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EXPERIMENTS
UPON
MAGNESIA ALBA, &C.,

By JOSEPH BLACK, M.D.

(1755).

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No. 1.

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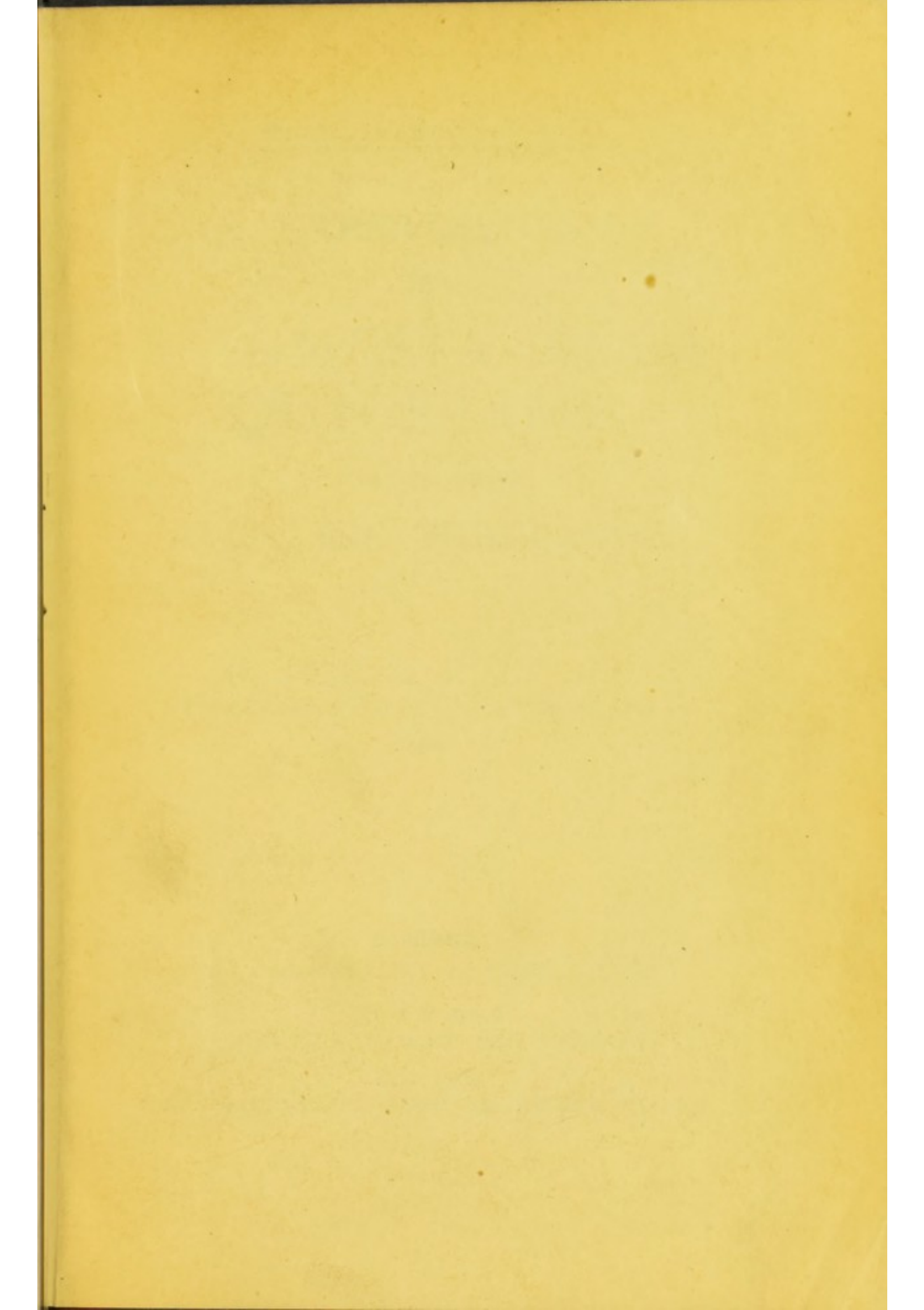
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EXPERIMENTS
UPON
MAGNESIA ALBA,
QUICKLIME,
AND SOME OTHER
ALCALINE SUBSTANCES

By JOSEPH BLACK, M.D.

