

XIII.—*On the Reaction between Sodium Thiosulphate and Iodine.
Estimation of Manganese Oxides and Potassium Bichromate.*

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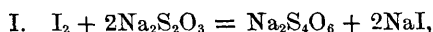
IN estimating the amount of manganese dioxide contained in various mixtures of the oxides of manganese, as described in a former paper, (this Journal, 1879), a modification of Bunsen's volumetric method was employed, which, although it had not been previously noticed by other chemists, appeared sufficiently obvious to require no special mention.

Instead of boiling the oxides with hydrochloric acid and collecting the evolved chlorine in a solution of potassium iodide (F. Mohr, *Lehrb. d. Chem. Analyt. Titrimethode*, 4 aufl., 278), or digesting them at 100° in a stoppered bottle containing hydrochloric acid and the iodide (*ibid.*, 281), the sample to be analysed was transferred to a beaker containing a large excess of this latter solution, a small quantity of acid added, and the liberated iodine determined by directly running into this mixture a standard solution of sodium thiosulphate. The oxides, if in a state of fine powder, and especially if recently precipitated, were found to be dissolved readily by very dilute acid in the presence of the iodide.

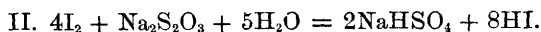
On comparing analyses made in this manner with those made according to Bunsen's directions, it was found that the former nearly always yielded slightly higher results than the latter: this fact led to the following investigation of the various circumstances which influence the reactions involved.

PART I.—*Reactions between Sodium Thiosulphate and Iodine.*

§ 1. *Amount of Sulphate formed.*—It is well known that in the reaction between iodine and sodium thiosulphate, if the liquid be warm, then, besides the action—



another action also takes place, resulting in the formation of a sulphate according to the equation—



Notwithstanding the statements of Rose (*ibid.*, 270) and others, a qualitative test sufficed to show that some sulphate is formed, even at

ordinary temperatures, and although the amount was not large, it was sufficient to admit of its being determined quantitatively.*

The sodium thiosulphate, which contained $\cdot 013704$ gram $\text{Na}_2\text{S}_2\text{O}_3$ per c.c., contained also some sulphate, and this had to be determined by blank experiments. The following numbers were obtained:—

100 c.c. of the sodium thiosulphate yielded.....	$\left\{ \begin{array}{l} \text{A } \cdot 000229 \\ \text{B } \cdot 000233 \\ \text{C } \cdot 000235 \end{array} \right\}$	$\cdot 000232$ gram BaSO_4 per c.c.
100 c.c. of the sodium thiosulphate added to an extremely slight excess of iodine at 20°C yielded.....	$\left\{ \begin{array}{l} \text{A } \cdot 000336 \\ \text{B } \cdot 000341 \\ \text{C } \cdot 000339 \\ \text{D } \cdot 000344 \end{array} \right\}$	$\cdot 000340$ gram BaSO_4 per c.c.

hence an amount of sulphate corresponding to $\cdot 000108$ gram BaSO_4 is formed in the oxidation of $\cdot 013704$ gram $\text{Na}_2\text{S}_2\text{O}_3$ by iodine at 20°C , or the number of molecules of iodine reacting according to the equations I and II is 1 and $46\cdot 6$ respectively.†

§ II. *Effect of Temperature.*—In order to obtain some idea as to the effect of temperature on these two reactions, a series of experiments was performed, in each of which 10 c.c. of an iodine solution (containing $\cdot 020672$ gram of iodine per c.c.) kept in a bath at a definite temperature was titrated by the thiosulphate. The results thus obtained are given in Table I.

Blank experiments were first performed to ascertain whether any appreciable loss of iodine took place from volatilisation during the titration of the warm solution. The iodine solution was heated to about 50°C . (the highest temperature employed in any of the experiments) in a stoppered bottle; some water was then run into it from the burette, the stopper replaced, and the solution cooled. It was then titrated; no loss of iodine has taken place during these operations.

Before the addition of the last drop of the thiosulphate solution the liquid was in every case allowed to attain the temperature of the room.

* Owing to this formation of sulphate the neutral solution of thiosulphate becomes distinctly acid after the addition of the iodine, as would be inferred from equation II.

In order that the thiosulphate used in these experiments should be as pure as possible it was recrystallised three or four times, and before the addition of the iodine to its solution both these reagents were mixed separately with a few drops of barium chloride solution and allowed to stand for 24 hours, so that any trace of sulphate present in them might be detected and eliminated.

