XVII. *On the Converſion of a Mixture of dephlogiſticated and phlogiſticated Air into nitrous Acid, by the electric Spark.* By Henry Cavendiſh, *Eſq. F. R. S. and A. S.*

Read April 17, 1788.

IN Volume LXXV. of the Philoſophical Tranſactions, p. 372. I related an experiment, which ſhewed, that by paſſing repeated electric ſparks through a mixture of atmoſpheric and dephlogiſticated air, confined in a bent glaſs tube by columns of ſoap-lees and quickſilver, the air was converted into nitrous acid, which united to the ſoap-lees and formed nitre. But as this experiment has ſince been tried by ſome perſons of diſtinguiſhed ability in ſuch purſuits without ſucceſs, I thought it right to take ſome meaſures to authenticate the truth of it. For this purpoſe, I requeſted Mr. Gilpin, Clerk of the Royal Society, to repeat the experiment, and deſired ſome of the Gentlemen moſt converſant with theſe ſubjects to be preſent at putting the materials together, and at the examination of the produce.

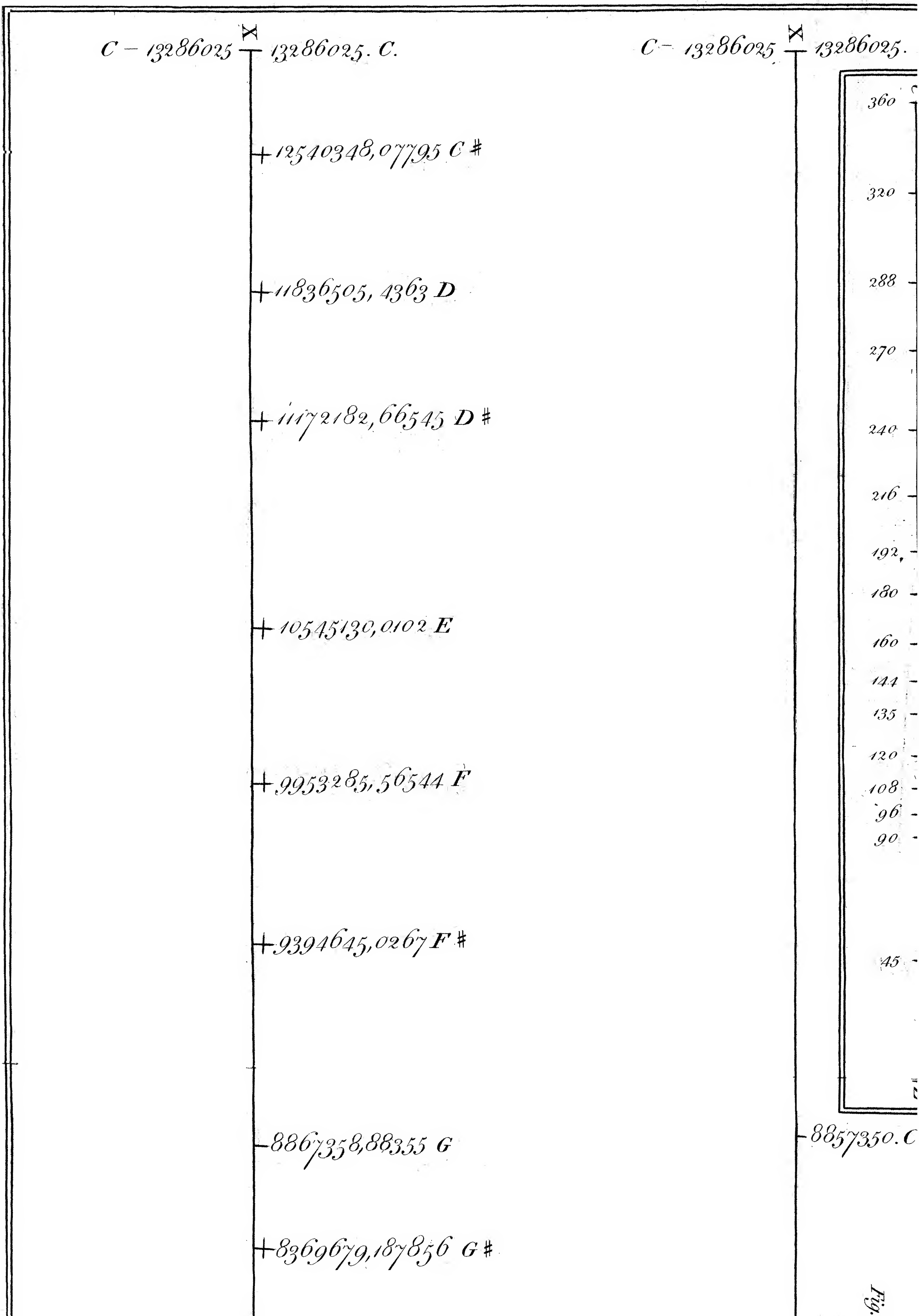
This laborious experiment Mr. Gilpin was ſo good as to undertake. It was performed in the ſame manner, and with the ſame apparatus, which was uſed in my own experiments, and which is deſcribed in the beginning of the above-mentioned Paper, and is accompanied with a drawing. The

 method

method ufed for introducing air into the bent tube, was that defcribed in the laft paragraph of p. 373. in that Paper, by means of the apparatus reprefented in fig. 3. or the refervoir, as I fhall call it. The foap-lees, like thofe of my own experiments, were prepared from falt of tartar, and were of fuch ftrength as to yield $\frac{1}{10}$ of their weight of nitre when faturated with nitrous acid. The dephlogifticated air was prepared from turbith mineral, and feemed by the nitrous teft to contain about $\frac{1}{18}$ part of phlogifticated air.

