

XXIII. *Experiments on the Alcohol of Sulphur, or Sulphuret of Carbon.* By J. Berzelius, M. D. F. R. S. Professor of Chemistry at Stockholm; and Alexander Marcet, M. D. F. R. S. one of the Physicians to Guy's Hospital.

Read May 13, 1813.

THERE has been, of late years, much discussion respecting the nature of a singular oily liquid, which was first noticed by Mr. LAMPADIUS,\* who procured it by distillation from a mixture of pyrites and charcoal, and gave it the name of *alcohol of sulphur*, on account of its very great volatility.

LAMPADIUS considered this liquid as a compound of sulphur and hydrogen; but Messrs. CLEMENT and DESORMES,† who obtained the same substance by subliming sulphur through red hot charcoal, were led by their researches to conclude, that the alcohol of sulphur was a combination of sulphur and charcoal, and that hydrogen was not one of its constituent principles.

Doubts, however, were entertained respecting the chemical nature of this compound. Mr. BERTHOLLET believed it to be a triple combination of sulphur, charcoal, and hydrogen.‡ Messrs. VAUQUELIN and ROBQUET,§ from a joint enquiry on the subject, considered it as a binary compound of sulphur and

\* CRELL'S Annals, 1796. II.

† Annales de Chimie, An. X. Vol. XLII. p. 121.

‡ Ibid. p. 286.

§ Ibid. Vol. LXI. p. 145.

hydrogen; and the late Mr. BERTHOLLET, jun.\* who resumed the subject, with much apparent accuracy, was induced, from his experiments, to adopt the last mentioned opinion, that the alcohol of sulphur was a compound of sulphur and hydrogen, and that no carbon entered into its formation.

Sir HUMPHRY DAVY, in the course of his brilliant career of chemical discovery, has repeatedly noticed this singular substance;† but it does not appear that he ever examined it minutely, and if he gave the preference to the opinion of the younger Mr. BERTHOLLET, respecting its chemical nature, it was principally from the circumstance of its having apparently yielded sulphuretted hydrogen by the agency of the Voltaic electricity, and sulphureous and sulphuric acid by combustion in oxygen.

These varieties of opinions, amongst such respectable authorities, having left on our minds much doubt and uncertainty with regard to the real nature of this compound, we undertook to examine it conjointly; in hopes that we might succeed in ascertaining its composition with a greater degree of certainty than our predecessors had done, and perhaps also in discovering the exact proportions of the elements of which it is composed, a circumstance which, in the present state of chemical science, would add considerable interest to an enquiry of this kind.‡

\* *Mémoires d'Arcueil*, Vol. I.; and *Annales de Chimie*, Vol. LXI. p. 127.

† *Phil. Trans.* 1809, page 464; and *Elements of Chemical Philosophy*, page 283 and 310.

‡ This enquiry was undertaken in London, in the months of July, August, and September, during Mr. BERZELIUS's stay in this country; and the leading points of the analysis were then ascertained, and mentioned to our chemical friends. Some parts of the work, however, and in particular the precise determination of proportions, remained to be completed; and this has been accomplished by Professor BERZELIUS

Whilst we were finishing this paper, and arranging our materials, in order to present them to the Royal Society, the *Annales de Chimie*, for the month of September last, reached this country, by which it appears that the alcohol of sulphur has recently been again submitted to examination in France, by Mr. CLUZEL, who supposed it to be a compound of sulphur, carbon, hydrogen, and azote.\* But MESSRS. BERTHOLLET, THENARD, and VAUQUELIN, the reporters of these experiments, have repeated them, and by a process of their own, quite different from the methods which we have employed, these celebrated chemists have revived the opinion of CLEMENT and DESORMES, that the alcohol of sulphur is a compound of sulphur and carbon, in the proportion of about eighty-five parts of the former to fifteen parts of the latter, no hydrogen entering into its composition. How near this conclusion agrees with our own, will be seen in the following pages.

Although some of the experiments on this substance which we are going to relate, have already been performed by others, yet as we have, in several instances, obtained different results, and as any considerable omission would interrupt the thread of our narrative, we shall beg leave to lay before the Society a complete, though concise, account of our analysis.

We shall, for the sake of arrangement, class the particulars of our enquiry under four heads: viz. 1. *Preparation and general*

since his return to Stockholm. There are also some important collateral objects, which are almost entirely his own, and which, together with his remarks on determinate proportions, have been added to the paper in the form of an appendix. (Note of Dr. MARCET.)

\* It appears that Mr. CLUZEL considered the sulphur in this oil, as being in a de-oxydated state, an idea which had some years ago occurred to one of us, and also to Sir H. DAVY. See *Phil. Trans.* for 1809, p. 465.

*properties of the Alcohol of Sulphur. 2. Experiments to ascertain whether Hydrogen be present in the Alcohol of Sulphur. 3. Experiments to ascertain the presence of Carbon. 4. Experiments to ascertain the proportions of the elements of the Alcohol of Sulphur.* And the Appendix will contain various elucidations and collateral objects.

§ 1. *Preparation and general Properties of the Alcohol of Sulphur.*

We prepared this substance according to the method pointed out by CLEMENT and DESORMES, that is, by slowly volatilizing sulphur through red hot charcoal in a porcelain tube, and condensing in water the oily liquid which is thus formed. The details of the process have so often been described elsewhere, that it would be superfluous to repeat them here. The fluid thus procured is of a pale yellow colour; being extremely volatile, it produces a remarkable degree of cold during its evaporation, and deposits in a crystalline form, some sulphur which it held in solution. The quantity of sulphur thus dissolved in the oily liquor, varies according to the circumstances of the process by which it is obtained;\* and its specific gravity, before it has been rectified, must, of course, be liable to corresponding variations.†

In order to obtain the alcohol of sulphur perfectly pure, it is only necessary to distill it at a very gentle heat, not exceeding  $100^{\circ}$  or  $110^{\circ}$ ; and some dry muriate of lime may be put into the retort, in order to obtain the liquor perfectly free from moisture. The fluid which comes over is quite pure, and some sulphur remains in the retort.

