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ART. I.—*An Iodine Titration Voltameter*; by D. ALBERT
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THE rapidity, accuracy and sharpness of the end reaction of several of the methods of volumetric analysis, particularly of the iodometric methods, have suggested the possibility of applying them to the voltameter. A rather extensive investigation of quantitative electrolytic oxidation and reduction methods, with this aim in view, has resulted in the evolution of a titration voltameter the accuracy of which may be depended upon to about one part in ten thousand. The advantages in point of manipulation and time required, as well as its applicability to a greater range of current density, will, in the writer's opinion, make it of service in many investigations.

The basis of the method is the electrolysis of potassium iodide and the titration of the liberated iodine by sodium thio-sulphate. Herroun* first suggested the use of iodine in this connection. He electrolyzed zinc iodide between a platinum anode and zinc cathode in a beaker; but gives the results of only one determination and leaves the method in an impracticable form.

Danneel† reports four comparative tests of Herroun's zinc iodide voltameter in series with a silver voltameter. The results show a difference of between +0.27 per cent and -1 per cent. His burette readings were made to only the nearest 0.1^{cc}; and the total quantity of thiosulphate was small; varying from 7. to 34^{cc}.

The work of Danneel, as well as that of Kistiakowsky‡ on a silver titration voltameter, seems never to have found its way

* Phil. Mag. [5], xl, 91, 1895.

† Zeitschr. für Elect. Chem., iv, 154, 1897.

‡ Zeitschr. Phys. Chem., vi, 97, 1890.

into the general literature. The work of both men, on voltameters, was incidental to another research and the titles of their articles fail to afford any clue to this particular contents. My own preliminary search of possible reactions had been completed and I had settled upon the form of the iodide voltameter before I learned of the work just mentioned.

Herroun rather erroneously points to the high electrochemical equivalent of iodine as its chief advantage; this is obviously immaterial in a volumetric method. As a basis of a titration method, however, iodine has peculiar advantages in the rapid action of sodium thiosulphate upon it and in the extreme sharpness of the end reactions, intensified when desirable by the addition of starch solution. Potassium iodide is, moreover, much to be preferred to the zinc salt. It is obtainable commercially quite free from iodates and its solutions may, therefore, be acidified without the liberation of iodine, except for the very slow action of atmospheric, or dissolved, oxygen.

It is, of course, impracticable to electrolyze the potassium iodide directly, when the liberated iodine is to afford a measure of the current; this is because of the recombination of the electrode products by diffusion. Acidifying prevents this recombination, or even after it has taken place, in an acid solution the original amount of iodine is liberated, providing the iodine has not been allowed to diffuse to the cathode during the electrolysis, where it would tend to combine with hydrogen and would be irrecoverable.

A most satisfactory action is obtained when the anode is submerged in a strong aqueous solution of the potassium iodide under dilute hydrochloric acid in which the cathode is suspended. With the electrodes thus placed vertically, the anode below, the liberated iodine, because of its great density and solubility in potassium iodide, diffuses very slowly. After a run of hours, and even on subsequent standing for hours more, the solution about the cathode remains perfectly colorless and free of iodine.

The Potassium Iodide Cell.

As a cell, I have employed a side-necked test tube, fig. 1, drawn out at the bottom to a long capillary. Into the junction of this capillary a glass rod was ground. The test tube was closed by a rubber stopper with three perforations, through the middle one of which the ground glass rod passes air tight, though not so tightly as to prevent easy motion when moist. The other perforations receive the glass tubes through which the wires connect with the platinum electrodes; anode at the

bottom of the tube, cathode above. The size of the electrodes was, in the small cell, 1.6×2.7 cm; in the large cell, 2.5×6 cm. In the latter case the cathode was somewhat smaller and corrugated. These electrodes were bent into cylindrical form and arranged coaxially with the tube. The smaller cell had a diameter of 2 cm, length, 12 cm, length of capillary, 7 cm. Its capacity was about 30 cc; about 7 cc being required to cover the anode. The larger cell was made in the same way, of a tube 3 cm in diameter and about 15 cm in length, with a capillary about 18 cm long. With the distance of 5 cm between the nearest edges of the electrodes, the total volume required to cover the cathode was about 60 cc, about 20 cc sufficing to cover the anode.

