IV. *On Oxalic Acid. By* Thomas Thomson, *M. D. F. R. S. Ed. Communicated by* Charles Hatchett, *Esq. F. R. S.*

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OXALIC acid, from the united testimony of EHRHART, HERMBSTADT, and WESTRUMB, appears to have been discovered by SCHEELE ; but it is to BERGMAN that we are indebted for the first account of its properties. He published his dissertation on it in 1776, and since that time very little has been added to the facts contained in his valuable treatise. Chemists have chiefly directed their attention to the formation of that acid, and much curious and important information has resulted from the experiments of HERMBSTADT, WESTRUMB, BERTHOLLET, FOURCROY, and VAUQUELIN, &c. but the properties of the acid itself, have been rather neglected. My object in the following pages is not to give a complete history of the properties of oxalic acid, but merely to state the result of a set of experiments, undertaken with the view of ascertaining different particulars respecting it, which I conceived to be of importance.

I. *Water of Crystallization.*

Oxalic acid is usually obtained in transparent prismatic crystals more or less regular; these crystals contain a portion of water, for when moderately heated they effloresce

and lose a part of their weight, which they afterwards recover
when left exposed in a moist place. When cautiously heated
on a sand bath they fall to powder, and lose about a third of
their weight. But as the acid is itself volatile, it is not probable
that the whole of this loss is water. To ascertain the quantity
of water contained in these crystals I had recourse to the fol-
lowing method.

1. Seventy grains of crystallized oxalic acid were dissolved
in 600 grains of water, constituting a solution which weighed
670 grains.

Fifty grains of pure carbonate of lime, in the state of cal-
careous spar, were dissolved in muriatic acid ; this solution
was evaporated to dryness to get rid of the excess of acid, and
the residue redissolved in water.

Into this muriate of lime the solution of oxalic acid was
dropt by little and little as long as any precipitate fell, and the
oxalate of lime thus formed was separated by the filter. Pure
oxalic acid is not capable of precipitating the whole lime from
solution of muriate of lime, the muriatic acid evolved being
always sufficient to retain the last portions in solution.

It was necessary to get rid of this excess of acid ; the method
which appeared the least exceptionable was to saturate the
muriatic acid with ammonia ; accordingly when the oxalic acid
ceased to occasion any farther precipitate, I cautiously added
pure ammonia, till the liquid ceased to produce any effect
upon vegetable blues. A copious additional precipitate of ox-
alate of lime was thus obtained. Oxalic acid was now added
again as long as it rendered the liquid muddy. By thus alter-
nately having recourse to the acid solution, and to ammonia,
and by adding both with great caution to avoid any excess, I

succeeded in separating the whole of the lime without using any sensible excess of oxalic acid.

558 grains of the acid solution were employed, a quantity which is equivalent to 58.3 grains of the crystallized acid.

2. The oxalate of lime, after being well washed and drained, and exposed for a week to the open air, at a temperature of about 60°, weighed 76 grains; but upon being left on the sand bath for some hours in a temperature between 200° and 300°, its weight was reduced to 72 grains.

3. These 72 grains of dry oxalate of lime were put into an open platinum crucible, and gradually heated to redness. By these means they were reduced to 49.5 grains, which proved to be carbonate of lime. The crucible was now exposed to a violent heat in a forge. Nothing remained but a quantity of pure lime weighing 27 grains.

4. From this experiment we learn, that 72 grains of dry oxalate of lime contain 27 grains of lime. Of consequence, the oxalic acid in this compound must be 45 grains. But the weight of crystallized oxalic acid actually used was 58.3 grains, a quantity which exceeds the whole acid in the oxalate by 13.3 grains. These 13.3 grains are the amount of the water of crystallization, which either did not unite with the salt, or was driven off by the subsequent exposure to heat. Hence crystallized oxalic acid is composed of

Real acid   -   -   45.
Water   -   -   13.3
                               ———
                               58.3

Now this is equivalent to

<div style="text-align:center">

Real acid   -   -   77

Water   -   -   23

___

100

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So that the crystals of oxalic acid contain very nearly the fourth part of their weight of water.*

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II. *Alkaline and Earthy Oxalates.*

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1. The preceding experiment gives us likewise the composition of oxalate of lime. This salt, when merely dried in the open air, still retains a portion of water which may be driven off by artificial heat. It is necessary to know that it parts with this water with considerable difficulty, so that a long exposure on the sand or steam bath, is necessary to get it thoroughly dry. It afterwards imbibes a little water if it be left in a moist place. Well dried oxalate we have seen is a compound of

<div style="text-align:center">

Acid   45 or per cent, 62.5 acid.

Base   27   -   -   37.5 base.

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72   100

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* Vauquelin in a late dissertation on cinchona, marked with that profound skill which characterizes all the productions of this illustrious chemist, has mentioned incidentally, that the crystals of oxalic acid contain about half their weight of water. He dissolved 100 parts of cinchonate of lime in water, and precipitated by means of oxalic acid; 22 parts of crystallized oxalic acid were necessary; and the oxalate of lime formed weighed 27 grains. From this experiment he draws the conclusion which I have stated, (See Ann de Chem. lix. 164.) But this ingenious chemist does not seem to have been aware of the real composition of oxalate of lime. 27 grains of that salt are composed very nearly of 10 grains of lime and 17 grains of acid. But the weight of the crystals used by Vauquelin was 22; the difference, 5, is obviously the water of crystallization in 22 grains of the crystals. But if 22 grains contain 5 of water, it is obvious, that 100 contain very nearly 23. So that his experiment in reality coincides with mine.

