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O F T H E
ACADEMY OF SCIENCES AT STOCKHOLM.
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THE
CHEMICAL ESSAYS

OF
CHARLES-WILLIAM SÖRELL

TRANSLATED FROM THE

FRANÇOIS

OF THE

ACADEMY OF SCIENCES OF PARIS

WITH ADDITIONS

LONDON

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MDCCLXXXV

T O

CHARLES-WILLIAM SCHEELE,

APOTHECARY AT KÖPING

IN SWEDEN,

T H I S A T T E M P T

T O

EXTEND THE KNOWLEDGE

OF HIS DISCOVERIES

IS RESPECTFULLY INSCRIBED.

TO

CHARLES WILLIAM SCHEFF

APOLOGUES OF SCIENCE

IN SWITZERLAND

THIS ATTEMPT

TO THE KNOWLEDGE

OF HIS DISCOVERY

IS RESPECTFULLY INSCRIBED

P R E F A C E.

I HAPPENED to be conversing, a few months ago, with a foreign gentleman of distinguished knowledge and abilities, on a circumstance which is observed by every foreigner, who is capable of making observations, and of which every native, whose information extends beyond the productions of his own country and one or two among the swarm of Parisian journals, must be sufficiently sensible: I mean, on the very slow and imperfect manner in which the improvements of literature and science, that are made in several countries abroad, become generally known in England; and to the accidental occurrence of this subject, the present publica-

tion entirely owes its rise. The train of such a conversation would naturally lead us to recollect many names, among the philosophers of Germany and Sweden in particular, of whom it may be said, almost in the strict acceptation of the terms,

Ἡμεῖς δὲ κλέος οἶον ἀκρόμεν, εἰδὲ τι ἴδμεν

with whose contributions to the sum of human knowledge, the Authors and Professors of Britain, how confident soever of their own superiority, might find it no disadvantage to be better acquainted than they in general appear to be.

In a review of this kind, it was impossible to leave, unnoticed, the merits of that original genius, whose essays are collected into this volume, and concerning whom it was well observed to me by a near relation of Bergmann, *that the greatest of BERGMANN'S discoveries was the discovery of SCHEELE*. It was not long before I learned, during a continuance of our conversation, that my friend had, lying among his papers, most of the following essays, which he had been induced to translate,
at

at different periods, in consequence of the solicitations of different persons, who were eager to obtain fuller information concerning them than could be had from any English book. I was no sooner apprised of this treasure, than I became desirous of laying it open to public access; and accordingly offered, when he hesitated, because the translation was, for the most part, written when his acquaintance with our language was very imperfect, and must therefore be altogether unfit for the press, to revise and correct it as well as circumstances would permit. And in performing this task of minute diligence, I have not contented myself with a bare perusal of the manuscript, but have almost constantly compared it with two German translations, one by Professor KAESTNER of Gottingen, which is by no means free from inaccuracies and mistakes, and the other by Dr CRELL or some of his coadjutors, which, though for the sake of brevity, some parts of different papers are omitted, and others abridged, I have found very exactly to

convey the author's sense. Hence, although the most careless reader of the following pages will undoubtedly be offended with many harsh constructions, and many phrases of foreign growth, yet I hope with some confidence, that few obscure passages will occur, and still fewer in which the meaning of the original has been misrepresented. The aids which I have just mentioned, have enabled me to exhibit a faithful translation; but in order to have stood any chance for attaining correctness of language, I must have transcribed the whole manuscript, a labour to which I would never have submitted, even if the various engagements which occupied my time had not rendered it impossible.

I have just alluded to the Swedish essays, as the original; but the truth is, as I have been credibly informed, and it is a curious circumstance, that Mr Scheele transmits his communications to the Stockholm Academy of Sciences, not in Swedish, but in German, his native language,

guage, from which they are translated by some Member, in order to be inserted in the Transactions. This may perhaps account for the obscurity of one or two passages of no great moment, which I am obliged to leave as I found them, not being able to clear them up by the help either of the German or the French translation, as it occurs in the *Journal de Physique*. These passages, which are, I think, not above two in number, I intended to point out to the reader; but I neglected to note them, and cannot now discover them.

I have, moreover, made some additions, such as the papers of Mr Wiegleb and Mr Meyer, together with those both of the author and of Dr Crell, which occur at the end of the volume, and are chiefly taken from the most excellent of modern journals. Other sources, too, would perhaps have afforded other additions to the author's discoveries and corrections of his opinions; but having so lately annexed to BERGMANN'S DISSERTATION ON E-

LECTIVE

LECTIVE ATTRACTIONS, much of what it would have been proper to observe concerning Mr Scheele's experiments and deductions, as far as I am acquainted with it, I chuse rather to refer to that publication, than repeat the same things in the present. I know not whether it can now be necessary to put any reader on his guard against the notions concerning the composition of HEAT which run through most of the essays, and are employed to explain the phænomena of phlogistic processes, as they have been denominated—phænomena, perpetually recurring in the operations of chemistry. Yet erroneous as this theory certainly is, it required for its formation no common talents; it is among the most striking proofs of a genius for discovery, and implies nothing less than accuracy of observation, and equal sagacity and boldness in deducing conclusions. The necessity of some body, which should supply both pure air and phlogiston, had never been so clearly stated, nor had this principle been applied in a systematical manner,

manner, to account for the appearances. The reader needs only to substitute WATER for HEAT, and all will be conformable to the most accurate experiments with which we are even yet acquainted. Had the author but fortunately fixed upon another element, as it was supposed to be, his view of chemistry would perhaps have been as just as it was extensive. But what analogy led to this? and who, without the most direct experiments, would have allowed himself to imagine, that water was more nearly allied to phlogiston than heat? I know indeed, that this great discovery, confirmed as it has been by several philosophers*, countenanced by all the phænomena which appear in the least connected with it, and, with a fate very different from that of most of the great advances in science, seeming at once likely to meet with universal reception, without cavil or contradiction, has been lately called in question. But if

the
 * WATT, PRIESTLY, LAVOISIER, even Mr KIRWAN, while he maintains an hypothesis seemingly quite inconsistent with it, seems to admit it.

the account of Mr Fontana's experiments, which has lately been given in a French Journal (*Journ. de Phys. Septembre 1785*) be not exceedingly defective, it is certain that they do not in the smallest degree tend to invalidate the conclusions of Mr Cavendish. They only shew, that Mr Lavoisier has formed some opinions with too much precipitancy.

The printer's mark sufficiently intimates the design of continuing this collection. At present, there are but few materials for a second volume. The continuation of the experiments on Prussian blue, and a few other papers of very recent date, being, I believe, all that the author has published, except the contents of this volume, and the *Treatise on Air and Fire*, I can only therefore promise to gratify the impatience of the public as soon as possible, and shall be willing to publish the second volume in three or four different parts, of which the first shall appear, as soon as the author himself shall have supplied materials for a few sheets.

The

The essays of Mr Scheele have been lately published in France, with notes by Mr Morveau; but as I have not hitherto been able to procure that translation, I could not borrow any assistance from it; but whatever it contains, more than the present, of useful or curious matter, shall be added in the second volume.

T H O M A S B E D D O E S.

EDINBURGH, *Feb. 12.* }
1786. }

P. S. Having fortunately procured the second part of the paper on Prussian blue since this preface went to the press, I have subjoined it at the end of the present volume, that the reader might not be left in a disagreeable state of suspense by the half-finished discussion of so interesting a subject.

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CHEMICAL ESSAYS;

ESSAY I.

ON FLUOR MINERAL, AND ITS ACID.
1771.

§ I.

FLUOR mineral is a kind of stone, especially remarkable on account of the beautiful phosphoric light which it yields in a dark place, when it has been heated. But its constituent parts are as yet little known. In order to discover them, I made several experiments with this substance. I made use of two sorts, one of a green colour, found at Garpenberg, and a white species from Gislöf in Scania.

§ II.

It is well known, that fluor mineral, after having been once thoroughly heated, loses its power of becoming phosphoric for ever after. In order to find out whether it thus loses any of its con-

stituent parts, I exposed three ounces in a covered crucible to a strong fire, so that it was thoroughly heated. It decrepitated, as soon as it grew red hot, with a loud noise, very like common salt. I took it out of the furnace, and found, after it was cooled, that it had lost hardly any of its weight, and that it appeared in every respect like fluor mineral which had not been burnt, only that it, *1st*, Neither showed any signs of decrepitation nor phosphorescence, on being heated anew; *2^{dly}*, That it was more friable than before; and *3^{dly}*, That the green sort had become reddish, and the white had lost its transparency.

§ III.

I put a piece of fluor heated to phosphorescence, into cold water: It immediately lost a great part of its light, retaining, however, some glimmering for very near an hour. The same thing happened when it was put into acids, instead of water; but the solution of fluor in acids, though made by boiling, shewed no kind of phosphorescence. A piece of fluor, in its luminous state, suspended by means of a brass wire in the vacuum of an air-pump, continued to emit light for about an hour, but it was faint during the last half hour.

§ IV.

§ IV.

The following experiments were made, in order to find whether the property of becoming phosphoric could be restored to the fluor, after it had been once lost.

Fluor mineral that had been thoroughly heated, was stratified with powder of charcoal in a crucible, which, after being well closed, was kept hot for two hours. It was then taken out of the fire, cooled and heated again, but no light appeared. Burnt fluor was exposed to the sunshine for a whole day, and afterwards heated, with as little success. I therefore conclude, that its phosphorescence does not depend upon a subtile inflammable matter.

§ v. *Effects of Acids on Fluor.*

I poured two ounces of concentrated vitriolic acid upon the same quantity of fluor, which had been previously powdered in a glass mortar, and then put into a retort, to which a receiver was adapted, and the juncture well closed with gray blotting paper: A gentle fire was then applied; the mass began immediately to effervesce and swell; invisible vapours penetrated every where through the joining of the vessels; and, towards the end of

the process, white vapours rose, and formed a white matter on the whole internal surface of the receiver. The lute was so much corroded as to be quite friable between the fingers, but its colour was unchanged. The mass remaining in the retort was as hard as stone, and could not be taken out without breaking the vessel.

§ VI.

The process (v.) was repeated exactly in the same manner, excepting only, that a quantity of distilled water was put into the receiver before the operation. When the mass began to grow warm, and to swell, a vapour rose, which was condensed upon the surface of the water in the receiver, and formed just in the centre of it, immediately under the mouth of the retort, a white round spot: This spot continually increased, till it at last occupied the whole surface of the water, forming a pretty thick crust, which prevented the communication of the water with the new vapours that came over; I therefore gently agitated the receiver, upon which this crust burst and fell to the bottom, and soon after a new crust like the former was produced. At last the receiver, and soon after likewise the retort, were become white in the inside. As soon as the vapours ceased to rise with a gentle
fire,

fire, the vessels were permitted to cool. Their internal surface was found much corroded. The liquid in the receiver was a mixture of water, and of an acid, which the vitriolic acid had expelled from the fluor. The great quantity of white matter which had settled at the bottom during the process, was separated from it by filtration.

§ VII.

The mass remaining in the retort was reduced to a fine powder, andedulcorated with distilled water, till no vestige of acid appeared. This lixivium was filtered, and a little evaporated by boiling. In a few days time selenite was deposited, with a little alum, weighing about two scruples. The lixivium was then evaporated anew, and its superfluous acid saturated with vegetable alkali; but no more crystals were deposited.

§ VIII.

The lixivium, thus inspissated by evaporation, became blue on the addition of phlogisticated alkali. In both processes, (v. vi.) I used the green fluor. In order to know whether the solutions of every kind of fluor mineral shewed signs of iron, I made an experiment with the white species, previously calcined with concen-

trated vitriolic acid in a crucible; but no Pruffian blue was obtained by means of the same phlogisticated alkali; the green colour therefore is owing to iron.

§ IX.

The remaining residuum of the former distillation, after being perfectly edulcorated by means of distilled water, was boiled repeatedly with rain-water, until seven kannes of water were used, whereby every thing soluble in water was dissolved, since nothing was precipitated from the last water employed, by adding alkali of tartar. The mass now remaining was $\frac{1}{4}$ of the whole employed. It was reduced to fine powder, and calcined with acid of vitriol to dryness. In the beginning of this operation, a quantity of corrosive vapours were separated from the mass, which at the same time swelled considerably. After the vessel was cooled, I reduced the mass to a very fine powder, boiled it in pure water, and found it entirely dissolved. On part of this solution I poured some caustic volatile alkali, which produced no precipitation; but, by means of alkali of tartar, true calcareous earth was precipitated. A kenne of the liquor, from which the precipitation was obtained, yielded upon evaporation vitriolated vegetable alkali. The alkali, at the same
time,

time, decomposed an earthy salt, (felenite,) which was dissolved in the water. The remaining fourth part, not soluble in water, was powder of fluor undecomposed.

§ x.

Fluor, therefore, consists principally of calcareous earth, saturated with a peculiar acid; the nature of which we shall investigate hereafter. Pure clay, or, as it is generally called, earth of alum and iron seem to be accidental ingredients. The following experiments will prove this synthetically.

I mixed diluted acid of fluor, obtained as in par. vi. with lime-water, upon which a white powder was immediately precipitated. When nothing more would precipitate, the water was found perfectly pure. The precipitate itself, though not of a crystalline form, proved however to be the same as fluor. It yielded phosphoric light when put upon a red hot stone in the dark, melted by means of the blowpipe, and still more readily by adding some gypsum. And when this fluor, thus artificially produced, was again decomposed by means of vitriolic acid, it shewed itself to be the same as the native.

§ xi.

The white matter, which, during the
A 4
processes,

processes, (No. v. vi.) was deposited in the receivers, after being welledulcorated and dried, shewed the following properties: 1. It was rare, friable, and white. 2. It was not sensibly soluble in acids. 3. It did not make a tough paste with water, but was loose and incoherent after being dried. 4. It dissolved by boiling in lixivium tartari, and the solution on cooling assumed a gelatinous consistence. 5. In its pure state it suffered no change in the strongest heat; but, 6. When mixed with a little alkali of tartar, it frothed and boiled in a melting heat, and formed a glass. 7. This glass, with three parts of fixed alkali melted in the fire to a bluish mass, which, when powdered and put into a cellar, first deliquiated, and then became gelatinous. The acids precipitated a powder from it. 8. It dissolved in borax without any intumescence. These several properties shew it to be siliceous earth.

§ XII.

That this siliceous earth was formed during the processes themselves, appears from several experiments.

(A) I poured vitriolic acid upon powdered fluor in a cylinder of brass, which was closed by an exact cover, after having suspended over the mixture an iron nail and a bit of charcoal. Two hours afterwards I opened
the

the vessel, and found the nail and charcoal unchanged. I now moistened them, and suspended them as before. The cover was put on again, and, being removed in two hours, I found the nail, as well as the coal, covered with a white powder, which had all the properties of siliceous earth. In this experiment I made no use of glass vessels. The siliceous earth, therefore, obtained in the experiments (v. vi.) was not the earth of the glass dissolved by the acid of fluor, and afterwards precipitated, as one might otherwise suspect, from the internal surface of the glass being so much corroded.

(B) The artificial fluor (x.) was treated in the same manner, by means of vitriolic acid, as the native, (vi.) and distilled water was poured into the receiver for the condensation of the acid. As soon as the fumes reached the surface of the water, a white crust of siliceous earth was formed. When no more acid came over, I filtered the liquor contained in the receiver, and found it to be fluor acid diluted with water. By means of lime-water, I obtained a precipitate, which, like the former, was an artificial fluor, and its acid was extricated by the vitriolic, with the same phenomena as in the former experiment. Upon repeating this experiment five times in the same manner, I constantly found
the

the filiceous earth and the acid diminish considerably, so that, after the last essay, the water had hardly any mark of acidity.

Thence I conclude, that all the fluor acid united itself by degrees with the vapours of water, and thus formed the filiceous earth. It may be objected, that the fluor acid is perhaps already united, by nature, with a fine filiceous powder, which it volatilises and carries over in distillation, but leaves it as soon as it finds water to unite with, just as muriatic acid parts from the regulus of antimony, when butter of antimony is dropped into water. But if this was the case, the fluor acid would leave the whole quantity of filiceous earth thus combined with it in the first distillation, and therefore show no mark of its presence in the following processes.

(c) When I put spirit of wine into the receiver instead of water, no filiceous earth was produced; but the alcohol became four.

(d) When I put an unctuous oil into the receiver, all the fluor acid penetrated through the crevices of the lute, and did neither unite with the oil, nor produce a filiceous earth.

(e) This also happened when acid of vitriol was put into the receiver. If, therefore, the filiceous earth was not a product
of

of each distillation, but, being previously contained in the acid, was only deposited from it, in consequence of the union of the acid with a third substance, I think the siliceous earth ought equally to appear when alcohol was put into the receiver, with which it unites, as well as with water; but as this does not happen, I conclude, that not all the siliceous earth, which is deposited upon the surface of water during the distillation of the fluor acid, was previously dissolved in this acid.

§ XIII.

I distilled one part of powdered fluor with two parts of concentrated nitrous acid, one part of which went over, together with the fluor acid, and upon the water of the receiver there was a thick crust formed. The mass remaining in the retort was calcareous earth, saturated with nitrous acid, of a porous texture and reddish colour, which attracted moisture from the atmosphere.

§ XIV.

Two parts of concentrated muriatic acid being distilled with one part of the spar, the fluor acid passed over into the receiver with a large quantity of the muriatic. The internal surface of the receiver, as well as the surface of the water

ter contained in it, was covered with a white crust. The residuum in the retort was reddish, attracted moisture from the air, and exhibited the properties of muriated lime, (fixed sal ammoniac).

§ xv.

If there had appeared no siliceous earth, except when vitriolic acid was employed for expelling the fluor acid, it might seem as if this earth owed its generation to the vitriolic acid. (Becher and Stahl pretend, that acid of vitriol contains siliceous earth). The fluor acid, reduced into vapours, might be supposed, in this case, to deprive the vitriolic acid of this earth, and to lose that power again in proportion as its vapours are condensed and unite with water; but as there is siliceous earth likewise produced, when no vitriolic acid has been employed, it is evident that this earth has not been separated from the acid of vitriol during the distillation.

§ xvi.

I dissolved some spar in the nitrous and in the muriatic acid, in a sand bath. From these solutions, a calcareous earth, capable of effervescing with acids, was precipitated, by aerated or common fixed alkali. But if the precipitation was performed

formed with caustic fixed, or with volatile alkali, the precipitate was fluor in fine powder. The same thing happened with aerated volatile alkali. When vitriolic acid was added to the above solutions, a precipitation took place immediately, and the precipitate was vitriolated lime. The same thing happens if vitriolated magnesia, (Epsom salt), vitriolated vegetable alkali, (vitriolated tartar), or vitriolated volatile alkali, (Glauber's sal ammoniac), were mixed with the above solutions.

§ XVII.

I digested powdered fluor with phosphoric acid, which dissolved a good deal of it. On distilling this solution, the fluor acid went over, together with the watery particles of the mixture; but the remaining mass in the retort had the properties of ashes of bones.

It has been lately discovered, that the earth of bones or horns is calcareous earth combined with phosphoric acid.

Distilled vinegar and acid of tartar had no effect in decomposing the fluor.

§ XVIII. *With Alkalis.*

I melted one part of fluor with four parts of caustic fixed alkali in a crucible, upon which I afterwards poured
water,

water, in order to dissolve all the soluble parts. I found the alkali had not in the least united with the fluor; this latter remaining unchanged after the water had dissolved the alkali.

§ XIX.

I melted one part of powdered fluor with four parts of aerated fixed alkali, and then poured water upon it, which dissolved all that was soluble; there remained at the bottom calcareous earth, which effervesced with acids. The liquor before mentioned was evaporated, and contained fixed alkali united with fluor acid, which remained dry in the air.

§ XX. *With neutral Salts.*

I distilled one part of powdered fluor with two parts of muriated volatile alkali (sal ammoniac). At first, caustic volatile alkali passed over, then sal ammoniac, at last yellow flowers, which attached themselves to the internal surface of the vessel with the sal ammoniac. The residuum in the retort was fluor unchanged.

The iron contained in the fluor was most probably the cause of the small decomposition of the sal ammoniac, which took place at first.

§ XXI.

§ XXI.

I sublimed one part of powdered fluor with two parts of vitriolated volatile alkali, (secret ammoniac of Glauber); and obtained, first, some caustic volatile alkali, then a kind of sal ammoniac. The residuum in the retort was vitriolated lime (felenite); the acid of fluor consequently united in this process with the volatile alkali, forming a kind of sal ammoniac; and its earth remaining in the retort, united with the vitriolic acid of the vitriolated volatile alkali. I dissolved this kind of sal ammoniac in lime-water, and obtained a precipitate, which was regenerated fluor. On mixing some of the same sal ammoniac with a solution of vitriolated magnesia, a precipitation likewise took place.

§ XXII.

I exposed equal quantities of powdered fluor and corrosive sublimate to sublimation. The mercurial salt rose unaltered; but a small quantity of muriatic acid went over towards the end of the process. The residuum in the retort was fluor unchanged. The muriatic acid obtained in the receiver had been probably first disengaged from the corrosive sublimate by the iron contained in the fluor; but was afterwards again separated from it by the
too

too great degree of heat, and was thus carried over into the receiver.

§ XXIII.

I exposed equal quantities of powdered fluor and vitriolated mercury in a close vessel to the fire, and obtained first a liquid; but soon after, when the retort became red hot, some fluor acid went over, and some globules of quicksilver adhered to the neck of the retort. The residuum was of a reddish colour. The small decomposition, which took place here, was likewise owing to the iron contained in the fluor; for, after the iron had united with a part of the acid of the vitriolated mercury, some quicksilver was necessarily disengaged, and rose; but, on increasing the heat, the vitriolated iron was again decomposed, and its acid left at liberty to unite with the calcareous earth of the fluor, and thus expel the acid of fluor.

§ XXIV. *With Sulphur and Arsenic.*

Fluor exposed to fire in close vessels, with an equal quantity of arsenic, suffered no change. The same thing happened with sulphur.

§ XXV. *On the Acid of Fluor.*

The effects produced by fluor acid upon
other

other bodies is very remarkable. By the smell alone it is not distinguishable from the muriatic acid; but the experiment in xiv. evidently shows, that these two acids are very different. Besides this, the fluor could not be fixed, permanent, and of a transparent and crystalline appearance, but would be constantly liquid, like muriated lime. The fluor acid, in some experiments, acts like muriatic acid; in others like acid of tartar; but in others it shows phænomena peculiar to itself.

§ XXVI.

The fluor acid, obtained in the manner described in vi. was filtered, and rectified in a glass retort, by means of a gentle fire. The whole liquor which ascended at first was of a sourish taste; at the end of the process the vapours were concentrated fluor acid; they formed a white crust upon the more diluted acid which came over first. After those vapours had done rising, I found the internal surface of the retort much corroded by the concentrated acid, and, at the bottom of the retort, some siliceous earth was left behind, which had been before dissolved in fluor acid, and may be separated from it besides by another method, of which I shall speak hereafter.

The filiceous earth thus produced towards the end of the process, was separated by filtration from the rectified acid, with which I then repeated the same process. At the end of it I again found filiceous earth in the retort, as well as in the receiver. After a third rectification, I obtained the same. Thence it seems to follow with certainty, that the acid also, by itself, might be changed entirely, with vapours of water, into filiceous earth, if the distillation was repeated with water always in the receiver.

§ XXVII. *Effects produced by this Acid on Alkalis.*

The solution of alkali of tartar in fluor acid immediately formed a gelatinous mass, almost without taste. I filtered and evaporated it, but was not able to bring it to crystallisation. I evaporated it then to dryness, and obtained a saline mass, which only was in weight the sixth part of the fixed alkali dissolved; did not change the colour of syrup of violets, but precipitated lime-water. The liquid above this precipitate was a solution of pure alkali in water. The same salt likewise precipitated the solutions both of muriated lime, and vitriolated magnesia. The precipitate obtained from the lime-water

water and solution of muriated lime, was regenerated fluor.

The gelatinous solution of fixed alkali in fluor acid was welledulcorated, dried, and exposed to the fire in a close covered crucible. It melted without any ebullition. I then took it out and powdered it. The taste was caustic. Exposed in a cellar, it deliquesced, and showed itself in every respect to resemble the liquor filicum.

§ XXVIII.

With mineral alkali fluor acid yielded exactly the same products as with the vegetable.

§ XXIX.

Volatile alkali dissolved in fluor acid likewise formed a jelly, which, when it was separated from the liquid, and welledulcorated, I found to be real siliceous earth. The supernatant liquid had a taste resembling that of the vitriolated volatile alkali, and yielded crystals, though indeed very small, with which I tried the following experiments :

(A) By sublimation, I at first obtained a little volatile alkali, and afterwards sal ammoniac, of a taste rather acid.

(B) Upon distillation, with a mixture

B 2

of

of powdered chalk and water, all the volatile alkali came over immediately.

(c) On the addition of lime-water, regenerated fluor was instantly precipitated.

(D) A precipitate of the same nature as the former was obtained, when the compound of fluor acid and volatile alkali was put into a solution of muriated lime. The liquor was a solution of common sal ammoniac.

(E) Regenerated fluor was likewise precipitated by a solution of lime in nitrous acid.

(F) A powder was precipitated from the solution of silver, which, by means of the blowpipe, was reduced to silver, losing, at the same time, its acid, which partly flew off, and in part uniting with the watery particles of the flame, generated filiceous earth, which appeared in the form of a white circular spot upon the charcoal, round the reduced silver.

(G) A mass was precipitated from the solution of quicksilver in nitrous acid, entirely volatile in heat; but a solution of corrosive sublimate remained unchanged.

(H) All the lead was precipitated from its solution in nitrous acid.

(I) A solution of vitriolated magnesia became turbid.

(K) Vitriolic

(K) Vitriolic acid, mixed with the solution of this kind of sal ammoniac, and distilled in close vessels, yielded pure fluor acid, which formed, at the same time, a thick crust upon the water in the receiver.

Regenerated fluor, obtained in the manner as mentioned c, D, E, is decomposed by digestion with aerated vegetable alkali. The acid of fluor unites with the alkali; but the calcareous earth, thus freed, uniting, at the same time, with the aerial acid, falls to the bottom of the vessel.

When the experiment was made with aerated volatile alkali, no decomposition ensued.

§ xxx. *On Absorbent Earths.*

(A) A solution of lime in fluor acid remained clear till the acid was saturated; but then the whole quantity of dissolved earth united with the acid into a mass, which partly precipitated and partly congealed with the liquid into a jelly in the open air, and proved to be regenerated fluor.

(B) Magnesia, dissolved in the fluor acid, partly precipitated immediately with it, and in part formed a jelly.

(c) Pure clay, or earth of alum, formed with the fluor acid a sweet solution, which also formed a jelly.

§ XXXI. *On Metals.*

The under mentioned metals were digested with fluor acid in separate glass vessels for six hours. The liquor was made to boil towards the end. They shewed the following phænomena :

(A) Gold was not attacked. The fluor acid shewing in some particulars a resemblance with muriatic acid, I was induced to try whether it would dissolve gold, when mixed with nitrous acid, as muriatic acid does ; but without success.

(B) Neither did silver undergo any change. The calx of silver, precipitated by an alkali, was partly dissolved ; but the remainder united with the fluor acid into an insoluble mass, which lay at the bottom of the vessel. On pouring vitriolic acid upon it, the fluor acid was expelled, under its common form of a corrosive vapour.

(C) Quicksilver was not dissolved ; but the calx of quicksilver, precipitated from nitrous acid by fixed alkali, was dissolved in part. The remaining insoluble part united with the acid, and formed a white powder, from which the vitriolic expelled the fluor acid in the form of vapour. The same powder formed, by means of the blowpipe, a yellowish glass, which, however, evaporated by degrees, leaving
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at the end a small globule of fixed glass behind.

(D) Lead was not dissolved; but with its calx the acid formed a sweet solution, from which the calx could be precipitated by vitriolic or muriatic acid, as also by sal ammoniac. After digesting a quantity of acid with calx of lead, which having been previously digested with the same calx, of course held some of it already dissolved, a spontaneous precipitation took place. The vitriolic acid expelled that of fluor from the precipitate, in the form of corrosive vapours. It was easily brought into fusion by means of the blowpipe, when the acid flew off, and the calx of lead was reduced. Part, however, of the glass remained fixed in the fire.

(E) Copper was partly dissolved; for the acid, after digestion with this metal, grew bluish, on the addition of volatile alkali. The calx of copper was readily soluble. This solution was gelatinous; yielding, however, blue crystals, partly of a cubic, partly of an oblong form, from which the acid could not be separated but by heat.

(F) Iron was attacked with violence. The vapours which arose during the solution were inflammable. The solution had a taste like vitriol of iron; it congealed during the evaporation, but was not reducible into crystals, forming only a hard

mass, after all the liquid was evaporated. Vitriolic acid expelled from this mass the fluor acid under the form of vapours. The same effect was likewise produced by simple heat; and in this case a red ochre or calx of iron was left behind. The calx of iron was likewise soluble in this acid; the solution had a taste like alum; it could not be reduced to crystals; upon the addition of alkali, it was decomposed, and the calx precipitated.

(G) Tin was not soluble; but the calx was easily dissolved; the solution became gelatinous; it had a nauseous taste.

(H) Bismuth was not dissolved; but its calx was dissolved by the acid, with the very same phenomena as the calx of lead.

(I) Zinc produced the same effects as iron with the fluor acid, excepting that the solution seemed to be more inclined to crystallise.

(K) The regulus of cobalt was not soluble; but its calx dissolved and formed a yellow gelatinous matter.

(L) The regulus of antimony was not attacked; neither was powdered crude antimony (*antimonium sulphuratum*) sensibly dissolved.

§ XXXII. *With Solutions of Salts.*

(A) Fluor acid precipitated something from a solution of silver. The small quantity

tity of precipitate, thus obtained, neither melted nor evaporated under the blow-pipe.

(B) Quicksilver, dissolved in nitrous acid, yielded precipitate, which melted upon the charcoal under the blowpipe, and was afterwards evaporated. The solution of corrosive sublimate was not changed by the fluor acid.

(c) The solution of lead in nitrous acid was not changed; but, from the solution of this metal in vinegar, all the lead was precipitated by the fluor acid. Upon adding more of this acid than was necessary for precipitating the calx of lead, the calx was dissolved, and found to be soluble afterwards in distilled vinegar.

(D) The solutions of vitriolated iron, copper, and zinc, of alum and vitriolated magnesia, were but little affected by the fluor acid.

§ XXXIII.

From what has been said of the fluor acid hitherto, it follows:

(A) That it dissolves siliceous earth, (XXVI.)

(B) That it parts from this earth as soon as it finds some other substance, alkali, (XXVII, XXVIII, XXIX,) absorbent earths, (XXX.) metals, (XXXI.) to unite with.

(c) That

(c) That the fluor, produced by art, (x.) was not quite pure, but mixed with filiceous earth; which however does not militate against the assertion mentioned in that paragraph; for the filiceous earth is obliged to remain always behind when it is decomposed, together with the gypsum that is formed at the same time.

(D) That the fluor acid will hardly ever be obtained pure, but always combined with some filiceous earth, which may be separated from it by volatile alkali.

(E) That if pure fluor acid is to be combined with some other substance, the surest way to effectuate this, is to make first a kind of sal ammoniac by uniting it with volatile alkali.

(F) A compound of fixed alkali and fluor acid is capable of combining with finely divided filiceous earth, *via humida*, (xxvii.)

E S S A Y II.

ON FLUOR MINERAL. 1771.

§ I.

IN the year 1771, I had the honour to present to the Royal Society some experiments made with fluor mineral, which were inserted the same year in the Transactions, and by which I proved, that the constituent parts of this fossil are calcareous earth, and a peculiar acid, to which I gave the name fluor acid. Two years afterwards, Mr *Boullanger**, in a little Treatise, endeavoured to shew, that this acid was nothing else than muriatic acid, intimately combined with some earthy substance. A short time after this again Mr *Monnet* † brought forward some experiments, made by himself upon the same substance. He maintains, that the acid, which I obtained from fluor mineral, is only vitriolic acid volatilised by means of some extraordinary combination with fluor.

§ II.

* *Expériences et observations sur le spath vitreux, ou fluor spathique, par M. Boullanger, 1773.*

† *Observations de phys. de M. l'Abbé Rozier, tom. x. p. 106.*

§ II.

Thus we have three different opinions on the origin of this acid. A natural philosopher, who seeks for truth, will naturally wish to know which of these opinions he is to follow. Far from adhering tenaciously to the propositions advanced in my former paper, I shall shortly examine the arguments adduced by both these Chemists in favour of their respective opinions.

§ III.

Mr Boullanger maintains, that fluor acid precipitates the solutions of silver and quicksilver, yielding with the former muriated silver, (*vulgo luna cornua*); and he asserts, that, by subliming half an ounce of the second precipitate, he obtained *mercurius dulcis*. It is indeed true, that the fluor acid precipitates silver and quicksilver, as I mentioned likewise in my Dissertation on the fluor mineral; but the precipitate obtained is in very small quantity; (for the fluor mineral, as well as all other mineral substances of a calcareous nature, is adulterated with a small quantity of muriatic acid); but the greatest abundance of the remaining acid will not precipitate the above mentioned metallic solutions; which however should
happen,

happen, if Mr Boullanger's opinion was true. He must have also made use of a very large quantity of fluor acid, in order to obtain such a considerable precipitate: For, from the quantity of acid, which I obtained from two ounces of perfectly pure fluor, I procured only half a drachm of luna cornua: But I shall shew how to separate this small quantity of muriatic acid from that of the fluor. A solution of silver made with nitrous acid is to be precipitated with alkali of tartar; and upon the precipitate, after beingedulcorated, so much acid of fluor is to be poured as is requisite for giving an excess of acid, and then the solution is to be filtered. Of this solution of silver, so much is dropped into the fluor acid, till no more precipitation ensues, then the acid is filtered through gray paper, and afterwards evaporated to dryness in a glass retort. Water first comes over into the receiver; this is followed by fluor acid, which covers the inside of both the vessels, together with the surface of the water in the receiver, with a thick siliceous crust. The acid, thus rectified, does not precipitate the solution of silver, and shews not the least mark of muriatic acid. Were Mr Boullanger's opinion just, the acid, notwithstanding it has been thus purified, should still precipitate the solution of silver, because he maintains, that, if
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the terrestrial part can but be separated from the acid, we should have nothing left but pure muriatic acid*. Now we know that this terrestrial part of fluor acid is a filiceous powder; if therefore Mr Boullanger is able to compose fluor acid with this powder, or any other filiceous substance and muriatic acid, I shall immediately give my assent to his opinion, but not before. Why does not fluor acid mixed with nitrous acid dissolve gold? Why is no corrosive sublimate produced when fluor acid is distilled with vitriolated mercury? Why do we not obtain plumbum cornuum on dropping this acid into a solution of lead made with nitrous acid? &c. Would not all this happen, if muriatic acid was contained in pure fluor acid? I readily believe that Mr Boullanger was not able to expel the fluor acid from the spar by the strong concentrated nitrous and muriatic acid. Had he made use of those acids a little less concentrated, or diluted as they commonly are, he would have surely seen the fluor mineral decomposed, as well as it was in my experiment; for these acids have not so strong an elective attraction for lime as vitriolic acid has; a small quantity of water is therefore required, and then the fluor is decomposed by means of a double elective attraction.

§ IV.

* Exp. & Obs. par M. Boullanger, p. 29.

§ IV.

I now come to Mr Monnet's Essay, who maintains, in opposition as well to mine as to Mr Boullanger's experiments, that fluor mineral contains neither acid nor lime, but that this substance, being volatilised when united with a sufficient quantity of vitriolic acid, forms the acid called fluor acid. The residuum in the retort, or the crystallised salt which I and Mr Boullanger call selenite, is in his opinion quite a different substance, since both this salt, and the crust which is sublimed, want only a small quantity of vitriolic acid, in order to be changed into fluor acid. Such are the conclusions of Mr Monnet. Thus we have a new kind of earth hitherto unknown to Chemists, and which will probably remain unknown to them to all eternity. It must be a curious kind of earth which is fixed by itself, but notwithstanding is able, without the assistance of fire, to volatilise the vitriolic acid; so that both united together form a kind of air, which even retains its elasticity in the cold. If I justly think that fluor acid contains not the least vestige of vitriolic acid, and if all the vitriolic acid, made use of for the process, is found in the retort, after the distillation, united with the basis of the fluor; and if this basis is lime or
pure

pure calcareous earth;—if I shall be able to prove this, I say, Mr Monnet's theory must fall of itself.

§ v.

Upon one ounce of pure levigated fluor with alcohol, I poured three ounces of concentrated acid of vitriol, and distilled the mixture in a sand-bath, having previously put twelve ounces of distilled water into the receiver. Then I took three other ounces (as exactly weighed as the former) of the same acid of vitriol, diluted with four-and-twenty ounces of water, to which I afterwards added lixivium tartari (liquid fixed alkali) previously weighed, till I attained the exact point of saturation; then I weighed again the remaining lixivium tartari, after the end of the distillation, which was continued for eight hours with such a degree of heat, that none of the vitriolic acid was carried over; I carefully broke the retort, took out the mass, and reduced it to powder in a glass mortar; it was then boiled in a glass vessel with four-and-twenty ounces of water, for some minutes; after which, I added just as much lixivium tartari as I had found before to be requisite for the saturation of three ounces of the vitriolic acid, and continued the boiling for a few minutes longer. When I at last came to
examine

examine the solution, I found it to be perfectly neutralised, neither the acid nor alkali prevailing. It was a perfect vitriolated vegetable alkali, (vitriolated tartar) and consequently not a drop of the vitriolic acid had passed over into the receiver. I afterwards lixiviated all the saline matter with hot water, dried the lime, and found it to weigh $9\frac{1}{2}$ drachms. I dissolved two drachms of this lime in diluted muriatic acid; there remained something which was insoluble, and seemed to be undecomposed fluor; it weighed, after being dried, nine grains. Upon one part of this solution I poured some acid of sugar, which immediately produced a precipitation of saccharated calcareous earth. To another part I added vitriolic acid, upon which small crystals immediately precipitated, which were found to be vitriolated lime or gypsum. The third part of the solution was evaporated to dryness, whence a salt was obtained, which was deliquescent in the air. The remaining part of the aerated lime being put into a crucible, and burned in a strong fire, I obtained a real quicklime, which made with water a perfect lime-water; and, when it was boiled with sulphur, dissolved it. It is probably unnecessary to adduce any more arguments, in order to prove that lime is the basis of fluor. After having thus shown, that the

whole quantity of vitriolic acid employed was retained by the lime, it would appear unnecessary to mention all the experiments which I made, in order to ascertain, whether, 1. fluor really contains vitriolic acid. But, in order to show the falsehood of Mr Monnet's assertion on this side also, I shall relate a few of them.

1. Pure acid of fluor does not precipitate the solution of the terra ponderosa.
2. Neither does it precipitate the solution of lead in nitrous acid.
3. Acid of fluor, saturated with alkali of tartar, and evaporated to dryness, then mixed with charcoal-powder, and melted, does not yield hepar sulphuris. Not to mention, that several other acids have the power of expelling the acid from fluor. Mr Monnet, however, might very easily say, in answer to this, that fluor mineral has the property of volatilising all acids, the fixed acids of phosphorus and of arsenic not even excepted. But no good chemist can possibly allow, that the crust, sublimed into the neck of the retort, and into the receiver, as likewise the selenitic mass remaining in the retort, distilled anew with vitriolic acid, is altogether converted into acid of fluor.

§ VI.

Mr Monnet, in order to give farther proof that fluor contains no calcareous earth, adduces the following experiments:

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He melts equal quantities of alkali and fluor together, and observes, that this mineral is thereby little or not at all changed; for, after having lixiviated the alkali employed, he dissolved the fluor remaining in the filter in nitrous acid; and to the solution he added vitriolic acid: and because he obtained no precipitate, he thinks it fully proved that fluor contains no lime. I maintain, on the contrary, that all solutions of fluor yield a precipitate of gypsum whenever vitriolic acid is added to them.

Was I to attempt an explication of Mr Monnet's experiment, I should be induced to think, that he diluted his solution with too great a quantity of water. But why does he take equal quantities of alkali and fluor, whereas, in my Dissertation on fluor, I say, that I took four parts of alkali to one part of fluor? I likewise mentioned in the same Dissertation, that fluor, melted with caustic alkali, undergoes no change. Now, Mr Monnet undoubtedly knows, that alkali, when exposed to a strong fire, without fusing, becomes caustic, the very thing which happens in his experiment. The result is quite different, if the experiment be made with four parts of alkali, here the fluor is decomposed by means of a double elective attraction; and this is the reason that Mr Monnet obtains pure lime in the filter.

ter. Mr Monnet is farther of opinion, that fluor may be precipitated by the phlogisticated alkali, because he obtained from its solution a much larger quantity of Prussian blue, though of a paler colour than was to be expected from the small quantity of iron contained in the fluor. Thus we should have, according to Mr Monnet's idea, a new discovery concerning the constituent parts of the fluor, *viz.* a new metallic earth, quite different from all others, since metallic calces alone have the property of being precipitated by phlogisticated alkali. If a chemist, however, speaks of the lixivium sanguinis, or phlogisticated alkali, he always understands a lixivium where the alkali does not predominate, but where it is perfectly neutralised; but of such an alkali Mr Monnet probably did not make use in this experiment; for I can affirm with certainty, that phlogisticated alkali does not precipitate the fluor. *Lastly*, Mr Monnet pretends, in contradiction to all those who have distilled the acid of fluor, that he has never observed the glass attacked by this acid. Every chemist, who has any fluor acid standing in a glass vessel, must be convinced of the contrary by his own ocular testimony; And thus, I hope, I have demonstrated, that the acid of fluor is and remains entirely a mineral acid sui generis.

ESSAY III.

CHEMICAL INVESTIGATION OF FLUOR ACID, WITH A VIEW TO THE EARTH WHICH IT YIELDS, BY MR WIEGLEB.

§ I.

THE observation communicated by Mr Margraaf to the Academy of Sciences at Berlin in 1768*, that a peculiar volatile earth might be obtained by distillation from fluor, to which vitriolic acid had been added, probably gave occasion to Mr Scheele to make some experiments with a view to this. They have served to shew the truth of what Margraaf had said concerning the volatile earth. But Mr Scheele has attempted to advance farther, and to explain the singular phænomenon which this earth exhibits.

§ II.

It appears from his Essay, that he does not consider the earthy matter as coming from the fluor, from which there is only a very peculiar acid sui generis expelled by the vitriolic acid. He supposes that the fluor acid, which arises in the form of

C 3 vapour,

* Memoires, tom. xxv. for 1768.

vapour, combines with the water as soon as it reaches its surface, and thus changes it into earth, constituting the crust which appears on the surface of the water during the operation. At the same time, he takes it for granted, without expressly mentioning it, that another portion of the acid is condensed, and forms with the water an acid liquor.

§ III.

Having moreover observed, that the liquor separated by filtration from the earthy crust, coagulated on the addition of alkaline salts, and, when it was more diluted, yielded a semitransparent, gelatinous, and viscid precipitate, he considered the coagulation as a property of the acid itself, not imagining that there took place a separation of any earthy substance that was combined with the proper acid: He therefore looked upon the gelatinous matter, which, afteredulcoration and deficcation, was found to possess the most distinguishing properties of siliceous earth, as newly formed from the water and acid. In short, Mr Scheele considers both the crust which forms upon the water during the distillation of the spar, and the siliceous earth obtained by precipitation, as an earthy substance originating from the acid of fluor and water.

§ IV.

§ IV.

Since the appearance of Mr Scheele's Essay, many hands have been set in motion by the singular phenomena related in it. Boullanger was probably led by the volatility of this acid, and the strong smell of pure marine acid, which the liquor emits after distillation, to look upon the acid of fluor as an acid of sea-salt. Monnet and Priestley, on the other hand, declared in favour of the vitriolic acid. With respect to the earth, Margraaf and Achard supposed that it must proceed from the fluor itself, and constitute an unknown species. Professor Weigel maintains, that it has its origin in a decomposition of the acid. Such are the principal opinions hitherto formed concerning the earthy matter which appears on this occasion.

§ V.

Mr Scheele's explanation of the phenomena appeared to me, on the first reading of his Essay, somewhat bold and improbable: For we are not acquainted with any instance in which water is thus changed into an earth by an acid, and still less with a transmutation of this liquid into siliceous earth. I endeavoured, therefore, to discover its origin by experiment. Having therefore first repeated several experiments

periments in the way described by Mr Scheele, accurately observed all the phænomena that occurred, and thus fallen upon a track which promised to lead to the solution of the whole problem, I proceeded to something which Mr Scheele had neglected, and from which I hoped that it might be ultimately determined whether the earth proceeded from the fluor, or was formed of the acid and water.

§ VI.

For this purpose, I first weighed the retort destined for the experiment in a very accurate manner, and found that its weight was two ounces and five drachms. I then put into it two ounces of calcined fluor in powder, and added, by means of a glass tube, $2\frac{1}{2}$ ounces of oil of vitriol. The retort was then placed on the furnace, and a receiver, which, when empty, weighed two ounces, two drachms, and thirty grains, and now contained two ounces of distilled water, luted to it. The distillation was conducted with all possible care, and at last pushed till the retort grew red hot. A few vapours could not be prevented from penetrating through the lute. The next day, the retort being separated from the receiver, was found to weigh, together with its contents, five ounces, five drachms, and thirty grains ;
it

it had therefore lost one ounce, three drachms, and thirty grains. The receiver, which, with the water, had originally weighed four ounces, two drachms, and thirty grains, now weighed five ounces and three drachms, and had therefore gained one ounce and thirty grains. This gain, compared with the loss of the retort, shews, that the retort lost more by three drachms than the receiver gained. These three drachms must have inevitably passed out of the vessels in the form of vapour.

§ VII.

But, from this inference, we can deduce nothing towards the determination of the point in dispute; it was necessary to examine more narrowly what had happened in the vessels. But, before I give any account of that, I shall, for the sake of perspicuity, briefly state what has been just said.

	Oz.	dr.	gr.
The empty retort weighed	2	5	0
The calcined fluor -	2	0	0
The oil of vitriol - -	2	4	0
<hr/>			
Total weight before distillation,	7	1	0
After it, - - -	5	5	30
<hr/>			
Loss, - - - -	1	3	30

The

	Oz.	dr.	gr.
The empty receiver weighed	2	2	30
The water put into it	-	2	0 0
<hr/>			
Total weight,	-	4	2 30
Weight after distillation,	-	5	3 0
<hr/>			
Gain,	-	1	0 30

If we now deduct this gain from the above loss, three drachms will be missing; and they must have been dissipated in the form of vapour.

§ VIII.

I now broke the retort, and, in the first place, separated, as accurately as possible, the dry earth, both in the neck and arch of the retort; it weighed three drachms. Then the residuum in the retort was tried, and found to weigh three ounces, two drachms, and forty grains. Now, as the mass in the retort had originally weighed four ounces and four drachms, it appears, by deducting the residuum, to have suffered, upon the whole, a loss of one ounce, one drachm, and twenty grains.

§ IX.

In order to determine the loss more accurately, I made the following calculation :

(A) The

ON FLUOR ACID. 43

	Oz.	dr.	gr.
(A) The white earth, separated from the neck and arch of the retort, amounted to	0	3	0
(B) The gain of the receiver,	1	0	30
(C) Lost in vapour,	0	3	0
Total	1	6	30

Here, to my great astonishment, the matter that had come from the retort amounted to more by five drachms, ten grains, than the mass in the retort had lost of its original weight (VIII). Now, nothing remained for the illustration of this circumstance but to weigh the retort and receiver themselves. The retort, or, more properly speaking, the pieces of it, which had been carefully preserved, weighed an ounce, seven drachms, and fifty grains; whereas, before the process, the weight of the retort was two ounces, five drachms; and hence it was obvious, that it had lost five drachms, ten grains, the precise quantity which the products of the whole operation had gained, and by which they exceeded the loss of the matter in the retort.

§ X.

This began at once to throw light on the controverted point. For where are the five drachms, ten grains, which the glass of the retort had lost, but in the products

products obtained out of the retort? In order to examine these, the fluid in the receiver was diluted with four ounces of distilled water, and poured on a filter, that the clear liquor might be separated from the earthy crust which floated in it; fresh water was poured on the filter as long as the earth retained any sour taste. The empty receiver was found, upon weighing, to have lost no sensible part of its original weight. The earth remaining on the filter, weighed, after it had been dried, fifty-seven grains.

§ XI.

The clear liquor was then diluted with more distilled water, and afterwards precipitated with spirit of sal ammoniac, prepared with fixed alkali and water, which was added till the smell of volatile alkali indicated the point of saturation. Before any precipitate began to fall, there was a brisk effervescence, that continued for some time. The precipitation itself took place without effervescence: There was present, therefore, a quantity of unsaturated acid. The semitransparent gelatinous precipitate not having quite reached the bottom the next day, the whole was poured upon a filter, and when the liquor had passed through, fresh water poured upon the precipitate as long as it retained
any

any saline taste. After drying, it weighed exactly two drachms.

§ XII.

