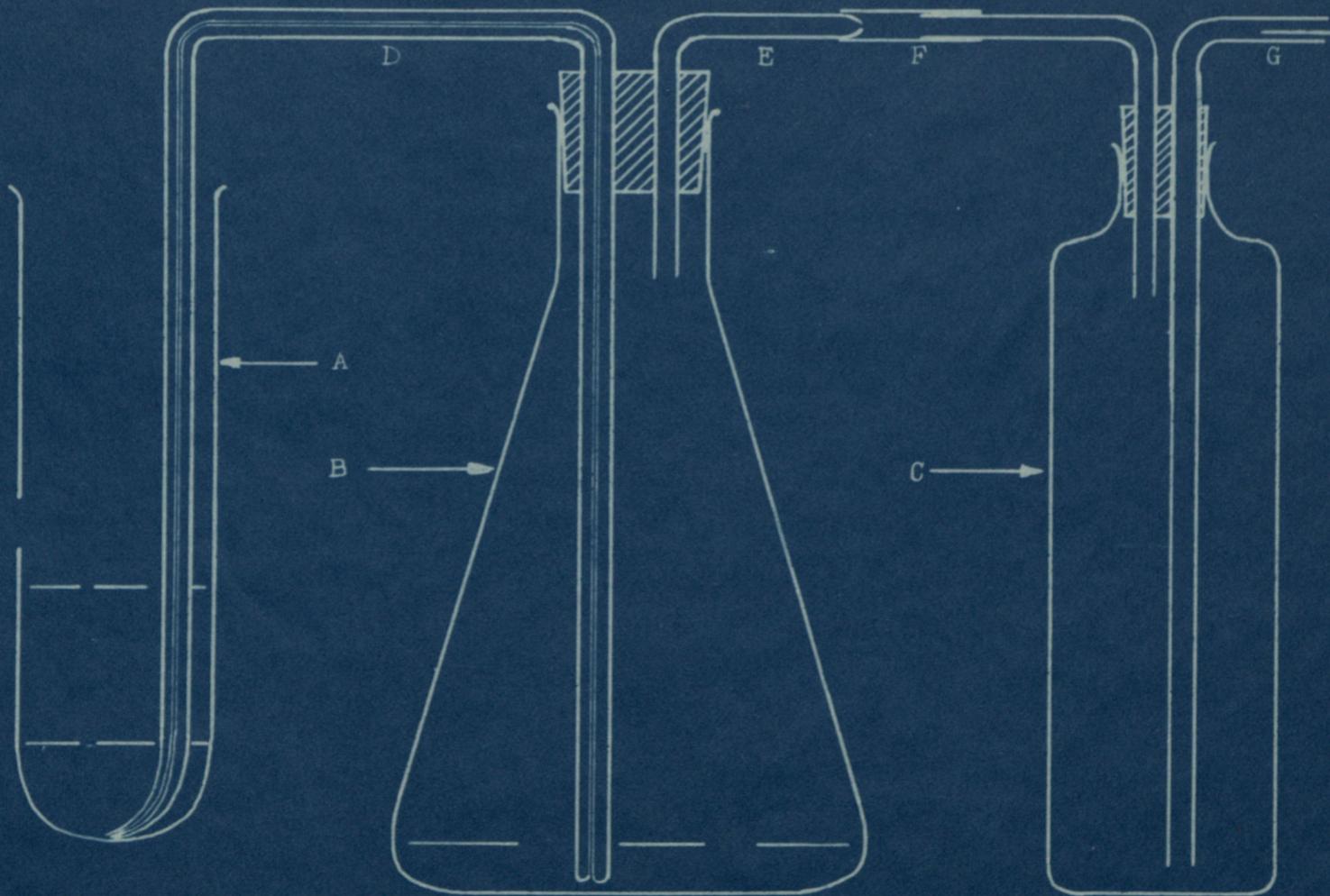


Figure 4. (Scale: 1 cm. = 1.5 cm.)

tube (G) was attached to a suction filter pump. The bottle (C) was inserted to make the filtering proceed more uniformly and also to act as a trap. The rubber tubing (F) was merely loosely attached to the tube (E) so that it could be detached easily and rapidly as soon as the siphoning had begun. Siphoning must proceed slowly to avoid spattering. When all of the iodine solution had been siphoned from the vessel (A), some of the clear chloride solution still being present, the process was interrupted. About a gram of potassium iodide crystals was introduced into the vessel (A). The resulting iodide solution dissolved any iodine which remained in the vessel. This was then siphoned over into the titration vessel (B). Then the vessel (A) and the anode, which was still in place, were rinsed by introducing about 20 cc of conductivity water into the vessel (A) and then siphoning it into the titration vessel. This washing process was repeated several times. Then the siphon was removed from the titration vessel, being rinsed off as it was removed.

The liquid in the titration vessel was stirred by rotating the flask and titration was continued

by adding thiosulphate solution from the weight burette. Extreme care was exercised at this point not to overstep the endpoint. As soon as the color of the iodine solution began to fade (at this point the color was a little darker than the shade of a solution of potassium chromate) the addition of thiosulphate solution from the weight burette was discontinued. The solution was now transferred to a 1000 cc beaker, a mechanical stirrer was introduced and the titration was continued by the addition of dilute thiosulphate solution from a volume burette. The end point was detected by means of the electrometric method¹⁷.

From the volume of dilute thiosulphate solution added until the end point was reached, the equivalent number of grams of concentrated thiosulphate solution was known. This added to the weight of thiosulphate solution added from the weight burette gave the number of grams of approximately normal thiosulphate solution equivalent to the iodine set free in the coulometer. Since the same thiosulphate solution was used in all of the analyses, the amounts used should be the same for the different coulometers of a given series. The agreement with which these amounts checked

was a measure of the precision attained. Thus it was not necessary to know the actual concentration of the thiosulphate solution to attain our purpose.