Though the oxalate of lime dried spontaneously can scarcely be considered as always in the same state, yet as the difference in the portion of water which it retains is not great, provided it be dried slowly in the temperature of 60°, and in a dry place, it may be worth while to state its composition. It is as follows :

Acid	45	or per cent	59.2	acid.
Base	27		35.5	base.
Water	4		5.3	water.
	76		100.0	

When rapidly dried, as by pressing it between the folds of filtering paper, it is apt to concrete into hard lumps, which retain more moisture. In this state I have sometimes seen it retain 10 per cent. of water after it appeared dry.

BERGMANN states the composition of oxalate of lime as follows :

Acid	-		48
Lime	-	-	46
Water	-	-	6
			100*

His method was to dissolve a determinate quantity of calcareous spar in nitric acid, and then to precipitate the lime by oxalic acid. 100 parts of calcareous spar thus dissolved, require, according to him, 82 parts of crystallized acid to precipitate them. But there must have been some mistake in this experiment; for, according to my trials (provided the nitric acid be carefully neutralized by ammonia as it is evolved), no

* Opusc. I. 262.

less than 117 grains of oxalic acid would have been required, and at least 145 grains of oxalate of lime would have been obtained instead of the 119, which was the result of Bergmann's experiment. It is obvious that Bergmann did not precipitate all the lime. He added oxalic acid till it ceased to produce any effect on the solution from the great excess of nitric acid evolved ; and then took it for granted that all the lime was separated. But had he added ammonia, he would have got an additional quantity of oxalate of lime, and the precipitation would have recommenced upon adding more oxalic acid. This explanation accounts in a satisfactory manner for the difference between Bergmann's statement of the composition of oxalate of lime, and mine.

2. Though the preceding experiment was made with care, yet as some of the most important of the following observations in some measure rest upon the analysis of oxalate of lime, I thought it worth while to verify that analysis in the following manner.

100 grains of crystallized oxalic acid were dissolved in 1000 grains of water, making a solution which weighed 1100 grains.

It is obvious that every 100 grains of the above solution contained 9.09 grains of crystal of oxalic acid, equivalent, according to the preceeding analysis, to 7 grains of real acid.

100 grains of this solution were gradually mixed with lime water till the liquid ceased to produce any change on vegetable blues. The oxalate of lime thus formed being well dried, weighed 11.2 grains. Exposed to a violent heat in a platinum crucible, this salt left 4.2 grains of pure lime. Hence it was composed of

7 acid, or per cent. 62.5 acid
4.2 lime   37.5 base
———   ———
11.2   100.0

Thus we have obtained exactly the same result as in the former experiment, both as far as relates to the composition of oxalate of lime, and likewise to the proportion of water of crystallization in crystallized oxalic acid.

The lime water necessary to saturate the acid amounted to 3186 grains. Hence, it contained only $\frac{1}{758}$th of its weight of lime.

3. The oxalates of barytes and strontian are white, tasteless powders, which may be obtained by mixing oxalate of ammonia with the muriates of these alkaline earths. It is said that these earths are capable of forming soluble superoxalates with this acid; but I have not tried the experiment. These oxalates, as well as oxalate of lime, are partially soluble in the strong acids.

4. Oxalate of magnesia is a soft white powder, bearing a considerable resemblance to oxalate of lime. It is tasteless, and not sensibly soluble in water; yet when oxalate of ammonia is mixed with sulphate of magnesia, no precipitate falls; but if the solution be heated and concentrated sufficiently, or if it be evaporated to dryness, and redissolved in water, in both cases the oxalate of magnesia separates in the state of an insoluble powder.

5. Oxalate of potash readily crystallizes in flat rhomboids, commonly terminated by dihedral summits. The lateral edges of the prism are usually bevelled. The taste of this salt is cooling and bitter. At the temperature of 60° it dissolves in thrice its weight of water. When dried on the sand bath, and afterwards

exposed in a damp place, it absorbs a little moisture from the atmosphere.

This salt combines with an excess of acid, and forms a superoxalate, long known by the name of *salt of sorrel.* It is very sparingly soluble in water, though more so than tartar. It occurs in commerce in beautiful 4-sided prisms attached to each other. The acid contained in this salt is very nearly double of what is contained in oxalate of potash. Suppose 100 parts of potash ; if the weight of acid necessary to convert this quantity into oxalate be x then $2\,x$, will convert it into superoxalate.

6. Oxalate of soda readily crystallizes. Its taste is nearly the same as that of oxalate of potash. When heated, it falls to powder, and loses the whole of its water of crystallization. Soda is said to be capable of combining with an excess of acid, and of forming a superoxalate. I have not tried the experiment.

7. Oxalate of ammonia is the most important of all the oxalates, being very much employed by chemists to detect the presence of lime, and to separate it from solutions. It crystallizes in long transparent prisms, rhomboidal, and terminated, by dihedral summits. The lateral edges are often truncated, so as to make the prism 6 or 8-sided. Sometimes the original faces of the prism are nearly effaced.