If we add together the three kinds of earth obtained in the above process, *viz.*

	Oz.	dr.	gr.
(1.) The earth in the neck, and arch of the retort, -	0	3	0
(2.) The earth that had formed a crust on the water, -	0	0	57
(3.) The earth that was precipitated out of the fluor acid, -	0	2	0
	<hr/>		

It amounts upon the whole to 0 5 57

and therefore only to forty-seven grains more than the retort had lost of its weight; which small excess is to be attributed in part to the acid inhering in it, and partly to some moisture attracted by it. To ascertain this, I made each by itself red hot in a small crucible, after which

	Oz.	dr.	gr.
(1.) Weighed - - - -	0	2	36
(2.) - - - -	0	0	21
(3.) - - - -	0	1	55
	<hr/>		

In all 0 4 52

which is less by eighteen grains than the loss of the substance of the retort (IX); they

they must certainly have escaped in the three drachms of vapour.

§ XIII.

Hence, I think, the origin of the earth which makes its appearance during the distillation of fluor, rendered quite evident. It proceeds, neither from the spar itself, and still less, as Mr Scheele supposes, from the fluor acid and water*, nor does it originate in any other way but from the solution of the glass,

§ XIV.

Hence the idea of the fluor acid assumes a totally different form. It is true, that fluor contains an acid before unknown, and

* To this I am induced, by my own experience, to accede. In distilling fluor with oil of vitriol, I have found the retort, as well as the receiver, very much corroded. I poured the acid obtained by the process into a phial furnished with a glass stopple, and observed, after some time, a considerable deposition. I then poured the liquor into another phial like the former; and that it might neither, on the one hand, attack the glass, nor, on the other, compose siliceous earth with the particles of water, according to Mr Scheele's hypothesis, I added highly rectified spirit of wine. I saw, however, after some time, another considerable deposition. This seemed also to proceed from the glass that had been before dissolved, which the acid let fall in consequence of the gradual combination with the spirit of wine; otherwise we must suppose, what to me appears incredible, that the acid decomposes the spirit, attracts the water, and forms the earth. CRELL.

and totally different from every other, which has the singular property not only of dissolving glass, but of carrying it off in the form of vapour: And moreover, that this acid forms, with all the alkaline salts, very peculiar neutral salts, of which the ammoniacal salt arising from the precipitation (XII. & XVI.) furnishes an instance.

§ xv.

I cannot leave untouched the singular property of this last salt, in which the fluor acid, though in the form of a perfect neutral salt, yet retains its power of dissolving glass unchanged: For, upon evaporating to dryness in a cup of Misnia porcelain, the liquor of § XII. which, by its smell, shewed an excess of volatile alkali, I obtained four drachms forty grains of an ammoniacal salt in thin prismatic crystals; but, upon examining the cup, I found all the glazing corroded, and the bottom as rough as a file. During the evaporation, the cup was covered with white paper, which, when dry, appeared full of small crystals of an acid taste, easily distinguishable with the naked eye. These, as well as the ammoniacal salt, forcibly attracted moisture from the air.

§ XVI.

§ XVI.

From the properties of fluor acid, with which we are now become acquainted, all Mr Scheele's other observations may be quite naturally explained; as, for instance, that regenerated fluor still continues to yield siliceous earth when it is distilled with vitriolic acid: That fluor acid, by being merely rectified, always leaves behind siliceous earth, and yet passes over still loaded with that earth: That the ammoniacal salt, in the formation of which the siliceous earth is separated by volatile alkali, yet yields an acid, when it is mixed with vitriolic acid, and distilled, that contains this earth. But the knowledge of so singular an acid may lead to much farther instruction, as we are already certain, that it completely and abundantly dissolves flint, quartz, and glass, the only refractory bodies. From this quality, it must also be apparent to every one, that the present can neither be the acid of salt nor of vitriol, but one totally different from all before known, and peculiar to fluor.

At the same time, we must perceive the almost insuperable difficulty of obtaining it pure, and ascertaining its effects on other bodies.

Additional

E S S A Y I V.

Additional Information concerning Fluor Mineral.* By Mr MEYER.

§ I.

IT is always of advantage to chemistry, when new and important experiments are controverted soon after their publication. If any mistakes, as so easily happens in chemical researches, be committed in the experiments themselves, or if a false theory be founded upon them, the error is not continued half a century, nor does it pass from one elementary book into another, till at last some sceptic thinks of enquiring more narrowly into the matter.

If the experiments be exact, and the theory founded on them true, such a controversy commonly gives occasion to new researches which otherwise would not have been made, and the subject is placed in a clearer point of view.

It were indeed to be wished that both parties held truth strictly in view; that they brought no false experiments into the dispute, and observed and explained the

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phænomena

* *Meyers Beytraage zur Kenntniß des fluspaths.* Schriften der Berlinischer Gesellschaft Natur-forscher-der-Freunde. B. 2. t. 319.

phænomena no otherwise than a friend to truth, uninterested in the controversy, would do, and advanced contradictory assertions with as much caution as possible. It is, by no means, rare, for a man, eager to convict his adversary of a mistake, to commit another in the very same experiment by which he thinks to attain his purpose.

Truth, however, let the dispute be carried on in whatever manner, is commonly a gainer; and this is no small advantage.

§ II.

This has been the fate of the fluor acid, a substance made publicly known by that excellent chemist Mr Scheele, in the Swedish Transactions.

Many doubted concerning it, but its most zealous avowed opposers were, as far as I know, Mr Boullanger and Mr Monnet. Though I had made but few experiments with it when I read Mr Monnet's essay, yet I easily perceived, that, while he charged Mr Scheele with having observed wrongly, his own observation had been still more faulty.

I resolved to defend my friend; but learning that he was himself making experiments in order to refute his adversaries, I willingly relinquished the task to
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his masterly hand. I read with satisfaction the experiments published by him with this view, in the first quarter of the Swedish Transactions for 1780; and moreover, translated them, in order to communicate them to my countrymen in some journal.

Hence I was led to repeat a few experiments, and these again suggested others; and, as I think them likely to contribute somewhat to a more intimate knowledge of this remarkable stone, I lay them before the Society.

§ III.

Among Mr Scheele's experiments, I was particularly struck by one in which he obtained no earthy crust on distilling fluor with vitriolic acid, when he had put spirit of wine into the receiver. I repeated this experiment, in hopes, that, by putting but little spirit into the receiver, I might procure a new kind of æther.

With this view, I put an ounce of finely powdered fluor, that had been before heated red hot, into a glass retort, and added three ounces of white English oil of vitriol; the receiver contained three ounces of highly rectified French brandy.

I had continued the distillation for three hours in a gentle heat, when the acid, having made its way through the bottom

of the retort, put a stop to the process, part of the mixture running into the sand.

On the surface of the spirit, I could not observe the least trace of any crust; but in the place where the receiver had been in contact with it, there was a thin ring of transparent jelly.

The same mixture of fluor and oil of vitriol was again put into a retort of very strong glass, and the same spirit, as in the former experiment, set in the receiver. The distillation was continued in a sand-bath for two hours, at first with a gentle, but afterwards with a stronger heat. When the distillation was half over, the spirit of wine began to change into a thin jelly; and, at the end of the process, I found some firmer pieces at the bottom. These I washed with some spirit of wine; and, in order to obtain the spirit, together with the acid, in a pure state, I poured it into a large retort; as the retort grew warm, the opal-coloured spirit grew clear and swelled; what passed over became again gelatinous. A good deal of earth remained behind, but did not adhere firmly to the retort, which was smooth in the inside, and yet full of broad shallow excavations: And it was evident, that it is not a mere crust which fixes itself to the glass, in treating fluor mineral with oil of vitriol, but that the glass is actually cor-
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roded, which Mr Monnet, contrary to all experience, denies.

§ IV.

I gave over my attempt to procure æther, thoroughlyedulcorated the jelly and the earth that remained in the retort after the rectification, and precipitated the earth that was dissolved by the water with spirit of sal ammoniac. The quantity of earth amounted in all to two drachms, and that which had separated spontaneously from the spirit was semi-transparent.

Neither of these earths suffered any change under the blowpipe, but they both flowed on the addition of a little salt of tartar.

This was a large quantity of earth from two ounces of fluor; and it could not be estimated as the whole, since the first process was cut short before it was completed.

As this earth shewed the properties of filiceous earth, and the glass, which was so much corroded, consists in great measure of it, the greatest part might come from the glass, and the rest perhaps be a constituent part of the fluor itself.

§ V.

In order to ascertain this, it was necessary to obtain the fluor acid quite free

from filiceous earth. I therefore exposed the ley, which I had procured by the precipitation of the earth with sal ammoniac, to a gentle evaporation in a slightly covered glass vessel. The product was one drachm fifty-six grains of an ammoniacal salt; the glass did not appear to have been attacked.

I sublimed half a drachm of this salt in a small retort, which, towards the end of the operation, I laid upon the bare fire. No crust appeared upon the surface of the water in the cover. At the bottom of the retort lay a little flocculent earth, of a light grey colour, above which the internal surface was covered with a white pellicle that reflected various colours, and in the neck there was a sublimate.

The thin pellicle easily separated in many places from the glass, which was quite smooth beneath, though it was not without small furrows.

I poured water both upon the ammoniacal salt and the crust, in consequence of which it acquired a very sour taste, and coloured the tincture of turnsol red.

The white crust that was left undissolved behind, weighed five grains, and under the blowpipe ran without addition into a green glass. This was nothing but the glass that had been corroded by the fluor acid; but, as this acid can be set loose
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only by a strong heat, it had done no more than corrode the glass, without passing over along with it in the form of vapour, and then depositing it again on the water. For, upon pouring two drachms of oil of vitriol upon half a drachm of this ammoniacal salt, a little moistened, and placed in a glass retort, a great foam arose, and the thick vapours that ascended covered the water in the receiver with a white crust.

A scruple of the salt on solution left behind a grain of earth, which, as I conjecture, it had taken up during the evaporation in the glass vessel.

§ VI.

In order to prevent this, I distilled half an ounce of fluor with an ounce of oil of vitriol for five hours. The crusts were separated from the water; they weighed, after being well washed and dried, eleven grains; they were white and very flocculent; thirty-two grains of siliceous earth were precipitated from the filtered water; the ley was then evaporated in a leaden vessel, and yielded eighty grains of salt.

Glass vessels were no longer to be trusted; a piece of a gun-barrel furnished with a cover and terminated by a bent tube, intended to serve instead of the neck of a retort, was used in the following experi-

ments, and the distillation was performed in a sand-bath. In this apparatus, to half a drachm of the newly procured ammoniacal salt I added two drachms of oil of vitriol, and distilled for two hours into a glass receiver, containing an ounce of water.

No vestige of a crust could be perceived on the water; but I saw some earth in the receiver, where the vapours having ascended through the tube came into contact with the wet glass; and here the surface was become sensibly rough.

On the addition of volatile alkali, a few flocculi of siliceous earth, amounting only to one-fourth of a grain, were thrown down out of the water.

Again, I added a drachm of oil of vitriol to $1\frac{1}{2}$ drachm of the salt in the same apparatus; but I now used a receiver of lead, containing an ounce of water.

At the close of the distillation, I found no crust on the water which had an unpleasant smell; and, on the addition of spirit of sal ammoniac, let fall a little grey earth that weighed half a grain.

A scruple of this salt, mixed with an equal quantity of white sand in fine powder, and distilled in the iron apparatus with $1\frac{1}{2}$ drachm of oil of vitriol, an ounce of water being put into the leaden receiver,

ver, shewed no vestige of a crust. The water had a putrid smell, and left on the filter $2\frac{1}{2}$ grains of grey earth, which ran under the blowpipe into a grain of lead; and, by volatile alkali, five grains of grey earth were precipitated, which melted on the addition of a little salt of tartar into a black globule, though the blowpipe alone produced no change on it. This probably arose from some dissolved lead; but as there was a more copious precipitate here than in the preparation of the ammoniacal salt without siliceous earth, it must unquestionably have arisen from a portion of that earth being dissolved and carried over by the fluor acid.

My ammoniacal salt being expended, I prepared more from a weaker acid, which I had remaining from another experiment, in a leaden vessel, but procured only thirteen grains.

To this quantity I added a drachm of oil of vitriol in the above described apparatus, putting in moreover two scruples of green glass in small pieces. Scarce had the iron tube grown warm, when I perceived on the water in the leaden receiver a great spot of siliceous crust; and I saw the same appearance on the moist sides of the vessel. I continued the distillation for two hours; but there did not seem to be any increase of the siliceous crust; $1\frac{1}{4}$ grain

grain remained on the filter, partly consisting of grey earth, partly of white films, which ran under the blowpipe into a greenish glass.

It seems therefore certain, that the earth which passed over in these experiments comes not from the stone, as any constituent part of it, but that it is filiceous earth dissolved by the acid. Did the stone contain an earth which so wonderfully altered acids, it must be thrown down by the volatile ley.

§ VII.

To set the matter in a still clearer light, I used a different species. Some yellow cubical fluor from Saxony being heated and pounded, and then distilled in the iron tube, with a double quantity of oil of vitriol, and with a drachm of water in the leaden receiver, yielded a thin pellicle, of the appearance of lead, but no filiceous crust. By precipitation with volatile alkali I got $2\frac{1}{4}$ grains of grey earth.

A drachm mixed with the same quantity of pulverized sand afforded a pellicle of lead, interspersed with a few particles of white crust, which ran into glass under the blowpipe. Volatile alkali precipitated eight grains, a striking difference.

A drachm mixed with an equal quantity of green glass, reduced to powder, swelled a good deal, and yielded a thick siliceous crust.

§ VIII.

Not yet satisfied with these experiments, I added to a drachm of green fluor, that had been heated and pounded, two drachms of oil of vitriol, still employing the iron tube. I also suspended a piece of wet charcoal in the inside, fixed a cover upon the tube, heated it in a sand-bath, and found, upon taking off the cover, in the space of fifteen minutes, that the charcoal was dry, and had no earth upon it. I now added a scruple of sand in fine powder, wetted the charcoal, and replaced it; but found after the same time nothing more than at first.

Some bits of green glass were now thrown into the mixture, when it began to foam so vehemently, that it ran over; and I did not now hang the charcoal in the tube, as it was no longer clean, nor was this at all necessary; for, after I had held it a few seconds over the orifice, it was covered with a white powder.

Mr Scheele, in his first Essay, says, That he observed the white powder on a piece of charcoal that had been moistened and suspended over fluor, to which vitriolic acid

acid was added. As this experiment was made in metallic vessels, I conjecture that the mortar used for reducing the fluor to powder was of soft glass, and that some particles being abraded by the trituration, had occasioned the phenomenon.

The GLASS was therefore the chief cause of the production of the siliceous pellicle on the surface of the water in the receiver.

§ IX.

In order to ascertain whether, when a quantity of glass sufficient for the saturation of the acid is added to it, it can carry over much more along with it, to half an ounce of fluor, $1\frac{1}{2}$ ounce of white oil of vitriol was added in a retort of glass, and three ounces of water put into the receiver. The retort was corroded through in an hour's time, and the crust on the water weighed ten grains. The water was filtered and divided into two equal parts, of which the one being precipitated with caustic volatile alkali, afforded twenty-five grains of siliceous earth, and the other with aerated vegetable alkali yielded sixty-eight grains of a precipitate which flowed under the blowpipe, ran into the pores of the charcoal, and gave out strong vapours of fluor acid.

In this case, therefore, the siliceous earth was precipitated in a state of purity by the
volatile

volatile alkali; but the precipitate by fixed alkali was a mixture of siliceous earth, fluor acid, and alkali, as Professor Bergmann has already observed.

§ x.

To a mixture of half an ounce of fluor, and the same quantity of glass in powder, $1\frac{1}{2}$ ounce of oil of vitriol being added in a retort that was thus half filled, the ingredients acted so violently on each other, that in a short time the mixture rose to the neck of the retort. It was left exposed to the open air on account of the vapour, and the next day I found the rim of the retort covered with fasciculated crystals as with hoarfrost.

The same mixture being on another occasion made in a capacious retort, and thoroughly blended by agitation, became a thick mass, and swelled like dough in fermentation; the bottom of the retort grew very hot, and the siliceous crust appeared, on three ounces of water, which had been put into the receiver.

At the end of the distillation, which was continued three hours, I found sixteen grains of siliceous earth on the surface of the water, and the precipitate by volatile alkali weighed fifty-six grains. The retort was not nearly so much corroded as usual.

On distilling thirty grains of this precipitate in a glass retort, with $1\frac{1}{2}$ drachm of oil of vitriol, I saw no filiceous earth on the water in the receiver, nor sublimate, nor did spirit of sal ammoniac throw down any thing, either out of the water in the receiver, or that with which the earth wasedulcorated. I mixed the ley of fluorated volatile alkali with a solution of chalk in nitrous acid, till no more precipitation took place. The mixture was passed through nitrous acid, and the precipitateedulcorated; it weighed, when dry, two drachms thirty-six grains.

Two drachms of oil of vitriol being added to a drachm of this precipitate contained in a glass retort, the precipitate was attacked in the cold, yet no crust appeared; but heat was scarce applied, when the whole surface of the water was covered, and all the phænomena which the natural exhibits were shewn by this regenerated fluor.

This shews, that Mr Scheele's theory of fluor acid is true, and that such an acid actually exists.

§ XI.

My first experiments were communicated to Mr Scheele, with a request that he would repeat them; by which means I hoped to guard against any new mistake.

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That worthy philosopher informed me, that he had long observed, that a mixture of fluor, as transparent as mountain crystal, and of oil of vitriol in a metallic cylinder, produced no appearance of siliceous earth on a wet sponge suspended in the inside.

At my request he made a new experiment, which consisted in adding oil of vitriol to portions of fluor of this transparent kind that were placed in two tin cylinders; some siliceous earth was put into one, a wet sponge suspended in both, and a cover fixed on them. The next morning the sponge that was suspended over the mixture to which siliceous earth had been added, was covered with that earth, while the other exhibited no such appearance.

However contrary this may appear to my experiment (§ VIII.), I have no doubt of the fact, having often experienced my friend's accuracy; I might have committed a mistake before.

§ XII.

The experiment was therefore repeated, but no heat was applied to the mixtures in the tin cylinders. After the expiration of fifteen minutes, neither sponge had any earth adhering to it; but after continuing suspended for a whole night, the
result

result was exactly such as Mr Scheele described.

Here, therefore, the filiceous earth alone, on mixture with fluor, had yielded the dry filiceous earth which I observed only when I added glass. Hence it became necessary to attempt a few more experiments.

§ XIII.

A drachm of fluor, mixed with a double quantity of oil of vitriol in the iron apparatus, afforded, after a distillation of two hours, a thin film of lead on the surface of the water in the receiver, but no filiceous earth. While I was washing it out, I perceived some few particles, which were like the filiceous crust, but they were too inconsiderable to be weighed. If the mixture had been treated in glass vessels, the filiceous earth would have amounted to $2\frac{1}{2}$ grains, which, on account of its rarity, makes a tolerable bulk. In order to be better able to observe it, the same mixture was disposed in the same manner, except that, instead of the leaden receiver, one of glass, with $3\frac{1}{2}$ ounces of water, was so applied, that the mouth of the iron retort nearly touched the surface of the water. In the beginning of the distillation, a small spot appeared under the neck of the retort, and the mouth it-
self

self was covered with white powder. But it all soon disappeared, and I saw no more of it, though the process was long continued.

The empty part of the receiver was corroded, yet I procured, after edulcoration, but half a grain of earth.

This seems further to shew, that nothing but the glass has any share in the production of the siliceous earth.

§ XIV.

It follows from these experiments, that uncombined fluor acid dissolves siliceous earth, and carries it up into the water in the receiver. If no water be present, it ascends in the form of a dry vapour; a remarkable fact, considering the fixity of this earth. May not this serve to illustrate the volatility of the diamond? I think it probable that fluor acid is a constituent part of this gem.

The origin of the siliceous crust on the surface of the water may be explained, by supposing, either that the acid dissolves an excess of the earth which is present in the glass, and already half prepared for solution, and that being oversaturated, it lets fall a part which it cannot retain when mixed with water, or that the alkali in the glass comes into action.

In Mr Scheele's experiment, the siliceous earth was deposited on the sponge, without any other circumstance to promote the volatilization. But it is, at the same time, to be noticed, how slowly this happened; for it, doubtless, did not begin to take place till the small quantity of water contained in the sponge was saturated with the siliceous earth dissolved in the acid. Fluor acid, which I have kept above a year in a phial, has corroded the glass in many points, which are surrounded with concentric circles, and deposited a powder that adheres to the bottom.

This remarkable fossil may still furnish a subject for many experiments. Golden vessels would, in my opinion, be the most convenient in such an undertaking, as also for keeping the acid*.

E S S A Y

* These experiments so clearly point out the origin of the siliceous crust, that Bergmann, who had adopted Mr Scheele's opinion concerning its formation during the process, candidly deserted it (Opusc. vol. iii. p. 397.). That this subject might not remain in obscurity for want of investigation, Mr Wenzel of Dresden likewise made a number of experiments on fluor, which coincide in every essential point with those of Mr Meyer, though they differ in a few particulars. The title of his pamphlet is, G. WENZEL'S *Chymische Untersuchung des Fluss-spaths*. Dresden bey Gerlach, 1783. 4to.

Mr Wenzel, in order to obtain the fluor acid free from siliceous earth, performed the distillation in a leaden retort, provided with a glass receiver; there appeared,

ESSAY V.

ON MANGANESE, MANGANESIUM, OR
MAGNESIA VITRARIORUM. 1774.

§ I.

THOUGH the different species of manganese have attracted the attention of chemists of late years, the result of
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appeared, however, upon the water in the receiver a variegated crust, and the acid, with fixed alkali, yielded a gelatinous precipitate. Upon examining the receiver, he found that the vapours had corroded its internal surface, so that it appeared as if it had been rubbed with coarse sand. Mr Wenzel, however, accomplished his purpose, by substituting a balloon of lead in the place of a glass receiver, and by distilling with a gentle heat. At the end of the operation, there was no appearance of any earthy crust, either in the retort, or on the surface of the water in the receiver: The acid liquor gave no jelly on the addition of alkali, though there was a precipitation of iron and earth of alum.

To complete his proof of the origin of the siliceous earth, he mixed fluor, quartz, and vitriolic acid, and performed the distillation in his apparatus of lead. But he now found the usual crust upon the acid liquor, and obtained a gelatinous precipitate on the addition of alkali.

Moreover, Mr Wenzel observed, that two ounces of fluor lost upon calcination in open vessels only two grains. When this experiment was performed in an air apparatus, some inflammable air was obtained, and a very small quantity of fluor acid, which attacked the
glass.

their experiments has gone no further than to disclose such of their qualities as serve to distinguish them from other minerals; at least nothing has been published to elucidate their nature any further, except a dissertation by Mr Westfeld, in the year 1767, in which this author first examined their constituent parts. My experiments, however, will shew, that his conclusions were too hastily made. I think it unnecessary to enumerate all the different kinds of manganese which I have examined, as they all agree in their principal qualities.

§ II. *Effects of Vitriolic Acid on Manganese.*

(A) Two drachms of manganese, levigated in a glass mortar, were digested with
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glass. Fixed alkali threw down a precipitate, amounting, after properedulcoration, to one ounce, twenty-two grains, from the acid expelled by oil of vitriol from two ounces of fluor. This precipitate was very fusible, and yielded fluor acid with oil of vitriol. Both fire alone and vitriolic acid expelled a little acid of fluor from the earthy crust. When the precipitation from the same quantity of acid was made by volatile alkali, two drachms and fifty-three grains of an infusible substance were obtained, which likewise, on addition of vitriolic acid, yielded some fluor acid. It appears then, that a portion of it is contained in the earthy crust, and that even fixed alkali is not capable of separating it completely from siliceous earth, but it remains united with some siliceous earth and alkali after precipitation.

The residuum, after distillation, contains calcareous and aluminous earth; this, at least, was the case with the German species examined by Mr Wenzel.

an ounce of diluted acid of vitriol for several days. No effervescence ensued, neither had the acid lost any of its taste, nor was the manganese diminished in quantity. I notwithstanding filtered the liquor, and saturated the acid with alkali of tartar, whence I obtained a yellowish white precipitate. (B) Upon the remaining manganese I poured another ounce of diluted acid of vitriol; which, however, appearing to have no action upon it, I put another half ounce of levigated manganese into the mixture, and boiled it. The solution still retained some acid taste; but on adding two drachms more of levigated manganese its taste grew bitter.

(c) I exposed an ounce of powdered manganese, mixed with as much concentrated acid of vitriol as to reduce the mass to the consistence of honey, in a glass retort to the fire, till it became red hot, during which operation some vitriolic acid mixed with water came over in the receiver. After breaking the retort, the mass was found hard, white in the inside, and red on the surface; it weighed $12\frac{1}{2}$ drachms. This mass was reduced to powder, and distilled water poured upon it; in consequence of which a great heat was generated, and a great deal of it dissolved. The solution, after being filtered, was edulcorated. Afterwards, when it was dry, it

appeared of a dark grey colour, and weighed one drachm and a half. This residuum was calcined in an open crucible with concentrated vitriolic acid, till no more vapours arose; then it was put into water, when one drachm remained undissolved, which was again calcined with concentrated vitriolic acid, and the undissolved residuum was a white powder, weighing half a drachm. (D) This white residuum was further insoluble in the vitriolic acid. During its fusion with borax, it made an effervescence, and yielded a transparent brown glass; it likewise effervesced with fixed alkali, changing into a brown mass, which yielded an hepatic smell with acids, becoming, at the same time, a gelatinous mass. (E) The solution of manganese obtained by calcination was evaporated, and, in the first place, a few small crystals were deposited, which were nothing but vitriolated lime (selenite). Afterwards, some very fine large crystals, of an oblique paralleliped form, were deposited, which increased in number as long as there was any liquid remaining. Their taste was very much like the taste of vitriolated magnesia (Epsom salt). Mr Westfeld pretends that they are alum; but they resemble alum in no other respect, except in containing the same acid.

§ III. *Effects of phlogisticated Vitriolic Acid.*

I dipped, according to Stahl's prescription, some rags into a solution of fixed alkali of tartar, and, after saturating them with the acid of burning brimstone, I put them into a retort, poured some acid of tartar upon them, and luted on a receiver which contained water and levigated manganese. The retort was put into a sand-bath, and, after a warm digestion of one day, the liquid of the receiver had become as clear as water, and a little fine powder was precipitated to the bottom, consisting, for the most part, of siliceous earth.

§ IV. *Effects of pure Nitrous Acid*.*

(A) I poured one ounce of pure colourless nitrous acid upon two drachms of levigated manganese. After this compound had been kept in a heat of digestion for several days, the menstruum was found to have lost nothing of its acidity, nor was there any appearance of effervescence. I abstracted the acid by distillation, poured the distilled liquor again upon the re-

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fiduum

* Under the name of pure nitrous acid I understand colourless nitrous acid—the fuming acid distilled in a gentle heat, till the mass remaining in the retort appears colourless, and yields white vapours when heated. Nitrous acid of this quality must be preserved in a glass vessel furnished with a ground stopple, in a dark room.

fiduum, and distilled it over again, but very slowly. The residuum was but very little dissolved. I again poured the distilled acid upon it, and afterwards added as much powdered manganese as was necessary for the perfect saturation of the acid, and found that nine drachms were required for this purpose. (B) The solution of manganese being by these means saturated, was filtered and divided into two equal portions. Into one of these I poured some drops of vitriolic acid, whereby a fine powder was precipitated, which, however, did not settle at the bottom till after some hours had elapsed. This powder was neither soluble in boiling water nor in acids. The limpid solution, after being evaporated, yielded some small crystals of selenite or gypsum; but would afford no others. (c) From the other half of this solution, after it had been evaporated in a gentle heat, I obtained small shining crystals, which, as well as the solution itself, were of a bitter taste, and weighed about ten grains. On pouring some drops of vitriolic acid into this solution, inspissated by a gentle heat, no precipitation ensued, except of a little selenite; but as soon as it was inspissated to the consistency of honey, some fine acicular crystals, verging towards the same centre, began to form, but they
grew

grew soft and deliquesced in a few days afterwards.

§ v. *Effects of phlogisticated Nitrous Acid.*

As this acid shews, in several experiments, quite different phænomena from those which the pure nitrous acid shews, I purposed to try its effects also upon manganese. I therefore put a little levigated manganese, mixed with some water, into a large receiver, to which I luted a tubulated retort, and poured through the opening some ounces of common nitrous acid, and added, at several different times, some iron filings, taking care to close the vessel always with a glass stopple. The nitrous acid thus combined with the phlogiston of the iron went over into the receiver, and there united with the black mass above mentioned. The manganese was thus entirely dissolved in a few hours time; the solution was as limpid as water, a little fine earth excepted, which was siliceous. There began now to precipitate a white earth, of the same kind as that mentioned in § IV. (B). In other respects, this solution agreed with that made in pure nitrous acid, as it is described in the preceding paragraph.

§ VI. *Effects of common Muriatic Acid.*

(A) I poured an ounce of purified muriatic

riatic acid upon half an ounce of levigated manganese. This acid, after standing quiet for an hour's time, grew dark brown. A portion of this solution was digested in an open glass vessel in heat. It yielded a smell like warm aqua regia. In a quarter of an hour, the smell was gone, and the solution became clear and colourless. (B) The rest of the brown solution was digested, with a view to see whether the muriatic acid would be saturated with manganese. As soon as it grew warm, the smell of aqua regia was considerably stronger, and an effervescence ensued, which lasted till the next day, when the solution was found saturated. Upon the residuum, which was not dissolved, I poured another ounce of muriatic acid, which was followed by the very same phenomena, and the manganese was entirely dissolved, a small quantity of siliceous earth remaining. (c) This yellow solution was divided into two portions. Into the one I poured some drops of vitriolic acid, and the solution in a few minutes turned white, and a fine powder was precipitated, which was not soluble in water. After the solution was evaporated, some small selenitic crystals formed, and the residuum exhibited the same phenomena as are described above, with the mixture of nitrous acid and manganese.

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(D) The other half was evaporated, and some small angular shining crystals were obtained, which, with regard to their crystallisation, agreed with those obtained by the nitrous acid.

§ VII. *Effects of Fluor Acid.*

But very little of the manganese, after being digested with this acid for several days, was dissolved; and it was necessary to add a very large quantity of levigated manganese before the acid was saturated. The solution had hardly any sensible taste; a little precipitation took place on adding alkali. But if a neutral salt, composed of this acid and volatile alkali, be added to the solution of manganese in any one of the above mentioned acids, a double decomposition takes place, and the manganese uniting with the fluor acid is precipitated.

§ VIII. *Effects of Phosphoric Acid.*

One drachm of phosphoric acid being boiled with half a drachm of powdered manganese, dissolved but little of it; and, though evaporated to dryness, the remainder had a very sour taste. At last, however, by adding more manganese, the acid was saturated. On adding microsmic salt to a solution of manganese, a decomposition follows, like that effected by the fluor acid.

§ IX. *Effects of Acid of Tartar.*

Pure acid of tartar, digested in the cold with manganese, produced a brown solution; but, on digesting in heat, more was dissolved with a kind of effervescence; the whole quantity, however, was not dissolved, but the acid was at last saturated by the addition of more manganese. On adding tartarized fixed alkali to a solution of manganese, a double decomposition happens, as § VII. VIII. IX.

§ X. *Effects of distilled Vinegar.*

In a boiling heat little of the manganese was dissolved by vinegar; but, after distilling the spirit of verdigrease several times from manganese, the acid was saturated. On adding vitriolic acid, I obtained a little white precipitate, (§ IV. B). Of the remaining manganese hardly any sensible quantity was dissolved by concentrated vinegar, though repeatedly distilled over it. The product of the solution upon evaporation to dryness was deliquescent in the open air.

§ XI. *Effects of Acid of Lemon.*

Two drachms of levigated manganese were digested with an ounce of the acid of lemon. The mixture, when cold, acquired a brown colour; but, on the application

application of heat, the liquid began to effervesce, which continued till the acid was saturated, when it had lost its brown colour. In the same manner the remaining manganese was dissolved. More acid was poured upon it, and thus the whole was in a few hours dissolved, a white earth excepted.

§ XII. *Effects of Aerial Acid.*

I saturated cold water, which contained a little snow unmelted, with aerial acid, and then put a little levigated manganese into it. The phial which contained this mixture was carefully closed, and left for several days in the cold, during which time it was now and then agitated. The liquor was afterwards filtered, and alkali added to it, upon which a white powder precipitated. The manganese likewise separated from its solution, on standing a few days in the open air.

§ XIII.

Such are the effects of acids upon manganese. What is most remarkable in them is, that some of the acids, such as the volatile sulphureous, the phlogisticated nitrous, the common muriatic acids, and the acid of lemon, completely dissolve it. Others during the solution cause a considerable effervescence; others again produce

duce the solution quietly, and others dissolve a part of the manganese only. Before I enter upon any explication of these singular phenomena, it will be necessary to point out the general properties of manganese.

§ XIV.

(1.) Manganese has a strong elective attraction for all phlogistic substances. (2.) This attraction becomes stronger, if there be a menstruum present which at the same time can unite with the phlogisticated manganese. In this situation the manganese is able to attract phlogiston more strongly than the nitrous acid does *viâ humidâ*. (3.) When manganese is saturated with phlogiston, it loses its black and assumes a white colour, which however disappears as soon as the phlogiston is separated from it again. (4.) Without combining it with phlogiston, there is no way of producing a colourless solution of manganese in any acid; and, whenever phlogiston is wanting, the solution becomes blue or red. By means of these four general qualities of manganese, discovered by a train of experiments, all its known effects are easily explicable, as will appear from the following observations.

§ XV.

§ xv.

Diluted vitriolic acid dissolves manganese only in part, whether digested or boiled with it, (§ II. A). This part therefore ought to be separated from the rest, because the solution of manganese is never colourless, except when combined with phlogiston, (§ XIV. No. 4.) Whence it follows, that this soluble part of it is united with phlogiston. That manganese naturally contains but little phlogiston, has been some time ago taught by Mr Westfeld; but the cause he assigns is not to be admitted, till it is confirmed by other arguments, especially as nitre, without the addition of phlogiston, may become alkalescent, and that the sooner, if there be a body present which is capable of uniting with the alkali, in which case a heat only half as strong is requisite. This happens in the calcination of manganese with nitre; for if the mixture is distilled, nitrous acid is obtained in the receiver: But that some phlogiston really enters into the composition of manganese, the following experiments will shew: (A) If the solution of manganese in vitriolic acid (§ II. A, B) be evaporated to dryness, and then the residuum distilled in the open fire in a glass retort, with a receiver applied to it, the vitriolic acid does not separate from the
manganese

manganese till the retort begins to melt; but it is then changed into volatile sulphurous acid. The residuum is black, and nothing but common manganese. (B) Let the solution of manganese in nitrous acid (§ IV. A) be put into a glass retort, all the liquid abstracted, and, when it begins to foam, let a receiver, with some water in it, be applied. By a slow fire, the nitrous acid, employed for the solution, will be driven over in the form of blood-red vapours, and yield green volatile nitrous acid. In the retort there will remain likewise real black manganese. (c) A solution of manganese in vitriolic or pure nitrous acid, (§ II. IV. B, A) precipitated by alkali of tartar, retains its colour; but, when calcined in the open air, grows black (§ XIV. No. 3.). Hence it follows, that manganese contains phlogiston; and, since the residuums in the retort have lost their phlogiston, by means of which they were united with the acids, they are no longer soluble in pure acids. If therefore vitriolic acid be poured upon the residuum (A), little or nothing of it will be dissolved; but if the volatile vitriolic acid, which was driven over into the receiver, be poured upon it, it will again dissolve it, a small portion excepted, for want of a sufficient quantity of acid; for there is some of the
acid

acid lost during the distillation through the lute. The same thing happens with the distillation and solution of manganese in nitrous acid, (B).

§ XVI.

Now, since only a part of this mineral is dissolved by the vitriolic acid, it may be asked, Why the remainder does not dissolve? To this I answer, The undissolved portion has parted with the little phlogiston it naturally possessed, to that portion of manganese which is taken up by the vitriolic acid during the first digestion; for, without that principle, manganese is insoluble. That the remaining manganese loses its phlogiston, is evident from this, that if nitrous acid be abstracted from it, there appears little or no red vapour. That manganese, according to its second general property, attracts phlogiston more strongly when it is combined with some acid, the following experiments will shew: (A) Levigated manganese digested or boiled with a solution of sugar, honey, gum Arabic, hartshorn, jelly, undergoes no change. But on mixing the manganese with some diluted vitriolic or pure nitrous acid first, afterwards adding some of these substances, and exposing the whole to digestion, you perceive with admiration how the black colour

lour vanishes by degrees, and the solution becomes as limpid as water. During this phænomenon, a quantity of air-bubbles is discharged with a violent effervescence; they are found to be aerial acid. Nay, manganese, in such a combination, shews such a strong attraction for phlogiston, that metals, not even the noble ones excepted, render it soluble in these acids in a limpid form; and what is still more remarkable, the volatile alkali, as well as the above mentioned vegetable and animal substances, is entirely destroyed. But of this I shall speak more fully hereafter. At present I conclude from these experiments, that the superficial particles of levigated manganese; on touching an acid, acquire a great attraction for phlogiston; and if such an acid contains no phlogiston, nor the manganese so much as is requisite for its entire solution (§ II. IV. A, A), those superficial particles attract as much of the phlogiston as is required from the particles next adjacent to them, which have not yet come in contact with the acid. This is the reason why the external particles dissolve in vitriolic or nitrous acid; and the internal, or those lying nearest under the external ones, having been deprived of their phlogiston, remain undissolved; but these likewise dissolve as soon as the requisite phlogiston is communicated

municated to them from the above mentioned substances, such as sugar, &c.

§ XVII.

We now come to speak of the effects of concentrated vitriolic acid on manganese, (§ II. c). It is remarkable, that this acid dissolves the manganese entirely without the addition of any phlogiston. It would be difficult to comprehend whence the phlogiston in this case should come, if we were not certain that several substances, which have a great attraction for phlogiston, can attract it in a red heat. Quicksilver, and silver when dissolved in the purest nitrous acid, really lose the phlogiston (§ IV.), which is a constituent part of these metals. This appears from the red vapours, under the form of which the nitrous acid arises; and the dissolved metallic earth cannot be again reduced to its metallic form, till it has again acquired the lost phlogiston, which is effected either by precipitation with complete metals, or else by means of heat alone. It is known, that nitrous acid, when combined with a little phlogiston, adheres afterwards to absorbent bodies so loosely, that it may be expelled from them by vegetable acids. If a small glass retort, filled with nitre, is kept upon the fire, till the nitre shall

have been in a red fusion for half an hour, it is found, after cooling, to have acquired some phlogiston. For, when rubbed with tamarinds, a strong smell of aquafortis rises; and it likewise deliquesces in the open air, though there is no mark of any superabundant alkali. And what else can be the cause, that fuming nitrous acid, when distilled, rises at last, when the retort is nearly of a white heat, in blood-red vapours, whereas it ascends during the distillation in a limpid form like water? I could adduce many more experiments to prove, that phlogiston is contained in fire, if I was not afraid of rendering this dissertation too long. This, however, I may add, that the following objection is void of foundation: Why; if what I assert was really the case, the calces of the ignoble metals are not equally reducible by heat? since all bodies have not an equal degree of attraction to phlogiston.

Thus manganese can attract the quantity of phlogiston necessary for its solution, by means of concentrated vitriolic acid, from heat. It is not probable, that the concentrated acid undergoes a decomposition in this degree of fire; for if you saturate half an ounce of this acid with alkali of tartar, and afterwards calcine in a retort, with a receiver applied, an ounce
and

and a half of powdered manganese, with an equal quantity of the same vitriolic acid, then dissolve the calcined mass in distilled water, and likewise wash well the receiver, which contains some drops of vitriolic acid, which are also to be added to the solution; and lastly, add the same quantity of alkali, there will be no mark either of abundant alkali or acid. Thence it may be concluded, that the phlogiston in the vitriolic acid (if there really exists any in it) contributes nothing to the solution. But the manganese, precipitated with alkali, contains a considerable quantity of it; in consequence of which, it is afterwards entirely soluble in acids, without the addition of any phlogiston.

§ XVIII.

Manganese is often mixed with heterogeneous earths, which are not to be reckoned as its constituent parts. Among these are, (1.) a little iron ochre. This was the reason why the mass in the retort, after distillation, was red on the outside (§ II. c), because it was there exposed to the greatest heat; whence the vitriolic acid, that was combined with the iron, quitted it. Calx of iron is besides easily obtained from the solutions of manganese in acids. If a few drops of a solution of alkali are

dropped in, the iron will be precipitated first, because it has less attraction for the acid than the phlogisticated manganese has. That this small quantity of calx of iron is only mechanically mixed with manganese, has been proved by Mr Pott, and afterwards by Mr Rinman, though Mr Westfeld looks upon it as a constituent part of manganese. (2.) Some siliceous earth is likewise found mixed with manganese, but it does not enter into the solution, (§ II. D). That the siliceous earth is not pure, appears from experiment; but it may be obtained quite pure by means of proper acids. (3.) A little calcareous earth, which, as far as I know, has not hitherto been taken notice of. It is this with which the separated siliceous earth is mixed, (§ II. D); and, in consequence of its absorbent nature combining with the vitriolic acid, it forms a neutral salt, which is soluble in water, and forms with borax a brown glass (§ II. D), on account of the sulphur produced during the fusion; of which I shall speak more particularly hereafter, § XXXII.

§ XIX.

If the salt, consisting of vitriolic acid and manganese (§ II. C), be again dissolved in distilled water, and afterwards crystallised, it will be obtained in a state of
purity,

purity, containing nothing of the admixtures, mentioned in the preceding paragraph. From it manganese, saturated with phlogiston, may be precipitated by alkali of tartar. That this manganese is really saturated with phlogiston, appears from this, that it cannot be united with more phlogiston, so as to yield any metallic substance. If Mr Westfeld had examined this precipitate a little more, he certainly would not have pronounced it to be the earth of alum. The earth, thus obtained, is without the least particle of iron, and is besides endowed with all the properties which mineralogists ascribe to manganese, after the phlogiston has been separated from it by calcination in the open air, (§ xv. c). Thence I infer, that Mr Westfeld's Dissertation affords no instruction whatsoever.

§ xx.

The effects of volatile sulphureous acid on manganese clearly prove what has been asserted (§ III.). The manganese attracts the phlogiston contained in this acid, which is the cause of its great volatility, and which renders the manganese soluble in the now pure vitriolic acid. If this solution be mixed with concentrated vitriolic acid, and distilled, no volatile sulphureous acid is obtained; and if it be precipitated

pitated by means of fixed vegetable alkali, vitriolated tartar is obtained. This proves that manganese has a stronger attraction for phlogiston than for vitriolic acid in the moist way.

§ XXI.

The effects of nitrous acid on manganese coincide, upon the whole, with those of vitriolic acid. If this acid could support such a degree of heat as the other in a state of concentration, it would also entirely dissolve the manganese without the addition of any phlogiston. But as this is not the case, it is necessary to supply the defect of phlogiston. The extraneous substances mixed with it appear in this process more clearly, (§ XVIII.). Here the pure siliceous earth remains undissolved at the bottom; but another unknown earth unites with the nitrous acid, and yields crystals, (§ IV. c). It likewise may be precipitated by the vitriolic acid; and this is the precipitate mentioned in the same place (H), as insoluble in water. The calcareous earth, with vitriolic acid, forms gypsum, and the small portion of iron is readily separated, by means of a few drops of alkali of tartar, (§ XVIII. No. 1.).

§ XXII.

§ XXII.

All this appears still more clearly with phlogisticated nitrous acid. The manganese decomposes this acid for the same reason as it does the volatile sulphureous acid (§ xx.). That the phlogiston of the acid really combines with the manganese, appears from this, that on adding to such a solution some vegetable acid, there is no smell of aquafortis observed, (§ xvii.) and the distillation with pure vitriolic acid yields limpid, by no means yellow, nitrous acid. There appears no effervescence here, as happens with the solution in pure nitrous or vitriolic acids, on adding a little gum or sugar (§ xvi. A). It is well known, that a great quantity of aerial acid is constantly developed in the decomposition of any animal or vegetable substance. Now, since manganese, assisted by acids, has the same effect upon those substances as air and other bodies have, which extract from them their phlogiston, there must necessarily be, in this process, a separation, or perhaps a generation of aerial acid. But, in the present case, with phlogisticated nitrous acid, no such effervescence can take place, because it is combined with pure phlogiston; and if this be again separated, I do not see why aerial acid should be extricated. Moreover, manganese,

ganefe, when united with nitrous acid and metals, arfenic or oil of turpentine, is entirely diffolved without fhewing any effervescence.

§ XXIII.

The vith paragraph fhews the effects of muriatic acid. In this cafe, perhaps, it does not immediately appear whence manganese fhould obtain its phlogifton; no phlogifton being added here, and the entire folution taking place without heat. There occurs, indeed, here a circumftance, which certainly proves that muriatic acid contains fome phlogifton; a property which one fhould have attributed to the nitrous acid, chemifts having been of opinion that this principle was prefent in a pretty large quantity, as one of its constituent parts. But this we now reverse, and attribute phlogifton to the muriatic acid.

Muriatic acid, when digefted in the cold with manganese, affumes a dark-brown colour (§ vi. A); for, fince this fubftance never affords a colourlefs folution without phlogifton, the prefent folution will be either blue or red (§ xiv. iv.), though the muriatic acid is capable of diffolving manganese, without the addition of the inflammable principle. In this cafe, the colour has more of brown than red, on account of the fine particles of the manganese

nese floating in the solution, and not easily sinking to the bottom; for, without these particles, the solution is red; and red mixed with black yields a brown colour. Manganese adheres here loosely to the muriatic acid; so that it may be precipitated by water; and the precipitate shews the same properties as common manganese. Whenever I exposed the mixture of manganese and muriatic acid to digestion, an effervescence ensued with a smell of aqua regia, (§ VI. B).

In order to set this new discovery in a clear light, I tied to the neck of a retort, which contained a mixture of manganese and muriatic acid, an empty bladder, and put it into hot sand. An effervescence ensuing, the bladder was filled. When the acid no longer occasioned any effervescence, which was a sign of its saturation, I took the bladder off, and found that the air had rendered the bladder yellow, as nitrous acid would have done; but there was not the least mark of aerial acid, only a very sensible pungent smell, highly oppressive to the lungs, and resembling the smell of warm aqua regia. The solution in the retort was clear, and of a yellowish hue, which was owing to the iron contained in it. If you wish to be convinced, that the manganese, thus dissolved, likewise contains phlogiston, you should precipitate the solution with alkali
of

of tartar, edulcorate the precipitate, and treat it in the manner above mentioned, (§ XVI. A, B, C). But whence did it acquire its phlogiston? From the muriatic acid. The matter of heat has no share here, because the solution becomes limpid without it, if it be only exposed to the air for a few hours. The following is the theory of the solution: The manganese is first attacked by the acid, and thus we have a brown solution. The manganese, when dissolved, acquires, by means of the acid, a strong attraction for phlogiston, (§ XIV. No. 2.) and really attracts it from the particles with which it is combined. These particles having thus lost one of their constituent parts, and being but very loosely combined with the phlogisticated manganese, are expelled from it by the remaining muriatic acid, which has not yet suffered any decomposition, and now appear with an effervescence, as an highly elastic air; the brown colour has now disappeared, and the solution is become limpid.

§ XXIV.

The marine acid separated from phlogiston, one of its constituent parts, unites with water in a very small quantity only, and gives it a slight acid taste: But, whenever it is enabled to combine with phlogiston,

giston, it assumes its former nature, and again becomes a true muriatic acid. In order to discover the properties of this aerial fluid, it is best to examine it in its elastic state. Common muriatic acid is to be mixed with levigated manganese in any quantity in a glass retort, which is to be put into warm sand, and a glass receiver applied, capable of containing about twelve ounces of water. Into the receiver put about two drachms of water; the joints are to be luted only with a piece of blotting paper tied round them. In a quarter of an hour, or a little longer, a quantity of elastic acid, going over into the receiver, gives the air contained in it a yellow colour, and then it is to be separated from the retort. At this time, if the paper has been closely applied, a portion of the aerial fluid will rush out with some force; and you therefore must have a cork ready to close it immediately; and then another receiver, with two drachms of water in it, should be applied to the retort as before; and thus several such vessels may be filled with dephlogisticated muriatic acid. In the process care should be taken, that the retort be fixed in such a posture, that if a few drops should rise into its neck, they may run back into the body. The water put into the receivers serves to condense the vapours of
marine

marine acid, should any go over. I fill several glasses at once, in order to get a good quantity, and to avoid the trouble of repeating the process as often as I want some of the fluid for my experiments. It is better to make use of small vessels for receivers, because a great part of the acid is lost every time the cork is taken out.

§ xxv.

