

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY.]

## THE DETERMINATION OF IODIC ACID AND SILVER BY ELECTROMETRIC TITRATION.

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In a recent paper the writer stated that he had determined by electrometric titration iodic acid and silver in essentially the same way as there described for dichromate, that is, by treating their solutions with an excess of a solution of pure potassium iodide, the value of which was known, and titrating this excess with permanganate in about 1 *N* sulfuric acid.<sup>2</sup> It was also stated that in the direct titration of iodide with iodate very nearly true values had been obtained in the case of about 0.05 *N* solutions in the presence of sulfuric acid.<sup>3</sup> Later work has shown that both 0.05 and 0.02 *N* solutions may thus be accurately titrated, due regard being paid to concentration in the titration vessel and sufficient time for the reaction to attain completion. The present paper contains a statement of this work and also of the influence of hydrochloric and nitric acids in such determinations.

In general the methods of work and apparatus were the same as described in the former paper. There being no further occasion to compare titrations in air and in an indifferent gas, a motor-driven stirrer of glass was used instead of compressed air or carbon dioxide. Except where otherwise indicated, all solutions used in the determinations were weighed. The data are given in grams, and to avoid the use of many ciphers in the tables, results are expressed in g. per 100 g. of solution, which is also the same as percentages.

**Determination of Potassium Iodate.**—Potassium biniodate prepared and sold to be used as a standard was recrystallized, dried over sulfuric acid and then to constant weight at 95° to 100°. Solutions were made by weight so as to be 0.02 and 0.05 *N* toward hydriodic acid, and standardized with thiosulfate solution which had been standardized with repeatedly sublimed iodine. The iodine was fused in glass-stoppered tubes which were left open over sulfuric acid for several hours before weighing. One g. of the iodate solutions set free from iodide 0.002611 and 0.006515 g. of iodine, showing a considerable excess over their theoretical values, and probably the iodate was more acid than the formula,  $\text{KHI}_2\text{O}_6$ , would indicate.

One g. of the permanganate solution used in Table I required 0.001328 g. of sodium oxalate, and the ratio of its weight to that of the iodide by

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<sup>2</sup> *THIS JOURNAL*, 43, 14 (1921).

<sup>3</sup> *Loc. cit.* (note).

electrometric titration was found to be 1.033:1. This value of the iodide was also confirmed with silver solution and weighing the silver iodide. Table I contains the original weights of iodate solution, and the weights of the iodide solution less the excess of iodide solution as determined with permanganate. Iodine found and calculated means to 100 g. of iodate solution.

TABLE I.—TITRATION OF IODATE WITH IODIDE AND PERMANGANATE, ALL ABOUT 0.02 *N*.

Expt.	KI. G.	HKI <sub>2</sub> O <sub>6</sub> . G.	I found.	I calc.	Deviation.
1.....	40.25	40.12	0.2607	0.2611	—4
2.....	52.69	52.55	0.2606	.....	—5
3.....	43.37	43.16	0.2611	.....	0
4.....	61.63	61.36	0.2610	.....	—1
5.....	49.90	49.58	0.2616	.....	+5
6.....	47.06	46.85	0.2610	.....	—1
7.....	45.42	45.25	0.2609	.....	—2

Average, —1

Determinations of the more concentrated solution of iodate with permanganate solution of which one g. oxidized 0.003195 g. of sodium oxalate, and the more concentrated iodide solution of which one g. was equivalent to 1.0182 g. of permanganate by titration, resulted as shown in the next table. Iodine found and calculated means to 100 g. of iodate solution.

TABLE II.—DETERMINATION OF IODATE WITH PERMANGANATE AND IODIDE, ALL ABOUT 0.05 *N*.

Expt.	KI. G.	HKI <sub>2</sub> O <sub>6</sub> . G.	I found.	I calc.	Deviation.
1.....	30.63	29.03	0.6502	0.6515	—13
2.....	31.35	29.63	0.6521	.....	+6
3.....	40.26	38.12	0.6509	.....	—6
4.....	34.11	32.26	0.6516	.....	+1
5.....	27.88	26.37	0.6516	.....	+1

Average, —2

**The Influence of Hydrochloric Acid.**—The work of Kolthoff<sup>1</sup> was referred to in the former paper by the writer. Following Crotogino whose work on the electrometric titration of iodide with permanganate has been discussed,<sup>2</sup> he rejects this oxidant for the purpose and gives the impression that sulfuric acid is not a suitable medium in which to determine iodide with dichromate or iodate, and he used hydrochloric instead. All the data submitted in this and the previous paper may be taken as evidence that these views are not well founded. Because of the fundamental importance of such titrations it seemed desirable to take up in some detail the influence of hydrochloric acid, when present in small amounts, in the ordinary titration of iodide with permanganate, using dil. sul-

<sup>1</sup> Hendrixson, THIS JOURNAL, 43, 23 (note).