On December 6, 1787, in the prefence of Sir JOSEPH BANKS, Dr. BLAGDEN, Dr. DOLLFUSS, Dr. FORDYCE, Dr. J. HUNTER, and Mr. MACIE, the materials were put together. The quantity of foap-lees, introduced into the bent tube, was 180 meafures, each of which contained one grain of quickfilver; and, as the bore of the tube was rather more than one-third of an inch in diameter, it formed a column of five or fix-tenths of an inch in length, which, by the introduction of the air, was divided into two parts, one refting on the quickfilver in one leg of the tube, and the other on that in the other leg. The dephlogifticated air was mixed with one-third part of its bulk of atmofpheric air of the room in a feparate jar, and the refervoir was filled with the mixture; and from thence Mr. GILPIN, as occafion required, forced air into the bent tube, to fupply the place of that abforbed by means of the electric fpark.

From what has been faid, it appears, that the mixture employed contained a lefs proportion of common air than that ufed in either of my experiments. This made it neceffary for Mr. GILPIN now and then to introduce fome common air by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+9953285,56544 F
+9394645,0267 F ♯
–8867358,88355 G
+8369679,187856 G ♯
X
C – 13286025 – 13286025.
–8857350. C
360
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Fig.

36025. *C.*

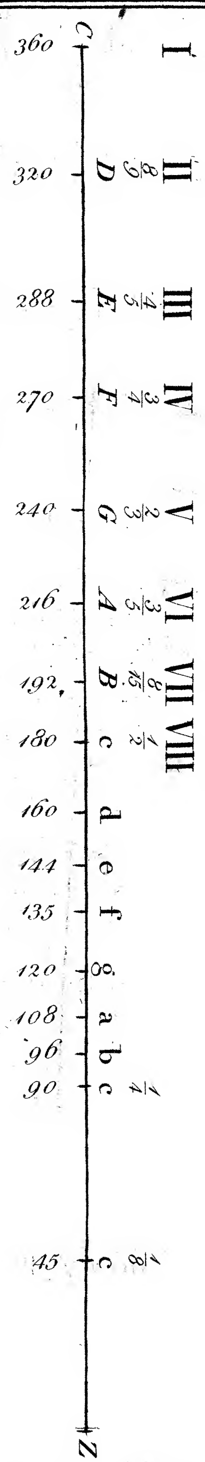
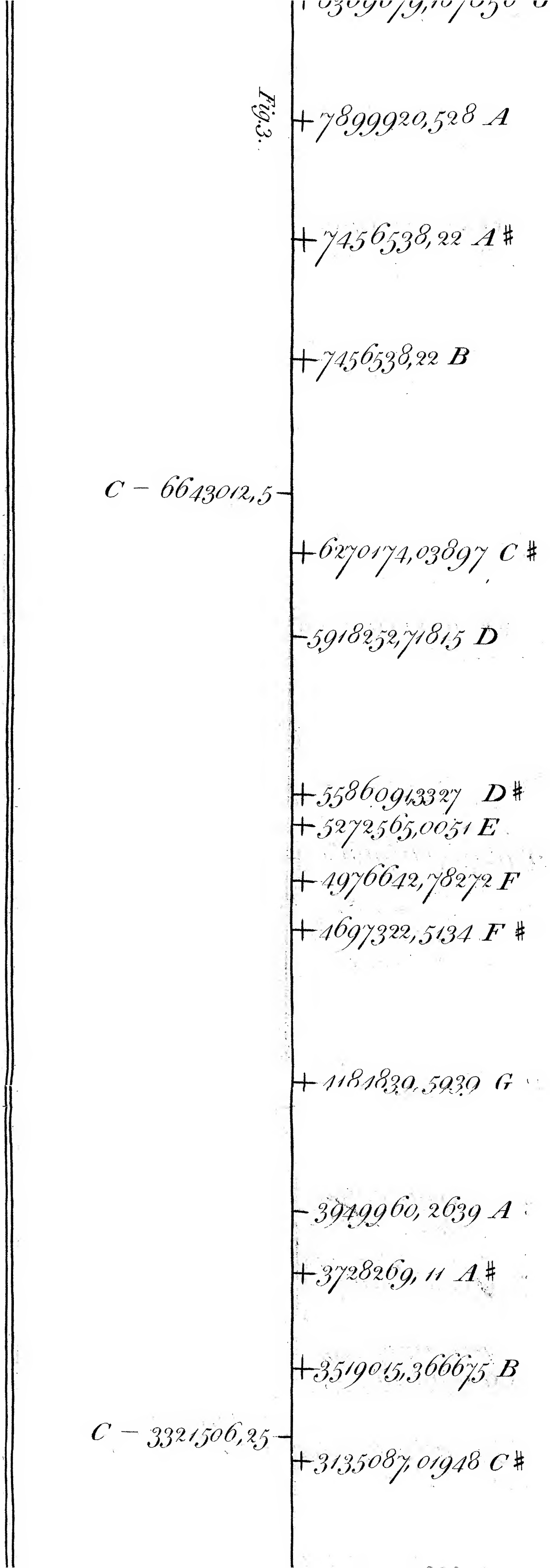


Fig. 1.