In titrating the iodine solution care was taken not to dilute the solution too greatly. According to Popoff and Whitman¹⁷ the final concentration of potassium iodide in the solution should be at least two per cent. Chapin²³ found that the concentration of potassium iodide in the solution at the end of the titration should be at least four per cent. The amount of potassium iodide in the original electrolyte was 19.28 grams. During electrolysis 6.18 grams of potassium iodide were decomposed. This left 13.1 grams of iodide in the solution. At the end of the titration 19.28 grams of iodide were again present. At the beginning of the titration the volume must not exceed 328 cc and at the end of the titration the volume must not exceed 482 cc in order to meet the specifications suggested by Chapin²³. According to Popoff and Whitman¹⁷ the dilution may be carried twice as far or to 964 cc. Apparently the end point could be determined more precisely at the higher dilution, so just before electrometric titration was begun, the solution was diluted to about

900 cc with conductivity water.

The detection of the end point at the different dilutions is illustrated below by giving data taken near the end point at each of the dilutions. In a preliminary trial made during the summer of 1952 the solution which had been titrated to near the end point by adding concentrated thiosulphate solution from a weight burette, as is discussed above, was transferred to a beaker and diluted to about 450 cc before finishing the titration by adding dilute thiosulphate solution from a volume burette. Near the end point the following data were taken and the end point was chosen according to the method suggested by Popoff and Whitman¹⁷.

cc reagent	34.56	34.51	34.67	34.83	34.99	35.15
E relative	.1690	.1608	.1518	.1420	.1333	.1253
dE		.0082	.0090	.0098	.0087	.0080

Since dE from 34.67 to 34.83 is greatest, the end point is somewhere between these values. Since dE (.0090) from 34.51 to 34.67 is greater than dE (.0087) from 34.83 to 34.99 the end point was chosen nearer to 34.67 and in this case was chosen one third of the way from 34.51 to 34.67 or at 34.56. The change in volume as

read on the burette (about 0.16 cc) represents the withdrawal of three drops from the burette. A similar iodine solution, after being titrated to near the end point by adding concentrated thio-sulphate solution from a weight burette, was transferred to a beaker and diluted to about 900 cc before finishing the titration by adding dilute thiosulphate solution from a volume burette. Near the end point the following data were taken and the end point was chosen according to the method suggested by Popoff and Whitman¹⁷.

cc reagent	47.46	47.52	47.57	47.62	47.67
E relative	.1787	.1733	.1672	.1605	.1555
dE		.0054	.0061	.0067	.0050

Since dE from 47.57 to 47.62 is greatest, the end point is somewhere between these values. Since dE (.0061) from 47.52 to 47.57 is greater than dE (.0050) from 47.62 to 47.67, the end point is nearer to 47.57 and in this case was chosen as 47.59. The change in volume as read on the volume burette (about 0.05 cc) represents the withdrawal of one drop from the burette.

At the higher dilution, the end point can probably be chosen as precisely as a volume burette can be read, that is, to within about 0.03 cc. At the lower dilu-

tion the end point cannot be chosen nearly so precisely. It is doubtful if it can be chosen to within two drops or about 0.10 cc. Matters were equally as bad at the lower dilution when the solution was added drop by drop, or two drops at a time for in either of the latter cases the change in the successive values of dE was so small that the end point could still not be detected any more precisely. Near the end point, several readings of the potentiometer (after a given addition of thiosulphate) varied as much as 0.0003 volts which was about as much as the change in dE for the addition of one drop. Hence it was found to be necessary to add three drops at a time in order to be certain of having the values of dE gradually increase to a maximum and then decrease again.

At the higher dilution the value of dE for three drops is 0.0178 volts or nearly double the value of dE for three drops (0.0090 volts) at the lower dilution.

Table 4.

Date	Series number	Cell	Sodium thiosulphate solution	% variation from mean value
7/23	1	#2	47.795 gms.	+0.095
7/23	1	#3	47.704 "	-0.095
7/26	2	#1	48.703 "	+0.035
7/26	2	#3	48.686 "	-0.035
7/29	3	#1	48.887 "	+0.012
7/29	3	#2	48.872 "	-0.018
7/29	3	#3	48.883 "	+0.004

In the first two series some difficulty was experienced since the method of handling the cells was being worked out. Reference to the table will show that cell #1 in series 1 and cell #2 in series 2 were not carried through the method successfully. The decrease in error in passing from series 1 to 3 is attributed to improvement in technique in handling of the coulometer after electrolysis was complete and to improvement in the method of transferring the iodine solution from the inner vessel of the coulometer to the titration vessel.

COMPARISON OF THE IODINE COULOMETER WITH THE SILVER COULOMETER.

THE SILVER COULOMETER AND ITS MANIPULATION.

The two silver coulometers used were approximately the same size and were made according to the specifications of the Bureau of Standards¹⁶.

The cathodes were 250 cc platinum bowls which weighed approximately forty grams each. A third platinum bowl of about the same size was used as a counterpoise in weighing. After the silver deposits had been weighed, they were removed by electrolysis, being simultaneously plated out on the bars of silver which served as the anodes in the silver coulometers. When practically all of the deposit had been removed, the platinum bowls were washed in hot dilute nitric acid. After being thoroughly washed with conductivity water, they were baked in an oven at 300° C. Then they were removed from the furnace with platinum tipped tongs and placed in a dessicator over sulphuric acid to cool. They were kept in the same desiccator while not in use.

The anodes were round bars of pure silver, about 1 centimeter in diameter and 6 centimeters

long, which were coated with electrolytic silver. Each time the coulometers were used the anodes were plated again during the removal of the previous silver deposit from the platinum bowls. A fresh ten per cent solution of silver nitrate was used during this plating process which was carried out at a low current density in order to get a good, adherent crystalline deposit. The anodes were then thoroughly washed with conductivity water and then baked at 300° C or more to expel any acid that may have come from the solutions. They were then placed in a desiccator over sulphuric acid where they remained while not in use.

A porous cup, 8 centimeters long and 3 centimeters in diameter was placed around each anode. This porous cup was suspended from the anode by passing a small glass tube through holes in the upper parts of the cup and anode. In preparation for use in the coulometer, these cups were boiled in nitric acid, washed thoroughly with conductivity water and then baked at 300° C. Thereafter, they were kept immersed in ten per cent silver nitrate solution which was kept in the dark.