Professor of Chemistry in the University of Edinburgh, 1766-1797
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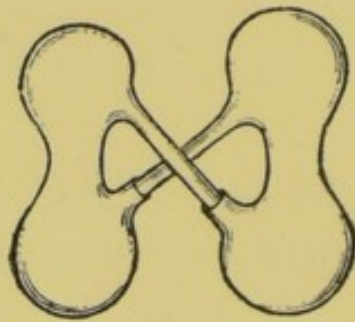
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PREFACE.

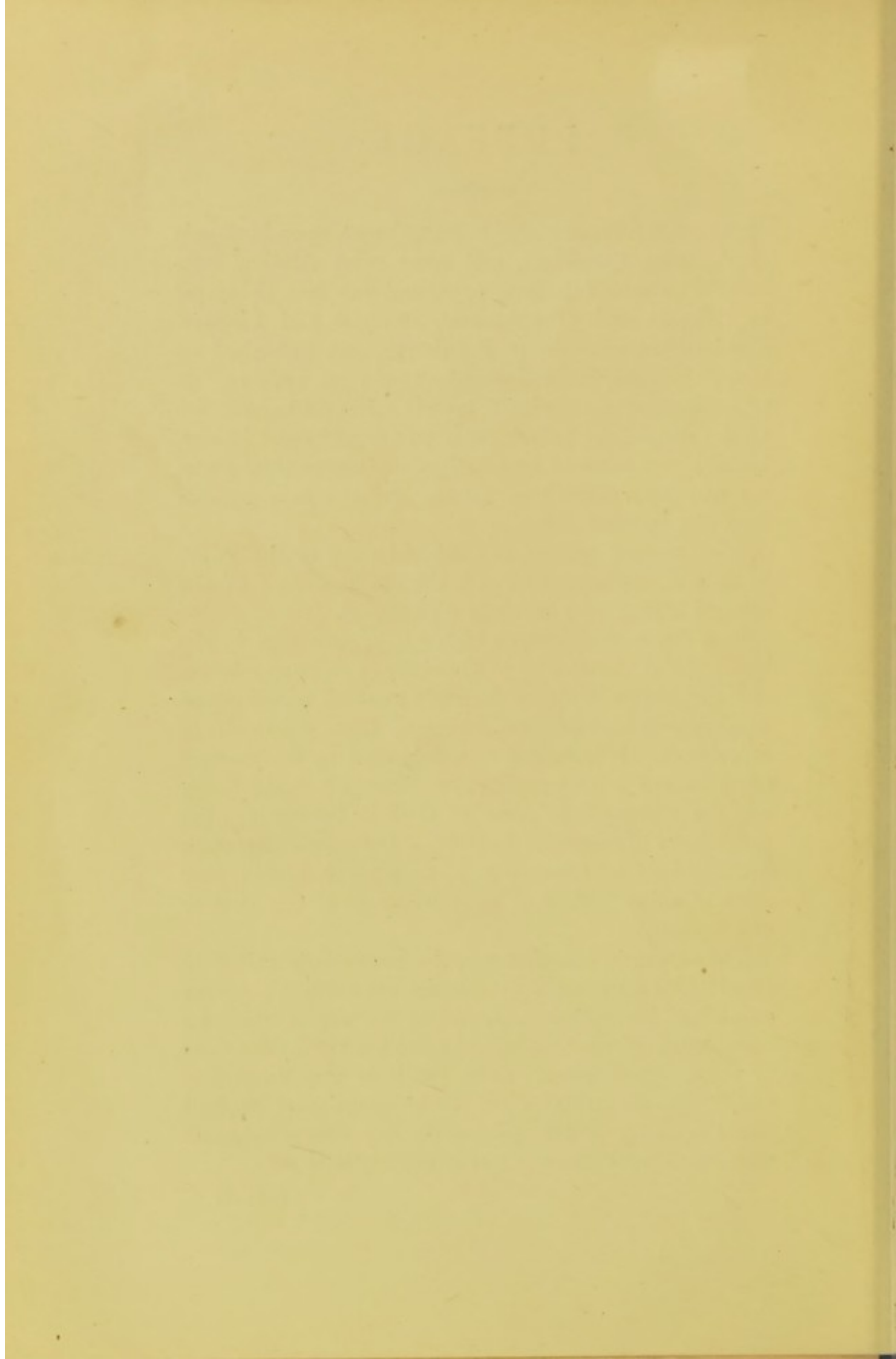
BLACK'S Paper entitled "Experiments upon Magnesia Alba, Quicklime, and some other Alcaline Substances" was read in June 1755, and was first published in "Essays and Observations, Physical and Literary. Read before a Society in Edinburgh, and Published by them," Volume II., Edinburgh, 1756; pp. 157-225. It was subsequently reprinted several times during the life of the author, not only in later editions of these Essays, but also in a separate form. Copies of the original Paper are now very difficult to obtain, and the later reprints have also become scarce.

