EXPERIMENTS

MADE IN ORDER TO ASCERTAIN

The Nature of ſome Mineral Subſtances;

AND, IN PARTICULAR,

To ſee how far the Acids of Sea-Salt and of Vitriol contribute to mineralize Metallic and other Subſtances.

BY PETER WOULFE, F. R. S.

Who was nominated by the Preſident and Council to proſecute Diſcoveries in Natural Hiſtory, purſuant to the Will of the late HENRY BAKER, Eſq. F. R. S.

EXPERIMENTS, &c.

Gray's-Inn,
April 25, 1776.

R. June 20, 1776. THE late HENRY BAKER, Eſq. a worthy member of this honourable Society, full of laudable zeal for the advancement of natural knowledge, has moſt generouſly bequeathed the ſum of one hundred pounds, for the uſe of this reſpectable body; the intereſt of which he intended ſhould be annually applied for the benefit of ſuch member whom the Council of this Society thought proper to nominate, for the taſk of making diſcoveries in natural hiſtory. Theſe gentlemen have this year done me that honour, which I moſt gratefully acknowledge; and in conſequence of this appointment, I have made experiments on a variety of mineral ſubſtances.

IN order to aſcertain how far the method, I propoſed to purſue in the following experiments, was calculated for the purpoſe of making a proper analyſis of the minerals I here treat of; and particularly to diſcover the exiſtence of the acids of ſalt and vitriol in them; I thought it expedient to make ſome artificial preparations, which I judged to be ſimilar to the natural ſubſtances, and I ſubmitted them to the ſame trials, and in ſimilar quantities; for as many of the minerals, which are the ſubject of the preſent paper, are exceeding ſcarce, I was under the neceſſity of uſing in theſe experiments ſmaller quantities of them, than I ſhould otherwiſe have employed.

[*a*] With that intent, I diſſolved half an ounce of refined ſilver in pure *aqua fortis*, and made a *luna cornea*, by adding to it a ſolution of ſea-ſalt in water; this was well edulcorated, dried firſt in the air, and afterwards with a ſtrong heat, but not ſo great as to melt it; the *luna cornea*, thus obtained, weigh five drams and one ſcruple, which is one-third more than the original weight. I muſt here obſerve, that I have uſed Troy-weights in all theſe experiments.

[*b*] The like quantity of the ſame ſilver, diſſolved in the ſame acid, and precipitated with a ſolution of tartar of vitriol, and treated as at [*a*], weighed five drams and twenty-two grains. It is worthy of obſervation, that if *ſal polychreſt* be made uſe of in the place of tartar of vitriol, its precipitate will not exceed three drams and fifty-

four grains; but if acid of ſalt, or a ſolution of ſea-ſalt, be added to the waſhings of this precipitate, the remainder of the ſilver is precipitated, and forms a *luna cornea.* This ſhews, that there is a difference between tartar of vitriol and *ſal polychreſt*, notwithſtanding what chemiſts think to the contrary; and indeed, upon trial, I found the *ſal polychreſt* to contain a ſmall portion of liver of ſulphur. Silver dipped into a warm ſolution of this ſalt becomes inſtantly black; thus the *ſal polychreſt* may be readily diſtinguiſhed from tartar of vitriol, which does not tarniſh ſilver.

The precipitate of ſilver, by tartar of vitriol put on a red-hot iron, melts and grows liquid like *luna cornea.* The precipitate of ſilver by *ſal polychreſt*, treated in the ſame manner, does not grow ſo liquid, but boils up and at laſt dries.

[*c*] Half an ounce of lead, diſſolved in *aqua fortis*, and precipitated by a ſolution of tartar of vitriol, edulcorated and dried, weighed five drams and a half.