\* The alcohol of sulphur can dissolve as much as  $\frac{1}{3}$  of its weight of sulphur.

† We ascertained the specific gravity of only one specimen of the impure oily liquor, which proved to be 1,321.

The alcohol of sulphur thus prepared has the following properties: it is eminently transparent, and perfectly colourless. Sometimes, immediately after distillation, the oily liquid appears somewhat opaque and milky; but the next day the liquor is found perfectly clear, the milky appearance having spontaneously disappeared. It has an acrid, pungent, and somewhat aromatic taste; its smell is nauseous and fetid, though distinctly differing from that of sulphuretted hydrogen. Its specific weight is 1,272; its refractive power, as ascertained by Dr. WOLLASTON, is 1,645. Its expansive force (the height of the barometer being thirty inches, and the temperature 53,5° FAHRENHEIT) is equal to the pressure of 7,36 inches of mercury; so that air, to which it is admitted, will dilate about one-fourth of its volume. It boils briskly under the common atmospheric pressure at a temperature between 105° and 110°.\* It does not congeal at a temperature as low as 60° below zero of FAHRENHEIT'S scale. It is highly inflammable, and takes fire at a temperature scarcely exceeding that at which mercury boils; it burns with a bluish flame, emitting copious fumes of sulphureous acid. If a long glass tube, open at both ends, be held over the flame, care being taken to keep the tube quite cold, no moisture whatever is deposited on its internal surface.

This oily liquid readily dissolves in alcohol and ether, † though not in all proportions; and if it contain sulphur in solution, the

\* The volatility of this liquid is very remarkable; it exceeds considerably that of ether; and in some experiments, tried since this paper was presented to the Society, on its power of producing cold by evaporation, some unexpected results have been obtained, which may, perhaps, become the subject of some future communication.

† Ether can dissolve about three times its own bulk of the oily liquor before any separation or turbidness takes place.

latter is rapidly precipitated in spicular crystals. The spirituous solution is rendered turbid, and the oily liquor precipitated by the addition of water. The alcohol of sulphur is not soluble in water, though it imparts to it some of its odour; this appears to be owing to its impregnating the atmospheric air contained in the water, rather than the water itself. It readily mixes, and perfectly incorporates with either the fixed or volatile oils; but if it hold sulphur in solution, the latter separates in a crystalline form. It dissolves camphor very rapidly, and forms with it perfectly transparent solutions. When kept for some time under water, the latter being in contact with atmospheric air, neither the air, nor the oily liquid, suffer any alteration. On being heated in contact with potassium, the alcohol of sulphur suffers no change or decomposition, when in its liquid state; but if it be brought to the state of vapour, by the exclusion of the air, and heat applied, the potassium becomes ignited in the vapour, and emits a reddish flame. During this species of combustion, a blackish film appears upon the potassium, (as happens when potassium is burnt in carbonic acid gas), and on introducing water, a greenish solution is obtained, which contains a quantity of carbonaceous matter, and has the smell and other properties of *hepar sulphuris*. Neither mercury nor amalgams of silver, or of lead, are at all acted upon by this liquor, if it has been carefully distilled; but if it contain any sulphur in solution, the amalgam blackens, and sulphurets of silver, or of lead, are produced, after which the liquor remains pure, and unsusceptible of further alteration. Mercury heated to ebullition in an atmosphere of this oil, comes over unaltered, and without the liquor undergoing any change. The alkalis dissolve it entirely, though but very slowly. None of the

acids exert any sensible action upon this liquor, except the nitro-muriatic acid, and oxy-muriatic gas in a humid state. If a globule of the alcohol of sulphur be brought into contact, under water, with a globule of the oily fulminating compound, lately described to this Society by Sir H. DAVY, the two globules remain in contact, side by side, without mixing, and without exerting any action upon each other; but when stirred together, they incorporate, forming a homogeneous amber-coloured globule, which does not detonate, even when exposed to ignition; and if olive oil be brought into contact with the two oils thus mixed, no detonation or other obvious effect takes place, a remarkable circumstance, of which advantage might be taken to attempt the analysis of the fulminating substance. The detonation of the fulminating compound with phosphorus, is also prevented by the presence of alcohol of sulphur; but if the quantity of the detonating compound preponderates over that of either the olive oil or phosphorus, the mixture inflames, though without detonation.\*

§ 2. *Experiments to ascertain whether Hydrogen be present in the Alcohol of Sulphur.*

1. We introduced into Volta's eudiometrical tube, over mercury, some pure oxygen gas, with one drop of the oily liquor. After letting these stand together for a few minutes, an electrical charge was passed through the tube, which produced a vivid explosion. The gas was first reduced to between one-

\* These experiments were tried in the presence of one of us, by Mr. WILSON, Assistant to the Chemical Lectures of GUY'S Hospital, who, conjointly with two other gentlemen, has lately published in NICHOLSON'S Journal, many curious facts on this extraordinary compound.

fifth and one-sixth of its volume, a circumstance which appeared to be owing to the destruction of the volatilized portion of the liquor; for the gas soon afterwards recovered its former volume. On examining the superior part of the tube, we perceived traces of a condensed liquid. Whether this liquid was concentrated sulphuric acid, or simply a small portion of the oily liquor, remained to be determined. We repeated the experiment in the following manner.