7350. *C.*

Fig.

Fig. 3.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+4697322,5134 F#
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Fig. 2.

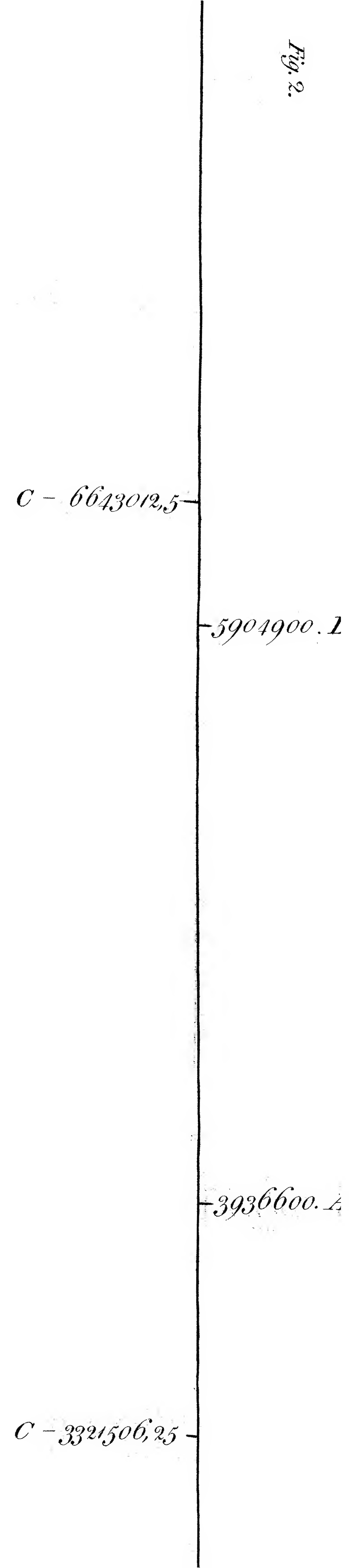
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Fig. 2.

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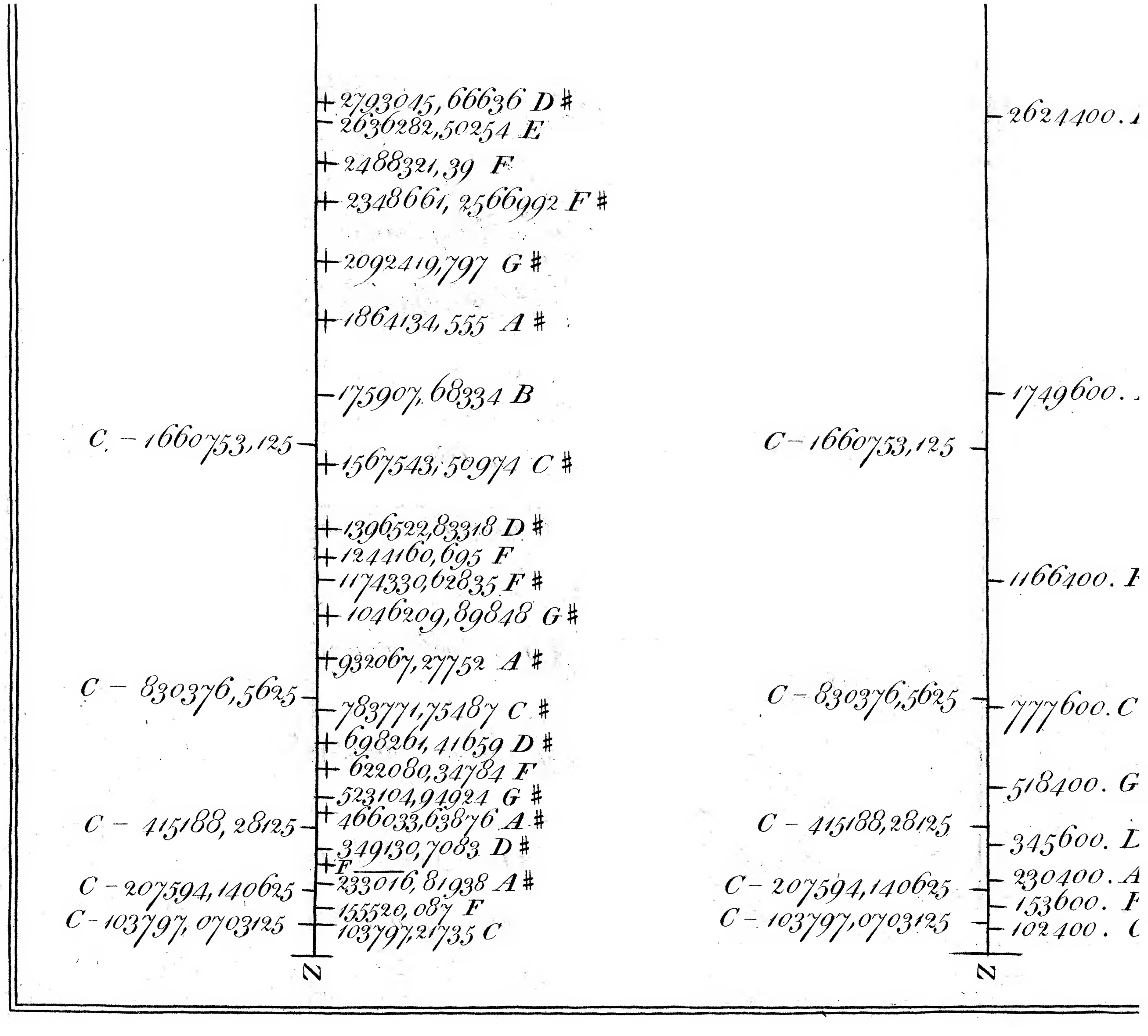

