ART. XL. — *The Determination of Persulphates*; by
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[Contributions from the Kent Chemical Laboratory of Yale University—CIII.]

IN a recent article by Namias, of which, however, only the abstract is at our disposal,* it is proposed to substitute for the method of reducing the persulphate by a ferrous salt and estimating the excess of the latter—a method which the author characterizes as inaccurate—the treatment of the persulphate by potassium iodide for a period of ten or twelve hours, and titration by thiosulphate of the iodine set free; and Grützner† has recently stated that a solution of arsenious oxide is well suited for the determination of the oxidizing power of persulphates, the reaction being hastened by heat and the presence of alkaline hydroxide. A test of the processes of Namias and Grützner led us to consider also the method of LeBlanc and Eckardt‡ as well as the previously proposed method of Mondolfo,§ in order that the indications of all these methods might be brought into comparison.

LeBlanc and Eckardt|| state and bring experimental results to show that when a mixture containing a persulphate, a sufficient excess of ferrous salt, and sulphuric acid, is heated at 60°–80°, or allowed to stand ten or twelve hours, the persulphate is reduced, and the amount of ferrous salt oxidized is the measure of the amount of persulphate originally present in solution. This is the method to which Namias takes exception. Marshall¶ is authority for the statement that persulphates liberate iodine from potassium iodide, and that the action is hastened by heat and affected little by the addition of dilute sulphuric acid. Upon this reaction Mondolfo** has based a method for the estimation of persulphates, which consists in heating a mixture containing the persulphate and potassium iodide in a stoppered bottle for ten minutes at 60°–80°, and titrating by thiosulphate the iodine set free. The process which Namias†† proposes for the estimation of persulphates—without knowledge of Mondolfo's method—differs from the iodometric method of Mondolfo in the point that the interaction between the iodine and the persulphate is carried out at the ordinary atmospheric temperature and prolonged ten or twelve hours, when the estimation is made by thiosulphate of the iodine set free in the action.

* Chem. Centralblatt, 1900, ii, p. 806.

† Zeit. f. Electrochemie, 5, 355–7.

‡ Loc. cit.

** Loc. cit.

† Ibid., 1900, i, p. 835.

§ Chem. Zeitung, 23, p. 699.

¶ Jour. Chem. Soc., 59, 771.

†† Loc. cit.

Method of LeBlanc and Eckardt.

The reagents used in our experiments were a solution of ammonium persulphate, 10 grm. of the salt to the liter; an acidified solution of ammonio-ferrous sulphate, 20 grm. to the liter; an approximately tenth-normal solution of potassium permanganate; and sulphuric acid of half strength. The standard of the potassium permanganate solution was determined by comparison with a solution of arsenious oxide.* The effect upon the reaction of variations in time, temperature, and amount of ferrous salt were tried, and the results given in Table I.

TABLE I.
Volume of liquid 100^{cm}³.

Ammonium persulphate, 10 grm. to liter. cm³.	(NH ₄) ₂ Fe(SO ₄) ₂ ·6H ₂ O solution 20 grm. to liter. cm³.	KMnO ₄ app. N/10, to oxidize the excess of ferrous salt. cm³.	Treatment.	(NH ₄) ₂ S ₂ O ₈ calculated from ferrous salt oxidized. grm.
A				
Heated 10 min.				
12·5	25	2·11	60°–80°	0·1216
12·5	25	2·18	"	0·1209
12·5	25	2·11	"	0·1216
12·5	25	2·11	"	0·1216
12·5	50	15·00	"	0·1218
25·0	50	4·21	"	0·2426
B				
Stood 11 hours.				
12·5	26	1·89	21°–25°	0·1214
12·5	26	1·80	"	0·1224
12·5	40	8·75	"	0·1221
12·5	40	8·75	"	0·1221
C				
Carbon dioxide above the liquid.				
Stood 11 hours.				
12·5	40	8·75	21°–25°	0·1221
12·5	40	8·78	"	0·1218

In section A are given the results of experiments obtained by heating the mixture of persulphate, ammonio-ferrous sulphate, sulphuric acid, and water, on the steam bath for ten minutes, at a temperature of 60°–80°. In section B are recorded the results of experiments in which the same mixture was allowed to stand 11 hours at the ordinary room tempera-

* Gooch and Peters, this Journal, viii, 125.

ture. In the experiments recorded in section C, the air above the liquid was replaced by carbon dioxide. It is seen that the results of the experiments given in the three sections of the table agree quite closely with one another, and the average of these experiments gives a value to the persulphate solution of 0.1217 grm. of the salt in 12.5 cm³.