The bodies which I wished to expose to the action of this dephlogisticated aerial fluid were fixed in a glass tube, which passed through the cork of the receiver. I observed that the corks (A) became yellow within the receiver, as from aquafortis, and the lute was likewise corroded during the distillation. (B) Paper coloured with lacmus became nearly white; all vegetable red, blue, and yellow flowers, grew likewise white in a short time; the same thing happened to green vegetables: Meanwhile, the water in the vessel was changed into a weak but pure muriatic acid. (C) The former colour of the flowers, or of the green vegetables, could not be recovered either by alkalis or acids (D), expressed oils and animal fat, whether dropped into the tube, or smeared upon it, grew in a short time as tenacious as turpentine. (E) Cinnabar grew white upon the surface, and, when it was washed

washed in water, a pure solution of corrosive sublimate was obtained; but sulphur was not changed; (F) vitriol of iron grew red and deliquescent; vitriol of copper and zinc remained unchanged; (G) iron filings, put into the tube, were dissolved. The solution, after being evaporated to dryness, and then distilled with the addition of some concentrated vitriolic acid, again yielded pure marine acid, in which gold remained undissolved. (H) All the metals were attacked; and, with regard to gold, it is remarkable that its solution in this dephlogisticated muriatic acid yields with volatile alkali aurum fulminans. (I) When some volatile alkali, prepared from sal ammoniac and quicklime, was dropped upon the tube, a white cloud was produced, and a great number of air-bubbles were discharged from them, which, on bursting, yielded a vapour. (K) Fixed alkali was changed into common salt, which decrepitated, but did not detonate in the fire. (L) Arsenic became deliquescent in this vapour; (M) insects instantly died in it; (N) and fire was instantaneously extinguished.

§ XXVI.

This sufficiently shews how strong an attraction dephlogisticated muriatic acid has for phlogiston. Perhaps STAHL obtained

tained such a dephlogisticated muriatic acid by means of iron, and, from the yellow colour of the cork, was led to suppose that the muriatic had been changed into the nitrous acid. If you make a mixture of manganese, muriatic acid, or diluted vitriolic acid and alcohol, and, after digesting it in a well closed phial for some days, distil it by a gentle fire, no effervescence ensues; but the spirit of wine goes over, and, what is very remarkable, has a strong smell of nitrous æther. The remainder in the retort will have lost its acidity, and be saturated with manganese. If metals, sugar, linseed, or oil of turpentine, be combined with a mixture of pulverized manganese and muriatic acid, no such dephlogisticated muriatic acid is produced; because, in this case, a sufficient quantity of phlogiston is present for the elastic acid to unite with. It is remarkable of quicksilver, that a great part of it enters into the solution, and may be afterwards again obtained by crystallisation with all the properties of corrosive sublimate. If plates of pure gold be put into a mixture of pulverized manganese and pure muriatic acid, it will afterwards appear that gold as well as manganese is contained in the solution.

§ XXVII.

As fluor acid yields a precipitate with manganese, (§ VII.), it is easily understood why it dissolves so little; for the salt forms a fine pellicle round the particles of the manganese, and thus prevents the acid from penetrating any further. The same thing happens with the acid of phosphorus, (§ VIII.); for microcosmic salt likewise produces a precipitation.

§ XXVIII.

The effects produced on manganese by the acid of tartar are remarkable, on account of the effervescence. Manganese does not enter with any acid into a colourless combination, without being first united with phlogiston. The small portion of phlogiston, which it naturally contains (§ XV. A, B, C), may serve to render it soluble in all acids; but this only in very small quantity. The effervescence which happens in the present case shews, that a part of the acid of tartar is entirely destroyed, in consequence of the combination of its phlogistic part with the manganese, as is explained in § XXII. in which the destruction of animal and vegetable substances is described. To this it may be added, that if you make the solution with a proper proportion of sugar, gum,

∴ there will not remain the least mark of those substances, (§ XVI. A). This is easily proved; for, if such a solution be filtered, inspissated, and slowly calcined with concentrated vitriolic acid, there should necessarily appear some blackness from the burned sugar, which however does not take place. During this decomposition of sugar or gum, there arises a vapour that vellicates the nose; and, if it be collected in a receiver, it appears to be pure vinegar. From diluted vitriolic acid, sugar and manganese, this acid is obtained in its purest state.

§ XXIX.

Among the vegetable acids, distilled vinegar combines most loosely with absorbents; for the acids of lemon and tamarinds expel it from its union with fixed alkali in acetated vegetable alkali, (*terra foliata tartari*). Its inflammable part is more closely united than in the rest of the vegetable acids, since it arises with it into the receiver, which is not the case with the other acids which are destroyed, except the volatile dry acids of benzoin and amber. Hence it appears, that vinegar acts upon manganese in no other manner than diluted nitrous and vitriolic acid do, (§ XV.—XXI.). If this acid had a greater attraction for phlogisticated manganese,

nese, or if its phlogiston was not so closely combined, the manganese would decompose it, as really happens with phlogisticated vitriolic acid, with volatile nitrous acid, and the acids of tartar and lemon.

§ xxx.

The acid of lemon is likewise decomposed by manganese, as well as that of amber. During putrefaction and combustion the acid of lemon also yields a great deal of aerial acid, which is here the real cause of the effervescence during the solution. The brown colour assumed at first by the solution, is a proof that the acid of lemon can dissolve the manganese, without its being first united with phlogiston. The acid of tartar produces likewise in the beginning a solution of a somewhat brown colour. The cause of this colour is the very same with that assigned with respect to the muriatic acid.

§ xxxi.

The xiiith paragraph shews that aerial acid too has some effect upon manganese. I have related this experiment to shew, that, from a solution in any acid, if there be an excess of the acid, all the manganese is not precipitated by vegetable alkali, though it be added till the acid is completely

pletely saturated ; for the aerial acid, which is extricated from the alkali, dissolves part of the manganese.

§ XXXII.

The peculiar kind of earth found in all the limpid solutions of manganese, and mentioned § XVIII. No. 4. remains to be more carefully examined. I shall here speak of a few particulars in which it differs from others.

(A) The small crystals which appear on the evaporation of the solution of manganese in nitrous and muriatic acids, § IV. C, § VI. D, consist of this earth combined with those acids. They are easily soluble in water, and may be freed from the adhering solution of manganese, by repeated evaporation and crystallisation. They are insoluble in spirit of wine, have an austere taste, and do not attract moisture from the atmosphere. (B) Dissolved in water, they are neither precipitated by fixed nor volatile caustic alkalis, nor by lime-water ; but, on addition of the mild, fixed and volatile alkalis, an earthy precipitation takes place. (C) This precipitate, after beingedulcorated and dried, is white, and effervesces with all the acids. If calcined, it grows a little bluish, and produces no effervescence with acids, but is dissolved by them when heat is applied. It is not
soluble

soluble in water, but expels the volatile alkali from sal ammoniac. (D) Exposed to the blowpipe, it is at last changed into an opal-coloured glass, which is again soluble in acids. (E) With fixed alkali it undergoes no change. (F) Borax dissolves it with effervescence, and thus forms a glass, which is colourless and transparent as long as it continues hot, but opaque when cold. (G) The solution of this earth in nitrous or muriatic acids is not precipitated either by phosphoric, tartar, or fluor acid, though it is by all ammoniacal salts containing these acids. (H) This solution is precipitated by vitriolic acid, and the precipitate is insoluble in water (§ IV. VI. B, C). It is likewise precipitated by vitriolated vegetable, fossil, volatile alkalis, and lime; as also by iron, copper, and zinc, combined with the same acid. (I) The vitriolic acid is not separable from this earth, either by alkali, lime, or solution of silver or quicksilver. The only means to effect this separation is to convert the acid into sulphur. This may be done, by mixing the edulcorated precipitate with alkali of tartar, and a little charcoal powder, fusing the mixture, afterwards dissolving the mass in water, and edulcorating the powder that lies at the bottom, which then may be again dissolved in nitrous acid, and thus purified from the charcoal. (K)

By fusing it with black flux and powder of charcoal I obtained no metallic substance.

Hence it appears, that this earth differs from all other earths hitherto known. But I am also convinced from experiments, that this earth is not found in manganese alone: For, when you lixivate potashes made of trees, or other smaller vegetables, in order to free them from vitriolated tartar, and afterwards dissolve them in pure nitrous or muriatic acid, filter the solution, and dilute it with water; then, on pouring into it some drops of vitriolic acid, you obtain, in a quarter of an hour's time, a fine white precipitate, which consists of this earth and vitriolic acid, and is exactly the same with the precipitate of (B).

§ XXXIII. *Manganese united with Phlogiston.*

In order to obtain the manganese in this state pure, it ought to be precipitated from limpid colourless solutions by alkali of tartar. The shortest way to obtain it in this manner has been already mentioned § XIX. It is white like chalk, and I shall call it for the future *phlogificated manganese*. That this precipitate contains phlogiston, has been already evinced by several experiments; and it has been likewise mentioned that it loses its white colour by calcination in an open fire. The same

same circumstance is observed when the solution of manganese is precipitated by fixed or volatile caustic alkalis: For thus a white precipitate is obtained, which, when exposed to the air, soon grows dark-brown, but retains its colour when kept in a close glass vessel. The manganese, however, precipitated by fixed vegetable alkali, retains its white colour in the open air. The reason of this is, because it is united not only with phlogiston, but likewise with aerial acid; the precipitate is consequently, properly speaking, a salt. No solution of manganese in acids is decomposed by air alone; whence it appears, that the acids enhance the attraction of manganese for phlogiston. The manganese, therefore, of which Mr Rinman speaks in his Essay, must be a white manganese prepared by art.

§ XXXIV.

(A) If you dilute a solution of manganese with a good deal of water, and afterwards precipitate it with caustic alkali, the precipitate from the very beginning is brown, and has all the properties of pure manganese. Here it evidently appears, that the air contained in the water is sufficient to attract the phlogiston of the manganese as soon as it is separated from the acid. For the same reason, manganese

precipitated from its solution by lime-water, is brown; but, on adding more of a concentrated solution of manganese, and afterwards some caustic alkali, the precipitate is white; because the air contained in the water, being already saturated with phlogiston, is not able to combine with any more.

(B) On distilling an ounce and an half of phlogisticated manganese in a glass retort with a strong fire, a great quantity of aerial acid, with some drops of water, came over. The retort being still warm, I poured the manganese out upon a piece of paper, when it immediately grew red hot, and set the paper on fire.

(C) The same experiment was repeated with a drachm; and an empty bladder was tied to the neck of the retort; the distillation was continued with a strong fire as long as the bladder was distended by the air.

This air occupied the space of three ounces of water. The residuum in the retort afterwards weighed thirty-five grains, was of a light grey colour, dissolved in acids, without the addition of phlogiston, with a great heat. At that degree of heat, at which sulphur smokes, but does not take fire, it grew black, and began to turn red hot. From these experiments, it follows, that, in close vessels, phlogiston
does

does not separate from manganese, if the access of air be prevented, (§ xiv. No. 3.)

§ xxxv.

In § xv. I observed that manganese decomposes nitre, and that the acid passes over. This does not happen till the mixture grows red hot. (A) If phlogisticated manganese be mixed with an equal quantity of pure nitre, and distilled in a glass retort provided with a receiver, it is observable, that the mixture begins to grow black before the retort becomes red hot, but no nitrous acid goes over. If it be afterwards lixiviated, there appears no mark of any uncombined alkali in the lixivium; but, on mixing the solution with tamarinds, an odour of aquafortis immediately arises. (B) If three parts of phlogisticated manganese, mixed with one part of finely powdered nitre, be distilled in the same manner, but the distillation be stopped as soon as the mixture grows black, the nitre is found to be alkalized; no nitrous acid, however, is found in the receiver. All this proves clearly, that phlogiston is contained in manganese.

§ xxxvi.

I likewise examined the effects produced on manganese by unctuous oils, and inflammable bodies.

(A)

(A) One part of finely powdered manganese, digested with four parts of olive oil, underwent no change; but as soon as the oil grew hotter, the mass began to effervesce violently, which is owing to the extrication of aerial acid. After the mass was become cold, the manganese was found to be dissolved, and had the consistence of salve. (B) A mixture of finely powdered manganese and charcoal was distilled in a small glass retort, to which an empty bladder was tied. When the retort began to melt, a quantity of aerial acid was extricated, and filled the bladder (§ XXII.). The remainder in the retort was for the greatest part soluble in spirit of vitriol, without the addition of any phlogiston. Spirit of wine, æther, oil of turpentine, produced no change upon manganese by themselves.

§ XXXVII.

(A) Half an ounce of powdered manganese mixed with two drachms of pounded sulphur were exposed to distillation in a glass retort. A part of the sulphur rose to the neck of the retort, and some of the volatile acid penetrated through the lute; at last the retort melted. After the residuum was cold, it weighed $5\frac{1}{2}$ drachms, and appeared of a yellowish grey colour. It dissolved in spirit of vitriol with effervescence,

vescence, and with an hepatic smell; when it was filtered, some sulphur remained on the filter. It is insoluble in water. Upon calcination in the open air, the sulphur was volatilised, and the mass assumed a brown colour. After this process a good deal of the mass dissolved in water, and shot into crystals, which were exactly like those of parag. xxii. The insoluble residuum being calcined with more sulphur in the same manner, was at last entirely reduced to such crystals. This has also been observed by Mr Westfeld; but he supposed them to be alum, to which I can by no means assent.

§ xxxviii. *With Nitre and fixed Alkali.*

(A) Nitre triturated with manganese to a fine powder, and strongly calcined in a crucible, loses its acid, and the manganese combines with the alkali, forming a dark-green mass, which is soluble in water, communicating to it a green colour. The colour is in reality blue (§ xiv. No. 4.); for, after the solution has been kept for a few days in close vessels, a fine yellow powder precipitates by degrees, which for the greatest part is nothing but crocus martis, and the solution afterwards turns blue. (B) In such a solution, the manganese is very loosely combined with the alkali; for it can be separated from it by
water

water alone. This mixture is at first of a violet colour, grows afterwards red, and when the red particles come into clofer contact with one another, the red colour disappears, and the powder precipitated has the natural colour of manganese. (c) The same thing happens if the blue solution of manganese be mixed with a few drops of an acid, or if the solution has been exposed for a few days to the open air; the caustic alkali, in this case, unites with the aerial acid, which is present in large quantity in the atmosphere, and for this reason the manganese must also fall down. (d) Probably the fine particles of manganese have naturally a dark-red colour, which becomes visible when they are separated from one another, without, however, being perfectly dissolved in a menstruum. (e) The precipitate, produced by an acid, is still real manganese, a part of which is soluble in acid of vitriol, but not the whole (§ II. A), unless there be added some phlogiston. Hence it follows, that nitre is not capable of depriving the manganese of its natural small quantity of phlogiston (§ xv.); consequently the alkalisation of nitre cannot be ascribed to the natural phlogiston of the manganese. (f) If the solution (A) be mixed with diluted vitriolic acid to saturation, the red colour disappears, and the solution grows colourless.

colourless. The reason of this is, because there is always some undecomposed nitre in the alkali of nitre, the acid of which has taken some phlogiston from the red heat (§ VII.). This phlogisticated nitrous acid is in the present case separated from its alkali by the vitriolic acid, and dissolves the manganese according to the reasons mentioned in § xx. xxii. (G) Manganese fused with alkali of tartar has nearly the same properties with that treated with nitre, the last excepted from the want of sulphur. (H) If charcoal in powder be mixed with the melted green mass, an effervescence ensues (§ xxxvi. B), and the mass assumes a light grey colour; it likewise yields a white solution with water; what remains on the filter is phlogisticated manganese. (I) If finely powdered arsenic be added to such an alkaline solution of manganese during its state of fusion, the green colour also disappears, and a white one is produced. If the mass be dissolved in water, phlogisticated manganese is precipitated. This is certainly a very remarkable phenomenon. I here see, that phlogiston actually enters into the composition of arsenic. The same thing likewise follows from par. xxii. in which I mentioned, that arsenic is capable of rendering the solution of manganese in acids limpid. I here also recollected the
 volatile

volatile nitrous acid that is produced by means of arsenic. I thought, if the arsenic could be deprived of its phlogiston, quite different properties would appear. The experiments which I made according to this conjecture were crowned with success, and I found out two ways of resolving arsenic into its constituent parts, which are a peculiar acid, and the universal inflammable principle.

§ XXXIX. *Effects of Sal Ammoniac.*

(A) Half an ounce of phlogisticated manganese, mixed with an equal quantity of powdered sal ammoniac, was distilled in a glass retort. I obtained in the receiver dry volatile alkali, and towards the end sal ammoniac in the neck of the retort. (B) Half an ounce of pure phlogisticated manganese (§ XXIV. B, C), mixed with two drachms of pounded sal ammoniac, were exposed to distillation, and I obtained caustic liquid volatile alkali. Both the residuums in the retort were fused; they were soluble in water. (C) An ounce of well triturated manganese was distilled with half an ounce of sal ammoniac, when a liquid volatile alkali came over, the same as that which is prepared by means of quicklime. There likewise sublimed a little sal ammoniac; the residuum was put into water, but there remained

mained a good deal of manganese undissolved. As manganese is not soluble in acids without being combined with phlogiston, a question arises, Whence the manganese obtains the phlogiston in this process? (D) If finely pounded manganese be exposed with pure nitrous acid and some volatile alkali to digestion for several weeks, you will observe a great number of air-bubbles rise to its surface. This kind of air, collected in a bladder tied to the neck of the flask, is not aerial acid, but of a quite different nature. During the digestion, the volatile alkali is entirely decomposed; for if the solution be mixed and distilled with a sufficient quantity of quicklime, not the least smell of volatile alkali appears in the receiver. In this process, the phlogiston, one of the constituent parts of volatile alkali, has combined with the manganese, and thus rendered the acid of nitre capable of acting upon the manganese. The elastic fluid, collected in the bladder, has been either separated from the volatile alkali, and is then its other constituent part, or it is a product arising from its decomposition. That the nitrous acid has no share here, is clearly proved by the following process: (E) I repeated the very same distillation with manganese and sal ammoniac, as in c; but, instead of the receiver, I applied

plied an empty bladder, which in these experiments is always to be fastened very exactly to the neck of the retort. It happened here as I expected; I obtained the same kind of air in the bladder as in the preceding experiment; and now I understand the nature of the process in E, and how this process is to be explained. The manganese had combined with the phlogiston of the sal ammoniac (resolved by the heat into vapours), that is, the phlogiston of the volatile alkali; and thence arose the elastic fluid; and the muriatic acid, which was before united with the volatile alkali, could not now but unite with the phlogisticated manganese. But since this alkali contains more phlogiston than the manganese requires to be combined with, in order to be soluble in muriatic acid (for *nitrum flammans* will de-flagrate, but not a solution of phlogisticated manganese in nitrous acid, after being evaporated to dryness), the rest of it combines with another portion of the manganese, which being thus phlogisticated, causes the alkali to go over in a caustic state, for the reason assigned in par. xxxix. B; and thus it likewise appears whence the air-bubbles come, which are obtained from caustic volatile alkali (§ xxv. 1.), viz. the dephlogisticated marine acid in this process combines, in consequence of its great attraction

attraction for phlogiston, with that of the volatile alkali, and thus a part of this salt is necessarily decomposed.

§ XL. *Effects of Arsenic, Orpiment, and Antimony.*

(A) Powdered manganese, mixed with an equal quantity of arsenic, was distilled, when all the arsenic came over, and the manganese remained behind unchanged.

(B) Manganese, distilled with an equal quantity of orpiment, yielded some volatile sulphureous acid, which was followed by a small portion of yellow sublimate, and at last a little red sublimate. I increased the fire by degrees, till the retort began to melt; but the orpiment remained attached to the manganese.

(C) The same thing happened when manganese was treated with an equal quantity of antimony, which likewise yielded a pungent sulphureous acid, but no sublimate. In this process, as well as when united with sulphur alone § XXXVII., the manganese bears a very strong resemblance to a metallic substance. It seems as if it cannot combine with sulphur before it is united with phlogiston; it therefore first attracts the phlogiston of the sulphur, and the vitriolic acid, still retaining some of this principle, goes over in the form of volatile sulphureous acid, and the remaining

fulphur is afterwards fixed by the phlogisticated manganese. By calcination in the open air, this is decomposed, as well as the compounds with orpiment and antimony, and the vitriolic acid unites with the phlogisticated manganese § XXXVII.

§ XLI. *With Cinnabar and corrosive Sublimate.*

(A) A portion of finely pounded manganese was mixed and distilled with an equal quantity of powdered cinnabar. A penetrating volatile sulphureous acid came over, and a little cinnabar was sublimed into the neck of the retort, which was followed by quicksilver. The residuum shewed the same properties as that mentioned § XXXVII. (B) Manganese, distilled with an equal quantity of corrosive sublimate, underwent no change; (c) but mixed with an equal quantity of mercurius dulcis and sublimed, there arose first corrosive sublimate, and then mercurius dulcis, into the neck of the retort. Now, as mercurius dulcis contains crude mercury united with phlogiston, but corrosive sublimate consists of calx of mercury and muriatic acid, it follows, that if part of the phlogiston of the mercurius dulcis is taken away, a kind of corrosive sublimate will be produced; and this portion of phlogiston is taken away in the present case by the manganese.

§ XLII.

§ XLII. *With Glass Fluxes.*

All the phænomena hitherto observed with manganese I have explained from the four general properties laid down in § XIV. ; and, from the same principles, I think the phænomena it shews with glass fluxes may be deduced. A colourless glass flux becomes constantly more or less red, on addition of manganese, according to the quantity (§ XXXVIII. D). If the flux be a little alkaline, the colour will approach to violet (§ XXXVIII. A). It is well known, that arsenic, gypsum, and calx of tin, destroy the red colour in those glasses, and thus render them clear and colourless. As to the arsenic, the reason appears from its constituent parts § XXXVIII. I. ; for in this case the phlogiston of the arsenic unites with the manganese that is dissolved in the red glass, and thus takes away the colour ; and the acid of arsenic unites with the alkali of the glass, (§ XIV. No. 3.). It is to be observed here, that the experiment likewise succeeds in a covered crucible, but it never succeeded with me when it was made in that way with gypsum and calx of tin ; but, on adding powdered charcoal, an effervescence ensues, the red colour disappears, and the glass becomes colourless. Thence it may be concluded, that the experiments made with a view to

change the red colour were made upon charcoal with the blowpipe ; and the phlogiston of the charcoal is therefore the cause of the destruction of the colour. The preceding effervescence is a necessary consequence of the separation of the phlogiston from the charcoal (§ XXII.).

(A) If glass coloured red by manganese be mixed with charcoal powder in a crucible, and fused, the colour disappears during the effervescence, without the addition of gypsum or calx of tin. (B) But on keeping the glass for a long time in fusion upon charcoal, by means of the blowpipe, the colour does not disappear. Nay, if the colourless glass (A) is kept in this state for a short time upon charcoal, by means of the blowpipe, it grows red again. (C) If to such a red glass globule a little sulphur be added, the colour disappears. The same thing happens on adding a little of any metallic calx, and any neutral salt containing vitriolic acid. Here it is to be observed, that all metals of which the calces colour glass, as, for instance, copper, iron, cobalt, give their peculiar colour to the glass, while they deprive it of the red colour communicated by manganese. (D) If to such a colourless glass nitre be added, though even in the smallest quantity, it immediately grows red again. The same thing happens

pens if such a colourless glass globule is kept in fusion upon an iron plate for a few minutes. (E) The appearance and disappearance of the red colour may be produced at pleasure: By only keeping the colourless glass apart from all phlogistic matter, and in fusion, for a few minutes, it will grow red; and then, by setting it upon charcoal, it will effervesce and grow colourless again. These last phenomena, however, will not succeed if the glass (A) be made use of.

From these experiments the following questions may be answered. Whence does it happen, that the additions, mentioned at letter E, so suddenly destroy the natural red colour of the manganese, since, sulphur excepted, they do not contain any considerable portion of phlogiston that can be separated from them, which, however, is necessary for the destruction of the colour? And why does not the red glass upon the charcoal become colourless by itself under the blowpipe, as happens on the addition of charcoal in the crucible?

Without contact the manganese cannot combine with the phlogiston of the charcoal, and the glass globule touches the coal only in one point, and thus takes the phlogiston only from that point; all the remaining points are in contact with the

H 3 surrounding

surrounding atmosphere, which deprives it of much more phlogiston (§ xv. c) than it is able to get from a single point of the charcoal, and thus the natural colour of the manganese must remain (B). The case is quite different in a crucible (A); for here the atmosphere touches only a part of the globule, and the whole mass receives a sufficient quantity of phlogiston from the surrounding charcoal powder to repair the loss, whence a colourless glass flux is produced. The same is the case when any vitriolic salt or metallic calx is added to a borax-glass globule in fusion under the blowpipe, and coloured red by manganese (c). For, since these substances attract the phlogiston with sufficient force from the charcoal, though they are dissolved in the glass, as is well known from the conversion of the vitriolic acid into sulphur, and the reduction of the metallic calces, and since manganese is able to separate the phlogiston from metals (§ xvi. xxxvii.), it follows, that in such a glass globule there is much more matter present which attracts the phlogiston from the point of the charcoal, upon which the globule rests, as is likewise sufficiently evident from the effervescence that takes place. If manganese comes into contact with any such substance when it is on the point of being converted into
sulphur,

fulphur, or reduced, it is in the same circumstances as if it were in contact with an equal quantity of charcoal powder. Hence, therefore, the glass must become colourless; and though the air every moment takes away phlogiston from the surface of the globule that is exposed to its action, the manganese will have, notwithstanding, a sufficient number of points through which the want of phlogiston is constantly supplied. This is proved by the constant effervescence which takes place as long as the glass globule remains in a liquid state upon the charcoal (§ XXII.).

§ XLIII.

From this explanation it plainly appears how manganese purifies glass. If the colour of the glass were to depend on a kind of carbonaceous matter, it would be imprudent to add more of the manganese than is required to saturate the phlogiston of that matter, for the natural colour of the manganese would certainly be produced. With regard to the green colour of the common bottle-glass, I was not yet fully convinced that it depended upon iron, and I therefore took this opportunity to examine whether I could separate iron from it. (A) I melted green glass with alkali of tartar by the blowpipe upon

a piece of the same substance, (for in using a crucible one may be deceived by the iron it contains). Upon this mass I poured a large quantity of pure muriatic acid, and added some drops of lixivium sanguinis, when the mixture grew a little bluish, and there is consequently some iron in the green glass. (B) This iron must be present nearly in a metallic form; for the calx of iron renders glass always yellowish. It is, therefore, the phlogiston to which the green colour is owing. As long as the iron retains part of its phlogiston, it also gives such a green colour to its solution in acids. But if manganese be added to such a solution, the green colour disappears during digestion, and a yellowish one is seen in its place. Nitrous acid likewise takes away this green colour during digestion. (c) If nitre be added to green glass in fusion, the green colour also disappears. Manganese added in due proportion produces the same effect. If Mr Westfeld had not added nitre in his experiment, by which the green colour of the glass was destroyed, he certainly never would have effected any change of the glass, nor would he have ascribed this property to the earth of alum. (D) But such a glass purified by manganese should have become somewhat yellowish; for manganese was incapable,

pable, in my experiment, of taking away the colour of glass tinged by calx of iron; and that a real calx of iron is present in this glass, though to all appearance pure, I have already shewn by the above experiment (A). I performed the fusion upon a plate of colourless glass. What can be the cause that it becomes clear and colourless under these circumstances? I believe, that the too small quantity of the calx of iron is the reason why its natural yellow colour cannot be distinguished. It is remarkable, that the rays of light passing through such an uncoloured glass when it is heated nearly red hot, appear yellow. Something like this is observed in red colours that are not changeable by fire; such as minium, crocus martis, cinnabar, red precipitate, which, during the time they are heated, appear of a black colour. Before I conclude, the following observations may deserve a place.

§ XLIV. *Presence of Manganese in Potashes.*

Chemists have often observed, that alkaline salts, when calcined, assume a bluish or greenish colour. The cause of this has been said to be phlogiston present in the alkali; but I have constantly found some nitre in the fixed nitre which was prepared with charcoal powder by a strong fire.

fire. Its presence was immediately discovered by the aquafortis smell that ensued on pouring some vitriolic acid upon the mass. To the common opinion, therefore, there arises an immediate objection; which is, that the green colour in this case should have been destroyed by the nitre still remaining. I observed, that such a green alkali fused with nitre did not, however, lose its colour. When fixed alkali is made to run over the crucible by a strong fire, the part that attaches itself to the outside acquires a dark green colour, in consequence of the ashes uniting with it. If one part of alkali of tartar be mixed with one-fourth of fine sifted ashes, and one-eighth of nitre, a dark green mass is obtained, which, when dissolved in water, yields a beautiful green solution, and, when filtered, turns red on adding a few drops of vitriolic acid (§ xxxviii. B, C). Some days afterwards I found a brown powder precipitated, which, though in a small quantity, appeared, on experiment, to be precisely the same substance as manganese.

A sufficient quantity of sifted ashes were dissolved in muriatic acid in a sand-heat. During the digestion, the same smell of aqua regia that arises from manganese and muriatic acid was perceptible. Some hours after I mixed a certain quantity of
vitriolic

vitriolic acid with this solution, in order to precipitate the greater part of the calcareous earth that was present. The second day I filtered it, and what passed through the filter had a yellow colour, and with alkali of tartar afforded a yellowish precipitate. This powder beingedulcorated, dried, and calcined in the open air upon an iron plate placed on burning charcoal, assumed a dark grey colour. It should have been quite black like manganese if an extraneous earth had not still been mixed with it (§ xv. c). This calcined powder was not entirely soluble in pure nitrous acid; but, on adding a little sugar, a clear solution was instantly procured. When mixed with alkali it yielded a green mass before the blowpipe; with glass of borax it assumed a yellow colour. From this latter phenomenon, however, it does not follow that it contains no manganese; the yellowness of the glass is a sign that iron is at the same time present, which is likewise confirmed by the yellow colour of the solution in muriatic acid: Now, since the calx of iron has the same property as gypsum and calx of tin (§ XLII. c), the red colour must also here disappear. If only a little nitre be added to the yellow glass, it becomes immediately dark red (§ XLII. d). Thence it is evident, that manganese

really

really enters into the composition of pot-ashes. In the ashes of thyme, (*thymus ferpillum*), however, I have observed very little; ashes from wood yield more.

§ XLV.

I shall now conclude with an account of some experiments which I made with a view to discover the constituent parts of manganese. But not having yet been able to produce manganese by art, or to confirm by synthesis what I have learnt by analysis, I am uncertain whether my conclusions, though founded on experiments, are just. I have observed, that from phlogisticated manganese, dissolved by vitriolic acid, there separates, after every calcination in the open fire, a quantity of gypsum. The gypsum is indeed in very small quantity; but I was curious to know whether the manganese loses of its weight in proportion? This led me to make the following tedious and troublesome experiments with the utmost accuracy: I calcined half an ounce of phlogisticated manganese, purified from all foreign particles, as described § XIX, upon a finely polished iron plate till it grew quite black. I then dissolved it in diluted vitriolic acid, with the addition of a little sugar, in a sand-heat, till the solution became limpid. After it was cooled, a fine shining powder precipitated, which proved

proved to be selenite ; this I separated by filtration ; then diluted the solution with six ounces of distilled water, and precipitated it with purified alkali of tartar ; but as in this process there is always a certain quantity of aerial acid expelled from the alkali by the acid, which may dissolve some manganese (§ xxxi.), it was necessary to place the whole mixture, with its precipitate, in an open vessel upon hot sand, in order to expel the aerial acid. In the space of a few hours it was filtered, and what remained in the filter wasedulcorated with hot distilled water. This phlogisticated manganese was afterwards dried, and exposed again to calcination in the same manner. All this was done with proper care not to lose any thing ; on which account the draught of air was carefully avoided. The manganese, when deprived of its phlogiston, was again dissolved in diluted vitriolic acid, with the addition of a little sugar, by which means I obtained as much selenite as before ; the solution was then made to pass through the same filter, on which the selenite remained behind mixed with that of the preceding operation. The filtered solution was precipitated by alkali of tartar, and, by means of heat, deprived of the aerial acid ; it was afterwards purified, as before, from the vitriolated tartar, by
means

means of the same filter,edulcorated, then dried, and again deprived of its phlogiston by a new calcination. This operation I repeated eleven times, till I grew tired of it. I dried the phlogisticated manganese which was last obtained upon the same blotting paper which had served as a filter, then subtracting the weight of this paper, which I had ascertained before the experiments were begun, I found the weight of the manganese to be three drachms and five grains, the selenite obtained forty-nine grains. It is impossible to avoid some loss in theedulcoration. The phlogisticated manganese thus obtained had the same property as in the beginning, and yielded, after the last calcination and solution, as much selenite as after the first. It therefore seems as if it was entirely changeable into calcareous earth, if the same operation was long enough continued. Mr Westfeld found it easy to fix his opinion about the constituent parts of manganese; but how near he advanced to the truth, those may determine who shall make experiments in the method just described. How this change of manganese into calcareous earth is produced, I dare not undertake to explain, having been, notwithstanding all possible trouble, never able to unite phlogiston with calcareous earth. I shall add but one observation,

vation, really remarkable in itself, and very well adapted to be inserted here. Having once abstracted muriatic acid from minium, I found that the acid had not only the smell of aqua regia, but that it also was capable of dissolving gold. If finely pounded minium be dissolved in pure nitrous acid, diluted with a triple quantity of water, a black powder remains, which is not soluble without the addition of a little sugar, upon which a clear solution is immediately obtained. If this black powder be digested with diluted vitriolic acid, no change happens; but, on adding some sugar, the powder grows white, and contributes to produce vitriol of lead. If muriatic acid be poured upon the black powder, an effervescence arises in a warm place, and the acid grows yellowish; the colour afterwards disappears, and a strong smell of aqua regia rises; but the black powder grows white, and is changed into muriated lead (*plumbum corneum*). If the black powder be distilled by itself in a glass retort, it grows yellow again, but not till it comes near the degree of heat at which it melts. This yellow powder shews in every respect the same properties as common yellow calx of lead, is entirely soluble in nitrous acid, and, on being mixed with muriatic acid, yields no further smell of aqua regia;

gia;—a proof of the presence of phlogiston in heat (§ XVII.). It seems as if the black powder was nothing else but calx of lead, which having lost its phlogiston entirely, or for the most part, during a gentle and slow calcination, has thus acquired such a strong tendency to unite again with it, as to be able to decompose muriatic acid.

Supplement

Supplement to the foregoing Dissertation on Manganese. By T. BERGMAN.

Mr Scheele, after having examined the composition of fluor, undertook, at my request, the examination of manganese, and has offered to the Society what he has learned upon the subject by his numerous and ingenious experiments, which were continued during the space of three years. After he had finished these experiments, I informed him that Mr Sage supposes manganese to be nothing else than a mineralised mixture of cobalt and zinc. He immediately made several experiments for this purpose, but found not the least mark of either of those metals.

Manganese has been classed by all mineralogists among the iron-ores. Mr Pott, however, thought the iron to be mixed only accidentally; and at last Mr Cronstedt, in his Essay on mineralogy 1758, placed it among the earths. For my part, however, I must own there are several circumstances which make me think that it is a metallic substance.

No pure earth colours glass; but all metallic calces have this property. Manganese, therefore, in this respect, shews a great resemblance to the latter, which is

further increased by its specific gravity, and its strong attraction for phlogiston. But what principally confirms me in my conjecture, is the following experiment, which I made with a view to determine its nature more particularly. It is well known, that fixed alkali, by a certain treatment with dried blood, *viâ siccâ*, or, what is more convenient, with Berlin blue in the moist way, may be almost completely neutralised. Phlogiston, it is true, is generally assigned as the cause of this change; but, in all probability, the whole depends principally on an animal acid. There appears at least on the addition of Berlin blue an evident effervescence, and the solution may be reduced to crystals. Alkali, thus changed and dissolved in water, is generally called *lixivium sanguinis*, and precipitates all metals dissolved in acids; but does not precipitate in the least any of the earths, except as far as there is any superfluous alkali present, which may be easily avoided by adding some distilled vinegar. Now, if a quantity of this alkali be added to a solution of manganese, a light yellowish grey earth immediately precipitates, which is not soluble in any of the mineral acids: Both which circumstances happen only with metals, and thus clearly shew the nature of the precipitate. But what kind of metal it is which manganese contains,

contains, is not so easily ascertained. The solution of cobalt does not lose its colour on adding sugar, or any other phlogistic substance; and zinc does not impart any colour to acids; these two substances consequently differ from manganese, which does not, indeed, entirely agree with any other of the known metallic earths. I have, however, great reason to conjecture that it must be platina, the earth of which is not yet known; or a new metal, which at least would agree with platina in the great difficulty with which it fuses. To ascertain this, a series of experiments is begun, which, if they shall confirm my conjecture, will make manganese a still more remarkable substance.

*Additional Remarks upon Mr SCHEELE'S
Analysis of Manganese, by GUSTAVUS
V. ENGESTROM.*

The experiments I made on manganese and its colour seem to differ in some measure from Mr Scheele's. Hence it will perhaps appear how difficult it is to measure the degree of fire in experiments with the blowpipe.

I melted manganese and borax together upon charcoal by means of the blowpipe. The glass at first assumed the common colour of manganese; but this colour I destroyed without any addition, and imparted it again to the glass; and this I did repeatedly to the same globule without adding any thing. During the operation I observed the following phenomena.

1. If I took a small quantity of manganese, the colour was light; if a larger portion, it became so dark as to appear black. This dark or light colour, which manifested itself during the first melting, appeared again in a second operation upon the same mass.

2. Manganese, on being melted with borax, unites with a violent effervescence, which, however, ceases as soon as the manganese is dissolved.

3. If

3. If the glass of borax was coloured by manganese, and I wished to make the colour disappear, I always directed the blue flame of the candle upon the glass, and that equally and constantly, but not very violently. As soon as I blew more faintly, and allowed the brown flame to touch the place, the glass grew dark again. According as the globule was larger or smaller, more or less coloured, it required a longer time to make the colour disappear. About the time when the glass becomes colourless, a kind of a section or partition is observed in it; and, as soon as the colour disappears, the blowing must be immediately discontinued, in such a manner that the brown flame shall not touch the glass. When it is afterwards taken out with the forceps, it appears perfectly colourless.

4. This destruction of the colour does not seem to happen suddenly and at once, but by degrees: For when I now and then discontinued the blowing, before the true mark had appeared, I found the glass generally lighter than it was before, and this more or less according as I had blown longer or shorter time.

5. After putting this colourless glass again upon the charcoal, and melting it by the brown flame of the candle, it again assumed its former colour, though I

kept it melted for a long time in the brown flame.

This change of colour I have effected several times with the same glass, always with the same success; but I cannot say whether it may be repeated often: Such an experiment would be too difficult to make. There is some room to doubt of this;—at least if the phenomenon in the following experiment was not owing to some accident.

6. Having already twice discharged the colour, I forced the blue flame with violence against the glass, in order to make the colour of the manganese the sooner disappear. I observed some little vesicles to rise in the glass, which afterwards burst, and at the same time dispersed a number of very small glass globules around. I had now continued the blowing for a whole hour, and had been blowing very violently, I therefore was obliged, after a short blast, to desist for two or three minutes.

I found the glass somewhat lighter than it was before; but on continuing the blowing with equal force, I found it impossible to expel the colour from the glass. After I had given over blowing, the mass appeared to be somewhat diminished, and was as dark as at first; but of the small globules dispersed around upon the charcoal some were clear and colourless, others were white and opaque. I

I attempted to give them colour by means of the blowpipe alone, but without success.

7. In one experiment I had taken a much larger quantity of manganese in proportion to the borax, and happening to give it a very violent heat, so as to cause an explosion of small particles, I found that the larger globule constantly retained a red colour, till at last it likewise grew clear and transparent during the blowing. On stopping suddenly, the glass was clear as long as it remained warm; but as soon as it began to grow cold, a dark cloud made its appearance upon the surface, which by degrees spread over the whole. On melting it suddenly anew, it recovered its transparency; but, as it grew cold, the same phenomenon as before appeared; and the oftener I repeated this, the more cloudy appeared the globule. As soon as it had become cold, I observed that it had lost its glassy splendour, and had assumed a very dry appearance, and was of a greyish red colour. The same thing happens likewise with glass of borax and lime; if the latter be added in too large quantity, the glass of borax loses its glassy appearance nearly in the same manner.

That the small globules separated by the violent heat (6.) remained colourless, though the great globule became red, seems

to shew, that manganese, or at least its colouring part, has a strong attraction for a small portion only of borax; and that, by means of a violent heat, the superfluous part may be separated, and the rest unite more closely with the earthy particles. The same thing happened likewise with the small globules which sometimes remained, after the mass was taken away, fixed to the charcoal by the violence of the flame. If this is really the case, it would follow, that, by repeating the experiment, some of these particles would always separate, if a sufficiently strong flame was applied, and it would be impossible to expel the red colour afterwards. I dare not, however, advance this conjecture, though it is grounded on some experiments, as a matter of certainty. Accidents may sometimes make a thing appear in a quite different light from what it really is, especially in experiments upon such a small scale, where one cannot be careful enough in forming conclusions.

More experiments would elucidate this point; but it would perhaps hardly be worth while to make them, since they seem to be more curious than useful.

Quite different is the case with regard to the destruction and restoration of the colour of manganese itself, by means of the
the

the simple flame; for the several experiments I made all agreed in the same result. In order to confirm them the more, I have made experiments lately with manganese, from Upton Pine, near Exeter, in England, and have observed no difference.

The brown flame of the candle has probably more phlogistic particles than the blue one.

The presence of phlogiston seems in most cases to communicate colour. Mineral substances, which contain little phlogiston, are often with great difficulty deprived of it; a violent and long continued heat is frequently required for this purpose; sometimes, however, we succeed on adding more phlogiston, and by means of certain management with regard to the fire itself.

Description

Description of a new spatheform Species of Manganese from the Iron Mines of Klapperud, in the Parish of Fresko in Dahlland.
By SEVEN RIUMAN.

This species was sent me by Baron Hermelin. It is not, as far as I know, mentioned in any system of mineralogy, unless that of Baron Born, entitled, *Magnesia texturâ lamellosâ, lamellis nitentibus*, from Hirschberg (Index Foss. p. 47.), belong to it. The present species, at first view, resembles a brown blend, or an impure calcareous spar: It consists of irregular cubes of the colour of colophony, or common resin; the thin lamellæ are semitransparent, and of a brownish-red colour; the surface has more splendour than that of blend or calcareous spar, and in this respect it is most like mountain-pitch. The specimens that I received were distinguishable, with respect to external appearance, into two varieties.

1. Sparry, shining, of the colour of colophony.

2. Compact, irregular in the fracture, with a duller surface, and of a darker colour.

The following general properties might moreover be distinguished:

(A) The

(A) The smooth surface, already described, is a sufficient intimation that it does not soil the hands; but, upon a part of the fossil, there appears a dark-brown calciform powder, seemingly produced by exposure to the atmosphere, which *does* soil the hands.

(B) Between the divisions of this sparry manganese, there are a few calcareous particles of a bright yellow.

(C) Against steel or the knife, it has no more hardness than common loose calcareous spar, and, when pulverized, affords a bright brown powder.

(D) Placed on a piece of charcoal, and heated with the blowpipe, it at first resembles zeolite, fusing with some effervescence and intumescence of the particles, which afterwards coagulate into a light-grey porous scoria, that is not fusible of itself by means of the blowpipe.

(E) It fuses easily with borax into a dark-red or garnet-coloured glass, and the fusion is accompanied with a brisk effervescence; but, in order to be transparent, it must be diluted with a good deal of borax, and it then appears of a beautiful red opposite the light.

(F) When heated red-hot in a test in an assay-furnace, it turns black with small shining scales; but in a stronger heat the
black

black colour passes away in part, and the powder becomes brown.

(G) The magnet does not attract any sensible quantity, either before or after roasting.

(H) This species of manganese in its crude state, and reduced to a fine powder, does not make any effervescence with strong aquafortis; but, in a gentle heat, it is almost entirely dissolved without imparting any colour to the solution.

(I) Fixed vegetable alkali precipitated a white powder out of this solution, which, when washed and dried, effervesced a little with acids, turned black upon being heated red-hot; and, when treated by the blowpipe upon charcoal with glass of borax, gave it a red colour.

(K) The roasted powder (F) effervesced still less with aquafortis; a great part of it, however, by gentle boiling, was dissolved, and yielded in like manner a white precipitate on the addition of vegetable alkali. This precipitate, when heated moderately red-hot, grows as black as soot, and gives a garnet-colour to borax. The residuum, which did not dissolve in aquafortis, was as black as before.

(L) When mixed with a large quantity of common enamel, consisting of siliceous powder and litharge fused together, so as to form a clear yellow glass, and exposed to a
stream

stream of air in a close crucible for a quarter of an hour, the roasted powder (F) yielded only a clear olive-coloured glass, in which many little grains of reduced lead were to be observed. That it did not assume a garnet colour,—I ascribe to the too great violence of the heat. The reduction of some of the lead indicates the presence of phlogiston in the pulverized manganese.

(M) Some of this roasted manganese was rubbed in a glass mortar with a quantity of the above mentioned enamel, to which a little more siliceous powder and some fixed alkali were added. With this mixture a piece of Cologne clay burnt white was covered, then placed in an heated assay-furnace, and taken out as soon as the enamel began to melt. It had acquired a clear and more beautiful colour than I could have produced with other manganese.

(N) One part of the roasted powder, mixed with two of siliceous powder, and four of white potashes, fused in a crucible, placed before the bellows, in seven minutes. It effervesced at first with violence, and afterwards yielded a clear violet-coloured glass, with which the crucible was likewise glazed.

The small quantity of which I was possessed, and the shortness of the time, would
not

not permit me to make any more experiments. From those which I have related, it appears that this species has nearly the same properties with that examined by Mr Scheele. There are, however, some points of difference to be noticed; as its shewing the same phenomena as zeolite under the blowpipe without addition, its containing in all probability but little iron, and its yielding a very beautiful violet-coloured enamel, for which, and especially for painting upon porcelain, it will be of great use, since, according to my information, the mine will yield a sufficiently large quantity.

It is to be observed of every species of manganese, that the colour is the deeper, the more violently it is roasted or calcined. Hence that which is used for enamel or glazing should be exposed for a long time to a strong heat.

E S S A Y

E S S A Y VI.

O N A R S E N I C A N D I T S A C I D. 1775.

§ I.

AFTER I had found, by my experiments on manganese, that the inflammable principle is not only present in arsenic, but that it may really be separated from it, I asked myself, What were the other constituent part or parts of arsenic? I found that it was an acid. Mr Macquer has given us some very satisfactory information concerning the properties of this mineral; but whether any one else has since made any experiments upon it, I know not.

§ II. *Analysis of the White Arsenic.**First Method.*

Put two ounces of arsenic, reduced to a fine powder in a glass mortar, into a retort of the same matter; pour seven ounces of pure muriatic acid* upon it, and lute on a receiver. The mixture is immediately

* The specific gravity of this acid to water is as 10 : 8. If a bottle of water weighs one ounce, a quantity of muriatic acid occupying the same space will weigh ten drachms.

immediately to be made to boil, and kept in this state till the arsenic is dissolved; then, while the solution is still warm, three ounces and an half of pure nitrous acid* are to be added to it, together with the acid which has already gone over into the receiver. The receiver is then to be applied again, but not luted. The mixture soon begins to foam, and volatile red nitrous acid goes over. Meanwhile the distillation is to be continued till no more red vapours appear, when again an ounce of finely powdered arsenic is to be added, the receiver applied as before, and a gentle ebullition continued, till this be likewise dissolved; and afterwards an ounce and a half of nitrous acid is to be added, whereupon a new effervescence and red vapours will arise; the recipient is to be applied, and the whole distilled to dryness; there will remain a white mass;—and, lastly, the fire is to be increased so far as to make this mass thoroughly red hot. The acid obtained in the receiver during the operation may serve for the same purpose several times. After the retort has grown cold, it is to be broken, and the white mass is to be put into a closed vessel, with this signature, *Dry acid of arsenic*; or, if you please, you may reduce

* Of the same specific gravity as the muriatic acid above mentioned.

duce it to coarse powder in a glass mortar, put it into a glass retort, pouring a double quantity of distilled water upon it, apply a receiver, and boil it for a few minutes till the acid is dissolved; the water that goes over is to be poured back into the retort. The solution is then to be filtered through blotting paper, which has been previously washed in hot water, and then to be preserved in a phial with a glass stopple, under the name of *Liquid acid of arsenic*.