A quantity of the oily liquor was suffered to evaporate in oxygen gas of known purity, and previously dried with muriate of lime. Some of this gas was introduced into the eudiometer, and exploded by the electrical spark. It lost between one-fifth and one-sixth of its volume; but we perceived, even then, traces of a condensed liquid in the superior part of the eudiometer. This liquid, in about a quarter of an hour, became opaque, and ultimately formed white specks, which we found to be sulphate of mercury. No oxygen gas remained in the tube after the explosion; but the gaseous residue consisted of sulphureous acid gas, and, as we shall see afterwards, of the carbonic acid, and the carbonic oxyd gases. This experiment having still left undetermined, whether the vestige of liquid we had observed, was or was not to be ascribed to the formation of water, we tried to decide this point by means of oxymuriatic gas, in the following manner.\*

2. We caused a succession of bubbles of oxymuriatic gas,

\* In relating the experiments in which oxymuriatic gas (or chlorine) is concerned, we have used the old nomenclature, and have explained the phenomena according to the notions, respecting the nature of this agent, which prevailed previous to Sir H. DAVY's ingenious experiments and speculations on the subject. But those who consider his views, as sufficiently established to supersede entirely the old hypothesis, may easily adapt to our statements the language which belongs to the new doctrine.



previously dried by muriate of lime, to pass through a portion of the alcohol of sulphur, and afterwards through a quantity of distilled water, over which it was collected. The oily liquid suffered no other change than that of acquiring an orange hue. After an hour and a half the process was stopped, and the liquor was found to have absorbed a considerable quantity of the gas, which had imparted to it a peculiar and extremely strong odour. Most of the gas, however, had passed through the water, in which it had deposited a portion of the oily liquid unaltered. The water had acquired a peculiar smell, and contained, after the expulsion of the oxymuriatic gas, a little muriatic acid, with a vestige of sulphuric acid. Here again it remained doubtful, whether the production of muriatic acid was owing to the alcohol of sulphur containing hydrogen, which, by uniting with the oxygen of the oxymuriatic acid, had formed water; or whether this appearance of minute quantities of muriatic and sulphuric acid, might not be explained in some other manner. It will hereafter be seen how the last conjecture was verified; but in the mean time it was sufficiently shewn, by the experiment just related, that if the alcohol of sulphur really contain hydrogen, it must be in very small quantity, and probably from some accidental circumstance, since the greater part of the liquor remained undecomposed, and with no other alteration than the absorption of the oxymuriatic gas. In the course of a few days, however, the oil gradually lost the smell of this gas, and acquired that of the muriated sulphur, described by Dr. THOMSON, (Sir H. DAVY'S sulphurane). The liquor thus treated, on being exposed to the action of water, lost its colour, and resumed its original

characters; and this was accomplished more quickly, if the water contained some alkaline substance.

3. Into a glass receiver, full of oxymuriatic gas, we immersed some of the oily liquor previously ignited in the air; it was instantly extinguished, and appeared to undergo no change, except that of absorbing a little oxymuriatic acid, and thereby acquiring a yellow colour.

4. A portion of the oily liquor, in the state of vapour, was caused to pass through liquified muriate of silver heated to a cherry red, and to condense again into a small receiver artificially cooled; neither the liquor, nor the muriate of silver, were altered by that operation, nor did the air contained in the apparatus appear, on examination, to contain the smallest quantity of acid. This shewed that the liquor did not contain any hydrogen, since if it had, the muriate of silver would have been decomposed, the hydrogen uniting with the oxygen to form water, so as to generate muriatic acid gas (which may be considered as a muriate of water, or more correctly a muriate of hydrogen), whilst some sulphuret of silver would have been produced.

5. Though the result just related appeared sufficiently conclusive, we thought it desirable to have it confirmed by some other mode of proceeding. With this view, we heated to incipient redness, in glass tubes, various metallic oxyds, such as red oxyd of iron, black oxyd of manganese, oxyd of tin; and we caused quantities of the oily liquor in vapour to pass through these ignited oxyds. The liquor was, by that means, entirely decomposed; the metallic oxyds were converted into sulphurets, and the gases acquired a strong smell of sulphureous

acid. But we could not, in any of our experiments, detect the least production of water, although our apparatus was so devised, as to render the smallest quantity of water conspicuous, and although we burnt, in some instances, as much as fifty or sixty grains of the liquor.

From all these experiments, we think ourselves warranted in concluding, that *the alcohol of sulphur contains no hydrogen.*

§ III. *Experiments to ascertain the presence of Carbon in the Alcohol of Sulphur.*

1. The gaseous residue obtained from the combustion of the vapour of the alcohol of sulphur in oxygen gas, by means of VOLTA'S eudiometer (§ II. 1.), being put in contact with water, was in a great degree absorbed, and the water acquired the taste and smell of sulphureous acid. The remaining gas being agitated with lime water was partly absorbed, and produced a precipitate of carbonate of lime. The unabsorbed portion being mixed with oxygen gas, and the electrical spark passed through the mixed gases, they detonated, and the remaining elastic fluid was found to have again acquired by this detonation the property of rendering lime water turbid, and of forming carbonate of lime. The residue of the first detonation was therefore gaseous oxyd of carbon.

2. We introduced into a glass receiver, filled with pure oxygen gas, and inverted over mercury, a small glass capsule full of the oily substance, which we kindled in the air before we plunged it into the gas. It continued to burn, and we were not a little surprised to find, that the heat of this combustion was sufficiently intense to melt a pretty strong platina wire, by which the capsule was suspended, so that it fell with its

contents upon the surface of the mercury, where the oily liquor continued to burn until it was all consumed. Water being then introduced, an absorption of gas took place, and the water became sulphureous. The unabsorbed portion of gas being introduced into lime water, rendered it turbid, and formed a quantity of carbonate of lime, which was sufficient to be carefully examined and accurately estimated.