Experiments were made in blank to discover the amount of ferrous salt oxidized in 11 hours by other agencies than the persulphate. The amount of oxidation in that time, however, was too small to be detected, but, when the solution was allowed to stand 36 hours a slight oxidation was noticed, which if calculated as persulphate, would be equivalent to 0.0006 grm. The correction for 11 hours standing, upon this basis; therefore, would be 0.0002 grm., which is obviously so small that it may be disregarded. This absence of any significant oxidation of the ferrous salt was undoubtedly due to the fact that the solution of ammonio-ferrous sulphate had been standing some time before standardizing and was devoid of any active oxygen.

Method of Grützner.

In testing the value of the persulphate solution according to the method of Grützner,* the mixture containing the persulphate, standard arsenite solution, and sodium hydroxide was raised to the boiling point, cooled, faintly acidified with sulphuric acid, then made alkaline with potassium bicarbonate, and after adding a large excess of the last, the arsenite remaining unoxidized was titrated by iodine. Experiments made in blank, that is experiments in which the mixture of arsenite and alkaline hydroxide was raised to the boiling point, cooled, made acid with sulphuric acid, then alkaline with potassium bicarbonate, and titrated with iodine, showed a deficiency of arsenious acid as compared with the experiments, similarly conducted, in which the mixture was not subjected to heat. The effects of various specimens of sodium and potassium hydroxide were tested in the process—sodium and potassium hydroxide made by the alcohol process, potassium hydroxide by the barium hydroxide process, sodium hydroxide especially prepared from sodium carbonate and calcium hydroxide—as well as a specimen of potassium carbonate. In the case of all but the potassium carbonate, more or less oxidation was observed, sometimes trifling, sometimes considerable. The same specimens of potassium and sodium hydroxides and potassium carbonate were tested in the absence of the arsenite solution, by dissolving them in water, heating the solution to the boiling point, cooling, adding sulphuric acid in faint excess and

* Loc. cit.

then potassium bicarbonate, and titrating with iodine to a color without starch. In all cases, save that of the potassium carbonate, the color of the first drop of iodine solution added was destroyed, and from 0.06–0.19^{cm³} were necessary to bring the permanent iodine color. The results of these experiments are given in Table II.

TABLE II.
Arsenic solution No. 1.

Arsenite solution taken. cm³.	NaOH present. grm.	KOH present. grm.	K ₂ CO ₃ present. grm.	Iodine solution required to bring color. cm³.	Remarks.
25	--	--	--	25.40	
25	2	--	--	25.36	NaOH by CaO ₂ H ₂ , average of 4 experiments. KOH by alcohol. KOH by BaO ₂ H ₂ .
25	--	6	--	25.29	
25	--	5	--	25.07	

Arsenic solution No. 2.

25	--	--	--	25.54	
25	--	6	--	25.42	KOH by alcohol.
25	--	6	--	25.30	KOH by BaO ₂ H ₂ .
25	--	--	6	25.56	
--	4	--	--	0.12	NaOH by CaO ₂ H ₂ .
--	6	--	--	0.06	NaOH by alcohol.
--	--	6	--	0.06	KOH by alcohol.
--	--	6	--	0.19	KOH by BaO ₂ H ₂ .
--	--	2	--	0.07	KOH by BaO ₂ H ₂ .
--	--	--	6	0.02	

Potassium carbonate proves to be inefficient as a substitute for an alkaline hydroxide, but by using definite amounts of the hydroxide, and introducing a correction for the oxidation determined by the blank tests, the real oxidizing effect of the persulphate upon the arsenite may be deduced. Table III contains the values found by Grützner's process thus corrected, as well as uncorrected results.

TABLE III.