The present reprint is a faithful copy of the Paper as it first appeared in 1756, the spelling, &c., of the original having been carefully reproduced.

The Paper constitutes a highly important step in the laying of the foundations of chemistry as an exact science, and furnishes a model of carefully planned experimental investigation, and of clear reasoning upon the results of experiment. It is neither so widely read by the younger chemists nor is it so readily accessible as it ought to be, and the object of the Alembic Club in issuing it as the first volume of a series of Reprints of historically important contributions to Chemistry, is to place it within easy reach of every student of Chemistry and of the History of Chemistry.

The student's attention may be particularly called to Black's tacit adoption of the quantitative method in a large number of his experiments, and to the way in which he bases many of his conclusions upon the results obtained in these experiments. Even yet it is very frequently stated that the introduction of the quantitative method into Chemistry (which did not by any means originate with Black) took place at a considerably later date.

L. D



EXPERIMENTS
UPON
MAGNESIA ALBA, QUICKLIME,
AND SOME OTHER
ALCALINE SUBSTANCES;
By JOSEPH BLACK, M.D.*

PART I.

HOFFMAN, in one of his observations, gives the history of a powder called *magnesia alba*, which had long been used and esteemed as a mild and tasteless purgative; but the method of preparing it was not generally known before he made it public.†

It was originally obtained from a liquor called the *mother of nitre*, which is produced in the following manner:

SALT-PETRE is separated from the brine which first affords it, or from the water with which it is washed out of nitrous earths, by the process commonly used in crystallizing salts. In this process the brine is gradually diminished, and at length reduced to a small quantity of an unctuous bitter saline liquor, affording no more salt-petre by evaporation; but, if urged with a brisk fire, drying up into a confused mass which attracts water strongly, and becomes fluid again when exposed to the open air.

* June 5. 1755.

† Hoff. Op. T. iv. p. 479.

To this liquor the workmen have given the name of the *mother of nitre*; and *Hoffman*, finding it composed of the *magnesia* united to an acid, obtained a separation of these, either by exposing the compound to a strong fire in which the acid was dissipated and the *magnesia* remained behind, or by the addition of an alkali which attracted the acid to itself: and this last method he recommends as the best. He likewise makes an inquiry into the nature and virtues of the powder thus prepared; and observes, that it is an absorbent earth which joins readily with all acids, and must necessarily destroy any acidity it meets in the stomach; but that its purgative power is uncertain, for sometimes it has not the least effect of that kind. As it is a mere insipid earth, he rationally concludes it to be purgative only when converted into a sort of neutral salt by an acid in the stomach, and that its effect is therefore proportional to the quantity of this acid.

ALTHO' *magnesia* appears from this history of it to be a very innocent medicine, yet having observed, that some hypochondriacs who used it frequently, were subject to flatulencies and spasms, he seems to have suspected it of some noxious quality. The circumstances however which gave rise to his suspicion, may very possibly have proceeded from the imprudence of his patients, who, trusting too much to *magnesia*, (which is properly a palliative in that disease,) and neglecting the assistance of other remedies, allowed their disorder to increase upon them. It may indeed be alledged, that *magnesia*, as a purgative, is not the most eligible medicine for such constitutions, as they agree best with those that strengthen, stimulate and warm; which the saline purges commonly used are not observed to do. But there seems at least to be no objection to its use when children are troubled with an acid in their stomach; for gentle

purging in this case is very proper, and it is often more conveniently procured by means of *magnesia* than of any other medicine, on account of its being intirely insipid.