The taste of this salt is bitter and unpleasant, somewhat like that of sal ammoniac. At the temperature of 60°, 1000 grains of water dissolve only 45 grains of this salt. Hence, 1000 grains of saturated solution of oxalate of ammonia contain only 43.2 grains of this salt. The specific gravity of this solution is 1.0186. As it may be useful to know the weight

of this salt contained in solutions of different specific gravities, I have thought it worth while to construct the following table :

Weight of oxalate of ammonia in 100 parts of the solution.	Specific gravity of the solution at 60°.	Weight of oxalate of ammonia in 100 parts of the solution.	Specific gravity of the solution at 60°.
4.32	1.0186	1.5	1.0075
4.	1.0179	1.	1.0054
3.5	1.0160	0.5	1.0030
3.	1.0142	0.4	1.0024
2.5	1.0120	0.3	1.0018
2.	0.0095	0.2	1.0012
		0.1	1.0006

8. To determine the composition of these salts, I took seven different portions of a diluted oxalic acid solution, each weighing 100 grains, and containing 7 grains of real oxalic acid. To each of these portions I added respectively potash, soda, ammonia, barytes water, strontian water, and lime water, till it ceased to produce any change. The liquid was then evaporated to dryness, and the residue, after being well dried on the steam bath, was weighed. Each of these salts contained 7 grains of acid ; the additional weight I ascribed to the base. Hence I had the following table, which exhibits the weight of each salt obtained, and its composition deduced from that weight.

Salts.	Weight obtained.	Composition.	
		Acid.	Base.
Oxalate of Ammonia	9.4	7	2.4
———— Magnesia*	9.5	7	2.5
———— Soda -	11.0	7	4.0
———— Lime -	11.2	7	4.2
———— Potash -	15.6	7	8.6
———— Strontian	17.6	7	10.6
———— Barytes -	17.0	7	10.0

The composition of these salts reduced to 100 parts, is given in the following table.

	Oxalate of Ammonia.	Ox. of Magnesia.	Ox. of Soda.	Ox. of Lime.	Ox. of Potash.	Ox. of Strontian.	Ox. of Barytes.
Acid	74.45	73.68	63.63	62.50	44.87	39.77	41.16
Base	25.53	26.32	36.37	37.50	55.13	60.23	58.84
Total	100.	100.	100.	100	100	100	100

* The oxalate of magnesia was obtained by neutralizing the oxalic acid solution with ammonia, then mixing it with sulphate of magnesia, evaporating the solution to dryness, and washing the insoluble oxalate of magnesia with a sufficient quantity of water.

But for practical purposes, it is more convenient to consider the acid as a constant quantity. The following table is constructed upon that plan.

	Acid.	Base.	Weight of Salt.
Oxalate of Ammonia	100	34.12	134.12
———— Magnesia	100	35.71	135.71
———— Soda -	100	57.14	157.14
———— Lime - -	100	60.00	160.00
———— Potash -	100	122.86	222.86
———— Strontian	100	151.51	251.51
———— Barytes -	100	142.86	242.86

9. In the preceding statement, no account has been taken of the water of crystallization which might still remain attached to the salts, notwithstanding the heat to which they were exposed. There is reason to believe, however, that in most of them this water must be so small, that it may be overlooked without any great error. Oxalates of soda and of ammonia, I have reason to believe, lose all their water of crystallization at a moderate heat. This is the case also with oxalates of lime and barytes, and I presume that the oxalates of strontian and magnesia are not exceptions; but oxalate of potash retains its water much more obstinately. I believe that in that salt the weight of acid and of base are nearly equal, and that when dried in the temperature of 212°, it still retains nearly 10 per cent. of water; but I have not been able to establish this opinion by direct experiment.

The composition of oxalate of strontian in the preceding table, was so different from what I expected, that I repeated

the experiment; but the result was the same. This induced
me to combine strontian and oxalic acid in the following
manner: 100 grains of a solution containing 7 grains of real
oxalic acid were neutralized by ammonia, and the oxalic acid
precipitated by means of muriate of strontian. The salt ob-
tained weighed 12.3 grains; of course it was composed of

Acid	7	or	56.9	or	100
Base	5.3		43.1		75.7
	12.3		100.0		175.7

Thus it appears that there are two oxalates of strontian, the
first obtained by saturating oxalic acid with strontian water,
the second by mixing together oxalate of ammonia and mu-
riate of strontian. It is remarkable that the first contains just
double the proportion of base contained in the second.

III. *Decomposition of the Oxalates.*

1. When oxalic acid, in the state of crystals, is exposed to
heat, it is only partially acted upon, a considerable portion
escaping without alteration; but when an alkaline or earthy
oxalate is heated, the acid remains fixed till it undergoes com-
plete decomposition. The new substances into which the acid
is converted, as far as my experience goes, are always the
same, what oxalate soever we employ. They are five in
number; namely, *water, carbonic acid, carbonic oxide, carbureted
hydrogen,* and *charcoal.*

2. The water is never quite pure. Though no sensible
portion of oil can be perceived in it, yet it has always the
peculiar smell of the water obtained during the distillation of
wood; a smell which is usually ascribed to oil. It commonly

shews traces of the presence of ammonia, changing vegetable blues to green, and smoking when brought near muriatic acid; but this minute portion of ammonia is probably only accidentally present. All the oxalates which I decomposed by distillation, were obtained by double decomposition from oxalate of ammonia; and though they were washed with sufficient care, yet I think it not unlikely that a minute portion of oxalate of ammonia might continue to adhere. Practical chemists know the extreme difficulty of removing every trace of a salt with which another has been mixed.