Ammonium persulphate solution taken. cm³.	Arsenite solution. cm³.	NaOH by CaO ₂ H ₂ . grm.	Calculated from Iodine actually used. grm.	(NH ₄) ₂ S ₂ O ₈ corrected for oxidation in blank. grm.
12.5	25	2	0.1223	0.1218
12.5	25	2	0.1223	0.1218
12.5	25	2	0.1225	0.1220
12.5	25	2	0.1229	0.1220

The average of the corrected figures gives a value to 12.5 cm^3 of the persulphate solution of 0.1219 grm. of the salt.

Method of Mondolfo.

In certain experiments conducted as described by Mondolfo* a mixture, 25 cm^3 in volume, containing 12.5 cm^3 of the persulphate solution, 1.0 grm. of potassium iodide, was heated in a stoppered bottle 10 minutes on the steam bath, and after cooling, the liberated iodine was titrated by thiosulphate. The readings were made without starch, which, however, was added afterwards to verify the observation. In other experiments, similarly conducted, the volume of the liquid containing the persulphate and the potassium iodide was increased to 100 cm^3 and the mixture heated 10 minutes on the steam bath, the temperature being 60° – 80° . The repeated return of the iodine color when the volume of the liquid was 100 cm^3 showed plainly that only a partial reduction of the persulphate had taken place.

When, however, the mixture at a volume of 100 cm^3 was heated on the steam bath for 30 minutes, the results agreed with those obtained by the treatment at a volume of 25 cm^3 . The results of these two sets of experiments are given in sections A and B of Table IV. After the iodine in the experiments which are recorded in section A of Table IV had been titrated by thiosulphate, sulphuric acid was added to the mixture and a blue color appeared immediately, showing, even in these experiments conducted at a volume of 25 cm^3 , that the reduction of the persulphate had been incomplete. This fact suggested a study of the effect of the presence of sulphuric acid on the process conducted otherwise as described by Mondolfo. Accordingly experiments were made similar to those already described excepting that a small amount of sulphuric acid was present. The results of these experiments are given in section C of Table IV.

In a blank test made with 1 cm^3 of sulphuric acid present, a small amount of iodine was liberated; and when, in a similar experiment the air over the liquid was replaced by carbon dioxide the amount of iodine liberated was less. The results of these experiments in blank are given in section D of Table IV. It is seen from the results of experiments given in sections A and B of the Table that the method as described by Mondolfo gives constant results provided the volume is small and the heating prolonged. The instantaneous appearance of the iodine color upon acidifying with sulphuric acid showed, however, that a very small amount of the persulphate had escaped reduction. Still, the presence of sulphuric acid in the

* Loc. cit.

TABLE IV.

Ammonium persulphate solution. cm ³ .	KI. gm.	H ₂ SO ₄ 1:1. cm ³ .	Volume. cm ³ .	Time of heating. minutes.	Na ₂ S ₂ O ₃ required. app N/10 cm ³ .	(NH ₄) ₂ S ₂ O ₈ calculated from sodium found. gm.
A						
12.5	1.0	----	25	10	10.65	0.1200
12.5	1.0	----	25	10	10.74	0.1210
12.5	1.0	----	25	30	10.73	0.1209
B						
{ 12.5	1.0	----	100	10	9.89*	0.1124 }
{ 12.5	1.0	----	100	10	8.99*	0.1013 }
12.5	1.0	----	100	30	10.70	0.1206
12.5	1.0	----	100	30	10.72	0.1208
12.5	1.0	----	100	30	10.72	0.1208
C						
12.5	1.0	0.05	25	30	10.78	0.1214
12.5	1.0	0.05	100	30	10.81	0.1218
12.5	1.0	1.0	100	30	10.81	0.1218
12.5	1.0	1.0	100	30	10.84	0.1221
D						
----	1.0	----	100	30	0.00	0.0000
----	1.0	1.0	100	30	0.07	0.0008
----	1.0	1.0	100	30	0.10	0.0011
----	1.0	1.0	100	30	0.03†	0.0003

process is hardly to be recommended, because of the sensitiveness of the hydriodic acid set free to the oxygen of the air and the oxygen dissolved in the water. The value of 12.5^{cm³} of the persulphate solution obtained by the method of Mondolfo, found by averaging the results of experiments in sections A and B (omitting the first two experiments under section B) is 0.1207 gm., while that found by averaging the results of experiments in section C and deducting the correction given in the experiments under section D is 0.1208 gm.