The apparatus was filled by raising the ground glass rod and by diminished pressure, effected through the side neck, drawing up through the capillary successively the required amount of hydrochloric acid and then the strong solution of potassium iodide in water. In this way the anode is completely submerged in the concentrated solution of iodide without the use of excessive quantities. The hydrochloric acid serves as an electrolyte, permitting the separation of the electrodes sufficiently to preclude the possibility of any interaction of the electrode products.

By this method of filling the cell the iodide is sufficiently acidified, and if not too rapidly drawn in, a sharp line will mark the junction of the two solutions of different density. The electrolysis results in a quantitative liberation of iodine unless the current density is too great. In the latter case oxygen is evolved along with the iodine. With the permissible current densities indicated in Table I, so long as the potassium iodide is not impoverished about the anode, not a trace of oxygen appears and the action is entirely satisfactory. As the iodine is liberated it sinks along the electrode and by its convection effect renews the iodide at the surface of the electrode without the slightest disturbance of the supernatant acid. In all cases where the current density has not exceeded the indicated maximum, or where the duration of the current has not been such as to exhaust the iodide (so that no oxygen is evolved) the supernatant liquid remains perfectly colorless and free of iodine, and continues to show a sharp line of demarcation between the iodine solution and the acid.

Table I shows the possible current densities, potential change, and permissible time of run, under the given conditions. In the first column, the first figure represents the num-

ber of grams of potassium iodide used and the second figure the volume of its solution in water. In the fifth column, where two figures are given, the first represents the fall of potential through the cell at the beginning of the experiment and the second figure that at the end of the run. The interval is found in the sixth column. An asterisk following the figures of the sixth column indicates that the current was continued until, and stopped at the moment of, the first appearance of gas on the anode. It is evident that the liberation of iodine is no longer quantitative for some time before this gas appears, the safety limit depending upon the current density. Within this safety limit the rise of potential is also not as great as that indicated in the fifth column. The fall of potential through the cell increases continuously and very regularly, after the first few minutes, in which it rises rather more rapidly. Just before the appearance of the gas the potential naturally rises quite rapidly. The gradual change of potential is doubtless due to the increased resistance of the potassium chloride solution which is formed during the electrolysis at the boundary of the two solutions. This part of the cell, especially the small one, is always considerably heated by the current, and a conspicuous line of increased density of the solution, but entirely colorless, gradually creeps up the tube to a distance of several centimeters in an hour's run. In the 7th experiment the solution became quite warm and small bubbles of gas appeared on the sides of the glass, long before there was any evidence of gas being evolved at the anode. To test the correctness of the supposition that this was merely dissolved gas, the 8th experiment was made with the cell in a water bath maintained at 9°. Under these conditions no gas appeared until it was evolved at the anode. This experiment also shows that the warming of the solution is, if anything, an advantage; due, doubtless, to the more rapid diffusion of the iodide or to the greater solubility of the iodine. In experiments 3 and 10 the current was varied; the time of run for each value of the current is given in the sixth column.

Three determinations with two of the small cells in series, each containing 2 grams of potassium iodide in 7.5 cc, with a current density of 0.015 amp./cm² showed the following satisfactory agreement in the amount of thiosulphate required:

(a) { 31.55 cc	(b) 28.60 cc	(c) 16.62 cc
31.58 "	28.66 "	16.60 "

A comparison between the values obtained by two of the iodine voltameters in series with each other and with one or more copper voltameters is shown in Table II. The titrations

in these cases were not as accurately made, nor the solutions standardized with the same care that characterized the later determinations, as will be seen from the sequel.

TABLE I.

(a) Small cell { Diam. of cell = 2^{cm}.
Length of cell = 12^{cm}.
Electrodes 1.6 × 2.7^{cm}.
Dist. between nearest edges of electrodes, 5^{cm}.

