

XV. *On some of the compounds of chromium.* By THOMAS THOMSON, M. D. F. R. S. L. and E. Professor of Chemistry, Glasgow.

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THE principal object of this Paper is to give an account of a singular combination of chromic acid, and chlorine, which I discovered about a year and a half ago. But as the investigation of this compound led me to a more careful examination of the oxides of chromium, and a more accurate knowledge of their composition than had been hitherto attained, I shall also state the facts which I have ascertained with respect to these bodies. In a Paper inserted in the Annals of Philosophy (1st Series, vol. 16, p. 321), I have shown that the atomic weight of chromic acid is 6.5. Two other compounds of chromium and oxygen being known, namely, the *green oxide*, and the *brown oxide*, I was induced, from analogy, to consider the atomic weight of the former to be 4.5, and that of the latter 5.5; and to make the atom of chromium 3.5. These views were rather favoured by some experiments on the chloride and muriate of chromium, which I have stated in my "First Principles of Chemistry," vol. ii. p. 52. But these experiments deviating more than two per cent from the theoretical number, could not be considered as decisive. How far my former notions on this subject were correct, will appear from the following statements.

I. *Chromium.*

The metallic chromium, which I employed in the following experiments, had been reduced by Mr. COOPER, of London, who possesses great skill in the management of furnaces. He was kind enough to give me a specimen of this rare metal several years ago; and I take this opportunity of thanking him for a present, which has been of considerable service in my investigations.

Pure metallic chromium is white, with a shade of yellow: it is very brittle, and easily reduced to a fine powder, which still retains the metallic lustre. It is not sensibly attracted by the magnet, even when in very fine powder. Magnetism then is not a property of this metal. The specimen found magnetic by RICHTER, must of course have contained iron. The specific gravity of chromium I found to be 5.093; but the specimen was not quite free from cavities.

Four grains of this metal, previously reduced to an impalpable powder, were boiled for an hour in nitric acid, without perceptible solution. The process was repeated with aqua regia instead of nitric acid, and the flask was left for two days on the sand bath. It was allowed to remain on the cold sand bath from the 3d June to the 18th July, 1826, during a period of uncommonly hot weather, when the thermometer in the shade was repeatedly at 86°. The acid liquid had assumed a green tinge, but the bulk of the powder was not sensibly diminished. The undissolved portion being separated, was found to weigh 3.73 grains: so that only 0.27 grain had been dissolved.

From this experiment it appears that acids do not answer

well for converting chromium into an oxide; I therefore had recourse to alkalies. 3·14 grains of metallic chromium in powder, were mixed with a sufficient quantity of hydrate of potash and nitre, in the proportion of about 5 parts of the former to one part of the latter, and kept for 20 minutes in a red heat in a silver crucible by means of a spirit lamp. The water of the hydrate gradually went off, and a reddish yellow matter remained, which was quite liquid while hot, but became solid on cooling. It dissolved completely in water, and the liquid had the usual yellow colour of a solution of chromate of potash. It was neutralized by nitric acid, and then precipitated by acetate of lead. The chromate of lead thrown down, after being washed and dried upon the filter, weighed 16·8 grains, but was reduced to 16·23 grains when exposed to a red heat over a spirit lamp.

By this process the metallic chromium had been converted into chromic acid. Now chromate of lead is composed of

1 atom chromic acid	-	-	6·5
1 atom protoxide of lead	-		14
			<hr/>
			20·5

From this constitution of the salt, it is easy to deduce the weight of chromic acid in 16·23 grains of chromate of lead: it amounts to 5·146 grains.

Thus it appears that 3·14 grains of chromium, when converted into chromic acid, become 5·146 grains. This gives us 3·966 for the atomic weight of chromium. For

$5·146 : 3·14 :: 6·5 \text{ (atom of chromic acid)} : 3·966 = \text{atom of chromium.}$

My stock of metallic chromium being small, I did not

choose to repeat this experiment ; but it had been made with such scrupulous attention, that I am satisfied it must approach very near the truth.

As 3.966 differs by less than one per cent from 4, we can scarcely hesitate about adopting 4 as the true atomic weight of metallic chromium. Indeed 4 must be the true number, if we adopt the law of Dr. PROUT, which I have so amply confirmed by numerous examples in my "First Principles of Chemistry," namely, that the atomic weights of all bodies are multiples of 0.125, the atom of hydrogen: for  $0.125 \times 32 = 4$ .

This conclusion will be corroborated by the experiments immediately to be detailed, which leave no doubt that the atomic weight of green oxide of chromium is 5. Now, as this oxide is a compound of 1 atom oxygen + 1 atom chromium, the atom of chromium must necessarily be 4. If we allow an error in weighing to have taken place in the preceding experiment to the amount 0.02 grain, the number 4 would come out as the result of the experiment. Now, I need hardly remark to practical chemists, how very difficult it would be to guarantee any similar experiment from so small an error as  $\frac{1}{50}$ th of a grain.

## II. *Green oxide of chromium.*

This oxide is always obtained by depriving chromic acid of a portion of its oxygen. Many processes have been followed. When chromate of potash is digested with alcohol or tartaric acid, the chromic acid is pretty speedily converted into green oxide. A solution of chromate of potash speedily lets green oxide fall when a current of sulphurous acid is passed through



the solution.\* The same change takes place if we boil a mixture of chromate of potash and muriatic acid together. The addition of a little alcohol greatly promotes the rapidity of this process. The method proposed by BERZELIUS is one of the most tedious and unproductive. He passes a current of sulphuretted hydrogen gas through a solution of chromate of potash, previously acidulated with muriatic acid.

In whatever way the green oxide of chromium is procured, it is always at first in the state of a hydrate. If we dry the precipitate in the open air, it is a greenish blue tasteless light substance, which may or may not contain carbonic acid, according to the re-agent employed in throwing it down. If we dry it on the filter by artificial heat, its colour becomes a good deal darker, and it retains almost exactly half its weight of water. When it is dried in the open air without artificial heat,  $\frac{1}{4}\frac{3}{5}$ ths of its weight are water. In this state of hydrate it dissolves readily in almost all acids. A moderate heat expels the water, and leaves the oxide in the state of an exceedingly beautiful green powder, scarcely soluble in any acid whatever. When this green oxide is heated nearly to redness in an open vessel, it generally *glows*, or becomes intensely red hot, so as to resemble the appearance of burning tinder. This glowing does not always take place, though it is a pretty common phenomenon. It has not yet been determined, upon what this curious property depends.

\* To prevent misapprehension, it will be proper to state, that the oxide thrown down by sulphurous acid has a brown colour; but if we dissolve it in muriatic acid, and throw it down by ammonia, the precipitate obtained will be green oxide. It will be shown hereafter, that brown oxide differs from green oxide, merely by retaining a small quantity of chromic acid, with which the green oxide is combined.

Many methods were tried to determine the atomic weight of this oxide. As it does not form crystallizable salts with acids, and as acids have the property of combining with it in various proportions, we cannot have recourse to the salts of chromium for this purpose. But as we know that the atomic weight of chromic acid is 6.5, it will be sufficiently satisfactory if we can determine exactly the number of atoms of oxygen, which must be abstracted from chromic acid, in order to convert it into green oxide of chromium. Now, sulphuretted hydrogen gas, and protosulphate of iron, possess the property of converting chromic acid into green oxide of chromium. I shall relate, in succession, the analysis of chromic acid made by means of these two bodies.

1. A quantity of neutral chromate of potash was dissolved in water, and a current of sulphuretted hydrogen gas passed through the solution till all action was at an end. A beautiful green-coloured precipitate fell: the liquid remained deeply coloured; but upon being heated sulphuretted hydrogen gas was exhaled, an additional portion of green precipitate fell, and the liquid became colourless. It was quite free from every trace of chromic acid or oxide of chromium.

The green precipitate being examined, was found to be a compound of one atom of sulphuretted hydrogen and one atom of green oxide of chromium. It was therefore a hydrosulphuret of chromium. This hydrosulphuret is tasteless, and insoluble in water. It dissolves with facility in acids, sulphuretted hydrogen gas being given off and sulphur remaining. From the experiment it appears, that this hydrosulphuret becomes soluble in water when an additional quantity of sulphuretted hydrogen is combined with it. Probably

this soluble portion was in the state of bihydrosulphuret of chromium.

The residual liquid being evaporated to dryness left a deliquescent salt, possessing the following properties. Its taste was strongly alkaline, and it acted powerfully on cudbear paper, giving it a deep purple colour, as alkalies always do. Muriate of barytes dropt into the aqueous solution of the salt threw down a white precipitate, which was re-dissolved by adding a few drops of nitric acid. Acetate of lead occasioned a white precipitate. Sulphuric acid occasioned an effervescence, sulphurous acid was driven off, and abundance of sulphur was thrown down. These properties leave no doubt that the salt was a *hyposulphite* of potash.

Thus it appears, that when a current of sulphuretted hydrogen gas is passed for a sufficient time through a solution of chromate of potash, the whole chromic acid is converted into hydrosulphuret of chromium, while the potash becomes hyposulphite of potash. Before the rationale of these decompositions, and new combinations can be given, it will be necessary to make the reader acquainted with the true composition of the *hyposulphurous acid* of Mr. HERSCHEL, which is the kind of acid formed in the process just described.

During the summer of 1825, which was remarkably hot and dry, there were formed in the soda leys of Mr. CHARLES TENNANT, of Glasgow, numerous octahedral crystals possessing the following properties.

The crystals seemed to be regular octahedrons, though they did not admit of accurate measurement. The taste of the salt was very hot, bitter, and sulphureous. It was not altered by twenty-four hours exposure to the air ; but when kept in

a phial, gradually deliquesced into a brown liquid. Its alkaline properties were as powerful as those of a strong caustic potash ley : that is to say, it rendered cudbear paper purple, and dissolved the cuticle and nails of the fingers very speedily. When heated, it underwent the watery fusion, then became a solid salt, which caught fire and glowed or burnt like tinder for a considerable time with a very low yellow-coloured flame.

This salt had been noticed by VAUQUELIN in 1802. He obtained it from the carbonate of soda manufactured by PAYER and BOURLIER, and described its characters under the name of hydrosulphuret of soda.\*

I dissolved 50 grains of these crystals in water, and added to the solution muriatic acid in sufficient quantity to saturate the soda, which I knew it, from previous trials, to contain. A smell of sulphuretted hydrogen was at first given out abundantly : this was soon followed by the odour of sulphurous acid, while at the same time sulphur was deposited. The solution being filtered and evaporated to dryness, left 25·3 grains of common salt, equivalent to 13·49 grains of soda.

50 grains of the salt being heated in a retort lost 29·2 grains of their weight. The retort was blackened by the action of the sulphur on the oxide of lead in the flint glass. The liquid collected in the receiver weighed 25·4 grains. It contained sulphuretted hydrogen and a small quantity of the original salt.

To determine the quantity of sulphur in this salt, 31·25 grains of sulphate of copper (containing 10 grains of oxide of

\* Ann. de Chim. 41, 190.

copper) were dissolved in water ; and it was found that when this liquid was mixed with a solution of 29·75 grains of the crystals the whole copper was thrown down, and no residual sulphur remained in the liquid ; for no effect whatever was produced by adding to it a few drops of the solution of sulphate of copper. Now, when sulphate of copper and a hydrosulphuret are mixed in the atomic proportions, the precipitate consists of bisulphuret of copper, composed of equal weights of sulphur and copper. But the copper in 31·25 grains of sulphate of copper is eight grains. Consequently, 29·75 grains of the crystals contain just 8 grains of sulphur ; or, which is the same thing, 14·875 grains of the crystals contain 4 grains of sulphur.

As 50 grains of the crystals gave 13·49 grains of soda, it is obvious that 14·875 grains must contain 4·013 grains, which differs by only  $\frac{1}{4}$ th per cent from 4.