Method of Namias.

In the process for the estimation of persulphates carried out as described by Namias,† a mixture containing 12.5^{cm³} of the persulphate solution, 1.0 gm. of potassium iodide, and water sufficient in some experiments to make a volume of 25^{cm³}, and in other experiments 100^{cm³}, was allowed to stand 11 hours in a stoppered bottle and the iodine set free was titrated by thiosulphate. After the titration by thiosulphate the mixture was allowed to stand still longer, and 16 hours later the blue starch iodide color which had developed in the experiments with the

* Color returned.

† Air over liquid replaced by carbon dioxide.

‡ Loc. cit.

volume of 100^{cm}³ was destroyed by thiosulphate. No more color appeared on standing. The results of these experiments are given in section A of Table V. In section B of Table V are recorded experiments in which the mixtures were allowed to

TABLE V.

Ammonium persulphate solution. cm ³ .	KI. gram.	Volume of liquid. cm ³ .	Time of standing. hrs.	Atmos- phere above liquid.	(NH ₄) ₂ S ₂ O ₈ calculated from iodine found 11 hours standing. gram.	After standing the number of hours indicated in the fourth column. gram.
A						
12.5	1.0	25	26	air	0.1203	0.1203
12.5	1.0	25	26	air	0.1196	0.1196
12.5	1.0	100	26	air	0.1191	0.1207
12.5	1.0	100	26	air	0.1190	0.1209
B						
{ 12.5	1.0	25	20	air	----	0.1211
{ 12.5	1.0	25	24	air	----	0.1213
{ 12.5	1.0	100	20	air	----	0.1211
{ 12.5	1.0	100	24	air	----	0.1211
{ ----	1.0	100	24	CO ₂	----	0.0000
{ 12.5	1.0	25	20	CO ₂	----	0.1216
{ 12.5	1.0	25	25	CO ₂	----	0.1214
{ 12.5	1.0	100	20	CO ₂	----	0.1212
{ 12.5	1.0	100	24	CO ₂	----	0.1217
C						
					H ₂ SO ₄ 1:1 cm ³ .	
{ 12.5	1.0	25	25	air	1.0	0.1248
{ 12.5	1.0	100	24	air	1.0	0.1220
{ 12.5	1.0	100	24	air	1.0	0.1226
{ 12.5	1.0	25	17	CO ₂	0.05	0.1217
{ 12.5	1.0	25	24	CO ₂	0.05	0.1212
{ 12.5	1.0	25	17	CO ₂	1.0	0.1222
{ 12.5	1.0	25	23	CO ₂	1.0	0.1223
{ 12.5	1.0	100	17	CO ₂	0.05	0.1214
{ 12.5	1.0	100	24	CO ₂	0.05	0.1214
{ 12.5	1.0	100	17	CO ₂	1.0	0.1214
{ 12.5	1.0	100	24	CO ₂	1.0	0.1219
{ 12.5	1.0	100	23	CO ₂	1.0	0.1220
{ ----	1.0	25	20	air	1.0	0.0014
{ ----	1.0	100	20	air	1.0	0.0006
{ ----	1.0	25	24	CO ₂	1.0	0.0011
{ ----	1.0	100	24	CO ₂	1.0	0.0003

stand 20–25 hours, the air about the liquid in some experiments being replaced by carbon dioxide. Though carbon dioxide shows no tendency to liberate iodine in the blank test, the persulphate appears to liberate in its presence a little more iodine than in its absence. This experience naturally suggests an effect of acidity. The effect of the presence of sulphuric acid in the process otherwise conducted as described by Namias was therefore tried, the air over the liquid being replaced by carbon dioxide. The results of these experiments are recorded in section C of Table V.