The carbonic acid remains partly combined with the base, which always becomes a carbonate, and partly makes its escape in the form of gas.

The carbonic oxide and carbureted hydrogen make their escape in the form of gas: the charcoal remains in the retort mixed with the base, to which it communicates a grey colour: the quantity of it depends in some measure upon the heat. If the oxalate was exposed to a very violent heat, no charcoal at all remains. Hence it probably acts upon the carbonic acid united to the base, converting it into carbonic oxide, as happens when a mixture of a carbonate and charcoal are heated.

3. I was induced to examine this decomposition with considerable attention, because I conceived that it would furnish the means of estimating the composition of oxalic acid; and I pitched upon oxalate of lime, as the salt best adapted for the purpose I had in view. A determinate quantity of this salt was put into a small retort, and gradually heated to redness. This retort was connected with a pneumatic trough by means of a long glass tube, having a valve at its extremity which allowed gas to issue out, but prevented any water from

entering the tube. The experiment was repeated three times.

4. A hundred grains of oxalate of lime, when thus heated, yield above sixty cubic inches of a gas, which is always a mixture of carbonic acid and inflammable air, nearly in the proportion of one part of the former to three and a half of the latter, reckoning by bulk. The specific gravity of the inflammable gas was 0.908, common air being 1.000; it burns with a blue flame, and when mixed with oxygen, may be kindled by the electric spark. The loudness of the report depends upon the proportion of oxygen.

The smallest quantity of oxygen, with which it can be mixed, so as to burn by the electric spark, is 1-9th; the combustion is very feeble, and is attended with no perceptible report. If the residue be washed in lime water and mixed with 1-9th of its bulk of oxygen, it may be kindled a second time: this may be repeated five times, after which the residue cannot be made to burn.

The combustion becomes more violent, and the report louder, as we increase the proportion of oxygen, and both are greatest when the oxygen is double the bulk of the gas. As we increase the dose of oxygen, the combustion becomes more and more feeble; and five parts of oxygen and one of gas is the limit of combustion on this side: for a mixture of six parts of oxygen and one of the inflammable air will not burn.

In these experiments the results differ materially from each other, when the proportion of oxygen used is small and when it is great. I am not able at present to account for this difference, which holds not only with respect to this gas, but

every compound inflammable gas which I have examined. This difference makes it impossible to use both extremes of the series: I make choice of that in which the proportion of oxygen is considerable, as upon the whole more satisfactory. The best proportion is one part of the gas and two parts of oxygen. The oxygen ought not to be pure, but diluted with at least the third of its bulk of azote, unless the gas be much contaminated with common air.

I have elsewhere detailed the method which I follow in analyzing gases of this nature.* The following table exhibits the mean of a considerable number of trials of this gas with oxygen.

Measures of inflammable Air consumed.	Measures of Oxygen con-sumed.	Carbonic Acid formed.	Diminution of Bulk.
100	91	93	98

that is to say, 100 cubic inches of the gas when burnt, com-bine with 91 cubic inches of oxygen; there are produced 93 inches of carbonic acid; and after the combustion these 93 inches alone remain, the rest being condensed. Hence we conclude that the other substance produced was water.

This result corresponds almost exactly with what would have been obtained, if we had made the same experiment upon a mixture of 70 measures of carbonic oxide, and 30 measures of carbureted hydrogen, as will appear from the following table.

* See NICHOLSON's Journal, 16. 247,

	Measures of inflammable Gas consumed.	Measures of Oxygen consumed.	Measures of carbonic Acid formed.	Diminution of Bulk.
Carbonic oxide	70	31.5	63	38.5
Carbureted hydrogen	30	60.0	30	60.0
Total	100	91.5	93	98.5

This coincidence is so exact, that I do not hesitate to conclude that the inflammable gas, which was the subject of experiment, was in reality a mixture of 70 parts of carbonic oxide, and 30 of carbureted hydrogen. The specific gravity indeed, which was 0.908, does not exactly agree with the specific gravity of such a mixture; for 2⅓ measures of carbonic oxide, and one measure of carbureted hydrogen, ought to form a mixture of the specific gravity 0.849, provided the specific gravity of carbonic oxide be 0.956, and that of carbureted hydrogen 0.600; but this objection cannot be admitted to be of much weight, till the specific gravity of pure carbureted hydrogen be ascertained with more accuracy than has hitherto been done.

The results contained in the preceding table, enable us to determine the composition of this inflammable air with considerable precision; for 100 cubic inches of it require 91 inches of oxygen, and form 93 cubic inches of carbonic acid. But it is known that carbonic acid gas requires for its formation a quantity of oxygen gas equal to its own bulk: therefore to form 93 inches of it, 93 inches of oxygen gas must have been employed; but only 91 were mixed with the gas: therefore the

gas itself must have furnished a quantity of oxygen, equivalent to the bulk of two cubic inches, besides all the carbon contained in 93 inches of carbonic acid.