3. We caused some alcohol of sulphur to dissolve in barytic water, in a well stoppered bottle. This solution proceeded very slowly, and was only completed at the end of three weeks. The barytic water had assumed a yellowish colour, and had deposited a white precipitate, which being well washed, and treated with liquid sulphureous acid, dissolved in it with effervescence. It was therefore carbonate of barytes.

4. A similar experiment being tried with lime water, an analogous result was obtained.

It follows from these experiments, that *the alcohol of sulphur contains carbon*, and therefore that this body, the nature of which has been the subject of so much doubt and speculation, is a true SULPHURET OF CARBON, a name by which, in compliance to the received chemical nomenclature, we shall henceforth usually designate it in the course of this paper.

#### § IV. *Experiments to determine the Proportions of Sulphur and Carbon, in the Sulphuret of Carbon.*

In attempting to analyse, with accuracy, the sulphuret of carbon, considerable difficulties occur from the great volatility of that compound, and from the inconsiderable action which most chemical agents exert upon it.

1. We first tried to ascertain the proportion of its constitu-

ent parts, by exploding it, in a state of vapour, with oxygen gas, in Volta's eudiometer; but this method presented insurmountable obstacles, and in particular that of our not being able to determine, with accuracy, the quantity of the oily substance actually decomposed by that process.

2. On the other hand, on attempting simply to burn in oxygen gas the sulphuret of carbon in its liquid state, the necessity of previously kindling it in the air, in order to avoid explosions, prevented our being able to ascertain, with accuracy, the quantity of the oily substance submitted to the experiment.

3. We also attempted the oxydation of the sulphuret of carbon by nitro-muriatic acid; but we obtained by this method, as we shall see afterwards, results and combinations which were quite different from those which we had expected.\*

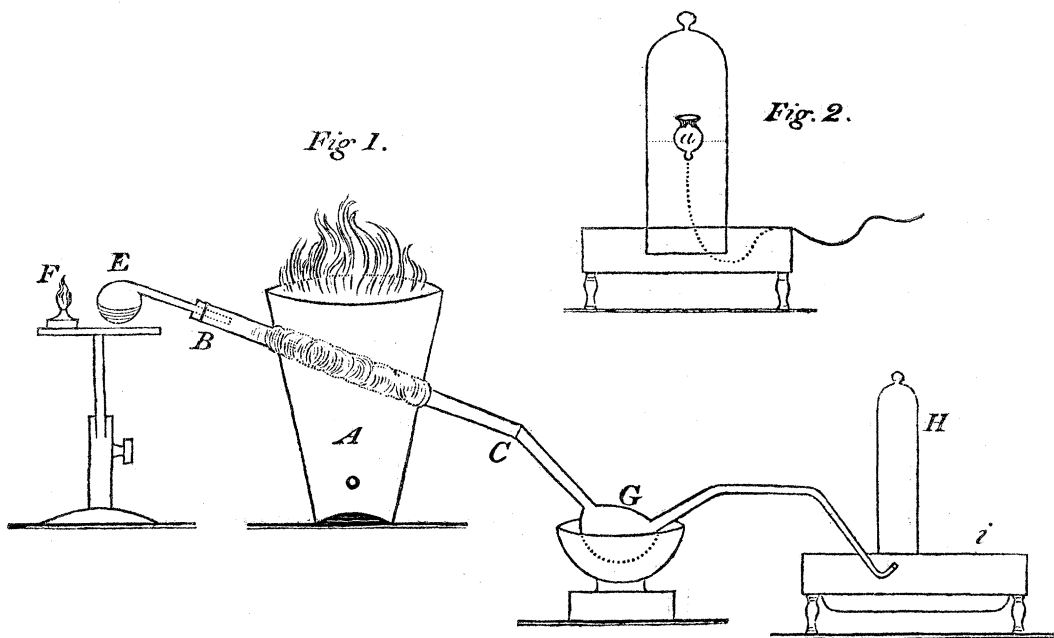
4. We then had recourse to the action of alkaline substances on the sulphuret of carbon, with a view to produce an alkaline sulphuret, and afterwards to convert this into a sulphate by means of nitro-muriatic acid. The sulphuric acid, precipitated by a barytic salt, was ultimately expected to indicate the quantity of sulphur contained in the oily compound. In order to try this method, we exposed portions of the sulphuret of carbon to the action of caustic potash, ammonia, barytic water, &c. and when the solutions appeared to be completed, we tried the effect of acids upon them; these separated from them a soft, reddish, glutinous substance, which, when exposed to distillation, yielded, first, a portion of the oily liquor undecomposed, and afterwards sulphur; thus shewing that the

\* A new and singular compound was obtained from the long continued action of nitro-muriatic acid on the alcohol of sulphur, the history and composition of which will be detailed in the Appendix.

whole of the sulphuret of carbon had not been decomposed. A black powder remained in the retort, which was found to be charcoal, and afforded us a new and unequivocal proof of the presence of carbon in the oily substance.

This imperfect decomposition of the sulphuret of carbon in alkaline solutions, was found an insurmountable objection to this mode of analysis; and induced us to try the method of distilling the sulphuret through ignited metallic oxyds.