THE above-mentioned Author observing, some time after, that a bitter saline liquor, similar to that obtained from the brine of salt-petre, was likewise produced by the evaporation of those waters which contain common salt, had the curiosity to try if this would also yield a *magnesia*. The experiment succeeded: and he thus found out another process for obtaining this powder, and at the same time assured himself by experiments, that the product from both was exactly the same.*

MY curiosity led me some time ago to inquire more particularly into the nature of *magnesia*, and especially to compare its properties with those of the other absorbent earths, of which there plainly appeared to me to be very different kinds, altho' commonly confounded together under one name. I was indeed led to this examination of the absorbent earths, partly by the hope of discovering a new sort of lime and lime-water, which might possibly be a more powerful solvent of the stone than that commonly used; but was disappointed in my expectations.

I have had no opportunity of seeing *Hoffman's* first *magnesia* or the liquor from which it is prepared, and have therefore been obliged to make my experiments upon the second.

IN order to prepare it, I at first employed the bitter saline liquor called *bittern*, which remains in the pans after the evaporation of sea water. But as that liquor is not always easily procured, I afterwards made use of a salt called *epsom-salt*, which is separated from the *bittern* by crystallization, and is evidently composed of *magnesia* and the vitriolic acid.

* Hoff. Op. T. iv. p. 500.

THERE is likewise a spurious kind of Glauber salt, which yields plenty of *magnesia*, and seems to be no other than the epsom salt of sea water reduced to crystals of a larger size. And common salt also affords a small quantity of this powder; because being separated from the bittern by one hasty crystallization only, it necessarily contains a portion of that liquor.

THOSE who would prepare a *magnesia* from epsom-salt, may use the following process.

DISSOLVE equal quantities of epsom-salt, and of pearl ashes separately in a sufficient quantity of water; purify each solution from its dregs, and mix them accurately together by violent agitation: then make them just to boil over a brisk fire.

ADD now to the mixture three or four times its quantity of hot water; after a little agitation, allow the *magnesia* to settle to the bottom, and decant off as much of the water as possible. Pour on the same quantity of cold water; and, after settling, decant it off in the same manner. Repeat this washing with the cold water ten or twelve times: or even oftner, if the *magnesia* be required perfectly pure for chemical experiments.

WHEN it is sufficiently washed, the water may be strained and squeezed from it in a linen cloth; for very little of the *magnesia* passes thro'.

THE alkali in the mixture uniting with the acid, separates it from the *magnesia*; which not being of itself soluble in water, must consequently appear immediately under a solid form. But the powder which thus appears is not intirely *magnesia*; part of it is the neutral salt, formed from the union of the acid and alkali. This neutral salt is found, upon examination, to agree in all respects with vitriolated tartar, and requires a large quantity of hot water to dissolve it. As much of it is therefore dissolved as the water can take up; the rest is

dispersed thro' the mixture in the form of a powder. Hence the necessity of washing the *magnesia* with so much trouble; for the first affusion of hot water is intended to dissolve the whole of the salt, and the subsequent additions of cold water to wash away this solution.

THE caution given of boiling the mixture is not unnecessary; if it be neglected, the whole of the *magnesia* is not accurately separated at once; and by allowing it to rest for some time, that powder concretes into minute grains, which, when viewed with the microscope, appear to be assemblages of needles diverging from a point. This happens more especially when the solutions of the epsom-salt and of the alkali are diluted with too much water before they are mixed together. Thus, if a dram of epsom-salt and of salt of tartar be dissolved each in four ounces of water, and be mixed, and then allowed to rest three or four days, the whole of the *magnesia* will be formed into these grains. Or if we filtrate the mixture soon after it is made, and heat the clear liquor which passes thro'; it will become turbid, and deposite a *magnesia*.

I had the curiosity to satisfy myself of the purgative power of *magnesia*, and of *Hoffman's* opinion concerning it, by the following easy experiment. I made a neutral salt of *magnesia* and distilled vinegar; choosing this acid as being, like that in weak stomachs, the product of fermentation. Six drams of this I dissolved in water, and gave to a middle-aged man, desiring him to take it by degrees. After having taken about a third, he desisted, and purged four times in an easy and gentle manner. A woman of a strong constitution got the remainder as a brisk purgative, and it operated ten times without causing any uneasiness. The taste of this salt is not disagreeable, and it appears to be rather of the cooling than of the acrid kind.