	KI grms. in cc. of solution	HCl (1:4) cc.	Current (approx.) amp.	Current density (approx.) amp./cm ²	P. D. Volts.	Time of run, mins.	
1	1 in 5	not measured	0.13	0.015	2.25	22*	
2	2 " 5		0.13	0.015	2.00	35*	
3	2 " 7.5	"	0.25	0.029		15	
		"	0.40	0.046		2 more	
		"	0.5	0.058		4½ more*	
4	2 " 7.5	"	0.5	0.058	7.1 to	7.8	15*
5	2 " 7.5	20	0.5	0.058	3. " "	4.7	13*
6	4 " 7.5	5	0.5	0.058	5. " "	12.5	47*
7	5 " 7.5	20	0.5	0.058	2.4 " "	4.8	85*
8	5 " 7.5	20	0.5	0.058	2.6 " "	5.8	54*
(b) Large cell { Diam. of cell = 3 ^{cm} . Length of cell = 15 ^{cm} . Electrode (anode) 2.5 × 6 ^{cm} . Distance nearest edges, 5 ^{cm} .							
9	5 " 20	40	0.5	0.017	2. " "	3.5	41*
10	10 " 20	40	0.5	0.017	1.5 " "	2.5	91
			1.0	0.033	4.1 " "	4.7	2 more
			1.5	0.050	5.7	1	more*

Solid iodine at anode
Solid iodine at anode
Solution alkaline
Solid iodine in large
quantity at anode

* Gas evolved at anode.

TABLE II.

Iodine voltameter.						Cu-voltameter.		
	Distance between elec- trodes, cm.	KI grms. in cc.	Cur- rent amp.	Amp./cm ²	Time, mins.	Na ₂ S ₂ O ₃ cc.	Copper equiv- alent, grms.	Copper grms.
1	(a) 5.4 in 7.5	{	0.5	0.058	25	73.90	0.2391	0.2379
	(b) 1.4 " 7.5					73.72	0.2385	
2	(a) 5.4 " 7.5	{	0.5	0.058	45	132.87	0.4202	0.4199
	(b) 5.4 " 7.5					132.71	0.4198	
3	5.5 " 7.5		0.5	0.058	45	134.21	0.4244	0.4234 0.4240

0.013
0.013
0.013

Standard Solutions.

Sodium thiosulphate is the most convenient medium for the titration of iodine, but it is not a very satisfactory standard where great accuracy is desired. The salt is readily obtained quite pure, but there is always some uncertainty as to the amount of extraneous water the crystals may contain. Further, on long standing, especially when exposed to the light, it undergoes a slight decomposition, with deposition of sulphur. However, this decomposition is so slow that, if kept in the dark, the solution will remain quite constant for months. In all of my titrations, except those that were merely relative, I have employed an approximately decinormal solution of sodium thiosulphate, standardized against arsenious oxide, by means of an iodine solution. The purest arsenious oxide obtainable was resublimed three times and weighed from a weighing bottle. This solution also was only approximately decinormal. The weight of the arsenious oxide was carefully determined and reduced to its weight in vacuo, and the solution accurately made up to one liter at 20° in a calibrated flask. The direct employment of the arsenic solution for the titrations is undesirable because it necessitates an excess of bicarbonate and the danger of loss of iodine in the neutralization requires a complicated series of traps. Moreover, the end reaction, when starch is employed, is much slower with arsenic than with the thiosulphate. With the latter it is practically instantaneous.

The Titrations.

The titrations were performed in Ehrlenmeyer beakers. In filling the cell, care was always taken to draw up the last of the iodide solution as far as the ground glass joint, but without admitting air which would stir up the solutions. To avoid a possible loss of iodine through a considerable leakage of the joint and vaporization from the concentrated solution, the Ehrlenmeyer beaker containing about 150^{cc} of water was placed under the cell during the electrolysis. The capillary extension of the cell (fig. 1) reached to the bottom of the beaker. Whenever the leakage of the ground glass joint was sufficient to allow the iodine solution to descend the full length of the capillary during an experiment, the joint was reground with the finest emery. Under these conditions a loss of iodine is impossible.