The electrolyte was a ten per cent solution of silver nitrate. This was freshly prepared before each electrolysis by dissolving 28 grams of the pure

salt (prepared as described above) in 252 grams of conductivity water. This solution was equally divided between the two coulometers.

The coulometer was assembled by placing the platinum bowl (the cathode was handled with platinum tipped tongs) in position on the stand of the coulometer. Then the anode was hung on its support immediately above the cathode bowl. The porous cup was placed around the anode and the anode and porous cup were lowered into the bowl. Then the electrolyte was poured into the bowl, a portion of it being pipetted into the porous cup. The base of the coulometer was made of bakelite. For convenience, two binding posts were mounted on the base of the coulometer, one of these was connected to the cathode bowl and the other was connected to the anode support and consequently to the anode. During an electrolysis the entire coulometer was covered with a large glass jar in order to keep foreign material from dropping into the electrolyte. No attempt was made to control the temperature of the coulometer since the temperature coefficient of the coulometer between 20° C and 50° C is negligible¹⁶. During an electrolysis 3600 coulombs were permitted to pass, that is, a current of 250 milliamperes

was permitted to flow for four hours.

Immediately after electrolysis was interrupted the anodes and porous cups were removed and set aside in the dark to await cleaning, which was done after the cathode had been properly treated. Then the electrolyte was slowly siphoned out of the platinum bowl. The silver deposit was repeatedly washed by adding conductivity water to the bowl and siphoning it out until the wash water did not give a precipitate when tested with potassium bromide solution. Several wash waters were used after no silver nitrate could be detected with the potassium bromide solution¹⁶. Care was taken not to loosen the silver deposit during the washing process nor to siphon off any loose silver¹⁶ which was seldom present. After thorough washing, the cathode bowls were dried at about 90° C in an electric oven and then baked at 300° C. They were removed from the oven with platinum tipped tongs and placed in a desiccator over sulphuric acid to cool before weighing.

While the cathodes were being cooled the anodes were removed from the porous cups and washed with conductivity water. Then they were baked at 300° C

and placed in a desiccator until it was convenient to plate them with silver. They were plated when the silver deposits were being removed from the platinum cathodes after they had been properly weighed.

Then the porous cups were cleaned, as described above, in preparation for the next electrolysis. They were not used around the bars of silver when the silver deposits were being removed from the platinum bowls.

The cathodes were not handled with the bare hands neither while assembling the apparatus nor after the electrolysis was finished. The weighings were made on a Volands and Sons chemical balance. The beam of the balance was graduated to tenths of a milligram and the sensitivity of the balance was such that it was possible to estimate the weight of the platinum cathodes to 0.05 milligrams. The weights of the silver deposits listed in table 5 are the actual weights corrected for inclusions as suggested by Vinal and Bovard⁹ of the Bureau of Standards. They found that on the average 0.004 per cent of the weight of the deposit was due to inclusions.

IODINE COULOMETER AND ITS MANIPULATION.

During the course of the comparison of the iodine coulometer with the silver coulometer, it was found that the form of the coulometer as well as its manipulation had to be varied somewhat. Hence, it is necessary to discuss the form and manipulation of the iodine coulometer with reference to table 5.

The first 6 series listed in table 5 were run during the summer of 1933. The iodine coulometer used in series 1, 2 and 3 was the same as the one diagramed in figure 3, except that the wax layer (T) was omitted and the rod (R) extended only about 2 centimeters above the rubber stopper. A wax layer (T), which passed through the rubber stopper and extended less than a half centimeter above and below the stopper, was put on the rod (R) before series 4, 5 and 6 were run. The remaining series listed in table 5 were run during the summer of 1934. Before these series were begun the rod (R) in the coulometer was replaced by a longer one which extended about 4 centimeters above the rubber stopper and had a layer of sealing wax on it which passed through the stopper and extended about 3 centimeters above and 2.5 centimeters below the stopper. The purpose of this layer

of wax is discussed below. In all of the series listed in table 5, the iodine coulometers were assembled in the manner discussed above, in connection with figure 3.

During an electrolysis, two iodine coulometers were connected in series with the two silver coulometers discussed above. In order to insure good insulation the silver coulometers were placed on asbestos boards (1 centimeter thick) which were in turn placed upon celotex boards that had been soaked in paraffin and the wire connections were all suspended in the air. In series 1 to 6 inclusive, the iodine coulometers were placed in a constant temperature mineral oil bath (30° C) since the temperature coefficient of the coulometers was to be determined as is discussed below. In series 8 and 10 the iodine coulometers were placed in an ice bath at 0° C. In series 7 and 9 the iodine coulometers (at room temperature) were placed on asbestos boards (1 centimeter thick) which were in turn placed upon celotex boards that had been soaked in paraffin. In each run the wire connections between all of the coulometers were suspended in the air. In all of the series, except series 3, a current of 250 milliamperes

was permitted to flow until about 3600 coulombs had passed. The source of the current was several storage batteries connected in series with a ballast resistance, an ammeter, two iodine coulometers and two silver coulometers. The ammeter was a standardized Weston milliammeter, model 1. The current seldom fluctuated more than 2 milliamperes during an electrolysis.

Immediately after electrolysis was interrupted, the silver coulometers were cared for as discussed above. While the silver nitrate was being siphoned out of the platinum bowls of the silver coulometers, the inner vessels of the two iodine coulometers were removed, a portion of the clear sodium chloride solution was carefully poured out of the holes of the side of the vessels and they were placed aside, (in the dark) to await analysis. The treatment of the silver coulometers required about two hours, so one of the iodine coulometers stood at least two hours before being titrated and the second iodine coulometer stood an additional one and one-half hours while the first titration was being made.

The analysis of the anode product was made by the method discussed above, in connection with figure 4. The only variation was that, in this case, a

standardized solution of sodium thiosulphate was used in place of the approximately normal solution. The standardization of this solution is discussed below. Thus it was possible to determine the amount of iodine which was set free during electrolysis. Then the equivalent amount of silver was calculated and listed in table 5. The amount of silver deposited during the same electrolysis is also listed in table 5. The last column in this table lists the per cent variation of the calculated amount of silver, equivalent to the iodine liberated, from the mean of the amounts of silver deposited in the silver coulometers. The series are numbered in the order in which they were run.