HAVING thus given a short sketch of the history and medical virtues of *magnesia*, I now proceed to an account of its chemical properties. By my first experiments, I intended to learn what sort of neutral salts might be obtained by joining it to each of the vulgar acids; and the result was as follows.

MAGNESIA is quickly dissolved with violent effervescence, or explosion of air, by the acids of vitriol, nitre, and of common salt, and by distilled vinegar; the neutral saline liquors thence produced having each their peculiar properties.

THAT which is made with the vitriolic acid, may be condensed into crystals similar in all respects to epsom-salt.

THAT which is made with the nitrous is of a yellow colour, and yields saline crystals, which retain their form in a very dry air, but melt in a moist one.

THAT which is produced by means of spirit of salt, yields no crystals; and if evaporated to dryness, soon melts again when exposed to the air.

THAT which is obtained from the union of distilled vinegar with *magnesia*, affords no crystals by evaporation, but is condensed into a saline mass, which, while warm, is extremely tough and viscid, very much resembling a strong glue both in colour and consistence, and becomes brittle when cold.

By these experiments *magnesia* appears to be a substance very different from those of the calcareous class; under which I would be understood to comprehend all those that are converted into a perfect quick-lime in a strong fire, such as *lime-stone*, *marble*, *chalk*, those *spars* and *marles* which effervesce with aqua fortis, all *animal shells* and the bodies called *lithophyta*. All of these, by being joined with acids, yield a set of compounds which are very different from those we have just

now described. Thus, if a small quantity of any calcarious matter be reduced to a fine powder and thrown into spirit of vitriol, it is attacked by this acid with a brisk effervescence; but little or no dissolution ensues. It absorbs the acid, and remains united with it in the form of a white powder, at the bottom of the vessel, while the liquor has hardly any taste, and shews only a very light cloud upon the addition of alkali.*

THE same white powder is also formed when spirit of vitriol is added to a calcarious earth dissolved in any other acid; the vitriolic expelling the other acid, and joining itself to the earth by a stronger attraction; and upon this account the *magnesia* of sea-water seems to be different from either of those described by *Hoffman*. He says expressly, that the solutions of each of his powders, or, what is equivalent, that the liquors from which they are obtained, formed a coagulum, and deposited a white powder, when he added the vitriolic acid; † which experiment I have often tried with the marine bittern, but without success. The coagulum thus formed in the mother of nitre may be owing to a quantity of quick-lime contained in it; for quick-lime is used in extracting the salt-petre from its matrix. But it is more difficult to account for the difference between *Hoffman's* bittern and ours, unless we will be satisfied to refer it to this, that he got his from the waters of salt springs, which may possibly be different from those of the sea.

MAGNESIA is not less remarkably distinguished from

* Mr. *Margraaf* has lately demonstrated, by a set of curious and accurate experiments, that this powder is of the nature, and possesses the properties, of the gypseous or selenitic substances. That such substances can be resolved into vitriolic acid and calcarious earth, and can be again composed by joining these two ingredients together. Mem. de l'Acad. de Berlin. an. 1750, p. 144.

† Hoff. Op. T. iv. p. 480 & 500.

the calcareous earths, by joining it to the nitrous and vegetable acids, than to the vitriolic. Those earths, when combined with spirit of nitre, cannot be reduced to a crystalline form, and if they are dissolved in distilled vinegar, the mixture spontaneously dries up into a friable salt.

HAVING thus found *magnesia* to differ from the common alkaline earths, the object of my next inquiry was its peculiar degree of attraction for acids, or what was the place due to it in Mr. *Geoffroy's* table of elective attractions.

THREE drams of *magnesia* in fine powder, an ounce of salt ammoniac, and six ounces of water were mixed together, and digested six days in a retort joined to a receiver.

DURING the whole time, the neck of the retort was pointed a little upwards, and the most watery part of the vapour, which was condensed there, fell back into its body. In the beginning of the experiment, a volatile salt was therefore collected in a dry form in the receiver, and afterwards dissolved into spirit.

