

XXXIV. *On the ultimate analysis of vegetable and animal substances.* By ANDREW URE, M. D. F. R. S.

Read June 27, 1822.

THE improvements lately introduced into the analysis of vegetable and animal compounds, with the investigation of the equivalent ratios, in which their constituent elements, carbon, hydrogen, oxygen, and azote are associated, have thrown an unexpected light into this formerly obscure province of chemical science. While the substitution by M. GAY LUSSAC, of black oxide of copper for the chlorate of potash, has given peculiar facility and elegance to *animal* analysis, it may be doubted whether, in those cases, where the main object of inquiry is the proportion of carbon, it has not, frequently, led to fallacious results. As the quantity of this element is inferred from the volume of carbonic acid evolved in the decomposition of the organic matters, such of their particles as happen not to be in immediate contact with the cupreous oxide, will remain unconverted into carbonic acid; and thus the proportion of carbon will come to be underrated; an accident which cannot occur with chlorate of potash, since the carbonaceous matter is here plunged in an ignited atmosphere of oxygen. It is probably to this cause, that we must refer the discrepant results in the analysis of pure sugar, between M. M. GAY LUSSAC, THENARD, and BERZELIUS, on the one hand, and Dr. PROUT, on the other; the former

MDCCCXXII.

3 N

gentlemen assigning about 43 parts in the hundred of carbon, while the latter states the carbon at only 40.*

The objects of the present paper are, first to indicate, and endeavour to remove several sources of fallacy attending the method with peroxide of copper; and next, to exhibit the results of its application to a considerable series of vegetable and animal compounds.

Peroxide of copper, prepared by igniting the pure nitrate of this metal, is, like yellow oxide of lead, and many other metallic oxides, readily absorbent of a small portion of humidity from the air, the quantity of which depends, in some measure, on the length of time during which it has suffered ignition. If exposed to a red heat, merely till the vapours of nitric acid are expelled, 100 grains of the oxide will absorb, in the ordinary state of the atmosphere, from one-tenth to two-tenths of a grain of moisture in the space of an hour or two; and about one half of the above quantity in a very few minutes. The French chemists, who have operated most with this agent, seem to be well aware of this circumstance, for they direct the peroxide to be used immediately after ignition, and to be triturated with the organic matter in a hot mortar of agate or glass. Yet this precaution will not entirely prevent the fallacy arising from the hygrometric action; for I find that peroxide thus treated does absorb, during the long trituration essential to the process, a certain quantity of moisture, which, if not taken into account, will produce serious errors in the analytical results. It is better therefore to leave the powdered peroxide intended for research, exposed for such time to the air, as to bring it to hygrometric repose,

* Dr. PROUT has informed me, since the above paper was written, that he re-triturated and re-ignited the contents of his tubes, in the analysis of sugar.

then to put it up in a phial, and by igniting one hundred grains of it in a proper glass tube, sealed at one end, and loosely closed with a glass plug at the other, to determine the proportion of moisture which it contains. This, then, indicates the constant quantity to be deducted from the loss of weight which the peroxide suffers in the course of the experiment. The mortar should be perfectly dry, but not warm.

Experimenters have been at great pains to bring the various organic objects of research to a state of thorough desiccation before mixing them with the peroxide of copper; but this practice introduces a similar fallacy to that above described. We ought, therefore, after having made them as dry as possible by the joint agencies of heat, and an absorbent surface of sulphuric acid in vacuo, to expose them to the air till they also come into hygrometric repose, noting the quantity of moisture which they imbibe, that it may be afterwards allowed for. The plan which I adopt for the purpose of desiccation seems to answer very well. Having put the pulverulent animal or vegetable matter into short phials, furnished with ground glass stoppers, I place the open phials in a large quantity of sand heated to 212° F. in a porcelain capsule, and set this over a surface of sulphuric acid in an exhausted receiver. After an hour or more the receiver is removed, and the phials instantly stopped. The loss of weight shows the total moisture which each of them has parted with; while the subsequent increase of their weight, after leaving them unstopped for some time in the open air, indicates the amount of hygrometric absorption. This is consequently the quantity to be deducted in calculating experimental results.

Many chemists, particularly in this country, have employed the heat of a spirit lamp, instead of that produced by the combustion of charcoal, for igniting the tube in which the mixed materials are placed. I have compared very carefully both methods of heating, and find that for many bodies, such as coal, and resin, which abound in carbon, the flame of the lamp is insufficient; while its application being confined at once to a small portion of the tube, that uniform ignition of the whole, desirable towards the close of the experiment, cannot be obtained. I was hence led to contrive a peculiar form of furnace, in which, with a handful of charcoal, reduced to bits about the size of small filberts, an experiment may be completed, without anxiety or trouble, in the space of half an hour. Since I have operated with this instrument, the results on the same body have been much more consistent, than those previously obtained with the lamp; and it is so convenient, that I have sometimes finished eight experiments in a day.