This carbon amounts in weight to   12.09 grains.

Two cubic inches of oxygen weigh   .68
_____

Total   12.77

But as 100 cubic inches of the gas weigh 28.15 grains, it is obvious that besides the 12.77 grains which it furnished to the carbonic acid, it must have contained 15.38 grains of additional matter; but as the only two products were carbonic acid and water, it is plain that the whole of this additional matter must, by the explosion, have been converted into water. Its constituents of course must have been

13.19 oxygen

2.19 hydrogen
_____

15.38

Adding this to the 12.77 grains formerly obtained, we get the composition of the gas as follows:

Oxygen   13.87

Carbon   12.09

Hydrogen   2.19
_____

28.15

which reduced to 100 parts, becomes

Oxygen   49.27

Carbon   42.95

Hydrogen   7.78
_____

100.00

5. The residue which remained in the retort, after the distillation was over, was a grey powder, not unlike pounded clay slate. To ascertain its constituents, it was dissolved in diluted nitric acid with the necessary precautions; the loss of weight indicated the quantity of carbonic acid. The charcoal remaining undissolved, was allowed to subside, carefully washed by repeated affusions of water, and then dried in a glass or porcelain capsule. It must not be separated by the filter, for it adheres so obstinately that it cannot be taken off the paper, nor weighed. The nitric acid solution was precipitated by carbonate of soda, and the carbonate of lime obtained was violently heated in a platinum crucible. What remained was pure lime.

6. I shall now detail one of my experiments more particularly. Eighty-nine grains of well dried oxalate of lime were exposed in a small retort to a heat gradually raised to redness; the products were the following :

			Grains.
45.6 cubic inches of gas* weighing			14.8
Water	-	-	6.4
Residue in retort	-	-	62.4
			83.6
Loss	-	-	5.4
		Total	89.0

The loss is obviously owing to the gas which filled the retort and tube when the experiment was concluded. We are

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* The gas obtained measured 60 cubic inches, but 14.4 inches of these were found to be common air which had previously filled the retort and tube ; this quantity was therefore deducted.

warranted therefore to add it to the weight of the gaseous pro-
ducts obtained.

Now the gas was composed of

Carbonic acid   10.5 cubic inches = 4.9 grains.

Inflammable air 35.1   -   -   = 9.9

so that one-third of the weight was carbonic acid, and two-
thirds inflammable air. If we divide the 5.4 grains of loss,
in that proportion we obtain 1.8 grains carbonic acid, and 3.6
grains of inflammable air. Adding these quantities to the
weight obtained, we get for the weight of the whole gaseous
product

Grains.

Carbonic acid   6.7

Inflammable air 13.5

‾‾‾‾

20.2

The 62.4 grains of residue in the retort were composed of

Grains.

Lime   -   -   33.4

Carbonic acid   26.4

Charcoal   -   2.6

‾‾‾‾

62.4

Now it is clear, that the 89 grains of oxalate of lime were
composed of

Lime   -   33.4

Acid   -   -   55.6

‾‾‾‾

89.0

The acid was completely decomposed and resolved into the
following products :

Carbonic acid   33.1
Inflammable air 13.5
Water   -   6.4
Charcoal - - 2.6
                          ————
                          55.6

Had the experiment been made upon 100 grains of oxalic acid instead of 55.6, it is clear that the proportions would have been as follows.

Carbonic acid   59.53
Inflammable air 24.28
Water   -   11.51
Charcoal   -   4.68
                          ————
                          100.00

The most remarkable circumstance attending the decomposition of oxalic acid by heat, is the great proportion of carbonic acid formed; the quantity amounts to 6-10ths of the whole weight of acid decomposed.

As the composition of all these products of oxalic acid is known with considerable accuracy, it is obvious that they furnish us with the means of ascertaining the constituents of that acid itself.

59.53 grains of carbonic acid are composed of

Grains.

Oxygen   42.86
Carbon   16.67
                ————
                59.53

24.28 grains of inflammable air, according to the analysis given in a preceding part of this paper, are composed of

Grains.

Oxygen   -   11.96
Carbon   -   10.43
Hydrogen   -   1.89
_____
24.28

11,51 grains of water are composed of

Oxygen   9.87
Hydrogen 1.64
_____
11.51

As for the charcoal, though it probably contains both oxygen and hydrogen as well as carbon, yet as the proportion of the two first ingredients is probably very small, and as we have no means of estimating them, we must at present rest satisfied with considering it as composed of pure carbon.