5. For this purpose, we introduced a glass tube (BC), in an inclined direction, through a small stove (fig. 1, A), the



tube being protected by lute, and filled with red oxyd of iron coarsely pulverized. The sulphuret of carbon, after being accurately weighed, was enclosed in a little retort (E), which we hermetically sealed to the upper extremity of the tube (B). To the other extremity (C), we adapted another glass tube

(CGI), terminating in a mercurial pneumatic apparatus (H), and having a bulb or expansion (in G), at about half way between its extremities, which bulb was cooled down to about 15° FAHRENHEIT, and kept at that temperature during the experiment by means of a mixture of ice and salt. The tube in the stove (BC) being now heated to redness, and an extremely gentle degree of heat applied to the retort, the oily liquor distilled slowly through the red hot oxyd of iron, and the whole of the experiment succeeded in a most satisfactory manner; for we found that the joints of the apparatus had remained perfectly tight during the process, and every vestige of the sulphuret of carbon had been decomposed.\* We could not perceive in the bulb the least appearance of moisture.

6. The oxyd of iron (the whole weight of which was about ten times that of the oil decomposed), was partly converted into sulphuret of iron, having a yellow colour and a brilliant metallic lustre. This sulphuret was dissolved by nitro-muriatic acid, and the oxyd of iron was separated by ammonia. The filtered liquid, being neutralized by muriatic acid, was precipitated by muriate of barytes, and the precipitate was well washed, and heated to redness.

7. During the process of decomposition above related, the mixture of sulphureous acid gas and carbonic acid gas had collected in the receiver (H) placed on the extremity of the

\* The process was so slowly conducted, that it required six hours and a half for the decomposition of about fifteen grains of the oil. The heat applied to the retort was merely that which radiated from a small lamp (F), placed at some distance from it, a screen being interposed between the furnace and the retort. In several previous trials, we had failed from not being sufficiently cautious and gradual in the mode of warming the retort.

tube. In order to separate these two gases from each other, we made use of the brown oxyd of lead, a substance which one of us had often employed for the purpose of combining with, and separating from other bodies, liquid sulphureous acid, with which that oxyd forms a neutral sulphate. The same method, to our great satisfaction, succeeded perfectly with the gaseous sulphureous acid. After a contact of about one hour, between the brown oxyd of lead and our mixed gases, the whole of the sulphureous acid gas was so completely absorbed, that the carbonic acid gas which remained in the vessel, had not the least sulphureous smell, and yet the carbonic acid itself remained perfectly unaltered in its bulk, after continuing in contact with the oxyd of lead for the space of three days.\*

8. The mode in which the respective weight of the two acids was ascertained was this; the oxyd of lead was placed in a small glass capsule (*a*, fig. 2), the orifice of which was carefully secured, by means of a thin piece of glove-leather, against the admission of quicksilver. A very thin flexible metallic wire was fastened to the capsule, so as to enable the operator to raise it through the mercury in the receiver containing the gases, as is expressed in the figure (fig. 2). After continuing the contact for several hours, and when the absorption had

\* The brown oxyd of lead, used in our experiments, was recently prepared, and had been long digested in weak nitric acid. In wiping this oxyd, and pressing the moisture out of it, we found it expedient to reduce it to the state of small laminæ, as in this form it is more easily penetrated by the acid gas than in the state of powder. It may be proper to remark, that when, for the sake of trial, gaseous mixtures, consisting of sulphureous acid gas and sulphuret of carbon in vapour, were used, the latter, as the absorption of the acid gas proceeded, was deposited in its liquid state upon the oxyd of lead.



ceased for a considerable time, the capsule was withdrawn, and another similar capsule filled with dry caustic potash (hydrate of potash), was introduced in a similar manner. The remaining gas (with the exception of a small residue),\* was immediately absorbed. Both capsules, after wiping off minute particles of quicksilver which adhered to their surface, were carefully weighed and were found to have undergone an increase of weight, which, of course, expressed the quantity of acid they had respectively absorbed. By combining these results with the examination above described (§ IV. 6.), of the sulphuret of iron found in the tube, the proportions of sulphur and carbon were deduced. Two such experiments were made which yielded very similar results; and by a mode of computation, which will be detailed in the Appendix, we were led to conclude that the alcohol of sulphur, or sulphuret of carbon consists of

Sulphur	-	84,83	or	100,00
Carbon	-	15,17		17,89.

If these proportions be compared with the numbers 13 and 5, which are assumed by Mr. DALTON as representing the respective weights of a particle of sulphur and a particle of carbon; or with those of 30 and 11,4, which are considered by Sir HUMPHRY DAVY as representing the same substances, we shall find that either of these modes of computation, as well as that detailed in the Appendix, make the above-mentioned proportions of sulphur and carbon, in the alcohol of sulphur, correspond very nearly to two atoms or portions of sulphur, to one of carbon; a result which is perfectly agreeable to the doctrine of determinate proportions. And as the

\* This small residue corresponded almost exactly to the quantity of air expelled from the tube in which the decomposition had been performed.

sulphur and carbon recovered by our analysis, were precisely equal in weight to the sulphuret of carbon subjected to examination, we are the more confident in believing that it does not contain any other element.

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## APPENDIX BY PROFESSOR BERZELIUS.

*A. Particulars respecting the Mode in which the Proportions of Sulphur and Carbon, in the Alcohol of Sulphur, were established.*

Two analytical experiments were made in succession, in the manner described in the paper (§ IV.), with the following results.