Fig. 1. (Plate L.) represents the whole apparatus, as when in action. Fig. 2 is a horizontal section of the furnace, in which we perceive a semi-cylinder of thin sheet iron, about 8 inches long and $3\frac{1}{2}$ wide, perforated with holes, and resting on the edge of a hollow prism of tin-plate, represented more distinctly in fig. 3, where *n* shows a slit, through which the sealed end of the glass tube may be made to project, on occasion. *i*, is a handle attached to the semi-cylinder, by which it may be slid backwards or forwards, and removed at the end of the process. *d*, is a sheath of platinum foil, which serves, by aid of a wire laid across, to support the middle of the tube, when it is softened by ignition. At *g*, the plates

which close the ends of the semi-cylinder and tin-plate prism, rise up a few inches to screen the pneumatic apparatus from the heat. A third occasional screen of tin-plate is hung on at *f*. All these are furnished with slits for the passage of the glass tube. This is made of crown glass, and is generally about 9 or 10 inches long, and $\frac{3}{10}$ of internal diameter. It is connected with the mercurial cistern by a narrow tube and caoutchouc collar. This tube has a syphon form, and rises about an inch within the graduated receiver at *e*. By this arrangement, should the collar be not absolutely air-tight, the pressure of the column of mercury causes the atmospheric air to enter at the crevice, and bubbles of it will be seen rising up without the application of heat. At the end of the operation, the point of the tube *e*, is always left above the surface of the mercury, the quantity of organic matter employed being such as to produce from 6 to 7 cubic inches of gaseous product, the volume of the graduated receiver being 7 cubic inches.

As the tubes with which I operate have all the same capacity, viz. half a cubic inch; and as the bulk of materials is the same in all the experiments, one experiment on the analysis of sugar or resin, gives the volume of atmospheric air due to the apparatus, which volume is a constant quantity in the same circumstances of ignition. And since the whole apparatus is always allowed to cool to the atmospheric temperature, the volume of residual gas in the tubes comes to be exactly known, being equal, very nearly, to the primitive volume of atmospheric air left after the absorption of the carbonic acid in the sugar or resin experiment.* Thus this

* If *a* be the capacity of the graduated receiver, and *b* the spare capacity of the tubes, then the above volume is $b - \frac{b}{a+b}$.

quantity, hitherto ill appreciated or neglected in many experiments, though it is of very great consequence, may be accurately found. At *k*, fig. 2, a little tin-plate screen is shown. It is perforated for the passage of the tube, and may be slid along, and left at any part of the semi-cylindric cage, so as to preserve from the influence of the heat, any requisite portion of the sealed end of the tube. At fig. 4 is seen the shape of the little bulb, into which I introduce the proper weight of ether, alcohol, naphtha, or other volatile liquids, which are destined for analysis. After weighing it exactly, it is immediately slid down to the bottom of the tube, and covered with 150 or 200 grains of peroxide of copper. The bulb has a capacity equal to 3 grain measures of water, and its capillary point is sometimes closed with an inappreciably small quantity of bees wax, to prevent the exhalation of the liquid, till the peroxide be ignited.

b is a cover to the furnace, with an oblong orifice at its top. It serves for a chimney, and may be applied or removed by means of its handle, according as we wish to increase or diminish the heat. *cc* are tin cases inclosing corks, through which the iron wires are passed, that support the whole furnace at any convenient height and angle of inclination.

The tightness of the apparatus at the end of the process, is proved by the rising of the mercury in the graduated receiver, by about one-tenth of an inch, as the tube becomes refrigerated.

My mode of operating with the peroxide of copper is the following:

I triturate very carefully in a dry glass mortar, from 1 to $2\frac{1}{2}$ grains of the matter to be analyzed, with from 100 to 140

grains of the oxide. I then transfer it, by means of a platinum-foil tray and small glass funnel, into the glass tube, clearing out the mortar with a metallic brush. Over that mixture I put 20 or 30 grains of the peroxide itself, and next, 50 or 60 grains of clean copper filings. The remaining part of the tube is loosely closed with 10 or 12 grains of amianthus, by whose capillary attraction the moisture evolved in the experiment is rapidly withdrawn from the hot part of the tube, and the risk of its fracture thus completely obviated. The amianthus serves moreover as a plug, to prevent the projection of any minute particles of filings, or of oxide, when the filings are not present. The tube is now weighed in a very delicate balance, and its weight is written down. A little cork, channelled at its side, is next put into the tube, to prevent the chance of mercury being forced backwards into it, by any accidental cooling or condensation. The collar of caoutchouc is finally tied on, and the tube is placed, as is shown in fig. 2, but without the plate *k*, which is employed merely in the case of analyzing volatile liquids. A few fragments of ignited charcoal are now placed under the tube at the end of the furnace next to the cistern, and the remaining space in the semi-cylinder is filled up with bits of cold charcoal. The top, *b*, may then be put in its place, when the operation will proceed spontaneously, the progressive advance of the ignition from one end to the other being proportioned to the expansion of glass, so that the tube very seldom cracks in the process. Indeed I have often used the same tube for a dozen experiments, in the course of which it became converted into *vitrite*, or Reaumur's porcelain.

Since the evolved gas is saturated with moisture, I reduce

it to the volume of dry gas, by help of the following table, computed by the well known formula from my table of the elastic force of steam, which the Royal Society did me the honour to publish in their Transactions for the year 1818.