The salt being in regular crystals, and not altered by exposure to the air, the water contained in it must be a determinate number of atoms. Now, 50 grains of the crystals gave 25·4 grains of liquid ; consequently, 14·875 grains would give 7·556 grains. But this liquid contained more than half a grain of saline matter : so that the quantity of water contained in 14·875 grains of the crystals does not amount to quite so much as 7 grains. If we suppose the water of the salt to be six atoms, its weight in 14·875 grains of the salt will be 6·75 grains. It is obvious from the experiment that it is not less than this, nor can it be more ; for 7 atoms of water would be 7·875, which was above the whole weight of the liquid obtained, and yet above half a grain of the weight found was owing to saline matter.

It appears from the preceding analysis, that 14·875 grains of the salt contain

2 atoms sulphur	-	-	4
1 atom soda	-	-	4
6 atoms water	-	-	6·75
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			14·75

The 0·125 wanting to make up the whole weight is equivalent to an atom of hydrogen. If we consider it as combined with the two atoms sulphur, making an atom of bisulphuretted hydrogen, then the constituents of the salt will be as follows:

1 atom bisulphuretted hydrogen	-	4·125
1 atom soda	- - -	4
6 atoms water	- - -	6·75
		<hr/>
		14·875

It will appear immediately that these numbers exhibit the true composition of this hydrosulphuret. It is not, as VAUQUELIN supposed, a compound of sulphuretted hydrogen and soda, but of bisulphuretted hydrogen and soda.

If we dissolve this salt in water and add to the solution sulphurous acid, as long as this acid continues to lose its smell, one half of the sulphur contained in the salt is thrown down, and the liquid will be found to contain nothing but a solution of hyposulphite of soda. If we concentrate the solution sufficiently, it shoots into large transparent crystals of hyposulphite of soda.

These crystals are flat four-sided prisms, terminated by a bihedral summit. They have very much the taste of GLAUBER salt. When sulphuric acid is poured upon this salt, or still better, into an aqueous solution of it, sulphur is thrown down,

and sulphurous acid is driven off, at least if heat be applied to the liquid. A careful analysis of this salt gave its constituents as follows :

1 atom hyposulphurous acid	-	-	5
1 atom soda	-	-	4
4 atoms water	-	-	4.5
			<hr/>
			13.5

It is obvious, that the hyposulphurous acid in this salt is a compound of 2 atoms sulphur and one atom oxygen, and that its atomic weight is 5. It is equally obvious, that the hydrosulphuret employed in its fabrication contains not sulphuretted hydrogen, but bisulphuretted hydrogen.

For, let us suppose a mixture to be made of 14.875 of the hydrosulphuret of soda and 4 sulphurous acid, 2 of sulphur will precipitate, and a neutral hyposulphite of soda will be formed.

14.875 hydrosulphuret contain 2 atoms sulphur and only 1 atom hydrogen. There remain in solution (as half the sulphur falls) 1 atom sulphur + 1 atom hydrogen.

The 4 sulphurous acid are composed of 1 atom sulphur + 2 atoms oxygen.

One of these atoms of oxygen in the sulphurous acid will combine with the atom of hydrogen in the hydrosulphuret, and form water ; so that there remain for the constituents of the hyposulphurous acid,

$$\begin{array}{rcl}
 2 \text{ atoms sulphur} & = & 4 \\
 1 \text{ atom oxygen} & = & 1 \\
 \hline
 & & 5
 \end{array}$$

There cannot have been more than 1 atom of hydrogen in the hydrosulphuret. For had there been two atoms, consti-

stituting a bihydrosulphuret of soda, the whole oxygen of the sulphurous acid would have been converted into water, and the hyposulphurous acid would have contained no oxygen at all.

Such is the composition of the hyposulphurous acid of HERSCHEL. I verified this constitution by the direct analysis of several hyposulphites; the most easily analyzed of which were the hyposulphites of barytes and of lead.\*

The reader being now aware of the composition of hyposulphurous acid, will be prepared for the theoretical explanation of the decomposition of chromic acid by sulphuretted hydrogen gas.

Let us suppose a solution of 125 grains of chromate of potash, containing 65 grains (equivalent to 10 atoms) of chromic acid. To reduce this to green oxide, 5 atoms of sulphuretted hydrogen gas are requisite, containing

5 atoms sulphur,  
5 atoms hydrogen.

The sulphur is converted into sulphurous acid and must combine with        -        -        -        10 atoms oxygen,

The hydrogen unites to        5 atoms oxygen,

forming water.

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Thus the 10 atoms chromic acid, in order to become green oxide, must part with 15 atoms of oxygen; or (which is the same thing) 1 atom of chromic acid is converted into green oxide when it is deprived of 1.5 atom oxygen. But chromic

\* There is another acid which exists, composed of 1 atom sulphur + 1 atom oxygen. Its atomic weight is 3. It may be distinguished by the name of *sub-sulphurous acid*.



acid weighs 6·5; and  $6\cdot5 - 1\cdot5 = 5 =$  atomic weight of green oxide.

The 5 atoms of sulphurous acid thus formed unite with 5 atoms of sulphuretted hydrogen; and these two bodies are mutually decomposed into 5 atoms hyposulphurous acid and 5 atoms water. The 5 atoms of hyposulphurous acid uniting to the 10 atoms of potash constitute dihyposulphite of potash, composed of

1 atom hyposulphurous acid	5	
2 atoms potash	-	-
		12
		<hr/>
		17

I conceive that this beautiful example of rather a complicated series of decompositions and new combinations, leaves no doubt that the atomic weight of green oxide of chromium is 5.

When we take bichromate of potash instead of neutral chromate, and treat it with sulphuretted hydrogen gas, the precipitated hydrosulphuret has a buff colour instead of a green. This may perhaps be ascribed to a portion of undecomposed chromic acid falling in combination with some part of the precipitate. For we shall see afterwards a similar coloured precipitate composed of chromic acid and green oxide.

This buff coloured precipitate is tasteless, and insoluble in water. It is either a hydrosulphuret of chromium, or at least contains a hydrosulphuret; for when it is heated sulphur sublimes, and sulphurous acid is given off. At a certain temperature it catches fire, and burns for some time with a yellow low flame. When digested in muriatic acid some sulphur precipitates. When digested in nitro-muriatic acid, a portion of the sulphur is converted into sulphuric acid. From 7·71 grains of the buff coloured precipitate I obtained

Green oxide of chromium	-	5.02
Sulphur	- - -	0.37

It was easy to drive off water, but not to determine its quantity. The 5.02 of green oxide contained  $\frac{1}{6}$ th of a grain of chromic acid. If we suppose the sulphur to be combined with hydrogen, and what is wanting to make up the weight to have been water, the constituents of the buff-coloured powder will be

Green oxide	- -	4.85 or 185.44 or 37 atoms.
Chromic acid	- -	0.17 or 6.5 or 1 atom.
Sulphuretted hydrogen	0.39 or	14.9 or 7 atoms.
Water	- -	2.30 or 87.94 or 78 atoms.

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7.71

The whole chromic acid, owing to an accident, was not collected; but from some experiments to be related afterwards, I am disposed to view the buff-coloured powder as a compound of

5 atoms hexa-chromate of chromium*	- -	36.5
1 atom hydrosulphuret of chromium	- -	7.125
12 atoms water	- - - -	13.5
		<hr/> 57.125

Green oxide of chromium, when prepared by the usual processes, is not always free from chromic acid; but in consequence of the property which sulphuretted hydrogen has of reducing chromic acid to green oxide, we have it always in our power to free it entirely from all such admixture. For this purpose it may be dissolved in muriatic acid, and a

\* By hexa-chromate of chromium, I mean a compound of 1 atom chromic acid, and 6 atoms green oxide of chromium.

current of sulphuretted hydrogen may be passed through the solution, previously rendered as neutral as possible by evaporating it to dryness, and re-dissolving the residual matter in water. If the green oxide was pure, no precipitate appears; but if chromic acid was present, a quantity of the above described buff-coloured precipitate will be thrown down.

When sulphate of chromium in the state of a dry powder is put into a glass tube and heated to redness over a spirit lamp, while a current of hydrogen gas is made to pass over it, water is at first given off, and afterwards sulphuretted hydrogen. When all action is at an end, a black, tasteless, insoluble matter remains in the tube, composed (judging from the loss of weight) of

1 atom sulphur	-	-	-	-	2
2 atoms green oxide of chromium	-				10
					<hr/>
					12

It is therefore a *disulphuretted oxide* of chromium; or, perhaps, a *dihydrosulphuret* of chromium.

2. I shall now relate the experiments by which chromic acid was converted into green oxide of chromium, by means of protosulphate of iron.

When a solution of protosulphate of iron is mixed with one of chromate of potash, a buff-coloured precipitate falls, which is a combination of peroxide of iron and green oxide of chromium. In this case, the protoxide of iron is peroxydized at the expence of the oxygen in the chromic acid, which becomes green oxide. Thus we have it in our power to convert chromic acid at once to green oxide, by mixing it

with a solution of protosulphate of iron. The determination of the quantity of protosulphate necessary to disoxygenise a given weight of chromic acid, will give us the quantity of oxygen which constitutes the difference between chromic acid and green oxide.

It will be necessary to remember that the atomic weight of protoxide of iron is 4.5, and that of peroxide 5; and that an atom of protoxide of iron is converted into peroxide by uniting with half an atom of oxygen. We must remember too, that crystallized protosulphate of iron is a compound of

1 atom sulphuric acid	-	-	5
1 atom protoxide of iron	-	-	4.5
7 atoms water	-	-	7.875
			<hr/>
			17.375

Consequently 17.375 of protosulphate of iron constitute the equivalent for 1 atom of protoxide of iron.

If chromic acid be a compound of

1 atom green oxide	-	-	5
$1\frac{1}{2}$ atom oxygen	-	-	1.5
			<hr/>
			6.5

as the analysis of it by means of sulphuretted hydrogen has shown it to be, it is obvious, that in order to reduce an atom of chromic acid to green oxide, we must mix it with three atoms of protoxide of iron. Now, 52.125 grains of protosulphate of iron contain the equivalent for 3 atoms of protoxide, while 12.5 grains of chromate of potash contain the equivalent for an atom of chromic acid. These facts being understood and remembered, we are prepared for following the details of the experiment.

12.5 grains of crystallized chromate of potash (containing 6.5 grains of chromic acid) were dissolved in a small quantity of boiling-hot distilled water. 52.125 grains of protosulphate of iron, recently crystallized, transparent, and of a light green colour, were dissolved in boiling-hot distilled water, after it had been kept boiling briskly for several minutes, in order to free it from air as completely as possible. These solutions being mixed, an abundant buff-coloured precipitate fell. It was separated by the filter, well washed and dried. The weight as dried on the filter was 25 grains, but by ignition it was reduced to 16.81 grains. It was a black shining powder, not magnetic, and similar in appearance to native *chromiron ore*, as it is called.

The residual liquid was neutral, and contained both peroxide of iron, and green oxide of chromium. It was diluted with water, and then mixed with benzoate of ammonia. The object of the dilution was to prevent any benzoate of chromium from being precipitated along with the benzoate of iron. The perbenzoate of iron, after being washed and dried, was found to contain 1.37 grain of per oxide of iron. The green oxide of chromium having been thrown down by an alkaline carbonate, washed, dried, and ignited, weighed 1.66 grains. It did not glow, and assumed a blackish colour.

From this experiment we see, that three atoms of protoxide of iron become peroxide when they are employed to reduce one atom of chromic acid to green oxide. But an atom of chromic acid weighs 6.5, and 3 atoms of protoxide of iron require 1.5 atom of oxygen to convert them into peroxide. Consequently, chromic acid is a compound of

Green oxide	-	-	5
Oxygen	-	-	1.5

and 5 is the atomic weight of green oxide of chromium.

The whole protoxide of iron used in this experiment, when converted into peroxide, became 15 grains, and the 6.5 chromic acid, when reduced to green oxide, became 5 grains. Hence the total weight of the oxides of iron and chromium ought to amount to 20 grains.