That the sulphate formed at ordinary temperatures in the reaction under discussion could not have been entirely, or even principally, due to any sulphite present in the thiosulphate, is shown by the fact that its amount is considerably reduced by a reduction of temperature.

† Molecule for molecule, potassium thiosulphate was found on oxidation with iodine to yield nearly the same amount of sulphate as the sodium salt.

TABLE I.—*Showing the Influence of Temperature on the Actions.*

Iodine solution taken.	Temperature.	Thiosulphate required.	Weight of iodine reacting to form tetrathionate.	Weight of iodine reacting to form sulphate.
10 c.c.	—	2·352 c.c.*	0	100
"	52° C.	18·18 } 18·17 c.c.	96·10	3·90
"	"	18·16 }		
"	50° "	18·207 c.c.*	96·32	3·68
"	43 "	18·32 c.c.	97·00	3·00
"	40 "	18·35 c.c.*	97·17	2·83
"	31 "	18·43 } 18·42 c.c.	97·63	2·37
"	"	18·41 }		
"	30° "	18·426 c.c.*	97·65	2·35
"	20 "	18·47 c.c. (see Table VI)	97·90	2·10
"	15 "	18·485 c.c.*	98·03	1·97
"	10 "	18·497 c.c.*	98·06	1·94
"	0 "	18·51 }		
"	"	18·52 } 18·51 c.c.	98·16	1·84
"	"	18·50 }		
"	—	18·816 c.c.*	100	0

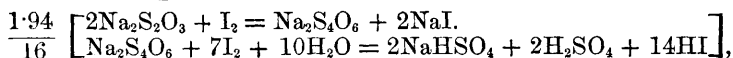
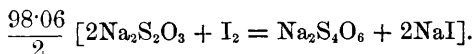
The above experiments are essentially a reproduction of those made by Wright in 1870† (*Chem. News*, 21, 103). He, however, does not appear to have recognised the formation of any sulphate at temperatures below 28° C. (the iodine not being in excess), and its formation above this temperature he attributes to the oxidising action of the iodine on the tetrathionate formed in the first stages of the reaction, and not to the direct oxidation of the thiosulphate according to equation II, page 128. The following considerations, however, appear to render such a view untenable:—

(1.) If the sulphate were formed by the oxidation of the tetrathionate, then, when the iodine is added to the thiosulphate, we should expect that less sulphate would be formed than when the thiosulphate is added to the iodine, for in the latter case some tetrathionate is in the presence of excess of iodine throughout the reaction, whereas in the former case no excess of iodine is present at any time. The experiments given in Table VI, however, show that the reaction is the same whether the iodine be added to the thiosulphate or the thiosulphate to the iodine.

* Interpolated.

† Wright did not make any direct determination of the sulphate formed: his experiments consisted chiefly in ascertaining the relative amounts of iodine required for the oxidation of a given quantity of sodium thiosulphate between the temperatures of 16° and 92° C.

(2.) In the case of the sulphate being formed by the oxidation of the tetrathionate, the results of the experiment at 10° C. (for instance) given in Table I would be represented by the following equations :—



from which, taking the titres of the various solutions and the quantities used as given above, we find that during the ten minutes allowed for the reaction .00352 gram of iodine has been used in oxidising some of the sodium tetrathionate formed into sulphate, the total quantity of tetrathionate formed being 0.216 gram.

In order to ascertain whether the oxidation of sodium tetrathionate does in reality take place at this rate, several portions of a pure sample of this salt, weighing .216 gram each, were dissolved in water, and 10 c.c. of the iodine solution added to each.* The residual iodine was subsequently determined after various intervals of time had elapsed, the temperature being kept constant at 10° C.

The following were the results obtained :—

	c.c.		gram.			
After 10 mins.	0.01	of iodine, or	.000207	I per 10 mins.	had disappeared.	
„	19 $\frac{5}{6}$ hrs.	0.38	„	„	.000066	„ „ „
„	24 $\frac{1}{6}$ „	0.40	„	„	.000057	„ „ „
„	46 $\frac{1}{3}$ „	0.70	„	„	.000052	„ „ „
„	69 „	1.05	„	„	.0000525	„ „ „

The amount of oxidation is thus seen to diminish considerably as the action proceeds,† but taking the first experiment, which gives by far the highest rate (possibly due in part to the difficulty of measuring such small differences as .01 c.c.), we find that this rate is less than one-twelfth of what it should be if the sulphate were formed (in the reaction of iodine on thiosulphate) by the oxidation of the tetrathionate, and not by the direct oxidation of the thiosulphate.