[*d*] The like quantity of lead, diſſolved as at [*c*], precipitated with a ſolution of ſea-ſalt, edulcorated and dried, weighed only half an ounce and eighteen grains. A ſolution of tartar of vitriol, added to the waſhings of this precipitate, cauſed a freſh precipitation, which, after edulcoration and exſiccation, weighed forty-two grains. Hence we ſee, that lead united to acid of ſalt is ſoluble in water, and on that account ſo ſmall a quantity of precipitate was obtained; but the tartar of vitriol precipitating its waſhings (for the acid of vitriol does the ſame) ſhews,

that

that lead has a greater affinity with this acid than with that of ſea-ſalt; it alſo ſhews, that this combination of lead with acid of vitriol is inſoluble. That moſt excellent chemiſt Mr. MARGRAF, in his experiments on the Bolognian *phoſphorus*, has ſhewn how the Bolognian ſtone and other ſuch ſpars, as well as the *gypſa*, are decompoſed by fixed alkalies; but, as it was neceſſary to employ an exceſs of alkaly to decompoſe them thoroughly, the quantity of neutral ſalt he thereby obtained could not be accurately aſcertained, on account of its mixture with the alkaly. I ſo far availed myſelf of this learned chemiſt's method; but contrived to remove that inconveniency, in ſuch a manner that the exceſs of alkaly was ſeparated, and the neutral ſalt left pure. This conſiſts in ſaturating the ſalt with diſtilled vinegar, evaporating the mixture ſlowly to dryneſs, and diſſolving the *ſal diureticus*, formed by the combination of the vinegar and exceſs of alkaly, in rectified ſpirit of wine, for this ſalt is very ſoluble in it; whereas the combinations of the acids of vitriol and of ſea-ſalt, with either vegetable or marine alkaly, are no way ſoluble in this ſpirit. I muſt here obſerve, that no fixed alkaly is quite free from neutral ſalt; but the pureſt is that made with good tartar. Two drams of the alkaly, I made uſe of for my experiments, contained two grains of tartar of vitriol, for which I made an allowance in all my experiments. The quantity of neutral ſalt in any alkaly may be accurately aſcertained by this method; and I can take upon me to ſay, that

that a ſingle grain of neutral ſalt in an ounce of *alkaly* may be diſcovered by this proceſs.

EXPERIMENT I.

Two drams of the horn ſilver [*a*] were well ground in a glaſs mortar, with an equal quantity of fixed alkaly of tartar, and diſtilled water enough to make the mixture of a ſoft conſiſtence; it was then taken out of the mortar, and deprived of its moiſture in a china cup fixed in a ſand heat. The mixture was then powdered and put into a common green ounce phial, and this into a crucible, and ſurrounded with ſand up to its neck. The crucible was fixed in a proper furnace, and a fire made round it, which was increaſed by degrees until the phial became of a dull red colour, in which ſtate it was kept for an hour. The crucible was then taken out of the fire, and, when quite cold, the phial was broken; care was taken to ſeparate the matter from the broken bits of glaſs. This matter was of a ſpungy texture, and would not powder, but flatted in the mortar, and then ſhewed its ſilvery appearance; it was, therefore, cut into thin ſlices and digeſted with four ounces of diſtilled water; the ſolution was poured off and filtered, and four ounces more of the like water added to what remained undiſſolved; this alſo, after digeſtion, was poured off, filtered, and added to the firſt ſolution. By this means the ſilver was deprived of all its ſaline part. The ſolution was evaporated ſlowly to about one-half, and then ſaturated with diſtilled vinegar; this was afterwards filtered, gently

evaporated to dryneſs, and freed from its *ſal diureticus* by three lotions with rectified ſpirit of wine. The neutral ſalt here remaining was diſſolved in a ſmall portion of diſtilled water, then filtered and put into a wine-glaſs, covered with filtering paper, to keep out the duſt. In about three months it was quite dry, and conſiſted of ſmall, flat, cubical cryſtals of regenerated ſea-ſalt, which altogether weighed fifty-five grains.

EXPERIMENT II.

Two drams of the precipitate of ſilver, by tartar of vitriol [*b*], treated as in the firſt experiment, produced one dram and ſeven grains of brown tartar of vitriol.