TABLE

Tempera- ture.	Multiplier.	Tempera- ture.	Multiplier.	Tempera- ture.	Multiplier.
53° F.	0.9870	61° F.	98.20	70° F.	0.9758
54	0.9864	62	98.13	71	0.9751
55	0.9858	63	98.06	72	0.9743
56	0.9852	64	97.99	73	0.9735
57	0.9846	65	97.93		
58	0.9839	66	97.86		
59	0.9833	67	97.79		
60	0.9827	68	97.72		
		69	97.65		

In certain cases, where the quantity of hydrogen is small, or where, as in the example of indigo, its presence has been denied, I employ pulverulent proto-chloride of mercury (calomel) instead of peroxide of copper. The organic compound being intimately mixed with that powder, and gently heated, the muriatic acid gas obtained, demonstrates the presence, though half of its volume will not give the total quantity of, hydrogen; for a proportion of this elementary body continues associated with oxygen in the state of water. Dry oxalate of lead, treated in this way, yields not the slightest trace of muriatic acid, for on passing the disengaged gas through a dilute solution of nitrate of silver, no precipitation or

even cloud of chloride is produced. But 5 grains of indigo, prepared from the de-oxidized solution of the dyer's vat, and freed from its lime and resin by the successive application of dilute muriatic acid and alcohol, gave 5 cubic inches of muriatic acid gas when heated along with 150 grains of calomel. Here we have a quantity of gas equivalent to $2\frac{1}{2}$ cubic inches of hydrogen. By means of peroxide of copper, however, nearly 4 times the above quantity of hydrogen may be obtained from the same weight of indigo.

I shall now give in detail, one example of the mode of computing the relation of the constituents from the experimental results, and shall then state the other analyses in a tabular form, subjoining a few remarks on the habitudes of some peculiar bodies.

1.4 grains of sulphuric ether, specific gravity 0.70, being slowly passed in vapour from the glass bulb through 200 grains of ignited peroxide of copper, yielded 6.8 cubic inches of carbonic acid gas at 66° F. which are equivalent to 6.57128 of dry gas at 60°. This number being multiplied by 0.127 = the carbon in 1 cubic inch of the gas, the product 0.8345256, is the carbon in 1.4 grains of ether; and $0.8345256 \times \frac{8}{3} = 2.2254 =$ the oxygen equivalent to the carbonic acid. The tube was found to have lost 4.78 grains in weight, 0.1 of which was due to the hygrometric moisture in the oxide, and 1.4 to the ether. The remainder, 3.28, is the quantity of oxygen abstracted from the oxide by the combustible elements of the ether. But of these 3.28 grains, 2.2254 went to the formation of the carbonic acid, leaving 1.0546 of oxygen, equivalent to 0.1318 of hydrogen. Hence, 1.4 ether, by this experiment, which is taken as the most satisfactory of

a great number, seem to consist of

Carbon	0.8345
Hydrogen	0.1318
Water	0.4337
	<hr/>
	1.4000

And in 1 grain we shall have

Carbon	0.5960	3 atoms	2.25	60.00
Hydrogen	0.1330	4 atoms	0.50	13.33
Oxygen	0.2710	1 atom	1.00	26.66
	<hr/>		<hr/>	<hr/>
	1.0000		3.75	100.0

Or, 3 volumes olefiant gas = $3 \times 0.9722 = 2.9166$

2 . . vapour of water . $2 \times 0.625 = 1.25$

4.1666

which suffering a condensation equal to the whole vapour of water, will give an ethereous vapour, whose specific gravity is 2.5.

The proportion of the constituents of sulphuric ether, deduced by M. GAY LUSSAC from the experiments of M. TH. DE SAUSSURE, are 2 volumes olefiant gas + 1 volume vapour of water, which 3 volumes are condensed into 1 of vapour of ether, having a specific gravity = 2.58. The ether which I used had been first distilled off dry carbonate of potash, and then digested on dry muriate of lime, from which it was simply decanted, according to the injunction of M. DE SAUSSURE. Whether my ether contained more aqueous matter than that employed by the Genevese philosopher, or whether the difference of result is to be ascribed to the difference in the mode of analysis, must be decided by future researches.

By analogous modes of reduction, the following results were deduced from my experiments. I ought here to state, that in many cases the materials, after being ignited in the tube, and then cooled, were again triturated in the mortar, and subjected to a second ignition. Thus, none of the carbon could escape conversion into carbonic acid. I was seldom content with one experiment on a body; frequently six or eight were made.

Table of organic analyses.

	Substance.	Carbon.	Hydrogen.	Oxygen.	Azote.	Water.	Excess.
1	Sugar - - -	43.38	6.29	50.33		56.62	Oxygen
2	Sugar of diabetes - -	39.52	5.57	54.91		51.13	10.35
3	Starch - - -	38.55	6.13	55.32		55.16	6.3
4	Gum Arabic - - -	35.13	6.08	55.79	3?	54.72	7.15
5	Resin - - -	73.60	12.90	13.50		15.20	Hydrogen
6	Copal - - -	79.87	9.00	11.10		12.5	11.20
7	Shell lac - - -	64.67	8.22	27.11		30.51	7.6
8	Resin of guaiac. - -	67.88	7.05	25.07		28.	4.82
9	Amber - - -	70.68	11.62	17.77		20.0	3.93
10	Yellow wax - - -	80.69	11.37	7.94		8.93	9.40
11	Caoutchouc - - -	90.00	9.11	0.88		.99	10.39
12	Splent coal - - -	70.90	4.30	24.80		27.90	9.00
13	Cannel coal - - -	72.22	3.93	21.05	2.8	23.68	1.20
14	Indigo - - -	71.37	4.38	14.25	10.	16.0	1.30
15	Camphor - - -	77.38	11.14	11.48		12.91	2.52
16	Naphthaline - - -	91.6	7.7	0.70?		0.79?	9.71
17	Spermaceti oil - -	78.91	10.97	10.12		11.34	9.71
18	Common oil of turpentine	82.51	9.62	7.87		8.85	8.64
19	Purified oil of turpentine	84.9	11.5	3.6		4.0	11.1
20	Naphtha - - -	83.04	12.31	4.65		5.23	11.73
21	Asiatic castor oil - -	74.00	10.29	15.71		17.67	8.33
22	Alcohol, sp. gr. 0.812 -	47.85	12.24	39.91		44.9	7.25
23	Ether, specific gravity 0.70	59.60	13.3	27.1		30.5	9.9
24	Bleached Silk - - -	50.69	3.94	34.04	11.33	35.43	Oxygen
25	Cotton - - -	42.11	5.06	52.83		45.56	2.55
26	Flax, by LEE's process	42.81	5.5	51.7		49.5	12.33
27	Common flax - - -	40.74	5.57	52.79	0.9	50.16	7.7
28	Wool - - -	53.7	2.80	31.2	12.3	25.7	8.2
29	Cochineal - - -	50.75	5.81	36.53	6.91	39.6	8.3
30	Cantharides - - -	48.64	5.99	36.29	9.08	40.83	Hydrogen
31	Urea - - -	18.57	5.93	43.68	31.82	49.14	14.1
32	Benzoic acid - - -	66.74	4.94	28.32		31.86	14.53
33	Citric acid - - -	33.00	4.63	62.37		41.67	0.47
34	Tartaric acid - - -	31.42	2.76	65.82		24.84	1.4
35	Oxalic acid - - -	19.13	4.76	76.20		42.87	Oxygen
36	Ferroprussic acid - -	36.82	27.89 of iron.		35.29		25.33
							43.74
							38.09