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C. -1660753,125
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+932067,27752 A #
C - 830376,5625
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+622080,34784 F
-523104,94924 G #
C - 415188,28125
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-349130,7083 D #
+F
C - 207594,140625
-233016,81938 A #
-155520,087 F
C - 103797,0703125
-103797,21735 C
N
-2624400.
-1749600.
C-1660753,125
-1166400.
C-830376,5625
-777600. C
-518400. G
C - 415188,28125
-345600.
C - 207594,140625
-230400.
-153600.
C - 103797,0703125
-102400.
N

4400. *E*.

9600. *B*.

5400. *F* ♯, *or G* ♭.

600. *C* ♯, *or D* ♭.

400. *G* ♯, *or A* ♭.

600. *D* ♯, *or E* ♭.
400. *A* ♯, *or B* ♭.
600. *F*.
400. *C*.

means of the bent tube reprefented in fig. 3. of the above-mentioned Paper, whenever from the flownefs of the abforption he thought there was too fmall a proportion of phlogifticated air in the tube.

My reafon for this manner of proceeding was, that as my firft experiment feemed to fhew, that the dephlogifticated air ought to be in a rather greater proportion to the phlogifticated than the latter did, I was fomewhat uncertain as to the proper quantities, and doubted whether I could proportion them in fuch manner as that it fhould not be neceffary, during the courfe of the experiment, to add either dephlogifticated or common air. I therefore mixed the airs in fuch proportion, that I was fure there could be no occafion to add the former; fince it was much eafier, as well as more unexceptionable, to add common air than dephlogifticated air.

On December 24, as the air in the refervoir was almoft all ufed, this apparatus was again filled in the prefence of moft of the above-mentioned Gentlemen, with a mixture of the fame dephlogifticated air and common air, in the fame proportions as before; and the fame thing was repeated on January 19.

On January 23, the bent tube was, by accident, raifed out of one of the glaffes of mercury into which it was inverted, by which it was filled with air, and a good deal of the foap-lees were loft; there, however, was enough remaining for examination.

On January 28, and 29, the produce of this experiment was examined in the prefence of Sir JOSEPH BANKS, Dr. BLAGDEN, Dr. DOLLFUSS, Dr. FORDYCE, Dr. HEBERDEN, Dr. J. HUNTER, Mr. MACIE, and Dr. WATSON. It appeared that 9290 meafures of the mixed air had been forced into the bent

bent tube from the refervoir *. Befides this, Mr. GILPIN had at different times introduced 872 meafures of common air, which makes in all 10162 of air, confifting of 6968 of dephlogifticated air, and 3194 of common air. But as there were 900 meafures of air remaining in the tube when the accident happened, the quantity abforbed was only 9262; but this is a much greater quantity that what from my own experiments feemed neceffary for this quantity of foap-lees.

The foap-lees were poured into a fmall glafs cup, and the tube wafhed with a little diftilled water, in order that as little as poffible might be loft. As they were by this means confiderably diluted, they were evaporated to drynefs; but it was difficult to eftimate the quantity of the faline refiduum, as it was mixed with a few particles of mercury.

Some vitriolic acid, dropped on a little of this refiduum, yielded a fmell of nitrous acid, the fame as when dropped on nitre phlogifticated by expofure to the fire in a covered crucible; but it was thought lefs ftrong. The remainder was diffolved in a fmall quantity of diftilled water, and the following experiments were tried with the folution.

It did not at all difcolour paper tinged with the juice of blue flowers.

It left a naufeous tafte in the mouth like folutions of mercury, and moft other metallic fubftances.

Paper dipped into it, and dried, burnt with fome appearance of deflagration, but not fo ftrongly or uniformly as when dipped in a folution of nitre. The marks of deflagration, however, were ftronger than when the Paper was dipped into a folution

* The method of afcertaining the quantity of air forced in was by weighing the refervoir, as mentioned in the above-mentioned Paper, p. 374.

of

of mercury in ſpirit of nitre, but not ſo ſtrong as when equal parts of this ſolution and ſolution of nitre were uſed.