When these different elements are collected under their proper heads, we obtain

1. Oxygen in carbonic acid   -   42.86
  —   —   inflammable air - 11.96
  —   —   water   -   -   9.87
_____
64.69

2. Carbon in carbonic acid   -   16.67
  —   —   inflammable air - 10.43
  —   —   charcoal   -   -   4.68
_____
31.78

3. Hydrogen in inflammable air - 1.89
  —   —   — water -   -   1.64
_____
3.53

Hence oxalic acid is composed of oxygen   64.69

— — — — — — — carbon   31.78

— — — — — — — hydrogen   3.53

100.00

7. The result of two other experiments on oxalate of lime was very nearly the same as the preceding. The following may be stated in round numbers as the mean of the whole. Oxalic acid is a compound of

Oxygen   64

Carbon   32

Hydrogen   4

100

8. The only other analysis of oxalic acid with which I am acquainted has been given by M. FOURCROY, as the result of his own experiments, in conjunction with those of VAUQUELIN.*
It is as follows:

Oxygen   77

Carbon   13

Hydrogen   10

100

It gave me considerable uneasiness to observe, that my experiments led to conclusions irreconcileable with those of chemists of such eminence and consummate skill, and it was not without considerable hesitation, that I ventured to place any reliance upon them. I am persuaded, however, that some mistake has inadvertently insinuated itself into their calculations; since the carbonic acid alone, formed during the distillation of

* *Systeme de Connois Chem.* VII. 224.

oxalate of lime, contains considerably more carbon than the whole quantity which they assign to the oxalic acid decomposed. M. FOURCROY informs us, that oxalic acid is converted into carbonic acid and water, when acted upon by hot nitric acid ; and this decomposition seems to have been the method employed, to ascertain the proportion of the constituents of oxalic acid ; but the numbers assigned by him do not correspond with this statement. For 10 parts of hydrogen require 60 of oxygen to convert them into water, and 13 of carbon require at least 33 of oxygen. So that instead of 77 parts of oxygen, there would have been required no less than 98 to convert the hydrogen and carbon into water and carbonic acid. It is true, that the surplus of oxygen may be conceived to be furnished by the nitric acid ; but if this be admitted (and I have no doubt from experience, that the nitric acid actually does communicate oxygen), it is difficult to see how the constituents of oxalic acid could be determined by any such decomposition, unless the quantity of oxygen furnished by the nitric acid were accurately ascertained.

IV. *Composition of Oxalic Acid.*

The knowledge of the relative weights of the elements which compose oxalic acid, though of importance, is not sufficient to convey a clear idea of this compound, and in what respect it differs from tartaric acid, alcohol, sugar, and various other bodies possessing very different properties, though composed of the very same elements in different proportions.

It has been ascertained, by numerous and decisive experiments, that elementary bodies always enter into combinations in determinate proportions, which may be represented by

numbers. For example, the numbers which correspond to the four elements, oxygen, azote, carbon, and hydrogen, are the following:

Oxygen   6
Azote   -   5
Carbon   -   4.5
Hydrogen   1

Now, in all compounds consisting of these ingredients, the proportion of the different constituents may always be represented by these numbers, or by multiples of them; thus, the composition of the following substances may be thus stated.

	Oxygen.	Hydrogen.	Carbon.	Azote.
Water - -	6	+ 1		
Carbonic oxide - -	6	- -	+ 4.5	
Carbonic acid -	2 × 6	- -	+ 4.5	
Carbureted hydrogen	- -	2 × 1	+ 4.5	
Olefiant gas - -	- -	1	+ 4.5	
Nitrous gas - -	6	- -	- -	+ 5
Nitric acid - -	2 × 6	- -	- -	+ 5
Nitrous oxide -	6	- -	- -	+ 2 × 5

From the knowledge of this curious law, it is difficult to avoid concluding that each of these elements consist of atoms of determinate weight, which combine according to certain fixed proportions, and that the numbers above given, represent the relative weights of these atoms respectively. Thus, an atom of oxygen weighs six, an atom of hydrogen one, &c. Water is composed of one atom of oxygen, and one atom of hydrogen; carbonic acid of two atoms of oxygen, and one of carbon, &c. This curious theory, which promises to throw

an unexpected light on the obscurest parts of chemistry, belongs to Mr. DALTON. I have elsewhere illustrated it at considerable length.*

The same law holds with respect to the salts. The acid and bases always combine in determinate proportions. We may affix numbers to all the acids and bases, which numbers, or their multiples, will represent all the combinations into which these bodies enter. Some of these numbers are given in the following table:

Sulphuric acid	33	Barytes	67
Muriatic acid	18	Soda	24
Carbonic acid	16.5	Lime	23
Nitric acid	17	Ammonia	6

These numbers may be conceived to represent the relative weights of an integrant particle of each of these substances; formed on the supposition that an atom of hydrogen weighs 1. It follows equally from this law, that the acids and bases combine particle with particle, or a certain determinate number of particles of the one with a particle of the other.

One of the most important points in the investigation of compound bodies, is to ascertain the number which denotes the weight of an integrant particle of each of them, that of an atom of hydrogen being 1; because this number, or a multiple of it, represents the weight of each, which enters into all combinations; and because it enables us to estimate the number of elementary atoms of which each is composed. From a careful comparison of the table of oxalates, given in a preceding part of this paper, with the weight of the different bases already

determined,* it appears that the weight of an integrant par-
ticle of oxalic acid must be represented by the number 39.5.