*Exp. 1.* 1,05 parts \* of sulphuret of carbon produced 0,24 parts of sulphureous acid gas, and 0,59 parts of carbonic acid. The sulphuret of iron found in the tube was dissolved in nitromuriatic acid; the oxyd of iron was precipitated from this solution by caustic ammonia in excess, and the filtered liquor was neutralized by muriatic acid. From this solution, muriate of barytes precipitated a quantity of sulphate of barytes, which, after ignition, weighed 5,6. From Mr. T. DE SAUSSURE'S experiments, as well as from inference from the doctrine of determinate proportions, 100 parts of carbonic acid contain from 27 to 27,1 parts of carbon. Therefore the above mentioned 0,59 parts of carbonic acid contain 0,1593 of carbon. From the experiments on the composition of sulphate of barytes, published by myself, 100 parts of that salt contain 13,66 of

\* The weights represented by these numbers were *grammes*; so that the quantity of sulphuret of carbon employed in this experiment, was 1,05 gramme, corresponding to about  $15\frac{1}{2}$  English grains.

sulphur; therefore the 5,6 parts of sulphate of barytes, are equivalent to 0,765 of sulphur, which, added to the 0,1224 parts of sulphur contained in the 0,24 parts of sulphureous acid gas, make 88,74 parts of sulphur. The sum total of sulphur and carbon is, therefore,  $88,74 + 15,93 = 104,67$ . But the quantity of the sulphur of carbon was 105 parts; consequently there is a loss of  $\frac{1}{3}$  per cent. From this experiment therefore, the sulphuret of carbon is composed of 15,7 parts of carbon to 84,83 parts of sulphur.

*Exp. 2.* 1,175 parts of sulphuret of carbon produced 0,66 of carbonic acid gas, = 0,1782 parts (which is equivalent to 15,167 per cent.) of carbon; and 0,271 parts of sulphureous acid gas = 0,138 of sulphur. In the superior extremity of the glass tube which contained the oxyd of iron, there was found, in that part of the tube which projected out of the stove, a small portion of sublimed sulphur weighing 0,029. The sulphuret of iron found in the tube afforded, by the mode of estimation above related, 6,06 parts of ignited sulphate of barytes = 0,829 of sulphur; therefore the sum total of sulphur is  $0,829 + 0,29 + 0,138 = 0,996$  parts of sulphur, which added to 0,1782 parts of carbon, makes 1,1742 parts, or 0,0008 less than the weight of the sulphuret of carbon employed in the analysis.

*B. Comparison of the above Proportions of Sulphur and Carbon, in the Sulphuret of Carbon, with those which might be inferred from the laws of determinate Proportions.*

The law respecting the combination of combustibile bodies between themselves, is that, *when two such bodies unite, the proportion in which this combination takes place is such, that if they*

be oxydated to a certain degree, they will either absorb an equal quantity of oxygen, or the one will absorb two, three, four, &c. times as much oxygen as the other. As to the metallic sulphurets in general, those which are called sulphurets *at the minimum*, are so composed that the sulphur requires twice as much oxygen in order to become sulphureous acid, or three times as much in order to become sulphuric acid, as the metallic body requires to become an oxyd or saline basis; and it is on that account, that the sulphurets in minimum produce, by their oxydation, neutral sulphites, or sulphates. Now, by comparing the quantities of oxygen required to convert the sulphur into sulphureous acid, and the carbon into carbonic acid, it appears that the first quantity is twice as great as the latter. The small difference is to be ascribed to the impossibility of obtaining perfectly accurate results in analytical processes so complicated as this; and therefore the sulphuret of carbon may be considered as constituted according to the same law as the other sulphurets; so that the sulphur which it contains requires twice as much oxygen to become sulphureous acid, as the carbon requires to become carbonic acid. Admitting, therefore, that the above views of the composition of those two acids are correct, the sulphuret of carbon would consist of 15,47 parts of carbon, to 84,53 parts of sulphur; and in that case the result of our analysis of the alcohol of sulphur would only differ by  $\frac{1}{3}$  per cent. from the proportions obtained by that mode of estimation.

### C. *Observations on the atomic doctrine of chemical Combination.*

Mr. DALTON has lately proposed a mode of viewing the subject of determinate proportions, which is distinguished by

its extreme simplicity. From that ingenious mode of expressing combinations, the sulphuret of carbon ought to consist of two atoms of sulphur to one of carbon, since, according to that system, both the sulphureous and carbonic acids are composed of two atoms of oxygen to one of radical. But it is probable, that the gaseous oxyd of carbon consists of two atoms of carbon to one of oxygen, because the quantity of carbon required to convert carbonic acid into carbonic oxyd, exactly doubles the volume of the acid. In this case, and if, according to Mr. DALTON's supposition, sulphureous acid consists of two atoms of oxygen to one of sulphur, the alcohol of sulphur would be, like all the other sulphurets at the minimum, composed of one atom of sulphur to one of carbon.

Sir H. DAVY, in his Elements of Chemical Philosophy, adopts, like Mr. DALTON, the idea that sulphureous acid gas consists of one portion of sulphur to two of oxygen; and agreeably to this, he supposes for instance that the sulphurets of copper, or of silver, are composed of one portion of sulphur to one of the metal. But on the other hand, he considers other sulphurets, such as those of antimony, of iron, and of lead, as consisting of two portions of sulphur to one of the metal, and the sulphuret of zinc would, according to his views, be composed of two portions of the metal to one of sulphur. Yet, notwithstanding this great diversity in the estimation of proportions, all these sulphurets are so constituted that, if the compound be fully oxydated, it remains in a state of perfect saturation. The cause of these apparent inconsistencies seems to be, that the supposed atom, or ultimate particle, or that which is to be regarded as the single portion of a body, requires to be fixed according to some determinate law, before Mr. DALTON's

ingenious method of expressing the proportions in which bodies combine, can be applied with certainty and precision.\*

D. *Experiments on the Combination of the Sulphuret of Carbon, with the Alkalies, the Earths, and the metallic Oxyds.*

The following experiments will shew in an unequivocal manner, that the sulphuret of carbon is capable of combining with saline bases. These combinations constitute a new class of bodies, for which there is no name in our present chemical nomenclature. I shall propose to call them *carbosulphurets*, a name quite consonant with the principles of the received chemical nomenclature.