§ III. *Effect of Dilution.*—The experiments given in Table II were performed in order to ascertain whether the amount of water present had any influence on the relative proportions in which the two above-

* This is, of course, a great exaggeration of the conditions existing in the experiment in Table I, for here we have both the maximum amount of tetrathionate, and also the maximum amount of iodine present at the same time, whereas in the ordinary determination when either of these substances is at a maximum the other is at a minimum.

† This diminution in rate is not due to the presence of the sodium sulphate formed, for on adding excess of this substance the rate of oxidation was not found to be appreciably altered.

mentioned reactions (page 128) take place. Dilution is here seen to cause a small increase in the amount of sulphate formed, less of the thiosulphate being required according as the quantity of water present is greater. Its effect, however, is very slight, for in order to make the experiments strictly comparable, a small correction must be applied, since it was found that a quantity of iodine ($\cdot 000042$ gram) equivalent to $\cdot 004$ c.c. of the thiosulphate was requisite for every 50 c.c. of solution to give a visible coloration with starch.

TABLE II.—*Showing the Effect of Dilution.*

Iodine solution taken.	Water added.	Thiosulphate solution required.	Thiosulphate corrected for final reaction.
10 c.c.	None	18·47 c.c. (see Table VI)	18·47 c.c.
"	50 c.c.	18·47	18·467 c.c.
"	"	18·47	
"	"	18·46	
"	100 c.c.	18·46	18·457 "
"	"	18·45	
"	"	18·46	
"	150 c.c.	18·45	18·447 "
"	"	18·42	
"	"	18·44	
"	"	18·45	18·435 "
"	"	18·43	
"	"	18·42	
"	200 c.c.	18·44	18·435 "
"	"	18·43	
"	250 c.c.	18·42	
"	"	18·43	18·435 "
"	300 c.c.	18·41	
"	"	18·42	

§ IV. *Amount of Potassium Iodide present.*—The experiments given in Table III show that the presence of an excess of potassium iodide over that necessary for the solution of the iodine, has no effect on the quantity of thiosulphate used.

TABLE III.—*Showing the effect of Excess of Potassium Iodide.*

Iodine solution taken.	Excess of KI added.	Thiosulphate solution required.
10 c.c.	None (see Table VI)	18·47 c.c.
"	1 gram	18·46 "
"	"	18·47 "
"	2 grams	18·47 "
"	"	18·47 "
"	3 "	18·46 "
"	"	18·47 "

§ V. *Influence of Time*.—A series of experiments were next performed with a view of ascertaining whether in a dilute solution of iodine in potassium iodide the amount of the former diminished appreciably on being kept for various lengths of time. The solutions to be titrated were placed in stoppered bottles inverted in a vessel containing starch water, so that any leakage might be detected. Some of them were kept in the dark, others in diffused daylight. In both cases, however, no sensible diminution in the amount of free iodine present was found to have taken place within four days,* that time being the extreme limit allowed in any of the experiments. The results are given in Table IV.

TABLE IV.—*Showing the Influence of Time.*

Iodine solution added.	Water added.	Interval between dilution and titration.	Thiosulphate required.
10 c.c.	150 c.c.	None	18·45 to 18·42 c.c. (see Table II)
"	"	$\frac{1}{2}$ hr.	18·44 c.c.
"	"	"	18·45 "
"	"	1 hr.	18·45 "
"	"	"	18·43 "
"	"	2 hrs.	18·43 "
"	"	"	18·44 "
"	"	$3\frac{1}{2}$ hrs.	18·42 "
"	"	5 "	18·42 "
"	"	6 "	18·45 "
"	"	7 "	18·45 "
"	"	$18\frac{1}{2}$ "	18·42 "
"	"	"	18·44 "
"	"	24 "	18·43 "
"	"	30 "	18·43 "
"	"	48 "	18·44 "
"	"	96 "	18·42 "

§ VI. *Influence of Hydrochloric Acid*.—In order to ascertain whether the reactions under consideration were influenced by the presence of hydrochloric acid, the amount of iodine liberated by treating potassium iodide with the latter substance had previously to be determined.

* It is scarcely necessary to mention that precautions were taken for detecting any change in the titre of the standard solutions; the iodine and thiosulphate were compared together, and the latter compared with a standard solution of potassium bichromate at least once in every 24 hours. In order to facilitate comparison of results in the tables given, the actual amount of thiosulphate employed is reduced to what it would have been had the solutions remained unaltered throughout.