After the current was cut off, the ground glass joint was opened slightly and the cell allowed to empty slowly. The great density of the iodine solution keeps it continuously covered with a layer of water of considerable depth in the

beaker, and the supernatant acid of the cell washed out the iodine completely.

A burette of 50^{cc} capacity was employed. This burette was carefully calibrated and was found to be surprisingly accurate. Its error indicates an extremely minute and regular taper of the tube and the graduations are such as to permit of accurate readings to 0.02^{cc}. In fact I have felt considerable confidence in reading it to 0.01^{cc}. This, with the strength of solution employed, was equivalent to about 0.1^{mg} of silver. In the earlier determinations, when more than 50^{cc} of the thiosulphate were required, the burette was in some cases refilled, which, of course, multiplied the error of reading. In other cases, where the amount of thiosulphate was approximately known, a sufficient quantity was added to the beakers from calibrated pipettes of various size, so that the additional amount required should be less than 50^{cc}. This is, of course, less exact and impractical as well, unless the amount required is approximately known.

In the later determinations a bulb burette, fig. 2, was employed. This contained 6 bulbs, each of approximately 25^{cc} capacity, connected by small tubes of about 2 to 3^{mm} internal diameter. At about the middle of these tubes marks were etched in such a way as to permit readings without error of parallax. The smallness of the tubes prevented filling the burette from the top and to avoid the uncertainty of rubber connections a small side tube, also about 2 to 3^{mm}, terminating in a funnel, *b*, was sealed on and supported by a section of cork as shown. A finger placed on *a* as the liquid is poured into *b* regulates the flow, so that air bubbles are not carried along and the burette is filled quietly and accurately. Inclining the discharge tube, as shown, is of great advantage in preventing any of the grease from the cock soiling the interior of the burette, a very troublesome feature of the usual burette.

The readings of this burette are naturally extremely accurate. It was employed in bleaching the larger part of the iodine. Experience enabled me to judge from the color about when the remaining iodine was less than that bleached by the contents of one bulb. If there was any difficulty in judging this, a comparison beaker of iodine solution could be employed. At any rate the 50^{cc} burette, with which the titration was com-

pleted, was equal to two of the bulbs, and no difficulty was experienced in keeping within that limit. In case of accidentally overstepping the amount of thiosulphate required, a measured volume of iodine solution may be added and the titration be repeated, subsequent deduction being made for the amount of thiosulphate necessary to bleach the added iodine.

The end reaction was in all cases taken as the bleaching of the iodine color, without starch. This in itself is quite delicate, and I have invariably been able to read it to a small fraction of a drop, when the beaker stood on white paper in a good indirect light. As a confirmation of the reading, 5^{cc} of starch solution was then added and produced a faint purple color. The delicacy of this end reaction was more thoroughly appreciated when, after a number of titrations had been made successively, as in the experiments of Table III, the addition of the starch produced almost precisely the same shade of color in all, despite the fact that a very small fraction of a drop of the thiosulphate produced a distinctly perceptible change in the color.

TABLE III.

	Electrodes, cm.	Dis. bet. electrodes, cm.	KI grms. in cc.	Amperes (approx.)	Amp./cm. (approx.)	Na ₂ S ₂ O ₃ cc.	Difference.	
							cc.	%
(1)	1.6 × 2.7	2	5 in 7.5	0.5	0.058	130.84	0.17	0.13
	1.6 × 2.7	5	5 " 7.5			130.67		
(2)	1.6 × 2.7	2	5 " 7.5	0.5	0.058	128.49	0.06	0.047
	1.6 × 2.7	5	5 " 8.5			128.55		
(3)	1.6 × 2.7	2	5 " 7.5	0.5	0.058	127.36	0.10	0.078
	2.5 × 6.0	5	10 " 20			127.46		
(4)	1.6 × 2.7	2	5 " 7.5	0.5	0.058	170.67	0.23	0.135
	1.6 × 2.7	5	5 " 7.5			170.67		
	2.5 × 6.0	5	10 " 20			170.90		