The large relative variation observed in series number 1 might have been due to one or more sources of error. It was thought that the current efficiency of the iodine coulometer might not have been 100 per cent at the current density used; that the iodine coulometers might have been shorted; or that the standardization of the thiosulphate solution might have been in error.

Series number 2 was run exactly as the first series except that the current density was decreased from

Table 5.

Series number	Coulometer number	Temp. °C	Amps. per sq. cm.	Silver deposit	Mean Ag. deposit	Ag. equiv. of iodine	Per cent variation
1	1	30	.0606	4.05495	4.05497	4.04045	-0.36
1	2	30	.0606	4.05499	4.05497	4.03958	-0.38
2	1	30	.0303	4.09216	4.09196	4.07765	-0.35
2	2	30	.0303	4.09177	4.09196	4.07610	-0.39
3	1	30	.00606	2.06939	2.06948	2.06145	-0.39
3	2	30	.00606	2.06957	2.06948	2.06192	-0.37
4	1	30	.1212	4.03884	4.03877	4.03660	-0.05
4	2	30	.1212	4.03870	4.03877	4.03775	-0.03
5	1	30	.0606	4.11833	4.11823	4.11444	-0.09
5	2	30	.0606	4.11813	4.11823	4.09848	-0.48
6	1	30	.0606	4.06535	4.06536	4.06146	-0.10
6	2	30	.0606	4.06537	4.06536	4.03411	-0.77

Table 5 (continued).

Series number	Coulometer number	Temp. °C	Amps. per sq. cm.	Silver deposit	Mean Ag. deposit	Ag. equiv. of iodine	Per cent variation
7	1	31.5	.0606	4.03206	4.03202	4.03037	-0.04
7	2	31.5	.0606	4.03198	4.03202	4.03160	-0.02
8	1	0.	.0606	4.05816	4.05819	4.06071	+0.06
8	2	0.	.0606	4.05821	4.05819	4.05977	+0.04
9	1	32.5	.0606	4.07824	4.07832	4.07846	+0.003
9	2	32.5	.0606	4.07840	4.07832	4.07783	-0.01
10	1	0.	.0606	4.04224	4.04221	4.04117	-0.03
10	2	0.	.0606	4.04217	4.04221	4.04201	-0.005

0.0606 amperes per square centimeter to 0.0303 amperes per square centimeter. Series number 3 was similar to series number 1 and 2 except that the current density (0.00606 amperes per square centimeter) was near the upper limit (0.005 amperes per square centimeter) used by Washburn and Bates¹⁰ and only about half as much electrolysis occurred in this case. Since the results in series 1, 2 and 3 were practically the same, the per cent variations listed in table 5 were probably not due to a variation of current efficiency with current density.

The thiosulphate solution was titrated against another sample of iodine in order to determine whether or not an error had been made in the standardization of this solution. The results listed in table 6 for sample 2 indicated that 1 gram of thiosulphate solution was equivalent to 0.07801 grams of iodine. This was about 0.038 per cent lower than the value obtained by using sample 1. This variation might have been due to chlorine or bromine in sample 2, since it received no special treatment before use as is discussed in connection with table 6. In order to account for the variations in series number 1, 2 and 3, (table 5) one gram of thiosulphate solution would need to have been equivalent to about 0.07835

grams of iodine. In view of the results listed in table 6 this was considered very unlikely.

As stated above, in series 1, 2 and 3 the rod (R), in figure 5, extended about 2 centimeters above the stopper and there was no layer of wax (T) around the rod. It was thought that a small fractional part of the current might have leaked over the surface of the rod, through the electrolyte (sodium chloride solution), over to the cathode (S). Such a short would cause the amount of iodine liberated to be low. A layer of wax (T) was put around the rod in order to prevent such a leak. In series 1, 2 and 3 the coulometers were connected in series so that the current passed in turn through iodine coulometer 2, iodine coulometer 1, silver coulometer 2 and silver coulometer 1. Thus there might have been an external short circuit across the two iodine coulometers which would permit them to check each other and yet not check the silver coulometers. This was considered somewhat unlikely though as the connecting wires between the coulometers were suspended in the air. However, the results obtained in series 1, 2 and 3 indicated that there must have been an external short circuit across the iodine coulometers or otherwise the internal leaks within the coulometers must have been of about the

same magnitude. In trying to locate a source of error, it was observed that the stirrer in the constant temperature bath and in turn the bath itself were short-circuited to the 110 volt line which was used to heat the bath and also drive the stirrer. Care had been taken to keep all leads leading to the coulometers well insulated from the bath itself but it is barely possible that a leak might have occurred. The possibility of the same external short circuit across the two iodine coulometers was eliminated in series 4, 5 and 6 by passing the current in turn through iodine coulometer 2, silver coulometer 2, iodine coulometer 1 and silver coulometer 1. In series 4 the agreement between the coulometers was fair so it was thought that the source of error had been removed.

The coulometers were placed in the same relative positions in series 5, but the variation in iodine coulometer 2 was greater than ever. The author suspected some gross error in the titration of this iodine sample and failed to examine the anodes as carefully as he did after a similar error was obtained in series 6. On inspection of the wax layers it was observed that the lower edge (next to the sodium chloride solution) of each of the wax layers

had been attacked. The wax in coulometer 2 was attacked even more than that in coulometer 1. The lower edge of the wax had turned a sort of grayish white and crumbled off when it was rubbed. Evidently a leak had occurred within the coulometers even over the wax layer and the wax had been attacked electrolytically. In series 4, the surface of the wax might have been less contaminated and thus prevented the internal short circuit during this run.