The addition of a little sodium hydrate greatly increases the stability of the thiosulphate (Harcourt and Esson, *Phil. Trans.*, 5, 156, p. 205).

5 c.c. of the acid employed (density 1.156 at 20° C. = 31.6 per cent. HCl) when added to 0.5 gram potassium iodide dissolved in 45 c.c. of water were found—

To liberate at once.....	·00123 gram I	{ (mean of many expts.)
To have liberated after 24 hours	·00515	„
„ „ another 24 hours	·00515	„
„ „ „	·00504	„
„ „ „	·00526	„
„ „ „	·00493	„
„ „ „	·00515	„
„ „ „	·00515	„
Mean	·00512 gram I per 24 hours.	

To have liberated after 96 hrs. ·01725 gram I = ·00431 gram I per 24 hours.

With the quantities of potassium iodide and water above mentioned the iodide liberated at once was found to be proportional to the hydrochloric acid added when the quantity of this latter was varied between 1 and 15 c.c., though with larger quantities than 5 c.c. the final action becomes rather uncertain.

The results obtained by titrating definite quantities of iodine solution in presence of hydrochloric acid are given in Table V, and show that the acid has no influence on the relative proportions in which the reactions I and II, page 128, take place. In these, and other similar experiments, the thiosulphate was run into the iodine solution as soon as it had been mixed with the acid and cooled down to 20° C., 10 minutes being allowed in every case for the reaction to complete itself.

TABLE V.—*Showing the Influence of Hydrochloric Acid present.*

Iodine solution taken.	HCl added.	Thiosulphate required.	Correction for I liberated by HCl.	Thiosulphate required, corrected.
10 c.c.	None	18.47 c.c. (see Table VI)	None	18.47 c.c.
„	1 c.c.	18.50 c.c.	·02 c.c. thiosulphate	18.48 „
„	3 „	18.53 „	·065 c.c. „	18.465 „
„	„ „	18.53 „	·065 „ „	18.465 „
„	4 „	18.56 „	·09 „ „	18.47 „
„	5 „	18.57 „	·11 „ „	18.46 „
„	„ „	18.58 „	·11 „ „	18.47 „
„	„ „	18.58 „	·11 „ „	18.47 „
„	10 „	18.69 „	·22 „ „	18.47 „
„	„ „	18.68 „	·22 „ „	18.46 „

§ VII. *Iodine added to excess of Thiosulphate.*—The results given in Table VI show that no difference in the amount of sulphate formed is made by adding the iodine solution to excess of thiosulphate, and subsequently determining that excess by means of a standard solution of iodine instead of adding the thiosulphate to the iodine.*

TABLE VI.

Thiosulphate added to Iodine.		Iodine added to excess of Thiosulphate.	
Iodine solution taken.	Thiosulphate required.	Iodine solution taken.	Thiosulphate required.
10 c.c.	18·47 c.c.	10 c.c.	18·46 c.c.
"	18·47 "	"	18·47 "
"	18·47 "	"	18·47 "
"	18·47 "	"	18·46 "
"	18·46 "	"	18·47 "
"	18·47 "	"	18·47 "
"		"	18·47 "

The case, however, is different if hydrochloric acid is present. The results obtained under these circumstances are given in Table VII,

TABLE VII.—*Iodine and Acid added to Thiosulphate.*

Iodine solution taken.	HCl added.	Thiosulphate required.	Correction for I liberated by HCl.	Corrected thiosulphate.	Iodine indicated by the thiosulphate used.
10 c.c. ..	None	18·47 c.c. (see Table VI)	None	18·47 c.c.	100·00
" ..	1 c.c.	18·48	{ ·02 c.c. thio-sulphate }	18·45 "	99·89
" ..	" "	18·46 } 18·47 c.c.		18·435 "	99·81
" ..	2 "	18·48 c.c.	{ ·045 c.c. thio-sulphate }		
" ..	3 "	18·45 } 18·475 c.c.	{ ·065 c.c. thio-sulphate }	18·41 "	99·67
" ..	" "	18·50			
" ..	4 "	18·46	{ ·09 c.c. thio-sulphate }	18·38 "	99·51
" ..	" "	18·48 } 18·47 c.c.			
" ..	" "	18·47			
" ..	5 "	18·43	{ ·11 c.c. thio-sulphate }	18·325 "	99·22
" ..	" "	18·40 } 18·435 c.c.			
" ..	" "	18·47			
" ..	" "	18·44			

* Finkener probably ascertained this fact, see Rose, *Handb. d. Anal. Chem.*, 6 Aufl., von Finkener, 2, 937.

and show that an increase in the amount of sulphate formed is occasioned by the presence of the acid, the greater being that increase according as the quantity of acid present is greater. In these experiments, since the acid liquid could not be added to excess of the thio-sulphate without causing its decomposition, the iodine solution, mixed with the acid, was added to nearly the necessary volume of thio-sulphate (18.3 c.c.) and the additional quantity required run into this mixture. It is also to be noticed that the individual experiments in this series are less concordant among themselves than in any other series.