It is to be observed, that arsenic must necessarily be deprived of its phlogiston before the acid can be obtained; this is principally effected by the nitrous acid. It may seem as if it should be sufficient to distil the nitrous acid from the arsenic, after which the acid of arsenic would remain behind; but in this manner only a very small portion of arsenic will be decomposed; for this salt requires first to be dissolved in water, in order that the nitrous acid may act upon it in all its points; but nitrous acid dissolves only a small quantity of arsenic, and that only in proportion to the water contained in the acid; the fuming nitrous acid dissolves still less; but muriatic acid has a strong attraction for arsenic, and the less water it contains the more it dissolves and carries over into the receiver. The above

mentioned quantity of muriatic acid is necessary, in order to keep the arsenic dissolved with the aid of heat. Now, if to such a solution nitrous acid be added, the arsenic will be calcined, because its phlogiston is taken away by that acid, as sufficiently appears from the red elastic vapours; whence likewise the attraction of the muriatic acid, for the now dephlogistigated arsenic is diminished, so that it is capable of dissolving more arsenic. Aqua regia might be poured upon arsenic at first, but then the great effervescence carries the arsenic up to the surface, and thus prevents it from being perfectly attacked by the menstruum. After all the acid has been distilled over, the fire ought to be increased, in order, if there should be any aqua regia remaining in the mass, to expel it entirely; the remaining acid weighs nearly as much as the arsenic employed for the experiment. One would hardly believe that it was an acid, because it has no taste; but after some days it grows moist in the air, and at last deliquesces, and then it has the appearance of vitriolic acid. As the deliquescency of this acid is very slow, I dissolve it in a certain quantity of water, when a small quantity of white powder remains undissolved, which comes from the retort, which is found much corroded after the process, and is therefore

therefore nothing but filiceous powder. This powder ought to be carefully separated from the acid, which may be effected by filtration; and in order to prevent the glue of the blotting paper from mixing with the acid, which might lead to a different result, the paper ought to be, as I said above, previously lixiviated with hot water.

§ III. *Another Method.*

A second method of decomposing arsenic is by means of manganese. Take one part of powdered manganese, and mix it in a tubulated retort with three parts of the above described muriatic acid. This mixture should fill one-fourth of the retort; a receiver containing one-fourth of white powdered arsenic, diluted with one-eighth of distilled water, is to be luted on, and the retort put into a sand-bath. The dephlogisticated muriatic acid going over into the receiver is immediately absorbed by the arsenic. Some hours afterwards the arsenic will be dissolved, and two different liquid strata, which will not mix together, be perceived in the receiver. This solution is now to be put into a clean glass retort, and distilled to dryness, and the fire at the end so much increased that the whole remaining mass may be perfectly red-hot. In this process also two dif-

ferent liquids go over into the receiver, which do not unite together.

Of this operation it is to be remarked, that the muriatic acid yields its phlogiston to the manganese; and as the dephlogistified acid attracts the phlogiston again, wherever it meets with it, very powerfully, it deprives the arsenic of its phlogiston, and hence it reassumes the nature of common muriatic acid. This acid dissolves a portion of the arsenic, and thus forms with it a liquor, called *butter of arsenic*; but the other portion of the arsenic, that has been decomposed, remains dissolved in the water, which was placed in the receiver, together with a little muriatic acid, and forms a liquid specifically lighter than the butter, which remains at the bottom. If these two liquids be now rectified, the undecomposed portion of the arsenic rises along with the muriatic acid, and goes over into the receiver in the form of an heavy oil, while the acid of arsenic remains behind in the retort. The acid obtained in this way has precisely the same qualities with that obtained by the former process. It is, however, remarkable, that the butter of arsenic does not combine with the muriatic acid when it is somewhat concentrated.

§ IV.

Before I subjected this acid to my experiments, I was curious to know whether it is as fatal as arsenic itself. I therefore mixed a little of it with honey, and exposed it to the flies, when I found that it killed them in an hour. I gave eight grains of the powdered acid, inclosed in a piece of meat, to a cat, which, two hours afterwards, seemed to be at the point of death; I then gave it some milk, upon which it vomited violently, and afterwards ran away.

§ v. *Effects of the Acid of Arsenic upon inflammable Substances.*

(A) If one ounce of dry acid of arsenic be exposed by itself in a small glass retort to such a degree of heat that it becomes nearly red-hot, it flows into a clear liquid, which, when cold, is of a milky colour; but if the heat be increased to such a degree that the retort begins to melt, the acid begins to boil, and a little arsenic rises into the neck of the retort. The longer the boiling is continued, the more arsenic is obtained. After I had kept up this degree of heat for an hour, the retort melted, and the acid ran into the fire. After the whole was cooled, I found that the acid had risen up the side

of the retort as high as the neck. (B) The same quantity of dry acid of arsenic, melted in a close crucible in a strong fire, boils violently, and disappears in the form of vapours in a quarter of an hour; if the crucible, during the time the acid is evaporating, be put under a convex glass vessel, the inside will be covered with a white powder, which is arsenic, and not acid of arsenic. In the crucible there remains a little clear and difficultly fusible glass, with which the crucible is likewise covered; it consists of clay and acid of arsenic. (c) Acid of arsenic digested with charcoal powder undergoes no change; but if this mixture be put into a retort, the moisture all driven off, a receiver then luted on, and the heat increased till the bottom of the retort begins to grow red-hot, the whole mass takes fire with violence, and all the acid is reduced and sublimed into the neck of the retort; a shining regulus is obtained, mixed with a little arsenic and charcoal dust. A few drops of water are found in the receiver, but they do not contain a particle of acid. The same thing happens when the acid of arsenic has been prepared with manganese. (D) The acid, after some days digestion with oil of turpentine, unctuous oil, and sugar, becomes thick and black. If some muriatic acid be abstracted with a gentle heat

heat from this mass, and then a few drops of nitrous acid dropped into it, and the abstraction repeated, a little arsenical acid will remain behind. It appears from this, that the arsenical acid attracts a little phlogiston from these oils, in consequence of which some arsenic is regenerated and carried over by the muriatic acid into the receiver. Spirit of wine undergoes no change, whether it be digested or distilled with arsenical acid. (E) Six parts of the acid, digested with one of sulphur, suffer no change; but when the mixture is evaporated to dryness, and distilled from a glass retort provided with a receiver, a violent combination takes place, as soon as the mixture is heated to that degree at which sulphur melts. The whole mass rises almost at the same instant, in the form of a red sublimate; and in the receiver there is found a penetrating volatile sulphureous acid.

It follows from these experiments, that the acid of arsenic has considerable fixity (A), and a strong attraction for phlogiston, without which it cannot be reduced to arsenic; whence it follows, that heat must necessarily contain phlogiston, since it is capable of reducing the arsenical acid (B). That it resembles metallic calces in this respect, that it is incapable of uniting with sulphur, except in a reguline state,

appears from the volatile sulphureous acid found in the receiver (c) ; for when the arsenic has attracted as much phlogiston as is necessary to that state, the vitriolic acid, that is extricated, retains so much of this principle as to form volatile sulphureous acid. That this is really the case, appears moreover from the sulphureous acid which arsenic, changed by sublimation with sulphur into red arsenic, affords.

§ VI. *Effects of saline Substances on Arsenic.*

Fixed vegetable Alkali.

(A) When acid of arsenic is saturated with alkali of tartar, a neutral salt is obtained, which cannot be reduced to crystals ; but, after being evaporated to dryness, and exposed to the open air, deliquesces. This neutral salt turns syrup of violets green, but produces no change on the solution of lacmus. (B) But if as much acid be added as shall produce no change on syrup of violets, and yet redden lacmus, the solution will afford fine crystals, resembling Macquer's arsenical neutral salt, both in form and other properties. (c) I have kept this salt in fusion for an hour in a crucible, exposed to a strong heat, upon which another was luted ; after the whole had grown cold, the crucible was found to be covered in the inside with a white glazing ; a salt still remained,

remained, which, after being dissolved in water, and evaporated, appeared to be the same salt, with excess of acid, as before.

(D) This neutral salt, as it is called, was mixed with one-eighth of charcoal powder, and distilled in a glass retort. When it began to grow red-hot, it set to boil violently, without taking fire, and a very fine regulus of arsenic was sublimed. The black residuum, when dissolved in water, proved to be of an alkaline nature, and shewed no vestige of the acid of arsenic. Mr Macquer thinks, that his neutral salt is an alkali mixed with arsenic in some peculiar manner; but it now appears, that it is only one of the constituent parts of arsenic with which the alkali is combined: And this is likewise the reason why acids do not precipitate any arsenic from this salt.

§ VII. *Mineral Alkali.*

(A) If mineral alkali be saturated with the acid of arsenic, crystals are obtained, the form of which is entirely the same with that of those just mentioned; but they do not change lacmus, and they make syrup of violets green. (B) If acid of arsenic be added, no crystallisation ensues, but the mass, after being evaporated to dryness, grows moist again in the air.

§ VIII.

§ VIII. *Volatile Alkali.*

(A) Volatile alkali, saturated with the acid of arsenic, affords, upon evaporation in the open air, an arsenical sal ammoniac, which, in its form, is very like the foregoing salts. This salt does not change lacmus, but turns the syrup of violets green; it loses its transparency when exposed to a gentle heat, and a part of the volatile alkali flying off, it afterwards shews a superabundance of acid. (B) When it is thus supersaturated with acid, it forms long radiated acid crystals, but deliquesces again in the air. (C) Arsenical sal ammoniac, when distilled, yields a liquid volatile alkali; it then flows, and arsenic is sublimed: A white mass remains, which likewise melts in a stronger heat, and proves to be the acid of arsenic. Since the acid of arsenic cannot be converted into arsenic without phlogiston, and such a change during the distillation cannot be ascribed to the heat, because the arsenic is sublimed before the residuum or acid begins to flow, it follows, that the acid of arsenic must decompose part of the volatile alkali during the process. In my experiments on manganese, I observed that a peculiar kind of air is obtained whenever volatile alkali is decomposed. (See *Diff. on manganese*, § xxxix.).

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The same thing happens here:—I distilled an ounce of arsenical sal ammoniac in a small retort, and applied a dry bladder instead of a receiver. Immediately as the arsenic rose into the neck of the retort, the bladder was filled. This air is perfectly the same with that which is obtained from manganese and sal ammoniac.

§ IX. *Vitriolated vegetable and fossil Alkali.*

(A) I dissolved one part of finely powdered vitriolated vegetable alkali, by boiling it in a retort in three parts of acid of arsenic; the liquid was first distilled off, then a dry receiver was applied, and the fire increased. When the retort grew red-hot, the mass melted into a transparent liquor, but no acid went over into the receiver; however, on increasing the fire still further, till the retort began to melt, the mass began to boil, and concentrated acid of vitriol went over. It had the smell of volatile sulphureous acid; no arsenic was sublimed. (B) Vitriolated fossil alkali, or Glauber's salt, was likewise decomposed, but seems not to require so much heat as vitriolated vegetable alkali.

§ X. *Nitre.*

I distilled a mixture of one part of purified nitre, and three parts of acid of arsenic. As long as there remained any humidity

midity in the acid, pure water went over into the receiver; but when the mass grew dry, nitrous acid rose, and the matter in the retort flowed clear. When no more acid came over with this degree of heat, I let the retort cool. The nitrous acid I obtained was not so volatile as that which is obtained from arsenic and nitre. The residuum, dissolved in water and evaporated, yielded crystals, perfectly agreeing with the neutral salt obtained by Macquer, together with a little undecomposed nitre.

Arsenic certainly could not decompose nitre, except by the power of a double elective attraction, *viz.* in consequence of the alkali of the nitre uniting with the acid of arsenic, and the acid combining with the phlogiston of the arsenic, by which this acid is rendered very volatile. If muriatic acid had a greater affinity with phlogiston, arsenic would likewise decompose common salt, as really happens with cubic nitre. Macquer obtained no neutral salt in the crucible, but alkali of nitre containing a little arsenic. I have found that this salt may likewise be prepared in a crucible. Let nitre be melted for this purpose in a crucible, which is to be red-hot only at the bottom, then let as much as will stand on the point of a knife of powdered arsenic be added, and, after the
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red vapours and effervescence are over, as much more arsenic is to be added, and so on, till the nitre begins to grow thick, and will no longer flow in the same degree of heat. If a part of the mass, thus obtained, be dissolved in water, it will redden paper stained with lacmus. After evaporating the solution, a quantity of arsenical neutral salt is obtained with a little nitre. But if the fire is a little increased, the mass begins to boil, and yield red vapours. When it grows thick, and the boiling with this degree of fire is over, a solution of it in water will not change paper coloured by lacmus, but syrup of violets will be turned green; yet no alkaline taste will be perceived. This solution does not shoot into crystals (§ VI. A).

If at last the fire be increased to such a degree, that the crucible and the saline mass are perfectly red-hot, a new ebullition begins, and a smell of aquafortis is perceived; at last the whole melts into a transparent mass. If this be dissolved in water, it proves to be strongly alkaline; but it contains as much acid of arsenic as the first solution. If one part of arsenic be exposed with two parts of nitre in a glass retort, to such a degree of heat as melts the retort, no neutral arsenical salt is obtained, but an alkaline mass mixed with some acid of arsenic. From this experiment

periment it appears, that Mr Macquer applied too strong a heat, and obtained, therefore, no neutral arsenical salt in the crucible. But it will be asked, Why a greater degree of heat alkalises the mass, whereas nitre in an equal degree of heat, or neutral arsenical salt in a still greater, is not alkalised (§ vi. c)? The following experiment gives the solution of this problem. If acid of arsenic be saturated with alkali of tartar, till the solution of lacmus is no longer reddened, and the solution be afterwards evaporated to dryness, and then distilled with double the quantity of nitre in a glass retort furnished with a receiver, the nitrous acid will be expelled as soon as the mass enters into fusion: This acid will be very volatile. If the distillation be continued with a strong fire till no more acid goes over, the residuum in the retort proves to be very alkaline. If a solution of hepar sulphuris be mixed with this imperfect neutral salt, the sulphur will be precipitated; in like manner, a solution of soap is rendered turbid by it. It is hence evident, that the acid of arsenic may be combined with a greater quantity of alkali than is necessary to its saturation; and that, in consequence of this, the nitrous acid is expelled, whence an arsenical salt, with a superabundance of alkali, arises. This attraction, however,
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has likewise its limits; for when a mixture of one part of acid of arsenic and six parts of nitre is melted in a covered crucible in a strong fire till all ebullition ceases, there will be found, besides the arsenical salt, a considerable quantity of undecomposed nitre. But concerning the alkalisation of nitre with arsenic, there is one principal point to be noticed, *viz.* that nitre always attracts a certain small quantity of phlogiston from the heat itself, and that this phlogisticated nitrous acid forms with the alkali but a loose union, so that vegetable acids are able to expel it from its basis. This property of nitre is the reason why acid of arsenic, by virtue of its attraction for the superfluous alkali, expels the nitrous acid phlogisticated by heat; whence it likewise follows, that, since common salt undergoes no change in the fire, the acid of arsenic is not able to alkalise it, as will appear from the following paragraph.

§ XI. *Muriated fossil Alkali, or common Salt.*

One part of common salt was distilled with three parts of acid of arsenic. Water first went over; when the mass was dry, I changed the receiver, and increased the fire till the retort grew red-hot, when the mass began to flow and to boil. This degree of heat was continued till the ebullition,

lition was over, when I found that some fuming muriatic acid had gone over into the receiver. After the residuum in the retort was cool, I dissolved it in water; the solution being filtered and evaporated, yielded crystals of common salt; but there remained a thick mass, which changed the colour of lacmus to red, and would not crystallise. In § VII. it has been observed, that mineral alkali, supersaturated with acid of arsenic, will not crystallise; wherefore I diluted this magma with distilled water, adding finely powdered chalk, till the solution shewed no more mark of acidity; I then filtered it. After evaporation in the open air, crystals were obtained, perfectly agreeing with the neutral salt § VII.

§ XII. *Upon Sal Ammoniac.*

One part of sal ammoniac was distilled with three parts of acid of arsenic. A portion of muriatic acid went over with the water; I then changed the receiver, and increased the heat, when fuming muriatic acid came over, and the mass entered into fusion. Immediately after this, the receiver was filled with a white smoke, and a white powder was sublimed into the neck of the retort; at last a pungent volatile alkali passed over into the receiver; and a residuum remained in the retort, which

which was acid of arsenic. The powder sublimed into the neck of the retort was dissolved in water, and the solution was filtered, when there remained a white powder, which proved to be arsenic. The liquor which passed through the filter contained sal ammoniac.

I repeated the same experiment, applying only a bladder instead of the receiver. When the heat became so strong as to drive the white powder into the neck of the retort, the bladder was distended. The air it contained is entirely the same with that of which I spoke § VIII. c. Hence it follows, that part of the arsenical acid has combined with a portion of the phlogiston of the volatile alkali, and that the arsenic sublimed into the neck of the receiver has been thus produced. Hence, too, the bladder was necessarily filled at the same instant with that air which arises from the decomposition of volatile alkali. Heat expels the volatile alkali from arsenical sal ammoniac § VIII. c; and as any acid converted into vapour, when it meets with volatile alkali, always produces a smoke, it is evident why the bladder at the end of the process was filled with it.

§ XIII. *Vitriolated Lime, (Gypsum), and Spathum Ponderosum.*

One part of powdered gypsum was mixed with two parts of dry acid of arsenic, and exposed to a red heat, when some vitriolic acid came over, with a strong smell of volatile sulphureous acid, and the mass entered into fusion. After the distillation was over, it had the appearance of a milky glass. (B) Spathum ponderosum produced the same phenomena, only the vitriolic acid was not expelled till the retort melted. The residuum was a little reddish. See § xx.

§ XIV. *Upon Fluor Mineral.*

One part of powdered fluor was mixed with four parts of acid of arsenic, and distilled, a little water being put into the receiver. When the retort grew red-hot, first a yellow, and afterwards a red substance, was sublimed. Volatile sulphureous acid went over, but no acid of fluor. The residuum, which was of a grey colour, was divided into two equal parts. Of these one was mixed with charcoal-powder, and distilled with a strong fire; but neither arsenic nor regulus was sublimed: Whence it appears, that I took too small a quantity of acid of arsenic to decompose

compose this fluor, which contained a small quantity of pyrites (§ v. c). The other half was mixed with four parts of acid of arsenic, and the mixture was distilled. When the mass grew dry, a little yellow sal ammoniac was sublimed, whereupon the water in the receiver was covered with a white crust. I frequently shook the receiver, in order to make this crust fall to the bottom, and continued the distillation as long as any crust formed upon the water. This crust was siliceous earth, and the water contained acid of fluor.

§ xv. *Effects of the Acid of Arsenic upon Earths.*

Lime.

(A) When acid of arsenic is dropped into lime-water, the lime precipitates, in combination with the acid of arsenic. If more acid be dropped in, the precipitate is again dissolved. If the solution be evaporated, small crystals shoot. If these be dissolved in a little water, and some vitriolic acid dropped into the solution, a precipitation of vitriolated lime takes place. (B) If the acid of arsenic be diluted with water, and some powdered chalk added, it will at first dissolve; but, on adding more chalk, the whole solution will coagulate into small crystals. (c) The acid of arsenic does not precipitate the solutions of nitrated, muriated,

and acetated lime; neither are these solutions precipitated by the neutral arsenical salt of Mr Macquer; but the arsenical salts (§ VI. VII. VIII. A, A, A,) decompose these solutions, and form a precipitate which is not soluble in water, though it is of easy solubility in acids. (D) If the precipitate of lime, combined with acid of arsenic, beedulcorated, and afterwards strongly calcined for an hour in a close crucible, it will form a thick flux; but it still retains the acid of arsenic. (E) If it be mixed with the same quantity (in measure) of charcoal-powder, and exposed to a strong fire in a retort, a shining regulus of arsenic will be sublimed. The residuum is quicklime, mixed with charcoal, still however containing some arsenic.

§ XVI. *Upon Magnesia.*

(A) Magnesia dissolves in acid of arsenic; but, when the solution comes to the point of saturation, the mass coagulates. This coagulum being dissolved in a larger quantity of acid of arsenic, and evaporated, the solution grows gelatinous; if the jelly be lixiviated with water, filtered and evaporated, a viscid mass remains, which will not crystallise. (B) The solutions of magnesia in vitriolic, nitrous, muriatic, and acetous acids, are not precipitated by the acid of arsenic, but very readily by
the

the neutral arsenical salts § VI. VII. VIII. A, A, A. The precipitate is easily soluble in acids, but not in water. (c) Exposed to the fire in a crucible with charcoal, it shews the same phenomena as the precipitate of lime § XV. D, E.

§ XVII. *Upon Earth of Alum.*

(A) The earth, which is precipitated from a solution of alum by alkali of tartar, after being washed with boiling water, is easily soluble in the acid of arsenic, till it becomes quite dry. The solution coagulates as soon as it arrives at the point of saturation. (B) Dissolved in the vitriolic, nitrous, and muriatic acids, it is not precipitated by the acid of arsenic, but it is, when dissolved in vinegar. The above solutions are precipitated by neutral arsenical salts; the precipitate easily dissolves in acids, but not in water. (c) Treated in the crucible, it shews the same phenomena as the precipitate of lime § XV. D. (D) If the solution (A) be evaporated to dryness, and then mixed with a little charcoal-powder, and exposed to distillation with a strong fire, a little yellow sublimate rises into the neck of the retort, as likewise some shining regulus; volatile sulphureous acid passes over into the receiver. The residuum dissolves with difficulty in vitriolic acid; some crystals of

alum, however, will form in the space of two months.

§ XVIII. *Upon white Clay.*

One part of white clay reduced to powder was mixed with four parts of acid of arsenic, and digested for a fortnight; but the acid would not dissolve any part of it. The mass was put into a retort, and distilled to dryness, and the fire increased till the retort began to melt. It was converted into a thick flux, and a little arsenic was sublimed. The residuum, powdered and mixed with a little charcoal-powder, was exposed to distillation in the same degree of heat when a shining regulus was sublimed.

§ XIX. *Upon Silex.*

Liquor silicum was precipitated by vitriolic acid, and lixiviated with boiling water. While it was still moist, acid of arsenic was added, and the mass was exposed to digestion for fourteen days, but no solution ensued. I afterwards evaporated it, and calcined the product, till the retort which I used began to melt. A little arsenic rose into the neck of the retort: Then the residuum was boiled in water, upon which the acid dissolved, but the flux remained at the bottom unchanged.

§ xx. *Upon Terra Ponderosa.*

The earth in the ponderous spar is not lime, as is generally believed, but a peculiar kind of earth. It is the same with that of which I related some experiments in my Dissertation on manganete. Mr I. G. Gahn afterwards informed me, that he found that this earth was the basis of the ponderous spar. Incited by this, I procured a larger quantity of it, in order to make more experiments. I shall here only mention the effects of acid of arsenic. (A) Terra ponderosa dissolves readily in the acid of arsenic; but, as soon as it has obtained its point of saturation, it again precipitates, combined with the arsenical acid. (B) Neither is its solution in nitrous, muriatic acetous acid, precipitated by the acid of arsenic; but the arsenical neutral salts (§ VI. VII. VIII. A, A, A,) precipitate these solutions. (C) In the crucible, this precipitate shews the same phænomena as the precipitate of lime; as also when treated with charcoal-powder. (D) The solution of ponderous earth in acid of arsenic is again precipitated by the acid of vitriol, in the form of a salt insoluble in water, *viz.* regenerated ponderous spar.

§ XXI. *The Effects of the Acid of Arsenic upon Metals.*

As the acid of arsenic cannot be kept long in the crucible without being converted into arsenic, in which state it sublimes (§ v. B); and as in a retort it continues long unchanged, and consequently acts longer upon metals, I rather chose to conduct my experiments in the latter way.

In long necked flasks I added four parts of the acid of arsenic to one part of filings of metals. After the water was evaporated, I poured fresh upon the mixture. This method I pursued in all the following experiments.

§ XXII. *Upon Gold.*

(A) The acid of arsenic has no effect upon gold in the heat of digestion. I put the mass into a retort, and abstracted all the liquid, then increased the heat till the acid flowed, and continued the same degree of heat for half an hour, during which time a small quantity of arsenic was sublimed. When the retort was grown cool, I poured a little water into it, and placed it in sand. The acid was dissolved; but the remaining gold being washed and dried, was found to be nearly of the same weight as at first. The retort was marked with red and yellow spots, which could
not

not be taken off by any menstruum. (B) The solution of gold was mixed with acid of arsenic, but no precipitation ensued; the mass was then abstracted in a retort to dryness, and the fire increased till it was in a perfectly fluid state; the gold was reduced, and some dephlogisticated muriatic acid came over into the receiver. The retort was spotted red and yellow. (C) The mixture of acid of arsenic and muriatic acid has no effect upon gold, neither has a mixture of acid of arsenic and nitrous acid.

§ XXIII. *Upon Platina.*

(A) Platina digested in the acid of arsenic is not attacked. After all the humidity was abstracted, I increased the fire till the retort melted. The platina lay at the bottom in the fused acid; a little arsenic was sublimed. After it was cool, I poured some water into the retort, which dissolved the acid. This acid was rendered opaque by a white powder, which was afterwards lixiviated with water, and then dried. It grew black upon charcoal before the blowpipe, had a smell like arsenic, and was attracted by the loadstone. The platina, after it was dried, had hardly lost any thing of its weight. Pure platina, consequently, is not attacked by the acid of arsenic. (B) The solution of platina

tina in aqua regia is not precipitated by the acid of arsenic, but readily by the arsenical neutral salts. The precipitate in this case is yellow; it is soluble in a large quantity of water; but it contains no mark of acid of arsenic. A mixture of acid of arsenic and muriatic acid has no effect upon platina, neither has a mixture of nitrous acid and the acid of arsenic.

§ XXIV. *Upon Silver.*

(A) Pure silver is not attacked by the acid of arsenic in digestion. After the whole of the liquid was abstracted, I increased the fire till the acid came into fusion. Here more arsenic was sublimed than in the foregoing experiments with gold and platina. This degree of heat being continued for half an hour, the silver dissolved. After the retort was grown cold, I broke it, and found that it contained a colourless glassy mass, nearly transparent. The retort was covered with a glazing of a flame-colour, which could not be separated from the glass by any solvent. (B) Upon the vitreous mass, after it was pounded, I poured some distilled water, and exposed it to a sand-heat, upon which it immediately lost its transparency, and assumed a brown-red colour; the acid of arsenic was dissolved, and a
brown

brown powder remained at the bottom. The acid contained a little of the silver in solution; for, on adding muriatic acid, some luna cornua was precipitated. (c) The brown powder was dried, and exposed to such a degree of heat that the retort melted. The powder entered into fusion, but no arsenic was sublimed. When the retort was cooled, I broke it, and, upon taking the mass out, I found it transparent at the margin. (D) As calx of silver is reducible without the addition of phlogiston, as is likewise the case with acid of arsenic (§ v. B), I tried what a greater degree of heat would effect. I therefore put the glassy mass into a crucible, over which I luted another, and afterwards applied as strong a heat as silver requires for being melted. After the apparatus was cooled, the silver was found reduced, and surrounded with a little white glass. (E) The solution of silver is precipitated by acid of arsenic, but not entirely; the precipitate is of a brown colour. More is precipitated by the neutral arsenical salt of Mr Macquer; but as this salt is supersaturated with acid, some silver is retained in the solution. The neutral arsenical salts (§ VI. VII. VIII. A, A, A,) decompose the solution entirely. (F) If this precipitate of silver be digested in muriatic acid, the acid of arsenic is expelled

pelled, and it is changed into muriated silver. In the same manner, this brown precipitate is soluble in spirit of sal ammoniac, prepared with lime. (G) Though neither the acid of arsenic nor the muriatic acid alone attack silver, a mixture of them has considerable action upon this metal. If the solution of silver in nitrous acid be precipitated by copper, and the precipitate well washed with hot water, and afterwards digested for fourteen days in a close vessel, with two parts of acid of arsenic, and two parts of muriatic acid, the silver is changed into a white powder, which, after beingedulcorated and dried, is found to be muriated silver. If the acid liquor be then distilled off, muriatic acid goes over, which contains arsenic; for, when mixed with a little nitrous acid, and again abstracted, a little acid of arsenic remains behind. Hence it follows, that the muriatic acid attacked the earth of silver during the digestion, while the acid of arsenic attacked its phlogiston; whence the arsenic was produced, which the muriatic acid afterwards took over with it into the receiver.

§ xxv. *Upon Quicksilver.*

(A) Quicksilver was not acted upon by the acid of arsenic during digestion. I next put the mixture into a retort, abstracted

ftracted all the watery part, and then increased the fire. The mass grew yellow, quicksilver rose into the neck, with a little arsenic, and a little yellow sublimate. The fire was then increased till the retort was near melting, but the mass would not enter into fusion. Of six drachms of quicksilver which I took for this experiment, I obtained three drachms and a half in the receiver. Thus the acid of arsenic contained $2\frac{1}{2}$ of fixed quicksilver. (B) After the retort was cold, I took the mass, which was a little yellow, out of it, and divided it into two parts. One I boiled in distilled water, but none of it was dissolved. Diluted nitrous and vitriolic acids had hardly any effect upon it, but muriatic acid dissolved it very readily. This solution being evaporated to dryness, then put into a retort, and distilled, corrosive sublimate rose into the neck. The residuum flowed upon applying a strong fire, and proved to be acid of arsenic. The other portion I mixed with two parts of common salt, and distilled it. Corrosive sublimate rose into the neck of the retort. (c) Calcined quicksilver and arsenical acid being reducible by heat without any addition of phlogiston, this residuum (A) must likewise be reducible by a sufficient degree of heat alone. One part of quicksilver was mixed with six parts of acid of arsenic,

arsenic, and after all the humidity was driven off, the fire was increased, and though the mass was heated white, it, however, lay unchanged in the retort; but when the retort melted, it ran likewise into fusion; the quicksilver was reduced, and rose, together with the arsenic, into the neck of the retort, a little quicksilver remaining behind. (D) It is known, that quicksilver, digested with muriatic acid is not attacked. But if two parts of muriatic acid, two parts of acid of arsenic, and one part of quicksilver, be exposed to digestion in a close phial for fourteen days, the acid acquires the taste of quicksilver, and that metal is changed into a yellow powder. If the acid be now distilled, muriatic acid impregnated with arsenic goes over. If the residuum in the retort be urged by a strong heat, corrosive sublimate rises, and the superabundant acid of arsenic remains behind in the retort. The yellow powder is turned black by lime-water and alkalis; if sublimed, it is changed into mercurius dulcis. (E) The solutions of quicksilver in vitriolic and nitrous acids are precipitated by the acid of arsenic in the form of a yellow powder; but the solution of corrosive sublimate is neither precipitated by the acid of arsenic, nor by any of the neutral arsenical salts; but arsenicated volatile

latile alkali (§ VIII.) precipitates the solution in the form of a white powder. (F) The acid of arsenic, when sublimed with corrosive sublimate, undergoes no change. But if, instead of corrosive sublimate, mercurius dulcis is employed, corrosive sublimate rises, and the residuum is the same as that of letter A. Some writers assert, that arsenic, distilled with corrosive sublimate, yields butter of arsenic; but they are mistaken. I have distilled such a mixture in different proportions, but have always obtained at first corrosive sublimate in the neck of the retort, and afterwards arsenic. Hence it would follow, that as the quicksilver in the corrosive sublimate is calcined, the muriatic acid has a stronger attraction for arsenic than for the calx of quicksilver. In order to ascertain this point, I mixed butter of arsenic with calcined quicksilver, and distilled the mixture. I first obtained some drops of the butter in the receiver, then corrosive sublimate rose into the neck of the retort, which was at last followed by arsenic. But the case is quite different with the regulus of arsenic; for if it be mixed with an equal quantity of corrosive sublimate and distilled, smoking butter of arsenic, mercurius dulcis, and a little quicksilver, are obtained. Hence it follows, that mercurius dulcis is decomposed

posed by a double elective attraction, that of the phlogiston of the regulus for the calx of mercury, and that of the muriatic acid for the calcined regulus of arsenic, whence the quicksilver is reduced, and butter of arsenic is produced. The same thing happens with a mixture of orpiment and corrosive sublimate.

§ XXVI. *Upon Copper.*

Copper is attacked by the acid of arsenic during digestion. The solution is of a green colour. A quantity of light blue powder is deposited, and attaches itself to the copper. This powder consists of acid of arsenic and calcined copper. (B) One part of filings of copper was mixed with two parts of dry acid of arsenic, reduced to a fine powder. The mixture was exposed to distillation, and the fire increased till the retort melted. Here some arsenic rose into the neck, the mass entered into fusion, and turned blue. After the retort was cooled, I poured some water upon it and boiled it; the solution was like that of letter A. In the retort there remained a little copper which was not dissolved, and the bottom of the retort was tinged with brown, red, and yellow spots, which were insoluble in any menstruum. (E) Copper dissolved in mineral acids was not precipitated by the acid of arsenic;

arsenic; but when it is dissolved in vinegar, a precipitation ensues. Neutral arsenical salts precipitate the solution of copper in the form of a blue powder, which I.edulcorated, dried, and exposed to a strong fire for an hour. After the mass was cooled, the powder appeared to be changed into a brown scoria, which had covered the whole internal surface of the crucible with a yellow enamel. (D) The scoria was finely powdered, mixed with a little lamp-black, and exposed in a small glass retort to the fire till it melted, when a fine regulus of arsenic was sublimed, and the copper in the residuum was found to be reduced.

§ XXVII. *Upon Iron.*

(A) Iron is attacked by the acid of arsenic during digestion, and at last the whole solution grows gelatinous. (B) But if the digestion be performed in a close phial, so that the air has no access to it, it does not grow gelatinous. One portion being exposed to the open air, in a couple of hours afterwards the solution was grown so gelatinous upon its surface, that the phial might be inverted without any thing running out of it. Another portion was mixed with alkali of tartar, whence a quantity of a whitish green powder was precipitated, which beingedulcorated and

distilled in a glass retort by a gentle fire, some arsenic was sublimed, and the residuum was red ochre. (c) One part of iron-filings was distilled with four parts of acid of arsenic. The mass made a great effervescence towards the end, and, when it became dry, it took fire in the retort upon increasing the heat, and then both arsenic and regulus of arsenic were sublimed. After it was grown cool, the residuum was found to be black; it was friable, and contained but little acid of arsenic. The retort was covered with yellowish-brown spots. (d) Solutions of iron in mineral acids are not precipitated by the acid of arsenic, but iron dissolved in vinegar is precipitated in the form of a dark-brown powder. Neutral arsenical salts precipitate all solutions of iron. The precipitated powders, if exposed to a strong fire, enter into fusion with an arsenical smell, and are changed into black scorix, which, when mixed with charcoal-powder, and calcined, yield copious vapours of arsenic, and are afterwards attracted by the loadstone.

§ XXVIII. *Upon Lead.*

(A) Lead digested with acid of arsenic turned black at first. Some days afterwards it was surrounded with a light-greyish powder, which is mixed with a little arsenic,

fenic, but this may be sublimed by a gentle fire. The acid contains no lead dissolved. (B) One part of shavings of lead was distilled with two parts of dry acid of arsenic reduced to powder. The lead was dissolved, and the mass flowed clear, a little arsenic rising into the neck of the retort. After the retort was grown cold, I found a milky glass in it, which I boiled in distilled water, and thus a quantity of white powder was separated; the superfluous acid of arsenic was dissolved in the water. (c) This powder was edulcorated, then put into a little retort, and kept in fusion for half an hour, but no arsenic was sublimed. I put some small pieces of charcoal into the retort, upon which a violent ebullition took place, and some regulus of arsenic was sublimed. (D) Lead dissolved in nitrous or muriatic acid or vinegar is precipitated by the acid of arsenic. This precipitate shews the phenomena mentioned at c.

§ XXIX. *Upon Tin.*

(A) Tin digested with acid of arsenic grows at first black, and is afterwards covered with a white powder; at last the whole mass grows gelatinous. (B) One part of tin-filings was mixed with two parts of acid of arsenic, and distilled. When the mass became red-hot, it took

fire in the retort, and immediately after both arsenic and a little regulus of arsenic were sublimed. The tin was dissolved, and formed a limpid flux, which, after growing cold, was of a milky colour. Upon this mass I poured water, and exposed it to heat, in order to dissolve the acid. A quantity of white powder was separated, which was insoluble in any acid, and contained very little acid of arsenic. (c) The solutions of tin in mineral acids are not precipitated by the acid of arsenic, but its solution in vinegar is. Neutral arsenical salts precipitate the solutions of tin. This precipitate is very difficult of fusion. When it is mixed with charcoal-powder, regulus of arsenic is sublimed.

§ xxx. *Upon Zinc.*

This is the only one of all the metals and semimetals that effervesces when digested with acid of arsenic. The zinc grows black, and the transparency of the acid is destroyed by a quantity of black powder. If this powder be separated,edulcorated, and dried, and then put upon an iron plate, heated nearly red-hot, in a dark place, it burns with a blue flame and a white arsenical smoke, and leaves a white powder behind; it is consequently for the most part regulus of arsenic. The effervescence soon ceases, because
each

each particle of zinc is surrounded with the regulus, which hinders the acid from having any effect upon it. (B) In order to ascertain what kind of air it is which rises during the solution, I tied an empty bladder to the phial in which the mass was contained. The air which I obtained had the following properties: 1. It would not unite with water, nor did it precipitate lime-water. 2. Mixed in a glass-vessel with two-thirds of common air, it was not absorbed. 3. When a burning candle was brought to the mouth of the vessel, the air in the vessel was inflamed with detonation; the flame took its direction towards the hand, which was thereby coloured brown: The matter that produced this colour proved to be regulus of arsenic, and left a disagreeable arsenical smell behind; the internal surface of the vessel too was covered with a brown pellicle. The air, therefore, which holds the regulus of arsenic in solution is of the inflammable kind. (c) One part of filings of zinc was mixed with two parts of dry and finely powdered acid of arsenic, and distilled. When the bottom of the retort began to be red-hot, a violent inflammation, accompanied with a very bright light, took place in the retort, which burst with an explosion. In the neck were found regulus of arsenic and flowers of zinc.

(D) Zinc dissolved in mineral acids is not precipitated by the acid of arsenic, but its solution in vinegar is precipitated. Neutral arsenical salts decompose all the solutions, and a white precipitate is obtained, which, when welledulcorated, fuses in a retort on the application of a strong heat, and, when mixed with charcoal-powder, yields regulus of arsenic.

§ XXXI. *Upon Bismuth.*

(A) Bismuth, during digestion with acid of arsenic, is covered with a white powder; water precipitates the solution. The powder consists of calcined bismuth and acid of arsenic. (B) One part of bismuth was distilled with three parts of dry acid of arsenic. The mass entered into fusion, the bismuth was calcined, but remained at the bottom undissolved; a little arsenic rose into the neck; after the retort became cool, water was poured upon the residuum, which dissolved the acid, but the calx of bismuth remained unchanged. (c) Bismuth dissolved in nitrous acid was precipitated by the acid of arsenic. This precipitate, as well as the calx (B), are very difficult of fusion; but on adding a little charcoal-powder, they melt immediately; the arsenic goes off in vapours, and the bismuth is reduced.

§ XXXII.

§ XXXII. *Upon Regulus of Antimony.*

(A) During its digestion with the acid of arsenic, a quantity of white powder is separated from the regulus of antimony. If a little of the clear solution be dropped into water, a white powder is likewise precipitated, which consists of calcined regulus of antimony, and of acid of arsenic. It is soluble only in muriatic acid, and may be again precipitated by water.

(B) One part of regulus of antimony was distilled with three parts of arsenical acid; as soon as the mass entered into fusion, an inflammation ensued, and regulus of arsenic and a little red sublimate were sublimed. A little volatile sulphureous acid came over into the receiver. The residuum was boiled in water, upon which the acid was dissolved; a white shining powder remained behind, which was mixed with charcoal-powder and distilled. An ebullition took place, some regulus of arsenic rose into the neck of the retort, and the antimony was reduced. (c) Butter of antimony was not precipitated by the acid of arsenic, but readily by the neutral arsenical salts. The solutions of glass of antimony in vinegar and cream of tartar are precipitated by the acid of arsenic.

§ XXXIII. *Upon Cobalt.*

(A) The acid of arsenic digested with cobalt assumed a rose-colour, but a great deal of the cobalt remained undissolved. (B) I put the whole mass into a retort, and abstracted it to dryness; then, on increasing the heat, it entered into fusion, and a little arsenic was sublimed. After the mass was grown cool, it had a semitransparent violet-colour. I then poured water upon it, and put it into hot sand; the acid was dissolved, the violet-colour disappeared, and the solution turned dark-red. The bottom of the retort was blue, and no menstruum was capable of taking this colour out of the glass. (c) Neither the solutions of cobalt, in mineral acids nor vinegar, are precipitated by the acid of arsenic; but the arsenical neutral salts produce a precipitation of a rose-colour. This precipitate is difficult of fusion in the crucible, and has the appearance of a dark-blue scoria.

§ XXXIV. *Upon Nickle.*

(A) The acid of arsenic digested with nickle assumes a green colour; a quantity of green powder mixed with arsenic is precipitated. The arsenic may be separated from it by a gentle heat. (B) One part of nickle was mixed with two parts
of

of dry acid of arsenic, and distilled by a strong fire. The mass melted with an appearance of inflammation, and some arsenic was sublimed. After it was grown cool, it proved to be a yellow mass, upon which a number of grey elevated streaks appeared; they were like a vegetation, and were formed during the distillation. This yellow mass was boiled in water, when the acid dissolved, and a yellow powder remained behind, which, when treated with charcoal-powder, yielded a regulus of arsenic, but was not reduced itself. (c) The solutions of nickle in acids are not precipitated by the acid of arsenic, neither is there any precipitation from its solution in vinegar; but the neutral arsenical salts precipitate a whitish-green powder.

§ xxxv. *Upon Manganese.*

(A) The acid of arsenic dissolves a little manganese during digestion; fixed alkalis precipitate a white powder from it. (B) When distilled with acid of arsenic, a little arsenic was sublimed. The mass entered into a kind of fusion, but the acid contained no more of the manganese than it did before. (c) Phlogisticated manganese dissolves readily in acid of arsenic; but whenever the acid arrives at the point of saturation, the solution coagulates into

to little crystals. (D) The solutions of manganese in the mineral acids are not precipitated by the acid of arsenic, though they readily are by the neutral arsenical salts. Manganese dissolved in vinegar is precipitated by the acid of arsenic. (E) These precipitates, which consist of phlogisticated manganese and of acid of arsenic, were distilled in such a heat that the retort at last melted, but no arsenic was sublimed, nor would they enter into fusion, but retained their white colour; however, when mixed with charcoal-powder in a crucible, they flowed, and regulus of arsenic arose in the form of vapour, while the manganese remained behind.

§ XXXVI. *Upon Regulus of Arsenic.*

(A) The regulus of arsenic digested with acid of arsenic, was covered with a white powder, which proved to be arsenic. (B) One part of the regulus was mixed with two parts of dry acid of arsenic, and distilled. The regulus rose into the neck, and the acid entered into fusion. (C) If small pieces of regulus of arsenic be put, one after another, into a retort where the acid of arsenic is in a state of fusion, an inflammation takes place, and arsenic is sublimed. (D) The regulus of arsenic is dissolved by unctuous oils in a boiling heat; the solution is black, and, after it grows cold, of the consistence of salve.

E S S A Y VII.

REMARKS UPON SALT OF BENZOIN. 1775.

THE common way to obtain the salt from benzoin is by sublimation. This salt is sold in the shops under the name of flowers of benzoin. I proposed to determine with exactness how much salt a given proportion of benzoin yields by sublimation. For this purpose, I distilled a pound of benzoin in a retort, and, after having perfectly separated the empyreumatic oil by lixiviation, I obtained between nine and twelve drachms of flowers. This salt may be likewise obtained by simply lixiviating the benzoin with water; but the salt thus obtained is less in quantity, and if the ley be made too hot, the resin easily runs together, and the whole labour is lost. The reason why simple lixiviation yields so little salt is easily assigned. The resinous particles of the benzoin do not transmit the water; the solution, therefore, takes place only on the surface of the particles of the powdered benzoin.

I further boiled powdered chalk and benzoin in water, and then filtered the decoction, but, on its cooling, obtained

no crystals; but on pouring some drops of vitriolic acid into this liquor, the salt of benzoin soon afterwards precipitated; for this salt, which is an acid, was united with the chalk. The quantity of salt obtained, however, was not greater than that obtained by lixiviation. I then fell upon the idea of communicating to the water the power of acting upon the resinous particles of the benzoin, and thought thus to extract all the salt existing in this resin. I therefore boiled pounded benzoin with alkaline ley, and afterwards saturated it with an acid. I thus obtained the salt of benzoin by precipitation; but I here likewise met with this inconvenience, that the powder of benzoin ran together during the boiling and floated on the surface in the form of a tenacious resin.

There remained one way more to be tried, *viz.* To boil the benzoin with quicklime. As the particles of the lime, by interposing themselves between the particles of the benzoin, might prevent their running together, and as lime has likewise the property of acting upon the resinous particles, this promised to be a good way of extracting the salt from the benzoin. The salt thus obtained is perfectly free from empyreumatic oil, with which the flowers of benzoin are commonly contaminated, it is consequently also free from the
smell

smell which they otherwise yield. An equal, if not a greater quantity of salt, is obtained by this process than by distillation. A pound of the resin yielded from twelve to fourteen drachms of salt by this new method, which is as follows :

Upon four ounces of unslaked lime pour twelve ounces of water, and, after the ebullition is over, add eight pounds more (the pound twelve ounces) of water ; then put a pound of finely pounded resin of benzoïn into a tinned pan, pour upon it first about six ounces of the above lime-water, mix them well together, and thus successively add the rest of the lime-water. If it be poured in all at once, it will not mix with the benzoïn, which will likewise coagulate, and run together into a mass. This mixture ought to be boiled over a gentle fire for half an hour with constant agitation ; then take it from the fire, let it stand quiet for an hour, in order that it may settle ; pour off the supernatant limpid liquor into a glass vessel. Upon the remainder in the pan pour eight pounds more of lime-water ; boil them together for half an hour, then take it from the fire and let it settle ; add the supernatant liquor to the former ; pour upon the residuum some more lime-water, boil it as aforesaid, and repeat the same process once more. At last, put all the residuum

fiduum upon a filter, and pour hot water several times upon it. During this process, the calcareous earth combines with the acid of benzoin, and separates it from the resinous particles of this substance. A small quantity of the resin is dissolved by the lime-water, whence it acquires a yellow colour. All these yellow leys and decoctions are to be mixed together, and boiled down to two pounds, which are then to be strained into another glass vessel.

These lixivia are inspissated thus much, because superfluous water would hold much salt in solution, which must afterwards be precipitated. Besides, a small quantity of the resin, suspended by the lime-water, likewise separates during the evaporation, not being soluble in a small quantity of water; it therefore remains in the strainer. After the two pounds of the evaporated leys are grown cold, muriatic acid is to be added, with constant stirring, till there be no further precipitation, or till the mass tastes a little sourish. As vegetable acids have in general a weaker attraction for absorbent earths than mineral acids, the muriatic acid combines with the calcareous earth, and the acid of benzoin, which requires a large quantity of water to its solution, must fall down; the solution, which had before but a very
weak

weak smell of flowers of benzoin, acquires, by this precipitation, a very strong one.

The precipitated coagulum is then to be put into a filter, and, after being well dried, it is to be edulcorated sufficiently, by repeatedly pouring cold water upon it; it should be dried afterwards in a gentle heat. But as the water made use of for the edulcoration contains a little of the salt of benzoin dissolved, it ought to be evaporated, and afterwards set by to crystallise. If you wish to give this salt a shining appearance, dissolve it in a sufficient quantity—in six ounces, for instance, of water, by gentle boiling, then strain it immediately, while it is yet warm, through a cloth, into a glass vessel which has been heated before; you will thus have the satisfaction to see a number of fine crystals shoot as soon as the solution is grown cold. The water is then to be strained from the crystals, and the rest of the salt, still suspended in this water, is obtained by repeated evaporation and crystallisation. But as the flowers of benzoin are, on account of their lightness, not easily pulverized, it may be best to keep the salt in the form of a precipitate, which is always the finest powder. To this consideration it may be added, that, during the crystallisation, a great deal of salt is lost.

I have recommended cloth for filtering the warm solution, because I found it answer best. If blotting paper be used, the salt sometimes crystallises in the filter itself, and obstructs it. The filtration itself might be omitted, if it were not unavoidable, in order to purify the salt from about two grains of resinous substance, which, having been mixed with it during the preceding boilings, remain united with it during the rest of the process.

E S S A Y VIII.

ON SILEX, CLAY, AND ALUM. 1776.

FROM the writings of Mr Baumé, it appears that he takes the earth of alum to be nothing else than filex, and common clay to be filiceous earth, combined with a little vitriolic acid. Alum he supposes to be the same earth, supersaturated with vitriolic acid. With regard to chemical opinions, it is my custom not to credit any, till I have brought them to the test of experiment. I therefore was obliged to try Mr Baumé's assertion, that filex is soluble in vitriolic acid, by this test. I took an ounce of mountain crystal reduced to powder, mixed it with three ounces of alkali of tartar, and fused the mixture by a strong fire. This alkaline mass I afterwards dissolved in twenty ounces of water, and poured as much diluted vitriolic acid to it, as was more than sufficient to saturate it; I then filtered the liquor, collected,edulcorated and dried, the precipitated filex which remained on the filter. From the filtered liquor, after it was evaporated, I obtained, besides a subacid vitriolated tartar, about $1\frac{1}{2}$ drachm of alum. The question now was, Whe-

ther the precipitated filix, repeatedly fused with alkali, would still yield alum? If this was the case, Mr Baumé's system would gain a strong confirmation; but, if it did not, a suspicion would arise, that some clay was mixed with the mountain crystal; I therefore dried the precipitate, and mixed it with a triple quantity of alkali; and, proceeding in the same manner as in the foregoing experiment, again obtained alum. This laborious experiment I repeated seven times, and always obtained alum; I now thought it reasonable to believe that Baumé was right. But, behold! on examining the crucibles, employed for these repeated fusions, I found them every where uneven in the inside, and full of little excavations, which they had not before the experiment. This created a suspicion that the alkali had perhaps dissolved part of the clay of these crucibles, and thus, with the superfluous vitriolic acid, produced alum; I therefore now took an iron crucible, and prepared the liquor filicum, which I treated in the same manner as before, and obtained no alum. How easily may one err in making experiments! Thus, all the alum, I obtained, came from my crucibles, and I was in a fair way to obtain conviction of a falsehood: Undoubtedly the same thing led Mr Baumé into the mistake. I afterwards

wards took precipitated siliceous earth while it was moist, and digested it for a fortnight with diluted vitriolic acid, in order to find out whether, as Mr Baumé asserts, any thing is dissolved, but could find not the least mark of solution.