EXPERIMENT III.

Two drams of precipitate of lead, by tartar of vitriol [*c*], treated as in the firſt experiment, produced one dram and five grains of brown tartar of vitriol.

EXPERIMENT IV.

Two drams of precipitate of lead, by ſea-ſalt [*d*], afforded one dram and one grain of cubical cryſtals of regenerated ſea-ſalt.

EXPERIMENT V.

Two drams of *mercurius dulcis*, treated in the like manner, produced thirty-eight grains of cubical cryſtals of regenerated ſea-ſalt.

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EXPERIMENT VI.

Two drams of turbith mineral (made by precipitating a ſolution of quickſilver in acid of nitre by a ſolution of tartar of vitriol, well edulcorated and dried), treated as in the firſt experiment, produced thirty-ſix grains of brown tartar of vitriol.

In the firſt and ſecond experiments, the ſilver regained its metallic form; in the third and fourth the lead was reduced to the ſtate of maſſicot; and, in the fifth and ſixth the quickſilver was totally diſſipated.

From the foregoing experiments it is clear, that combinations of the acids of ſea-ſalt and of vitriol with ſilver, lead, and quickſilver, are decompoſed by theſe means; and alſo, that the quantity of neutral ſalt, which their acids form by combination with the alkaly, is aſcertained. Having premiſed theſe experiments on artificial ſubſtances, I now come to thoſe made with natural ones, which are the ſubject of the preſent paper.

OF NATIVE HORN SILVER.

Horn ſilver is found of various colours, *viz.* green, yellow, brown, purple, and alſo black. When cryſtallized, it forms perfect cubes; it readily melts when put upon a red-hot iron, but does not ſmoke; it may be eaſily cut with a knife, for it is ſomewhat malleable; we muſt, however, except the black ſort, which is brittle, and may be powdered. Some authors will have it, that

this mineral is compoſed of ſilver, ſulphur, and arſenic; ſome, of ſilver ſulphur, arſenic, and fixed alkaly; others, of ſilver, arſenic and acid of ſea-ſalt; but Meſſ. CRONSTEAD and LE SAGE aſſert, that it is compoſed of ſilver and acid of ſalt only. I know of no experiments that have been made public with a view to determine this affair, except thoſe of M. LE SAGE; but he and I differ widely in the reſult of our experiments.

EXPERIMENT VII.

Two drams of brown, native horn ſilver, cut into very thin ſlices, and well ground with the like quantity of fixed alkaly of tartar and a little water, treated as in the firſt experiment, produced forty-three grains of neutral ſalt, compoſed of flat cubic cryſtals of regenerated ſea-ſalt, intermixed with brown cryſtals of tartar of vitriol; this laſt did not appear to be above one-third of the firſt.

The brown colour of the horn ſilver is owing to an ochre of iron; a thin ſlice of it, viewed through a magnifying glaſs, looks in ſome parts of a ſmooth pearly colour, but in others of a powdry brown one.

The ſilver, which remained after this operation, had the ſame texture and ſilvery appearance as that of the firſt experiment. It was digeſted with diſtilled vinegar, then filtered and evaporated to one-fourth, with a deſign to diſſipate the exceſs of acids. A freſh infuſion of galls mixed with it becomes of a dark purple colour, which precipitates; an inconteſtible proof of the iron it contains,

Silver, in its metallic ſtate, is not ſoluble in diſtilled vinegar.

EXPERIMENT VIII.

Two drams of the pearl-coloured horn ſilver, treated with the like quantity of fixed alkaly as in the firſt experiment, produced fifty-one grains of neutral ſalt, compoſed of flat cubic cryſtals of regenerated ſea-ſalt, with a mixture of brown cryſtals of tartar of vitriol; this laſt, in appearance, is about a fourth or more of the firſt. The ſilver here remaining had the ſame appearance as that of the firſt experiment; it alſo gave marks of its containing iron, but not near ſo great a quantity as that of the ſeventh experiment.