WHEN all was cool, I found in the retort a saline liquor, some undissolved *magnesia*, and some salt ammoniac crystallized. The saline liquor was separated from the other two, and then mixed with the alkaline spirit. A coagulum was immediately formed, and a *magnesia* precipitated from the mixture.

THE *magnesia* which had remained in the retort, when well washed and dried, weighed two scruples and fifteen grains.

WE learn by the latter part of this experiment, that the attraction of the volatile alkali for acids is stronger than that of *magnesia*, since it separated this powder from the acid to which it was joined. But it also appears, that a gentle heat is capable of overcoming this superiority of

attraction, and of gradually elevating the alkali, while it leaves the less volatile acid with the *magnesia*.

DISSOLVE a dram of any calcarious substance in the acid of nitre or of common salt, taking care that the solution be rendered perfectly neutral, or that no superfluous acid be added. Mix with this solution a dram of *magnesia* in fine powder, and digest it in the heat of boiling water about twenty four hours; then dilute the mixture with double its quantity of water, and filtrate. The greatest part of the earth now left in the filtre is calcarious, and the liquor which passed thro', if mixed with a dissolved alkali, yields a white powder, the largest portion of which is a true *magnesia*.

FROM this experiment it appears, that an acid quits a calcarious earth to join itself to *magnesia*; but the exchange being performed slowly, some of the *magnesia* is still undissolved, and part of the calcarious earth remains yet joined to the acid.

WHEN a small quantity of *magnesia* is thrown into a solution of the corrosive sublimate of mercury, it soon separates part of the mercury in the form of a dark red powder, and is itself dissolved.

IMAGINING that I perceived some resemblance between the properties of *magnesia* and those of alkalis, I was led to try what change this substance would suffer from the addition of quick-lime, which alters in such a peculiar manner the alkaline salts.

TWENTY seven grains of *magnesia* in fine powder were mixed with eighteen ounces of lime-water in a flask, which was corked close and shaken frequently for four days. During this time, I frequently dipp'd into it little bits of paper, which were coloured with the juice of violets; and these became green as soon as they touched the water, until the fourth day, when their colour did not seem to be altered. The water being now poured off,

was intirely insipid, and agreed in every chemical trial with pure water. The powder, after being perfectly well dried, weighed thirty seven grains. It did not dissolve intirely in spirit of vitriol ; but, after a brisk effervescence, part of it subsided in the same manner as the calcarious earths, when mixed with this acid.

WHEN I first tried this experiment, I was at the trouble of digesting the mixture in the heat of boiling water, and did not then know that it would succeed in the heat of the air. But Dr. *Alston*, who has obliged the world with many curious and useful discoveries on the subject of quick-lime, having had occasion to repeat it, I learned from him that heat is not necessary ; and he has moreover added an useful purpose to which this property of *magnesia* may be applied ; I mean the sweetening of water at sea, with which lime may have been mixed to prevent its putrefaction.

THAT part of the dried powder which does not dissolve in spirit of vitriol, consists of the lime separated from the water.

QUICK-LIME itself is also rendered mild by *magnesia*, if these two are well rubbed together and infused with a small quantity of water.

By the following experiments, I proposed to know whether this substance could be reduced to a quick-lime.

AN ounce of *magnesia* was exposed in a crucible for about an hour to such a heat as is sufficient to melt copper. When taken out, it weighed three drams and one scruple, or had lost $\frac{7}{12}$ of its former weight.

I repeated, with the *magnesia* prepared in this manner, most of those experiments I had already made upon it before calcination, and the result was as follows.

IT dissolves in all the acids, and with these composes salts exactly similar to those described in the first set of experiments : but what is particularly to be remarked,

it is dissolved without any the least degree of effervescence.

IT slowly precipitates the corrosive sublimate of mercury in the form of a black powder.

IT separates the volatile alkali in salt ammoniac from the acid, when it is mixed with a warm solution of that salt. But it does not separate an acid from a calcarious earth, nor does it induce the least change upon lime-water.