The siliceous earth, therefore, still remains a peculiar earth. Mr Baumé pretends, that clay contains a little vitriolic acid, and is on this account soluble in a large quantity of boiling water. I likewise tried this experiment, but found, that of several kinds of pure argillaceous earth not the smallest quantity was dissolved, which is easily ascertained by means of alkali of tartar. I here likewise made different experiments, in order to obtain vitriolic acid from pure argilla, but without success. I could never obtain any hep-
par by means of alkali of tartar, nor by means of powder of charcoal; neither have I obtained with clay a vitriolic neutral salt from the residuum of the distillation of muriatic and nitrous acid.

I have made several experiments with alum, in order to ascertain its effects when mixed with other substances. A solution of alum is decomposed (A) by lime-water. If no more lime-water be added than is exactly requisite for the precipitation, the earth of alum forms a transparent precipitate, of the appearance

of boiled starch. If the clear water is filtered, it proves to be a solution of gypsum. (B) If more lime-water be added to the solution of alum than is requisite for its precipitation, a white precipitate is formed, but nothing gelatinous, as in the foregoing experiment. If the whole be left together for a quarter of an hour, and frequently agitated during this time; and if it then be filtered, no gypsum, nay, not even lime, is found in the supernatant water, unless there has been added too much lime-water; but it will be found to be pure water. I was at first at a loss to imagine what was become of the gypsum. (c) On examining the precipitate, I found it to consist of earth of alum, selenite, and lime; for, after putting it to dissolve in muriatic acid, the gypsum, which is not so easily soluble, remained behind. The clear solution being saturated with caustic volatile alkali, a transparent gelatinous earth, which was the earth of alum, was precipitated. Upon straining it again, and pouring lixivium tartari to it, I obtained a precipitate, which was lime. Hence I saw that the lime and gypsum had separated from the water, and united with the earth of alum.

In order to acquire a more distinct idea of this phenomenon (D), I precipitated a solution of alum with a quantity of caustic volatile

volatile alkali, more than sufficient to saturate the acid, in order that I might be quite certain of separating all the vitriolic acid, which might perhaps still adhere to the precipitate. The precipitated earth wasedulcorated, and mixed with a solution of gypsum, that I might see whether the gypsum would separate from the water and precipitate with the solution of alum; but this did not happen. (E) I further wished to know how lime-water would act upon the earth of alum. I found that it very soon lost its caustic taste, and that the clear earth of alum grew opaque. I strained part of this water, and dropped some lixivium tartari into it, but it remained clear; neither was there any precipitate formed by corrosive sublimate. I afterwards added muriatic acid to the last mentioned precipitate, when it dissolved entirely without leaving any gypsum behind. Thus the earth of alum had united itself with lime, and formed a peculiar compound.

I now thought that this compound of the earth of alum and lime might separate gypsum from water; (F) I therefore prepared a large quantity of this compound earth, mixed it with a solution of gypsum, and set it to rest for a quarter of an hour, when I saw, to my surprise, that the gypsum remained suspended in the water,

and that the precipitate was still soluble in muriatic acid, without leaving any gypsum behind. (G) I now mixed a solution of gypsum with lime-water, adding also pure earth of alum. This mixture perfectly agreed with that mentioned at B. The precipitate was white, and contained gypsum as well as lime. From these experiments I conclude, 1. That the vitriolic acid in gypsum is able to combine with more lime than is requisite for its perfect saturation. 2. That calcareous earth is capable of uniting with the earth of alum. 3. That gypsum cannot combine with the earth of alum; but if a superfluous quantity of lime be united with vitriolic acid, it then will serve as a means of union, to combine gypsum with the earth of alum, and thus form a combination, consisting of three earths. Pure clay has no effect upon lime-water.

E S S A Y IX.

ANALYSIS OF THE CALCULUS VESICÆ.

1776.

HAVING collected a sufficient number of calculi, taken from persons of both sexes, I undertook an enquiry into their nature, and I now communicate some observations, which, to my knowledge, have not hitherto been communicated to the public.

All the calculi which I have examined, whether flat and polished, or rough and angular, were of the same nature, and consisted of the same constituent parts.

§ I.

I put a quantity of calculus, reduced to powder, into a small glass retort, poured some diluted vitriolic acid upon it, and exposed it to digestion, but the powder was not at all attacked. After the humidity was abstracted by distillation, the concentrated acid began to attack the powder, and the stone was dissolved. After the acid was abstracted to dryness by an increased heat, a black coal remained; the liquid which passed over was vitriolic acid,

with a strong smell of the volatile acid of sulphur.

§ II.

Neither concentrated nor diluted muriatic acid had any effect upon the calculus, not even when boiled with it.

§ III.

(A) The diluted nitrous acid, or aquafortis, had some effect upon the calculus, even in the cold. On the application of heat, an effervescence ensued, and red vapours arose; the calculus was entirely dissolved. If the experiment be made in a retort, and lime-water be put into the receiver, it will be precipitated.

(B) This solution is acid, though the menstruum be boiled with a superabundant quantity of powder, so that there may remain a portion of it undissolved.

(C) This yellow solution produces deep red spots upon the skin in half an hour after it is applied. If the saturated solution be a little more evaporated, it assumes of itself a blood-red colour, which, however, disappears on dropping in a single drop of nitrous acid.

(D) A solution of ponderous earth in muriatic acid precipitates nothing from this solution.

(E) Me-

(E) Metallic solutions are not sensibly changed by this solution.

(F) It is not precipitated by alkalis, but only grows a little yellower when the alkali is superabundant, and then this mixture, in a strong digesting heat, likewise assumes a rose-colour, and produces spots of the same colour very quickly, and without any sense of burning upon the skin. This mixture likewise precipitates metals of different colours; vitriol of iron, black; vitriol of copper, green; silver, grey; corrosive sublimate, zinc, and lead, white.

(G) Lime-water decomposes this solution, and precipitates a white powder from it, which I haveedulcorated and dried. This precipitate is soluble in muriatic and nitrous acids without any effervescence. Though there be an excess of the precipitated powder, the solution will be acid. (The same thing happens likewise with animal earth and fluor spar, if they be dissolved in the same acids). If the solution be evaporated to dryness, it will at last take fire. If the precipitate be heated only to a dull-red heat in a close crucible, it grows black, smells like burnt alum, and effervesces with acids. Before the blowpipe it changes into quicklime.

(H) Neither the acid of sugar nor salt of sorrel precipitate this solution. The
alkaline

alkaline mixture (F) is also not precipitated by these acids.

§ IV.

The calculus, when pounded and boiled with a solution of alkali of tartar, remains unchanged. But perfectly pure or caustic alkali, such as shews not the least mark of aerial acid, dissolves the calculus, even in the cold. The solution is yellow, and tastes sweetish; it is precipitated by all the acids, even by the aerial. Lime-water is not precipitated by this solution, but metallic solutions are decomposed. Iron is precipitated brown, copper grey, silver black, zinc, corrosive sublimate, and lead, white. If there be a little superabundance of alkali in the solution, it yields a smell of volatile alkali. Dry volatile alkali has no effect upon the stone, but the caustic, prepared with quicklime, dissolves it; a pretty large quantity, however, is required for this purpose.

§ V.

Lime-water likewise dissolves the stone by means of digestion. Twelve grains of calculus require four ounces of lime-water. The lime-water thereby loses its caustic taste. On adding acids to this solution, the calculus is partly precipitated.

§ VI.

§ VI.

Pure water dissolves the calculus entirely, but a large quantity is requisite for this purpose. If eight grains of finely powdered calculus be boiled for a short time with five ounces of water, they will be dissolved. The tincture of lacmus is turned red by this solution. Lime-water is not precipitated. As it grows cold, the greatest part of the calculus separates again in the form of fine crystals.

§ VII.

On distilling, in a small glass retort, one drachm of calculus in the open fire, I obtained a volatile alkaline liquor, like that from hartshorn, but no oil. In the neck of the retort there was a brown sublimate. Upon heating the retort thoroughly red-hot, and then leaving it to cool, I obtained a black coal, weighing twelve grains, which, when put upon red-hot iron in the open air, retained its black colour. The sublimate, which seemed to have been somewhat fused, weighed twenty-eight grains, and on being purified by a new sublimation, it grew white. It had no smell, but a somewhat sourish taste, and was easily soluble in boiling water. It also dissolved in spirit of wine, but a larger quantity than of water was requisite

site for this purpose. Lime-water was not precipitated. The sublimate seemed to agree, in some respects, with the *sal succini*.

From these experiments I conclude, that since the *terra ponderosa* (§ III. D) is not precipitated, which would, however, be a necessary consequence, if vitriolic acid were a constituent part of the calculus; and since the acid of sugar (§ III. H) does not produce any precipitation, which certainly would take place if lime were a constituent part of it,—I conclude, I say, that calculus is neither calcareous nor gypseous, but consists of an oily, dry, volatile acid, united with some gelatinous matter. The calculus is an oily salt, in which the acid prevails a little, since it is soluble in pure water (§ VI.), and imparts to the tincture of *lacmus* a red colour. That it contains phlogiston, appears by its solution in caustic alkalis and lime-water (§ IV. V.), but especially from the effects produced by means of nitrous acid, from which it acquires quite different properties than from being dissolved in alkalis, nor can it be precipitated from this solution (§ III. F). The animal gelatinous substance appears on distillation, by which a liquor is obtained resembling spirit of hartshorn, and a fine coal is left behind.

§ VIII.

I have found calculus dissolved in all urine, even in that of children. If four kannes of limpid fresh urine be evaporated to two ounces, a fine powder is deposited as it cools, and a part firmly adheres to the glass. This powder dissolves very readily in a few drops of caustic alkali, and has moreover all the properties of a calculus vesicæ. The lateritious sediment, which is deposited from the urine of those who labour under an ague, is of the same nature. I suspected in the beginning, that there was an unknown menstruum in this urine, which, being volatile in the open air, was the cause of such a large quantity of this powder being kept suspended in the urine; but as such urine likewise grows turbid, and deposits the same sediment when kept in close vessels, and redissolves it again on being exposed to a sufficient degree of heat, it appears evident that such a menstruum is neither present nor requisite.

§ IX.

All urine contains some animal earth or lime combined with phosphoric acid, and, by the superabundance of acid, this earth is kept dissolved. It is owing to this superabundance that urine imparts a red
colour

colour to paper coloured with lacmus. If this superabundant acid be saturated with volatile caustic alkali, a white powder is precipitated. Three drachms and a half of this powder, when dried, are obtained from four kannes of urine. I dissolved it in nitrous acid; on adding vitriolic acid some gypsum was precipitated. After all the nitrous acid was evaporated, an acid remained, which precipitated lime-water, and, when mixed with lamp-black, yielded phosphorus on distillation; consequently this powder really contains lime and phosphoric acid.

§ x.

According to these experiments, all urine contains, besides the substances already known, (*viz.* sal ammoniac, common salt, digestive salt, Glauber's salt, microcosmic salt, sal perlatum, and an oily extractive matter) a concrete acid, hitherto unknown or the calculus, and animal earth. It is remarkable that the urine of the sick is more acid, and contains more animal earth than that of healthy persons.

Supplement to the foregoing Dissertation.

By T. BERGMAN.

Without knowing any thing of Mr Scheele's analysis of the calculus vesicæ, I was employed at the same time upon the same subject. My experiments lead nearly to the same conclusion, *viz.* that these animal stones consist of a concrete acid. There are, however, some circumstances in which they differ from those of Mr Scheele. Perhaps the calculi on which we made our experiments were really different in their nature; but as the differences I remarked were constant with all the calculi on which I made experiments, I thought it worth while to communicate them to the public, especially as they relate to a matter so interesting to mankind.

I could not succeed in entirely dissolving stones of the bladder or kidney, either in distilled water, or in nitrous acid; though it is true that the undissolved part is the less, the more finely the calculus has been previously pounded; but even in this case a part remains undissolved, as appears clearly when the experiment is made in a small cucurbit; so that, after the mass is cooled, the undissolved part may settle at the bottom in one place. This appears in the
 clearest

clearest manner, if small pieces, or small calculi, of a few grains weight only, be put into a superabundant quantity of menstruum, and be kept in a degree of heat, very near to that which makes water boil. Here it will be observed, that the greatest part of the piece is dissolved, but that at the same time some small white spongy particles remain, upon which water, spirit of wine, acids, or caustic volatile alkali, have no sensible effect. If the heat be increased to full boiling, these particles divide into white rare flocculi, and become almost imperceptible, but without being dissolved, at least not entirely. I have not been as yet able to collect a sufficient quantity of them, in order to determine exactly their nature. This, however, I know, that, when exposed to fire, they are reduced to a coal, which burns slowly to ashes, and is not soluble in diluted nitrous acid.

When calculus vesicæ is dissolved in nitrous acid, no precipitation ensues on adding the acid of sugar; whence one is readily induced to conclude, that there is no calcareous earth present, because this experiment is the surest way to discover it. But I have found, in a variety of experiments concerning elective attractions, that the addition of a third substance, instead of disuniting two already united,
often

often unites with both very closely. That the same thing happens here, I had the more reason to believe, because the acid of sugar contains some phlogistic matter, though of so subtle a nature, that, on being burned, it does not produce any sensible coal; and the event of my experiment has shewn, that I was not mistaken in my conjecture. In order to ascertain this point, I burned coals of the calculus to ashes, which were quite white, and shewed in every respect the same phænomena as lime, caused some effervescence during their solution in acids, united with vitriolic acid into gypsum, were precipitated by the acid of sugar, and were partly soluble in pure water, &c. Notwithstanding this, there remains about one hundredth part of the ashes insoluble in aquafortis; the remainder of the above mentioned substance, which, together with the concrete acid, constitutes the calculus. If the calculus be dissolved in nitrous acid, the solution filtered, and evaporated to dryness, and the dry mass calcined to whiteness; a calcareous powder is thus likewise obtained.

As pure vitriolic acid contains no phlogistic matter, I expected that it would, in the present case, immediately shew the presence of lime, a circumstance which really happened. I dropped some pure

concentrated vitriolic acid into a solution of calculus in nitrous acid, and found, that when the solution was saturated, some small crystals immediately separated from it: They proved, on examination, to be gypsum; and, after being dissolved in distilled water, they were precipitated by the acid of sugar. When the solution of the calculus was very much diluted, there appeared no change in the beginning; but, after a little evaporation, the above mentioned crystals began to appear. Some calculi of the bladder or kidneys at least certainly contain lime, but seldom more than one-half in a hundred parts, or one in two hundred parts.

Concentrated vitriolic acid dissolves the calculus, when assisted by heat, with effervescence; the solution is dark-brown. If a little water be afterwards added, there seems to take place a kind of coagulation; but, on adding more water, all grows clear again, and assumes a yellowish brown colour.

The muriatic acid seems to have no effect upon it. I am however in doubt, whether it will not extract at least a portion of the calcareous earth, and shall for this reason make some farther experiments to determine this point.

The red colour which the solution of the calculus in aquafortis may be made to assume, is remarkable. A saturated solution

lution discovers no smell of nitrous acid, and if evaporated by itself in a large open vessel, the liquor assumes at last a deep-red colour, and it hardly contains any nitrous acid; for, on the one hand, paper tinged with lacmus scarce shews any signs of its presence; and, on the other hand, the colour is destroyed by the addition of any acid, without being ever afterwards recoverable, either by alkalis, or any other means known to me. If the solution be quickly evaporated upon a heated furnace, it at last swells into innumerable bubbles. This foam grows redder and redder, and, after it is quite dry, it appears dark-red. This dry mass communicates its colour to a much larger quantity of water than before, and dissolves very readily in all acids, even in such as have no action on the calculus; but they entirely destroy the colour, and that the more quickly, the stronger they are. Even alum, with its small excess of acid, has this effect. Caustic alkalis dissolve the colouring matter, and destroy it, but more slowly.

The nitrous acid has a peculiar effect upon all phlogistic substances; and, as the colour of bodies is especially dependent on phlogiston, it appears why no other acid has the power of educing such a colour from the calculus. But, in order to

obtain it, a proportional quantity of acid is requisite. The diluted acid of nitre ought therefore to be made use of, in order not so easily to transgress the proper limits; for if too much be used, it will not produce the proper effect; but, in proportion to its superabundance, goes further, and destroys more or less, or the whole of it. If it be poured undiluted upon powdered calculus, it is converted in a few moments, and without any assistance of heat, into a mere foam.

The acid of calculus is the more easily separated from the aquafortis by evaporation, as the latter is rendered more volatile by the inflammable particles of the former. Alkali added to them both united, does not produce any precipitation, a circumstance which is generally observed when two acids are combined; but both the acids unite with the alkali, according to the law of their attraction. The red mass obtained after desiccation, is however very different from the concentrated acid, such as is contained in the calculus; for it is of a darker colour, and very deliquescent; the least particle gives to a considerable quantity of water a rose-colour; it is attacked by the muriatic and other strong acids with violence, which sooner or later produce a quite colourless solution. Such a remarkable change depends, as much as

I have hitherto been able to ascertain, more on the action of the nitrous acid upon the inflammable part than upon any thing remaining behind. Such red spots, as are produced upon the skin by the solution, are likewise produced upon bones, glass, paper, and other substances; but then more time is required before they become visible, which however may be a little accelerated by heat.

I pass over a number of other experiments, made partly in a different manner from those of Mr Scheele, which, however, prove no more than may be learned from his excellent paper. I was also prevented from finishing some of them by other engagements. I have been these several years collecting the different stony concretions of animal bodies, in order to investigate their component parts; I have been promised still more of them, and hope to be assisted in this matter, so interesting to medical science, by such as have collections of this kind. The only thing from which we may reasonably expect the discovery of proper remedies, for the relief of people labouring under this complaint, is the just knowledge of the nature of the calculus. Did we not already know from experience, that lime-water and the caustic lixivium are among the best remedies against the stone of the bladder or kidneys,

neys, we might conclude this from its properties, as they are now discovered. From a further enquiry, we may perhaps be led to find out a still more convenient remedy. Whether all urinary calculi are of the same nature, I hope to ascertain soon.

E S S A Y

E S S A Y X.

METHOD OF PREPARING MERCURIUS
DULCIS VIA HUMIDA. 1778.

§ I.

TAKE half a pound of quicksilver, and as much pure common aquafortis, pour it into a small cucurbit, with a pretty long neck, stop the mouth with a little paper, and put it into warm sand. Some hours afterwards, when the acid appears no longer to act upon the quicksilver, the fire is to be so much augmented as nearly to make the solution boil. This heat is to be continued for three or four hours, and the vessel now and then to be shaken*.

Towards

* One would imagine, that when the acid no longer effervesces with the quicksilver, it should be saturated; but this is far from being the case. If the heat is increased, this solution is still able to dissolve a great quantity; with this difference, however, that whereas the quicksilver in the beginning is calcined, a great deal of quicksilver, in a metallic form, is afterwards dissolved, as appears clearly from this, that not only no more elastic vapours ascend, but also, that with fixed and volatile caustic alkalis a black precipitate is obtained, otherwise, when the solution contains only calcined quicksilver, the precipitate is yellow. If the black precipitate be gently distilled, quicksilver arises, and there remains a yellow powder, which

Towards the end, regulate the heat so that the solution shall gently boil for a quarter of an hour *. In the mean time, dissolve $4\frac{1}{2}$ ounces of pure common salt in six or eight pounds of water; pour this solution, still boiling, into a glass-veffel, and immediately afterwards mix with it the above mentioned solution of quicksilver, which must also be boiling, in small quantities at a time, with constant agitation. When the precipitate has settled, decant off the clear liquor and pour hot water again on the precipitate, with which it is to beedulcorated, till the water standing upon it shall be entirely tasteless. Put the whole obtained by these means together; filter and dry it in a mild heat †.

§ II.

is precisely that part of quicksilver, which, in the beginning of the operation, was calcined by the acid of nitre.

* The fire must necessarily be augmented, in order to keep the nitrated mercury dissolved, which is very much inclined to crystallise, even in the heat. There commonly remains some undissolved quicksilver; but it is always better to take too much than too little, for the more metallic substance the mercurial solution contains, the more mercurius dulcis is obtained.

† The mercurial solution must be cautiously poured into that of the common salt, that no mercury may follow. Two ounces of salt would be sufficient for the precipitation of all the quicksilver; but when so small a quantity is used, it may easily happen, that
some

§ II.

If we consider how mercurius dulcis is obtained in the dry way, or by sublimation, it will not be difficult to account for the method I have proposed. Mercurius corrosivus albus is a middle salt, and consists, as is well known, of marine acid, combined with calx of mercury. This salt can dissolve a good deal of quicksilver in its metallic form: In order to this, they must meet one another when separated into their smallest particles, which happens when, by means of heat, they are converted into vapour. The same thing takes place with the solution of mercury that is obtained in the method above described. This contains the calx of mercury and quicksilver, divided into its finest particles. If there be now added marine acid, or, to save expence, common salt, the marine acid will unite with the calx of mercury,

some superabundant corrosive sublimate may adhere to the precipitate, which water alone is incapable of entirely separating; this is doubtless the reason why it is generally supposed that white precipitate is corrosive. I have found, that common salt, as well as sal ammoniac, is capable of dissolving a considerable quantity of corrosive sublimate. It is on this account that I take $4\frac{1}{2}$ ounces of salt, in order completely to separate all the corrosive sublimate. From the above mentioned quantity of quicksilver, about $8\frac{1}{2}$ ounces of mercurius dulcis are commonly obtained.

cury, by which genuine mercurius corrosivus albus is produced; and as the solution contains quicksilver in its metallic form, it immediately attracts as much of the corrosive salt as is necessary to its saturation; and thus is produced a real mercurius dulcis, which, on account of its insolubility in water, must be precipitated.

§ III.

Experiments prove, that this precipitate is nothing else than a good mercurius dulcis; as, *1st*, It is entirely tasteless. *2^{dly}*, I have sublimed the precipitate, and examined what ascended in the beginning of this process, which ought to be corrosive, if the precipitate contained this salt in abundance, because it is well known, that corrosive sublimate rises sooner than mercurius dulcis; but this, as well as that which was afterwards sublimed, was pure mercurius dulcis, and entirely like to that obtained in the common manner. *3^{dly}*, I also mixed the precipitate with one-fourth part of quicksilver (thinking that, if it had contained too much mercurius corrosivus, it ought now to be able to unite with more quicksilver), and sublimed it, when I found my quicksilver again with its former weight undiminished. *4^{thly}*, It is known, that caustic alkalis

lis and lime-water give mercurius dulcis a black colour. The same thing appeared with mine. The black colour is nothing else than quicksilver divided into very minute particles.

§ IV.

That the method above described is really more advantageous than that usually employed, I cannot doubt; because,

1st, The mercurius dulcis can be prepared with less difficulty, with less expence, and without employing mercurius corrosivus.

2^{dly}, It can never become either more or less corrosive, if it be only welledulcorated, and consequently it is always safe.

3^{dly}, One is never exposed to the vapour which rises in the old method during the saturation of corrosive sublimate with quicksilver, and which is so dangerous to the health.

4^{thly}, This mercurius dulcis is much finer than the common, which never can be reduced to so fine a powder, however long it is triturated.

and this water gives mercurius sublimatus
black colour. The same thing appears
with mine. The black colour is no
thing else than quicksilver dissolved into
very minute particles.

§ 14

That the method above described is
fully more advantageous than the usual
method employed, I cannot doubt; because
the mercurius sublimatus can be prepared
with less difficulty, with less expense, and
without employing any violent processes.
It can never become either more or
less corrosive, if it be only well sublimated,
and consequently it is always safe.
Ours is never exposed to the vapour
which rises in the old method during
the formation of corrosive sublimate, which
is dangerous, and which is so dangerous to
the health. This mercurius sublimatus
is much finer than the common, which
never can be reduced to fine powder,
however long it is triturated.

E S S A Y XI.

A CHEAPER AND MORE CONVENIENT
METHOD OF PREPARING THE PUL-
VIS ALGAROTHI. 1778.

THE preparation of this powder, as has hitherto been practised, is an operation very difficult, and dangerous to the health. As this powder is requisite, in order properly to prepare antimonial or emetic tartar, I resolved to try whether the preparation would not succeed without corrosive sublimate, by which means two considerable advantages would be gained; the chemist would be out of danger, and the great quantity of the first mentioned mercurial preparation, which is now employed for making this powder, would be saved. Both these purposes we obtain by preparing *mercurius dulcis via humida*. For the objection, that no cinnabar of antimony is obtained, is groundless; because this cinnabar, purified by sublimation, is in no respect different from the common pure cinnabar.

Before I proceed to describe the new process for preparing the *pulvis algarothi*, it will be necessary to enquire into the theory which has been hitherto received, concerning

concerning the production of butter of antimony, when regulus of antimony is distilled with corrosive sublimate. It is said, that the decomposition of the corrosive sublimate, which in this case happens, takes place, because the elective attraction of the regulus of antimony for the muriatic acid is greater than that of the quicksilver for the same acid; that it therefore leaves the acid, and that this latter uniting with the regulus goes over into the receiver in the form of butter; that at last, on increasing the heat, the mercury goes over by itself, or that it is sublimed in union with the sulphur of antimony, under the name of cinnabar of antimony, provided crude antimony (antimonium sulphuratum) be taken for this purpose instead of the regulus.

This explication does not agree with the late observations in chemistry; for the butter of antimony, or, as it is sometimes called, the antimonial caustic, contains not the least regulus of antimony; but the portion of antimony which it contains is half calcined, and this calcination cannot be owing to the muriatic acid. But as it is well known, that the mercury in the corrosive sublimate is not in a reguline form, but in the state of a calx, and that the mercurial calx in this metallic salt may be reduced, by being put upon live coals; that

that fuming muriatic acid goes over, if the corrosive sublimate is distilled with phlogistic substances; and further, that the corrosive sublimate is by no means decomposed when distilled with pulvis algarothi, or with a half calcined regulus of antimony; it follows that, in the present process, the mercurial calx, as one constituent part of the corrosive sublimate, attracts the phlogiston necessary for its reduction from the regulus of antimony, whereby the muriatic acid is set free, and then attacks the regulus of antimony, which is dephlogisticated in the same proportion, and goes over united with it in the form of a thick substance, resembling butter.

The butter of antimony consists, therefore, of concentrated muriatic acid, and of a half calcined regulus of antimony; and it is from this partly dephlogisticated regulus that the antimonial tartar is obtained when it is united with cream of tartar. The regulus of antimony must be only partially calcined, in order to be soluble either in the muriatic acid, or by cream of tartar; for, in its metallic form, it is entirely insoluble; and the bezoar mineral proves, that this is also the case if the metal be entirely dephlogisticated; consequently, if regulus of antimony, partially dephlogisticated, be digested in muriatic

riatic acid, this acid is not able to dissolve more of it than what has already undergone that degree of calcination, or what has lost so much phlogiston, as the regulus of antimony generally loses when it is distilled with corrosive sublimate.

It is a known fact; that emetic tartar may be prepared from liver of antimony and cream of tartar; and that, when this emetic tartar is dissolved in muriatic acid, and the solution distilled, the causticum antimoniale is generated; there must therefore be contained in the liver of antimony a regulus, so far calcined as to be fit for this purpose; and we should gain our end completely, if the half calcined regulus contained in the hepar could be entirely freed from the hepar. This is the more requisite, as the solution by the cream of tartar in the other case is not only very slow, but likewise contains (if the emetic tartar, which is thus prepared, be not contaminated with superfluous cream of tartar) vitriolated tartar, which, though it be lixiviated with boiling water, cannot be extracted from the vitrified regulus with which it has been united by fusion. The most proper menstruum for extracting the half dephlogisticated regulus is muriatic acid, which afterwards quits the antimony if the butter be diluted with boiling water. If this solution be
distilled,

distilled, butter of antimony is likewise obtained: As, however, the hepar, prepared with equal parts of antimony and nitre, contains not only antimony still undecomposed, but likewise hepar sulphuris, as easily appears, when this hepar is digested with muriatic acid, not only from the hepatic smell, but also from the remaining insoluble black powder, it is necessary to add more nitre; and, instead of muriatic acid, which is dearer, a mixture of diluted vitriolic acid and common salt should be poured upon it, with which it is afterwards to be digested. Thus a real butter of antimony is obtained, from which, when diluted with water, the pulvis Algarothi is precipitated. The salts contained in this antimonial solution, *viz.* Glauber's salt and vitriolated tartar, remain behind in the water, and do not in the least change the precipitate.

The process is therefore the following: Take of powdered crude antimony one pound, powdered nitre one pound and a half, which, after being well dried and mixed, are to be detonated in an iron mortar. The hepar, obtained in this manner, is to be powdered, and a pound of it to be put into a glass vessel, on which, first a mixture of three pounds of water and fifteen ounces of vitriolic acid is to be poured, and afterwards fifteen ounces of powdered

dered common falt are to be added ; the glafs vefsel is then to be put in a fand-bath, and kept in digeftion for twelve hours ; during which period the mafs is to be constantly ftirred. The folution, when cool, is to be ftained through linen. Upon the refiduum one-third of the above mentioned menftruum is to be poured, the mixture digefted and ftained. From this folution, when it is diluted with boiling water, the pulvis algarothi precipitates, which is to be well edulcorated and dried.

E S S A Y XII.

EXPERIMENTS UPON MOLYBDÆNA. 1778.

I Do not intend to treat here of the common molybdæna which is to be met with in the shops, for that is very different from the sort concerning which I am now communicating my experiments to the Royal Society. Mine is that kind which Cronstedt in his mineralogy calls *molybdæna, membranacea, nitens*, and with which Mr Quist and several others made their experiments. The specimens, which I had an opportunity to examine, were taken from different places, but were all found to be of the same nature, and to consist of the same constituent parts.

§ I.

I first wished to know what effects molybdæna would produce in the moist way: It was necessary for this purpose to have it very finely powdered. This being impossible to effect without some addition, on account of its flexible lamellæ, I triturated it in a glass mortar, with some pieces of vitriolated vegetable alkali, and thus I at last reduced it to a fine powder; upon which, after it was sifted, I poured hot

water, stirring the mass well together. After the molybdæna had sunk to the bottom, I poured off the solution, and repeated the same process several times, till all the vitriolated tartar was entirely washed off; I then dried the powder that remained.

§ II.

I both digested and boiled this mineral in all the known acids; but among them all I found but two which have any effect upon it, *viz.* the acid of arsenic and the acid of nitre. The molybdæna not attacked by the acid of arsenic till the water is evaporated. If then the heat be increased a little, arsenic rises into the neck of the retort, and towards the end yellow arsenic or orpiment is sublimed. Volatile sulphureous acid goes over into the receiver.

I poured two parts of concentrated nitrous acid upon one part of powdered molybdæna. The mixture was hardly lukewarm in the retort, when it passed all together into the recipient with great heat, in the form of dark-red vapours. I doubt not but this mixture would have taken fire if its quantity had been larger; and therefore thought it more advisable to repeat the experiment with diluted nitrous acid.

§ III.

§ III.

I poured six ounces of diluted acid of nitre on one ounce and a half of powdered molybdæna, and put it into a glass retort, provided with a luted recipient, and placed it in a sand-bath. During the digestion the acid had no effect upon the powder; but, as soon as the mixture began to boil, red elastic vapours rose, with a great intumescence; the retort therefore ought to be taken large enough. The distillation was continued to dryness. Upon the residuum in the retort, which was now of a grey colour, I poured the same quantity of diluted acid of nitre, when the mass began to effervesce considerably as before. After the mixture was again distilled to dryness, the residuum appeared to be of a whiter colour than before. I poured upon it the same quantity of the same acid, distilled and abstracted it as before, and repeated the same operation the 4th and 5th time, till at last a powder as white as chalk remained in the retort. This residuum, after beingedulcorated with hot water, till it was poured off perfectly tasteless, was dried. At this time it weighed six drachms and a half; I shall call it *terra molybdæna*. The limpid liquor obtained from theedulcoration was evaporated to half an ounce; it

then assumed a fine blue colour, and grew thick; it contained a little iron, but was, besides, chiefly acid of vitriol. On diluting the acid with water, the colour disappeared; fixed and volatile caustic alkalis have no effect upon molybdæna in the moist way.

§ IV.

From the fine experiments of Mr Quist on molybdæna, we know that this mineral contains sulphur, and is almost entirely volatile in the open fire. A small piece of it exposed upon a silver-plate to the blow-pipe makes a beautiful appearance, when the white vapours attach themselves to the plate in the form of small shining scales, in the direction of the flame. This white sublimate becomes blue whenever it is in contact with the blue flame, but disappears and changes again to white whenever the extreme point of the flame is directed against it. This white sublimate is the same earth that is obtained with the acid of nitre (§ III.), and shews the same phenomena in the flame of the blowpipe.

§ V.

One ounce of pulverised molybdæna was mixed with four ounces of purified nitre, and detonated in a crucible heated thoroughly

roughly hot. The mass thus obtained was of a reddish colour; I dissolved it in water; the solution was clear and colourless; to the bottom of the vessel a small quantity of red powder subsided, which, after being dried, weighed eleven grains, and proved to be an iron ochre. From the solution I obtained, upon evaporation, both vitriolated tartar and nitre in crystals; but a good deal of lixivium remained, which refused to crystallise, though there was no mark of superfluous alkali. I mixed it with a little water, to which I afterwards added diluted acid of vitriol, till there appeared no more precipitation. This precipitate, whenedulcorated with lime-water, and dried, weighed three drachms. If too much acid of vitriol is added in the foregoing process, the precipitate will be redissolved, and the water itself retains a part of it in solution. Nay, while the solution is hot, no precipitation ensues. A precipitate is likewise obtained by means of nitrous or muriatic acid.

§ VI.

In order to become better acquainted with this kind of earth, I first examined that obtained by means of nitrous acid, *via humida* (§ III.).

P 4

(A) I

(A) I reduced a scruple of it in a glass-mortar to a very fine powder, and boiled it with two ounces of distilled water for a quarter of an hour. The liquid was then poured into another vessel, and the remainder again boiled with two ounces more of water, which, when poured off, had a peculiar acid, and somewhat metallic taste. I therefore repeated the same process ten times over, always with two ounces of fresh water, and found at last that nearly the whole was dissolved. (B) Thinking that perhaps some vitriolic acid might have adhered to the earth, and thus be the cause of its solubility in water, I exposed part of the terra molybdæna in a glass retort to the open fire, till the retort was very near beginning to melt, and really found in the recipient some smell of sulphureous acid. Afterwards I exposed the earth in a crucible, upon which another inverted one was luted to the fire for a quarter of an hour, when, on opening the crucible, the earth was found to be melted, and immediately a smoke ascended, which fixed itself to a cold iron plate, that was held over it, in the form of small shining white and yellowish scales. As soon as the covercle was put on, the fumes ceased; but as soon as the air had access to it, the earth melted, and began again to fume, on which account

count I could not collect any flowers in the upper crucible. The melted earth was poured upon a plate, when it assumed a light-grey colour, with rays emanating from the centre to the circumference.

Under the blowpipe this earth is soon absorbed by charcoal; but when placed upon a silver-plate, it melts, and yields vapours with the same phænomena as molybdæna (§ iv.). I was now desirous to know, whether this melted earth was still soluble in boiling water. (c) It was therefore pulverised, and a little of it boiled in water, as before (A); but it exhibited the same phænomena, and the solution acquired the same taste. This fused earth of molybdæna I made use of for all the following experiments. The flowers which attached themselves to the iron-plate shewed the same phænomena as this earth.

§ VII.

The earth of molybdæna is of an acid nature. The solution (§ vi. c) reddens lacmus, coagulates the solution of soap, and precipitates hepar sulphuris. (B) It has likewise some effect upon metals. If it be boiled with filings of all the ignoble metals, the solution is of a bluish cast. (c) If there be added to it a little alkali of tartar, the earth becomes soluble in greater quantity in water, and after evaporation

poration shoots into small confused crystals. This small quantity of alkali prevents the earth from being volatilised in the open fire (§ VI. B). (D) This solution, while hot, more clearly shews its acid property, and tinges lacmus of a deeper red. It effervesces with chalk, with magnesia, and with earth of alum, with which earths it forms neutral salts, which are very difficult of solution in water. (E) It precipitates silver, quicksilver, and lead dissolved in nitrous acid, as also lead dissolved in marine acid. These precipitates are reduced upon charcoal, and the melted earth runs into the pores of the charcoal. The other metals are not precipitated, nor is corrosive sublimate. (F) It also precipitates the earth of the ponderous spar from nitrous or marine acid. This precipitate is not a regenerated spar, because it is soluble in cold water, a property which regenerated ponderous spar does not possess; the solutions of other kinds of earth are not precipitated. (G) This solution also expels the aerial acid from the fixed and volatile alkalis, and forms with them neutral salts, which precipitate all metallic solutions. Gold, corrosive sublimate, zinc, and manganese, are precipitated in the form of a white powder; iron and tin, from their solution in marine acid, of a brown; cobalt, of

a rose colour; copper, blue; the solutions of alum and quicklime, white. If the ammoniacal salt formed by the earth of molybdæna and volatile alkali be distilled, the earth parts with its alkali in a gentle heat, and remains itself in the retort, in the form of a grey powder.

§ VIII.

(A) Concentrated vitriolic acid dissolves, with the assistance of heat, a great quantity of this kind of earth. The solution acquires a very fine blue colour, and becomes thick on cooling; the colour disappears on the application of heat, but returns again when it grows a little cool; as also in water (§ III.): In a stronger heat, the earth parts with the vitriolic acid, and remains behind unaltered. (B) The nitrous acid has no effect upon it; (c) But when boiled with muriatic acid it dissolves in considerable quantity; and when this mixture is distilled to dryness, there remains a dark-blue residuum. If the heat be increased, there arise white flowers, with a little blue sublimate, and in the receiver is found smoking muriatic acid. The residuum is grey. The sublimate and the flowers moisten in the open air, stain metals wetted with the solution blue, and are only earth of molybdæna volatilised by muriatic acid. (D) If one part of
this

this earth be distilled with two parts of vitriolated tartar, there goes over at last, when the heat is very strong, a little vitriolic acid. The remaining earth is more soluble in water than before. (E) Distilled with two parts of nitre, it expels smoking nitrous acid. The residuum dissolved in water is a neutral salt which precipitates all metallic solutions, and resembles the salt of § VII. G. (F) When it is distilled with two parts of pure common salt, the acid is expelled in a fuming state, and there arise into the neck of the retort white, yellow, and violet-coloured flowers, which become moist in the air; and, when sprinkled on metals, give them a blue colour (C).

§ IX.

That this metal is not incapable of attracting phlogiston, appears from the blue colour which the sublimate receives from the flame of a candle; that it attracts it also via humida, the blue colour likewise evinces (§ VII. B). (A) In order to acquire more certainty on this point, the earth of molybdæna was dissolved in boiling water, with the addition of a little alkali. Into this solution were poured some drops of muriatic acid, and it was divided into several parts; into each part there were put filings of different metals; the solutions

tions soon acquired a bluish colour, which grew deeper and deeper, and, in an hour's time, during which the bottle was now and then shaken, the colour became a very fine and dark blue: That this colour depends upon phlogiston, may be concluded from the following considerations: *1st*, If, instead of the metals, you take the different calces, no change of colour takes place. *2^{dly}*, If there be dropped into the blue solution a few drops of acid of nitre, and the solution be then put into a warm place, the colour disappears. It is therefore not a matter of surprise, that both silver and quicksilver should be attacked, since a double attraction takes place, the muriatic acid uniting with the metallic calx and the earth of molybdæna with the phlogiston of the metals, gold, however, is not attacked. (B) If too much muriatic acid be added to the solution, it acquires not a blue but a yellowish colour, which at last turns brown if the metallic mixture be digested. Here the earth seems to attract more phlogiston; for if this solution be added to a solution of earth of molybdæna, the phlogiston is more divided, and the mixture grows blue. (c) Lixivium sanguinis, in which the acid prevails, precipitates this earth dissolved in water brown, and the infusion of galls, dark-brown.

§ x.

I have tried the earth of molybdæna with black flux and charcoal, in order to see if I could reduce it; as also, with glass of borax and charcoal, but in vain. I could not discover the least metallic principle. I conjectured that inflammable bodies might have the same effect upon earth of molybdæna as the air, *viz.* to volatilise it (§ VI. B). I therefore moistened some of this earth with olive oil, put the mixture into a glass retort, and continued the fire till the retort began to melt. But here arose no sublimate; the residuum in the retort was like a black powder: Some of this powder was put into a crucible, and exposed to a strong fire, when it became red-hot, and sublimed in the form of white flowers. I then put the other part into a crucible, and luted on it another inverted crucible, which was likewise exposed to a strong fire. An hour afterwards, when the whole mass was grown cool, I opened the crucibles; but the earth was found with its black colour unchanged, without any sign of fusion. This black powder shewed the following phenomena: 1. It did not dissolve in boiling water; 2. Nor when alkali was added, and the boiling heat continued, did it dissolve, notwithstanding alkali on other occasions

occasions so readily dissolves it (§ VII. G).

3. But, when mixed with a triple quantity of alkali of tartar, and exposed to fusion into a crucible, there arose a strong effervescence. If the mass be then dissolved in water, and the superfluous alkali saturated with nitrous acid, the product will be a neutral salt, consisting of the earth of molybdæna and alkali, which decomposes all other neutral salts (§ VII. G).

4. Nitrous acid attacks the phlogisticated earth very violently in digestion, and deprives it of its phlogiston, upon which it grows white, and regains its former property. Vitriolic and muriatic acids have no effect upon it.

§ XI.

The earth of molybdæna, which is procured by nitre (§ v.), is in several circumstances different from that just mentioned.

1st, It requires much more water for its solution; two ounces of water, dissolved by continued boiling, 11½ scruples. 2^{dly}, It expels not the vitriolic acid from vitriolated tartar. 3^{dly}, It is more easy of fusion. 4^{thly}, It does not sublime in an open crucible. 5^{thly}, When fused with charcoal-powder, it affords a solution with water, containing a neutral salt, which precipitates all other neutral salts.

§ XII.

§ XII.

The cause of this great difference lies in the alkali, of which this precipitate obstinately retains a part: That it contains alkali, though it be purified by repeated solutions and crystallisations, is easy to infer from the following experiments: 1. When to a hot solution some concentrated nitrous acid is added, and the boiling continued, the greatest part of the dissolved earth falls to the bottom, in the form of small crystals. If afterwards the clear liquor is evaporated, some nitre is obtained. These small crystals have the same properties with that earth of molybdæna that is procured by nitrous acid (§ III.) 2. The salt which is obtained by fusion (§ XI. 5.) proves the same. This neutral salt is produced in the following manner: The earth which contains only a small quantity of alkali, and yet operates like an acid, because it changes the colour of lacmus to red, attracts phlogiston from the charcoal-powder that is added; but alkali prevents as much earth from entering into this union, as is necessary to its saturation. It appears from § X. 3, that alkali more strongly attracts the earth than the earth does phlogiston. This is a neutral salt, which is soluble in water, and is entirely like the salt of § VII. G; the charcoal which remains after the
lixiviation

lixiviation yields vapours in an open crucible, and gives a sublimate, containing phlogisticated earth of manganese. 3. This alkali fixes the earth in the open fire (§ XI. 4.). 4. Hence appears likewise the reason why this earth does not expel the vitriolic acid from vitriolated tartar; for its attractive power for the alkali must diminish in proportion as it comes nearer to the point of saturation; and as the pure earth contains no alkali, it attracts a little from the vitriolated tartar, consequently there can appear but a slight vestige of vitriolic acid (§ VIII. D). This small quantity of alkali occasions its more easy solubility in water. The same earth is found in § VII. c.

§ XIII.

Having now analysed molybdæna, by means of the experiments which I have communicated, it still remained to be able to recompose this mineral of its proximate constituent parts. That molybdæna contains sulphur, is already known, and my experiments shew the same thing. Some very fine pulverised earth of molybdæna (§ VI. c) was mixed with three parts of sulphur. The mixture was distilled in the open fire in a glass retort, furnished with a luted recipient. The retort was placed in the beginning,

in such a manner, that the sulphur which rose to the neck should run back again ; but at last this substance was entirely driven off. The recipient, besides the sulphur, was filled with a stinking smell of volatile spirit of sulphur. The residuum in the retort resembled a black powder, which, when rubbed between the fingers, stained them of a shining black colour, and shewed the very same phenomena in every other respect, as native molybdæna itself. We have then a kind of earth in molybdæna, which has probably to this time been unknown, and which one may properly call acid of molybdæna, as it has all the properties of an acid. But I think I already hear it objected that it may be some metallic earth, combined with an acid hitherto unknown, or else *vice versa*. I am content to let this opinion rest upon its own merit, as long as it remains unconfirmed by convincing proofs, deduced from unequivocal experiments ; and although in certain circumstances it resembles a metallic earth, I believe with confidence, that molybdæna consists of an acid mineralised by sulphur.

ESSAY XIII.

EXPERIMENTS ON PLUMBAGO. 1779.

I HAD the satisfaction of seeing my experiments on molybdæna inserted in the third quarter of the Transactions of last year; and as, in the beginning of that paper, I advanced that the black lead or plumbago which is generally known in commerce, is very different from molybdæna, I shall now shew by experiments, that this is really the case. The mineral of which I am to speak at present is called by Cronstedt, "*Molybdæna texturâ micaceâ et granulâtâ.*"

§ I.

Finely levigated and sifted plumbago, after being digested and boiled in all the known acids, both concentrated and diluted, shewed no sign of decomposition, excepting that the menstrua were impregnated with a small portion of iron. The acid of arsenic is the only acid which has any effect upon this mineral, but it produces it only in the dry way. I mixed two parts of dry acid of arsenic with one part of pulverised plumbago; and after having distilled this compound in a retort,

found the neck of the vessel filled with arsenic. That this reduction of the acid of arsenic was not owing to the heat, I shall shew in the sequel of this paper.

§ II.

(A) Corrosive sublimate had likewise no effect upon plumbago when they were subjected to sublimation together. (B) With sal ammoniac, by the same operation, I obtained flores martiales and a little caustic volatile alkali. The remainder was unchanged. (c) When I mixed plumbago with a double quantity of sulphur, and again separated it by sublimation, I found the weight of the plumbago to be the same as before. (D) Upon fusing it with four parts of vitriolated vegetable alkali in a covered crucible, I obtained hepar sulphuris. (E) When one part was exposed to the action of heat with eight parts of litharge in a close crucible, the calx of lead was reduced; but no reduction followed when it was treated with glass of antimony. That the calx of lead acts more powerfully upon phlogiston than the calx of antimony, appears upon mixing and fusing litharge with regulus of antimony; for by this means regulus of lead and black glass of antimony are obtained. (F) By distillation with common salt none of the acid was expelled. (G)

On

On distillation with nitre, no detonation took place in the retort.

§ III.

(A) I put two drachms of levigated plumbago, together with an ounce of purified nitre, into a red-hot crucible. At first a strong effervescence, and afterwards a violent detonation, took place. There remained in the crucible a black shining liquid matter, which still contained a great deal of plumbago. (B) I then mixed one part of levigated plumbago with six parts of nitre, and the same detonation followed. The mass remaining in the crucible was exactly the same as the former. (C) The same process was repeated with eight parts of nitre, and here a little plumbago remained, which was not calcined by the nitre. All the masses remaining in the crucibles were dissolved in water, when a good deal of undecomposed plumbago fell to the bottom. The limpid solution neither contains hepar nor vitriolic acid; consequently there is no sulphur in pure plumbago. (D) At last I mixed one part of levigated plumbago with ten parts of nitre, and put it into a red-hot crucible; a detonation followed, and after it was kept for a few minutes in a state of fusion, a white alkaline mass appeared, which I poured

out upon a copper plate, and afterwards dissolved it in water, upon which a little brown powder was precipitated. From an ounce of plumbago thus calcined with nitre, I obtained fifteen grains of this brown powder, which I found to be ochre of iron. Upon pouring some vitriolic acid into the alkaline solution, an effervescence ensued, and the air expelled was aerial acid mixed with nitrous air (*acidum nitri phlogisticatum*), and the whole mixture became gelatinous. I filtered the whole together, and found that what remained in the filtre was siliceous earth, mixed with a little earth of alum. The saturated solution yielded, after evaporation, nothing but vitriolated vegetable alkali. (E) But not being convinced by this experiment of the existence of clay in plumbago—for I have elsewhere more particularly shewn (*Dissertation on flux, clay, and alum*) how unsafe all experiments of this kind are in common crucibles—I made the same detonation with plumbago and nitre in an iron crucible, and found that I was right in my suspicion, for not the least mark of clay was now to be discovered.