EXPERIMENT IX.

The brittleneſs and colour of the black horn ſilver made me at firſt doubt of its being horn ſilver; and I thought, that, if it contained any, it muſt be mixed with ſome other mineral ſubſtance. Volatile alkalies having the property of diſſolving all combinations of ſilver with acids, I availed myſelf of that well-known property on this occaſion. I took, therefore, ſeven drams of the black horn ſilver, and digeſted it at three different times with a large portion of volatile ſpirit of hart's-horn; this ſpirit I preferred to that of *ſal ammoniac*, as I knew it to be free from acid of ſalt. The three ſolutions were mixed, filtered, and ſlowly evaporated to dryneſs, and produced two drams and two ſcruples of a dark ſlate-coloured horn ſilver.

ſilver. Forty-ſix grains of artificial horn ſilver [*a*], diſſolved in ſpirit of hart's-horn, and dried in the ſame ſlow manner, increaſed only two grains in weight, and was of the ſame dark colour; owing, no doubt, to a ſmall portion of volatile ſpirit adhering to it.

The two drams and two ſcruples of horn ſilver, obtained by means of the ſpirit of hart's-horn, were well mixed with an equal quantity of ſalt of tartar; and being treated as in the firſt experiment, produced one dram and eleven grains of neutral ſalt, conſiſting of flat cubical cryſtals of regenerated ſea-ſalt, intermixed with brown cryſtals of tartar of vitriol, which laſt appeared to be in leſs proportion than in the former experiments. The ſilver, after this operation, had the ſame ſpongy, ſilvery appearance as in the former experiments. The undiſſolved part of of the horn ſilver, which remained after its horn ſilver was extracted by the ſpirit of hart's-horn, retained its black colour. It was calcined in a crucible, and, during the calcination, a ſulphureous ſmell was obſerved; the calcination was continued until this ſmell ceaſed. It had now an aſh-colour, ſilvery appearance, and, during the operation, ſlightly caked together, which made me think it had yet ſome horn ſilver; I therefore digeſted it with more ſpirit of harts-horn; and, having evaporated the ſolution ſlowly to dryneſs, I obtained thirty-four grains of horn ſilver; the undiſſolved part here remaining, being melted with black flux, produced two drams and a half of pure ſilver, ſo that black horn ſilver is compoſed of horn ſilver and ſulphurated ſilver. The ſolution of the

the three ſorts of horn ſilver in ſpirit of hart's-horn were as colourleſs as water; a proof they contain no copper.

To give a proof of the exiſtence of the acid of ſalt in the horn ſilver, I took four grains of the cubical cryſtals obtained in the ſeventh, eighth, and ninth experiments, and having put them into ſeparate wine-glaſſes, poured a little oil of vitriol on each, which made them all boil up, efferveſce, and ſend forth copious fumes of acid of ſalt, juſt as the like quantity of ſea-ſalt would have done.

In order to give alſo a convincing proof, that the horn ſilver contained acid of vitriol, I availed myſelf of M. MARGRAF's diſcovery, who ſays, that a ſolution of calcareous earth in acid of nitre is precipitated by a ſolution of tartar of vitriol; for the acid of vitriol forſakes its alkaly to unite, and form a ſelenite with the calcareous earth. I therefore diſſolved twelve grains of tartar of vitriol in diſtilled water, and having filtered the ſolution, I added to it a ſufficient quantity of a ſolution of chalk in acid of nitre, which cauſed a precipitation; this precipitate, being edulcorated and dried, weighed ſeven grains: this ſerved as a comparative experiment. It is probable, from the ſmall quantity of this precipitate, that the whole of the tartar of vitriol was not decompoſed. It ſhews, however, that ſeven grains of this precipitate require twelve grains of tartar of vitriol to their formation.

The neutral ſalt of the ſeventh experiment, treated in the like manner, produced eight grains of ſelenite; that

of

of the eighth, ſeven grains and a half; and that of the ninth ten grains.