<sup>2</sup> *Ibid.*, p. 22.

furic as the main acid medium, and then proceed to study comparatively the electrometric titration of iodide directly with iodate in hydrochloric and in sulfuric acid.

Titration of iodide with permanganate in sulfuric acid were made in the usual way except that increasing amounts of hydrochloric acid were added to the titration vessel, which contained in all cases at the end of the experiments about 250 cc. of solution. In each of the following series 25 cc. of 0.02 *N* iodide, 25 cc. of 10 *N* sulfuric acid and the recorded permanganate were used. The concentration of the hydrochloric acid given refers to the total solution at the end of the determinations.

Expt.	1	2	3	4	5	6	7
Normality HCl.....	0.0	0.01	0.02	0.04	0.08	0.16	0.5
Cc. permanganate.....	25.25	25.27	25.22	25.25	25.30	25.38	(?)

The nearly straight line representing the sudden rise of voltage as shown in Fig. 1, Curve 5, which represents the usual iodide-permanganate curve when titrated in sulfuric acid was gradually shortened and more inclined till in Expt. 6 the curve closely resembled Curve 2 in the cut. The end-point cannot be accurately determined from such a curve. The curve in Expt. 7 was quite useless.

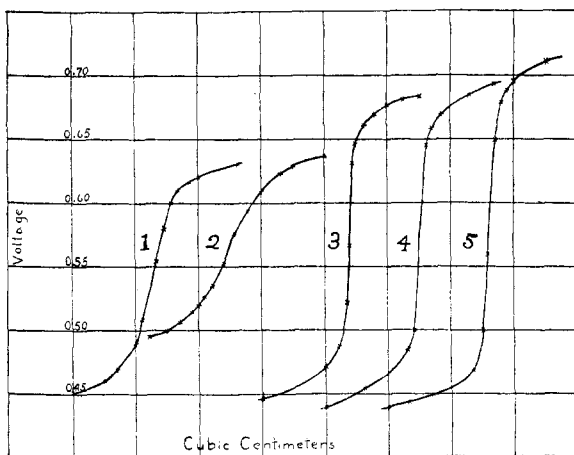


Fig. 1.

A similar series of determinations was carried out using about 0.05 *N* solutions of permanganate and iodide, all volumes being about the same as in the first series. The results are given as in the previous series.

Expt.	1	2	3	4	5	6	7	8
Norm. HCl.....	0.0	0.01	0.02	0.04	0.08	0.16	0.32	0.5
Cc. permanganate.....	26.24	26.25	26.27	26.28	26.20	26.25	26.3	(?)

With these solutions the curves were better but the end-points were obscured and uncertain beyond Expt. 6. The end-point in Expt. 7 is

quite uncertain, and not to be determined in Expt. 8. It follows that iodide may be determined with fair accuracy by use of permanganate solution and sulfuric acid in the presence of chloride, if the latter does not exceed about 0.1 *N* in the titration vessel. In these series iodide was about 0.002 and 0.005 *N* in the whole solution. Hence it is evident that iodide may be determined in the presence of many times its equivalent of chloride.

**Direct Titration of Iodate and Iodide in Hydrochloric Acid.**—Many such titrations were made using about 0.02 and 0.05 *N* solutions of iodate and iodide in hydrochloric acid of concentrations 0.1 to 0.5 *N* in the titration vessel, and of course without sulfuric acid. (The curves were plotted on paper ruled in inches and tenths.) In no case in which the volume in the titrating vessel was 250 cc. was a curve obtained from which the end-point could be determined. The nearest approach to it was a curve about the same as Curve 2 in Fig. 1, obtained with 0.05 *N* solutions in 0.2 *N* acid. By reducing the volume in the vessel to about one-half and in 0.2 *N* acid, Curve 2 was obtained with 0.02 *N* solutions, and Curve 1 with 0.05 *N* solutions. Curve 2 is of course valueless for accurate work and Curve 1 is inadequate. It seems probable that accurate titrations of dilute solutions of iodate and iodide in hydrochloric acid as the medium are impracticable. As in the determinations of iodide with permanganate in the series in which known amounts of hydrochloric acid were added, so here increasing acid caused poorer curves, and at most the limit of acid is apparently about 0.2 *N*. to provide a usable curve for end-point.