A ſolution of fixed vegetable alkali, dropped into ſome of it diluted, produced a ſlight reddiſh-brown precipitate, which afterwards aſſumed a greeniſh colour.

A bit of bright copper being dipped into it, acquired an evident whitiſh colour, though not ſo white as when dipped into the ſolution of mercury in ſpirit of nitre.

From theſe experiments it appears, that the mixture of the two airs was actually converted into nitrous acid, only the experiment was continued too long, ſo that the quantity of air abſorbed was greater than in my experiments, and the acid produced was ſufficient, not only to ſaturate the ſoap-lees, but alſo to diſſolve ſome of the mercury. The truth of the latter part is proved by the metallic taſte of the reſiduum, its not diſcolouring the blue paper, the precipitate formed by the addition of fixed alkali, and the white colour given to the copper; and the nitrous fumes produced by the addition of oil of vitriol, as well as the manner in which paper impregnated with the reſiduum burnt, ſhew as plainly, that the acid produced was of the nitrous kind. It is remarkable, however, that during this experiment there were no ſigns which ſhewed when the ſoap-lees became ſaturated. The only time when the diminution proceeded much ſlower than uſual was on January 4. It then ſeemed to go on very ſlowly; but as the air abſorbed at that time was only 4830 meaſures, which is much leſs than what ſeems requiſite to ſaturate the alkali, and as the diminution immediately went on again upon adding more common air, it ſeems not likely, that the ſoap-lees were ſaturated at that time.

On January 10, Mr. Gilpin obſerved a ſmall quantity of whitiſh ſediment on the ſurface of the mercury; which ſeems

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to ſhew, that the ſoap-lees were then ſaturated, and that the acid was beginning to corrode the mercury. The quantity of air abſorbed was alſo 6840 meaſures, which is about as much as I expected would be required. However, as I was perſuaded, from the event of my own experiments, that the diminution would either intirely ceaſe, or go on very ſlowly, as ſoon as the ſoap-lees were ſaturated; and as I was unwilling to ſtop the experiments before that happened, I thought it beſt to continue the electrification.

On the ſame morning Mr. GILPIN found, that about 120 meaſures of the air in the bent tube had been ſpontaneouſly abſorbed during the night, the quantity therein being ſo much leſs than it was the preceding evening, though the electrical machine had not been worked, or any thing done to it during the intermediate time. The reaſon of this in all probability is, that as the acid was then corroding the mercury, the ſoap-lees became impregnated with nitrous air, which, during the night, united to the dephlogiſticated air, and cauſed the diminution.

Though in reality the event of this experiment was ſuch as to eſtabliſh the truth of my poſition, that the mixture of dephlogiſticated and phlogiſticated air is converted by the electric ſpark into nitrous acid, as fully as if the experiment had been ſtopped in proper time; yet, as the event was in ſome meaſure different from that of my own experiments, and might afford room for cavil, I was deſirous of having it repeated; and as Mr. GILPIN was ſo obliging as to undertake it again, the materials were, on February 11. put together for a freſh experiment, in the preſence of moſt of the above-mentioned Gentlemen. The ſoap-lees employed were the ſame as before, but 183 meaſures were now introduced. The dephlogiſtcated air was different,

different, the former parcel being all uſed. It was prepared, like the former, from turbith mineral, but was rather purer, as it ſeemed to contain only $\frac{1}{32}$ of phlogiſticated air. The proportion in which it was mixed with common air was that of 22 to 10; ſo that a greater proportion of common air was now uſed, in conſequence of which it was not neceſſary for Mr. GILPIN to introduce common air ſo often.

On February 29, the reſervoir was again filled with air of the ſame kind, in preſence of ſome of the ſame Gentlemen. As it was found by the laſt experiment that we muſt not depend on the ſaturation of the ſoap-lees being made known by any alteration in the rate of diminution, the proceſs was ſtopped as ſoon as the air abſorbed was ſuch as from my own experiments I judged ſufficient to neutralize the ſoap-lees. This was effected on the 15th of March. The air remaining in the tube, when Mr. GILPIN left off working, was 600 meaſures; but at the time the produce was examined, it was reduced to about 120, ſo much having been abſorbed without the help of any electrification, which is a ſtill more remarkable inſtance of ſpontaneous abſorption than what occurred in the former experiment. A few days after the experiment began, a black film was formed in one of the legs, which, I ſuppoſe, muſt have been a mercurial *ethiops*; but whether owing to ſome ſmall degree of foulneſs in the mercury or tube, or to any other cauſe, I cannot tell. This foulneſs ſeemed not to increaſe; but on March 10, when the air abſorbed was about 5200, a whitiſh ſediment began to appear on the ſurface of the mercury.

On March 19, the produce was examined in the preſence of Dr. BLAGDEN, Dr. DOLLFUSS, Dr. FORDYCE, Dr. HEBERDEN, Dr. J. HUNTER, Mr. MACIE, and Dr. WATSON.

The mixed air forced into the bent tube from the refervoir was 6650 meafures, befides which Mr. GILPIN had at different times introduced 630 of common air, which makes in all 7280, containing 4570 of dephlogifticated, and 2710 of common air.