Now the buff-coloured precipitate was	-	-	16.81
In solution { peroxide of iron	-	-	1.37
{ green oxide of chromium	-	-	1.66
			<hr/>
			19.84
Loss	-	-	0.16

The cause of this loss became evident when the residual liquid was concentrated to a few drops. It should have contained sulphuric acid, potash, and the alkali employed to throw down the green oxide, and nothing else. But after the concentration had made considerable progress, the liquid assumed a perceptibly yellow tinge, showing that it still retained a small portion of chromic acid. The colouring powers of this acid are so great, that a very minute portion of it becomes visible. The protosulphate of iron, though I had been at great pains to have it as pure as possible, was not quite free from all admixture of peroxide. For when a crystal of it was put into a solution of prussiate of potash, a green colour was immediately struck. This incipient peroxidization of the iron rendering the quantity employed insufficient to reduce the whole chromic acid, a minute portion still remained in the state of chromic acid.

Various repetitions of this experiment were made, but I was never able to obtain a solution of protosulphate of iron absolutely free from all admixture of peroxide. There was therefore always a loss. When the preceding quantities were employed, the smallest loss amounted to 0.07 grain, and the greatest to 0.2 grain; but notwithstanding this loss, never exceeding 1 per cent, and sometimes less than a half per cent, the experiment is conclusive, that 5 is the atomic weight of green oxide of chromium; and that 6.5 chromic acid become green oxide when deprived of 1.5 oxygen.

It is obvious that the 16.81 grains of black matter obtained were composed of

Peroxide of iron	-	-	13.63 or 20.404
Protoxide of chromium	-	-	3.34 or 5
			<hr/>
			16.97

That is to say, it is a compound of 4 atoms peroxide of iron, and 1 atom green oxide of chromium. On subjecting a portion of it to analysis, I obtained

Peroxide of iron	-	-	8.77 or 21.286
Green oxide	-	-	2.06 or 5

Now, if we subtract from the 3.34 of green oxide the 0.16 of loss, it is obvious that the true composition of the powder will be

Peroxide of iron	-	21.11
Green oxide of chrome	-	5

The analysis therefore, notwithstanding the smallness of the scale, comes near enough the truth to show that it had been conducted with care.

Having thus established the true atomic weight of chromium, and protoxide of chromium, the experiments which

were made to determine the composition of phosphuret of chromium will be readily understood by the reader.

3.2 grains of phosphorus and 5.08 grains of anhydrous green oxide of chromium were put into a green glass tube, shut at one end and open at the other. The phosphorus occupied the bottom of the tube and the oxide the middle portion, extending about two inches, and distant rather more than one inch from the phosphorus. The tube was laid horizontally across a choffer, and the portion of it containing the green oxide was raised to a red heat by means of a charcoal fire. The phosphorus was then sublimed through the green oxide by means of a spirit lamp. A brilliant combustion took place, and the oxide was converted into phosphuret of chromium.

The phosphuret thus formed still continued an incoherent powder. It had a brown colour, was tasteless, and insoluble in water and acids. Before the blow pipe it was agglutinated together, but did not undergo complete fusion. It weighed 6.21 grains.

5.08 grains of green oxide of chromium are equivalent to 4.065 grains of chromium. Hence, the phosphuret was a compound of

Chromium	-	-	4.065 or 4
Phosphorus	-	-	2.145 or 2.11

$1\frac{1}{2}$  atom phosphorus weighs 2.25, which comes near 2.11. The compound thus seems to consist of 1 atom of chromium united to  $1\frac{1}{2}$  atom phosphorus. It is therefore a sesqui-phosphuret.

I digested this phosphuret for a week in nitric acid. No solution took place, but the matter assumed a fine green



colour. By this process the powder was converted into a phosphate of chromium. Part of the phosphoric acid was withdrawn, and remained dissolved in the liquid; for the phosphate weighed 9.545 grains. It was obviously a compound of

Protoxide of chromium 5.08    or 5    or 1 atom.

Phosphoric acid    -    4.465    4.394     $1\frac{1}{3}$  atom.

There is still an excess of acid; but the excess, instead of being half an atom, as in the phosphuret, was only  $\frac{1}{3}$ d of an atom.

My attempts to form a sulphuret of chromium by a similar process were not attended with success.

3. Besides the preceding experiments, by which the atomic weight of green oxide of chromium was determined, many others were tried, which did not terminate so satisfactorily. It will be worth while to give a short account of a few of the most promising of these methods, though they did not prove successful.

1. A quantity of chromate of lead was heated to whiteness in a charcoal crucible. It became black and agglutinated, and globules of metallic lead were visible in it. The under side of the cohering mass consisted chiefly of green oxide of chromium. 23.06 grains of this black matter were digested for a month in dilute nitric acid, and then filtered. The undissolved green oxide of chromium being collected on a filter,edulcorated, dried, and ignited, weighed 5.589 grains. The nitric acid solution being evaporated to dryness, left 27 grains of pure nitrate of lead, equivalent to 18.216 grains of protoxide of lead. Thus the 23.06 grains of black matter furnished

Green oxide of chromium	-	5.589
Protoxide of lead	- -	18.216
		<hr/>
		23.805

which exceeds the weight of the matter employed by 0.745 grains. The oxygen in 18.216 grains of protoxide of lead amounts to 1.301. Of this only 0.556 gr. existed in the black powder. From this experiment it appears that  $\frac{4}{7}$ ths of the lead were reduced to the metallic state, while  $\frac{3}{7}$ ths still remained in their original state of protoxide.

The lead here exceeds the quantity which would have been obtained, had I been able to analyse the whole altered chromate of lead. The true proportions would have been

Green oxide of chromium	-	5.589
Protoxide of lead	- -	15.645

The excess of  $2\frac{1}{2}$  grains was owing to this: I took the bottom of the cake, because the upper part was not free from charcoal; and the great weight of the reduced lead occasioned an excess of it to be found in the bottom of the cake. Now the oxygen in 15.645 grains of protoxide of lead is 1.117, of which 0.556 gr. is very nearly the half. From this we see, that when chromate of lead is exposed to a white heat in a charcoal crucible, the chromic acid is totally converted into green oxide, while half the protoxide is reduced to metallic lead. The black matter formed is a compound of

2 atoms green oxide of chromium	-	10
1 atom protoxide of lead	- - -	14

42 grains of chromate of lead, in powder, were put into a green glass tube, which by means of a charcoal fire was kept at a cherry red heat, while a current of dry hydrogen gas

was made to pass through the tube till all action was at an end. The chromate underwent combustion, and water was evolved pretty copiously. The loss of weight was 4·6 grains.

Now, the constituents of 42 grains of chromate of lead may be represented as follows :

	Lead.	Oxygen.
28·68 protoxide of lead composed of	26·63	+ 2·05
	Green oxide.	
13·32 chromic acid composed of	- 10·246	+ 3·074
Total oxygen	- - -	5·124

By the process the chromic acid was totally reduced to green oxide. Globules of metallic lead could be detected in the residual matter. But had the whole lead been reduced, the loss of weight would have amounted to 5·124 grains, instead of 4·6 grains. The difference is 0·524, which rather exceeds  $\frac{1}{4}$ th of the oxygen in the protoxide of lead.

The whole of the residual matter having been digested in nitric acid for about a week, was dissolved, and formed a very dark bluish green liquid, from which the lead was precipitated by sulphate of soda, and the green oxide by carbonate of ammonia. When this last precipitate was dried it had a blue colour ; when heated to redness it did not glow, as green oxide usually does, but assumed a dirty green colour. The weight was 9·36 grains. There had remained undissolved of the original matter 3·46 grains. It had a brownish yellow colour, and was chromate of lead, probably reproduced during the action of the nitric acid on the green oxide. It was composed of

Protoxide of lead	-	-	2·36
Chromic acid	-	-	1·10
			<hr/> 3·46

If we subtract the 1.1 chromic acid from the 13.32, originally present in the chromate of lead, there will remain 12.22, which had yielded 9.36 of green oxide. According to this analysis chromic acid is composed of

Protoxide of chromium	-	9.36 or 4.9
Oxygen	- - -	2.86 or 1.5
		<hr/>
		12.22

The atomic weight of protoxide of chromium, by this experiment, comes out 4.9, instead of 5; but a few flocks of the green oxide of chromium accidentally escaped, and could not be weighed. Were we to estimate them at  $\frac{1}{20}$ th of a grain (and I think they amounted to that quantity), the atom of protoxide would amount exactly to 5.

This mode of experimenting is susceptible of considerable accuracy. The error was only 2 per cent, and the source of it was evident.

2. 6.62 grains of anhydrous green oxide of chromium were heated with hydrate of potash, over a spirit lamp, till water ceased to escape. The silver crucible containing the mixture was then raised to a red heat, and kept in that temperature for 15 minutes. The whole was now digested in water: 1.49 grains of the anhydrous green oxide still remained in its original state; so that by the process, 5.13 grains of green oxide had been converted into chromic acid. The yellow-coloured alkaline solution was saturated with acetic acid, and precipitated by acetate of lead. The chromate of lead obtained weighed after ignition 20.29 grains, equivalent to 6.433 grains of chromic acid.

According to this experiment chromic acid is composed of

Green oxide	-	-	5.13	or 5.183	or 5.89
Oxygen	-	-	1.303	or 1.317	or 1.5
			<hr/>	<hr/>	
			6.500	7.39	

This makes the atomic weight of green oxide 5.183, instead of 5; and if we consider 1.5 as the excess of oxygen in chromic acid over green oxide, we have the atomic weight of chromic acid 7.39, instead of 6.5, which is the true number.

The experiment was repeated twice, but without coming nearer the truth. I shall briefly mention the results of these two experiments.

10 grains of anhydrous green oxide were boiled in a silver crucible with a strong potash ley till water ceased to be driven off. The whole was then heated to redness, and kept in that state for a quarter of an hour. The dry mass being digested in water and filtered, there remained on the filter a blackish matter, which, dried on the sand bath, weighed 0.66 grain. When heated it glowed, and the weight was reduced to 0.33 grain. Thus 9.66 grains of green oxide had been converted into chromic acid. The potash solution treated as before gave 41.492 grains of chromate of lead, equivalent to 13.156 grains of chromic acid. Consequently, chromic acid is composed of

Protoxide	9.66	or 4.145	or 4.775
Oxygen	- 3.496	or 1.5	or 1.727
		<hr/>	<hr/>
		13.156	5.645    6.5

12.99 grains of anhydrous green oxide were mixed with a great excess of bicarbonate of potash which had been triturated with a little nitre. This mixture was slowly raised to

a red heat: it was then brought into fusion, and kept in that state for about 20 minutes. The fused mass on cooling had a fine yellow colour. Being digested in water a dirty brown matter remained, weighing when dried on the filter 1·89 grain. When ignited it became green, but did not glow, and the weight was reduced to 1·19 grain. Thus 11·8 grains of green oxide were converted into chromic acid. The potash solution treated as before gave 49·21 grains of chromate of lead, equivalent to 15·603 grains of chromic acid. Thus, 11·8 grains of green oxide became 15·603 chromic acid. According to this experiment, we have chromic acid composed of

Protoxide	11·8	or 4·654	or 4·915
Oxygen	3·803	or 1·5	or 1·585
	<hr/>	<hr/>	<hr/>
	15·603	6·154	6·5

These experiments all deviate a good deal from the truth. The mean of the three gives us the constituents of chromic acid, as follows:

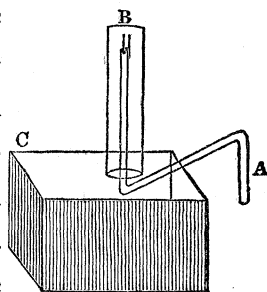
Protoxide	-	-	4·957
Oxygen	-	-	1·543

This gives us 4·957 for the atomic weight of green oxide. The deviation from the truth does not amount to 1 per cent. I expected by this mode of experimenting to have obtained much more satisfactory results.