§ IV.

Mr J. G. GAHN, in roasting plumbago upon a test, experienced a loss of ninety parts

parts in an hundred of plumbago, without any visible smoke; and Mr P. J. HJELM, upon repeating the same experiment, obtained the same result. The remainder is nothing but ochre of iron. One should be easily tempted to believe, that whatever has been volatilised during the ustulation was nothing but phlogiston! For there is not any sulphureous smell perceived from pure plumbago, and the calcination requires the free access of air; and, *2dly*, from its detonation with nitre, &c. But then, the phlogiston would, according to this supposition, constitute the greatest part of the weight of the plumbago; but it is not probable that such a small quantity of iron should fix such a large quantity of phlogiston; which would then be present in a much larger quantity in plumbago than even in charcoal; for five parts of nitre are sufficient to decompose one part of charcoal; whereas ten parts of nitre are required to produce the same effect upon one part of plumbago. This induced me therefore to examine the vapours which arise from it in such large quantity during detonation.

§ v.

One part of levigated and sifted plumbago was mixed with ten parts of powdered nitre, and a little of this mixture was

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put

put at intervals into a red-hot tubulated retort, to which a large glass receiver was adapted. At last the receiver was found full of nitrous air, and covered with a white crust, which was easily soluble in water, and proved, on an exact examination, to be nothing else than nitre. Thence it is evident, that, during the ustulation and distillation of plumbago, no sublimate, or any thing like a sublimate, is driven off.

§ VI.

There was one circumstance observable, which deserves the greatest attention, *viz.* the aerial acid which was expelled during the saturation of the fixed alkali (§ III. D). I was led by this to mix fifteen grains of levigated plumbago with eight scruples of nitre, and to put it into a small retort of thick glass. A large empty bladder was adapted to the retort, and it was placed upon live coals. As soon as the nitre entered into fusion, the mass in the retort took fire, and the bladder became distended. After the whole was cooled, I detached the bladder from the neck of the retort, and found that the air contained in it occupied as much room as thirty-six ounces of water. Lime-water absorbed one-third of this air, and by the remainder flame was supported. Plumbago therefore

fore contains likewise aerial acid; a great part of which is attracted by the alkali of nitre.

§ VII.

One might perhaps suppose, that this aerial acid arose from the nitre itself. To this I answer, If such was really the case, we should obtain aerial acid in all other detonations with nitre. I therefore mixed (A) half a drachm of tin filings with two drachms of nitre, and detonated the mixture in the manner above mentioned. I thus obtained as much air as occupied the space of four ounces and a half of water; but this air contained not the least mark of aerial acid; it did not extinguish a candle. (B) From one drachm of regulus of antimony, detonated with two drachms of nitre, a quantity of air was obtained, which occupied the space of eight ounces of water: It contained no aerial acid, but extinguished flame; neither in the detonation of brimstone is there any aerial acid obtained. But, in order to remove all doubts and objections, I contrived to decompose plumbago without nitre. (C) For this purpose I repeated the experiment already mentioned with the acid of arsenic § I. I applied an empty bladder to the retort instead of a receiver. When the arsenic rose into the neck of
the

the retort, the bladder was distended, and I obtained pure aerial acid. (D) I mixed four parts of calcined quicksilver with one part of pulverised plumbago, and distilled this mixture in the same manner as before. The quicksilver was reduced, and the bladder distended with air. This air was aerial acid, and mixed with one-third of pure air. (E) One part of litharge reduced to glass *, and then ground to powder, mixed with two parts of plumbago, was reduced in the retort, and the bladder contained pure aerial acid. (F) One part of powdered plumbago, mixed with caustic fixed alkali, and exposed to distillation by a strong fire, yielded inflammable air. The mass remaining in the retort had lost its causticity, and made a strong effervescence with acids.

§ VIII.

Hence I am convinced, that plumbago is a kind of mineral sulphur or charcoal; the constituent parts of which are aerial acid and a considerable quantity of phlogiston. The small quantity of iron can hardly be taken into the account; for *1st*, It seems to be mixed with it only mechanically; and, *2^{dly}*, I have treated
plumbago,

* Litharge generally containing a little aerial acid, it was requisite to fuse it first, in order to separate the air.

plumbago, from which I obtained, after calcination, a little more ochre of iron than usual; and when one part of this kind of plumbago was detonated with six parts of nitre, I have found some hepar at last. When therefore plumbago, during calcination, yields a sulphureous smell, it must be mixed with a little pyrites. That pure plumbago does not enter into any union with sulphur, appears from § II. c; and that it contains no sulphur, appears from § I.; for if this were the case, I should have certainly obtained in the neck of the retort either a red or a yellow sublimate. See likewise § III. c.

If cast-iron be dissolved in diluted vitriolic acid, a black mass remains, which is insoluble in acids, and which has been supposed to be plumbago. I shall therefore take this opportunity to relate the experiments I made with this residuum. I extracted an ounce of it by means of aqua regia, which thereby acquired a dark-yellow colour. After having decanted the solution, I poured some new menstruum upon the residuum, and continued in the same manner, till there appeared no more iron in the menstruum. I dried the residuum, and found that it had a shining black colour, and between the fingers it felt like plumbago. It now weighed no more than three drachms and a half. Mr
P.

P. J. Hjelm having roasted this residuum under the muffle, found that it calcined somewhat more quickly than plumbago. The remainder of this calcination was a very small quantity of white ashes.

One part of the above mentioned residuum of cast-iron was mixed with five parts of nitre, and put into a red-hot crucible; a detonation followed, as with plumbago; the alkaline mass remaining in the crucible, which was of a white colour, I dissolved in water, whence after some time a little white sediment precipitated, which however was not sufficient for making any decisive experiment. The solution or lixivium effervesced with acids, and shewed the same effects as the lixivium of § III. D. The air, separated during this detonation, was also collected. It appeared to consist of three parts of aerial acid, and one part of foul or corrupted air. Hence I conclude, that this residuum of cast-iron is plumbago; but as less nitre is requisite for its decomposition than for the decomposition of plumbago, it must contain less phlogiston than that substance.

E S S A Y XIV.

METHOD OF PREPARING A NEW GREEN
COLOUR. 1778.

CHEMISTRY is well known to be indispensably necessary in the preparation of colours for painting, and it often discovers new ones. It was the desire of the Royal Academy, that the green colour which I observed during my experiments on arsenic might be made more generally known, together with the mode of preparation. In compliance with this desire I give the present account of it, and that with the greater pleasure, as I have found the colour useful both in oil and water painting, and as it has not undergone the slightest alteration in the course of three years.

Dissolve two pounds of vitriol over the fire in a copper vessel, in six kannes of pure water, and, as soon as it is dissolved, take the kettle from the fire.

Then dissolve in another copper kettle two pounds of dry white potashes, and eleven ounces of pounded white arsenic *, in two kannes of pure water over
the

* It is always better to pound the arsenic one's self than to buy it ready pounded; for this is often adulterated with gypsum, of which any one may readily convince himself, by laying a little with the point of a knife upon a red-hot coal. If the whole evaporate without leaving any residuum, the arsenic is pure.

the fire. When all is dissolved together, strain it through linen into another vessel.

Of this arsenical ley a little is to be poured at a time into the above mentioned solution of vitriol of copper, while it is kept constantly stirred with a wooden spoon *. When the whole has been added, the mixture should be left to stand still for a few hours, during which the green colour will be deposited at the bottom. The clear ley is then to be poured off, and a few kannes of hot water added under continual agitation. When the colour has fallen again to the bottom, the clear water is to be poured off. This lixiviation with hot water should be repeated a second time.

When the matter has been thus well washed †, the whole together is to be shaken out on a stretched linen cloth; and when the water has all dropped away, the colour is to be placed in small lumps on grey paper, and dried by a gentle heat. From the quantities above prescribed, one pound, together with six ounces and a half of a fine green colour, are obtained.

E S S A Y

* As an effervescence takes place in this operation, the vessel in which the mixture is made should not be too small. It should contain about sixteen kannes.

† The water with which the colour is lixiviated contains a little arsenic, and must therefore be thrown out in a place to which cattle have no access.

E S S A Y XV.

OF THE DECOMPOSITION OF NEUTRAL
SALTS BY UNSLAKED LIME AND IRON.

1779.

IT is looked upon as a demonstrated truth in chemistry, that fixed alkalis have a stronger attraction for acids than absorbent or metallic earths, and that the latter are precipitated by the former. There seems to be only two exceptions to this rule, namely, in favour of ponderous earth, which has a stronger affinity for all acids, and lime which unites more readily with most acids than alkalis do. That the foregoing tenet should be still farther limited, I have discovered by the following experiments.

I once found in a cellar a wooden vessel hooped with iron hoops, and containing salted turnips. The iron hoops were covered over with a salt which appeared perfectly to resemble mineral alkali. This accident appeared very singular, as I well know that the acid of salt has a weaker attraction for iron than for mineral alkali; I could not therefore believe that the common salt, oozing out through the wood, could be decomposed by the iron hoops.

To

To resolve this doubt, a clean plate of iron was dipped into a saturated solution of common salt, and hung up in a moist cellar. In fourteen days mineral alkali was found on the plate. There appeared also some yellow drops containing iron, which was precipitated when a little of the alkali that was beside them was brought close to them. I afterwards covered over another iron plate, with a saturated solution of Glauber's salt, and hung it up for some weeks in the cellar. The result was, that the fossil alkali effloresced on its surface like wool. The same thing happened upon repeating the experiment with a solution of cubic nitre; but, when I used plates of lead, tin, copper, or silver, no decomposition took place. I afterwards prepared a mass, consisting of unflaked quicklime moistened with a solution of common salt, and placed it in a moist cellar; in a fortnight afterwards the surface was covered over with mineral alkali, which I scraped off, and left the remainder in the cellar. In another fortnight more alkali was visible on the surface, which was scraped off. Water was poured on the remaining mass, and it was well stirred and filtered. The solution had a strong taste of lime-water, on which account I let it stand a few days in the open air, by which means the lime was precipitated. And to
determine

determine with more certainty, whether the lime was all precipitated, I poured on it a solution of corrosive sublimate, which remained colourless. The whole was then filtered, and a solution of the efflorescent mineral alkali added to it, by which a considerable quantity of aerated lime was precipitated.

In the same manner I made a mass of quicklime and solution of Glauber's salt and cubic nitre, when the same effect was produced, and an efflorescence of fossil alkali was observed: But this did not happen, when, instead of quicklime, aerated or calcined magnesia, or aerated lime, were used instead of unslaked lime.

It is certain that fossil alkali always precipitates solutions of iron and lime; and it is a consequence of this, that fixed alkalis more readily combine with acids than these substances. The experiments, however, which I have related, point out a limitation in certain cases. It is therefore probable, that alkalis have a stronger attraction for acids when they contain a certain quantity of water; but, when this is diminished, it is not impossible that an earth or a metal should obtain the superiority, especially if the alkali which is separated, should, at the instant of its separation, meet with a weaker acid with which it can unite. Such is the aerial

acid in this case, which is always present in considerable quantities in cellars.

It appears strange, that the fossil alkali, efflorescing upon the iron plate, should not be able to precipitate the drops of the martial solution resting upon it : But the cause is this, that the solution of iron in muriatic acid, when it has become dry, strongly attracts moisture, and the alkali which is then separated and effloresces, cannot afterwards produce any effect upon it.

If vegetable alkali, like the fossil, had the property of efflorescing, the neutral salts into which it enters would probably be decomposed in the same manner ; but as they have not this property, this does not happen.

E S S A Y X V I.

ON THE QUANTITY OF PURE AIR WHICH
IS DAILY PRESENT IN OUR ATMOSPHERE. 1779.

IT is a known fact, that our atmosphere ought not to be considered as a simple fluid substance, for, when freed from all heterogeneous admixture, it is found, according to the late discoveries, to consist of two very different kinds of air; the one is called *corrupted air*, because it is very dangerous and fatal, as well to living animals as vegetables; it constitutes the greatest part of our atmosphere. The other is called *pure air, fire air*. This kind of air is salutary, supports respiration, and consequently the circulation; without it we could form no distinct idea, either of fire, or how it is kindled. It constitutes but the smallest part of the whole atmosphere. Now as we know that this air is of the most immediate necessity for the support of our health, but as it is uncertain whether there is always the same quantity of it present in the atmosphere, I proposed to make observations upon it through the course of a whole year.

When this pure air meets with phlogiston uncombined, it unites with it, leaves the corrupted air, and disappears, if I may say so, before our eyes *. If, therefore, a given quantity of common atmospheric air be included in a vessel, and meet there with some loosely adhering phlogiston, it will at once appear, from the quantity of corrupted air remaining, how much pure air was contained in it before. Though there is a variety of inflammable substances and mixtures fit for this purpose, I however found a mixture of iron-filings and sulphur the most serviceable.

I reduced a pound of sulphur to very fine powder, and mixed it with two pounds of iron filings, which were not rusty, moistening the whole with a little water. This mixture I immediately afterwards put into several small flasks, which I corked very exactly †, taking care, at the same time, not to press the powder too hard into the flask; for, in twelve hours, in which time the union of iron and sulphur takes place, as the black colour which it affumes

* That light arises from this union, I have already proved in my Treatise on air and fire.

† The phials must be frequently opened, and if one contained the whole mixture, it would be soon spoiled by the fresh air that is admitted.

assumes shews, the space occupied by this compound is greatly increased; the flask, therefore, would burst if it were pressed too hard. I shall now take the liberty to describe my apparatus.

In a pedestal of lead (B) placed in the middle of a vessel (A), I fixed a glass tube; upon the top of the tube was fastened a flat piece of wood, such as would support a small vessel filled with the above mentioned mixture of iron and sulphur. This apparatus was covered with an inverted glass cylinder (D), and the vessel (A) was filled with water*. When the cold was so intense as to freeze the water, I made use of brandy. The glass cylinder (D) was capable of containing thirty-four ounces of water. The little vessel (C), with its mixture of iron and sulphur, and its stand, occupied the space of an ounce of water. There remained, therefore, room for thirty-three ounces.

Having already learned, from the experiments of others as well as my own, that pure air never constitutes more than one-third of the whole atmosphere, I pasted on the outside of the glass cylinder a piece of paper, which was equal in length to

R 3 one-

* The original Essay is accompanied with a figure of this apparatus; but such assistance is perfectly unnecessary, as no one can be at a moment's loss to comprehend so very simple a contrivance. T.

one-third of the contents of the glafs, or 11 ounce-measures of water. I divided this paper into equal parts, which I marked with black lines and small cyphers, so that each line shewed $\frac{1}{3}$ part of the space in the glafs. The whole piece of paper I varnished over with oil-varnish, in order to prevent the effect of water upon it.

On the first of January 1778 I began my observations. After having filled the vessel (c) with the mixture of iron and sulphur, I inverted the cylinder over it, observing the degree of the barometer and thermometer. The water began slowly to ascend into the cylindrical glafs. After eight hours it stopped at No. 9. Though I left the glafs for six hours longer in the same situation, the water did not rise any higher. In the mean time the barometer and thermometer had undergone no change. The next day I repeated the experiment, by admitting fresh air into * the cylinder; but the water remained at the same mark. The 3d of
January

* In order to be sure that there may not be any corrupt air remaining from the first experiment, I always fill the vessel with water, whereby the air is entirely expelled. This water I afterwards pour out in the air. When I make experiments upon air inclosed in a chamber, I proceed in the same manner, and pour the water out of the glafs into a vessel in the same room.

January the air was the same. The 4th, upon making a new experiment, the water rose more slowly, and arrived only at its former height in fourteen hours time; whence I concluded, that the mixture in the vessel (c) had lost most of its loosely adhering phlogiston; I therefore afterwards filled, on occasion of every fourth experiment, the vessel with a new mixture. With these experiments I continued daily the whole of January, filling the glass often, even in the night-time, with new air, but constantly found the same proportion of pure air contained in our atmosphere. Sometimes the water rose a little higher, sometimes it was lower; but this seemed to depend on the rise or fall of the barometer and thermometer. I was led to think it sufficient to make my experiments for the following months only four times a-week. In the month of February the air appeared to be the same as in January, but on the 23d of March the water rose only to No. 8. which was the more remarkable, as the cold had increased, and the barometer had risen. The 19th of April the water rose to No. 10. though neither the thermometer nor barometer suffered any change during that time. Thus the air continued till the 21st, after which the water remained every day at No. 9. In May and June

between No. 8. and No. 9. The 30th of June it rose to No. 10. The whole month of August it was between 8. and 9. But from the 3d to the 15th of September at No. 9. The 6th of October it again rose to No. 10. It afterwards kept, during a continuation of very tempestuous weather, between 8. and 9. till the 4th of November, when it rose no higher than to No. 8. The same was the case on the 5th of November, though the barometer rose very high. After this it kept between No. 8. and 9. On the 10th it rose to No. 10. when the barometer was as high as the 4th and 5th. The 21st it rose only to No. 8. Afterwards it kept between 8. and 9. till the 8th of December, when it rose to No. 9. the barometer being low; but afterwards, till the 31st, it rose no higher than between 8. and 9.

Our atmosphere, therefore, contains always, though with some little difference, nearly the same quantity of pure or fire air, *viz.* $\frac{2}{3}$, which is a very remarkable fact; and to assign the cause of it seems difficult, as a quantity of pure air, in supporting fire, daily enters into a new union; and a considerable quantity of it is likewise corrupted, or changed into aerial acid, as well by plants as by respiration; another fresh proof of the great care of our Creator for all that lives.

E S S A Y XVII.

ON MILK AND ITS ACID. 1780.

§ I.

IT is well known, that milk contains butter, cheese, sugar of milk, some extractive matter and a little salt,—the rest is water. But we are yet far from having a just chemical knowledge of this substance. I shall first consider a little the separation of the cheese from the serum, &c. and afterwards enquire into the acid, and the properties which whey or milk acquires in a warm place.

§ II.

(A) If any vegetable or mineral acid be mixed with milk, it is well known, that the separation of a cheesy matter ensues. This cheese becomes perfect, if the mixture be assisted by the application of heat, since in this case the cheesy particles all coagulate into one mass. Mineral acids yield less cheese than the vegetable.

(B) If you put into boiling milk as much of any neutral salt as will dissolve in it, the cheesy parts will also separate from the serum or whey. The same thing happens with all

all earthy and metallic salts, and likewise with sugar and gum Arabic.

§ III.

Caustic alkalis will dissolve the curds by the aid of a boiling heat; and it may be again precipitated by acids. Hence one may easily be induced to conjecture, that the cheesy part is dissolved in the milk by means of an alkali. In order to find out whether this was really the case, I coagulated some milk with a little nitrous acid, filtered and evaporated the whey, but not the least mark of nitre was discovered in it, but only the common sugar of milk. The coagulation of the milk by acids must consequently be owing to some other cause.

§ IV.

(A) The curds obtained by means of mineral acids always manifests signs of acidity. It is likewise partially soluble in boiling water.

(B) If with eight parts of water mixed with one part of precipitated, but not dry curds, so much mineral acid be mixed that the water acquires a sourish taste, and it be afterwards boiled, the cheese will be dissolved. Vegetable acids and the acid of milk dissolve little or nothing of the curds. Hence it appears why
more

more curds are obtained by vegetable than by mineral acids (§ II. A). Hence it is likewise evident, why milk coagulates with acids. The curds attract a certain quantity of acid, and this compound requires much more water in order to be kept in solution than the milk contains.

(C) If milk be mixed with ten parts of water, no curds are obtained by mineral acids.

(D) If to these acidulous solutions of curds a small quantity of some concrete mineral acid be added, the greatest part of the curds will be again precipitated. They also precipitate on the addition of alkalis and lime-water, but if too much of these latter be added, the curds will be redissolved.

(E) If curds dissolved in quicklime or caustic alkali be precipitated by vinegar, a disagreeable hepatic smell is produced.

The reason why neutral salts, whether saline or terrestrial, gums, and sugar, produce a coagulation of milk (§ II. B), lies probably in the stronger attraction of water for those salts than for the curds. Infusions of vegetable astringents always shew marks of an uncombined acid. It is easily understood why milk is coagulated by them, and many, if not all vegetables, contain some caseous substance. It thence likewise appears why emulsions
are

are coagulated by decoctions of the bark of the *cinchona officinalis*.

§ v.

As to the constituent parts of curds, they are probably, like all animal gelatinous substances, still involved in obscurity. This much is certain, that the earth of cheese is the universal animal earth, and consists of phosphoric acid supersaturated with lime. For after several times abstracting nitrous acid from curds, I at last obtained a white residuum, which was nitrated lime and animal earth. The same earth I obtained from the residuum remaining after the distillation of curds and its further calcination in a crucible by means of nitre,—for without nitre this residuum proves very difficult to be reduced to ashes. Thirty parts of dried curds contained about three parts of animal earth.

§ vi.

No substance is more like curds than the white of eggs boiled. It is indeed nothing else but pure cheese. The white of eggs coagulated by heat dissolves by means of boiling in very diluted mineral acids, which solution is again precipitated on adding some concentrated acid. During this precipitation, there is likewise a smell, exactly

exactly like that of hepar sulphuris, produced, which is a very singular phænomenon. Silver is coloured by it, and acetated lead rendered black; properties, all of which, are likewise common to the curds of milk (§ iv.). It is also a singular fact, though it be generally known, that heat alone coagulates the white of eggs, and this without any loss of its weight. The true cause of this is, as far as my information reaches, hitherto unknown, but seems to me to be the following: As curds and the white of eggs combine with acids, and are thereby coagulated, and as all the substances which enter into an union with acids may be likewise combined with the matter of heat, a circumstance in which this principle often resembles acids, it is very probable that it enters into a chemical union with the white of eggs, and is thus the cause of coagulation. What confirms me more in this opinion is, that I have observed such a coagulation of the white of eggs produced in the following manner: I mixed one part of white of eggs with four parts of water, and added a small quantity of a solution of caustic alkali, mixing at the same time as much muriatic acid as was necessary for its saturation; the white of the egg then coagulated like curds. I mixed the water with the white of eggs,
with

with the view of preventing the heat, which is expelled by acids from caustic alkalis from becoming sensible, to which the whole phænomenon otherwise might easily be ascribed. Here therefore a double decomposition takes place, the alkali uniting with the muriatic acid, and the principle of heat with the white of the eggs. If aerated alkali be employed instead of the caustic in the same process, no coagulation takes place.

§ VII.

It is a known fact, that milk in a short time grows sour and thick during the summer. This sourness daily increases, and is the strongest after a fortnight has elapsed. If the whey be then filtered and evaporated to one-half of its quantity, a few curds settle to the bottom. If it be filtered again, and a little acid of tartar be added, some time afterwards a great number of small crystals are generated, which fall to the bottom, and appear on examination to be tartar. The origin of this tartar I cannot ascribe to the small quantity of muriated vegetable alkali, which the milk always contains; for this salt exists in milk in too small a quantity to produce any effect here; it is rather to be ascribed to an essential salt contained in the milk. This is further evident from
this,

this, that when whey evaporated by itself to dryness, and afterwards reduced to charcoal in a crucible, by which process this essential salt is destroyed, it is found that this coal contains vegetable alkali, mixed with a little muriated vegetable alkali, which may be obtained by lixiviation with water. The whey also contains in solution a portion of animal earth, as may be seen, when it is saturated with caustic volatile alkali, as also with lime-water. Thus the acid of milk contains an essential salt, animal earth, sugar of milk, a little muriated vegetable alkali, and some mucilaginous matter. We have only then to separate all these heterogeneous bodies from the acid, in order to obtain it as pure as possible. Distillation would indeed be the shortest way, but this will not answer; for though some vestiges of an acid appear in the receiver, which acid is a kind of very weak vinegar, and the cause of the sourish smell of the whey, almost all the acid remains in the retort; and if the heat be increased, this acid will be decomposed; I therefore make use of the following process.

§ VIII.

I evaporated four whey till one-eighth only remained. The cheesy part being then perfectly separated, I strained the
acid.

acid. In order now to obtain the animal earth, as I knew that this kind of earth is precipitated by lime-water (§ VII.), I saw no other way than to saturate the acid with lime. I then filtered the solution, and diluted it with a triple quantity of water. To separate the lime again from its solvent, the acid of sugar was a most excellent medium. I therefore dissolved a quantity in water, and afterwards added this solution to the solution of lime, till no more saccharated lime precipitated, observing carefully not to add more acid of sugar than was requisite, which I could easily discover by means of lime-water. There now remained the other substances to be separated from the acid of milk. For this purpose I evaporated it to the consistence of honey, then dissolved it in highly rectified spirit of wine, and thus separated from it both the sugar of milk and the remaining heterogeneous substances. The acid alone being thus dissolved in spirit of wine, I filtered it, and then mixed some pure water with this solution; and after separating the spirit of wine by distillation, the acid of milk remained in the retort as pure as in my opinion it ever can be got by a chemical process.

§ IX.

The nature of this acid, and its effects upon earths, alkalis and metals, I found to be as follows: 1. Evaporated to the consistence of a syrup, it yields no crystals; and, when evaporated to dryness, it deliquesces again. 2. When distilled, water first comes over, then a weak acid, like spirit of tartar; afterwards, some empyreumatic oil, with more of the same acid, aerial acid, and inflammable air; in the retort there remained a coal. 3. Saturated with fixed vegetable alkali, it yields a deliquescent salt, soluble in spirit of wine. 4. A salt of the same kind is obtained with fixed mineral alkali, which does not crystallise, but dissolves in spirit of wine. 5. Combined with volatile alkali, it produces a kind of sal ammoniac, which however deliquesces, and, when distilled, yields a great deal of its volatile alkali before the acid is destroyed by the heat. 6. Combined with terra ponderosa, lime and clay, it forms deliquescent neutral salts; but with magnesia it yields small crystals, which however at last are again deliquescent. 7. This acid of milk has no effect either in a digesting or a boiling heat on bismuth, cobalt, regulus of antimony, tin, quicksilver, silver and gold. This acid, however, having been digested

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with tin, precipitated the gold from its solution in aqua regia, in the form of a black powder. 8. It dissolves iron and zinc, and produces inflammable air. The solution of iron was brown, and yielded no crystals; but the solution of zinc crystallised. 9. Copper communicated to this acid first a blue, then a green, and at last a dark blue colour, without crystallising. 10. Lead was dissolved after some days digestion; the solution had a sweet astringent taste, and would not crystallise. I observed afterwards a small quantity of a white sediment in this solution, and found it to be vitriol of lead. Thus there is likewise some vestige of vitriolic acid in milk.

§ x.

From these experiments it appears, that the acid of milk is an acid of a peculiar kind; and though it expels the vinegar from the acetated vegetable alkali, yet it seems destined, if I may so speak, to be vinegar; but, from the want of such substances, as, during fermentation, produce some spirituous matter, it seems not to be volatilised, though a portion of it indeed arrives at this point, and really becomes vinegar; for without a previous spirituous fermentation, or, without brandy, there never arises any vinegar: But that the
milk

milk enters into a complete fermentation, though there is no sign of brandy present, appears from the following experiment: If a bottle full of fresh milk be inverted into a vessel containing so much milk, that the mouth of the bottle reaches below the surface; and if you expose this bottle to a degree of heat, a little greater than our summer heat, you will find in the space of twenty-four hours, that the milk is not only coagulated, but likewise diminished in the bottle, and that in a couple of days afterwards, the aerial acid, extricated from the milk, will have expelled the greater part of it out of the bottle. I said above, that the acid of milk cannot be converted into vinegar, from the want of such substances, as, during fermentation, produce brandy. This appears to be evident from this: If to a kanne of milk you add five spoonfuls of good brandy, and expose the vessel, well corked, to heat, in such a manner, however, that you give now and then to the air, developed during fermentation, a little exit, you will find in a month, sooner or later, the whey changed into good vinegar, which, when strained through a cloth, may be kept in bottles.

E S S A Y XVII.

ON THE ACID OF SACCHARUM LACTIS.

1780.

§ I.

THE sugar of milk is an essential salt, which is contained in solution in milk, and which, on account of its sweetish taste, has been called sugar. The taste of milk is the sweeter and the more agreeable the more sugar it contains. Pharmaceutical chemistry teaches the manner of preparing it.

§ II.

Sugar of milk yields by distillation the very same products as other sugars do. There is, however, one remarkable circumstance, that the empyreumatic oil smells somewhat like the salt of ben-zoin. We know that common sugar contains an acid, which, on account of its strong attraction for all kinds of earths, especially for lime, is indispensably necessary in chemical experiments. The origin of this acid is the dephlogistication of the sugar, by means of nitrous acid. What effects are produced on the sugar of

milk by the latter acid, the following experiments will shew:

§ III.

I poured twelve ounces of diluted nitrous acid upon four ounces of finely powdered sugar of milk, contained in a glass retort, to which a receiver was annexed. The retort was placed in a sand-bath. As soon as this mixture acquired a certain degree of heat, it began to effervesce violently; I therefore took the retort out of the sand, with the receiver, and put it upon the table. The mixture however grew hotter and hotter, and the effervescence stronger and stronger, with dark-red vapours, and continued to do so for about half an hour upon the table, without any fire. A considerable quantity of nitrous air and aerial acid were extricated during that time. Whoever therefore wishes to repeat this experiment, must not take too small a retort, nor lute the retort too tight to the receiver. After the effervescence had subsided in some measure, the retort was again placed in the sand-bath, and the nitrous acid was thus distilled off, till the mass acquired a yellowish colour; whereupon the retort was immediately taken out of the fire. In two days time the solution seemed to have undergone no remarkable change; there was no appearance

pearance of crystals; I therefore added eight ounces more of the same nitrous acid, and exposed it to the same degree of sand heat. As soon as the mass grew warm, the yellow colour disappeared, an effervescence ensued as before, though it was not so strong. After it was over, I again abstracted the nitrous acid, till the solution, which meanwhile had been rendered opaque by a white powder, assumed a yellowish colour, whereupon the retort was removed from the sand. After it was grown cool, I found the mass in the retort inspissated; I therefore redissolved it in eight ounces of water, and passed the whole through a filter. There remained on the filter a white powder, which, after being edulcorated and dried, weighed $7\frac{1}{2}$ drachms. The solution which passed through the filter was very sour; I now evaporated it to the consistence of a syrup, poured four ounces more of nitrous acid on it, and evaporated it again in a sand heat. After the whole was cool, some small long acid crystals were found together with a small quantity of white powder, which I separated from it, and then poured some more nitrous acid upon the remaining mass, and, on evaporation, more such crystals appeared. The same process was repeated several times, by which means the whole mass was at

last changed into such crystals, which weighed about five drachms. This salt shewed in every respect phænomena like those produced by the acid of sugar.

§ IV.

The above mentioned white powder, which weighed $7\frac{1}{2}$ drachms, I took at first to be saccharated lime, because I thought that as milk always contains a little lime, it might enter into the sugar, as one of its constituent parts, and then, by combining with the acid of sugar, would consequently form the saccharated lime. But two experiments, which I made with it, shew that I was mistaken in my conjecture. I poured a solution of acid of sugar into a solution of sugar of milk, but no precipitation ensued. I further found that this powder burned in a red-hot crucible like oil, without leaving any mark of ashes behind.

§ V.

Lime-water seemed to have no sensible effect upon this powder; but boiling water dissolved some of it, though but a very little; for one part of this powder required sixty parts of boiling water for its solution. After the solution was cooled, one-fourth part of the powder separated again from the water in the form of very
small

small crystals. The remaining mass being then collected by evaporating the water from it, a small quantity of acid of sugar, constituting about one-tenth of the powder, remained, which at first was not so exactly separable by edulcoration. I now found that this powder was a salt, because it was soluble in water;—it was now purified by means of the solution and crystallisation. The properties of this salt are the following :

§ VI.

Half an ounce of it was dissolved in a glass vessel in thirty ounces of boiling water; and after the solution was cool, it was filtered. It had a sourish taste. The tincture of lacmus was reddened by it. It made an effervescence with chalk. Two drachms of this salt were exposed to an open fire in a glass retort, when it immediately melted, grew black, and frothed very much. Into the neck of the retort a brown salt was found sublimed, which smelled like a mixture of the salt of ben-zoin and salt of amber. Eleven grains of coal remained in the retort. The receiver contained a brown liquid, without any mark of oil; its smell was like the sublimed salt; it also contained some of this salt dissolved, which was separated from it by a gentle evaporation. The salt
that

that was sublimed weighed thirty-five grains, had a sour taste, was easily soluble in spirit of wine, more difficultly in water, and burned in the fire with a flame. Concentrated vitriolic acid exposed to distillation with this salt became black, frothed very much, and decomposed the salt entirely. All these circumstances shew that this salt is to be classed among the vegetable acids, under the title of *acid of sugar of milk*.

§ VII. *Its Effects upon Alkalis.*

I poured depurated acid of sugar of milk, in small quantities at a time, into a hot solution of alkali of tartar, till there appeared no more effervescence. A coagulation immediately took place, in consequence of the formation of small crystals, which required eight times the quantity of boiling water for their solution. After it was cold the greatest part of the crystals separated again from it. With mineral alkali this acid shewed the same phenomena, with this difference, that the neutral salt thus arising requires only five parts of boiling water for its solution. If to a solution of it, a solution of alkali of tartar be added, a number of small crystals will be soon formed at the bottom of the vessel, on account of the greater affinity of this acid with the latter alkali.

Both

Both these salts are perfectly neutral.—Saturated with volatile alkali it forms a kind of sal ammoniac, which, after being gently dried, has a sourish taste. When distilled, the volatile alkali is first separated, the lime-water precipitates, the acid remaining in the retort afterwards yields, with a stronger heat, the same products as in § VI.

§ VIII. *With Earths.*

The acid of the sugar of milk forms, with all the earths, salts insoluble in water. I shall, therefore, only relate the experiments which I made with it in the way of precipitation. If a solution of the ponderous earth in muriatic or nitrous acid be dropped into a cold solution of our acid (§ VI.), the earth is immediately precipitated, in combination with this acid. With the same solutions of lime this acid exhibits the same phenomena; but the solution of gypsum remains undecomposed. The same thing happens with the solutions of magnesia in vegetable or mineral acids, and with earth of alum; all of which, however, are decomposed by the neutral salts above mentioned.

§ IX. *With Metals.*

It produces the same effects with the metals as with the earths. With regard to the weakness of the menstruum, since the water dissolves so little of our acid, it has no sensible effects upon metals; but with the metallic earths, salts are formed very little or not at all soluble in water. Argentum nitrated silver is precipitated by our acid in the form of a white powder: and in the same manner is the nitrated mercury and lead. Vitriolated iron, copper, zinc, and manganese, are not hereby precipitated. Muriated tin and mercury are not hereby decomposed, but muriated lead is precipitated. By the neutral salts (§ VII.) all metallic solutions are decomposed.

E S S A Y XVIII.

ON THE CONSTITUENT PARTS OF LAPIS PONDEROSUS, OR TUNGSTEN. 1781.

IT is probable that the constituent parts of this species of fossil have been hitherto unknown to the chemists. Cronstedt enumerates it among the ferruginous stones, under the name of, *Ferrum calciforme terrâ quâdam incognitâ intimè mixtum*. That which I employed in my experiments was of a pearl colour; it was taken from the iron mines of Bitzberg; and as I made many experiments upon it, and have discovered its constituent parts, I take the liberty of communicating the following account to the Royal Academy.

§ I.

(A) In the fire tungsten does not undergo any perceptible change, nor does glass of borax produce any sensible effect upon it; (B) but with microcosmic salt it forms, by means of the blowpipe, a glass of a sea-green colour. If the globule be kept in fusion at the extreme point of the flame, the colour gradually disappears; a very little nitre also very soon destroys the

the colour; but it returns whenever the blue part of the flame is driven on the globule; consequently, it is the phlogiston of the flame which is the cause of the colour. (c) One part of tungsten, reduced to a fine powder in a glass mortar, was mixed with four parts of alkali of tartar, and placed in the fire in an iron crucible. The mixture, when melted, was poured out on an iron plate, and dissolved in twelve parts of boiling water. After standing some hours, the lixivium was poured off from a portion of white powder which had subsided to the bottom. (d) This powder wasedulcorated, and nitrous acid added to it, till no more effervescence could be perceived, by which operation great part of it was dissolved. (e) The undissolved part of the powder was dried, and being again mixed with four parts of alkali of tartar, was fused as before: This mass being also dissolved in water, and nitrous acid poured upon the remaining powder, only a very small portion of grey powder was left behind undissolved. (f) The ley (c) was saturated with nitrous acid; it grew thick by the precipitation of a white powder, which was afterwards washed with cold water and dried. (g) The solution in nitrous acid (d) afforded, on the addition of alkali of tartar,

tartar, a white precipitate, which was dried.

§ II.

(A) Boiling water has no action upon tungsten reduced to powder. (B) On one part of finely powdered tungsten were poured two parts of concentrated acid of vitriol, and the mixture was distilled. The acid passed over unchanged; and the residuum, which was of a bluish colour, was boiled a short time in distilled water, which was then filtered off, and upon cooling deposited some vitriolated lime. (c) On four scruples of tungsten, reduced to a very fine powder, were poured twelve scruples of common nitrous acid, or pure aquafortis: No effervescence ensued; the mixture was then exposed to a strong digesting heat, whereupon the powder soon assumed a citron-yellow colour. The acid was then decanted off into a separate phial; and the yellow powder, having beenedulcorated with water, was put into another phial. (D) On this yellow powder I poured eight scruples of caustic volatile alkali, and exposed the phial to heat; the yellow colour presently vanished, and the powder became white. This solution was then in like manner poured into a separate flask, and the powderedulcorated. As the matter was sensibly diminished by these

these operations, I repeated them many times on the same powder, digesting it first in the nitrous acid, and then in the volatile alkali, till at length the greatest part of it was dissolved. What remained undissolved weighed three grains, and seemed to be siliceous earth. Muriatic acid produces the same effect upon tungsten as the nitrous, but the solution was of a deeper yellow.

§ III.

(A) The solutions made in the foregoing manner with the nitrous acid being all mixed together, some drops of phlogisticated alkali were added, upon which about three grains of Prussian blue were precipitated. (B) The mixture was then saturated with caustic volatile alkali; but as no precipitate appeared, some solution of alkali of tartar was added; a white powder now fell to the bottom, which, when washed and dried, weighed two scruples and five grains, and was found to be aerated lime unadulterated; so also is the earth obtained § I. (C). (c) The extracts procured by volatile alkali were precipitated with nitrous acid; the precipitate was washed with cold water and dried; it is exactly the same as that mentioned § I. (F). (D) It is of an acid nature, not easily soluble in water, for near
twenty

twenty parts of boiling water are required to one of the precipitate; it colours the tincture of litmus red, and has an acid taste.

§ IV.

Now, as the earth separated from tungsten by the nitrous acid is calcareous (§ III. B), it became necessary to try whether the above mentioned acid, combined with calcareous earth, would constitute a regenerated tungsten. Having this in view, and knowing that tungsten is not soluble in boiling water (§ II. A), I mixed one part of the acid solution (§ III. D) with six parts of clear lime-water, upon which the mixture became a little turbid; but as, after an interval of some hours, there was no deposition, the mixture was made to boil, when immediately a white heavy powder separated, which, after being dried, gave a sea-green colour to glass of microcosmic salt, became bluish on being boiled in the vitriolic acid, and of a lemon colour with the nitrous and marine acids, and consequently was pure tungsten.

§ V.

To ascertain more completely the nature of this acid, the following experiments were made. (A) Under the blow-pipe the dry acid became first of a red-

dish-yellow colour, then brown, and at last black: It neither smoked, nor gave any signs of fusion. (B) With borax it produced a blue, and with microcosmic salt a sea-green glass. This colour is subject to the same changes as are related of the glass § I. B. (C) When pulverised acid of tungsten is boiled with a small quantity of the nitrous or marine acids, the powder becomes yellow; and, with the acid of vitriol, bluish. (D) If the solution of the acid of tungsten in water (§ III. D.) be saturated with alkali of tartar, a neutral salt is obtained in very small crystals. (E) With volatile alkali this acid forms an ammoniacal salt, in shape like the points of small pins. This salt, on distillation, yields its alkali in a caustic state; the acid remaining behind in the retort, in the form of a dry powder of a yellow colour. This ammoniacal salt decomposes nitrated lime, in consequence of which regenerated tungsten is produced. (F) With magnesia the acid of tungsten forms a neutral salt of difficult solubility in water. (G) It produces no change on solutions of alum or lime, but it decomposes acetated ponderous earth, and the precipitate is altogether insoluble in water. (H) The following metallic solutions are precipitated, of a white colour, by the acid of tungsten, *viz.* vitriolated iron, zinc, and

and copper; nitrated silver, quicksilver, and lead, as also muriated lead; but tin, combined with the same acid, is precipitated blue; and corrosive sublimate, and the solution of gold, undergo no change.

§ VI.

When the acid of tungsten is calcined in a crucible, it loses the property of being soluble in water. That the acid is much disposed to attract phlogiston, appears from the blue colour it acquires with fluxes (§ V. A, B). This circumstance induced me to mix the dry acid with a little linseed oil, and to expose the mass to a strong fire in a luted crucible. When it was grown cold, I found the acid black, but in other respects quite unchanged. I also mixed one part of the dry acid with two parts of sulphur, and distilled off the latter; I then mixed with the residuum two parts more of sulphur, and again distilled it off: The acid had acquired a grey colour, but was in other respects unaltered. Solution of liver of sulphur was precipitated of a green colour, by acid of tungsten, but the phlogisticated alkali white; the latter precipitate is soluble in water. If a few drops of marine acid be added to a solution of the acid of tungsten in water, and the liquor be spread on polished iron, zinc, or even tin, the acid ac-

quires a beautiful blue colour ; and the same thing happens if these metals be put into the acid.

§ VII.

As the acid of molybdæna likewise acquires a blue colour from these metals, it might be natural to suppose that the acid of tungsten is the same as that of molybdæna ; but as, in other respects, it shews very different properties, it must be of a totally different nature. For, *1st*, The acid of molybdæna is volatile, and melts in the fire*, which is not the case with the acid of tungsten (§ V. A). *2^{dly}*, The former of these acids has a stronger attraction for phlogiston, as appears from its combining with sulphur, and the change it undergoes on calcination with oil. *3^{dly}*, Lime combined with the acid of molybdæna is not turned yellow by the acid of nitre, and is readily soluble in it : With tungsten it is quite the contrary. *4^{thly}*, Ponderous earth, combined with the acid of molybdæna, is soluble in water ; but the combination of the ponderous earth with the acid of tungsten is insoluble. And, *5^{thly}*, The acid of molybdæna has a weaker attraction for calcareous earth than the acid of tungsten has ; for if the combination

* See the dissertation on molybdæna.

combination of lime and acid of molybdæna be digested in a solution of the above mentioned ammoniacal salt (§ v. A), a regenerated tungsten will be obtained.

The iron procured from some sorts of tungsten is to be considered as accidentally present.

T 3

Supplement

Supplement to the foregoing Essay. By
T. BERGMAN.

Several years ago I began an investigation of the constituent parts of tungsten. Its great specific gravity induced me to seek for ponderous earth in it; but the process by which this earth is usually extracted, gave, instead of it, common calcareous earth; and when the first alkaline solution, made in the moist way, was poured off, and an acid added to the solution, it gave on saturation a white precipitate of an acid nature. I need not relate the experiments, as I obtained the same results as Mr Scheele: Some small differences, however, in my experiments with the blowpipe, deserve to be mentioned.

Tungsten, by itself, decrepitates with the blowpipe, but does not melt.

In a small gold or silver spoon it unites with mineral alkali with some effervescence, and the bit of tungsten falls into powder.

With microcosmic salt it effervesces a little at first, and then leaves a residuum of difficult solubility; but the glass globe assumes a bright sky-blue colour, without the least sign of that redness, when it is held between the eye and the light, which is produced when cobalt is used.

used. If more tungsten be added, the globule becomes brownish, but remains still transparent: With a further addition, it becomes black and opaque.

Borax dissolves it without motion, and almost without colour; but when the globule is overloaded with tungsten, it at length becomes brown or white, and opaque, in cooling.

The acid earth by itself produces some effervescence with mineral alkali. With microcosmic salt it gives a globule which is at first light-blue, more of the acid makes it dark-blue, but it still remains free from redness by refraction: With a further addition it becomes brown. Borax acquires a slight tinge of blue, and with more of the acid becomes of a yellowish brown colour; but remains transparent, provided no further addition be made.

This ultimate brown colour I have not been able to drive off, either with nitre, or the point of the flame.

A very easy method of distinguishing tungsten from all other fossils hitherto known, is, to pour upon it, when it is reduced to powder, aquafortis or marine acid, and to set the mixture in a digesting heat. It will soon be perceived, especially when the latter acid has been employed, that the powder gradually acquires a fine light-yellow colour. This happens not only with the species from Bitiberg,

but likewise with all the foreign sorts I have hitherto had an opportunity of trying. What is usually called *white tin ore, in clusters like grapes*, often belongs to this species.

With respect to the nature of the acid earth, it is nearly allied to that obtained from molybdæna; and both are in a state much resembling that of white arsenic. It is well known, that arsenic, in its semi-metallic state, is nothing but a peculiar acid, saturated with phlogiston; and that the white calx is in an intermediate state between acid and metal, containing just phlogiston enough to coagulate the acid; but remaining still soluble in water, and shewing signs of acidity. If a conclusion from analogy be admissible, all the other metals should consist in a combination of the same nature, of the different radical acids, which, with a certain quantity of phlogiston, are coagulated to a dry earthy substance, and, on complete saturation, are brought to the state of complete metals.

The reasons which induced me to suppose that the above mentioned acid earths are metallic acids, reduced by phlogiston to that form of metallic calces in which the acid is still perceptible, are the following:

i. They

1. They both shew a striking resemblance to white arsenic in form, in producing effects like acids, and in their little solubility in water.

2. Their specific gravity; that of white arsenic is 3,750, that of the earth of molybdæna 3,460, and that of the acid earth of tungsten about 3,000.

3. Their precipitation with phlogisticated alkali. None but metallic substances are hitherto known to be precipitated by this alkali: Moreover, arsenic, properly dissolved in the marine acid, gives with the phlogisticated alkali a precipitate soluble in water, just as the acid earth of tungsten.

4. Their property of tinging vitreous fluxes. Metallic calces, but, as far as I know, no other substances, have the property of communicating a colour, each according to its peculiar kind, to clear glass. The effect of white arsenic, in this respect, is well known; that of the earth of tungsten has been described above; and the earth extracted from molybdæna is not less powerful; for it gives to microcosmic salt a beautiful green colour; and borax well saturated with it appears grey when viewed by the reflected rays, but, by the refracted, of a dark-violet colour.

These

These reasons have induced me to consider the acid earths obtained from molybdæna and tungsten as metallic calces. Other occupations have hitherto prevented me from confirming my opinion by reduction; but I thought proper, nevertheless, to mention it on this occasion, as perhaps some other person before me may be inclined, for the promotion of science, to undertake the necessary proofs.

E S S A Y

ESSAY XIX.

EXPERIMENTS AND OBSERVATIONS ON
ÆTHER. 1782.

UNDER the term *æther* chemists understand a very volatile, penetrating, colourless oil, which has an aromatic smell, and is soluble in water. The first method of preparing this oil from vitriolic acid and spirit of wine has been long known. In later times, several methods of preparing a liquor of the same kind from nitrous and marine acids, with alcohol, have been proposed; but it has been observed, that this latter acid was not of itself strong enough for this purpose, but that, in order to produce the desired effect, it must be united with tin, or with regulus of antimony. The theory of the generation of æther is still very imperfect, from the want of sufficiently decisive experiments;—the following may perhaps contribute to elucidate this intricate subject.

§ I.

(A) If, in the preparation of vitriolic æther, a large retort be made use of, and the fire be much increased towards the end of the process, it is found, that the
volatile

volatile fulphureous acid in the receiver is mixed with vinegar, without any mark of aerial acid, either in the cavity of the retort or of the receiver. (B) If one ounce of pulverised manganese be put into a retort, with half an ounce of vitriolic acid, and an ounce of rectified spirit of wine, and this mixture be exposed to a sand-heat, in a few minutes it will begin to grow hot, and will soon boil by itself. During this time some æther, of a most agreeable smell, goes over into the receiver. If the fire be increased, towards the end a small quantity of vinegar will pass over, without any mark of volatile fulphureous acid. The air in the receiver is now found to be mixed with aerial acid, and in the retort there will remain a residuum of vitriolated manganese, without any excess of acid. (c) If two parts of pounded manganese and one-half part of vitriolic æther be mixed with one part of vitriolic acid, and the process carried on as in (B), the mixture will likewise grow hot of itself in about an hour's time. The æther which, a small portion excepted, is again obtained after the process, has a finer smell than before. There is likewise obtained some vinegar, and some aerial acid.

§ II.