The foap-lees were evaporated to drynefs as before. The refiduum weighed two grains, but there were two or three globules of mercury mixed with it, which might very likely weigh half a grain. This being diffolved in a fmall quantity of water, the following experiments were made with it.

It did not at all difcolour paper tinged with blue flowers.

Slips of paper were dipped into it, and dried; and, by way of comparifon, other flips of paper were dipped into a folution both of common nitre and phlogifticated nitre, and alfo dried. The former burnt in the fame manner, and with as ftrong marks of deflagration, as the latter.

It had a ftrong tafte of nitre, but left alfo a flight metallic tafte on the tongue.

It did not give any white colour to a piece of clean copper put into it.

In order to fee whether the whitifh fediment, which was before faid to be formed in the bent tube, contained any mercury, the remainder of this folution was diluted with fome more diftilled water, and fuffered to ftand till the white fediment had fubfided. The clear liquor being then poured off, the remainder, containing the fediment, which feemed to amount only to a very fmall quantity, was put on a piece of bright copper, and dried upon it; a piece of clean gold was then laid over it, and both were expofed to heat. Both metals acquired a whitifh colour, efpecially the gold, but which was very indeterminate.

Fig. 1

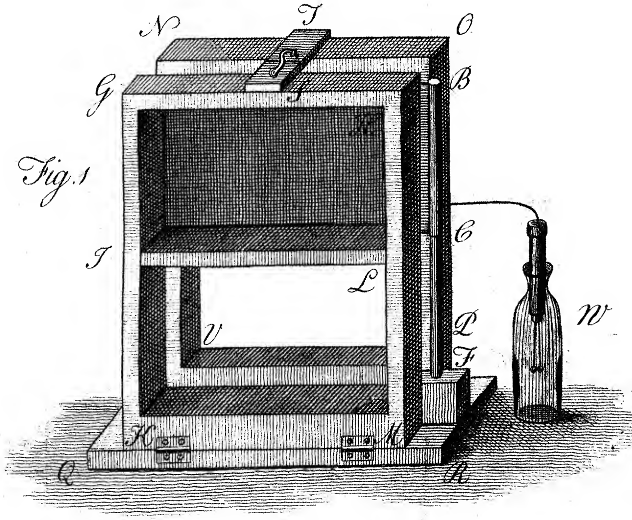
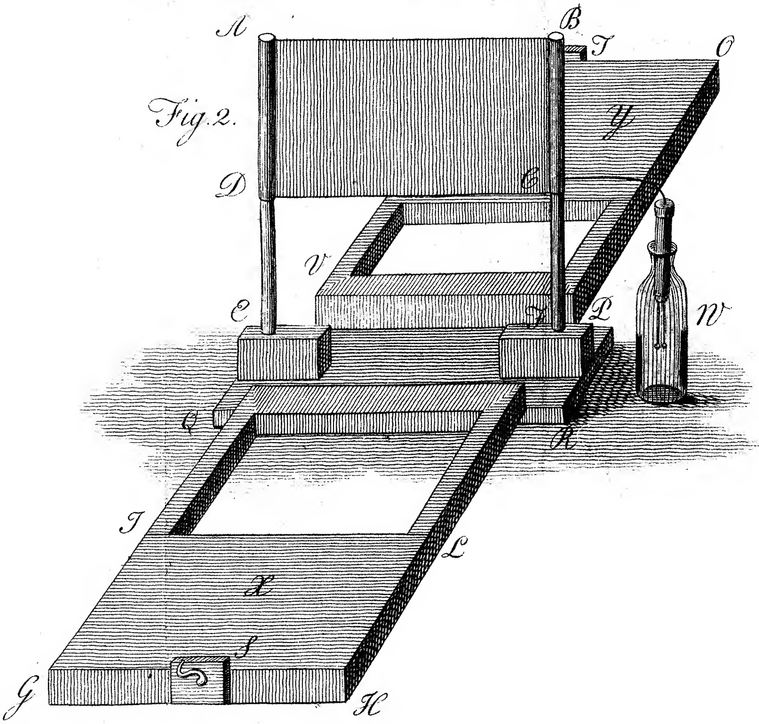


Fig. 2.



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In order to diſcover how nice a teſt of alcalinity the paper tinged with blue flowers was, a ſaturated ſolution of common nitre was mixed with $\frac{1}{120}$ of its bulk of the ſoap-lees; and this mixture was found to turn the paper evidently green; ſo that, as the ſolution of nitre contains about twice as much alkali as the ſoap-lees, it appears, that if the reſiduum had wanted only $\frac{1}{240}$ part of being ſaturated, it would have diſcoloured the paper.

From the foregoing trials it appears, that the mixture of dephlogiſticated and common air in this experiment was actually converted into nitrous acid, and was ſufficient not only to ſaturate the ſoap-lees, but alſo to diſſolve ſome of the mercury. The quantity diſſolved, however, was very ſmall, and not ſufficient to diminiſh ſenſibly the deflagrating quality of the nitre; ſo that the proof of the air being converted into nitrous acid was as evident as if no mercury had been diſſolved.