The remaining series were made during the summer of 1954. In each of these runs the current passed in turn through the silver coulometer 1, iodine coulometers 1 and 2 and then through silver coulometer 2. Before these runs were begun the rods (R) in the coulometers were replaced by longer ones which extended about 4 centimeters above the rubber stoppers and had layers of sealing wax on them which passed through the stoppers and extended about 3 centimeters above and 2.5 centimeters below the stopper. After each of the following runs, the lower edge of the wax was inspected and was found not to have been attacked. Evidently, the layer was long enough to prevent a leak over its surface for the iodine coulometers checked each other better and were

in much better agreement with the silver coulometers.

It will be observed that in series 7, 9 and 10 the silver equivalent of the iodine set free in the iodine coulometers was lower than the mean silver deposit in the silver coulometers. In series 8 the silver equivalent of the iodine was higher. This was accounted for at the time of the experiment. After the electrolysis was begun, the room became filled with chlorine gas from an adjoining laboratory where a chlorination of some organic compound was being made on a rather large scale by using chlorine gas from a cylinder of chlorine. So much chlorine gas was escaping that one could scarcely remain in the room. The chlorination was continued during the greater part of the day, hence the room was filled with chlorine gas during the electrolysis and the analysis of series 8. Before any more runs were made, methods of proper disposal of the excess chlorine, in the adjoining laboratory, were introduced, and the room in which this investigation was continued remained free from chlorine.

The mean per cent variation of the 8 iodine coulometers, used in series 4, 7, 9 and 10, from the silver reference coulometers was -0.023 per cent. The

maximum variation was -0.05 per cent. The mean per cent variation of the 6 iodine coulometers, used in series 7, 9 and 10 (1954), from the silver reference coulometers was -0.017 per cent and the maximum variation was -0.04 per cent.

One will observe that of the 8 iodine coulometers, used in series 4, 7, 9 and 10, the value of the silver equivalent of the iodine liberated in 7 of them is less than the mean silver deposit. In calculating the silver equivalent of the iodine the atomic weight of silver was used as 107.880 and that of iodine was used as 126.92. If the atomic weight of iodine were lower, the above values would be thrown into closer agreement. Several of the more recent atomic weight determinations have given lower values than that recommended by the Committee on Atomic Weights of the International Union of Chemistry⁵. Guichard²⁴ obtained 126.915, Baxter and Butler²⁵ obtained 126.905, and Hönigschmidt and Striebel²⁶ obtained 126.917 for the atomic weight of iodine. Recently, Guichard²⁷ recommended the use of 126.91 as the atomic weight of iodine for the present. The Committee on Atomic Weights of the International Union of Chemistry⁵ recommends the use of 126.92.

STANDARD SODIUM THIOSULPHATE SOLUTION.

The method used, during the summer of 1934, in the standardization of the sodium thiosulphate solution was the same as that used during the summer of 1933. The method of storing and using the thiosulphate solutions was the same throughout the investigation. Hence a detailed discussion of the standard thiosulphate solution used in 1933, and merely the results of the standardization of the thiosulphate solution used in 1934 will be given here.

Two and one-half liters of approximately N/2 solution of the thiosulphate was made up and transferred to a dark bottle. This bottle was kept submerged to the neck in a large tank of water at 30° C to prevent condensation of moisture on the upper part of the inside of the bottle due to temperature changes in the surroundings¹². The bottle was fitted with a siphon so that solution could be withdrawn without removing the stopper. This solution stood for 24 days before being standardized. A portion of this solution was diluted to exactly one-hundredth the concentration of the approximately N/2 solution. This was done by weighing 20.40744 grams of the concentrated solution from a

weight burette and diluting it with 2020.337 grams of water. The weight burette was weighed on a Voland and Sons chemical balance. The water was weighed on a Sartorius balance of large capacity. The set of weights was calibrated by the Bureau of Standards and weighings were corrected to vacuum. The dilute solution was stored just as the concentrated solution was. The specific gravity of the concentrated solution was found to be 1.0817 at 30° C and that of the dilute solution was found to be 1.0009 at 30° C. These were determined by means of a Parker and Parker²² pycnometer.

The concentrated solution was standardized against iodine as follows. About 4.7 grams of iodine (4.7352 grams are liberated by 3600 coulombs) were weighed out in a glass stoppered weighing bottle. This was immediately dropped into a glass stoppered Erlenmeyer flask which contained about 13 grams of potassium iodide in about 150 cc of triple distilled water. The stopper of the weighing bottle was loosened but not removed before dropping it into the Erlenmeyer in order not to lose any iodine as vapor. This is similar to the method used by Foulk and Morris²⁰ and

that given by Treadwell²⁸. When the weighing bottle was introduced, the Erlenmeyer was tilted so that the solution came near the mouth of the flask. In this manner the bottle would slide in so smoothly that the stopper would not be removed. The weighing bottle was weighted with an agate marble so it would sink in the solution. Then an amount of the thiosulphate solution, which was a little less than the amount equivalent to the sample of iodine, was added to the Erlenmeyer flask from a weight burette. By rotating the flask the stopper of the weighing bottle came out readily and the iodine was beneath the surface of the solution. When the iodine was all dissolved the titration was continued by adding thiosulphate solution from the weight burette. As soon as the color of the solution began to fade, the addition of thiosulphate solution from the weight burette was discontinued and the solution was transferred to a 1000 cc beaker and diluted to about 900 cc. A mechanical stirrer was used to stir the liquid in the titration beaker and titration was continued by the addition of dilute thiosulphate solution from a volume burette, which had been calibrated by the Bureau of Standards.

The end point was detected by means of the electrometric method¹⁷.

From the volume of the dilute thiosulphate solution added, the equivalent number of grams of concentrated thiosulphate solution was known. This amount added to the weight of thiosulphate solution used from the weight burette gave the number of grams of concentrated solution which was equivalent to the number of grams of iodine used. Thus it was found that 1 gram of the concentrated solution was equivalent to 0.0780395 grams of iodine (atomic weight 126.92) and 0.066532 grams of silver (atomic weight 107.880).

The results of the standardization of the thiosulphate solution used during the summer of 1933 are listed in table 6.

Table 6.