Now, what number of atoms of oxygene, carbon, and hydro-
gen, go to constitute an integrant particle of oxalic acid ? We
have assigned the relative weights of each of these atoms,
and we have ascertained the relative proportions of the respec-
tive elements of oxalic acid. From these data it is easy to
solve the problem. An integrant particle of oxalic acid con-
sists of 9 atoms combined together, namely, 4 atoms of oxygen,
3 of carbon, and two of hydrogen.

$$
\begin{aligned}
4 \text{ atoms of oxygen weigh } & 4 \times 6 && = 24 \\
3 \text{ atoms of carbon } \quad - \quad - \quad & 3 \times 4.5 && = 13.5 \\
2 \text{ atoms of hydrogen } \quad - \quad & 2 \times 1 && = 2 \\
\hline
\text{Total} && & 39.5
\end{aligned}
$$

which together make up the weight of an integrant particle
of oxalic acid.

According to these proportions, 100 parts of oxalic acid is
composed of

$$
\begin{aligned}
\text{Oxygen} \quad & - \quad - \quad && 61 \\
\text{Carbon} \quad & - \quad - \quad && 34 \\
\text{Hydrogen} \quad & - \quad - \quad && 5 \\
\hline
&&& 100
\end{aligned}
$$

numbers which do not indeed exactly correspond with the
result of the preceding analysis, but which approach suffi-
ciently near it to give the reasoning employed considerable
probability at least, if it does not lead to certainty.

* For these weights, and the method of determining them, I refer the reader to my
System of Chemistry, 3d Edition, III. 619. The numbers which I have there assign-
ed are, I am persuaded, rather too low.

We may now examine the decomposition which takes place when oxalate of lime is exposed to heat. Let an atom of oxygen be w, an atom of carbon c, and an atom of hydrogen h. An integrant particle of oxalic acid may be represented by $4 w + 3 c + 2 h$. We may represent the composition and weight of an integrant particle of each of the substances into which oxalic acid is decomposed by heat, by the following symbols and numbers :

Carbonic acid -	$2 w + c$ weight	16.5
Carbureted hydrogen	$c + 2 h$ -	6.5
Carbonic oxide -	$w + c$ -	10.5
Water -	$w + h$ -	7
Charcoal - -	c -	4.5

We may now conceive 3 particles of oxalic acid to be decomposed at once, and to resolve themselves into these substances, in the following proportions :

$$
\begin{array}{lll}
\text{4 particles of carbonic acid} & = & 8 w + 4 c \\
\text{2 particles of carbureted hydrogen} & = & \quad\; 2 c + 4 h \\
\text{2 particles of carbonic oxide} & = & 2 w + 2 c \\
\text{2 particles of water} \quad - \quad - & = & 2 w \quad\;\; + 2 h \\
\text{1 particle of charcoal} \quad - \quad - & = & \quad\;\; 1 c \\
\hline
\text{Total} & & 12 w + 9 c + 6 h
\end{array}
$$

3 particles of oxalic acid $= 12 w + 9 c + 6 h$

We see that such a decomposition is possible. It remains only therefore to see whether the weights of these substances, which result from this hypothesis, correspond with the preceding analysis. Now,

4 particles of carbonic acid weigh $4 \times 16.5 = 66$

2   -   - carbureted hydrogen $2 \times 6.5 = 13$

2   -   - carbonic acid $2 \times 10.5 = 21$

2   -   - water   -   - $2 \times 7 = 14$

1   -   - charcoal   -   -   - $4.5 = 4.5$

        Total   118.5

Reducing these proportions to 100 parts of acid, and joining together the two inflammable gases, the numbers come out as follows :

Carbonic acid 55.70 we actually obtained 59.53

Inflammable air 28.69 - - 24.28

Water - 11.81 - - - 11.51

Charcoal - 3.80 - - - 4.68

    100.00   100.00

It is impossible to expect exact correspondence between the theory and hypothesis, till the numbers representing the weights of the elementary atoms be ascertained, with more rigid accuracy than has hitherto been done. I satisfied myself with taking the nearest round numbers, which are sufficient at least to show an evident approximation to the proportions obtained by experiment.

V. *Composition of Sugar, and Formation of Oxalic Acid.*

When a compound body is decomposed, and resolved into a number of new substances, the products are almost always simpler, or consist of integrant particles, composed of fewer atoms than the integrant particles of the original body. Thus, though oxalic acid is composed of 9 atoms, none of the pro-

ducts evolved, when that acid is decomposed by heat, contain more than 3 atoms. Hence it is probable that sugar is a more compound body than oxalic acid, because nitric acid resolves it into a variety of new compounds, one of which is oxalic acid. It may be worth while to examine the action of nitric acid on sugar, and the formation of oxalic acid, more closely than has hitherto been done, as the investigation will furnish some data for estimating the composition of sugar.

Two hundred grains of pure crystallized sugar being treated with diluted nitric acid in the usual way, yielded 200 cubic inches of carbonic acid, 64 cubic inches of nitrous gas, and 70 cubic inches of azotic gas. But these numbers, though the result of a good many experiments, are not to be considered as very exact. The uncertainty depends upon the property which the solution has of producing more gas after the sugar is decomposed, at the expence of the oxalic acid formed. Now, it is difficult to stop at the precise point.

The whole weight of oxalic acid, which can be obtained from 200 grains of sugar, amounts to 116 grains. If the experiment be properly conducted, the whole of the sugar is decomposed, or at least the quantity of residuary matter is small.

From the preceding statement, there is reason to conclude that 100 grains of sugar, when decomposed by nitric acid, yield,

Grains.