In order to ascertain whether the vitriolic acid is to be looked upon as a real constituent part of the vitriolic æther, the superfluous vitriolic acid ought to be separated from it. In order to effect this, I found the rectification of the æther with dry alkaline salt insufficient, because the alkali does not touch the æther in all its points. I therefore dissolved caustic alkali in spirit of wine, and in this alkalised spirit I dissolved as much æther as it would take up. I then distilled the mass again by means of a gentle heat. Upon the æther thus obtained, after it was rectified, I cautiously poured two parts of pure concentrated nitrous acid. The mixture had perfectly the smell of nitrous æther. I evaporated the whole to within a few drops, and then added a little of the solution of terra ponderosa, which instantly grew white; consequently a regenerated spathum ponderosum was here produced. This I think will be quite sufficient to prove that vitriolic acid is a constituent part of vitriolic æther.

§ III.

That calx of zinc, dissolved in muriatic acid, and that butter of antimony and smoking spirit of libavius, on distillation

tion with spirit of wine, produce æther, is a known fact, and my experiments confirm it. I shall only add here, that in all these distillations no aerial acid is produced. Why no æther can be produced from muriatic acid and spirit of wine alone, the following experiment may teach: (A) I mixed an ounce of pulverised manganese with four ounces of common muriatic acid, and two ounces of rectified spirit of wine, and put this mixture, after I had covered it well, aside for seven whole months; during which period it was now and then agitated. This mixture at last yielded an odour of nitrous æther, and I saw some drops of oil floating upon it. From this observation I was led to put into a tubulated retort two ounces of common salt, and as much vitriolic acid; and after luting on a receiver, which contained three ounces of spirit of wine, I placed it in a sand-bath. After some time I poured this spirit, which was now fuming, into a retort which contained three ounces of powdered manganese. The mixture instantly assumed a fine green colour, but a few minutes afterwards it grew hot, upon which I immediately applied a receiver. The heat increased so much, that the mass began to boil of itself, and at the same time the green colour disappeared. After the ebullition had ceased,

I put the contents of the receiver into a flask, into which I had previously poured a little water, the æther instantly separated; it resembled in its smell nitrous æther, when it is mixed with dephlogisticated muriatic acid. I luted the receiver again to the neck of the retort, and continued the distillation to dryness, by which operation I obtained more æther; some of which floated upon the surface, and the rest kept at the bottom. (B) I then distilled a mixture of three ounces of powdered manganese, one ounce of vitriolic acid, and three ounces both of common salt and of spirit of wine, and observed the same phenomena, and obtained the same products as in (A). (C) I mixed three ounces of powdered manganese, with the same quantity of common muriatic acid, in a retort, placed the mass in warm sand, and applied a receiver, which contained three ounces of spirit of wine. The muriatic acid now went over in a dephlogisticated state into the spirit of wine, which soon grew very warm, though the neck of the retort was cold. Some time after all the effervescence had subsided in the retort, I poured the spirit out of the receiver into another retort, and distilled it by a gentle heat. At first some æther went over, having the smell of nitrous æther. At the end of the process, another kind of æther, or rather oil, came over,
which

which sunk to the bottom, and at last muriatic acid passed over. (D) I dissolved some bismuth in aqua regia, consisting of three parts of muriatic, and one part of nitrous acid. This solution I evaporated to the consistence of a syrup, then mixed it with an equal quantity of spirit of wine, and distilled the mass by a gentle fire. At first pure spirit of wine passed over, which was followed by some æther, that had exactly the smell of vitriolic æther. (E) Iron was the last among the metals, by means of which I could produce æther with muriatic acid. I saturated muriatic acid, by boiling it with crocus martis (for with iron filings no æther can be produced). The solution I evaporated to the consistence of honey, and then proceeded as in (D). The æther, thus obtained, was perfectly like the preceding. I several times poured spirit of wine as well upon this residuum as upon the residuum of bismuth, and constantly obtained some æther upon a new distillation. In this distillation no aerial acid is generated.

§ IV.

In order to determine with certainty, whether the muriatic acid is to be looked upon as a constituent part of this æther, it was first necessary to free it from the
superfluous

superfluous muriatic acid as well as possible; and with this view I proceeded with this æther as I had done before with the vitriolic § II. The æther, thus purified from muriatic acid, was mixed with a solution of silver; but observing no precipitation to take place, I poured the whole mass into a glass vessel, and set it on fire after the æther was consumed; I found the solution of silver turbid, and as it were coagulated by the muriated silver; consequently my conjecture that the muriatic acid was a constituent part of this æther was well founded.

§ v.

The action of nitrous acid upon spirit of wine is well known; on which account I shall take no further notice of it; but the action of the fluor acid upon spirit of wine I was curious to learn. (A) For this purpose I mixed powdered fluor with an equal quantity of vitriolic acid in a retort, to which I luted a receiver, containing three ounces of spirit of wine, and placed the retort in warm sand. The day following I poured the spirit, which now smoked, into another retort, and distilled it in the common manner. The fluor acid penetrated every where through the lute, but no mark of æther was perceptible. (B) I then mixed the spirit which

was contained in the receiver with fluor acid air as before; and having poured the mixture into a retort upon three ounces of pounded manganese, I subjected it to distillation. I here obtained a quite different result; no acid penetrated through the lute; I only perceived the smell of æther through it; and, after I had driven over all the spirit, I poured it into another retort, rectified it by a gentle heat, and by this means obtained a small quantity of æther of a very agreeable smell, resembling nearly that of nitrous æther.

§ VI.

In order to procure a sufficient quantity of concentrated vinegar, I distilled the acid vinegar from acetated copper, and rectified it by another distillation. My view was to prepare and to examine the acetous æther of Count Lauragais. But, notwithstanding all the trouble I bestowed for this purpose, I was not able to produce the least vestige of such an æther; the same disappointment I met with, when I used vinegar obtained by distillation from acetated vegetable alkali. It is singular enough that so many of our modern chemists should have acquiesced in the assertion of the Count as an indisputable certainty. Upon communicating my unsuccessful experiment to Professor Bergman,

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man, he had the kindness to inform me in answer, that Dr Pörner was the only chemist who had not blindly admitted the Count's assertion, and had asserted, that he had not been able to obtain any æther, according to the Count's process. But though this be certainly true, I however found the means of obtaining such an æther; it requires only the addition of a little mineral acid before the distillation. Add, for instance, (A) to an ounce of concentrated vinegar (which may be obtained from verdegrease, crystals of verdegrease, saccharum saturni, or acetated vegetable alkali, by means of vitriolic acid), two ounces of spirit of wine, and two drachms of common muriatic acid. Distil this mixture, till all the spirit has been driven over, and then, upon distilling it off a second time to one-half into a receiver, which should contain a little water, acetous æther will be obtained. If, instead of the muriatic acid, vitriolic, nitrous, or fluor acid be employed, the same æther will be produced. This æther is obtained in a larger quantity than any other, and may be prepared in several different ways. (B) If an ounce of alkali saturated with vinegar be dissolved in three ounces of spirit of wine, and then as much of any of the above mentioned four mineral acids be added as is requisite

not only to decompose the acetated alkali, but that there shall likewise be some superfluous mineral acid, and the mass be then distilled, the same æther will be obtained. (C) If acetated lead be triturated with a sufficient quantity of muriatic acid, then mixed with spirit of wine and distilled; (D) if crystals of verdegrease be dissolved in a sufficient quantity of muriatic acid, and distilled with spirit of wine; (E) if one part of concentrated vitriolic acid be mixed with three parts of spirit of wine, one part of common salt, and one-half part of powdered verdegrease, and distilled, an æther of the same kind is likewise obtained. In the same manner, if (F) one part of vitriolic acid be mixed with four parts of concentrated vinegar, and four parts of spirit of wine, then put aside in a well corked phial for a few days, if to this mass some water be added, the same sort of æther will be separated. All the æther obtained floats upon the water, but is not near so volatile as nitrous or vitriolic æther; it burns with a blue flame like spirit of wine. The union of the component parts of the acetous æther is much easier destroyed than that of the other kinds, as the following experiments will prove: (G) I dissolved one part of acetous æther in as much water as was necessary for the solution, and afterwards

afterwards added two parts of caustic fixed alkali. On distilling it by a gentle fire, I hardly obtained the eighth part of the æther dissolved. The acetous æther, thus depurated, did not indeed any longer affect tincture of lacmus as it did before; but, on pouring some drops of it upon blue paper, it immediately turned it red. I dissolved this æther anew in a weak alkaline ley, and distilled the solution again. Here it disappeared entirely; the first liquor that went over retained only a faint smell of æther. I saturated the remainder in the retort with vitriolic acid, and obtained by distillation acetous acid.

§ VII.

Some phosphoric acid which was prepared by burning phosphorus was mixed with two parts of spirit of wine. I distilled the mixture in the common way, till there was nothing remaining in the retort but the acid. The spirit which came over into the receiver had a disagreeable smell. I rectified it, in order to get the æther, by a more gentle degree of heat, but I obtained not a vestige of it. On mixing water with this spirit it grew white like milk, and some days afterwards I found a white powder precipitated, which was pure phosphorus. Should the phosphoric acid perhaps contain always a

small quantity of phosphorus undecomposed, the spirit of wine would be a good medium to separate it. The disagreeable smell, as it would seem, arose from the phosphorus dissolved in the spirit; but that the spirit of wine should carry over along with it into the receiver acid of phosphorus, as Mr Morveau * maintains, is not in the least probable, as I found not the slightest mark of it in the spirit thus distilled.

§ VIII.

The crystallised acid of benzoin mixed with spirit of wine yielded no æther; but on distilling one part of the acid of benzoin with three parts of spirit of wine and one-half part of common muriatic acid, pure spirit first came over, whereupon I observed two different liquids in the retort, one white, the other brown. I therefore changed the receiver; and, on continuing the distillation, afterwards obtained an æther, one portion of which floated upon water, while the other, which was the larger portion, subsided to the bottom. This æther had the smell of salt of benzoin, was not more volatile than acetous æther, burned with a clear flame, and with smoke. When dissolved in alkalised

* *Elemens de Chemie Théorique et Pratique*, tom. iii. p. 338.

kalised spirit of wine, and then distilled, it was as easily decomposed as acetous æther; and, on dissolving the remainder in the retort in water, and adding some acid, the whole mixture was coagulated by the precipitation of salt of benzoin.

§ IX.

I must not conceal the rest of my unsuccessful experiments made upon this subject, as they may perhaps afford some illustration with regard to the theory of the generation of æther. The acid of tartar had no effect upon spirit of wine, not even when a mineral acid was added; neither did the addition of manganese afford any æther. Concentrated acid of lemon gave, in every respect, the same result. Neither does the acid of borax afford any æther, either with or without manganese. The acid of amber acts in the same manner, as likewise does the phosphoric acid with manganese, with concentrated vinegar and acid of tartar, with concentrated vinegar and manganese. These substances distilled with spirit of wine yield no æther. The same thing takes place with the following salts: Acetated zinc, acetated mercury, muriated mercury and iron, muriated manganese, nitrated silver, muriated magnesia, salt of benzoin and manganese, fixed caustic al-

kali and manganese, acid of arsenic, acid of arsenic and manganese.

§ x.

From the foregoing experiments I should be unwilling to attempt an explanation of the generation of æther; for though it might be concluded, with some degree of certainty, that there is always required a substance to attract the inflammable principle of the spirit of wine, because all the experiments coincide in shewing this; yet still I do not see how this opinion can be held with regard to æther of vinegar and benzoin, as these two vegetable acids have as little affinity with phlogiston as fluor and muriatic acids have. But if you were even to allow that they attract phlogiston, though but weakly, a question still remains, In what manner does this *oil of spirit of wine or æther* separate from the water with which it was so intimately united? Perhaps, however, this phænomenon might be explained upon the same principle as the separation of sulphur from hepatic air. It is known that this air is, like spirit of wine, soluble in water, and that it consists of phlogiston, the matter of heat and sulphur. If any substance be added which disunites the phlogiston from this air, the matter of heat flies off, and the sulphur precipitates.

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This I apply to the explication of the generation of æther; and we know beforehand, that manganese, when united with an acid, has a strong attraction for phlogiston. Now, if this metallic calx, spirit of wine, salt and vitriolic acid be mixed, the manganese will unite with a part of the phlogiston of the spirit of wine, and the matter of heat, which becomes so evident in this process that the mixture boils of itself (§ I. A; § III. A), is set free, by its separation from the phlogiston; and thus the oil of spirit of wine, or æther, is separated from the water. The æther, in this case, commonly carries along with it a small admixture of the acid, which served to its separation from the water (§ II. IV.); but this small quantity of acid is so insignificant in rectified æther, that it cannot be maintained with certainty that there exists no æther at all without some mineral acid. The small portion of vinegar and aerial acid which I observed in some distillations (§ I. c), arises from the total decomposition of a small portion of æther; for it is very probable that the oil of spirit of wine consists of acetous acid and phlogiston; whereas calx of iron, dissolved in muriatic acid (§ II. c), and distilled with spirit of wine, yields æther; whence it appears why the tinctura ferri of the Pharmacopœia Suecica in time acquires a smell like nitrous æther.

ESSAY XX.

OBSERVATIONS ON A METHOD OF PRESERVING VINEGAR. 1782.

IT is a fact generally known, that vinegar, of whatever kind, will not keep long; but, in the course of a few weeks, especially in the warm temperature of summer, grows turbid, and that its surface is covered with a thick mucilaginous substance; during which period the acid disappears by degrees, and at last is entirely lost; whence the vinegar must very often be thrown away. Now, in order to avoid this corruption of the vinegar, four methods have been discovered. The first is, to prepare the vinegar very strong and four at first. It is well known, that such vinegar keeps for several years; but as there are few people who prepare their own vinegar, and as most content themselves with buying it as it is to be had in the shops, there are of course but few who can make use of this method. The second method is to concentrate the vinegar by congelation; after which a hole is made in the crust of ice which covers it, through which the part that is not congealed is let out, and afterwards put
into

into bottles. This manipulation answers well enough; but as nearly one-half is lost, because that which forms the crust of ice is, for the most part, nothing but water, good œconomists dislike it. The third method is to prevent the access of air, *viz.* To fill the bottles full, and keep them perfectly well corked. Though vinegar by this method keeps very long, it is not much employed; probably, because it is troublesome to fill the bottle immediately again, every time you have made use of part of its contents, with clear vinegar from another bottle; after which, the vinegar in the bottle that is not full, and to which consequently the air has access, soon grows turbid and vapid. The fourth method is to distil the vinegar: Such vinegar suffers not the least change, though exposed to a warm air for years; but, being more expensive than that which is not distilled, this method is seldom made use of, especially as the following method to preserve vinegar is the easiest of all.

It is only necessary to put your vinegar into a well tinned kettle, and make it boil for a quarter of a minute over a strong fire. It is then to be immediately bottled carefully; or, if any one should be afraid of tin being pernicious to health, he may fill his bottles first, and then put them into a kettle full of water upon the fire.

After

After the water has boiled for about an hour's time, the bottles are taken out of the pot and corked. The vinegar thus boiled keeps for several years, as well in open air as in half-filled bottles, without growing turbid or mucilaginous. It likewise may be used with advantage for pharmaceutical purposes, instead of common vinegar; for the preparation of the compound vinegars, which, if not prepared with distilled vinegar, soon grow turbid, and lose their acidity.

E S S A Y

E S S A Y XXI.

EXPERIMENTS ON THE COLOURING
MATTER IN BERLIN OR PRUSSIAN
BLUE. 1782.

TOWARDS the beginning of the present century, Mr Diesbach, a manufacturer of colours at Berlin, with the assistance of Dr Dippel, accidentally discovered the blue colour, since called Berlin or Prussian blue. They kept this preparation with great secrecy, till Woodward published the whole process in 1724. After this period, several chemists have endeavoured as well to improve the colour as to give an explanation of its origin. Brown, both the Geoffroys, and the Abbé Maynan, are known on account of their papers written upon this subject; but it was reserved for Macquer, who published a dissertation upon it in 1752, to represent the whole in a connected view. After him several have attempted to determine the nature of the matter, which in general unites with the metallic calces, when they are precipitated from their solutions by the *lixivium sanguinis*, and which in the preparation of the Prussian blue gives to the iron a blue colour: But they have
advanced

advanced no further. Some are of opinion that it is phlogiston which comes into action here, and thence the name *phlogisticated alkali*. Others think that it is an animal acid. The cause of this uncertainty is, that there has been hitherto no method discovered to obtain this colouring matter in a perfectly pure state, it being hitherto always united with some heterogeneous substance. Having at last, after many repeated trials, found means to obtain it in this pure state, and unmixed, so that I was able to make several experiments with it, I now take the liberty of presenting an account of them to the Royal Society.

§ I.

(A) If the *lixivium sanguinis*, the preparation of which is universally known, be exposed for some time to the open air, it loses its property of precipitating the iron of a blue colour; and the precipitate, thus obtained, is entirely dissolved in the acid. Now, in order to ascertain whether the air had hereby undergone any change, I put some recently prepared *lixivium* into a glass vessel, which was well sealed with rosin; but some time afterwards I found the inclosed air as before, and the *lixivium sanguinis* unchanged; whence I conclude, that the colouring
matter

matter is not absolutely simple phlogiston*. It occurred to me, that the aerial acid, which was not present in sufficient quantity in air confined, as in the preceding experiments, but exists in a much larger quantity in the open air, might be the principal cause of the separation of this colouring matter from the lixivium. (B) I therefore filled a glass vessel with aerial acid, and poured a little lixivium sanguinis into it, carefully preventing the access of the external air. On examining this lixivium the day after, I found that my conjecture was well founded; for calx of iron, precipitated with this lixivium, was entirely soluble in acids. (c) I further tried, whether other acids had the same effect upon the lixivium sanguinis. For this purpose I supersaturated that preparation with all the known acids, adding afterwards a solution of vitriolated iron to them; but neither did I now obtain any precipitate.

§ II.

(A) I now inverted my experiments; I mixed a little vitriolated iron with lixivium sanguinis, which immediately grew yellow; I then poured some of this mix-

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† Le bleu de Prusse est un précipité de fer, avec surabondance de phlogistique. Macquer Dict. de Chimique, 2de edition.

ture into a glass vessel filled with aerial acid. The day after, I poured this lixivium into a solution of vitriolated iron, then supersaturated the lixivium with acid, and obtained a considerable quantity of Prussian blue. (B) To the same lixivium sanguinis, in which I had dissolved a little vitriolated iron, I added of the other acids somewhat more than was necessary for saturation; and, on mixing afterwards a solution of vitriol with them, I instantly obtained Berlin blue. (c) I precipitated a solution of vitriolated iron with alkali, and boiled the greenish precipitate for some minutes in lixivium sanguinis, which dissolved part of it; I then filtered the lixivium. This lixivium underwent no change, when exposed to the open air, or to the aerial acid; it precipitated the solution of iron of a blue colour, as well before as afterwards; and although the lixivium was supersaturated with acid, and some vitriolated iron was added, a very beautiful Prussian blue was obtained. Hence it appears, that the calx of iron in some manner fixes the colouring matter in the lixivium; so that neither aerial acid, nor any other acid, is capable of separating this matter from the alkali. This is likewise the reason why the colouring neutral salt, which is formed on boiling alkali with Prussian blue, does not so easily

ly lose its power of precipitating iron of a blue colour, either by the action of the aerial or any other acid. (D) But if lixivium sanguinis be boiled with a perfectly calcined calx of iron, (which I prepared for this purpose from vitriolated iron, by boiling it in nitrous acid, and precipitating with caustic alkali) no part of it is dissolved; for if the lixivium be afterwards supersaturated with acid, and vitriolated iron added to it, no Prussian blue is obtained. The same thing happens, if such a solution of perfectly calcined iron be precipitated with lixivium sanguinis, and some acid be afterwards added to it. Hence it likewise appears how much the small quantity of phlogiston, which the calx of iron retains in the vitriol, contributes to the fixing of the colouring matter.

§ III.

(A) In order now to learn whither the colouring matter had gone in the experiments § I. A, B, C, I poured some lixivium sanguinis into a glass vessel, filled with aerial acid; it was kept well corked during the night, and the next day I fixed to the cork a piece of paper, that had been dipped in a solution of vitriolated iron, and then pencilled it over with a couple of drops of a solution of alkali in water.

The piece of paper was soon covered with precipitated iron. A couple of hours afterwards I took the paper again out of the vessel, and besmeared it with some muriatic acid, when, to my great surprize, I saw it immediately covered with the most beautiful Prussian blue. (B) The same experiment was repeated with lixivium sanguinis, supersaturated with vitriolic acid. This mixture was put into a glass vessel, and the piece of paper treated as in the last mentioned experiment. (A) I here likewise observed, that the air was filled with the colouring matter; for the piece of paper became blue on applying muriatic acid to it. (c) Though acids expel this matter from alkali, a considerable quantity of it nevertheless remains in the lixivium sanguinis supersaturated with acids; for the same mixture, removed into another vessel, imparts to the air the colouring quality, and that repeatedly, according to the quantity of air. (D) When I applied upon the pieces of paper a solution of perfectly dephlogisticated calx of iron, instead of a solution of vitriol, no Prussian blue was formed; but the muriatic acid dissolved the calx entirely. This agrees with what is said in (§ II. D).

§ IV.

Being now aware that acids really attract the alkali more strongly than the colouring matter does, I wished to know what effect would be produced by distillation. (A) I therefore poured lixivium sanguinis, supersaturated with vitriolic acid, into a glass retort, luted on a receiver closely, and distilled by a gentle fire. When about one-third of the mass had passed over, I changed (B) the receiver, and distilled, till half of the remainder went over. (C) The watery liquor, which came over first, had a peculiar smell and taste. The air in the receiver was filled with the same colouring matter as the glass vessels (§ III.) had been; paper tinged with lacmus was turned red by this liquor; but, upon discovering afterwards, by means of the solution of terra ponderosa, some vitriolic acid in it, I perceived that I could not depend upon this phenomenon for any conclusion. I mixed with one part of this water a little phlogisticated calx of iron, or what comes to the same thing, a little precipitate from vitriolated iron; and a short time afterwards I added some drops of vitriolic acid to it, by which I obtained a fine Prussian blue. (D) Part of this water being exposed for some hours to the open air, entirely lost

its colouring quality. (E) The water obtained by the second distillation (B) produced the same effects as pure water mixed with a little vitriolic acid.

§ v.

When I had thus discovered the possibility of obtaining the colouring matter in its greatest purity, I proceeded to make some experiments, in order to obtain it separate from the blue itself; and this with a view partly to procure a larger quantity of it than the lixivium yields; partly also to avoid the troublesome calcination of the blood, and preparation of the lixivium. This matter, though it may be separated from the Prussian blue by distillation, yet it is thus mixed with so many heterogeneous particles, that it would not serve my purpose. On examining several sorts of Berlin blue, I found in them marks of sulphur, volatile alkali, vitriolic acid, and volatile sulphureous acid, which substances are found as well in the lixivium sanguinis as in the lixivium of foot, and adhere to the precipitate in the preparation of Prussian blue. On distilling one sort of this preparation, I obtained in the receiver a liquid, which had a smell of spiritus cornu cervi, precipitated vitriolated iron, and, on the addition of an acid, was changed into Prussian blue. In the neck

neck of the retort there was a sublimate, which proved to be a kind of neutral salt, consisting of volatile alkali and volatile sulphureous acid; the air in the receiver was full of aerial acid, volatile alkali, and the colouring matter. The remainder in the retort was black, obedient to the loadstone and yielded hepatic air with acids. Being unable by these means to attain my purpose, I resolved to examine a little more closely a neutral salt known in chemistry, which is formed when lixivium tartari is boiled with a sufficient quantity of Prussian blue. This salt consists of the colouring matter of the lixivium, of calx of iron, and of alkali, and is especially made use of for discovering iron in mineral waters; but is not entirely to be depended upon for this purpose, as long as chemistry is unable to free it perfectly from iron; and this cannot be effected without decomposing this salt, of which the iron is constantly a constituent part, and is the medium by which the colouring matter is attached to the alkali (§ II. c). The lixivium sanguinis is more to be depended upon for this purpose, though it likewise, as well as the lixivium of foot, shews marks of the presence of iron. Though I have mentioned (§ I.), that on supersaturating lixivium sanguinis with an acid, and then adding vitriolic acid,

no sign of Prussian blue is perceived ; but as blood and foot contain a little iron, there is no reason to be surpris'd that lixivium sanguinis should contain iron ; whence it happens, that, in such cases, there may really appear some mark of Prussian blue, and this the more readily, if the calcined mass be boiled in an iron vessel. But if the vitriol be first put into the lixivium, and then an acid be added to it, a great difference is found with regard to the quantity of Prussian blue obtained. If a perfectly pure lixivium sanguinis be taken, supersaturated with an acid, and vitriolated iron be added to it, not the least mark of blue appears. Such a pure lixivium is not obtained in the common way, but on mixing the colouring matter in its purest state (§ x.) with alkali of tartar.

§ VI.

To return to the above mentioned neutral salt, I dissolved an ounce of it in a glass retort in four ounces of water, adding three drachms of concentrated vitriolic acid (other acids produce the same effect, but I prefer the vitriolic acid in this process), and distilled this mixture into a luted receiver by a gentle fire. As soon as the mass began to boil, it grew thick, from the production of a great quantity
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of Prussian blue, which was separated. I perceived at the same time a smell, which penetrated through the lute, and perfectly resembled the smell of water impregnated with the colouring matter (§ IV. c). I continued the distillation, till an ounce had passed over into the receiver, and then poured the water containing the colouring matter into a phial. The air in the receiver had likewise absorbed this colouring matter, which I detected as in § III. A. The blue mass remaining in the retort I put upon a strainer, and into the liquid, which passed through, I put a piece of vitriolated iron, in order to see whether there was still remaining any of the neutral salt undecomposed. But no Prussian blue was produced, and thus the salt was decomposed during the boiling. The blue which now remained on the filter, and was free from the neutral salt, I again boiled with *lixivium tartari*; the solution was freed by filtration from its ochre of iron, and the mass was then distilled a second time, with the addition of vitriolic acid in excess. It now shewed the same phenomena as at first; for as soon as it began to boil, Prussian blue was again separated, though in less quantity, and the colouring matter came over into the receiver. After one-third of the mass had passed over, I added it to that obtained

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ed by the first distillation, and then separated the regenerated Prussian blue from its acid, which I again extracted by *lixivium tartari*, and then distilled it the third time. Here I again obtained some blue, and it thus evidently appears, that, by repeated extractions and distillations, all Prussian blue might at last be entirely decomposed.

It is not difficult to account for the series of phenomena that occurred in this whole process. The neutral salt consists of alkali, a little iron, and the colouring matter; it is therefore a triple salt. Now, when an acid is added to this salt, the colouring matter, in consequence of the stronger attraction of acids for alkalis, must be expelled, which immediately, on account of its volatility, goes over into the receiver during the distillation. But as the acids are not capable of expelling this colouring matter from the iron, the calx of iron will contain as much as is requisite for its saturation, or, what comes to the same, as much as is requisite for the production of Prussian blue; and this is the part which separates from the salt during the distillation. If Berlin blue be extracted by lime or *terra ponderosa*, these extracts shew the same phenomena during distillation with vitriolic acid.

§ VII.

If Prussian blue be extracted by volatile alkali, a compound arises, which likewise constitutes a kind of triple neutral salt, consisting of volatile alkali, iron, and the colouring matter. With vitriolic acid it shews the same phænomena as the salt of § VI. If this neutral salt be distilled by itself, after having been dissolved in water, the solution grows thick, in consequence of the separation of Berlin blue, and a volatile alkaline liquor goes over into the receiver. If the distillation be continued till but little liquid remains with the Berlin blue in the retort, no more salt will be found in the retort, but all will have gone over into the receiver. The liquor in the receiver consists of volatile alkali and the colouring matter. It is not precipitated by lime-water; but vitriolated iron is decomposed by it, and, on adding an acid, Prussian blue is generated. If a piece of paper dipped into a solution of vitriolated iron be suspended in the receiver, this solution is soon decomposed, the air of the receiver being impregnated with volatile alkali. If afterwards the same paper be pencilled over with muriatic acid, it grows blue. If the whole liquor of the receiver

ver be exposed to the open air, it all evaporates, leaving behind pure water.

§ VIII.

Among several other fruitless attempts to separate this colouring matter from the Prussian blue in a more commodious way, I found that calcined quicksilver afforded an excellent medium for accomplishing this purpose. I observed, that mercurius dulcis grew black in air impregnated with this colouring matter. The same thing likewise happened if it was put into the tinging water (§ IV. c); and this water thence acquired an acid quicksilver taste. Hence it was probable that this matter had united with the sublimate in the mercurius dulcis, or at least with the calx, which is its basis, and expelled the muriatic acid, which would give rise to the acid taste; and as quicksilver, in its metallic state, is not soluble in muriatic acid, it must therefore separate from it; and this is the cause of its black colour. I therefore boiled the liquor with corrosive sublimate, and the mixture hardly began to boil, when the blue colour had already disappeared. I then boiled calcined mercury or red precipitate with Prussian blue and water. The colour disappeared entirely, and the filtered solution had a strong taste of quicksilver; it contained

no iron, and, what is remarkable, it could not be precipitated either by acids, lime, or alkalis; but, by a long digestion with metals, the mercury was reduced to its metallic state, by means of a double elective attraction. If the union of the colouring matter with metals be prevented, it becomes free and uncombined, and may be easily separated by distillation. This may be effected by means of an acid. After different trials, I found the following method the best.

§ IX.

To two ounces of powdered Prussian blue, and one ounce of calx of quicksilver, prepared by means of nitrous acid, I added six ounces of water in a cucurbit; I boiled this mass for some minutes with constant agitation, when it assumed a yellowish grey colour. I then poured it out on a filter, and upon what remained in the filter I poured a couple of ounces of hot water, in order to elixivate the whole thoroughly. The strained mercurial solution was then poured upon an ounce and a half of iron-filings, free from rust, and contained in a glass vessel, there being added three drachms of concentrated vitriolic acid. The whole mass was well agitated, during which, in a few minutes, it was turned quite black by the reduced quicksilver,

quickfilver, and thereby completely lost its quickfilver taste. It, at the same time, acquired the peculiar smell of the colouring matter. I left the mixture a few minutes at rest; then poured off the clear liquor into a retort; and distilled the fourth part of it off into a well luted receiver. Here I obtained the same colouring matter as from the neutral salt (§ vi.). It is sufficient to distil off one-fourth; for this matter is much more volatile than water, and goes over first.

§ x.

A slight vestige of vitriol easily appears in this (§ ix.), as well as in the preceding distillation of the neutral salt (§ vi.). This little vitriolic taint must consequently be likewise separated from the colouring matter. I have remarked (§ i.), that aerial acid is capable of dislodging this matter from alkali and lixivium sanguinis. The same thing happens if this matter be combined with lime. It is therefore not difficult to separate the vitriolic acid from it. I mixed a little pounded chalk with the distilled water impregnated with this matter, and distilled the mass a second time by a gentle fire. The vitriolic acid united during this process with the chalk, and the colouring matter went over in its greatest purity. In order to hinder, as
much

much as possible, the escape of this volatile matter through the lute, and in order to prevent the air in the receiver from absorbing too much of it, I make use of a small receiver, pouring a little distilled water into it, and place it so that the greatest part of the receiver, during the operation, shall be immersed in cold water. This matter has a peculiar, but not disagreeable smell, a taste somewhat approaching to sweet, and warm in the mouth, at the same time exciting cough. Of its nature and constituent parts, as likewise of its action upon other substances, I shall speak in the second part of this dissertation.

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water into it, and place it so that the
lower part of the receiver, during the
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proaching to sweet and warm in the
mouth, as the same time exciting cough,
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the result of its action upon other substan-

ESSAY

E S S A Y XXI.

ON THE INFLAMMABLE PRINCIPLE IN
CRUDE CALCAREOUS EARTH*.

YOU entreat me, my worthy friend, to communicate to you my thoughts on Dr Weber's publication, entitled, *The Nature and Properties of Lime and Caustic Substances newly discovered*. I cannot but wonder, that the controversy concerning fixed air and the *acidum pingue* should not yet have ceased with you: That this acid is a mere chimæra, is acknowledged both by Dr Weber, and, I believe, by all chemists: But it would appear that the Doctor wishes, by his phlogiston, to supplant fixed air, as this has supplanted the *acidum pingue*. Whoever is desirous of attempting satisfactorily to prove any opinion in chemistry, ought to be thoroughly acquainted with the bodies with which he makes his experiments, and on which he rests his proofs: But, when this knowledge is wanting, how easily may wrong conclusions be drawn! I do not indeed

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* This is a letter from Mr Scheele to Mr Meyer of Stettin. The original was published in CRELL's *Neuesten Entdeckungen*, Th. 1. p. 30. &c.

by any means flatter myself that we are acquainted so completely as could be wished with the constituent parts of all bodies, but so much is certain, that all oily compounds, derived from the animal and vegetable kingdoms, yield, when they are entirely destroyed, an inflammable principle, a mild acid in an elastic form, or the true aerial acid (to which the author assigns the old appellation, fixed air), more or less, or no humidity; as also, more or less, or no earth. Could Dr Weber decompose pure fixed air, and shew demonstrably, that phlogiston actually is one of its constituent parts, his opinion would acquire much weight. Were this effected (which it can never be by conjectures), it will next be asked, What is the other principle contained in fixed air? The author's supposition, that it is the electrical fluid, is a mere hypothesis, just as much as if I were to suppose that it is some acid of a stronger nature. The author can by no means establish his opinion concerning the presence of phlogiston in fixed air, by saying that the vapours of fixed air, extricated from chalk by muriatic acid, have a smell; fixed air separated from magnesia alba by vitriolic acid is inodorous, and the same fluid expelled from *lapis suillus* by muriatic acid has a stinking smell; and yet both these

species

species of air coincide entirely with respect to their principal qualities. Dr Black's experiments are so solid and convincing, that it seems to me impossible to form any objection against them. He has, indeed, pushed his conclusion rather too far in saying, that the explosion of fulminating gold, and the increase of weight in metallic calces, prepared by heat, are owing to fixed air; but the chief discovery does not suffer from these mistakes*. Dr Weber cannot maintain, upon the authority of his first and second experiments, that crude calcareous earth contains phlogiston as a constituent part; for, in the *first* place, that which appears, is to be deduced from a small residuum of decaying mineral substances; and, in the *second*, saltpetre can be alkalised, by being kept long in a red-heat, provided some body be mixed with it to prevent its fusion. Neither will his opinion, that, in the distillation of crude calcareous earth (experiment 3.), the phlogiston it contains passes over along with the moisture, and precipitates the lime-water in the receiver, easily find admittance. Will any

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reflecting

* It is but justice to this great philosopher, whose lectures not only teach the principles of a science, and the operations of an art, but contain likewise a system of practical logic, that he never contended strenuously for these conjectures, and that he has long abandoned them. T.

reflecting chemist readily suffer himself to be persuaded that pure phlogiston parts from a body, without at the same time being in immediate contact with another body, for which it has a stronger attraction. We cannot shew that water has the smallest disposition to attract phlogiston, considered in a state of purity; and we find in general, that acids must be employed as the means of effecting such an union. The theory of Dr Black explains this precipitation so clearly, that nothing can be objected to it. When the author allows the lime-water to remain in the receiver to the end of the process, while there is at the same time an excess of chalk in the retort, he finds that the lime-water redissolves the regenerated calcareous earth. Now, if we assume with him that phlogiston in excess can dissolve even crude calcareous earth in water, his phlogiston must either be an acid or not an acid; in either case a few drops of nitrous acid must precipitate the solution, (he must grant this, as, according to his first experiment, nitrous acid is capable of attracting it from lime in the fire); but no such thing happens. I have scarce any inclination to advert to the 4th experiment, as it contradicts all experience. The fixed air, expelled by nitrous acid from a quarter of a pound of calcareous earth, does not precipitate

precipitate more than a quart of lime-water. In the fifth experiment, the author precipitates lime-water with an alkaline spirit obtained from horns; but finds that the earth, after it has been dried, is lighter than the lime employed. It cannot be unknown to the author, that the fixed air, separated from the alkaline spirit during the precipitation (for express mention is made of an effervescence), has the properties of an acid, and can therefore dissolve part of the lime. The lime dissolved in this manner will not fall down, until a good quantity of alkaline spirit is added; and why is so much required? because it is the caustic part only of this spirit which effects a precipitation, as it has a stronger attraction for the superfluous fixed air, which holds the earth in solution. His supposed reciprocal attraction has no place here. Alkaline spirit, obtained from horns and hoofs, should never be used in exact chemical experiments. That from common sal ammoniac is the best for these purposes; and this is the reason why the author, after he had saturated the spirit from hoofs with muriatic acid, and distilled the ammoniacal salt with spirit of vitriol, obtained at the last a volatile spirit in the receiver, which effervesced with acids. Had the author distilled pure but common sal

ammoniac with oil of vitriol, his volatile spirit would certainly not have effervesced with acids: But why did the spirit obtained by the author effervesce? because it contained some oily matter, which was destroyed by the vitriolic acid on the application of the heat; as, during the decomposition of oil, fixed air is always separated (let any one distil oil of vitriol with a little fat, he will easily discover fixed air in the receiver); and as it combines with the spirit driven over into the receiver, the spirit must of course effervesce with acids. That the vitriolic acid should remain in the retort, is owing to its fixity, a property which it has in common with other known acids, which are more or less fixed as the phosphoric and arsenical acids, and sedative salt. The author certainly does not know, that a quantity of fixed air is separated from coal during its combustion, as being one of its constituent parts, otherwise he never would have related his 6th experiment. As the atmosphere always contains some uncombined fixed air, what wonder that quicklime should return in time to crude calcareous earth? Putrid vapours contain a far greater quantity of this fixed air, consequently we know that phlogiston must be combined in the air with some substance; for were it uncombined, so that it
could

could unite with lime (I very much question, however, whether phlogiston can unite with pure lime), it would much sooner combine with pure air, for which it has a very strong attraction: But we know, that in this case the air becomes unfit for respiration, and therefore the earth must have long since lost its inhabitants. He thinks that the 10th experiment is so clear and convincing, that no doubt can remain respecting his new doctrine. But had he been better acquainted with oils, he would not have looked on his experiment as incontrovertible; for as the vitriolic acid in sulphur fixes the phlogiston, even so does the fixed air in oils fix the same principle. As, when we mix lime with sulphur, phosphorus, or regulus of arsenic, and afterwards separate those inflammable bodies from the lime by burning, and obtain in the first gypsum, in the second animal earth, and in the third lime combined with arsenic: So also must lime, when linseed oil is burned with it, exhibit a combination of lime and fixed air. With respect to the 13th experiment, I can assure the author, that iron, dissolved in vitriolic acid, yields but very little fixed air; the air is mostly inflammable. The author must not then compare this with that air which is extricated from chalk by acids;

for the inflammable air is formed during the solution of the metal in vitriolic or marine acid; but fixed air is present beforehand in chalk. That the air which is expired from the lungs carries along with it fixed air, is absolutely certain, on which account lime-water is precipitated by this air. Fixed air is actually a constituent part of the atmosphere; and the more exactly the phlogiston combined with it is separated from it, the more pure air must make its appearance. Fixed air is also present in putrefying water. That the earth in lime-water is restored to its crude state by phlogiston, the author can neither persuade me nor any intelligent chemist. Had the author examined a little less carelessly the precipitate which appears on pouring lime-water into human urine, he never would have pronounced it to be calcareous earth, as in experiment 19. I can assure him that this precipitate does not effervesce with any acid, but is animal earth, precipitated by the phosphoric acid in urine. The same may be said of the 20th experiment, which the author made very unnecessarily. No exact chemical experiments should be made with the volatile alkali from putrid bodies. Other chemists, as well as myself, have obtained by sublimation good sal ammoniac, from volatile alkali separated
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from fal ammoniac by lime, and afterwards saturated with muriatic acid. Neither is the fixed nor volatile alkali in neutral salts caustic; neither is the lime contained in *fixed ammoniac*, as it is called. These substances are caustic only, in consequence of being combined with a considerable portion of the matter of heat, which separates as soon as an acid is poured on them, the acid having a stronger attraction for the bodies than heat. I need not touch upon the 25th experiment. When the lime does not flake, it can only make the ley a little caustic; for, in the last case, or when the ley is to be thoroughly caustic, it must touch the corrosive sublimate in all possible points. As the matter of heat consists of phlogiston and pure air, while metallic calces, prepared by heat, contain much heat, which must be heavier than phlogiston alone, what wonder that a metallic calx should be heavier than the perfect metal? Such a calx does not, as Dr Black supposes, contain fixed air. When it is reduced by means of charcoal, the fixed air is to be deduced from the charcoal, and not from the metallic calx. As long as the author considers fixed air as phlogiston and æther, he will easily be able to explain, why dry volatile alkali, abstracted from a metallic calx, becomes caustic. But a prudent
chemist

chemist will not so lightly yield his assent, much less will he reason so much at random; for, in this case, we have a double attraction, the fixed air, which is united with the volatile salt, and constitutes with it a kind of sal ammoniac, since it is a species of acid—the fixed air, I say, uniting with the metallic calx, as at other times it does with lime, and the matter of heat in the calx joining the alkali. In experiment 31. the author distilled sal ammoniac, prepared with volatile spirit of urine and oil of vitriol, and he obtained an alkaline spirit, which effervesced with acids. I have repeated the experiment, with this difference, that I used spirit of sal ammoniac, and not oily spirit of urine for saturating the vitriolic acid. My Glauber's ammoniac melted during the distillation, and I obtained caustic volatile alkali, which neither rendered lime-water turbid, nor effervesced with acids. The residuum in the retort was vitriolic acid; some of the ammoniac was also sublimed. The 40th experiment, too, proves nothing. He burns *terra foliata tartari*, or acetated vegetable alkali, and obtains a salt which effervesces with acids. The injudicious and uninstructed may indeed be easily led into mistakes by such experiments as this. He should know that there are oily particles in vinegar, and that, if they were
away,

away, it would be no vinegar at all. These oily particles, an essential part in all vegetable acids, are destroyed by the heat; upon which the fixed air, the other constituent part of this oil, and indestructible in the fire, combines with the alkali; and what wonder that this elastic acid should be expelled by a stronger? Experiment 34. is very easy to be explained; (for if the author's assertions were admitted, calx of iron would have a stronger attraction for phlogiston than nitrous acid). Alkalis, as well as nitre, when they are mixed with metals, or metallic calces, in order to prevent their fusion, lose their acids on a long continued calcination, and immediately afterwards the matter of heat unites with the alkalis, which is the only cause of their causticity.

Lead is a metal which contains very little phlogiston; for I have observed scarce any sensible mark of liver of sulphur upon stratifying it with vitriolated tartar in a close crucible. Should vegetable alkali have reduced any calx of lead, this might have arisen from the glue that the ley carried along with it, on being filtered through bibulous paper, or perhaps from some impurity adhering to the alkali or minium. Why is not a solution of lead reduced by alkali in the humid way? Experiments 42. and 43. have turned out
very

very differently, when made by all other chemists, even by the late Mr Meyer himself, as well as by me; for caustic fixed alkali always precipitates a solution of calcareous earth in a caustic state. The author here did not pay attention enough. Experiments 44. 45. and 46. are also insignificant. According to the 47th, ashes adhering to red-hot coals should have lost their phlogiston. But, if so, Why do they effervesce with acids? For, according to the hypothesis, the earths effervesce, because they contain phlogiston. P. 137. and 145. the author mentions some phenomena, which, in his opinion, cannot be explained at all; as, for instance, that alkali does not totally precipitate vitriol; that vitriolated tartar does not entirely precipitate the solution of quicksilver; as also, that the mother ley of common salt cannot be completely precipitated by alkaline spirit. But an intelligent chemist, accustomed to experiment, finds no difficulty in assigning the causes of phenomena, to the author so incomprehensible; but as they do not belong to the present subject, I pass them over.

These observations will, I hope, my very worthy friend, convince you, that the doctrine of Black is not only applicable to all the experiments, but that it will maintain its ground in the principal points,
and

and is consequently true. Refer to the author's analysis of sea salt, and you will find (p. 160.) that Glauber's salt, together with the lime dissolved by marine acid, are to be separated by crystallisation. In like manner, he supposes, (p. 167.), that Epsom salt and Glauber's salt are contained in the mother ley, together with calcareous earth, dissolved by marine acid. He speaks, too, of these salts at p. 175. Now, it has been known since the time of Neumann, that vitriolic acid, and the neutral salts into which it enters, separate calcareous earth from the muriatic as well as other acids.

E S S A Y XXII.

SOME INCIDENTAL REMARKS ON THE
AFFINITY OF BODIES *.

THE few following observations on Mr Wenzel's doctrine of the affinity of bodies, are not made with a view to detract from his merit, but to shew both my attention to his valuable book, and how necessary it is to repeat the experiments of others, when they do not coincide with the principles of chemistry.

Page 9. That metals dissolved in acids are unchanged, and remain just in their former state, is contrary to all experience in chemistry; which shews, that they lose their inflammable principle during solution.

P. 14. The position, that salts do not act, unless in solution, fails in many cases. When

* The name of the excellent Mr Scheele, a German, and at present settled as an apothecary at Koping, in Sweden, will serve as a sufficient recommendation to all his productions. The present remarks, though they have a reference only to Mr Wenzel's *Doctrine of the Affinity of Bodies*, bear, like all his other works, the stamp of acuteness and truth; and as they are delivered with proper candour, they rather do honour to Mr Wenzel, to whose merits I here subscribe my testimony. CRELL *Chem. Journ.* th. 4.

When powdered chalk, for instance, is boiled with Prussian blue, reduced likewise to powder, the former attracts the colouring matter of the latter, and yet chalk is insoluble in water.

P. 40. Mr Wenzel does not explain the decomposition of vitriolated tartar right. For, if the fixed alkalis had not the property of combining with vitriolic acid in excess, the nitrous and marine acids would neither change vitriolated tartar nor Glauber's salt into acid neutral salts, and therefore one should never be able to pour off the vitriolic acid from the crystals of nitre; but it is always combined with fixed alkali, and cannot be separated by any nitrous acid.

P. 41. I have great difficulty in believing, that caustic volatile alkali precipitates the solutions of lime and lead. Spirit of sal ammoniac is always obtained when that salt is distilled with chalk and water. Simple experiments give sufficient testimony in this case.

P. 54. Both alkaline salts have not an equal affinity for vitriolic acid. Pour oil of tartar, *per deliquium*, into a solution of Glauber's salt, and vitriolated tartar, will fall to the bottom in the course of a few minutes.

P. 72. and 73. The inflammable air of the zinc and iron should have been taken into the account in the weighing.

P. 81. This earth of alum can scarce be without vitriolic acid; for we know, that a part of this acid is very difficult to be separated from it; and, on this account, it could not attract any fixed air. Were the author to dissolve his earth in distilled vinegar, and then to add a few drops of a solution of terra ponderosa, the vitriolic acid would immediately shew itself.

P. 95. If coals consist of phlogiston and a little earth, where does the quantity of fixed air, which makes its appearance during their decomposition, reside? This must contribute very much to their weight.

P. 133. The solution of magnesia becomes a little turbid on the addition of caustic volatile alkali. How, indeed, should it be otherwise? Since there is formed a triple salt, consisting of the earth, the vitriolic acid, and the volatile alkali; and since as much of the earth must be disengaged as the acid attracts of the alkali. If some Glauber's ammoniac be first added to the solution of magnesia, no precipitate will be occasioned by the caustic alkali.

P. 135. In my experiments, iron has never been precipitated, in its metallic form, from its solution in muriatic acid by zinc.

P. 149. The calx precipitated from the butter of antimony by oyster-shells, is not a pure precipitate; but, according to my experiments, still contains some muriatic acid. I could not accomplish the dulcification of muriatic acid in the way mentioned by the author.

P. 155. If much nitrous acid be taken for the solution of quicksilver, and the whole be boiled together, the quicksilver is completely calcined, and then it affords a white precipitate, on addition of spirit of sal ammoniac. The quicksilver in corrosive sublimate is in a calcined state; the black matter is nothing but exceedingly fine revived mercury.

P. 177. It is said, that platina is not precipitated by mineral alkali; but although many agree in this opinion with the author, a precipitation does actually take place.

P. 248. As the neutral salt, consisting of lemon juice and fixed alkali, is capable of dissolving iron, it is no wonder that alkali does not cause a precipitation. The same thing has been observed by the author (p. 303.) concerning the solution of iron in tartar, and the reason is the same.

P. 273.

P. 273. The want of fixed air is said to be the cause why acetated lead, prepared from minium, does not crystallise; but it is totally different. The author has not mentioned, that his solution, after he had introduced fixed air to it by means of his apparatus, became white, though this was really the case. This white matter in the solution of lead is nothing but calx of lead saturated with fixed air; that is to say, real white lead. If this superfluous calx is separated from the solution, the compound of lead and vinegar will immediately crystallise; and this may be effected by the addition of gum Arabic, or by adding more vinegar, in order to dissolve the abundant calx of lead. Fixed air is seldom necessary to bring the difficultly crystallisable salt to shoot. Too much is attributed to this mild acid; and I cannot agree with the author in thinking that the explosion of gold is owing to it.

P. 286. It would be difficult to shew, that all the fixed air obtained by Mr Lavoisier came from the minium. Part, indeed, does; but as we know that charcoal consists of phlogiston and aerial acid or fixed air, to abide by the author's appellation, I ask, What becomes of that fixed air, which those particles of the

charcoal that part with their phlogiston to the lead, yield? Recent minium gives out much fixed air when it is distilled with charcoal.