Remarks on the preceding analyses.

1. Sugar. The sugar which I employed had been purified by Mr. HOWARD's steam process, and was so well stove-dried, that it lost no appreciable portion of its weight, when enclosed along with sulphuric acid in *vacuo*. The diabetic sugar has a manifest excess of oxygen, which I believe to be the case with all weak sugars, as they are called by the sugar refiners. I consider this excess of oxygen as the chief cause which counteracts crystallization, and therefore the great obstacle to the manufacturer. The smallest proportion of carbon, which I have ever found in any cane sugar, was upwards of 41 per cent. The experiments on starch and gum were among the earliest which I made, and the results differ so much from those given by other experimenters, that I shall repeat the analyses at the earliest opportunity. The constituents of the above three bodies, referred to the prime equivalent scale, will be approximately as follows :

Sugar.				Starch.				Gum.		
Carbon	5 atoms	3.75	45.4	5 atoms	3.75	40.5	4 atoms	3.0	35.25	
Oxygen	4 —	4.00	48.5	5 —	5.00	54.0	5 —	5.0	58.90	
Hydrogen	4 —	0.50	6.1	4 —	0.50	5.5	4 —	0.5	5.85	
		8.25	100.0		9.25	100.0		8.5	100.00	

I conceive the purest and strongest sugar to be constituted as here represented.

All the elementary principles of organic nature may be considered as deriving the peculiar delicacy of their chemical equilibrium, and the consequent facility with which it may be subverted and new modelled, to the multitude of atoms

grouped together in a compound. On this view, none of them should be expected to consist of a single atom of each component. The allurements of theoretic simplicity has led some ingenious philosophers to represent sugar by 1 atom of carbon, 1 atom of oxygen, and 1 atom of hydrogen; or of 40 carbon, $59\frac{1}{3}$ oxygen, and $6\frac{2}{3}$ hydrogen in 100 parts. But I am satisfied that all sound specimens of sugar will yield considerably more carbon than 40 *per cent*.

Starch is liable to a similar deterioration with sugar; that is, some species of it make a much firmer coagulum with hot water than others; a difference probably due to the proportion of oxygen. The starch here employed was that of commerce, and was not chemically desiccated: hence, the redundancy of water beyond the equivalent proportion. A little hygrometric moisture was present also in the gum, as it was not artificially dried. A note of interrogation is placed after azote. That doubt will I trust be solved, when I complete my analyses of grains, roots, and leaves, with the view of tracing the origin of azote in the bodies of graminivorous animals.

We now come to a class of bodies in which the hydrogen predominates over the oxygen. With regard to resin, I believe the quantity of its carbon to be somewhat underrated in the table. Though three experiments were made on it, I now perceive that I had omitted to re-triturate and re-ignite; and the carbon of resin is very difficult of oxygenation. Its true composition is probably,

Carbon	8 atoms	6.0	75.00
Hydrogen	8 ———	1.0	12.50
Oxygen	1 ———	1.0	12.50
		<hr/>	<hr/>
		8.0	100.00

A still more symmetric arrangement would be derived from

Carbon	8 atoms	. .	6.0	. . .	73.9
Hydrogen	9 ———	. .	1.125	. .	13.8
Oxygen	1 ———	. . .	1.000	. .	12.3
			8.125		100.0

This proportion corresponds to 8 atoms of olefiant gas and 1 atom of water; and I think it is very possibly the true constitution of resin. Had the loss of weight suffered by the contents of the tube, during their ignition, been a few hundredth parts of a grain more, the experimental result would have coincided with this theoretical view. Copal approaches to

Carbon	10 atoms	. .	7.5	. . .	80.30
Hydrogen	7 ———	. .	0.875	. .	9.36
Oxygen	1 ———	. .	1.000	. .	10.34
			9.375		100.00

Lac may be nearly represented by

Carbon	6 atoms	. .	4.5	. . .	64.3
Hydrogen	4 ———	. .	0.5	. .	28.5
Oxygen	2 ———	. .	2.0	. .	7.2
			7.0		100.0

or 2 atoms of olefiant gas + 1 atom carbonic oxide; that is equal weights of these two binary compounds; for

$$2 \text{ atoms of olefiant gas} = 2 \times (0.75 + 0.125) = 1.75$$

$$1 \text{ atom carbonic oxide} = 1.75$$

Referred to volumes, we shall have lac to consist of equal parts of the two gases.