**Direct Determinations of Iodate and Iodide in Sulfuric Acid.**—As already stated,<sup>1</sup> preliminary titrations of iodate and iodide in dil. sulfuric acid gave results only slightly below the true value of the iodate, and good curves were obtained when 0.5 *N* solutions were used. A new solution of permanganate, having an oxalate value 0.003366 was used to standardize the iodide solution. The ratio of their weights found by titration was 1.0277:1. The iodate solutions were redetermined with re-standardized thiosulfate, and their former values confirmed.

In determining iodate with iodide in sulfuric acid the volume in the titration vessel was reduced to 150 cc. and the time near the end-point was much increased. Before taking the end-point one should assure himself that the galvanometer-mirror reflection is perfectly stationary, and that the voltage corresponds closely with the center of the abrupt rise shown in curves of previous experiments. To attempt to complete the titration in less than 5 minutes as may easily be done with permanganate will surely lead to large negative errors. The end-points are about as sharply indicated in titrating iodide with iodate in sulfuric acid as when

<sup>1</sup> *Loc. cit.* (note).

permanganate solution is used. Curve 5 in Fig. 1 was made with permanganate solution; Curve 4 was made with 0.05 *N* iodate solution with the total volume in the titrating vessel of 250 cc., and Curve 3 with 0.02 *N* solutions of iodide and iodate in a volume of 150 cc. The advantage of sulfuric acid is shown by contrasting Curve 3 with Curve 2, which was made with the same 0.02 *N* solutions but by titration in 0.2 *N* hydrochloric acid, the final volumes and other conditions being the same.

Several titrations of iodate with iodide of concentration just given are summarized in Table III. Again "Iodine found" and "Iodine calc.," mean the iodine set free from iodide by 100 g. of iodate solution.

TABLE III.—DIRECT DETERMINATION OF IODATE WITH IODIDE IN SULFURIC ACID.

Expt.	Iodide. G.	Iodate. G.	Iodine found.	Iodine calc.	Deviation.
1.....	33.84	34.02	0.6518	0.6515	+3
2.....	37.26	37.49	0.6513	.....	-2
3.....	43.07	43.35	0.6513	.....	-2
4.....	33.39	33.60	0.6513	.....	-2
5.....	37.41	37.64	0.6513	.....	-2
6.....	29.53	29.70	0.6516	.....	+1
					—
Average,					-0.7

It was found practicable to titrate the 0.02 solutions of iodide and iodate in sulfuric acid. The iodide solution used showed the relation 1 to 1.006 toward the permanganate solution which was redetermined and showed an oxalate value 0.001323 to 1 g. of solution.

TABLE IV.—DIRECT TITRATION OF IODATE AND IODIDE IN SULFURIC ACID.

Expt.	Iodide. G.	Iodate. G.	Iodine found.	Iodine calc.	Deviation.
1.....	36.77	35.50	0.2611	0.2611	0
2.....	35.64	34.44	0.2610	.....	-1
3.....	42.66	41.25	0.2608	.....	-3
4.....	40.78	40.08	0.2625	.....	+14
5.....	24.00	23.29	0.2608	.....	-3
6.....	47.33	45.77	0.2607	.....	-4
7.....	36.33	35.10	0.2609	.....	-2
					—
Average,					0

It was observed in the attempted determination of iodide with iodate in hydrochloric acid that on adding a few drops of iodate when near the end-point the reaction completed itself and the reflection in the galvanometer mirror became stationary much more quickly than when sulfuric acid was used in large excess as the acid medium. Possibly this increased speed may be explained by the fact that hydrochloric acid itself reduces iodic acid when they are in moderate concentration, but the reaction is reversible. In the present case the reverse action may be prevented by the fact that any chlorine from the direct one could at once replace iodine in the remaining unstable hydriodic acid, and the end of the reaction

between iodic and hydriodic acid would be quickly reached through this catalytic action of hydrochloric acid.