3. A quantity of liquid chromic acid was evaporated to dryness, forming, as usual, a very deliquescent red mass, which I found by analysis to consist of

Pure anhydrous chromic acid	-	-	88·97
Protoxide of chromium	-	-	4·30
Water	-	-	6·73
			<hr/>
			100·00

12·1 grains of this dry acid were put into a green glass tube, shut at one end, and bent as the tube (A) in the margin, so as to serve the purpose of a retort. The open end ascended to nearly the top of a glass jar (B) standing in the mercurial trough (C), and containing 3 cubic inches of air over a column of mercury 3·6 inches long. While the barometer stood at 30·13 inches, and the thermometer at 52°. The flame of a spirit lamp being applied to the end of the tube (A), containing the acid, fusion took place, and water was given out. A little of the acid assumed the form of vapour, and was deposited in the upper part of the tube. As soon as the tube became red hot, the acid began to give out oxygen gas. The heat was continued till all evolution of gas was at an end, and till the acid in the tube had assumed a fine green colour.



The oxygen gas evolved when reduced to the temperature of 60°, under a pressure of 30 inches of mercury, was 5·634 cubic inches, the weight of which is 1·909 grain. The real acid heated amounted to 10·765 grains. According to this experiment, chromic acid is a compound of

Protoxide	-	-	8·856 or 6·95
Oxygen	-	-	1·909 or 1·5
			<hr/>
			10·765

What makes this result so erroneous, is partly the impossibility of determining the quantity of chromic acid which had sublimed unaltered ; but chiefly the impracticability of reducing the acid completely to the state of protoxide by the application of the greatest heat which the glass could bear

without fusion. I made an attempt to determine how much of the acid still remained undecomposed, but did not succeed. Water would not separate the acid from the oxide, and fusion, or even digestion with an alkali could not be had recourse to, because it might have brought back a portion of protoxide to the state of acid.

### III. *Brown oxide of Chromium.*

This oxide was first noticed by VAUQUELIN, who remarked at the same time that it contained only a very little more oxygen than the green oxide. It may be most conveniently prepared by passing a current of sulphurous acid gas through a solution of chromate, or bichromate of potash: the brown oxide soon precipitates, and may be easily collected on the filter, and washed and dried.

It has a flea-brown colour, and is destitute of taste, and does not undergo any alteration by several days exposure to the air. It is not quite insoluble in water. A quantity of it was put into a large glass jar, which was filled with water, and the powder well agitated in the liquid. When the oxide had subsided, the water was drawn off with a syphon, and clean water substituted. This was continued regularly every day for above two months. The water always assumed a yellow colour, and some chromic acid could be detected, dissolved in it, to the very last.

I did not succeed by this method in altering the colour of the oxide; but when caustic ammonia was substituted for water, the colour of the oxide, after the second washing, had become black; and after two or three more washings, it



assumed the green colour of protoxide of chromium. From these trials I was led to suspect, that this supposed oxide might be nothing else than common green oxide of chromium combined with a certain determinate quantity of chromic acid. The following experiments were made with a view of determining how far this suspicion was well founded.

8 grains of brown oxide of chromium were heated on the sand bath till they ceased to lose weight. The brown colour was not altered, but the weight was reduced to 6·8 grains. When this matter was exposed to a red heat it did not glow, but became black, and similar to brown oxide after it has been once or twice washed in ammonia. The weight was reduced to 6·24 grains.

Brown oxide, when digested in nitric acid, was dissolved. The solution had a green colour, a very sweet taste, and possessed the usual characters of nitrate of chromium. It dissolved likewise in muriatic acid. The solution was green-coloured, sweet tasted, and precisely similar to common muriate of chromium.

These facts seemed to show decisively, that this supposed brown oxide does not combine with acids; and that when treated either with acids or alkalies, it is resolved into common green oxide and chromic acid.

To determine the quantity of chromic acid in brown oxide of chromium, the following experiments were made: 6·81 grains of brown oxide, previously exposed to an incipient red heat, were put into a green glass tube, through which a current of dry hydrogen gas was made to pass, while the oxide was kept at a red heat by means of a spirit lamp. No combustion took place; but a little water was formed, and

the oxide assumed a fine green colour. The loss of weight was 0.18 grain.

12 grains of the brown oxide in its original state, as prepared, were put into a green glass tube, shut at one end and bent into a retort-like form, as before described. The open end of the tube rose to the top of a small glass jar, standing over mercury, and containing 3 cubic inches of air. Heat was applied to the oxide in the tube by means of a small charcoal fire. No gas was extricated till the oxide became red hot. At that temperature 1.169 cubic inch of oxygen gas came over. The heat was raised as high as the tube could bear, and it was continued till the evolution of gas had been for some time over, and till the oxide had assumed a fine green colour. During this process the oxide did not glow. The weight of 1.169 cubic inch of oxygen gas is 0.4009 grain.

From a preceding experiment it is evident, that 12 grains of the brown oxide employed, when exposed to a strong red heat, were reduced to 9.36 grains; or, the loss of weight was 2.64 grains. From the experiment just stated, it appears that 0.4009 gr. of that weight is oxygen. Consequently, the constituents of the brown oxide may be represented as follows:

Green oxide	-	-	9.36
Oxygen	-	-	0.4009
Water	-	-	2.2391
			<hr/>
			12.0000

But the oxygen must have been combined with green oxide, so as to constitute chromic acid. We may therefore represent the constitution of brown oxide of chromium in the following manner.

Green oxide    8·024    or 30·02 or 6 atoms.

Chromic acid   1·7369 or 6·5        1 atom.

Water    -    -    2·2391 or 8·38     $7\frac{1}{2}$  atoms.

From the preceding analysis it appears, that brown oxide of chromium is a compound of 1 atom chromic acid and 6 atoms green oxide. The combination is not very intimate, since the chromic acid is gradually separated by water. It is not capable of combining either with acids or alkalies, or of forming peculiar compounds. When it is digested in acids, the common salts of green oxide of chromium are obtained. To alkaline solutions it gives out chromic acid, while green oxide of chromium remains.

In my "First Principles of Chemistry," vol. ii. p. 54, I mention that I formed a combination of brown oxide of chromium and soda, and I describe the process followed. I merely inferred the existence of brown oxide in this liquid, from its colour. I have since analyzed it, and found it a mixture of nitrate of soda and chromate of chromium. When nitric acid is digested on green oxide of chromium, and the liquid after being evaporated to dryness is fused in a crucible, the nitric acid is destroyed, and abundance of chromic acid formed. By this process, if we stop in time, we may form a brown-coloured liquid, which, when evaporated to dryness, leaves a substance quite similar in its properties to brown oxide of chromium.

From the preceding investigation it follows, that chromium combines with two proportions of oxygen, forming green oxide and chromic acid. The atomic weights and constituents of chromium and its oxides are as follows:

	Atomic weight.
Chromium - - - - -	4
Green oxide 4 chromium + 1 oxygen =	5
Chromic acid 4 + 2.5 =	6.5
Brown oxide 4 + 1.2142857 =	5.2142857

Two atoms and a half, the proportion of oxygen united to an atom of chromium in chromic acid, has not yet been observed, except in the hyposulphuric acid of GAY-LUSSAC, which is a compound of 1 atom sulphur, and 2.5 atoms oxygen.

#### IV. *Chloro-chromic acid.*

I proceed now to describe the properties of a rather remarkable compound, which I discovered about a year and a half ago, and which, from the great energy with which it acts upon combustible substances, will be very acceptable to those persons who are fond of exhibiting brilliant chemical experiments.

Chloro-chromic acid may be obtained with great facility by the following process. Triturate together in a mortar 190 grains of bichromate of potash, and 225 grains of common salt, till they are intimately mixed. Pour the dry powder into a tubulated retort: insert the beak of the retort into a dry glass receiver, fitting it by means of a perforated cork, which should not be quite air tight. Pour into the retort 500 g ains of the sulphuric acid of commerce, and by agitation make it into a magma with the salts. Then apply the flame of a lamp to the bottom of the retort. An effervescence takes place, and beautiful red fumes soon make their appearance. These condense in the beak of the retort, and gradually drop into the receiver under the form of a red-

coloured liquid. This process lasts about ten minutes, or a quarter of an hour, when the evolution of the red fumes suddenly stops. The matter in the retort has now assumed a fine green colour. If the distillation be continued, a liquid passes into the receiver, consisting chiefly of acidulous water, and destroys the red liquid. The process therefore must be stopped as soon as the evolution of red fumes is at an end.

The quantity of red liquid obtained from the above stated proportions of materials is about 200 grains; but it varies somewhat with the care with which the process is conducted. The quantity of protoxide of chromium remaining in the retort is also various. With the above proportions it usually amounts to 27.3 grains, equivalent to 35.5 grains of chromic acid, or  $\frac{3}{11}$ ths of the whole chromic acid in the salt; but it varies with the quantity of common salt employed. If we introduce only a portion of the common salt at first, and add the rest at intervals, till the matter in the retort has assumed a green colour, the protoxide of chromium remaining in the retort is a maximum, and the quantity of red liquor obtained a minimum. When the atoms of chlorine in the common salt are to those of chromic acid in the bichromate as 3 to 2, the product of red liquor is greatest. We may vary the sulphuric acid considerably, but the process is easiest when the quantity of acid used is sufficient to convert the salt into a semifluid magma. Chromate of lead or chromate of potash may be substituted for bichromate of potash.

The red liquid possesses the following properties: its colour is a deep, but lovely crimson; so intense indeed as to render the liquid opaque, except in very thin films.

Its taste is sweetish, astringent, and acid.

It has a smell of chlorine fully as strong and as disagreeable as chlorine gas itself.

It reddens vegetable blues.

Its specific gravity at  $50^{\circ}$ , was 1.9134; but its extreme volatility makes it rather difficult to estimate the specific gravity with very great exactness.

When dropt into water it falls to the bottom, and exhibits the appearance of a drop of oil. Globules of chlorine gas issue from it rather copiously. This evolution continues till the red liquor *dissolves* in the water, forming a yellow-coloured mass, which contains muriatic acid, chromic acid, and a little green oxide of chromium.

151.5 grains of the red liquor were poured into about an ounce of water. The temperature rose at once to  $212^{\circ}$ , and chlorine gas was given off in such abundance as to occasion an effervescence.

When the red liquid is dropt upon oil of turpentine, much heat is evolved and the oil catches fire, and burns with a lively flame, but having more of the blue tint than is usual with the flame of that oil. After the combustion, we find green oxide of chromium mixed with vegetable matter from the oil of turpentine.

When dropt into alcohol, even of a specific gravity not lower than 0.840, it sets it on fire. The combustion goes on tranquilly, the flame is lively, and has a beautiful bluish white colour.

When the red liquid is poured on flowers of sulphur, a pretty violent action takes place. After a few seconds the sulphur catches fire, and burns with a fine red flame.

When we drop it into olive oil, a violent action takes place;

great heat is evolved, a kind of effervescence is produced, and a quantity of green oxide of chromium formed ; but the oil does not take fire.

The effects upon pyroxylic spirit are nearly the same as upon olive oil.

The red liquid has scarcely any action upon phosphorus. Even when the phosphorus is heated till it is brought into a state of fusion no action takes place. If the phosphorus be set on fire, the combustion is instantly extinguished by bringing the red liquid in contact with the burning body.

Neither does it produce any sensible effect upon charcoal powder, nor upon indigo.

When it is poured upon camphor no immediate action takes place ; but after two or three minutes the camphor begins to swell out, and it gradually occupies many times its former bulk. By this action the camphor loses its smell and consistence, and seems as if it had been partially charred, the colour being changed into a dark brown.

The red liquid effervesces rather strongly when dropped into naphtha. Much heat is evolved, and the naphtha loses its oily nature, but does not catch fire.

Zinc and tin filings effervesce with the red liquid, but the action is gentle and soon at an end. On iron filings it does not act till we apply heat, when the iron dissolves with effervescence ; but the volatility of the liquid prevents the process from going far. On copper and antimony it has no sensible action. When brought into contact with mercury, it forms with it a matter of the consistence of hog's lard. The mercury loses its fluidity, but retains its colour and metallic lustre.