In calcining the different ſpecimens of horn ſilver with the alkalies in the foregoing experiments, I could perceive no ſmoke or ſmell iſſue out of the phials. Hence I conclude, that the horn ſilver contained no arſenic; and that none of it was diſſipated during the operation.

From the foregoing experiments it appears, that the horn ſilver is compoſed of ſilver united to the acids of ſalt and of vitriol; and that this laſt is nearly one-third of theſe firſt.

OF HORN MERCURY.

I diſcovered this mineral about four years ago, when I was collecting minerals at Obermoſchel, in the Dutchy of Deux Ponts. I have ſince ſeen it in a fine collection abroad; but no one ſuſpected what it was until I had made it known, for it was taken for an inſignificant ſpar. I have found this mineral of three colours; white, and of a ſhining brightneſs; yellow, and alſo black; this laſt owes its colour to a mixture of minute particles of live quickſilver. This ſubſtance cryſtallizes in various forms; but the cryſtallization is too ſmall to be deſcribed without the help of a microſcope.

EXPERIMENT X.

I took three drams of horn mercury, picked as clean as poſſible from the cinnabar and ſtony matter to which it adhered, and treated it with two drams of ſalt of tartar

as

as in the firſt experiment. The quantity of neutral ſalt here obtained was only half a dram, and it was compoſed of flat, cubical cryſtals of regenerated ſea-ſalt, intermixed with about an equal quantity of brown cryſtals of tartar of vitriol. The quickſilver was all diſſipated in the operation, as in the fifth experiment. Four grains of the cubic cryſtals, mixed with oil of vitriol, boiled up, and ſent out copious fumes of acid of ſalt. The remainder of the neutral ſalt was diſſolved in diſtilled water, and mixed with a ſufficient quantity of a ſolution of chalk in acid of nitre; the precipitate, here obtained, being edulcorated and dried, weighed eight grains and a half. Hence we may conclude, that this mineral is compoſed of quickſilver united to a greater proportion of acid of vitriol, than of acid of ſalt.

The horn-mercury uſed for this experiment was intermixed with minute *globules* of quickſilver, which could not well be ſeparated, to which the ſmall produce of half a dram of neutral ſalt was owing; and, indeed, to obtain the three drams of horn-mercury employed for this experiment, it was neceſſary to deſtroy ſeveral beautiful ſpecimens.

The ingenious M. LE SAGE, of the French Academy of Sciences, has publiſhed many experiments to ſhew, that the acid of ſalt contributes to mineralize a great variety of mineral ſubſtances; but I have tried a great number of them without obtaining an atom, either of acid of ſalt, or acid of vitriol. Among theſe are the

following, which were ſubmitted to the ſame trials as in the firſt experiment.

White ſpathoſe iron ore from Bayreuth.

Corniſh and Bohemian tin grains.

Mendip calamine.

Semi-pellucid calamine, from Wales.

Sooty kobalt, from Saxony.

Somerſetſhire manganeſe; this is the only ſort I ever ſaw which is mixed with calcareous ſpar, and, on that account, effervеſces with acids without help of heat.

Ceruſſa nativa, in lump, from Lorraine; I found this to conſiſt of a *calx* of lead, mixed with an argillaceous earth.

White, tranſparent, lump lead ore, from Somerſetſhire.

Cat's-tooth white lead ore, from Ireland.

White lead ore, from Poulaſent in Low Brittany.

Black, whitiſh lead ore, from Tſchoppan in Saxony.

Green lead ore, from ditto.

Green lead ore, from Freibourg in Briſcau.

In all theſe experiments the lead was converted to maſſicot; but, in the two laſt, the maſſicot had a pale greeniſh caſt, owing to iron, and not to copper: for if theſe green lead ores, after having been calcined with fixed alkaly and edulcorated, be digeſted with acid of vitriol, we obtain a greeniſh ſolution; this being then deprived of its exceſs of acid by an alkaly, filtered and mixed with infuſion of galls, gives a black, inky colour.