Table III is a record of a number of determinations of the constancy of this voltameter. Two or more of the cells were connected in series, and the conditions in each varied as shown. The time of run for 1 to 3 inclusive was about 45 mins., for the 4th, one hour. The amount of hydrochloric acid (1:4) was not measured. Enough of the acid was drawn in to insure the covering of the cathode when the iodide solution was drawn in, and to keep the solution acid throughout the experi-

ment. The iodide was roughly weighed. No correction was made for the blank determinations, nor was special care taken to maintain exact constancy of temperature.

Table IV shows the results of the only two determinations that were made by three of the iodine voltameters in series with each other and with one normal silver gravimetric voltameter. The original readings of the burettes for the required thiosulphate is given in the 6th column. In the 7th column is given the value corrected for the blank determinations. A number of blank determinations for the small cell, when 5 grams of iodide were used, gave, with the blank shown in (2), an average value of 0.07^{cc} of thiosulphate, which is the correction applied to all of the small cells. The large cell, with 10 grams of potassium iodide, showed an average value for a blank determination of 0.21^{cc} of thiosulphate. This is three times instead of twice the value of the small cell, as would be expected were the result due to traces of iodate in the iodide. The uncertainty as to the amount of iodine liberated by iodate, or by dissolved oxygen, or by possible oxidizing impurities of the acid, make it rather more desirable to employ known weights of the iodide and known volumes of the acid and then to correct for the blank determination, than the alternative of securing absolute freedom from these extra sources of liberation of iodine.

In the silver voltameter employed, the cathode was a platinum bowl about 8^{cm} in diameter and 3.5^{cm} in depth. The anode was a silver disc, 5.8^{cm} in diameter, 0.8^{mm} thick, and supported by three platinum wires bent over its edges. This was wrapped in filter paper. The solution was made up of 20 grams of pure silver nitrate, dissolved in 106^{cc} of distilled water. The deposited silver was washed with water and allowed to stand under water over-night. Then washed again with water, finally with absolute alcohol and heated for 4 hrs. in an oven at 160°. Then allowed to cool for an hour in a desiccator before weighing.

TABLE IV.

	Electrodes, cm.	Distance between Electrodes, cm.	KI grms. in cc.	Amp. (approx.)	Amp./cm ² (approx.)	Na ₂ S ₂ O ₃ cc.	Na ₂ S ₂ O ₃ corrected for blank, cc.	Silver equivalent, grms.	Silver (in vac.) ag. voltameter, grms.	Difference.	
										Grms. of silver.	%
1	1.6 × 2.7	2	5 in 7.5	0.5	0.058	152.07	152.00	1.63386	1.63236	0.00150	0.092
	1.6 × 2.7	5	5 " 8.5		0.058	152.06	151.99	1.63375		0.00139	0.085
	2.5 × 6.0	5	10 " 20		0.017	152.19	151.98	1.63364		0.00128	0.078
2	1.6 × 2.7	2	5 " 7.5	0.0	0.00	0.06			1.67934		
	1.6 × 2.7	5	5 " 7.5	0.5	0.058	156.40	156.33	1.68042		0.00106	0.063
	2.5 × 6.0	5	10 " 20		0.017	156.55	156.34	1.68053		0.00119	0.071

The titrations in the experiments recorded in this table were made with due regard to all possible sources of error. The solutions were brought precisely to the temperature of 20° , at which temperature the room was maintained. The burettes had been thoroughly cleaned with chromate solution, and of course, ample time was allowed for the burettes to drain to a constant reading. The results show that the iodine voltameter, even after the correction for the blank determinations, run uniformly higher by from 0.06 per cent to .09 per cent; but that they agree among themselves to an order of accuracy of about 1 part in 10,000.

Sloane Physical Laboratory,
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