

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.

4 K 2

E X P E R I M E N T S, &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 propos'd 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 judg'd 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 dissolv'd 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 welledulcorated, 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 us'd Troy-weights in all these experiments.

[b] The like quantity of the same silver, dissolv'd in the same acid, and precipitated with a solution of tartar of vitriol, and treated as at [a], weigh'd five drams and twenty-two grains. It is worthy of observation, that if *sal polybreft* 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, afteredulcoration 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 spongy 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.

EXPE-

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, welledulcorated 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 mafficot; 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 alkali, 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 powdery 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 flow 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 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

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, beingedulcorated 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, beingedulcorated 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, effervesces 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 Brisgau.

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 andedulcorated, 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

622 *Mr. Woulfe's Experiments to ascertain*

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.

Somerfetshire 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 trials, 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.