LASTLY, when a dram of it is digested with an ounce of water in a bottle for some hours, it does not make any the least change in the water. The *magnesia*, when dried, is found to have gained ten grains; but it neither effervesces with acids, nor does it sensibly affect lime-water.

OBSERVING *magnesia* to lose such a remarkable proportion of its weight in the fire, my next attempts were directed to the investigation of this volatile part, and, among other experiments, the following seemed to throw some light upon it.

THREE ounces of *magnesia* were distilled in a glass retort and receiver, the fire being gradually increased until the *magnesia* was obscurely red hot. When all was cool, I found only five drams of a whitish water in the receiver, which had a faint smell of the spirit of hartshorn, gave a green colour to the juice of violets, and rendered the solutions of corrosive sublimate and of silver very slightly turbid. But it did not sensibly effervesce with acids.

THE *magnesia*, when taken out of the retort, weighed an ounce, three drams, and thirty grains, or had lost more than the half of its weight. It still effervesced pretty briskly with acids, tho' not so strongly as before this operation.

THE fire should have been raised here to the degree

requisite for the perfect calcination of *magnesia*. But even from this imperfect experiment, it is evident, that of the volatile parts contained in that powder, a small proportion only is water; the rest cannot, it seems, be retained in vessels, under a visible form. Chemists have often observed, in their distillations, that part of a body has vanished from their senses, notwithstanding the utmost care to retain it; and they have always found, upon further inquiry, that subtile part to be air, which having been imprisoned in the body, under a solid form, was set free and rendered fluid and elastic by the fire. We may therefore safely conclude, that the volatile matter, lost in the calcination of *magnesia*, is mostly air; and hence the calcined *magnesia* does not emit air, or make an effervescence, when mixed with acids.

THE water, from its properties, seems to contain a small portion of volatile alkali, which was probably formed from the earth, air, and water, or from some of these combined together; and perhaps also from a small quantity of inflammable matter which adhered accidentally to the *magnesia*. Whenever Chemists meet with this salt, they are inclined to ascribe its origin to some animal, or putrid vegetable, substance; and this they have always done, when they obtained it from the calcareous earths, all of which afford a small quantity of it. There is, however, no doubt that it can sometimes be produced independently of any such mixture, since many fresh vegetables and tartar afford a considerable quantity of it. And how can it, in the present instance, be supposed, that any animal or vegetable matter adhered to the *magnesia*, while it was dissolved by an acid, separated from this by an alkali, and washed with so much water?

Two drams of *magnesia* were calcined in a crucible, in the manner described above, and thus reduced to two scruples and twelve grains. This calcined *magnesia* was

dissolved in a sufficient quantity of spirit of vitriol, and then again separated from the acid by the addition of an alkali, of which a large quantity is necessary for this purpose. The *magnesia* being very well washed and dried, weighed one dram and fifty grains. It effervesced violently, or emitted a large quantity of air, when thrown into acids, formed a red powder when mixed with a solution of sublimate, separated the calcareous earths from an acid, and sweetened lime-water: and had thus recovered all those properties which it had but just now lost by calcination: nor had it only recovered its original properties, but acquired besides an addition of weight nearly equal to what had been lost in the fire; and, as it is found to effervesce with acids, part of the addition must certainly be air.

THIS air seems to have been furnished by the alkali from which it was separated by the acid; for Dr. *Hales* has clearly proved, that alkaline salts contain a large quantity of fixed air, which they emit in great abundance when joined to a pure acid. In the present case, the alkali is really joined to an acid, but without any visible emission of air; and yet the air is not retained in it: for the neutral salt, into which it is converted, is the same in quantity, and in every other respect, as if the acid employed had not been previously saturated with *magnesia*, but offered to the alkali in its pure state, and had driven the air out of it in their conflict. It seems therefore evident, that the air was forced from the alkali by the acid, and lodged itself in the *magnesia*.

THESE considerations led me to try a few experiments, whereby I might know what quantity of air is expelled from an alkali, or from *magnesia*, by acids.

Two drams of a pure fixed alkaline salt, and an ounce of water, were put into a Florentine flask, which, together with its contents, weighed two ounces and two drams.