In this experiment, as well as the former, no indication of the ſoap-lees becoming ſaturated was afforded by any ceſſation in the diminution of the air; whereas, in my experiments, it was very manifeſt. I do not know what this difference ſhould be owing to, except to Mr. Gilpin's giving much ſtronger electrical ſparks than I did. In his experiments the metallic knob which received the ſpark, and conveyed it to the bent tube, was uſually placed at about 2½ inches from the conductor, ſo that the ſpark jumped through 2½ inches of air, in paſſing from the conductor to the knob, beſides from 1½ to 2½ inches of air in the tube; whereas in my experiments, I believe, the knob was never placed at the diſtance of more than 1¼ inch from the conductor, and the quantity of air in the tube was much leſs; but the conductor and electrical machine were the ſame.

Except this, the only difference I know in the manner of conducting the experiment is, first, that Mr. GILPIN usually continued working the machine for half an hour at a time, whereas I seldom worked it more than ten minutes; and, secondly, that in Mr. GILPIN's Experiments the common air in the reservoir bore a less proportion to the dephlogisticated air than in mine; in consequence of which it was necessary for him frequently to introduce common air. On this account, the proportion of the two airs in the bent tube would be considerably different at different times; but on the whole, the common air absorbed bore a greater proportion to the dephlogisticated than in mine.

Though the whole quantity of air absorbed in these experiments is known with considerable precision, yet it is impossible to determine, with any accuracy, how much of each kind was absorbed, on account of our uncertainty about the nature of the air which remained at the end of the experiment. But if in the last experiment we suppose that the air absorbed spontaneously between the 15th and 19th of March was intirely dephlogisticated, and that what remained at the end of that time was of the purity of common air, it will appear, that 4090 of dephlogisticated and 2588 of common air, which is equivalent to 4480 of pure dephlogisticated air and 2198 of phlogisticated air, were absorbed at the time the electrification was stopped, and consequently the dephlogisticated air is $\frac{204}{100}$ of the phlogisticated air; whereas in my first experiment it seemed to be $\frac{220}{100}$, and in my last $\frac{253}{100}$.

But the quantity of acid produced, and consequently, I suppose, the saturation of the soap-lees, depends only on the quantity of phlogisticated air absorbed; and the effect of the greater or less quantity of dephlogisticated air is only to make the

nitre

nitre produced more or lefs phlogifticated. Now, in this experiment, the bulk of the phlogifticated air was $12\frac{2}{10}$ that of the foap-lees. In my firft experiment it was $11\frac{9}{10}$, and in my laft $10\frac{8}{10}$.

As many perfons feem to have fuppofed that the diminution of the air in thefe experiments is much quicker than it really is, though I do not know any thing in my Paper which fhould lead to fuppofe that it was not very flow, it may be proper to fay fomething on this head. As the quicknefs of the diminution depends fo much on the power of the electrical machine, I can only fpeak as to what happens with the machine ufed in thefe experiments. This was one of Mr. NAIRNE's patent machines, the cylinder of which is $12\frac{1}{2}$ inches long, and 7 in diameter. A conductor of 5 feet long, and 6 inches in diameter, was adapted to it, and the ball which received the fpark was placed at two or three inches from another ball, fixed to the end of the conductor. Now, when the machine worked well, Mr. GILPIN fuppofes he got about two or three hundred fparks a minute, and the diminution of the air during the half hour which he continued working at a time, varied in general from 40 to 120 meafures, but was ufually greateft when there was moft air in the tube, provided the quantity was not fo great as to prevent the fpark from paffing readily.

The only perfons I know of, who have endeavoured to repeat this experiment, are, M. VAN MARUM, affifted by M. PAETS VAN TROOTSWYK; M. LAVOISIER, in conjunction with M. HASSENFRATZ; and M. MONGE. I am not acquainted with the method which the three latter Gentlemen employed, and am at a lofs to conceive what could prevent fuch able philofophers from fucceeding, except want of patience. But M. VAN MARUM, in his *Premiere Continuation des Expériences,*

faites

faites par le moyen de la Machine électrique Teylerienne, p. 182. has described the method employed by him and M. VAN TROOTSWYK. They used a glass tube, the upper end of which was stopped by cork, through which an iron wire was passed, and secured by cement, and the lower end was immersed into mercury; so that the electric spark passed from the iron wire to the soap-lees. After so much of a mixture of five parts of dephlogisticated and three of common air as was equal to twenty-one times the bulk of the soap-lees * was absorbed, some paper was moistened with the alkali, which by its burning appeared to contain nitre, but shewed that the alkali was not near saturated. The experiment was then continued with the same soap-lees till more of the air, equal to fifty-six times the bulk of the soap-lees, was absorbed, which is near double the quantity required to saturate them; but yet the diminution went on as fast as ever. It was then tried, by the burning of paper dipped into them, how nearly they were saturated; but they still seemed far from being so.