It is seen from the experiments conducted as described by Namias that the reduction of the persulphates in the time stated by Namias, 10–12 hours, is plainly incomplete unless the volume of the liquid is small. If the experiments are conducted at the greater dilution the time of standing must be increased in order that subsequent standing may not result in the return of color. In the presence of sulphuric acid more iodine is liberated than in its absence, and the amount is greater when the air above the liquid is not replaced by carbon dioxide, and when the volume is small. The amounts of iodine liberated under similar conditions in blank experiments prove to be appreciable and naturally greater when the atmosphere above the liquid is air. When these amounts, averaging the equivalent of 0.0007 gram. of the persulphate when the atmosphere is carbon dioxide, and about 0.0010 gram when the atmosphere is air, are deducted from the actual indication, the figures agree well with those found for the same amount when sulphuric acid is not present. Plainly, the addition of the acid adds nothing to the regularity and value of the process. The value of 12.5 cm³ of the persulphate solution obtained by the method of Namias is 0.1208 gram.

Arseniate—Iodide Method.

The estimation of chlorates is accomplished according to Gooch and Smith* by allowing a mixture containing the chlorate, a definite amount of standard potassium iodide solution, an arseniate, 20^{cm} of 1:1 sulphuric acid, to boil from a volume of about 100^{cm}³ to 35^{cm}³; the difference between the amount of iodine required to oxidize the arsenious acid produced and the amount of iodine in the potassium iodide originally present being the measure of the chlorate taken. It is interesting to note that persulphates can be estimated in a similar manner. Mixtures containing 12.5^{cm}³ of the persulphate solution, 0.5 gram. of potassium iodide, 2.3 gram. of hydrogen

* This Journal xlii, 220.

potassium arseniate, and 20^{cm}³ of 1:1 sulphuric acid, and water enough to make the total volume about 100^{cm}³, were boiled in a trapped Erlenmeyer beaker until the volume decreased to 35^{cm}³, and the arsenite present after the solution was made alkaline with potassium bicarbonate was estimated with iodine. The results of these experiments are given in Table VII.

TABLE VII.

Ammonium persulphate solution. cm ³ .	KI present. grm.	Iodine required for oxidation of arsenite. grm.	Iodine liberated by persulphate. grm.	(NH ₄) ₂ S ₂ O ₈ equivalent to iodine liberated. grm.
12.5	0.1875	0.0514	0.1361	0.1225
12.5	0.1875	0.0522	0.1352	0.1217
12.5	0.1875	0.0514	0.1361	0.1225
12.5	0.1875	0.0516	0.1359	0.1222

These results agree closely with one another and in the average, 0.1222 grm., accord well with the results of the process of Grützner and of LeBlanc and Eckhardt.

To compare the values obtained for the persulphate solution the averages of the results obtained by the different methods, together with the average of all the experiments, are given in Table VI.

TABLE VI.

Process.	Number of experiments.	Average of results. grm.
Mondolfo	6	0.1207
Namias	8	0.1208
LeBlanc and Eckhardt	12	0.1217
Grützner (corrected)	4	0.1219
Arseniate-iodide method	4	0.1222
Average of whole		0.1213

The results obtained by the process of Mondolfo and the process of Namias, both of which involve the liberation of iodine from potassium iodide and the titration of that iodine by thiosulphate, are practically identical and lower than the results obtained by the other three methods. The results obtained by the process of LeBlanc and Eckardt in which the persulphate is reduced by a ferrous salt, by the process of Grützner in which an arsenite solution is the reducing agent, and the arseniate iodide method in which the persulphate is determined by the difference between the amount of iodine in

an iodide added and the amount necessary to oxidize the arsenite remaining after boiling the solution, are all in quite close agreement and are all higher than those obtained by the processes of Namias or Mondolfo.

It is readily seen that the results of the experiments obtained by the process of LeBlanc and Eckardt are nearer the average of the results of all the methods than those of Namias or the similar process of Mondolfo, and this fact would show that the statements of Namias regarding the inaccuracy of the method of estimating persulphates by the reduction with a ferrous salt is without foundation.

The process of LeBlanc and Eckardt is simple, rapid and convenient. The method of Grützner is advantageous in that the ordinary arsenite solution is the standard for the process, but requires the application of a correction. The method of Mondolfo is simple and fairly rapid, but tends to give low results. The method of Namias is slow because the experiments must stand 10 to 12 hours, and the results of these experiments, like those obtained by the method of Mondolfo, are lower than the results obtained by the other methods. The arseniate-iodide method introduced as a control, is accurate but less simple than the other methods.

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