#### Determination of Silver.

The accurate electrometric determination of iodide seemed to make possible a new, simple and accurate volumetric determination of silver. One might precipitate the silver with an excess of pure iodide of known value and titrate the excess with permanganate solution, and on account of the extreme insolubility of silver iodide the determination might be carried out without filtering it off. Experience seems to confirm this view. The first means of testing the method was a solution of silver sulfate made up by weight so that each gram of solution contained 0.0021573 g. of silver. Determinations of this solution were made with carefully restandardized permanganate solutions requiring 0.001323 and 0.00319 g. of sodium oxalate and whose ratios to the corresponding iodide solutions were 1.033 and 1.0182 g. respectively to 1 g. of iodide. Preliminary titrations showed irregularities in the curves, when the ordinary platinum electrode exposing to the solution only a bit of fine wire was used. This was due apparently to a disturbing amount of silver deposited in spite of the smallness of the currents that could have passed, considering the fact that the galvanometer was held as nearly as possible to the neutral point, and the circuit was broken while readings were being taken. The substitution of an electrode exposing about 2 sq. cm. of metal entirely removed this difficulty and the curves obtained were as good as those with iodide and permanganate alone. This electrode was kept in nitric acid when not in use.

In carrying out the determinations the weighed silver solution in the titration vessel was treated with a small excess of iodide and subjected to the stirrer a few moments, after which and without filtering the excess of iodide was determined with permanganate. In a few determinations the silver iodide was filtered off before titrating the excess of iodide but without apparent difference.

In all the following tables the weights of silver found and calculated are given in terms of 100 g. of silver solution.

TABLE V.—DETERMINATION OF SILVER WITH IODIDE AND PERMANGANATE.

Expt.	Ag. sol. G.	KI sol. G.	Ag. found.	Ag. calc.	Deviation.
1. ....	25.42	24.92	0.2157	0.21573	0
2. ....	24.26	23.81	0.2160	.....	+3
3. ....	24.96	24.46	0.2157	.....	0
4. ....	49.98	49.04	0.2159	.....	+2
5. ....	48.59	47.60	0.2156	.....	-1

Average, +0.6

To test the method further portions of the same silver solution were titrated with the 0.05 *N* solutions of iodide and permanganate. Since

silver must often be determined in the presence of nitric acid, after the third experiment in the next table the amounts of nitric acid designated in terms of normality in the titration vessel were added, and in Expt. 8 no sulfuric acid was used.

TABLE VI.—DETERMINATION OF SILVER WITH IODIDE AND PERMANGANATE AND THE EFFECT OF NITRIC ACID.

Expt.	Ag. sol. G.	KI. G.	Normality HNO <sub>3</sub> .	Ag. found.	Ag. calc.	Deviation.
1.....	49.62	20.51	0	0.2162	0.21573	+5
2.....	49.55	20.43	0	0.2157	.....	0
3.....	50.04	20.64	0	0.2157	.....	0
4.....	50.11	20.67	0.04	0.2157	.....	0
5.....	49.90	20.57	0.08	0.2156	.....	-1
6.....	50.66	20.89	0.16	0.2157	.....	0
7.....	50.01	20.67	0.32	0.2162	.....	+5
8.....	49.71	20.50	0.64	0.2157	.....	0
Average,						+1

More than a year ago, as stated in the first paper the influence of nitric acid on the titration of iodide with permanganate was studied with the result that very little effect was observed up to a concentration of 2 *N*, nitric acid in the titration vessel and this effect could be ascribed largely to the presence of small amounts of nitrous acid. Table VI seems to confirm the former experience. In the present instance the nitric acid used was taken from the original bottle which had been kept in darkness, and on testing with iodide and starch it showed scarcely a trace of nitrous acid. Nevertheless, though the results do not show it, according to the work of Eckstadt,<sup>1</sup> nitric acid apart from nitrous acid it may contain does slowly decompose hydriodic acid. The rate is, however, so slow in such concentrations as here used that the effect should not be apparent in titrations of silver carried out with reasonable speed.

A method for the determination of silver and without filtration seemed of sufficient importance to make it desirable to test the method more rigorously than could be done on the bases of silver sulfate. To this end, since nitric acid had shown no harmful effect, a solution of silver nitrate was prepared from pure silver that had been prepared by the writer many years ago, and whose purity had often been tested. To prepare this silver a quantity of the nitrate was fused, dissolved and precipitated as chloride, which was reduced with lactose. The reduced metal was fused into large masses which were used as positive electrodes and the silver electrolyzed in nitric acid. The crystalline deposit was fused into buttons on charcoal made of sugar and in a gasoline flame. A weighed portion of this metal in the present instance was dissolved in a small excess of nitric acid and most of the excess was evaporated. The solution made up by weight

<sup>1</sup> Eckstadt, *Z. anorg. Chem.*, **29**, 51 (1901).

should contain 0.004714 g. of silver to each gram of solution. Determinations of silver in this solution are shown in Tables VII and VIII. To ascertain whether chloride from the capillary of the calomel electrode might possibly influence the results an extra calomel electrode vessel filled with a concentrated solution of pure sodium nitrate was interposed between the calomel electrode and the titration vessel, and the last 5 experiments of Table VII were carried out with this arrangement.