Resin of guaiac. gives

Carbon	7 atoms	. .	5.25	. . .	67.7
Hydrogen	4 ———	. .	0.50	. .	6.5
Oxygen	2 ———	. . .	2.00	. .	25.8
			7.75		100.0

Although the experiments on amber were conducted carefully with re-trituration and re-ignition, no good atomic configuration of it has occurred to me. It approaches to 10 carbon + 10 hydrogen 10 hydrogen + 2 oxygen.

Wax is apparently composed of

Carbon	13 atoms	.	.	9.75	.	.	80.4
Hydrogen	11 —	.	.	1.375	.	.	11.3
Oxygen	1 —	.	.	1.000	.	.	8.3
				<hr/>		<hr/>	
				12.125		100.0	

or in other words, of 11 atoms olefiant gas + 1 atom carbonic oxide + 1 atom carbon. Had the experiment given a very little more hydrogen, we should have had wax as consisting of 12 atoms olefiant gas + 1 atom carbonic oxide. This is possibly the true constitution.

Caoutchouc seems to consist of

Carbon	3 atoms	.	.	2.25	.	.	90
Hydrogen	2 —	.	.	0.25	.	.	10
				<hr/>		<hr/>	
				2.50		100	

Or it is a sesqui-carburetted hydrogen. The oxygen deduced from experiment is in such small quantity, as to leave a doubt whether it be essential to this body, or imbibed in minute quantity from the air during its consolidation.

Splent or slate coal, specific gravity 1.266, abstracting its incombustible ashes, approaches in constitution, to

Carbon	7 atoms	.	.	5.25	.	.	70.00
Hydrogen	3 —	.	.	0.375	.	.	3.40
Oxygen	2 —	.	.	2.000	.	.	26. 6
				<hr/>		<hr/>	
				7.625		100.0	

Cannel coal from Woodhall, near Glasgow, specific gravity 1.228, resembles a compound of

Carbon	9 atoms	. .	6.750	. .	73.9
Hydrogen	3 ———	. .	0.375	. .	4.2
Oxygen	2 ———	. .	2.000	. .	21.9
			<hr/>	<hr/>	
			9.125		100.0

In both of these bodies there is an excess of carbon beyond the 3 atoms of olefiant gas and 2 of carbonic oxide. The former coal has 2 extra atoms of carbon, and the latter 4 atoms. Hence, this coal is found at the Glasgow gas works to yield a very rich burning gas. I do not know whether the azote be essential to the constitution of this coal, or accidentally introduced from animal remains at the formation of the strata.

The elements of indigo may be grouped as follows :

Carbon	16 atoms	. .	12.0	. .	72.70
Hydrogen	6 ———	. .	0.75	. .	4.55
Oxygen	2 ———	. . .	2.00	. .	12.15
Azote	. 1 ———	. . .	1.75	. .	10.60
			<hr/>	<hr/>	
			16.50		100.00

or, in other terms, we shall have

1 atom cyanogen, 6 atoms olefiant gas, 2 atoms carbonic oxide, and 6 atoms of carbon in excess.

I had intended to pursue, at considerable detail, my researches on this curious azotized product of vegetation, but the subject having been lately taken up, and ingeniously prosecuted by my pupil and friend, Mr. WALTER CRUM, I was induced to leave it in his hands. He announced to me the presence of hydrogen in indigo, before I had analyzed this substance myself; and drew my attention, particularly, to

the fallacy occasioned by the hygrometric water of the peroxide of copper. It is likely that some slight modification may require to be made in my tabular proportion of the constituents, for I did not resume the subject of indigo, after I had become most familiar with the manipulations.

Camphor is very nearly represented by

Carbon	10 atoms	.	.	7.5	.	.	78.02
Hydrogen	9 —	.	.	1.125	.	.	11.58
Oxygen	1 —	.	.	1.0	.	.	10.40
				<hr/>			
				9.625		100.00	

or 9 atoms olefiant gas + 1 atom carbonic oxide. Naphthaline is, in my opinion, a solid bi-carburet of hydrogen, consisting of

Carbon	2 atoms	.	.	1.5	.	.	92.9
Hydrogen	1 —	.	.	0.125	.	.	7.1
				<hr/>			
				1.625		100.0	

It is very difficult, even by the best regulated ignition, to resolve the whole carbon of this very volatile body into carbonic acid; hence, the carbon may come to be underrated in the result. Naphthaline is obtained during the rectification of the petroleum of the coal gas works. It is found encrusting the pipes in the form of a greyish crystalline mass; and when purified by a second sublimation at the temperature of about 220°, it forms beautiful thin plates, white and glistening. It has a powerful petroleum odour. With brine of the specific gravity 1.048, these plates, when once thoroughly wetted (which is difficult to effect) remain in equilibrium; that is, float in any part of the liquid. That number, therefore, represents the specific gravity of naphthaline. It is insoluble in water, but very soluble in ether, and moderately so in alcohol. With iodine, it fuses at a gentle

heat into a brown liquid, forming as it cools a solid resembling plumbago, which dissolves readily in alcohol, and is thrown down by water. Naphthaline is soluble in oils. In water heated to 168° F. it fuses, and remains like oil at the bottom of the liquid; but when stirred it rises, and spreads on the top in little oily patches. At 180° it rises spontaneously from the bottom in oily globules, which, as the temperature is raised, dissipate in the air, undergoing motions similar to those of camphor floating on water.