Trial	Sample iodine	Iodine equivalent	% variation from mean
1	1	.078039	-0.0006
2	1	.078038	-0.002
3	1	.078039	-0.0006
4	1	.078042	+0.003
5	2	.078009	
6	2	.078012	

Sample number 1 was purified (1933) according to the method discussed above, under the heading, "Purification of materials". Sample number 2 was given no special treatment. It was a sample of Mallinkrodt's, analytical reagent, chlorine and bromine free iodine. Column 3 of table 6 lists the number of grams of iodine equivalent to 1 gram of the standard concentrated sodium thiosulphate solution. Trials 5 and 6 were not included in computing the mean iodine equivalent of 1 gram of concentrated thiosulphate solution mentioned above.

The results of the standardization of the thiosulphate solution used during the summer of 1934 are listed in table 7.

Table 7.

Trial	Sample iodine	Iodine equivalent	% variation from mean
1	3	.0898113	+0.003
2	3	.0897991	-0.014
3	3	.0898108	+0.003
4	3	.0898117	+0.004
5	2	.0897608	
6	2	.0897724	

Sample number 3 was purified (1934) according to the method discussed above, under the heading, "Purification of materials". Sample number 2 was given no special treatment. It was some of the same sample 2 used in 1933. Column 3 of table 7 lists the number of grams of iodine equivalent to 1 gram of the standard concentrated thiosulphate solution. The mean iodine equivalent, obtained by using the values for trials 1, 2, 3 and 4, only, was found to be .0898085. The specific gravity of the concentrated thiosulphate solution at 50° C was found to be 1.0940 and that of the dilute solution was found to be 1.0008.

TEMPERATURE COEFFICIENT OF THE IODINE COULOMETER.

In the comparison of the iodine coulometer with the silver coulometer, the temperature of the iodine coulometer was maintained approximately constant during any given run. Column 5 of table 5 lists the temperature of the bath surrounding the iodine coulometer to within 0.5° C. The temperature of the solution in the outer vessel, outside of the jacketing cylinder, of the iodine coulometer was measured at the end of every run and was found to be from 1° C to 1.5° C higher than that of the surrounding bath.

Reference to table 5 shows that at 0° C (series 10) the mean value of the silver equivalent of the iodine liberated was about 0.02 per cent lower than the silver deposit. Series 8 was made at 0° C too, but as is stated above, it is unreliable due to the presence of chlorine gas in the room while this run was being made. Series 7 at 31.5° C gave a silver equivalent which was about 0.03 per cent low. Series 9 at 32.5° C gave a corresponding value which was 0.006 per cent low.

The variation of the amount of iodine liberated, due to a temperature change of about 32°C , appears to be within experimental error. Thus we may conclude that for temperatures from 0°C to 32.5°C the temperature coefficient of the iodine coulometer is negligible at the current densities here employed.

VARIATION OF THE NATURE OF THE CATHOLYTE.

The iodine coulometer used in this investigation has been discussed in detail in connection with figure 3. Reference to that discussion will show that hydrochloric acid was used around the cathode to prevent the accumulation of hydroxyl ions which upon migration to the anode region would produce a loss in iodine. No doubt a number of other chemicals would serve the purpose as well. Gallo⁸, and later Washburn and Bates¹⁰ and Vinal and Bates¹² used a solution of iodine in potassium iodide around the cathode.

Hydrochloric acid served the purpose well. The specific gravity of a 2 N solution of hydrochloric acid²⁹ at 30° C (1.0283) is less than that of a 10 per cent solution of sodium chloride³⁰ at 30° C (1.06676). Therefore, when the acid is introduced carefully, a distinct meniscus is formed between the two solutions. Greater care must be exercised in introducing the acid than the potassium iodide solution, since the specific gravity of a 50 per cent solution of potassium iodide³¹ at 30° C (1.53822) differs more from that of a 10 per cent solution of

sodium chloride than the sodium chloride solution differs from a 2 N solution of hydrochloric acid. Undue mixing must be avoided, for the acid must not reach the anolyte. Oxygen of the air will liberate iodine from an acid solution of potassium iodide. No trouble was experienced in this respect, however, and one would hardly expect to, since the hydrogen ions tend to migrate toward the cathode as soon as the electrolysis is begun.

Cady¹⁵ made no attempt to prevent the accumulation of the hydroxyl ions at the cathode, but increased the length of the path between the anode and cathode to such an extent that during the period of electrolysis the hydroxyl ions did not have time to migrate over to the anode region. Increasing the length of this path increases the internal resistance of the coulometer.

An attempt was made to determine the effect of omitting the acid from the coulometer diagramed in figure 3. If it were possible to omit the acid and still attain the desired precision it would be desirable, for the proper introduction of the acid into the coulometer requires special care.

In each run made in this part of the investigation four iodine coulometers were connected in series. Current from the source (Edison cells) passed in turn through a ballast resistance, an iodine reference coulometer (number 1), two iodine test coulometers (numbers 2 and 3) and then through another iodine reference coulometer (number 4). The same precautions were taken to insulate the coulometers as are discussed under the heading, "Comparison of the iodine coulometer with the silver coulometer". A current of 250 milliamperes passed for the length of time indicated in table 8. These runs were made at room temperature. Series 1 and 2 were made at 35° C and series 3 was made at 30° C.

Iodine reference coulometers were used in place of silver reference coulometers since they are much more convenient. The minimum time required to properly care for two silver coulometers and get them ready for another electrolysis is about 24 hours, while the author found that he could determine the amount of iodine liberated and have two iodine coulometers ready for another electrolysis within 5 hours after an electrolysis was finished.

The results of three series are listed in table 8.