The unavoidable presence of water, in either caustic potash or soda, induced me to try, in the first instance, the action of ammoniacal gas on the sulphuret of carbon.

*Carbosulphuret of Ammonia.* Some ammoniacal gas, and some liquid sulphuret of carbon were successively introduced into a receiver filled with mercury, the sulphuret being enclosed in a small glass bulb having an open orifice. The first effect of this contact was a dilatation of the gas; the surface of the sulphuret soon covered itself with a pulverulent straw-coloured substance, as if a portion of sulphur had been precipitated. After a few hours, the gaseous mixture had sensibly

\* It appears to me that the best way to form a system of definite proportions, and to make it harmonize with the general views of chemistry, would be to take oxygen as the base of the scale, because most chemical combinations turn upon the proportion of that ingredient; and as gaseous bodies unite in equal or multiple volumes, I would consider as *the atom* of any other gas, the proportional weight of an equal measure of that gas.

diminished in bulk, and as this diminution proceeded, the gas gradually deposited on the surface of the glass a saline yellowish substance, which did not exhibit, even with the aid of a microscope, the least appearance of crystallization. The mercury having at last filled the receiver, an additional portion of ammoniacal gas was introduced, and this was repeated till no further absorption took place. The whole of the sulphuret of carbon was then found converted into the yellowish uncrystallized matter just described. This substance had a strong smell of ammonia, and was so deliquescent that it could not be transferred from one vessel into another, without undergoing an obvious alteration. The solution of this substance in water is first red, but it very soon passes to a deep orange colour, shewing that it undergoes a partial decomposition; and if it be distilled in its solid, though humid state, it sublimes and deposits small shining crystals of hydrosulphuret of ammonia; whilst, on the contrary, if it be heated in the same vessel in which it is formed, that is, without any access of air or moisture, the carbosulphuret of ammonia sublimes unchanged, from one part of the vessel to the other, and no vestige of hydrosulphuret is perceived. It appears therefore, that the sulphuret of carbon can enter into combination with pure ammonia without depositing its carbon; but if moisture or air be admitted, an alkaline hydrosulphuret, or sulphuret is formed, and carbonic acid is generated.

*Carbosulphuret of lime.* If some pure quick lime be heated in a glass tube, by means of a lamp, and some sulphuret of carbon in vapour be made to pass through the heated earth, the latter becomes ignited at the moment the vapour comes into contact with it, and this ignition continues till the earth is

saturated. During this process, none of the sulphuret of carbon escapes, the whole of it being absorbed by the lime. The earth, at its surface, is found yellowish, owing to the formation of a little sulphuret of lime, but this appearance ceases on removing the surface, shewing that it arises from the contact of air. The earthy mass is tasteless, when first applied to the tongue, but a bitter taste, with a smell of sulphuretted hydrogen are soon perceived. It is no longer susceptible of being heated or dissolved by water. If digested with water in close vessels, a solution of hydrosulphuret of lime is obtained, and the undissolved portion is mostly found to be carbonate of lime.

*Carbosulphurets of barytes and strontian* may be produced in a similar manner, and are found to possess analogous properties.

There can be no doubt but that the two fixed alkalies, in a state of perfect dryness, would form, with the sulphuret of carbon, *carbosulphurets of potash and soda*, quite analogous to those just described; but as these alkalies cannot be obtained in an anhydral state, I could only examine their action on the sulphuret of carbon when in a state of solution. The general result of these trials was, that if a quantity of the sulphuret of carbon be long digested, at a very gentle heat, with a solution of caustic potash, the sulphuret of carbon is decomposed, and the mixture resolves itself into a hydrosulphuret, and carbosulphuret, and a carbonate of potash.

In the same manner, if sulphuret of carbon be long digested with liquid caustic ammonia, it dissolves very slowly, forming an orange coloured solution analogous to that in caustic potash just described.



I tried also to produce *carbosulphurets of metallic oxyds*. The process simply consisted in precipitating metallic solutions, by solutions of the sulphuret of carbon in caustic potash. The precipitates which were thus obtained, had characters sufficiently distinct to shew that they were chiefly metallic carbosulphurets; but as the presence of a hydrosulphuret, and of carbonate of potash, in the solutions used for these precipitations, necessarily interfered with the distinctness of the results, I shall not trouble the Society with a detail of these experiments.

E. *Experiments to determine the nature of a particular Substance, produced by the action of nitro-muriatic Acid, on the Sulphuret of Carbon.*

We have already alluded, Dr. MARCET and myself, in the course of our paper, to a new and singular substance, which we produced by the long continued action of nitro-muriatic acid on the sulphuret of carbon. This compound was discovered in the following manner.

A portion of sulphuret of carbon was exposed to the action of a mixture of fuming nitric acid with concentrated muriatic acid. The acid instantly acquired a peculiar odour resembling that of muriated sulphur. Upon trying to promote the combination by applying heat, the sulphuret of carbon was expelled in the form of vapour, which obliged us to leave the mixture to its own spontaneous action, under the temperature of the atmosphere, which was then at least 70°.\* The sulphuret of carbon soon passed to a reddish orange colour, which it communicated to the acid; and during this change,

\* In August, 1812.

nitrous gas, with a strong smell of muriated sulphur, was slowly evolved. After the space of a week, the liquor began to cover itself with a white crystalline substance, losing at the same time its colour. On stirring the mixture, these crystals fell to the bottom, where they were immediately dissolved by the remaining sulphuret of carbon. This, however, in proportion as it saturated itself with the new formed substance, gradually lost its colour, acquired a greater consistence, and at last, at the end of three weeks, it was entirely converted into a solid white crystalline body, having the appearance of camphor.