When the protohydrate of acetic acid, in the liquid state, which it always has during the summer, is mixed with the red liquid, no immediate decomposition takes place; the mixture continues red and opaque, and as liquid as ever. The smell of the chlorine was much weakened, or overpowered by the acetic acid. No alteration in this mixture had taken place in a week; but in a fortnight the chloro-chromic acid was decomposed, and a quantity of reddish brown matter had precipitated.

A quantity of the red liquid was put into a receiver, and a current of ammoniacal gas was made to pass into the receiver from a small retort filled with a mixture of sal ammoniac and quick lime, to which the flame of a spirit lamp was applied. When the receiver was filled with ammoniacal gas, it was turned round so as to bring the red liquid in contact with it. A brilliant combustion took place, the red liquid assumed the form of a dark brown solid, and glowed for some time with an intense red heat. The residual matter being digested in water left a quantity of green-coloured muriate of chromium, or chloride of chromium, which would neither dissolve in water, nor nitric acid; but I ascertained the presence of muriatic acid by heating it with caustic potash. By this process much sal ammoniac is formed, and a quantity of muriate of chromium.

It is obvious from the preceding facts, that the property of supporting combustion, which this liquid possesses to so great a degree, is not owing solely to the chlorine which it contains, but likewise to the oxygen of the chromic acid; which, as we shall see afterwards, constitutes so considerable a portion of it. So that chromic acid is a supporter of combustion, as



well as nitric acid, and nearly to as great an extent. Indeed this might have been inferred from several facts already known. I may mention, as an example, the property which it has of effervescing with tartaric acid, and giving out abundance of carbonic acid.

Neither nitric acid, muriatic acid, iodine, oxygen, or chlorine, have any sensible action on the red liquid.

When the red liquid is exposed to heat it gives out chlorine, and is gradually converted into a brown mass, solid while cold, but readily melting when heated. This brown matter deliquesces when left exposed to the air. When strongly heated it swells out, and at last assumes the form of a light grey slaggy looking matter. This in a strong red heat assumes a green colour, and is insoluble in acids. It resembles green oxide of chromium. I did not try whether or not it contained muriatic acid.

After various trials, I employed the following method to determine the constituents of this red liquid.

A cylindrical glass vessel, containing a few ounces of distilled water, was accurately balanced, and a quantity of the red liquid poured into it. The weight of this quantity was found to be 90·1 grains. By a little agitation, a complete solution was soon obtained, and the water assumed nearly the colour of sherry. A solution of carbonate of soda was gradually added till the acids contained in the liquid were saturated. The colour of the liquid had become darker, and upon applying heat a precipitate fell. This precipitate, after being collected on the filter, washed, and dried, weighed 1·37 grain. By ignition it glowed, and the weight was reduced to 0·71 grain. It was green oxide of chromium.

The liquid thus deprived of green oxide, and perfectly neutral, was mixed with a solution of nitrate of barytes, as long as any precipitate continued to fall. By this process the liquid was deprived of its yellow colour, the chromic acid having fallen in the state of chromate of barytes. This method of separating chromic acid does not succeed unless care be taken to leave no excess of acid in the liquid; for chromate of barytes dissolves easily in even dilute acids. If this inadvertency has been committed, the best way is to pour caustic ammonia into the liquid till you have supersaturated the acid. This will throw down all the chromate of barytes, previously held in solution, without acting upon nitrate of barytes, should an excess of that salt have been introduced. The chromate of barytes thus obtained being washed, dried, and ignited, weighed 148·37 grains. Chromate of barytes is a compound of

1 atom chromic acid	-	-	6·5
1 atom barytes	-	-	9·75
			<hr/>
			16·25

148·37 grains of the salt therefore contain 59·34 grains of chromic acid.

The residual liquid thus freed from chromic acid was precipitated by nitrate of silver. The chloride of silver obtained, weighed, after being washed, dried, and fused, 164·42 grains, equivalent to 40·54 grains of chlorine.

Thus the constituents obtained from 90·1 gr. of the red liquid were

Green oxide of chromium	-	0.71
Chromic acid	- - -	59.34
Chlorine	- - -	40.54
		<hr/>
		100.59

The weight of the products is more than 10 per cent. greater than that of the red liquid subjected to analysis.\* But 59.34 is to 40.54 as 6.5 to 4.4. I was induced from this to consider the red liquid as a compound of 1 atom chlorine and 1 atom chromic acid; and the following experiment was made to verify this supposition.

15.32 grains of the red liquid were dropt into a quantity of distilled water, and 50.15 grains of crystallized carbonate of soda were dropt into the bottom of the vessel containing the liquid. The solution of this salt took place slowly, and the carbonic acid escaped gradually, and without carrying with it any perceptible quantity of chlorine, as is apt to happen when a solution of carbonate of soda in water is poured into the dilute red liquid. The liquid being heated and agitated, to expel the carbonic acid gas, a slight flocky precipitate fell, and the liquid was found quite neutral; for it neither altered the colour of litmus nor cudbear paper.

The reason why 50.15 grains of carbonate of soda were used was this: if the red liquid be a compound of

1 atom chromic acid	- - -	6.5
1 atom chlorine	- - -	4.5
		<hr/>

11

\* This augmentation of weight was occasioned by using a carbonate of soda, not quite free from common salt; and by adding the alkali slightly in excess. From these two causes there was an excess of chloride of silver, and the chromate of barytes was mixed with a little carbonate.

its atomic weight will be 11, and 11 grains of it will contain just the equivalent of 1 atom of chromic acid, and 1 atom of chlorine. The crystals of carbonate of soda being composed of

1 atom carbonic acid	-	-	2.75
1 atom soda	-	-	4
10 atoms water	-	-	11.25
			<hr/>
			18

It is clear, that in order to neutralize 11 grains of the red liquid, we must employ 36 grains of the carbonate; but  $11 : 36 :: 15.32 : 50.15 =$  quantity of carbonate of soda employed. As this quantity just neutralized the liquid, it is plain that the quantity of acid in the red liquid was rightly estimated.

If 11 grains of the red liquid contain 6.5 gr. chromic acid, 15.32 gr. must contain 9.052 of that acid, which will require for complete precipitation 22.98 grains of nitrate of barytes.

The liquid was freed from the trace of green oxide of chromium which it contained by filtration, and a solution of 22.98 grains of nitrate of barytes was mixed with it. After the chromate of barytes had subsided the liquor was colourless, and was not altered by sulphate of soda. Consequently it contained no sensible quantity of chromic acid, or of barytes. It is plain that the quantity of chromic acid in the red liquid had been rightly determined.

The liquid thus freed from chromic acid still retained its chlorine, which, if the constitution of the red liquid has been rightly determined, should amount to 6.268 grains, and would just require 29.94 grains of nitrate of silver to throw it down. This quantity was therefore dissolved in distilled water, and mixed with the liquid. After the chloride of

silver had subsided, the residual liquid was neither affected by common salt nor by nitrate of silver.

From this analysis it is clear, that the red liquid is a compound of 1 atom chromic acid, and 1 atom chlorine, and that its atomic weight is 11.

From an experiment formerly given, it is easy to deduce that 11 grains of the red liquid contain likewise 0.0866 grain of green oxide of chromium, doubtless, from the sweet taste of the liquid, held in solution by chlorine or muriatic acid. It would seem at first sight that this quantity, not taken into consideration in the analysis, vitiates the whole of the conclusions. But from the length of time taken up in weighing the liquid, I have no doubt that just as much moisture evaporated as this increase amounts to. The reader will observe, that the amount of green oxide is less than 1 per cent of the whole.

As this liquid possesses acid properties, I have given it the name of chloro-chromic acid. Water having the property of decomposing it, we have scarcely the means of trying whether it be capable of uniting with bases. The few trials which I made were not attended with success.

This body, so liquid and so volatile, is a compound of a solid and a gas. One cubic inch of chloro-chromic acid contains 259.22 inches of chlorine gas. Thus the gaseous particles are about  $6\frac{1}{2}$  times nearer each other than when they are in the gaseous state. This, together with the looseness of the combination, accounts for the abominable smell which distinguishes this liquid.

100 grains of the acid contain very nearly 41 grains, or  $31\frac{1}{4}$  cubic inches of chlorine.

When chloro-chromic acid is left exposed to the air, it gradually loses its smell and its red colour, and is converted into an opaque dark brown liquid, having an acid and astringent taste, without the least perceptible sweetness. When this liquid is saturated with carbonate of ammonia, a yellowish brown precipitate falls, which becomes blue when washed, and is merely protoxide of chromium. The filtered liquid is yellow-coloured, and consists of a mixture of chromate of ammonia and sal ammoniac.

In some cases, when the chloro-chromic acid had been left for some days exposed to the air, it was converted into a solution of muriate of chromium in water; but this change was not constant. I ascribed it at first to small pieces of cork which had accidentally fallen into the liquid which had undergone this alteration; but upon trying whether I could convert chloro-chromic acid at pleasure into muriate of chromium, by leaving it in contact with cork, the experiment did not succeed. I am disposed however to ascribe the alteration to the action of combustible matter, as spirits and oils cautiously added convert it into a green coloured matter which has a considerable resemblance to muriate of chromium.

When chloro-chromic acid is exposed to heat in an open vessel much chlorine flies off, and a black scaly matter remains, which speedily deliquesces in the air, and when heated melts and gives out the odour of chlorine gas. 31 grains of this scaly matter were left for a month in an open dish covered with paper in my laboratory, which is rather damp. It was converted into a brown opaque liquid, weighing 58.36 grains. It had therefore absorbed 27.36 grains of water. The liquid being diluted with water and filtered,

left 0·25 grain of a brown matter, which did not glow when heated to redness.

The filtered liquid was very dark-coloured, but not muddy. Its opacity was not destroyed by very large dilution with water. It reddened vegetable blues slightly, and had the sweet taste which characterizes muriate of chromium.

Being mixed with ammonia, abundance of green flocks fell, which weighed after ignition 10·22 grains.

The filtered liquid was mixed with nitrate of barytes as long as any precipitate fell. The chromate of barytes weighed after ignition 27·77 grains, equivalent to 11·108 grains of chromic acid.

The residual liquid being precipitated by nitrate of silver, the chloride of silver obtained weighed after fusion 23·6 grains, equivalent to 5·819 grains of chlorine.

Thus the constituents of the 31 grains analysed were

Brown insoluble matter	-	0·25
Protoxide of chromium	-	10·22
Chromic acid	- - -	11·108
Muriatic acid	- - -	5·980
Loss, considered as water	-	3·442
<hr/>		
31		

These numbers are not precisely in atomic proportion. There is a slight redundancy of muriatic acid or chlorine, amounting to very nearly half a grain. The constituents approach

1 atom muriate of chromium	{ acid 4·625 oxide 5·000 }	9·625
1 atom bichromate of chromium	{ acid 13 oxide 5 }	18
3 atoms water	- - - - -	3·375
		<hr/> 31·000

And the matter when allowed to absorb as much water as possible contains 27 atoms of that liquid.

It is not easy to form a conception of the way in which the reduction of the chromic acid to green oxide takes place. The heat employed was never sufficient to drive off the oxygen. Had the chlorine been converted into muriatic acid, the oxide of chromium should have been acidified, at least in part. Hence I am disposed to think that it is not muriatic acid which the black matter contains, but chlorine. A similar disorganisation takes place, if chromic acid itself be left for some time on the sand bath. Hence, I am disposed to ascribe the reduction to the tendency which chromic acid has to unite with protoxide of chromium. We may conceive that the elasticity communicated to the oxygen of the acid by the heat, together with the affinity of chromic acid for protoxide, may occasion the reduction of a portion of the acid, and cause the oxide formed to unite with the acids in the liquid.

### V. *Salts of chromium.*

The green oxide of chromium combines with the different acids and forms a genus of salts, not one of which, so far as I know, has been described by chemists. I shall therefore embrace the present opportunity to give a short account of them.