Table 8

Series number	Coulometer number	Amps. per sq. cm.	Time in hrs.	Sodium thiosulphate soln. (gms.)	Mean of reference coulometer	Per cent variation from this mean
1	1	.1437	4.	50.9855	50.9773	+0.02
1	2	.0606	4.	50.7181		-0.51
1	3	.0606	4.	50.9034		-0.15
1	4	.0606	4.	50.9690	50.9773	-0.02
2	1	.1437	1.5	19.2021	19.1981	+0.02
2	2	.0606	1.5	19.1880		-0.05
2	3	.0606	1.5	19.1850		-0.07
2	4	.0606	1.5	19.1941	19.1981	-0.02
3	1	.1437	4.	51.0024	51.0004	+0.004
3	2	.0606	4.	50.6624		-0.66
3	3	.0606	4.	50.6727		-0.64
3	4	.0606	4.	50.9983	51.0004	-0.004

Since iodine reference cells were used, it was not necessary to use a standardized solution of sodium thiosulphate. The thiosulphate solutions used here were prepared and used similarly to the method discussed above, under the heading, "Standard sodium thiosulphate solution". Column 5, table 8, lists the grams of thiosulphate solution used in titrating the iodine liberated in the various coulometers. Any variation in these masses would represent a corresponding variation in the iodine liberated in the coulometers. These variations are indicated in column 7, table 8.

In each series, coulometers 2 and 3 were made up just as the reference coulometers 1 and 4, with the exception that the catholyte (hydrochloric acid) was omitted in coulometers 2 and 3.

In series 1, coulometers 2 and 3 did not check so well. Hence this series was repeated and the results are listed as series 5. This would indicate that when 5600 coulombs are permitted to pass, the coulometers can not be used without the hydrochloric acid if precision of 0.1 to 0.01 per cent is desired. In series 2 the coulometers were assembled in exactly the same

manner as in series 1 and 3. Series 2 lasted only 1.5 hours instead of 4 hours, that is, only about 1350 coulombs passed instead of 3600 coulombs, as had been used in most of the series throughout this investigation. The results of series 2 indicate that one might use the iodine coulometer without any catholyte (other than sodium chloride) and still attain greater precision than 0.1 per cent if the duration of the electrolysis is short enough not to permit the hydroxyl ion to migrate over to the anode region.

At the end of the electrolysis some of the sodium chloride solution from the inner vessel, just above the anolyte, was tested for alkalinity. In series 1 and 3 it was found to be distinctly alkaline to phenolphthalein, indicating that the hydroxyl ions had migrated to the anode region. In series 2, it was very slightly alkaline to phenolphthalein, indicating that 1.5 hours is near the limit of the time necessary for the hydroxyl ion to reach the inner chamber.

USE OF SO-CALLED C. P. MATERIALS.

As a matter of convenience, it would be advantageous to be able to use so-called C. P. materials in place of the specially purified substances used above. An attempt was made to determine whether or not C. P. materials can be used and still attain precision of 0.1 to 0.01 per cent.

In each run made in this part of the investigation four iodine coulometers were connected in series. Current from the source (Edison cells) passed in turn through a ballast resistance, an iodine reference coulometer (number 1), two iodine test coulometers (number 2 and 3) and then through another reference coulometer (number 4). The same precautions were taken to insulate the coulometers as was discussed above under the heading, "Comparison of the iodine coulometer with the silver coulometer". A current of 250 milliamperes was passed for 4 hours, that is, 3600 coulombs were permitted to pass before the electrolysis was interrupted. These runs were made at room temperature. Series 5 and 6 were made at 32° C. Series 4 was made at 36° C and series 7 was made at 50° C.

The results of four series are listed in table 9.

Table 9

Series number	Coulometer number	Amps. per sq. cm.	Time in hrs.	Sodium thiosulphate soln. (gms.)	Mean of reference coulometer	Per cent variation from this mean
4	1	.1437	4.	51.0694	51.0652	+0.009
4	2	.0606	4.	51.0537		-0.02
4	3	.0606	4.	51.0419		-0.05
4	4	.0606	4.	51.0608	51.0652	-0.009
5	1	.1437	4.	51.0122	51.0133	-0.002
5	2	.0606	4.	51.0001		-0.03
5	3	.0606	4.	51.0205		+0.01
5	4	.0606	4.	51.0143	51.0133	+0.002
6	1	.1437	4.	51.5229	51.5149	+0.02
6	2	.0606	4.	51.5155		+0.001
6	3	.0606	4.	51.5186		+0.007
6	4	.0606	4.	51.5069	51.5149	-0.02

Table 9 (continued).

Series number	Coulometer number	Amps. per sq. cm.	Time in hrs.	Sodium thiosulphate soln. (gms.)	Mean of reference coulometer	Per cent variation from this mean
7	1	.1437	4.	51.1509	51.1467	+0.008
7	2	.0606	4.	51.1813		+0.07
7	3	.0606	4.	51.1932		+0.09
7	4	.0606	4.	51.1425	51.1467	-0.008

Since iodine reference cells were used, it was not necessary to use a standardized solution of sodium thiosulphate. The same thiosulphate solutions were used in these series as were used in the series under the heading, "Variation of the nature of the catholyte". Column 5, table 9, lists the grams of thiosulphate solution used in titrating the iodine liberated in the various coulometers. Any variation in these masses would represent a corresponding variation in the iodine liberated in the coulometers. These variations are indicated in column 7, table 9.

SODIUM CHLORIDE.

In series 4, Mallinckrodt's, analytical reagent, sodium chloride was used in making up the 10 per cent solution of sodium chloride for coulometers 2 and 3. In every other respect these coulometers were similar to the iodine reference coulometers 1 and 4. It is interesting to note here that the sample taken directly from the bottle, without any special treatment, met the tests applied to the specially prepared sodium chloride discussed under the heading, "Purification of materials". It did not give a precipitate with 50 per cent potassium iodide solution as the commercial

samples used during the summers of 1932 and 1933 did (Purification of materials). This commercial sample was not available in our laboratory during the summers of 1932 and 1933. The results of series 4 indicate that one may use this quality of commercial sodium chloride and obtain precision of 0.1 to 0.01 per cent.

POTASSIUM IODIDE.

The tests listed under "Purification of materials", were applied to Mallinckrodt's, analytical reagent, potassium iodide. It was alkaline to phenolphthalein and contained iodates or some other oxidizing material which liberated enough iodine to color a 50 per cent solution of the sample, which was placed in the dark, distinctly within 8 hours. A sample of this potassium iodide was heated to slightly above 400° C for four hours. After being heated it still tested alkaline but appeared to have less, if any, oxidizing agents remaining for it gave a negative test for iodates (Purification of materials). A 50 per cent solution of this sample did not become colored while it stood in the dark for 24 hours. Since the solution was alkaline any liberated iodine would tend to be used up.