Spermaceti oil is constituted apparently of

Carbon	10 atoms	.	.	7.5	.	.	78.0
Hydrogen	9 ———	.	.	1.125	.	.	11.8
Oxygen	1 ———	.	.	1.0	.	.	10.2
				<hr/>		<hr/>	
				9.625		100.0	

or, in other words, of 9 atoms olefiant gas + 1 atom carbonic oxide. The experimental proportion is, however, more nearly,

Carbon	10 atoms	.	.	7.5	.	.	79.0
Hydrogen	8 ———	.	.	1.0	.	.	10.5
Oxygen	1 ———	.	.	1.0	.	.	10.5
				<hr/>		<hr/>	
				9.5		100.0	

There is here an atom of carbon in excess.*

Common oil of turpentine, specific gravity 0.888, comes very closely to the following arrangement:

Carbon	14 atoms	.	.	10.5	.	.	82.35
Hydrogen	10 ———	.	.	1.25	.	.	9.80
Oxygen	1 ———	.	.	1.00	.	.	7.85
				<hr/>		<hr/>	
				12.75		100.00	

* This is probably the truer view. The former would make it coincide with camphor.

Oil of turpentine, purified with alcohol by Dr. NIMMO's method, seems to approach to the constitution of naphtha, or of a mere carburet of hydrogen. Its specific gravity is 0.878. But as from the mode of preparing it, a minute portion of alcohol may remain in it, I do not think it necessary to investigate its atomical structure.

Naphtha, specific gravity 0.857, obtained by distillation from petroleum, is very nearly represented by,

Carbon	22 atoms	.	.	16.50	.	.	82.5
Hydrogen	20 ———	.	.	2.50	.	.	12.5
Oxygen	1 ———	.	.	1.00	.	.	5.0
				<hr/>			
				20.00			100.0

It therefore consists of 20 atoms olefiant gas, 1 atom carbonic oxide, and 1 atom of carbon held in solution.

Castor oil is an interesting unctuous body, from its great solubility in alcohol. It consists nearly of

Carbon	7 atoms	.	.	5.25	.	.	75.00
Hydrogen	6 ———	.	.	0.75	.	.	10.70
Oxygen	1 ———	.	.	1.00	.	.	14.30
				<hr/>			
				7.00			100.00

It is composed therefore of 6 atoms olefiant gas + 1 atom carbonic oxide; or in volumes of 3 olefiant gas + 1 carbonic oxide.

Alcohol, specific gravity 0.812, is composed very nearly of

Carbon	3 atoms	.	.	2.250	.	.	46.15
Hydrogen	5 ———	.	.	0.625	.	.	12.82
Oxygen	2 ———	.	.	2.000	.	.	40.03
				<hr/>			
				4.875			100.00

or, of 3 atoms olefiant gas = 2.625.

2 ——— water . = 2.25.

And in volumes, 3 olefiant gas = $.9722 \times 3 = 2.9166$

4 aqueous vapour = $.625 \times 4 = 2.500$

Thus alcohol of 0.812, by the above analysis, which I believe merits confidence, from the care and consistency of the experiments, differs from M. GAY LUSSAC's view of absolute alcohol, deduced from M. TH. DE SAUSSURE's experiments, in containing an additional volume of aqueous vapour. At the specific gravity .814, alcohol would have exactly this atomic constitution. If the condensation be equal to the whole 3 volumes of olefiant gas, that is if the 7 volumes of constituent gases become 4 of alcohol vapour, we shall have its specific gravity at this strength = 1.3722; the additional volume of aqueous vapour producing necessarily this abatement in the density.

We have already considered sulphuric ether.

The next 4 bodies which occur in the table are of fibrous texture, and are chemically characterized by an excess of oxygen beyond the hydrogen equivalent.

Fibres of the bleached threads of the silk-worm were subjected to analysis. Their composition is apparently,

Carbon	10 atoms	.	.	7.5	.	.	50.8
Hydrogen	4 —	.	.	0.5	.	.	3.4
Oxygen	5 —	.	.	5.0	.	.	34.0
Azote	1 —	.	.	1.75	.	.	11.8
				<hr/>			
				14.75			100.0

or, 4 of olefiant gas, 5 of carbonic oxide, and 1 of nitrous oxide; or of 1 atom prussic acid, 3 atoms olefiant gas, and 5 atoms carbonic oxide.

Cotton fibres, unbleached, seem to consist of

Carbon	11 atoms	. .	8.25	. .	42.85
Hydrogen	8 ———	. .	1.00	. .	5.30
Oxygen	10 ———	. .	10.00	. .	51.85
			<hr/>	<hr/>	
			19.25		100.00

Flax, by LEE's patent process, consists of

Carbon	7 atoms	. .	5.25	. .	44.25
Hydrogen	5 ———	. .	0.625	. .	5.25
Oxygen	6 ———	. .	6.000	. .	50.50
			<hr/>	<hr/>	
			11.875		100.00

It contains more carbon, and is therefore probably stronger than common flax, prepared by a putrefactive maceration.

This seems composed of

Carbon	1 atom	. .	0.75	. .	40.0
Hydrogen	1 ———	. .	0.125	. .	6.6
Oxygen	1 ———	. .	1.000	. .	53.4
			<hr/>	<hr/>	
			1.875		100.0

But this is the theoretical representation of sugar by M. GAY LUSSAC and Dr. PROUT; and, hence, these chemists would readily explain, how linen rags may pass into the form of sugar, by the action of sulphuric acid.