The circumstance of using the iron wire appears evidently objectionable, on account of the danger of the iron wire being calcined by the electric spark, and absorbing the dephlogisticated air; and when I first read the account, I thought this the most probable cause of the difference in the result of our experiments; but I am now inclined to think that the case was otherwise. From the manner in which M. VAN MARUM expresses himself, it seems that the only circumstance, from which they concluded that the alkali was not saturated, was the imperfect marks of deflagration, that the paper dipped into it exhibited in burning; which, as we have seen, might proceed as well from some of the mercury having been dissolved

* This is rather more than half of that requisite to saturate the soap-lees.

as

as from the alkali not being ſaturated. I am much inclined to think, therefore, that, ſo far from the ſoap-lees not having been ſaturated, the quantity of acid produced was in reality much more than ſufficient for this purpoſe, and had diſſolved a good deal of the mercury; for the quantity of air abſorbed favours this opinion, and the phænomena agree well with Mr. GILPIN's firſt experiment, in which this was certainly the caſe; whereas, if the diminution had proceeded chiefly from the dephlogiſticated air being abſorbed by the iron, the tube towards the end of the experiment would have been filled chiefly with phlogiſticated air, which would have made the diminution proceed much ſlower than before; but we are told, that it went on as faſt as ever. It is moſt likely, therefore, that the apparent diſagreement between their experiment and mine proceeded only from their having continued the proceſs too long, and from their not having properly examined the produce.

M. VAN MARUM then proceeds to ſay: "Surpris de cette "différence de réſultat j'envoyai une deſcription exacte de nos "expériences à M. CAVENDISH, le priant en même tems de m'in- "ſtruire s'il pourroit trouver la cauſe de cette différence; et "comme la ſeule différence eſſentielle, par laquelle notre expé- "rience différoit de celle de M. CAVENDISH, conſiſtoit en ce que "nous avons employé de l'air pur produit du précipité rouge ou "du minium, au lieu de l'air pur produit de la poudre noire "formée par l'agitation du mercure avec le plomb, dont M. "CAVENDISH ne donne pas la maniere de le produire*, je le "pria;

* The uſing the iron wire formed a material difference in our manner of conducting the experiment, and one which may, perhaps, have had great influence on the reſult; but I do not ſee how the uſing ſome other kind of dephlo-

" priai de me communiquer de quelle maniere il étoit venu a " cet air, parceque je desirois de répéter l'expérience avec ce " même air: mais comme il ne m'a fourni aucune élucidation " sur la cause vraisemblable de la différence du resultat de nos " expériences, et qu'il ne lui a pas plu de me communiquer sa " maniere de produire l'air pur qu'il avoit employé pour les ex- " périences, m'écrivant, qu'il s'étoit proposé d'en parler dans un " écrit public, la longueur ennuyante de ces expériences nous " a fait prendre la resolution de différer leur continuation, pour " obtenir une parfaite saturation de la lessive, jusqu'à ce que M. " CAVENDISH ait publié sa maniere de produire l'air pur, dont il " s'est servi, nous contentant pour le present d'avoir vu, que " l'union du principe d'air pur et de la mofette produit de l'acide " nitreux, suivant la découverte de M. CAVENDISH."

As I should be sorry to be thought to have refused any necessary information to a Gentleman who was desirous to repeat one of my experiments, and who by his situation was able to do it with less trouble than any one else, I hope the Society will indulge me in adding a copy of my answer, that they may judge whether this is in any degree a fair representation of it.

" TO M. VAN MARUM.

" SIR,

" I received the honour of your letter, in which you inform " me of your ill success in trying my experiment on the con-

dephlogisticated air, instead of that prepared from Dr. PRIESTLEY's black powder, can in the least degree form an essential difference, as in the same paragraph in which I mention my having used this kind of air in my first experiment, I say, that in my second experiment I used air prepared from turbith mineral.

" version

"version of air into nitrous acid by the electric spark. It is "very difficult to guess why an experiment does not succeed, "unless one is present and sees it tried; but if you intend to "repeat the experiment, your best way will be to try it with "the same kind of apparatus that I described in that Paper. "If you do so, and observe the precautions there mentioned, I "flatter myself you will find it succeed. The apparatus you "used seems objectionable, on account of the danger of the "iron being corroded by absorbing the dephlogisticated air."

"As to the dephlogisticated air procured from the black "powder formed by agitating mercury mixed with lead, as "it was foreign to the subject of the Paper, and as I proposed "to speak of it in another place, I did not describe my me- "thod of procuring it. As far as I can perceive, the success "depends intirely on carefully avoiding every thing by which "the powder can absorb fixed air, or become mixed with par- "ticles of an animal or vegetable nature, or any other inflam- "mable matter: for which reason care should be taken not to "change the air in the bottle in which the mercury is shaken, "by breathing into it, as Dr. PRIESTLEY did, or even by "blowing into it with a bellows, as thereby some of the dust "from the bellows may be blown into it. The method which "I used to change the air was, to suck it out by means of an "air-pump, through a tube which entered into the bottle, "and did not fill up the mouth so close but what air could "enter in from without, to supply the place of that drawn "out through the tube.

"I am, &c."

With regard to the main experiment, it was not in my power to give him further information than I did; as I pointed out the

the only circumſtance to which, at that time, I could attribute the difference in our reſults. And with regard to the manner of preparing the dephlogiſticated air from the black powder, I have mentioned all the particulars in which my manner of proceeding differed from Dr. PRIESTLEY's, and have alſo explained on what I imagine the ſucceſs intirely depends; ſo that, I believe, no one at all converſant in this kind of experiments will think that I did not communicate to him my method of procuring that air.