The greater number of them have a deep green colour ; though some of them are blue, and some of them purple. The intensity of the colour is such, that the aqueous solutions of most of them are opaque, even when dilute. They have a very strong and rather agreeable sweet taste, very often slightly acidulous, from the great difficulty of freeing them from all excess of acid. None of them can be crystallized ; but when evaporated to dryness, they assume the form of dark green, or nearly black powders.

When the infusion of nutgalls is dropt into a solution of muriate of chromium a *green* flocky precipitate falls.

Prussiate of potash occasions no precipitate, but when the mixture is heated it becomes dark brown and opaque, though no perceptible precipitate falls.

Sulphuretted hydrogen occasions no precipitate, provided the salt of chromium be free from all traces of chromic acid ; but hydrosulphuret of ammonia usually throws down green flocks, owing, I presume, to an excess of ammonia, which that hydrosulphuret frequently contains.

Both carbonate of ammonia and caustic ammonia throw down the green oxide from muriate of chromium. But carbonate of ammonia does not answer for precipitating oxalate of chromium or acid phosphate of chromium, probably because it forms compound salts with the acid and base. Caustic potash throws down the green oxide, but an excess of the alkali again dissolves the precipitate.

When benzoate of potash is dropt into a concentrated solution of muriate of chromium, a green flocky precipitate falls, but no precipitate falls when the solution is dilute.

We must attend to this circumstance, when we employ a benzoate to free a salt of chromium from iron.

### I. *Muriate of chromium.*

Muriatic acid dissolves the hydrated green oxide of chromium with great facility ; but neither this nor any other acid answers as a solvent of anhydrous green oxide. Exposure to a red heat almost entirely destroys the solubility of this oxide. The muriatic solution has a very deep green colour, and always retains a great excess of acid. When evaporated to dryness, and kept for some time on the sand bath, much of this excess is driven off. The salt assumes a red colour and a scaly appearance. It still retains an excess of acid and dissolves readily in water, forming a deep green liquid, having a sweet, and slightly acidulous taste. The scales rapidly absorb moisture from the atmosphere, and deliquesce into a green liquid. In this state the salt is composed of

$1\frac{1}{4}$ atom muriatic acid	-	-	5.781
1 atom green oxide	-	-	5.000
1 atom water	-	-	1.125
			<hr/>
			11.906

If we raise the heat sufficiently high to drive off all excess of acid, and to convert the salt into a chloride, we obtain it in the form of light, tasteless, green scales. In this state it is insoluble in water and acids. I did not analyse it, but conceive it to be a simple chloride composed of

1 atom chlorine	-	-	4.5
1 atom chromium	-	-	4
			<hr/>
			8.5

As long as muriate of chromium is soluble in water it contains an excess of acid, varying from one half to one fourth of an atom according to the heat in which it has been dried.

*2. Nitrate of chromium.*

Nitric acid dissolves the hydrated oxide of chromium readily enough, if we assist the acid by the application of heat. The solution has a reddish blue colour, and always retains an excess of acid, what quantity soever of hydrated oxide we employ in the preparation. The solution is opaque, and if sufficiently diluted to be transparent, has a deep brownish purple colour by transmitted light. When evaporated to dryness it leaves a deep reddish blue matter, readily soluble in water, but not by any means so deliquescent as the muriate. A quantity of hydrate equivalent to 27.5 grains of green oxide was dissolved in nitric acid, and the solution evaporated to dryness. The residual matter was redissolved in water, and again evaporated to dryness. This process was repeated thrice. The weight of the dry salt was now 69 grains; its taste was acidulous, and very sweet, and the salt still reddened vegetable blues. The green oxide being thrown down by ammonia, and the liquid remaining evaporated to dryness, I obtained 33.53 grains of nitrate of ammonia, equivalent to 22.63 grains of nitric acid. This would make the composition of the salt

Nitric acid	-	-	22.63 or $\frac{2}{3}$ atom.
Green oxide	-	-	27.50 or 1 atom.
Water	-	-	18.87 or 3 atoms.
			<hr/> 69.00

But no confidence can be put in this analysis ; for nitrate of ammonia is apt to be decomposed by too high a temperature ; and the salt had been left for 24 hours upon the sand bath.

When nitrate of chromium is exposed to heat in a platinum crucible, it melts, and copious fumes of nitrous gas are given off. When the heat is continued till these fumes cease to be disengaged, a great part of the green oxide is converted into chromic acid. The residue is soluble in water, and forms a dark brown acid liquid, consisting of chromic acid holding green oxide in solution. This affords an easy way of getting pure chromic acid ; for the small quantity of green oxide present will not interfere with the application of the chromic acid to most purposes for which chemists are likely to employ it. When we prepare chromic acid by VAUQUELIN's method, besides the expence of the process, it is by no means easy to free the acid from all traces of sulphuric acid.

### 3. *Sulphate of chromium.*

I mentioned before. that when hydrated green oxide of chromium is dried in the open air, without the application of artificial heat, it contains  $\frac{1}{5}$ ths of its weight of water. When dried on the sand bath, it retains about half its weight of water. The last of these is darker coloured than the first. It is much easier to dissolve the former of these hydrates in sulphuric acid than the latter. With the former we can obtain a neutral salt ; but I never was able to saturate sulphuric acid by digesting it over the latter hydrate.

Sulphate of chromium, while in solution, forms a dark green opaque liquid, having a sweet, and slightly acidulous taste. Like all the salts of chromium it reddens vegetable

blues. When evaporated to dryness, there remains a dark matter, having a green colour, so intense, that it appears black. It is tasteless, does not affect vegetable blues, and is easily reduced to a fine powder. It is not altered by exposure to the air, and seems at first to be insoluble in water; but when we pour water over it, and apply heat, the sulphate gradually dissolves in the liquid, and the solution has the same colour and the same sweet acidulous taste as at first.

To determine the composition of this salt, 345 grains of the hydrated oxide, dried in the open air (containing 55 grains of oxide), were digested in a flask with a quantity of sulphuric acid of commerce, containing just 55 grains of real acid. The solution was complete; and the liquid being evaporated to dryness, the dry tasteless residue weighed 151·4 grains. Now, as the acid and oxide together amounted to 110 grains, it is clear that the water in the salt must amount to 41·4 grains. Thus the constituents of sulphate of chromium are

Sulphuric acid	-	-	55	or 1 atom.
Green oxide of chrome			55	or 1 atom.
Water	-	-	41·4	or $3\frac{1}{3}$ atoms.
<hr/>				
				151·4

We may therefore without sensible error consider sulphate of chromium as composed of

1 atom sulphuric acid	-	-	5
1 atom green oxide	-	-	5
3 atoms water	-	-	3'375
			<hr/>
			13'375

Twenty grains of the dry salt being heated to incipient

redness lost 9.97 grains of their weight, and when kept for ten minutes in a wind furnace, in a heat approaching to whiteness, the weight was reduced to 8.58 grains. 20 grains (as is evident from the preceding analysis) of this salt contain 7.26 grains of green oxide. The salt, after exposure to an incipient red heat, retained nearly  $\frac{2}{5}$ ths of its acid; and almost  $\frac{1}{5}$ th of the acid was retained after the strong heat of a wind furnace. I was unable by heat to bring sulphate of chromium to the state of green oxide.

#### 4. *Carbonate of chromium.*

When muriate of chromium is precipitated by carbonate of soda, and the precipitate, after being welledulcorated, is collected on a filter, and dried in a heat not exceeding  $212^{\circ}$ , we obtain a light blue-coloured matter, which is very light, tasteless, and insoluble in water. In this state it is a dicarbonate of chromium composed of

1 atom carbonic acid	-	-	2.75
2 atoms green oxide of chrome			10
4 atoms water	-	-	4.5
			<hr/>
			17.25

I exposed 30.06 grains of this dicarbonate to a strong red heat. The loss of weight was 12.9 grains. The same quantity being dissolved in nitric acid effervesced, and lost 4.6 grains. This experiment requires some care, for the solution does not take place without the application of heat. Thus the constituents of the salt were found to be

Carbonic acid	-	4·6	or	2·75
Green oxide	-	17·16	or	10·25
Water	-	8·3	or	4·96
<hr/>				
30·06				

The slight excess of green oxide and water in this analysis was, I believe, occasioned by the great caution employed in dissolving the salt in nitric acid ; for I was so apprehensive of evaporating a portion of the nitric acid that I applied heat very cautiously, and stopt the process before the whole powder was dissolved. In another analysis of a portion of a similar dicarbonate, prepared in a different way, I obtained

Carbonic acid	-	-	2·75
Green oxide	-	-	9·33
Water	-	-	3·87

Here there is a deficiency of oxide and water ; but this might be owing to errors in the analysis.

Finding that carbonate of soda, when employed to precipitate muriate of chromium, gives only a dicarbonate, I thought it not unlikely that a neutral carbonate might be formed by employing a solution of bicarbonate of potash to precipitate muriate of chromium. The matter obtained by this process was light blue, and resembled the dicarbonate in its external qualities. It was dried without the application of any artificial heat. Its composition determined in the same manner as above described was found to be

1 atom carbonic acid	-	2·75
5 atoms protoxide	-	25
21 atoms water	-	23·625
<hr/>		
51·375		

The result of the analysis was

Carbonic acid	-	-	2.75
Green oxide	-	-	26.44
Water	-	-	23.69

In this analysis, as in the preceding, there is a slight excess both of oxide and water ; I ascribe this to the same cause. Such analyses can scarcely be made with very great accuracy.

Thus I obtained a penta-carbonate instead of a neutral carbonate, when I employed bicarbonate of potash as a precipitant ; a result quite unexpected, and not easily explained.

I tried to form a neutral carbonate by passing a current of carbonic acid through newly precipitated dicarbonate, still suspended in water ; but the process did not answer.

### 5. *Phosphate of chromium.*

Phosphate of soda precipitates exceedingly dilute solutions of muriate of chromium. The precipitate while in the liquid state has a dirty whitish green colour. But when phosphate of chromium is in the state of a dry powder, it has a very fine deep but lively green colour. It is quite tasteless, and insoluble in water. To determine the composition of this salt, 16 grains of anhydrous phosphate of soda (containing 7.46 grains of acid) were dissolved in water and mixed with an excess of muriate of chromium, previously rendered as neutral as possible by evaporation to dryness. The mixed liquids were placed on the sand bath, in a porcelain dish, and evaporated to dryness. Water was digested over the dry residue till it ceased to dissolve any more. The insoluble



matter weighed 18·75 grains. It was a fine chromium green powder, tasteless, and insoluble in water. When heated to redness it smoked, gave out the smell of muriatic acid, and became greenish black. The weight was reduced to 12·72 grains.

The water digested over this salt being examined by reagents, no phosphoric acid could be detected in it. Consequently the 12·72 grains of phosphate of chromium contained all the phosphoric acid employed in the experiment. It is clear that the phosphate formed was composed of

Phosphoric acid	- -	7·46 or 7·09 or 2 atoms.
Green oxide of chrome		5·26 or 5 or 1 atom.
		<hr/>
		12·72
Water	- - -	6·03 or 5·68 or 5 atoms.

The salt was a biphosphate, and obviously composed of

2 atoms phosphoric acid	-	7
1 atom green oxide	- -	5
5 atoms water	- - -	5·625
		<hr/>
		17·625

The slight excess of water was probably owing to the presence of a little muriatic acid in the salt before it was exposed to a red heat.

I did not succeed in my attempts to obtain a neutral phosphate of chromium. The biphosphate is soluble in phosphoric acid, and forms a deep green, sweet, and acidulous liquid; but the acid does not dissolve an atomic quantity; at least I did not succeed in obtaining such a solution. It is not unlikely that a quadro-phosphate of chromium exists.

6. *Arseniate of chromium.*

Arseniate of soda, when dropt into a solution of muriate of chromium, though very dilute, occasions a green flocky precipitate, at first dissolving in the liquid, but becoming permanent after the addition of a certain quantity of arseniate. This precipitate is an arseniate of chromium. When dry, it has a fine green colour, is tasteless, and insoluble in water.