Wool approximates to

Carbon	10 atoms	. .	7.5	. .	55.0
Hydrogen	3 ———	. .	0.375	. .	2.8
Oxygen	4 ———	. .	4.000	. .	29.4
Azote	1 ———	. .	1.750	. .	12.8
			<hr/>	<hr/>	
			13.625		100.0

Cochineal seems to be made up of

Carbon	15 atoms	-	11.250	-	50.20
Hydrogen	11 ———	-	1.375	-	6.15
Oxygen	8 ———	-	8.000	-	35.85
Azote	- 1 ———	-	1.750	-	7.80
			<hr/>		<hr/>
			22.375		100.00

Cantharides approximate to

Carbon	11 atoms	-	9.75	-	49.4
Hydrogen	10 ———	-	1.25	-	6.3
Oxygen	7 ———	-	7.00	-	35.4
Azote	- 1 ———	-	1.75	-	8.9
			<hr/>		<hr/>
			19.75		100.0

My result with urea differs so considerably in the proportion of azote, from that of Dr. PROUT and M. BERARD, that I am disposed to doubt of the accuracy of my experiments, though they were made with the utmost care, and were most consistent in the repetition. I could perceive no smell whatever of nitrous gas in the gaseous products, which were made to traverse a column of copper filings 3 inches long, in a state of ignition. I shall renew the inquiry on urea, and employ the lowest temperature compatible with the formation of carbonic acid.

The prime equivalent of benzoic acid crystals, I find by saturation with water of ammonia, to be 14.5; and it consists apparently of

Carbon	13 atoms	-	9.75	-	67.24
Hydrogen	6 ———	-	0.75	-	5.16
Oxygen	4 ———	-	4.00	-	27.60
			<hr/>		<hr/>
			14.50		100.00

Of crystalline citric acid, the prime equivalent is 8.375 by my experiments ; and it consists probably of

Carbon	4 atoms	.	.	3.000	.	.	35.8
Hydrogen	3 —	.	.	0.375	.	.	4.5
Oxygen	5 —	.	.	5.000	.	.	59.7
				<hr/>			
				8.375			100.0

or, of 4 atoms carbon, 3 water, and 2 oxygen. 2 of these atoms of water are separated, when citric acid is combined with oxide of lead in what is called the dry citrate. Hence, the acid atom is in this case 6.125.

The prime equivalent of crystalline tartaric acid is 9.25 by my results ; and it seems made up of

Carbon	4 atoms	.	.	3.0	.	.	32.43
Hydrogen	2 —	.	.	0.25	.	.	2.70
Oxygen	6 —	.	.	6.00	.	.	64.87
				<hr/>			
				9.25			100.00

or, of Carbon	4 atoms	.	.	3.0	.	.	32.43
Oxygen	4 —	.	.	4.0	.	.	48.24
Water	2 —	.	.	2.25	.	.	24.33
				<hr/>			
				9.25			100.00

From my experiments I have been led to conclude, that into dry tartrate of lead these two atoms of water *do* enter as a constituent ; and, hence, that the crystals of tartaric acid are as dry as is compatible with its constitution.

Oxalic acid crystals have 7.875 for their prime equivalent ; and are composed of

Carbon	2 atoms	.	.	1.500	.	.	19.04
Hydrogen	3 —	.	.	0.375	.	.	4.80
Oxygen	6 —	.	.	6.000	.	.	76.16
				<hr/>			
				7.875			100.00

or, of 2 atoms Carbon	.	.	1.5	.	.	19.14
3 ——— Oxygen	.	.	3.0	.	.	40.72
3 ——— Water	.	.	3.375	.	.	40.14
						<hr/>
						7.875
						<hr/>
						100.00

Into the dry oxalate of lead these 3 atoms of water do *not* enter. Hence, I find the dry acid to be composed of

Carbon 2 atoms	.	.	1.5	.	.	33.33
Oxygen 3 ———	.	.	3.0	.	.	66.66
						<hr/>
						4.5
						<hr/>
						100.00

or, of 1 atom carbonic acid + 1 atom carbonic oxide, as was first suggested, I believe, by DOBEREINER. Crystallized oxalate of ammonia consists of 1 atom acid, 1 atom ammonia, and 2 atoms water = 8.875. By a gentle heat 1 atom of water may be separated; and an oxalate of ammonia, as dry as is compatible with its neutrality, remains.

I have analyzed, by the peroxide of copper, the citrate, tartrate, and oxalate of lead; and on comparing the results thus obtained, with those derived from the analysis of the crystalline acids, I have come to the above determinations.

Ferroproussic acid, the ferrocyanic acid of the French chemists, has proved, hitherto, a stumbling block to me, in reducing the results of my experiments to the atomic theory. I have subjected it to very numerous trials in many states of combination, and have sought, with great pains, to accommodate the results to the doctrine of prime equivalents; but hitherto without success. The following facts, however, may perhaps be deemed of some consequence.