Having

Having now tried in my manner, without ſucceſs, a great number of the minerals which M. LE SAGE affirms to contain the acid of ſalt, it became alſo neceſſary to try his method; and I choſe ſuch ſubſtances as he ſays are the moſt replete with that article.

EXPERIMENT XI.

White, ſpathoſe, iron ore from Bayreuth, tried in M. LE SAGE's manner.

I put into a ſmall glaſs retort three ounces of this mineral powder, and poured on it an equal quantity of oil of vitriol. The retort was placed in a proper reverberatory furnace, and a quilled receiver luted to it; an ounce meaſure of oil of tartar, *per deliquium*, was previouſly put into the receiver, and ſhaken ſo as to moiſten all its internal parts: a very ſlow fire was made under the retort, ſuch as cauſed no moiſture to riſe; and this gentle degree of heat was continued for five hours. In a little time the upper part of the receiver was lined with long ſpiculine cryſtals; and, after the operation, the oil of tartar, which was at the bottom of the receiver, was, for the moſt part, cryſtallized.

EXPERIMENT XII.

Somerſetſhire manganeſe, treated in the like manner, produced the ſame ſpiculine cryſtals in the upper part of the receiver; and the oil of tartar was, in like manner, cryſtallized. It was here neceſſary, on account of the

efferveſcence of the mixture, to make uſe of a larger retort, and to let it ſtand for twelve hours before any fire was made under it, in which time the ſpiculine cryſtals appeared.

EXPERIMENT XIII.

Somerſetſhire white-lead ore, treated in like manner, ſhewed the like appearances; but here there was only a very ſlight efferveſcence.

EXPERIMENT XIV.

Corniſh tin-grains, treated in this manner, cauſed no change in the oil of tartar; nor was there the leaſt appearance of cryſtallization in the receiver.

EXPERIMENT XV.

White ſpathoſe iron ore, diſtilled *per ſe* with a ſtrong fire, ſhewed the ſame appearance of cryſtallizations in the oil of tartar and in the upper part of the receiver, as when diſtilled with oil of vitriol; ſee the eleventh experiment.

I now ſaturated each of the cryſtallized alkalies of the eleventh, twelfth, thirteenth, and fifteenth experiments, with diſtilled vinegar, and having filtered them, they were ſlowly evaporated to dryneſs, and diſſolved with rectified ſpirit of wine, as in the firſt experiment, but no neutral ſalt was left; from hence we may certainly conclude, that theſe minerals contained neither acid of ſalt, nor acid of vitriol. The cauſe of the cryſtallization of

the oil of tartar is owing to the phlogiſtic fixed air of the the minerals; but of this I ſhall treat more fully in another paper; and will now only add, that chalk, diſtilled *per ſe*, with a ſtrong fire, makes the oil of tartar in the receiver alſo cryſtallize. I muſt, however, own, that no cryſtallization is obſerved in the upper part of the receiver; nor was it to be expected, on conſidering the moiſture which the chalk affords in diſtillation.

M. LE SAGE ſays, that the cryſtallizations in the upper part of the receivers in his experiments were compoſed of cubic cryſtals; but in all mine they were ſpiculine.

By the foregoing experiments it appears, that ſilver and quickſilver are the only ſubſtances which are mineralized by the acid of ſalt, and that they are alſo combined with acid of vitriol.

Though the reſult of my experiments has been very different from that of the ſame ſubſtances examined by M. LE SAGE, yet I have too high an opinion of him, and know him too well, to call his veracity in queſtion. I am rather inclined to ſuſpect that this difference may proceed, from his having uſed oil of vitriol that contained acid of ſalt. Mr. HOLKER, who prepares this acid in France, owned to me, that he had, in his firſt tryals, mixed ſea ſalt in the preparing of it, with a view to increaſe its quantity. Might not M. LE SAGE have made his experiments with ſuch an acid; and of conſequence obtained acid of ſalt from the ſubſtances he tried.