P. 193. When speaking of tartar, Mr W. mentions an inflammable earth, which is separated on saturating tartar with alkali. But the tartar contains some calcareous earth, which, with the acid of tartar, constitutes a salt very difficult of solution; on which account, it falls to the bottom. Acid of tartar contains much oily matter, wherefore a compound of that acid and lime must burn.

P. 297. We obtain caustic alkali, and not a neutral salt, as the author affirms; for the latter is obtained only when chalk is boiled with tartar; in which case, it is not surprising that the caustic alkali should chrySTALLISE on the addition of an acid.

P. 366. It is said that fixed air is the cause of the crystallisation of the neutral salt prepared from nitre and arsenic; and as Mr W. could not have been acquainted with arsenic and its constituent parts, he is not to be blamed for entertaining such an opinion.

P. 379. The fixing of arsenic by caustic spirit of sal ammoniac is truly remarkable. But it is certain, that caustic volatile alkali always contains some lime. It
appears,

appears, when it is kept long in glaffes that are frequently opened, in the form of a hard pellicle deposited on the glass. Is it not this lime which adheres to the arsenic, and fixes it? If not, and the experiment be exact, the problem is one of the most difficult in chemistry.

P. 404. It is said that volatile alkali easily dissolves precipitated magnesia; but the solution is entirely owing to the water in which alkali is dissolved. The separation of the earth, when the solution is exposed to the open air, arises not from the evaporation of the volatile alkali, but from the escape of the aerial acid, which held the earth in solution in the water; for, from a pound of Epsom salt, dissolved in 64 pounds of water, no precipitate can be obtained by pure potashes without boiling; but, when the air is driven off by boiling, the magnesia is obtained.

P. 423. "Fixed alkalis precipitate a solution of silver prepared with volatile alkali." How is that possible? It is indeed true that a precipitation takes place; but what a great quantity of fixed alkali must be added before all the silver is precipitated. With what does the alkali combine? It has no attraction for the volatile alkali; and, without a new combination, it is impossible to conceive a precipitation. Saturate pure salt of tartar with abstract-

ed vinegar, or even precipitated nitrous acid, and you will find that the solution of silver yields some precipitate. I have never met with alkali which did not shew some vestiges of muriatic acid. When the author comes to examine the precipitate again, he will not fail to recognise it for luna cornea.

P. 472. Mr W. has no doubt of the presence of a great quantity of fixed air in nitre. For my part, I entertain many doubts whether fixed air can be obtained from nitre, and still more, from nitrous acid. I have already observed, that a great deal of fixed air is procured from charcoal distilled with recently prepared minium; and the same thing holds when the phlogiston of the charcoal unites with the acid of the nitre. Why is no fixed air obtained when metals are deflagrated with nitre? In this case, *corrupted air* is obtained, which does not precipitate lime-water. Moreover, only one-sixth part of the air obtained from gunpowder is fixed air; the rest is corrupted air.

P. 480. Mr W. maintains, after Beaumé, that calcareous earth may be converted by a very violent fire into a vitriform earth; but in this point I can neither give credit to Mr Beaumé nor the author.

Letter

Letter from Mr SCHEELLE to Dr CRELL.

I have often prepared the colouring neutral salt, contained in lixivium sanguinis, in the following manner: I extract Prussian blue with thoroughly caustic fixed alkali. To the liquor containing the extract, after it has been filtered, I add highly rectified spirit of wine, upon which the salt falls in the form of flocculi to the bottom*. With respect to every other method for the purification of the lixivium (those of Scopoli and Westrumb † not excepted), I am convinced that they are imperfect; for it is only necessary to boil a sufficient length of time their yellow solution with vitriolic or muriatic acid, and Prussian blue will be separated. My salt continues unaltered, even when exposed to the open air; for the iron

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* Truth obliges me to mention, that three months before I received this letter, Mr Westrumb described the same experiment for purifying the lixivium sanguinis. I can say nothing further to decide the priority of the discovery. CRELL.

For an account of Mr Westrumb's method, see the notes on Bergman's Dissertation on Elective Attractions, p. 337. T.

† Mr Scheele means here the method proposed by Mr Westrumb, in his *Essay on the Constituent Parts of the Blood, and the lixivium sanguinis*, (*Crell's Neueste Entdeck.*), and not that alluded to in the last note. T.

strengthens the connection between the colouring acid and the alkali, and fixes it so, that the aerial acid cannot expel it; which otherwise will happen in a few days, provided it be not combined with iron or some other metal in the colouring ley. I have not yet observed whether the *tinging acid*, for such is the name which Professor Bergman has bestowed upon it, saturated with alkali or lime, will yield crystals? If you desire to know this, the combinations and evaporations must be performed in close vessels.

On the Crystallisation of the Acid of Lemons.*

It has hitherto been a matter of doubt, whether the juice of lemons could be reduced to the form of crystals; for it appeared, from a great variety of experiments, that this juice, though evaporated to the consistence of a syrup, would not shoot into crystals. I was led to make some trials upon this subject, which I have communicated to our Academy of Sciences, and which point out the method by which I at length accomplished my purpose. I conjectured at first, that the mucilaginous matter in the juice prevented its crystallisation; on which account I mixed the inspissated juice with strong spirit of wine, and thus produced a coagulation of the whole. I then poured it out upon a filter, and evaporated the acid liquor which passed through; but it could not be made to shoot by these means.

I therefore concluded the great quantity of saponaceous matter, which the spirit holds in solution, is the impediment to crystallisation. In order to separate it, I employed the same method that is followed when the essential acid of tartar is to be obtained from cream of tartar. I saturated

* Crell's Chemische Annalen. Th. 7, s. 3.

turated the lemon-juice, as it was boiling in the cucurbit with pulverised chalk, the weight of which was observed; the compound fell immediately to the bottom in the form of a middle salt, nearly resembling tartarised lime. The water, at the bottom of which the precipitate lies, contains the saponaceous and mucilaginous matter, and the pure acid remains in combination with the calcareous earth. The precipitate is to beedulcorated with lukewarm water, till it appears colourless on being poured off. The compound agrees with gypsum, in being very sparingly soluble in water. There is next to be added to it a quantity of English oil of vitriol, diluted with ten times its bulk of water, equal in weight to the chalk used for saturating the juice. This mixture is to be boiled in the cucurbit for a few minutes; When the whole has grown cold, the acid is to be separated from the gypsum by means of the filter, and to be treated in the same way as the acid of tartar. It is however necessary to try, by evaporating the acid to the consistence of a thin syrup, whether it still contains any calcareous earth. This appears upon mixing a small quantity with oil of vitriol, as, in that case, there will be a precipitation of gypsum; and it will be necessary to add more oil of vitriol to the whole quantity of acid, as
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the presence of a small quantity of lime in solution totally prevents the crystallisation. The crystals will shoot just as well in a hot temperature as in the cold; and should there be any superfluous vitriolic acid, it will be found in the residuum. This crystallised acid of lemons cannot be changed by the action of nitrous acid into acid of sugar; but the saponaceous extract may be totally converted into that acid.

Discovery

Discovery of a peculiar sweet and volatile Matter, which is a constituent part of expressed Oils, and the Fat of Animals.*

Several years ago, upon dissolving litharge in olive oil, I observed a peculiar sweet matter, distinct from the oil floating on the surface, which, when inspissated and treated with nitrous acid, appeared to be a modification of the acid of sugar. I have since more particularly examined this peculiar phenomenon, and have discovered the sweet matter, as well in linseed oil, oil of almonds, and of rape-seed, as in oil of olives; and, still more lately, both in hog's grease and butter. In my experiments, I made use of the following process: One part of pulverised litharge was dissolved in two parts of some one or other of the unctuous substances above mentioned, and some water, the mixture being made to boil all the time. As soon as it was inspissated to the thickness of salve, the whole was left to cool, and then the water was poured off. The water is found to contain the sweet matter in question; and it is to be evaporated to the consistence of syrup. If the oil
or

* This is taken from the second part of Crell's *Chemische Annalen*, p. 99.

or fat be fresh, there does not appear any sign of dissolved calx of lead, on addition of the vitriolic acid; but should either the one or the other be old and rancid, some calx will then be dissolved, and should be precipitated by a proper quantity of vitriolic acid. If this inspissated matter be strongly heated, the vapours that arise will take fire on the application of a candle. In order to make it pass over from the retort into the receiver, a degree of heat is requisite, equal to that which must be employed for the distillation of vitriolic acid. Half of the sweet matter goes over unaltered, in the form of a thick syrup, and still retains its sweet taste; what rises afterwards has an empyreumatic smell, and this is followed by an oil of a brown colour, which smells like spirit of tartar. There remains in the retort a light spongy coal, which does not contain the smallest particle of lead. This sweet matter cannot be made to crystallise; nor, when mixed with water, and set in a warm place, does it run into fermentation; for, after the mixture had stood for four months, tincture of turn-sol did not undergo the least change when mixed with it. It will mix with tincture of caustic vegetable alkali; though neither simple syrup nor honey will do this; but they attract the alkaline salt
from

from the spirit of wine, and then fall to the bottom, in the form of a thick mucilage. If nitrous acid be abstracted from off this unctuous sweet substance, it is at last, after many repetitions of the operation, converted into acid of sugar, and the nitrous acid is very much phlogisticated. It would seem to follow, from these experiments, that the sweet matter in question is combined with more of the principle of inflammability than sugar and honey.

I have also boiled litharge with olive oil, separated from soap by vitriolic acid, with the same result; for I here likewise obtained the sweet matter. I likewise separated the oil from the common salve (*Empl. Simp.* *); which must be done in consequence of the laws of double attractions. Let the salve be sliced and rubbed in a glass mortar, with a mixture consisting of eight parts of strong spirit of wine, and one part of oil of vitriol. This white mixture is to be poured on a filter, and water is to be added to the liquor that

* The author means, undoubtedly, the *emplastrum commune* of the *Pharm. Suecica*, in which there is no salve with the denomination *simplex*. The *empl. comm.* is prepared from two parts of oil of olives, and one of litharge, which are boiled over a slow fire, with continual agitation, and the addition of a little boiling water now and then, till they combine. *Pharm. Suec.* 1779. p. 74. T.

that runs through, upon which the oil that was contained in the salve will be separated. I wished to recompose salve, by boiling this oil again with litharge; but it grew thick before it could be made to boil. From the water, which I took care to decant, I obtained some of the sweet matter so often mentioned, though indeed but in very small quantity.

Letter

Letter from Mr SCHEELÉ to Dr CRELL.*

It seems as if the opinion maintained by many chemists and philosophers, that fixed air is a combination of pure or dephlogisticated air, with a certain portion of phlogiston, is not yet so completely proved. Many rather suppose, that the pure air must be further dephlogisticated, in order to become aerial acid; and that, when it is totally free from phlogiston, it constitutes nitrous acid. Pure air, fit for supporting of combustion, is a kind of sulphur, consisting of phlogiston and the matter of heat.—

In my Essay upon æther, I have related a great number of experiments made with manganese, spirit of wine, and acids. I have, at the same time, shewn, that acetous æther is never generated without the assistance of muriatic or nitrous acid.—

In your *New Discoveries*, (Part 8. p. 111.), there is an observation on my method of preparing the flowers of benzoin †. Lime-water

* *Chemische Annalen.* Th. 8 f. 123.

† This observation comes from Mr Gren of Bernburg, and is to the following purport :

Mr Scheele's method of preparing flowers of benzoin, by boiling the resin in lime-water, and then precipitating them with vitriolic acid, is not without its difficulties,

water is directed in the Swedish Pharmacopœia ; but, in the original paper, (*Transactions of the Royal Academy*), I have mentioned milk of lime ; for the particles of the lime not only dissolve the acid of benzoin, but prevent, in consequence of the boiling, the gum from adhering to it, which happens when alkaline salts are employed.

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difficulties, since the precipitated acid of benzoin is mixed with the selenite that is produced, and it becomes necessary to separate it by boiling water ; but the hot water that is requisite for this purpose, dissolves a considerable quantity of the selenite, by which the salt of benzoin is rendered impure. Mr Gottling has therefore proposed (*Almanack for Chemists, 1782. p. 157.*) to use vegetable alkali instead of lime-water ; no great advantage will result from this change, as long as vitriolic acid is used for separating the salt of benzoin from the alkali, as the vitriolated tartar is difficult of solution in cold water ; and therefore hot water must be used for the edulcoration of the salt of benzoin, which, at the same time, dissolves a considerable portion of it. If then the vegetable alkali is to be used for the extraction, it will be necessary to use some other acid for the separation, in order to form a salt, which cold water will carry off by solution, from the acid of benzoin. In order to extract this acid, I use mineral alkali. I boil sixteen parts of benzoin, with two or three of the alkali, adding a sufficient quantity of water : I then allow it to settle ; repeat the boiling with fresh alkali and water ; filter the solution while it is hot, and evaporate it till it becomes a little thick. After it has grown cool, I add vitriolic acid as long as any salt of benzoin is seen to precipitate. I separate this salt by means of the filter from the ley, which contains Glauber's salt, and edulcorate it with cold water. T.

I have by no means made use of the vitriolic acid for separating the salt of benzoin, but have directed the muriatic acid for this purpose; and in this manner are flowers of benzoin prepared here.

There does indeed (as Mr Gren afterwards observes) take place, a separation of mineral alkali, when Glauber's salt is boiled with unslaked lime. We obtain, however, but a very small quantity of caustic alkali; for the greater part of the Glauber's salt shoots again into crystals. If they be again boiled, some alkali will indeed be obtained, and so on continually; but, With what immense trouble is this mode of proceeding attended?

Concerning what Mr Hermbstaedt has said (*Part 9. p. 66.*) on the subject of lapis infernalis, it may be remarked, that the dark colour of this caustic arises from copper; for even the finest silver-leaf contains copper, which is dissolved at the same time; but, in the melting heat, the copper loses its solvent sooner than the silver, and being then in the state of a calx, it acquires its natural dark colour; and for this reason it is that lapis infernalis is commonly black. If it be dissolved in water, a black powder will remain behind, which is nothing but calx of copper.

Letter

Letter from the Same to the Same.*

I believe that the volatile sweet matter contained in various oily and fat substances (p. 364.), may be totally destroyed by repeated distillations. I have at least obtained, after every rectification, a product resembling spirit of tartar, and the sweet substance became every time more acrid and bitter. The strong heat, which is necessary in order to drive over, is the cause of this destruction.—

Mr Kirwan's experiments, which are adduced to prove that the aerial acid consists of phlogiston and pure air, seem liable to some objections, as long as iron-filings are used for the revivification of red precipitate, and a burning-glass for the calcination of iron in pure air; for iron commonly contains some aerial acid, as it is more or less mixed with plumbago, and as this mineral consists of phlogiston and aerial acid †. If these experiments

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* Chemische Annalen. St. 10. p. 328.

† Mr Cavendish has likewise made the same observation on this experiment; and Mr Kirwan, when he came to repeat the experiment himself, for it was not originally his, as Mr Scheele seems to suppose, but Dr Priestley's, found, upon distilling recent and clean iron-filings with red precipitate, or precipitate *per se*, in the
proportion

were repeated with copper, they would be more convincing; but the filings of copper must be free from dust, and all other impurities.

ESSAY

proportion of two to one, that no aerial acid, nor any other air is produced, but the whole unites with the iron which is calcined, while the mercury passes over. (*Journal de Phys. Août 1785, p. 146.*)

Upon this Dr Metheric observes, that the appearance of air depends on the quantity of precipitate and iron-filings employed. I have distilled, says he, equal quantities of these substances in a mercurial apparatus; and a little air has appeared, which might probably have been that contained in the vessels; it was however more impure than atmospheric air. The mercury was revived, and arose into the neck of the retort. There was neither any extrication nor absorption of air, and the neck of the retort was covered with a considerable quantity of moisture; the filings were calcined, and lime-water introduced into the retort, was precipitated. On repeating the experiment, with two ounces of precipitate, and 72 grains of filings, a quantity of air was extricated, which contained a little aerial acid, but consisted chiefly of pure air. T.

E S S A Y XXIII.

UPON THE RESEMBLANCE WHICH VEGETABLE ACIDS BEAR TO ONE ANOTHER, PARTICULARLY THOSE OF MUST AND SUGAR*. By Dr CRELL.

THE acids that exist in the vegetable kingdom differ, in many respects, from one another. They may be divided into the ESSENTIAL, the FERMENTED, and the EMPYREUMATIC.

The essential are almost entirely pure, as those of lemons, sorrel, and sorrel-dock; or but little altered by the admixture of other matters, as the acids of cherries, barberries, apples, unripe grapes, gooseberries, currants, tamarinds, &c. They are so much covered, as to be hardly distinguishable in many sweet fruits, when they are ripe, in grapes, in various roots,

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* *Chemische Annalen*, St. 7. p. 89.

The obscurity and importance of this subject would alone justify me in the eyes of the intelligent chemist, for adding this and the two following papers; but Mr Scheele has had so great a share in the discovery of the new acids, that they form a peculiarly proper addition to his Essays. It was another strong inducement with me to subjoin them, as they form an excellent supplement to what is said, both by *Bergmann* himself in his Essay on Attractions, and in the *Notes*, p. 334. T.

as carrots, parsnips, in sugar, &c. These latent acids become more evident, partly in consequence of fermentation, by which almost all plants (a few, particularly those which bear cruciform flowers, excepted) are made to yield vinegar, and partly by dry distillation. In the two last operations, all vegetables, however different from one another in taste and other sensible qualities, seem to yield products very nearly resembling one another. But however alike, on the one hand, the results may be, when different plants are treated in the same manner, the products, on the other, which are obtained from the same plant by different operations, are as widely different. How different are the qualities of sugar, when it is dissolved in water, and left to ferment under proper management, till it is converted into vinegar, when it is distilled dry by itself*, and when the acid of sugar is obtained by means of nitrous acid †? In order to be thoroughly convinced of this, it is only necessary to compare, in the two last cases, the experiments made by Mr Schrickel and Professor Bergmann on earths, alkalis, and

* SCHRICKEL *Diss. de salibus saccharin. vegetab. ex sacch. albi analysi acidoque hujus spiritu speciatim.* Giesæ, 1776.

† Bergmann. *Opusc.* vol. I. p. 251.

and metals, with one another. I intend to treat, on some other occasion, of the causes of the different products that are obtained from the same plant, treated in different ways. I shall at present confine myself to the extrication of the same constituent parts from different vegetables, when the same method is applied to each.

The acid which passes over in dry distillation, along with an empyreumatic oil, is scarce perceptible beforehand, though it is procured from very various plants. All vegetables that run into the acetous fermentation yield a vinegar, which has, in all cases, the same essential qualities. This gave rise, in the minds of many chemists, to this very natural conjecture, that the acid diffused through the whole vegetable kingdom, may be of the same kind, and the species may proceed only from the different proportion of oily and mucilaginous particles intermixed with it. Thus it is said by Mr Morveau*, among others, that the acid basis is probably the same in all plants, and only modified by the various constituent parts by which it is neutralised. Most chemists maintain, that vinegar is the basis of the essential vegetable acids: Others, as Mr Westrumb†, suppose,

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* Elemens de Chemie Theor. et Prat. T. 2. p. 9.

† Neu. Entdeck. Th. 11. s. 109.

pose, that the acid of sugar, or rather*, as Mr Hermbstaedt, that the acid of tartar constitutes the essence of the other vegetable acids. We have not, I believe, facts enough to ascertain this matter; neither do I think that, as yet, the case of two specifically different acids, co-existing in one plant, has been considered; but their properties have been constantly deduced from one single acid. This, however, seems frequently to take place: Thus, Mr Scheele was not able to convert the crystallised acid of lemons into acid of sugar, by means of nitrous acid; though he perfectly succeeded in effecting this with the saponaceous extract, which accompanied the acid before it was crystallised. Mr Hermbstaedt, in analysing the juice of four cherries, obtained acid of sugar with a middle salt containing an excess of acid, which was probably tartar. In order to answer this question, it would be proper to enquire, whether the constituent parts and the products of sugar, and the constituent parts of wine, the purest source of vinegar, are in reality so very much alike (as is taken for granted, and commonly supposed to be proved

* Others hold the acid of sugar to be an artificial product, and not a natural salt. See Mr Wiegleb. Chem. Ann. Th. 7. f. 12. and Mr Hermbstaedt N. Entdeck. Th. 9. f. 17.

proved by too few circumstances)? or, Wherein they differ?

The first question then would be, Whether sugar can be extracted from the expressed must, in the same way as Margraaf obtained it from various roots? This admits of but little doubt, since the same chemist asserts, that he has obtained sugar from very fine raisins. It is, moreover, necessary to submit this sugar of wine, or at least the must, after it has been properly purified and evaporated, to a dry distillation, in order to see whether these substances would afford the same products as sugar; and whether the acid that is obtained acts upon alkalis, earths and metals, in the manner which Mr Schrickel has particularly described with respect to his acid. The sugar of wine, or the must, should be treated with nitrous acid, in order to determine whether acid of sugar can be obtained from it in equal quantity: I say, in equal quantity; for some of this acid may well be expected, as wine contains tartar, which, according to Mr Hermbstaedt, may be converted into acid of sugar. On the other hand, a kind of wine, according to the proper way of proceeding, must be obtained from sugar. Preserve it carefully in vessels, and take notice whether any tartar is deposited from it. Another part of the fermented
sugar

sugar must be allowed to pass into vinegar, and afterwards combine the vinegar with all the common salts, earths and metals, in order to compare the effect of vinegar obtained from wine upon the same substances, and to determine how far both kinds of vinegar coincide. The first kind of experiments with must, may be very easily made in countries that produce wine; the last, with sugar, any one may make who has opportunity, patience and time. These points, however, if they were clearly decided, would not furnish an answer quite satisfactory to the question. Concerning the circumstances which it would be further necessary to ascertain, I shall take the liberty of giving my opinion on some future occasion.

On the Conversion of Vinegar into Acid of Tartar, or of Sugar, by the Same.*

I have already thrown out some reflections, both on the resemblance between the acids contained in must and in sugar, and on the difference between them. Now, when must has undergone the fermentative process, its acid appears under the two forms of vinegar and of tartar. Are both these acids newly generated by the process? or but one? or are they only separated? To the production of tartar, fermentation is not necessary; for, according to Rouelle (Bucquet *Introd. à l'étude des corps natur.* T. 2. p. 177.), it may be procured from the juice of unripe grapes. Pure acid of tartar consists, after distillation *per se*, of an empyreumatic acid, and the coal that is left behind of oily particles and calcareous earth (*Bergmann de tubo ferrum*, § 12.), may not then the acetous acid be mere acid of tartar, which did not meet with alkaline salt and earth enough with which it might combine, and become more fixed; but, on the contrary, attracted more subtile oily particles, and thus became more volatile. The fixed vitriolic acid is converted by phlogiston into the sulphureous acid which is so volatile, that the acetous acid may acquire its characteristic properties,

perties, from the want of fixed constituent parts, with which it might unite, may be deduced from the changes which it undergoes, when combined with some fixed matter, and then distilled. Acetated vegetable alkali (*terra foliata tartari*) yields, according to Mr Beaumé (Chym. exp. et raison. T. 2. p. 21.), on distillation by itself, but $\frac{1}{80}$ of pure acid. All the rest of the acid, employed for saturation, is totally destroyed, and the residuum, both in the retort and receiver, quite alkaline, just as the acid of tartar is almost wholly destroyed by dry distillation, the empyreumatic acid, which is obtained, being very weak. According to Beaumé (T. 1. p. 315), if calcareous earth, egg-shells, for example, be dissolved in vinegar, and the crystallised salt be distilled, $\frac{2}{3}$ of a red and very spirituous and inflammable fluid, that smells like empyreumatic acetous æther, and reddens tincture of turnsol, is got. This also shews the change that has been wrought, and the reduction of the strength of the former acid. The acid in sugar of lead is in like manner entirely destroyed by distillation (*Macquer's Dict. vol. 1. p. 328. of the German translation*). It is still further in confirmation of this, that must, distilled even before fermentation, yields nothing but an empyreumatic acid, a kind of spirit of tartar. Whoever shall doubt

of

of the great difference, which the close combination or absence of earthy particles occasions in an acid, would do well to compare lime combined with somewhat of an excessive portion of vitriolic acid, with the same acid uncombined (Beaumé, l. c. p. 273): Let him at the same time imagine the earth to be so intimately combined as to be inseparable. In this manner, may, I think, tartar be conceived, since, according to Bergmann's experiment, it contains calcareous earth; but it is united with acid in excess, tastes sour, and is soluble. The contrary appears, when acid of tartar is completely saturated with lime; for the selenite is exceedingly difficult of solution, and has scarce any taste.

Is it then a conjecture altogether improbable, that vinegar and tartar have for their basis the same species of acid; and that this acid is only combined with a greater quantity of subtile oil in one case, and with more earth in the other? Will it not be possible to bring vinegar again in some measure nearer towards the state of tartar? In order to accomplish this, we must endeavour to take away the fine volatilising phlogiston of the former, to combine it with more fixed matter, and to restore its grosser oil. The latter seems to be extremely difficult, nor will the former be easily effected. Mr Westrumb

(*Chem.*

(*Chem. Ann. St. 3. f. 340.*), in examining whether vinegar did not contain acid of sugar, added nitrous acid to it in various proportions; but he only produced a phlogistication of the nitrous acid, and rendered the vinegar more free from phlogiston. The properties of vinegar, so much dephlogisticated, elude, he adds, further examination, as it would be impossible entirely to separate the one acid from the other. I think, however, that this might have been done by vegetable alkali, lime and heavy earth. The nitrous acid, combined with vegetable alkali, would have shot into the ordinary hexangular crystals; the acetous acid, had it remained unchanged, would have formed the difficultly crystallisable compound; and had it approached to acid of sugar, it would still have constituted a neutral salt, that does not readily crystallise. Nitrous acid only forms difficultly crystallisable compounds, while the crystals vinegar forms with it are so little liable to deliquesce, that they effloresce in the open air*. The effects produced by these acids on heavy earth would have been directly opposite, the nitrous acid forming salts difficult of solution, the acetous such as deliquesce (*Bergm. Op. vol. 3. p. 391.*). But should the latter have approached to
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* Perhaps also spirit of wine would separate nitrated from acetated lime.

the nature of acid of fugar, transparent crystals would immediately have fallen down (l. c. p. 392.). I think therefore that one might several times distil off nitrous acid from vinegar; and when the former, upon being newly added, yields no more red vapours, saturate with calcareous or heavy earth, and separate the ley, that will not shoot, from the crystals. The nature of the salt, which does not contain nitrous acid, may be more certainly determined by its figure, or the effects of other salts, in consequence of a double elective attraction. One might add fresh nitrous acid to the separated salt, or to the whole mixture, without any separation of the nitrous salt, till the earthy salt, which does not contain nitrous acid, be saturated. Were the vinegar unaltered, it would distil off; if it were converted into acid of fugar, it would not be dislodged from the lime by nitrous acid.

In like manner, distilled or Westendorf's vinegar, should be saturated with chalk; the compound should be reduced to crystals, and then exposed to as strong a fire as it can bear without the expulsion of the acid, in order to separate some of the phlogistic particles. Next, let it be dissolved, filtered, and set to crystallise again; then let it be treated with nitrous acid. The vinegar may, perhaps, by such a combination,

bination, acquire more fixity; so that the nitrous acid shall be able to produce a greater change. Should it pass over again in the form of vinegar, let it be combined once more with calcareous earth, and let the foregoing experiment be repeated, in order to try whether some sensible change will not ensue. Should this method fail, let the opposite be tried; endeavour to add more gross phlogistic matter to the vinegar; try to combine strong vinegar, and that of Westendorf, with unctuous oils (*See Macquer's Dict. Tb. 2. f. 126. G. T.*) as, for instance, with oil from tartar, by means of digestion or distillation; and afterwards it may be joined with calcareous earth. Thus we might attempt to bring it nearer to tartar, and again, by means of nitrous acid, to convert it into acid of sugar.

Extract

Extract of a Letter from Dr CRELL to Mr D'ARCET *.

The chemists have always been much occupied in the investigation of the nature of the vegetable acids; and the discovery of their constituent parts would certainly be an highly interesting event. I think I can shew that they may all be converted into one; and that this primitive acid is contained in the purest spirit of wine. The following are my proofs:

1. If the residuum of dulcified spirit of nitre be boiled with a large quantity of nitrous acid, care being at the same time taken to condense the vapours by a proper apparatus; and if the liquid which has passed over be saturated with vegetable alkali, nitre and *terra foliata tartari* will be obtained. If the latter be separated by means of spirit of wine, the vinegar may be got by the ordinary process.

2. Upon boiling the residuum over again with nitrous acid, the same products are obtained. The oftener this process is repeated, the less is procured of acid of sugar, and at length no vestige of it is to be found.

3. If pure acid of sugar, completely formed, be boiled with twelve or fourteen

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Journal de Physique. Octob. 1785. p. 297.

times its quantity of nitrous acid, the former disappears, and the receiver is found to contain phlogisticated nitrous acid, vinegar, aerial acid, phlogisticated air; and in the retort there remains a little calcareous earth.

4. If acid of sugar be boiled with six times its quantity of vitriolic acid, there are found in the receiver, vinegar, phlogisticated vitriolic acid, aerial acid, and in the receiver pure vitriolic acid.

5. By saturating the residuum of dulcified spirit of nitre with chalk, there is formed an insoluble salt, which, on being treated with vitriolic acid, yields a real acid of tartar; for, with vegetable alkali, it constitutes cream of tartar.

6. If the liquor, from which the tartarised lime (tartareous selenite) was procured, be evaporated, there will remain a dark-coloured matter, which yields, on distillation, empyreumatic acid of tartar, and a spongy coal. Hence it appears, that spirit of wine consists of acid of tartar, of water, and phlogiston; so that it is a native dulcified acid; and nitrous acid, on being mixed with it in moderate quantity, dislodges the acid of tartar. If more nitrous acid be added, the acid of tartar is converted into acid of sugar and phlogiston; and, by adding a new portion

tion of nitrous acid, the acid of fugar is changed into vinegar.

7. If one part of acid of fugar, together with one and one half part of manganese, be boiled with a sufficient quantity of nitrous acid, the manganese will be almost entirely dissolved, and vinegar, with phlogisticated nitrous acid, pass over into the receiver.

8. If acid of tartar and manganese be boiled with vitriolic acid, the manganese will be dissolved, and vinegar, with vitriolic acid, be obtained.

9. When acid of tartar, manganese and nitrous acid, are boiled together, the manganese is dissolved, and vinegar, together with phlogisticated nitrous acid, is obtained.

10. If acid of tartar and spirit of wine be digested together for several months, the whole is converted into vinegar, and the air in the vessel becomes partly fixed, and partly phlogisticated air.

11. If spirit of wine be boiled with vitriolic acid and manganese, it will be converted into vinegar, and phlogisticated air.

12. Spirit of wine, by being distilled upwards of twenty times from off caustic alkali was changed into vinegar, and a considerable quantity of water was obtained.

Hence it follows, that the acids of tartar, and fugar, and vinegar, are modifications of the same acid, as it contains more or less phlogiston. The acid of tartar has the greatest quantity; the acid of fugar, a little less; and vinegar has the smallest quantity. In these experiments, it is necessary to employ nitrous acid and fixed alkali, without any admixture of marine acid; otherwise the observer will be led into mistakes.

14. By distilling vitriolic acid from off manganese, an acid is obtained, which is alone capable of dissolving gold, silver, and mercury, very readily.

The analysis of camphor has been entered upon. By several distillations with red bole, a substance like an æthereal oil is obtained. It has all the properties of such an oil, being soluble in spirit of wine, and separable again on the affusion of water.

On distilling dephlogisticated nitrous acid eight times with camphor, a salt is obtained in the form of a parallelepiped, having an acid and bitter taste, and changing the juice of violets and turnsol to red. This salt, when combined with vegetable alkali, assumes a hexagonal form, yields regular crystals, with fossil alkali; and, with volatile alkali, constitutes partly crystalline masses, and partly
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acicular and prismatic crystals; with magnesia, it forms a white powder, which dissolves in water. It dissolves copper and iron. The latter solution yields, upon evaporation, a yellowish white powder, which is insoluble. It likewise dissolves zinc, bismuth, arsenic and cobalt. With manganese, it forms crystals, of which the planes are parallel, and which, in some measure, resemble basalt. It does not precipitate lime from the marine acid, a circumstance, which, together with its effects on iron and magnesia, distinguishes it from acid of sugar.

According to Mr Westrumb's analysis, a resin may be obtained from the residuum of vitriolic æther, which contains vitriolic acid, vinegar, Glauber's salt, selenite, calcareous earth, flint, iron, and phosphoric acid.

Three varieties of zeolite have been discovered in the mountains of the Hartz, and the Tourmalin, or Mount Gothard in Switzerland.

In Cornwall, two mines have been found, extremely rich in the new mineral or acid, tungstein, which the experiment of Bergmann and Scheele have rendered so famous.

Prussian blue is half composed of iron, although Bergmann has maintained the contrary.

Mr Scheele has just discovered, that the salt obtained from urine, and known under the name of *acidum perlatum*, is not a peculiar acid; but that it is only phosphoric acid, disguised by a small quantity of fossil alkali, that is united with it. The analysis is confirmed by synthesis; for, by combining fossil alkali, with phosphoric acid, the author has obtained a true perlate acid. *Journal de Physique*, p. 316. Octobre 1785.

DISSER-

DISSERTATION ON PRUSSIAN BLUE.

Part II. 1783.

§ XI.

(A) **T**HE colouring liquor rectified, as directed in the preceding paragraph (p. 335.), appears to be neither acid nor alkaline; for it neither reddens paper dyed with lacmus, nor does it restore the colour of such paper after it has been made red; but it renders turbid the solutions of soap and hepar sulphuris.

(B) The same liquor, mixed with fixed alkali, produces a compound, which, though it contains a superabundance of the colouring matter, restores the blue colour of paper reddened by an acid. If this compound be distilled to dryness, there goes as much of the colouring matter over as can disengage itself from the alkali. The residuum is soluble in water, and the solution has all the properties of the best lixivium sanguinis. This solution is decomposed by all acids, even by the aerial acid (§ III.).

(c) Combined with caustic volatile alkali, it forms a kind of ammoniacal salt, which has the smell of volatile alkali, though the colouring matter be superabundant in the compound. This salt instantly rises by distillation, and there

remains nothing but pure water in the retort. I doubted at first whether this matter could enter into an union with the volatile alkali; but was soon convinced, when I saw that the solution of magnesia in the colouring matter was precipitated by volatile alkali. Besides, this ammoniacal salt shewed the same phænomena in the precipitations as the pure lixivium sanguinis does. (D) Magnesia, precipitated from Epsom salt by caustic volatile alkali, was found dissolved in the colouring matter, after they had been allowed to stand together for several days in a well closed bottle. When this solution was exposed to the open air, the magnesia separated from it, on account of its greater elective attraction for the aerial acid, and formed on the surface of the water a pellicle like that of cream of tartar. This solution was likewise decomposed by alkalis and by lime-water. (E) This matter dissolves but a very small quantity of terra ponderosa (*barotes* of Mr Morveau), which may be afterwards precipitated by vitriolic acid, and even by aerial acid. (F) Pure clay, or the basis of alum, is not attacked by it. (G) Lime is dissolved in a certain quantity by this matter. The superabundant portion should be separated by means of the filter; and as the liquor contains, besides the combined lime, the portion

tion which water itself is able to take up, in order to free it from this, precisely the same quantity of water, impregnated with aerial acid, is to be added, as is requisite for precipitating an equal quantity of lime-water. The colouring matter, thus saturated with lime, is to be filtered again, and then to be preserved in a well closed bottle, in order to prevent the access of the aerial acid. All acids, even the aerial, and the fixed caustic or pure alkalis, decompose this solution. Moreover, if it be distilled to dryness, a portion of the colouring matter is disengaged at the very beginning of the distillation from the lime; and there remains, at the end of the distillation, nothing behind but pure lime. As it appeared to me that the colouring matter was, if I may say so, completely neutralised by the lime, in the manner just mentioned, (though this solution, as well as that of magnesia and terra ponderosa, still restores the blue colour of turn-sol which has been turned red), I resolved to employ it, in preference, for precipitating all the metallic substances; and I shall consequently call it the *precipitating liquor*.

§ XII.

(A) The colouring matter has no sensible action, either upon metals or upon metallic

metallic solutions, except upon nitrated silver, which is precipitated in the form of a white powder; nitrated mercury, which is precipitated in the form of a black powder; and the solution of iron in aerial acid, which is precipitated first of a sea-green colour, but at last changes to a blue colour. The other metallic solutions undergo no change. (B) This matter has a more sensible action upon the calces and metallic precipitates: All the calces, however, are not attacked; for it produces no effect upon the calces of platinum, tin, lead, bismuth, iron, manganese, and antimony; as little does it act upon the acids of molybdæna and of arsenic. The following are the phenomena which it presents with the other metallic calces: Gold, precipitated by aerated alkali, becomes white. From silver, precipitated by the same alkalis, it disengages the aerial acid with a slight effervescence, but the calx preserves its white colour. It dissolves the calx of quicksilver, and yields crystals by means of a gentle evaporation. The calx of copper, precipitated by aerated alkali, effervesces, and assumes a faint citron colour. Calx of iron, precipitated from its solution in the vitriolic acid by the same alkali, effervesces, and assumes a dark blue colour. Precipitated cobalt shews some signs of an

an effervescence, and changes into a yellowish brown colour. Calx of manganese, precipitated from its solution by aerated alkali, is not attacked.

§ XIII.

The precipitating liquor (§ XI. G) acting upon the metallic solutions by means of a double elective attraction, must present phænomena with these solutions different from those which the pure colouring matter produces. (A) If a quantity of this liquor be poured into a well saturated solution of gold, the gold precipitates in the form of a white powder; but if it be added in excess, the precipitate will be redissolved. This solution is colourless, like water. The precipitate is not soluble in acids. (B) The solution of platinum is not changed. (C) Silver is precipitated of a white colour, and of a consistence like that of cheese. If more of the liquor be added, the precipitate is redissolved. This solution is not decomposed either by sal ammoniac or by muriatic acid. The white precipitate is insoluble in acids. (D) Corrosive sublimate seems to undergo no change on pouring this liquor into a solution of it, though it is really decomposed, being, of all the metallic calces, the only one which can be dissolved by the colouring matter (§ XII. B). (E) Mercury

cury dissolved in nitrous acid, without the application of heat, is precipitated in the form of a black powder, which is reduced mercury. (F) Tin dissolved in aqua regia is precipitated of a white colour; but as the mixture gave out a smell very much resembling the smell of the colouring matter, I examined the precipitate, and found that it was nothing but the pure calx of tin soluble in acids. (G) The solution of bismuth shewed the same phenomena. (H) The liquor also produced the same effects upon the solution of butter of antimony; (I) as likewise upon the solution of well dephlogisticated calx of iron. (K) Vitriolated copper, dissolved in water, was precipitated of a yellow citron colour. If more of the precipitating liquor be added, the precipitate will be redissolved, and this solution will be colourless. This precipitate likewise dissolves in volatile alkali without any colour. If more of the solution of vitriolated copper be added, the precipitate likewise disappears, and the solution assumes a green colour. Acids dissolve a portion of this precipitate, and what remains of it is white. The muriatic acid dissolves the yellow precipitate completely; but it is again precipitated by water. (L) The solution of vitriol of zinc in water yields a white precipitate, which is not redissolved

solved on adding more of the precipitating liquor; but it is soluble in acids. These solutions have the smell of the colouring matter, which latter may really be separated from them by distillation. (M) Vitriol of iron is first precipitated of a yellowish brown colour, which soon changes to green, and then becomes blue on the surface. Some hours afterwards the precipitate subsides to the bottom of the vessels, and then the whole mixture turns blue; but, on adding any acid, the precipitate becomes instantly blue. If a very small quantity of vitriolated iron be put into the precipitating liquor, the precipitate entirely dissolves, and imparts to the mixture a yellow colour (§ II. A, C). (N) From the solution of cobalt, a brown yellow precipitate is thrown down, which does not dissolve on adding more of the precipitating liquor; neither will it dissolve in acids. (O) Lead dissolved in vinegar is precipitated in the form of a white powder, which more liquor does not dissolve; but, when welledulcorated, it is soluble in acids. If the solution be distilled, the colouring matter goes over into the receiver.

(P) Vitriolated manganese suffers no decomposition.

§ XIV. *On the constituent Parts of the colouring Matter.*

I met by accident with a very remarkable phenomenon : As I was one evening about to pour the liquor of the first distillation of the colouring matter out of the receiver into a bottle (§ VI.), and a burning candle happened to be standing near the orifice, the air contained in the receiver instantly took fire, without, however, any explosion. As long as the mass continued warm in the receiver, (for the distillation was forced rather a little too much), I was able to inflame this air several times, till at last it would no more take fire. As all the phlogistic substances, from the vegetable as well as animal kingdom, contain aerial acid as one of their constituent parts, I wished to know whether there was any of this acid contained in the colouring matter. I therefore filled a small retort half full with this latter, and, after applying a receiver, gave it immediately a pretty strong heat. The receiver soon grew hot, and as it was at the same time filled with thick vapours of the colouring matter, I separated it from the retort, and presented to its orifice a little burning sulphur*, which I introduced
even

* When we make use of a candle for this purpose, we can never be sure that the aerial acid does not
come

even into its cavity. The air in the receiver took fire instantly. I afterwards poured some very clear lime-water into it, which was immediately precipitated. Hence it may be concluded, that the aerial acid and phlogiston exist in this colouring matter. But several chemists having asserted that the Prussian blue constantly yields volatile alkali upon distillation, in order to verify this observation, I prepared on purpose some perfectly pure Prussian blue from vitriol of iron, and from the precipitating liquor.

§ xv.

I distilled this Prussian blue in a glass retort, to which I adapted a receiver, in which I had put a little distilled water. I pushed the fire till the bottom of the retort was red hot. After the distillation was over, I found that the water in the receiver contained colouring matter and volatile alkali, but no oil. The air in the receiver was impregnated with the same matter, and with aerial acid. What remained in the retort was black, and obeyed the loadstone. It therefore appears, that

come either from the tallow or from the wick. I was thus deceived several times, on setting fire to inflammable air. It is, therefore, better to use a little brimstone fixed upon the end of an iron wire.

that the volatile alkali enters into the composition of the colouring matter. I thought it, however, of importance to examine what phænomena the other metallic precipitations, prepared with the same precipitating liquor, would shew when distilled in the same manner. (B) The yellow brown precipitate of cobalt (§ XIII. N) yielded just the same products as the precipitate of iron. The residuum in the retort was black. (c) The yellow precipitate of copper took fire, and emitted, from time to time, slight sparks during the distillation. It yielded but a very small quantity of colouring matter; but much more aerial acid and volatile alkali than the precipitates before mentioned. There was likewise a sublimate in the neck of the retort; but in too small a quantity for making experiments. The residuum in the retort was reduced copper. (D) The precipitate of zinc shewed the same phænomena as Prussian blue. (E) The precipitate of silver yielded likewise volatile alkali and aerial acid, but chiefly colouring matter. There was likewise a little sublimate in the neck of the retort, which contained some silver in combination. The residuum was reduced silver. (F) The compound formed by the calx of mercury dissolved in the colouring matter, and crystal-

lised

hsed (§ XII. B), yielded, by means of distillation, a little of the colouring matter; but hardly any mark of volatile alkali. In the neck of the retort there was likewise some mercury sublimed, with a portion of the original compound.

(G) Hence I was disposed to believe, that the constituent parts of the colouring matter were volatile alkali, and an oily substance. In this opinion I was the more confirmed, when I saw, that, on dissolving martial vitriol in spirit of hartshorn, recently distilled, and adding to it muriatic acid, I obtained Prussian blue. I however distilled oxes blood, till nothing more would pass over into the receiver, and the retort was red hot. I filtered the liquor of the receiver, in order to separate from it the empyreumatic oil, and then dissolved a little martial vitriol in it, and added a superabundant quantity of acid; and thus likewise obtained Prussian blue. (H) I then resolved to make several experiments, the principal purpose of which should be, to unite the volatile alkali with some oily substance. For this purpose, I distilled a mixture of concrete volatile alkali and unctuous oil; a mixture of the same alkali with animal fat; and, on another occasion, with oil of turpentine; a mixture of quicklime, sal ammoniac and axunge; the same mixture with

oil of hartshorn; likewise a mixture of potashes, sal ammoniac, and empyreumatic oil; the same mixture with axunge; but all in vain. The liquors obtained in the receiver, which consisted of phlegm, mixed with volatile alkali and oil, never yielded even the slightest mark of Prussian blue. Hence I concluded, that, though aerial acid and phlogiston are obtained every time any oil is decomposed, it at the same time contains water intimately combined with the other constituent parts, and that it is absolutely necessary that this water should be separated from them, before a perfect union of the volatile alkali can take place. We know that charcoal-powder, brought into fusion with fixed alkali, yields likewise a kind of lixivium sanguinis, though weak. I digested the colouring matter with concentrated vitriolic acid, and the mixture remained colourless. If this matter had contained any oily principle, the mixture would have become black or brown. Having reduced some pulverised blood, by calcination, to a coal, *viz.* the residuum in the retort (§ xv. c), I mixed with it an equal quantity of alkali of tartar, and exposed this mass in the ordinary manner to a red heat, and thus I obtained a very good lixivium sanguinis. It is hence evident, that no oily matter is required
for

for the production of the colouring matter.

§ XVI.

Lastly, I made the following experiments, which convinced me of the truth of my conclusion. I mixed three table-spoonfuls of charcoal-powder, with an equal quantity of pulverised alkali of tartar, and put the mixture into a crucible. I filled another crucible with a like mixture, and placed both of them at the same time upon burning charcoal. I kept them red hot for a quarter of an hour, and then threw one of the portions, which was perfectly red hot, into eight ounces of water. At the same time, I put into the other half an ounce of sal ammoniac, in small pieces, agitated the whole briskly together, taking care at the same time to push the sal ammoniac down towards the bottom of the crucible, which I then again placed in the fire. Observing, a couple of minutes afterwards, that there arose even then no more ammoniacal vapours, I threw the whole mass, red hot as it was, into eight ounces of water. I now filtered the first lixivium, and trying it in the ordinary way, with vitriol of iron and acids, it yielded little or no Prussian blue, (or at least not any sensible quantity); but it would perhaps have yielded

a little, if the fire had been pushed till the mass ran into fusion. I now filtered the second lixivium, and tried it in the same manner, with vitriol of iron, which immediately grew yellow, as if lixivium sanguinis had been added; and, on adding a sufficient quantity of acid, the same phenomena were observed, as the best lixivium sanguinis would have produced, and a great quantity of Prussian blue was procured. I mixed plumbago with the same alkali, and proceeding in the same manner with sal ammoniac, obtained a middling lixivium. From these experiments, it appears, that the volatile alkali is capable of uniting with the carbonaceous matter, after it has been subtilised by a strong heat; that it thus acquires the remarkable property of combining so firmly with alkali of tartar, as to be able to support the most violent degree of heat, (§ XI. B); and when this alkali is dissolved in water, there is obtained lixivium sanguinis, as it is called. It is now easy to explain what happens in the distillation of Prussian blue, as well as of the other above mentioned metallic precipitates, (§ XV. A—F). In the distillation of Prussian blue, for instance, the calx of iron attracts a portion of phlogiston from the colouring matter. The aerial acid being thus disengaged, must go over into the receiver

receiver with the volatile alkali, which is set free at the same instant; but as the calx of iron in the heat of this distillation cannot unite with more phlogiston, a portion of the colouring matter, not decomposed, must likewise arise. If the calx of iron could combine with the whole of the phlogiston, there would come nothing over into the receiver, but aerial acid and volatile alkali. In order to prove this, I distilled a mixture of six parts of manganese, finely powdered, and one part of pulverised Prussian blue, and I obtained in the receiver nothing but aerated volatile alkali, without the least mark of colouring matter.

It may be observed, 1. That it is probable that this matter may be made to assume aerial form, though I have hitherto not been able to effect this.

2. It is remarkable, that our colouring matter, after it has united with the alkali, or with the lime, forms a menstruum, capable not only of dissolving metallic calces, but also of constituting a triple salt, which is not decomposed by the aerial acid, as happens with the lixivium sanguinis and the precipitating liquor, when exposed to the free access of air. Iron is not the only metal which has the property of fixing the colouring matter (§ II. c), the same quality belongs
likewise

likewise to gold, silver, copper, and probably to several other metallic calces; for if after these calces have been precipitated, a sufficient quantity of precipitating liquor be added, in order to redissolve them, the solution remains clear in the open air, and in this state the aerial acid does not precipitate the metallic calx.

3. It is another remarkable circumstance, that except nitrated silver, nitrated mercury, and aerated calces (§ XII. A), this matter does not decompose metallic solutions by a single elective attraction. Now, as we know that Prussian blue is not soluble in acids, it naturally follows, that the colouring matter has a greater affinity with iron than acids have, notwithstanding there is no precipitation perceived when this matter is mixed with the solution of vitriol of iron. It may not be an easy matter to give a satisfactory explication of this phenomenon.

F I N I S.