1. Oxalic acid crystals 58 grains, or real acid   45
2. Carbonic acid 100 cubic inches, equivalent to   46.5

while these are evolved obviously by the decomposition of the nitric acid.

Grains.

   1. Azotic gas 35 cubic inches equivalent to   10.62

   2. Nitrous gas 32 cubic inches equivalent to 10.85

Now, as nitric acid contains no carbon, it is obvious that the oxalic acid formed, and the carbonic acid evolved, must contain the whole carbon contained in 100 grains of sugar.

Grains.

   45   grains of oxalic acid contain of carbon 14.40

   46.5 grains of carbonic acid contain of ditto 13.02

                                               —————

                                Total   27.42

therefore 100 grains of sugar contain $27\frac{1}{2}$ grains of carbon.

The azotic gas and nitrous gas must have been originally in the state of nitric acid, and must have given out oxygen when they were evolved. But nitric acid is composed of

                                   Oxygen.

      Azote – – 10.62 + 25

      Nitrous gas   10.85 +   4.5

                                 —————

                                 29.5

Therefore they must have parted with 29.5 grains of oxygen. We are at liberty to suppose that the whole of this oxygen went to the formation of carbonic acid. Now, 46.5 grains of carbonic acid are composed of

                               Grains.

        Oxygen –   38.5

        Carbon – – 13.0

                        —————

                      46.5

From this it appears, that in the carbonic acid there were 4 grains of oxygen more than was furnished by the nitric acid. I confess I am disposed to ascribe this surplus to errors

in the experiments, and to believe that the whole of the oxy-
gen of the carbonic acid was furnished by the nitric acid. This
being admitted, it follows that the carbon of the carbonic acid,
and the whole constituents in the oxalic acid, were furnished
by the sugar. These are as follows:

	Grains.
Carbon - - -	27.5
Oxygen in 45 grains oxalic acid	28.8
Hydrogen in ditto - -	1.8
	58.1

If this total be subtracted from the 100 grains of sugar used,
there will be a remainder of 41.9 grains. As this quantity of
the sugar has disappeared, and is no where to be found among
the products, we must suppose that it has assumed the form
of water. Now 41.9 grains of water are composed of

Oxygen	35.9
Hydrogen	6
	41.9

Adding these quantities to the preceding products, we obtain
the composition of sugar, as follows:

Oxygen	64.7
Carbon	27.5
Hydrogen	7.8
	100.0

Though the process of reasoning, which led to this analysis
of sugar, is too hypothetical to be trusted implicitly, yet I am
persuaded that it is to a certain degree correct, and that the
result obtained does not deviate very far from the truth. If

we compare LAVOISIER's statement of the composition of sugar obtained in a different manner, though by a mode of reasoning not less hypothetical, we shall be surprised at its near coincidence with mine. His numbers are

<div align="center">

Oxygen 64

Carbon 28

Hydrogen 8

——

100

</div>

It is true that two different hypotheses may lead to the same result, and yet be both wrong; but this becomes infinitely improbable in the present case, when we consider that the proportion of carbon, which I assign to sugar, must at all events be nearly correct.

We have no direct method of determining the weight of an integrant particle of sugar; but if the accuracy of the preceding analysis be admitted, it furnishes us with an indirect one, which cannot be rejected; for it is clear, that the atoms of oxygen, carbon, and hydrogen, will be to each other respectively, as the numbers $\frac{64}{6}$, $\frac{28}{45}$, $\frac{8}{1}$; and these numbers reduced to their lowest terms become 5, 3, 4, nearly, which being primes with respect to each other, must represent the number of atoms, of which an integrant particle of sugar is composed. Sugar then is a compound of 12 atoms; namely, five of oxygen, three of carbon, and four of hydrogen; the weight of an integrant particle of it is 47.5, and its symbol is $5\,w + 3\,c + 4\,h$. It differs from oxalic acid merely in containing an additional atom of oxygen and two of hydrogen. If we had any method of removing these substances, without altering the proportion of the other constituents, we should

obtain a much greater quantity of oxalic acid from sugar than we can at present; but nitric acid acts by removing one-half of the carbon in the form of carbonic acid; the sugar deprived of this, resolves itself into oxalic acid and water. Suppose two particles of sugar acted on at once, the symbol for them will be $10\,w + 6\,c + 8\,h$. Let three atoms of the carbon be removed by the action of the nitric acid, there will remain $10\,w + 3\,c + 8\,h$. Now

$$
\begin{array}{l}
\text{A particle of oxalic acid} = 4\,w + 3\,c + 2\,h \\
\text{Six particles of water}\quad\; = 6\,w - \quad - + 6\,h \\
\hline
\phantom{\text{Six particles of water}\quad\;} 10\,w + 3\,c + 8\,h
\end{array}
$$

which is just the quantity of oxalic acid left. This will give us some idea of the way in which the formation of oxalic acid by nitric acid is accomplished. And although the series of changes is probably more complicated, yet they are ultimately equivalent to the preceding statement. I allude to the formation of malic acid, which is said to precede the oxalic acid, and afterwards to be converted into it by the subsequent action of nitric acid; but on the composition and formation of this latter acid, I avoid making any observations at present, as I propose to make them the subject of a separate dissertation.