In the first place, the prime equivalent of the crystallized ferroproussiate of potash is 13.125, compared to oxide of lead

14, and to nitrate of the same metal 20.75; that is, 13.125 of the former salt neutralize 20.75 of the latter. In the second place, 14 parts of oxide of lead yield 21 parts of dry ferroprussiate of lead; or the atomic weight of dry ferroprussic acid is 7:

The mean of my analyses of ferroprussiate of lead, gives the relation of the constituents of the acid, as marked in the table. These proportions, reduced to the atomic weight 7, afford

Carbon	.	.	.	2.5774
Azote	.	.	.	2.4703
Ferrous matter				1.9523
				<hr/>
				7.0000

Were we to suppose the prime equivalent of the ferroprussic acid 7.5 instead of 7; and were we farther to suppose that the carbon in the above result should be $2.25 = 3$ atoms, and the azote $= 3.5$, or two atoms, then we might conceive an atom of dry ferroprussic acid to be made up of

Carbon	3 atoms	2.25
Azote	2	<hr/> 3.50
Iron	1	<hr/> 1.75
		<hr/>
		7.50

But experiment does not permit me to adopt this theoretical representation.

The best mode that has occurred to me for analyzing ferroprussiate of potash, is to convert it, by the equivalent quantity of nitrate of lead, into the ferroprussiate of this metal; then to separate the nitrate of potash by filtration; and, after evaporation, to determine its weight. In this way,

13.125 grains of crystallized ferroproussiate of potash afford 12.33 grains of nitre, which contain 5.8 of potash.* By heating nitric acid in excess on 21 grains of ferroproussiate of lead, I obtained 2.625 grains of peroxide of iron, equivalent to 1.8375 of the metal. Hence I infer, that the iron in the ferroproussiate of lead is in the metallic state; for the joint weights of the carbon and azote contained in 7 grains of the dry acid is 5.0477; and the difference, 1.9523, approaches too closely to the above quantity, 1.8375, for us to suppose the metal to be in the state of protoxide. In fact, 2.625 parts of peroxide $\times 0.9 = 2.3625$ of protoxide, is a quantity much beyond what experiment shows to be present.

* By careful desiccation, 1.69 grains of water, may be separated from 13.125 grains of the salt.

Horizontal Section.

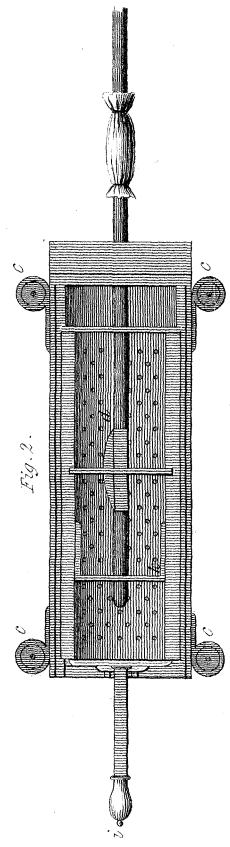


Fig. 3.

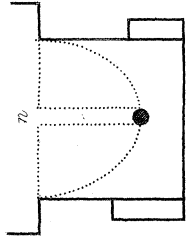


Fig. 4.



Side Elevation.

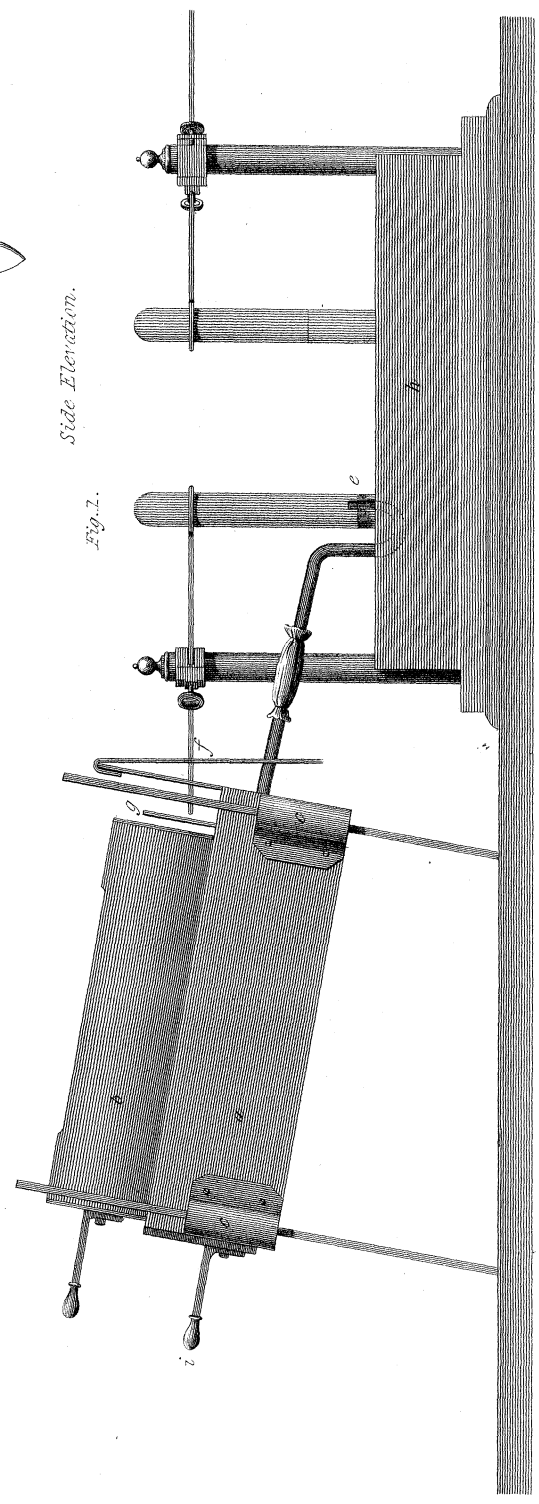


Fig. 2.