This substance being separated from the acid, and washed with cold water, presented the following characters: it was colourless; its smell resembled both that of muriated sulphur and of oxyd of osmium; its taste was both acrid and acid; it was very volatile, melted at a gentle heat, and sublimed without residue. In fact, this body very closely resembles camphor in its external properties. It is insoluble in water, but readily dissolves in alcohol and ether, from which it is precipitated by water; it is also soluble in the oils, whether fixed or volatile, with which it forms transparent solutions. The spirituous solution of this substance has a peculiar, disagreeable, and very acid taste. It reddens litmus paper, and dissolves zinc with the disengagement of an extremely fetid gas. From this solution, a spirituous liquor is obtained by distillation, which possesses the same smell, and leaves a residue of muriate and sulphate of zinc. When a pure solution of the peculiar substance in alcohol is submitted to distillation, the products are, first, some sulphureous acid gas, and then alcohol strongly impregnated with muriatic ether; after which the air of the

vessel is found to contain portions of sulphureous and carbonic acid. The peculiar substance, in its dry state, does not alter litmus paper; but it reddens it strongly if the paper be moistened. When exposed to the action of boiling water, this body volatilizes through the water, but the remaining liquor contains some muriatic and a little sulphuric acid. Water, therefore, has the power of decomposing, though very slowly, this substance. Indeed if it be left a long time in contact with a small proportion of water, the liquor becomes strongly acid. Liquid caustic potash assisted by heat, dissolves the peculiar substance without any disengagement of gas. This solution is colourless; when neutralized by sulphuric acid no precipitation takes place from it, which shews that the alkali decomposes the peculiar body. Sulphuric acid, however, produces a slight effervescence, and the liquor exhales a smell of sulphureous acid. On adding to it a solution of sulphate of silver, muriated silver is precipitated,

These results tend to shew, that the substance in question contains sulphur and carbon in combination with oxygen, that is in the state of sulphureous and carbonic acid; for otherwise, some carbon would have been precipitated, or some sulphuret or hydrosulphuret of potash would have been formed.

And again, a portion of the problematic substance being sublimed through ignited lime in a glass tube, it was absorbed by the lime without any vestige of sulphuret of lime being formed, or any carbon deposited. And a similar experiment being tried with ignited metallic iron, instead of lime, some muriate of iron and a sulphuret of oxyd of iron\* were formed, and carbonic acid gas was disengaged. This last

\* *Sulphure d'oxidule de fer.*

experiment in particular shewed clearly that the substance in question contains carbonic acid.

The existence of three acids united in this compound, being thus ascertained, their respective proportions remained to be determined. It was by an experiment similar to the last described, that this object was obtained. The outline of this analysis, a minute detail of which would unnecessarily prolong this communication, was as follows :

A portion of the compound, after being weighed with great accuracy, was sublimed through a tube containing some very fine spiral iron wire in a state of ignition, the weight of which was three times that of the compound submitted to analysis. A decomposition took place, the products of which were, as in the experiment above related, muriate of iron, sulphuret of oxyd of iron, and a mixture of the carbonic oxyd and acid gases. These being carefully examined by appropriate reagents,\* so as to form an estimate of the quantities of the muriatic, sulphureous, and carbonic acids contained in the peculiar compound, the following ultimate result, respecting the nature and proportions of its constituent parts, was obtained, viz.

Muriatic acid	-	-	48,74
Sulphureous acid	-	-	29,63
Carbonic acid (and loss)			<u>21,63</u>
			100,00

\* The proportion of muriatic acid was estimated by dissolving the muriate of iron in water, and precipitating the acid by nitrate of silver ; that of the sulphureous acid was ascertained by treating the sulphuret of iron with nitro-muriatic acid, and precipitating the sulphuric acid formed by muriate of barytes : from the known relation between the sulphureous and sulphuric acid, the quantity of the former was easily deduced. And, lastly, the proportion of carbonic acid was gained by reducing the gaseous mixture to the state of carbonic acid, and absorbing this by caustic potash.

From the mode of computation adopted by Mr. DALTON, this triple acid would be composed of two atoms of muriatic acid, to one of the sulphureous, and one of the carbonic acid. It is a remarkable circumstance that the proportions of sulphur and carbon which prevail in the sulphuret of carbon, no longer obtain in this compound; one of the atoms of sulphur being expelled during the formation of the triple acid, and converted into sulphuric acid, which is found in the nitro-muriatic liquor.

The reason why the combination in question does not take place on burning the sulphuret of carbon in oxymuriatic gas, is that this gas does not yield a sufficient quantity of oxygen to acidify the sulphur and carbon, which are to unite with the muriatic acid, so that either nitric acid must be added, or a portion of muriatic acid must be detached from the oxymuriatic gas, by the agency of water, or of some other oxydated body.

It will be necessary to give a name to this triple acid. The combination of the fluoric with the boracic acid has been called *fluo-boric acid*; but the word *fluo* does not express the degree of acidification of the radical, which would be of great advantage in systematic language. In the Essay on the Latin Chemical Nomenclature, which I published some time ago, I proposed the name of *acidum boracico-fluoricum*. Upon the same principle, the combination, of the muriatic and carbonic acid, discovered by Mr. J. DAVY, would be named *acidum carbonico-muriaticum*; the combination of the sulphureous and muriatic acid (should such a compound be discovered), would be called *acidum sulphuroso-muriaticum*; and our triple acid would be *acidum muriaticum sulphuroso-carbonicum*, a name inconvenient by its length, but perfectly consonant to the principles of Chemical Nomenclature.