I dissolved in muriatic acid a quantity of hydrated green oxide of chromium, containing 10 grains of oxide, evaporated the solution to dryness, and re-dissolved the salt in water. This solution was mixed with a solution of 41.5 grains of arseniate of soda (containing 15.5 grains of arsenic acid). This mixture was evaporated to dryness in a porcelain dish, and the saline residue digested in water till nothing more could be taken up. The water did not contain any trace of arsenic acid; but it still retained a green colour, and was found to contain 1.125 grain of green oxide of chromium. The arseniate formed was a compound of

Arsenic acid    -    15.5    -    -    8.73    -     $1\frac{1}{8}$  atom.

Green oxide    -    8.875 - or 5    -    1 atom.

An accident prevented me from weighing the arseniate. It was very nearly, though not quite neutral.

There exists also a binarseniate of chromium, which was obtained in the following manner. A quantity of liquid arsenic acid was digested over hydrated oxide of chromium till it refused to take up any more. A dark green liquid was obtained, which was evaporated to dryness. There remained a dark green matter, which being digested in water gave out arsenic acid, and a dark green insoluble salt remained, which was

binarsenate of chromium. It was tasteless, and insoluble in water. When heated to redness it became rose red, but on cooling the colour became a dingy buff. This salt was analyzed in the following way.

Six grains by ignition lost 1·45 grains, which were considered as water. 12 grains were dissolved in caustic potash, and the alkali being neutralized by muriatic acid, the green oxide of chromium was thrown down by carbonate of ammonia. The precipitate dried on the filter weighed 4·3 grains : but by ignition the weight was reduced to 2·18 grains. Hence the constituents were

Arsenic acid	-	-	6·92 or 15·8
Green oxide of chrome			2·18 or 5
Water	-	-	2·90 or 6·65
			<hr/>
			12·00

If we consider it as a compound of 2 atoms acid, 1 atom green oxide, and 6 atoms water, the constituents will be

2 atoms arsenic acid	-	-	15·5
1 atom green oxide	-	-	5
6 atoms water	-	-	6·75
			<hr/>
			27·25

numbers which approach very near the actual result of analysis.

#### 7. *Chromate of chromium.*

When chromic acid is digested on hydrated green oxide of chromium, a solution takes place, and the liquid assumes a dark brown colour. When we dissolve as much of the oxide as possible, and evaporate the solution to dryness, a brown

insoluble matter is obtained, quite similar in appearance to brown oxide of chromium.

When we mix together solutions of chromate of potash and muriate of chromium, the mixture acquires the same brown colour, and a brown precipitate falls, evidently composed of chromic acid and green oxide of chromium. But this precipitate being soluble in water could not beedulcorated, or freed from the foreign salts with which it was contaminated.

#### 8. *Acetate of chromium.*

When strong acetic acid is digested in a flask over hydrated oxide of chromium, several days elapse before any solution takes place, though the action be assisted by heat. By degrees, however, the acid acquires a green colour, which gradually deepens. I was unable by this process to saturate the acid completely. The smell of acetic acid still continued strong, and the liquid had an acid, though sweet taste. This solution was evaporated to dryness in a low temperature. The matter which remained had a fine dark green colour, but it was insoluble in water, though a solution was again obtained by digesting it in acetic acid.

Acetate of chromium then may be formed, but I was not able to obtain it in a state fit for analysis.

#### 9. *Oxalate of chromium.*

Oxalic acid when digested over hydrated green oxide of chromium, dissolves it with considerable facility. The solution has a deep violet colour, and an excessively sweet taste. When evaporated to dryness it deliquesces again; but if we

heat it so as to expel a considerable portion of the water of crystallization, we obtain a greenish-black matter quite tasteless, and similar to charcoal in its appearance. If this powder be digested in water it gradually dissolves, and the solution has the usual colour and taste of a solution of oxalate of chromium. It reddens vegetable blues.

A quantity of oxalic acid crystals, containing 45 grains of real acid, was dissolved in water and digested for several weeks over an excess of hydrated oxide. The quantity of oxide dissolved was exactly 45 grains, and the weight of the oxalate after evaporation to dryness was 120 grains. Hence, the constituents were,

Oxalic acid	-	-	45 or 5	-	or $1\frac{1}{10}$ atom.
Green oxide	-	-	45 or 5	-	or 1 atom.
Water	-	-	30 or 3.333	-	or 3 atoms.

---

120

This oxalate was very nearly though not quite neutral. We see here the difficulty in obtaining exact chemical compounds of bodies which are not capable of crystallizing. Probably, I might have rendered the salt neutral by means of a slight admixture of ammonia.

#### 10. *Tartrate of Chromium.*

Tartaric acid gradually dissolves hydrated oxide of chromium, and forms a dark blue-coloured liquid, having the usual sweet acidulous taste which characterises these salts. When the liquid is evaporated to dryness, a black, brittle, tasteless powder remains, which is tartrate of chromium.

To determine the composition of this salt, 148 grains of

hydrated oxide (containing 23.58 grains of green oxide), were digested in a flask with 40.2 grains of crystallized tartaric acid, previously dissolved in water. This quantity contains 35.55 grains of real tartaric acid. After several weeks digestion the liquid was filtered. There was separated a light-blue powder, weighing afteredulcoration and drying on the filter 24.52 grains. When heated it glowed, and its weight was reduced to 16.64 grains. Thus, 35.55 grains of tartaric acid had dissolved 16.64 grains of green oxide. The weight of the salt was 58.8 grains. Consequently, its constituents were,

Tartaric acid	-	-	35.55	or	10.68	or	$1\frac{1}{4}$	atom.
Green oxide	-	-	16.64	or	5	-	or	1 atom.
Water	-	-	6.61	or	1.99	or	2	atoms nearly.
			<hr/>					
			58.80					

This salt, like most of the others, contains an excess of acid. My attempts to obtain a neutral tartrate were not successful.

#### 11. *Potash-tartrate of Chromium.*

This salt was accidentally formed in one of my processes to reduce the chromic acid in bichromate of potash to green oxide by means of tartaric acid. The liquid had assumed a deep green colour; but I was surprized that no precipitate could be obtained when ammonia was poured into it; though in a process of the same kind, which I had performed the day before, the green oxide had been readily thrown down by that alkali. On investigating the cause of this anomaly, I found that it depended upon the quantity of tartaric acid employed. If just the proportion requisite for decomposing

the chromic acid be used, we can always throw down the green oxide of chromium by ammonia; but when such a quantity of tartaric acid had been employed that a notable portion of it remained undecomposed in the liquid, then no green oxide could be thrown down by ammonia, or by any other alkali. Knowing that the compound metalline tartrates are not precipitable by alkalies, I was naturally led to suspect that I had formed potash-tartrate of chromium. To verify this suspicion, I put bitartrate of potash and protoxide of chromium in the atomic proportions into a flask, with the requisite quantity of water, and digested the mixture for some days. By degrees the oxide entered into combination with the salt, and formed a deep-blue liquid, having a sweet acidulous taste. When evaporated to dryness, there remained a powder almost black and tasteless. It was still soluble in water, unless too much heat had been employed, and possessed exactly the characters of the substance obtained by digesting bichromate of potash with tartaric acid in such quantity as to form the compound not precipitable by ammonia.

This compound salt was subjected to analysis, and its constituents found to be,

2 atoms tartaric acid	-	-	16.5
1 atom potash	-	-	6
1 atom protoxide of chromium			5
2 atoms water	-	-	2.25
			<hr/>
			29.75

The three first constituents are given exactly as they came out in the analysis. The water actually procured was only

2 grains. But as 29.75 grains of the salt contain 27.5 grains of the anhydrous salts, it is plain that the 2.25 grains wanting to make up the total must be water.

## VI. *Chromates.*

In my "First Principles of Chemistry" I have given an account of twenty species of chromates, or combinations of chromic acid with a base. I shall take the present opportunity to give a short account of a few more of these salts which I have had occasion to examine, but without pretending to exhaust the subject.

### 1. *Perchromates of Iron.*

As the protoxide of iron has the property of reducing chromic acid to protoxide, it is evident that no protochromate can exist; but I thought it worth while to try whether I could not obtain a combination of chromic acid and peroxide of iron. 35 grains of iron were dissolved in dilute nitric acid, the solution was heated on the sand-bath and evaporated to dryness. The red-coloured residue, consisting chiefly of peroxide of iron, was redissolved by means of muriatic acid, and the muriatic solution was made as neutral as possible; first, by evaporation, and then by adding a few drops of ammonia.

125 grains of chromate of potash in crystals were dissolved in water.

These two solutions being mixed together, a dark reddish brown precipitate fell in large flocks. This precipitate was collected on the filter,edulcorated, and dried on the sand-bath. The brown matter thus collected weighed 30.45



grains; but when it had been exposed to a red heat the weight was reduced to 23.368 grains. It had a brown colour with a slight shade of red, was tasteless and insoluble in water, and was not in the least attracted by the magnet.

10 grains of this matter, as it had been dried on the filter, were dissolved in muriatic acid and precipitated by ammonia. The peroxide of iron thus collected beingedulcorated, dried and ignited, weighed 6.14 grains. The residual liquid was saturated with acetic acid and precipitated at a boiling temperature by acetate of lead. The chromate of lead obtained weighed after ignition 4.82 grains, equivalent to 1.53 grain of chromic acid. From a preceding experiment, it is plain that the 10 grains of matter analyzed contained 2.33 grains of water; so that the constituents were,

Chromic acid	-	-	1.53	or	6.5	or 1 atom.
Peroxide of iron	-		6.14	or	26.08	or 5 atoms.
Water	-	-	2.33	or	9.87	or 9 atoms nearly.
			<hr/>			
			10.00			

We see that the salt is a compound of 1 atom chromic acid and 5 atoms peroxide of iron. Or it is a pentachromate of iron.

1 atom chromic acid	-	-	6.5
5 atoms peroxide of iron	-		25
			<hr/>
			31.5

It would appear from this, that when per-muriate of iron and chromate of potash are mixed in equal atomic proportions, one-half of the peroxide of iron falls united to one-tenth of the chromic acid, forming a pentachromate of iron.

The liquid which passed through the filter had a dark

brown colour and was opaque. It was cautiously evaporated to dryness. An orange-coloured matter precipitated, which was sparinglyedulcorated, because it was not quite insoluble in water. Of this orange powder I dissolved 10 grains in muriatic acid and threw down the peroxide of iron by ammonia. This precipitate after ignition weighed 4.102 grains. It was strongly magnetic, and therefore the oxidum ferroso-ferricum of BERZELIUS = 4.243 grains of peroxide.

The residual liquid was neutralized by acetic acid and thrown down by acetate of lead. The chromate of lead obtained weighed after ignition 9.46 grains, equivalent to 3 grains chromic acid. Thus, the constituents of the orange powder are,

Chromic acid	-	-	3.000 or 6.5	or 1 atom
Peroxide of iron	-	-	4.243 or 9.193	or 2 atoms nearly.
Water	-	-	2.757 or 5.973	or 5 atoms
			<hr/>	
			10.000	

Thus, the orange matter was a *diperchromate* of iron.

I could not ascertain the weight of the diperchromate formed ; but if we suppose the whole peroxide of iron in the liquid to have been in the state of diperchromate, it is obvious that ( supposing it anhydrous ) it would amount to

2.5 atoms chromic acid	-	16.25
5 atoms peroxide of iron	-	25
		<hr/>
		41.25

Thus, only about  $\frac{1}{3}$  of the chromic acid had combined with the peroxide of iron, the remainder must have still continued in the state of chromate of potash.

2. *Dichromate of Lead.*

Chromate of lead constitutes one of the richest orange coloured pigments in existence ; but it is too well known to require any description. The dichromate of lead is easily formed by digesting chromate of lead in caustic potash. Half the chromic acid combines with the potash, the remainder continues united with the oxide of lead. Dichromate of lead has a rich scarlet-colour : like chromate of lead it is tasteless, and insoluble in water. When heated to redness it becomes brick-red, but recovers its original colour on cooling. When digested in nitric acid, one-half of the oxide of lead is dissolved and chromate of lead restored. The following experiment will show the constituents of this salt. 58.96 grains of anhydrous chromate of lead were digested in caustic potash. The undissolved scarlet powder beingedulcorated and ignited weighed 49.58 grains.