PART II.—*Estimation of Manganese Oxides and Potassium Bichromate.*

§ I. *Valuation of Manganese Oxides.*—In valuing the oxides of manganese according to Bunsen's method three different forms of apparatus were employed:—(1) The oxide was boiled in a small flask fitted with a thistle funnel, the chlorine evolved being absorbed in three other flasks containing potassium iodide solutions; the flasks were fitted with india-rubber stoppers, and a current of air was drawn through the whole apparatus during the experiment. (2) The oxide was boiled with the acid in a small retort, the neck of which was bent down and fitted by means of an india-rubber plug into the first of three U-tubes containing potassium iodide solution; no current of air was employed. With this, and also with the first apparatus, no chlorine ever passed beyond the second absorption vessel. (3) The ebullition was performed in a small retort, as in the second case, the neck of which passed into a larger inverted retort containing potassium iodide solution.

With the first two arrangements identical results were obtained; with the third one, however, a small loss of chlorine was found to take place, owing to there being but one vessel for its absorption. In most cases apparatus (1) was employed as being found the most convenient of the three.

Traces of chlorine were found to be retained by the acid liquid even after prolonged boiling, and these were estimated by pouring some solution of potassium iodide into the flask before disconnecting it from the absorption vessels, and determining the iodine liberated in this flask separately from that liberated in the others.* A given number of minutes was allowed for the ebullition, cooling, and determination of the iodine, the amount of iodine liberated by boiling a given quantity of hydrochloric acid alone being determined in each special case by blank experiments.

* It was ascertained that neither the acid nor the oxides employed contained any traces of iron.

From 0.2 to 0.3 gram of the oxide was used in each analysis, this quantity requiring 20—30 c.c. of the thiosulphate.

Method employed.	Percentage of available oxygen found.	Relative quantity of available oxygen found.
Modification of Bunsen's method	6·938	100·00
" " " " "	6·922	
" " " " "	6·940	
" " " " "	6·923	
" " " " "	6·936	
Bunsen's method; using 10 c.c. HCl and no water	6·922	99·97
" " " " "	6·938	
" " " " "	6·934	
" " " " "	6·918	
" " " " "	6·938	
Ditto; using 10 c.c. HCl, and 5 c.c. water	6·900*	99·54
Ditto; using 10 c.c. HCl, and 10 c.c. water	6·877	99·24
" " " " "	6·881	
Ditto; using 10 c.c. HCl, and 15 c.c. water	6·864*	99·01
Ditto; using 10 c.c. HCl, and 20 c.c. water	6·872	98·904
" " " " "	6·862	
" " " " "	6·840	
" " " " "	6·850	
Ditto; using 10 c.c. HCl, and 30 c.c. water	6·824	98·56
" " " " "	6·841	
" " " " "	6·831	
Ditto; using 10 c.c. HCl, and 50 c.c. water	6·794	98·30
" " " " "	6·801	
" " " " "	6·832	
" " " " "	6·829	

* Interpolated by means of a curve.

§ II. *Analyses of Potassium Bichromate*.—A series of experiments, similar to those just described, were performed, substituting potassium bichromate for the manganese oxide. The results are given in Table II, and are found to agree with those in Table I; they show, however, that in the case of potassium bichromate the discrepancy between results obtained by the two methods is greater than with manganese oxide, and thus, even when the acid employed in Bunsen's method is undiluted, a notable deficiency of chlorine is observed.

TABLE II.—*Analyses of Potassium Bichromate*.