TABLE VII.—DETERMINATION OF SILVER IN SOLUTION MADE FROM PURE METAL.

Expt.	Ag. sol. G.	KI sol. G.	Ag. found.	Ag. calc.	Deviation.
1.....	50.60	45.62	0.4716	0.4714	+2
2.....	25.30	22.81	0.4716	.....	+2
3.....	25.11	22.62	0.4711	.....	-3
4.....	50.45	45.45	0.4712	.....	-2
5.....	25.64	23.14	0.4720	.....	+6
6.....	25.12	22.66	0.4718	.....	+4
7.....	50.15	45.28	0.4722	.....	+8
8.....	25.50	22.98	0.4713	.....	-1
					—
				Average,	+2

Portions of the same solution were titrated with another pair of iodide and permanganate solutions, the same as used in the direct titration of 0.05 *N*, iodate and iodide in sulfuric acid.

Essentially the same values were found as in the previous table, as shown in the next table.

TABLE VIII.—DETERMINATION OF SILVER WITH NEW IODIDE AND PERMANGANATE.

Expt.	Ag. sol. G.	KI sol. G.	Ag. found.	Ag. calc.	Deviation.
1.....	50.56	42.79	0.4714	0.4714	0
2.....	30.31	25.67	0.4719	.....	+5
3.....	50.67	42.84	0.4710	.....	-4
4.....	25.66	21.69	0.4709	.....	-5
5.....	25.32	21.43	0.4715	.....	+1
					—
				Average,	-0.6

It is obvious that this method of determining silver may also serve as an accurate method of standardizing permanganate and iodide solutions at the same time provided the latter is free from other halogens. Few substances can easily be prepared in such a high state of purity as metallic silver which would serve as the basis. Even silver sulfate might meet ordinary requirements.

Bromate and dichromate solutions have also been directly titrated against iodide in dil. sulfuric acid, and chlorine has been indirectly determined by the electrometric method. The details will be given in a later communication.



### Summary.

1. Iodate may be determined accurately by reducing it with an excess of known iodide solution in dil. sulfuric acid, and titrating the excess with permanganate solution, electrometrically.
2. Iodide can be titrated directly with iodate in dil. sulfuric acid, by the electrometric method.
3. Hydrochloric acid may not be substituted for sulfuric except within very narrow limits of concentration in the determination of iodide with either permanganate or iodate.
4. These determinations may be made in the presence of chloride not exceeding about 0.1 *N*, or in presence of nitric acid of higher concentration if it contains only traces of nitrous acid.
5. Silver may be accurately determined electrometrically with pure iodide and permanganate solution.
6. Pure silver may be used as a standard in determining the values of both iodide and permanganate.

The writer takes this opportunity to express his appreciation of the generosity of the Johns Hopkins University in providing for this work, the cordial cooperation of the Staff in the Department of Chemistry, and especially the friendly advice and criticism of Professor B. F. Lovelace, with whom he has been more closely associated.

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[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY.]<sup>1</sup>

## THE PRINCIPLE OF SIMILITUDE AND THE ENTROPY OF POLYATOMIC GASES.

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In a previous article,<sup>2</sup> the author has shown the possibility of using the principle of similitude for predicting the relation between the entropy of a monatomic gas and its molecular weight. It is possible to extend the mode of attack so as to treat diatomic and polyatomic gases, provided they can be thought of as composed of rigid particles having a definite molecular weight, and definite moments of inertia around their centers of gravity.

The purposes of the present article are, (1) to give a brief introduction to the theory of similitude<sup>3</sup> or relativity of size, using a method of pre-

<sup>1</sup> Published by permission of the Chief of Ordnance.

<sup>2</sup> Tolman, *THIS JOURNAL*, **42**, 1185 (1920).

<sup>3</sup> Tolman, *Phys. Rev.*, **3**, 244 (1914); **4**, 145 (1914); **6**, 219 (1915); **8**, 8 (1916); **9**, 237 (1917); *Gen. Elec. Rev.*, **23**, 486 (1920). See also Karrer, *Phys. Rev.*, **9**, 290 (1917); Davis, *Science*, **50**, 338 (1919).