The potash solution was saturated with acetic acid and thrown down by acetate of lead. The chromate of lead obtained weighed after ignition 29.5 grains. But 29.5 is almost exactly the half of 58.96 grains, the original quantity of chromate of lead employed. It is plain, from this, that just one-half of the chromic acid in the salt had been removed. All the oxide of lead remaining, and the original salt having been neutral, it is clear that the red powder is a compound of

1 atom chromic acid	-	6.5
2 atoms protoxide of lead		28
		<hr/>
		34.5

3. *Bichromate of Silver.*

In the year 1820 I received a letter from Mr. DOWLER, who was at that time in the laboratory at Guy's Hospital, informing me that "if a few drops of dilute nitric or sulphuric acid be added to a solution of chromate or bichromate of potash, so as to disengage the chromic acid; or, indeed, if a little of either of these acids be added to a solution of chromic acid, and, subsequently, a dilute solution of nitrate of silver be added, a precipitate will form, consisting of very small transparent scales, composed, I believe, of chromic acid and silver." He then mentions that he had not analyzed this salt, and that the same salt may be formed by adding dilute muriatic acid to the pulverulent chromate of silver, but not in sufficient quantity to decompose the whole, and applying heat. He mentions also some other cases in which these crystalline scales appeared during his experiments.

I have hitherto abstained from noticing this salt, from a notion that Mr. DOWLER might perhaps have some intention of laying the analysis and properties of it before the public. But as six years have elapsed without any farther observations from Mr. DOWLER, I think it right to state here the result of my trials to determine its nature.

If we dissolve bichromate of potash in water, and acidulate the solution with nitric acid, nitrate of silver cautiously added will occasion no precipitate; but on setting the liquid aside for 24 hours, if it be sufficiently concentrated, a number of small crystals are deposited: they are sometimes feather-shaped, sometimes oblique, four-sided prisms, terminated by rhomboidal faces, placed obliquely. They are opaque, have

a splendid and metallic lustre, and a reddish-brown colour. They are tasteless, and insoluble in water. When digested in potash ley, chromic acid is separated, and oxide of silver remains. By this process I obtained from 2·95 grains of the crystals

Chromic acid        -        -    1·27 or 13    -    2 atoms.

Oxide of silver    -        -    1·68 or 17·19     $1\frac{1}{6}$  atom.

I consider the salt as a bichromate composed of

2 atoms chromic acid	-	13
1 atom oxide of silver	-	14·75
		<hr/>
		27·75

The small excess of silver in the analysis was probably owing to the digestion in the potash ley not having been continued long enough. The scale was rather too small to entitle me to expect very accurate results.

#### 4. *Potash-chromate of Soda.*

This compound salt is easily formed by adding carbonate of soda to a solution of bichromate of potash in the atomic proportions. The carbonate of soda dissolves with effervescence, and the solution has the yellow colour of neutral chromate of potash. When the liquid is evaporated, crystals of the compound salt are deposited. These crystals have a yellow colour, and are four sided oblique prisms, but so irregular, that it was very difficult to make out the shape. When heated, they decrepitated and became red; but recovered their colour on cooling. 23·57 grains by exposure to a red heat lost 0·57 grain of their weight. Hence the constituents of the salt are

1 atom chromate of potash	-	12.5
1 atom chromate of soda	-	10.5
$\frac{1}{2}$ atom of water	-	0.5625
		<hr/>
		23.5625

Though the water happens to amount almost exactly to half an atom, it is probable from the decrepitating property of the salt, that it is only mechanically lodged between the plates of the crystals.

This compound salt differs exceedingly from a mere combination of chromate of potash and chromate of soda. Chromate of potash is anhydrous, but chromate of soda contains 12 atoms of water. All this water is excluded when the compound salt is formed.

#### 5. *Potash-chromate of Magnesia.*

Bichromate of potash, when digested over carbonate of magnesia, dissolves it with effervescence, and gradually assumes the yellow colour of the neutral chromates. This happens when the excess of acid in the bichromate is saturated with magnesia; so that 19 grains of bichromate of potash just dissolve 2.5 grains of magnesia. When the liquid is concentrated, it deposits a crust of the compound salt at the bottom of the vessel. This crust consists of a congeries of small hard crystals, so closely interwoven that it is scarcely possible to make out the shape. Some of the facets appear to belong to octahedrons, while others are more like faces of a prism, seemingly four sided, and rectangular. The colour is a fine yellow, and the salt is not altered by exposure to the air. The taste is bitter and unpleasant. The salt is pretty soluble in

water. When heated, the colour becomes red, and it remains so, though with a stronger tint of yellow after the salt has become cold. In a strong red heat it fuses and effervesces, as if a gas were making its escape. The colour becomes brown, and the salt is no longer completely soluble in water.

To determine the composition of this salt, 190 grains of bichromate of potash were dissolved in water, and a quantity of magnesia alba, which contained 25 grains of magnesia, was digested in the liquid till the whole was dissolved. The colour of the solution was now a fine yellow, and no more magnesia would dissolve in it. The liquid being evaporated to dryness, the potash-chromate of magnesia obtained weighed 244·4 grains. Its constituents were obviously

Chromic acid	-	130	or 13	2 atoms.
Potash	- -	60	or 6	1 atom.
Magnesia	- -	25	or 2·5	1 atom.
Water	- -	29·4	or 2·94	2½ atoms.

In another experiment the quantity of water was only 2·12 grains. We may therefore consider the salt as composed of

2 atoms chromic acid	-	-	13
1 atom potash	-	-	6
1 atom magnesia	-	-	2·5
2 atoms water	-	-	2·25
			<hr/>
			23·75

This salt is a compound of 1 atom chromate of potash and 1 atom chromate of magnesia, containing the usual quantity of water of crystallization.

VII. *Chromiron Ore.*

In my "First Principles of Chemistry," vol. ii. p. 55, I express an opinion, that this mineral is a compound of 2 atoms brown oxide of chromium and 1 atom peroxide of iron. The facts stated in this Paper, showing that this opinion was ill founded, it became necessary to endeavour to determine the composition of the mineral by experiment.

The following table exhibits the result of all the analyses of this mineral that have come to my knowledge.

	* VAUQUELIN.	† LAUGIER.	‡ KLAPROTH.	§ SEYBERT.	¶ SEYBERT.	BERTHIER.	BERTHIER.	THOMSON.	THOMSON.
Green oxide of chrome	43	53	55.5	39.514	51.562	36	51.6	47.92	52.45
Peroxide of iron - -	34.7	34	33	36.004	35.140	37.2	37.2	34.08	24.33
Alumina - - - -	20.3	11	6	13.002	9.723	21.8	9.7	11.76	17.80
Silica - - - -	2.0	1	2	10.596	2.901	5	2.9	1.06	2.29
White matter - - -	.....	.....	.....	.....	.....	.....	.....	4.18	1.61
Moisture - - - -	.....	.....	.....	.....	.....	.....	.....	1	
	100	99	96.5	99.116	99.326	100	101.4	100	98.48

\* Jour. de Mines, x. p. 521. The specimen was sent from the departments of the Var. No description is given. Sp. gr. 4.0326.

† Philosophical Magazine, xxiv. 7. The specimen was from the Uralian mountains. Sp. gr. 4.0579.

‡ BEITRAGE, iv. 132. The specimen was from Styria. Sp. gr. 4.5.

§ SILLIMAN'S Jour. iv. 321. The specimen was from the Bare Hills, Baltimore. Sp. gr. 4.0639.

¶ Ibid. p. 323. The specimen was from Chester, Pennsylvania.

|| Ann. de Chim. et de Phys. XVII. 55. The first specimen from Isle de Vache, near St. Domingo; the second from the neighbourhood of Philadelphia. Obviously the same as SEYBERT's second specimen.



The first of the specimens in the table analysed by me was from the Bare Hills, Baltimore ; its sp. gr. was 3.949. Its constituents differed so much from those given by SEYBERT of a specimen from the same place, that I was induced to repeat the analysis four times. The results did not coincide with each other, but all gave nearly the same ratio between the green oxide of chromium and the peroxide of iron.

The second of the specimens analysed by me was from the Shetland Isles. Its specific gravity was 4.164 when purified by floating off the lightest portions, after reducing the mineral to powder.

My method of analysis was this : the mineral was reduced to a fine powder, and heated in a silver crucible with a mixture of caustic potash and nitre, amounting to thrice the weight of the powder. I usually operated on 25 grains of the mineral. After keeping the mixture in a state of fusion for half an hour, it was raised to a red heat, and kept in that temperature for about ten minutes ; it was then allowed to cool, and lixiviated in water. A fine yellow alkaline liquid was obtained. The undissolved portion being digested in muriatic acid, the whole dissolved except about  $\frac{1}{4}$  grain of brown matter, obviously consisting of ore that had escaped decomposition. It was deducted from the portion of ore subjected to analysis.

The alkaline solution was supersaturated with acetic acid, and then mixed with carbonate of ammonia in slight excess. The alumina was thrown down. After washing and ignition it was dissolved in muriatic acid to separate a little silica with which it was mixed.

The muriatic solution was concentrated, and then diluted

with water. It became milky, and deposited a small quantity of white matter, which possessed the following properties:

Its colour was white, it was tasteless, and insoluble in water: it dissolved in muriatic acid, and was again precipitated by dilution. When digested in caustic potash it became black. This black matter again dissolved slowly in muriatic acid, and was precipitated white by potash. I had never more of it at once than half a grain. It seems to be a metalline salt. The characters agree best with a salt of base of manganese. The acid is neither the chromic, phosphoric, nor arsenic. This matter existed in all the specimens of chrome iron ore that I examined. The muriatic solution thus freed from the white matter was precipitated by caustic ammonia. The peroxide of iron after washing and ignition was dissolved in muriatic acid, to separate a little silica with which it was mixed.

Finally, the chromic acid solution was mixed with an excess of acetic acid, and the chromic acid thrown down by acetate of lead.

A glance at the preceding table, shows clearly that no deduction can be drawn from the analyses which it exhibits, because the ore was never pure. There is reason to believe that, in most cases, it is mixed with more or less of octahedral iron ore, besides the earthy matter with which it is obviously contaminated. I therefore reduced a quantity of the Baltimore ore to a coarse powder, and picked out a number of the small octahedrons, which constituted the pure chromium ore. They had more or less of the form of octahedrons, a brown colour with a splendent and almost metallic lustre. The specific gravity was 4.321. All the particles the least

acted on by the magnet were scrupulously withdrawn. 25 grains of this pure ore being subjected to analysis, I obtained the following constituents :

Green oxide of chrome	-	52.95	or	10
Peroxide of iron	-	29.24	or	5.52
Alumina	-	12.22	or	2.30
White matter	-	3.09		
Water	-	0.70		
<hr/>				
		98.2		

A trace of silica.

If we exclude the unknown salt, which I have called white matter, we see that the ore is a compound of

2 atoms green oxide of chrome	10
1 atom peroxide of iron	5
1 atom alumina	2.25

The very slight excess of iron and alumina, together with the trace of silica, were probably derived from some small green particles (obviously the gangue of the ore), which I could detect with a glass in the portion of the picked ore that had not been pounded. It is more than likely that one or two of them had got mixed with the pounded ore.

From the analysis of the Shetland ore, in the table, it seems to follow, that it contains no admixture of octahedral iron ore ; for in it alone the green oxide of chromium, and the per oxide of iron, bear to each other the ratio of 2 to 1. All the other specimens subjected to analysis have been contaminated with iron ore.

## APPENDIX.

Since the preceding paper was drawn up, I have found that when green oxide of chromium is precipitated by a fixed alkaline carbonate, we cannot free it from the fixed alkali by washing. This probably occasioned the want of success which attended some of the experiments related in the second section of the paper.