In series 5, Mallinckrodt's, analytical reagent, potassium iodide, which had been heated, was used in making up the anolyte for coulometers 2 and 3. In every other respect they were similar to the iodine reference coulometers 1 and 4. The results indicate that one may use such a sample and still obtain precision of 0.1 to 0.01 per cent.

In series 7, Mallinckrodt's, analytical reagent, potassium iodide, which had not been heated, was used in making up the anolyte for coulometers 2 and 3. In every other respect they were similar to the iodine reference coulometers 1 and 4. The variations of these coulometers from the reference coulometers were greater than in series 5, in which the iodide was first heated. While the variation is still within the limits of the precision (0.1 to 0.01 per cent) aimed at in this investigation, coulometer 3 approached the limit rather closely.

SODIUM IODIDE.

The tests which were applied to the above mentioned potassium iodide sample were applied to a sample of Mallinckrodt's C.P. sodium iodide. The results were identical to those obtained for potassium iodide in every detail.

In series 6, a sample of this sodium iodide, which had been heated to slightly above 400° C for four hours, was used in making up the anolyte for coulometers 2 and 3. In every other respect they were similar to the reference coulometers 1 and 4. The results indicate that one may use such a sample and still obtain precision of 0.1 to 0.01 per cent.

RANGE OF CURRENT DENSITIES PERMISSIBLE.

Reference to the discussion following table 2 will show that the permissible current density depends, among other factors, upon the physical dimensions of the coulometer, the total quantity of electricity which is to pass through the coulometer and the volume of anolyte used. For a coulometer as is diagramed in figure 3, when 25 cc of 50 per cent potassium iodide solution is used and for a total quantity of electricity of 0.05 faradays the upper limit of current density is near 0.3 amperes per square centimeter for an anode of 8.25 square centimeters. Under the same conditions, except for an anode of 4.125 square centimeters, the upper limit of the current density is somewhat above 0.2 amperes per square centimeter. Under the same conditions, except for an anode of 1.74 square centimeters, the upper limit is near 0.2 amperes per square centimeter.

The above (table 2) somewhat qualitative data proved valuable in designing the coulometer for the quantitative experiments, the results of which are listed in tables 5, 8 and 9. In all of the cells listed in these tables 25 cc of 50 per cent potassium

iodide was used as anolyte. The physical dimensions of the coulometers used were the same as the one diagramed in figure 3. In each electrolysis, to be considered here, 3600 coulombs were permitted to pass before it was interrupted. In table 5, series 4, an anode of 4.125 square centimeters was used. In this case 0.1212 amperes per square centimeter was successfully used. This is not the maximum indicated in table 2 but it happens to be the highest current density used in this investigation, with this size anode. In table 5, series 7, 9 and 10, an anode of 4.125 square centimeters was used. The current density in these series was 0.0606 amperes per square centimeter and the results show that such a current density is permissible. In each of the series listed in tables 8 and 9, reference coulometer 4 had an anode of 4.125 square centimeters, and the current density was 0.0606 amperes per square centimeter. In the same series, reference coulometer 1 had an anode of 1.74 square centimeters and the current density was 0.1457 amperes per square centimeter. Since it is known (Table 5) that a current density of 0.0606 amperes per square centimeter is permissible, the results in tables 8 and 9 justify the use of a cur-

rent density of 0.1437 amperes per square centimeter even with as small an anode as 1.74 square centimeters. The variation of reference coulometer 1 from reference coulometer 4 was well within the experimental error in each series listed in tables 8 and 9.

Vinal and Bates¹² have shown that current densities of 0.005 and 0.001 amperes per square centimeter are permissible. Since oxygen is more liable to be liberated at a higher current density, it seems safe to conclude that when 3600 coulombs or less pass through the above designed iodine coulometer current densities from 0.001 to 0.1437 amperes per square centimeter, at least, are permissible. The data in table 2 indicate that even higher current densities are permissible.

SUMMARY

A review of previous investigations on the iodine coulometer has been made.

Platinum and platinum-iridium alloy were not attacked when used as anodes in potassium iodide solutions, when current densities ranging from 0.02 to 0.51 amperes per square centimeter were used.

Specifications for an iodine coulometer which will permit 0.05 faradays to pass were determined.

By varying the form of the coulometer, its resistance was reduced to 5.9 ohms, a marked economy of electrode material resulted and the coulometer was simplified until it can be used in about one fifth of the time required to operate a silver coulometer.

By manipulation this coulometer was varied until precisions lying between 0.1 to 0.01 per cent were obtained.

In the direct comparison of the iodine coulometer with the silver coulometer the mean per cent variation of 6 series of electrolyses was -0.017 per cent and the maximum variation was -0.04 per cent. The mean variation was within the desired experimental

error. However, it should be noted that in 5 of the 6 series the iodine coulometer was low.

The temperature coefficient of the iodine coulometer was found to be negligible for temperatures ranging from 0° C to 32.5° C at the current densities here employed.

When 3600 coulombs were permitted to pass through the iodine coulometer discussed above, it was found to be essential to use a catholyte (hydrochloric acid or some other reagent which would serve the same purpose) to prevent the accumulation of hydroxyl ions around the cathode. When the hydroxyl ions did not have time to reach the anode region during the period of electrolysis, the special catholyte was not required.

When Mallinckrodt's, analytical reagent, sodium chloride was used as electrolyte, the desired precision was obtained. Mallinckrodt's, analytical reagent, potassium iodide caused the amount of iodine liberated to be too high by nearly 0.1 per cent. When this iodide or Mallinckrodt's C. P. sodium iodide was heated to slightly above 400° C for four hours before being used to prepare the anolyte, the desired precision was obtained.

It was found that when 3600 coulombs or less pass through the above designed iodine coulometer, current densities of 0.001 to at least 0.1437 amperes per square centimeter are permissible. Qualitative tests indicated that even higher current densities are permissible.

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