Method employed.	Potassium bichromate taken.	Thiosulphate required.	Relative quantity of thiosulphate used.
Modification of Bunsen's method	·1522 gram	35·05	100·00
" "	"	35·04	
" "	"	35·04	
" "	"	35·04	
" "	"	35·05	
" "	"	35·04	
" "	"	35·04	
Bunsen's method; using 10 c.c. HCl, and no water	·1522 gram	34·84	99·40
" "	"	34·83	
" "	"	34·83	
" "	"	34·83	
" "	"	34·84	
" "	"	34·84	
" "	"	34·75	
Ditto; using 10 c.c. HCl, and 3 c.c. water	"	34·75	99·17
" "	"	34·76	
" "	"	34·76	
" "	"	34·75	98·984
Ditto; using 10 c.c. HCl, and 5 c.c. water	"	34·69* c.c.	
Ditto; using 10 c.c. HCl, and 7 c.c. water	"	34·66	98·90
" "	"	34·66	
Ditto; using 10 c.c. HCl, and 10 c.c. water	"	34·625* c.c.	98·80
Ditto; using 10 c.c. HCl, and 15 c.c. water	"	34·595* c.c.	98·713
Ditto; using 10 c.c. HCl, and 17 c.c. water	"	34·59	98·70
" "	"	34·60	
" "	"	34·58	

§ III. *Loss of Chlorine*.—In order to ascertain whether the well-known formation of hydrochloric acid in chlorine water at ordinary

* Interpolated by means of a curve.

temperatures was sufficiently increased at 100° C. to account for the low results obtained by Bunsen's method, some chlorine water was heated for various times at different temperatures, either in stoppered bottles or in sealed tubes, and the numbers thus obtained are given in Table III, the chlorine water here used not being saturated, but containing 0·002192 gram Cl per c.c. All the experiments, except the last one, were performed in weak diffused daylight; the amount of hydrochloric acid formed, however, does not appear to be increased to any great extent by the action of light.

TABLE III.—*Showing the Loss of Chlorine produced by Heating Chlorine Water.*

Chlorine water taken.	Temperature.	Time.	Thiosulphate required.	Loss of free chlorine experienced.
50 c.c. ..	Before heating	—	25·98	—
" ..	"	—	26·01	
" ..	"	—	26·03	
" ..	"	—	26·02	
" ..	Heated to 100° C. and cooled slowly	about $\frac{1}{2}$ hr.	24·94	3·90 p. c.
" ..	"	"	25·04	
" ..	At 100° C.	for $\frac{1}{2}$ hr.	24·48	6·06 "
" ..	"	"	24·39	
" ..	"	for 1 hr.	23·61	9·16 "
" ..	"	"	23·58	
" ..	"	"	23·67	
" ..	"	"	23·68	
" ..	"	for 2 hrs.	22·37 c.c.	14·00 "
" ..	At 62° C.	for 1 hr.	24·81 c.c.	4·63 "
" ..	" 41 "	"	25·28 "	2·80 "
" ..	" 20 "	for 24 hrs.	24·62 "	0·22 " per hr.
" ..	"	"	24·89 "	0·18 " "
" ..	in the dark			

These experiments show that a very considerable loss of free chlorine takes place at 100°, and also at lower temperatures,* being quite sufficient to account for the loss experienced in Bunsen's method, especially as the chlorine is then in a nascent condition; and, that

* Some chlorine water was heated over mercury that the oxygen liberated might be collected; in place, however, of this gas being evolved, the mercury was oxidised, an oxychloride being probably formed. When some mercury was shaken with strong chlorine water it was converted at once into a fine grey powder, which, on subsiding, left the liquid quite colourless. Lead immersed in chlorine water became oxidised immediately, the metal, and especially the parts of the glass vessel near it, becoming coated with a film of what appeared to be lead dioxide.

this is the true explanation of this loss is supported by the fact that the results obtained are lower in proportion as more prolonged boiling is necessary to liberate the chlorine, *i.e.*, the results are lower as the acid used is more dilute, and also lower in the case of potassium bichromate than with manganese oxide. Nor can any of this loss be considered as mechanical, for, if it were so, it would be extremely improbable that an entire change in the apparatus used should not alter its amount, and impossible that no loss should take place when undiluted acid is employed for the solution of the oxide.

§ IV. *Conclusion.*—It hence appears that Bunsen's method is capable of yielding accurate results only in the case of manganese oxides, using the strongest acid. The modification of it here investigated has the advantage of being, not only accurate, but far more expeditious and less troublesome than the original method; a smaller quantity of acid being required (2 to 5 c.c. for a determination), and the correction due to the iodine liberated by this acid being determinable with greater ease and certainty than in Bunsen's process. Unfortunately, however, it has the disadvantage of not being applicable to manganese ores, since the ferric oxide present in them would also liberate iodine from the potassium iodide, and therefore in these cases Bunsen's method must be employed, using all the precautions here indicated.