Some oil of vitriol diluted with water was dropt in, until the salt was exactly saturated ; which it was found to be, when two drams, two scruples, and three grains of this acid had been added. The vial with its contents now weighed two ounces, four drams, and fifteen grains. One scruple, therefore, and eight grains were lost during the ebullition, of which a trifling portion may be water, or something of the same kind. The rest is air.

THE celebrated *Homborg* has attempted to estimate the quantity of solid salt contained in a determined portion of the several acids. He saturated equal quantities of an alkali with each of them ; and, observing the weight which the alkali had gained, after being perfectly dried, took this for the quantity of solid salt contained in that share of the acid which performed the saturation. But we learn from the above experiment, that his estimate was not accurate, because the alkali loses weight as well as gains it.

Two drams of *magnesia*, treated exactly as the alkali in the last experiment, were just dissolved by four drams, one scruple, and seven grains of the same acid liquor, and lost one scruple and sixteen grains by the ebullition.

Two drams of *magnesia* were reduced, by the action of a violent fire, to two scruples and twelve grains, with which the same process was repeated, as in the two last experiments ; four drams, one scruple, and two grains of the same acid were required to compleat the solution, and no weight was lost in the experiment.

As in the separation of the volatile from the fixed parts of bodies, by means of heat, a small quantity of the latter is generally raised with the former ; so the air and water, originally contained in the *magnesia*, and afterwards dissipated by the fire, seem to have carried off a small part of the fixed earth of this substance. This is probably the reason, why calcined *magnesia* is saturated with

a quantity of acid, somewhat less than what is required to dissolve it before calcination: and the same may be assigned as one cause which hinders us from restoring the whole of its original weight, by solution and precipitation.

I took care to dilute the vitriolic acid, in order to avoid the heat and ebullition which it would otherwise have excited in the water; and I chose a Florentine flask, on account of its lightness, capacity, and shape, which is peculiarly adapted to the experiment; for the vapours raised by the ebullition circulated for a short time, thro' the wide cavity of the vial, but were soon collected upon its sides, like dew, and none of them seemed to reach the neck, which continued perfectly dry to the end of the experiment.

WE now perceive the reason, why crude and calcined *magnesia*, which differ in many respects from one another, agree however in composing the same kind of salt, when dissolved in any particular acid; for the crude *magnesia* seems to differ from the calcined chiefly by containing a considerable quantity of air, which air is unavoidably dissipated and lost during the dissolution.

FROM our experiments, it seems probable, that the increase of weight which some metals acquire, by being first dissolved in acids, and then separated from them again by alkalis, proceeds from air furnished by the alkalis. And that in the *aurum fulminans*, which is prepared by the same means, this air adheres to the gold in such a peculiar manner, that, in a moderate degree of heat, the whole of it recovers its elasticity in the same instant of time; and thus, by the violent shock which it gives to the air around, produces the loud crack or fulmination of this powder. Those who will imagine the explosion of such a minute portion of fixed air, as can reside in the *aurum fulminans*, to be insufficient for the excessive loudness of the noise, will consider, that it

is not a large quantity of motion communicated to the air, but rather a smart stroke which produces sound, and that the explosion of but a few particles of fixed air may be capable of causing a loud noise, provided they all recover their spring suddenly, and in the same instant.

THE above experiments lead us also to conclude, that volatile alkalis, and the common absorbent earths, which lose their air by being joined to acids, but shew evident signs of their having recovered it, when separated from them by alkalis, received it from these alkalis which lost it in the instant of their joining with the acid.

THE following are a few experiments upon three of the absorbent earths, made in order to compare them with one another, and with *magnesia*.

Suspecting that *magnesia* might possibly be no other than a common calcarious earth, which had changed its nature, by having been previously combined with an acid, I saturated a small quantity of chalk with the muriatic acid, separated the acid from it again by means of a fixed alkali, and carefully washed away the whole of the salt.

THE chalk when dryed was not found to have suffered any alteration; for it effervesced with the vitriolic acid, but did not dissolve in it; and when exposed to a violent fire, was converted into a quick-lime, in all respects similar to that obtained from common chalk.

IN another experiment of the same kind, I used the vitriolic acid with the same event.

ANY calcarious matter reduced to a fine powder, and thrown into a warm solution of alum, immediately raises a brisk effervescence. But the powder is not dissolved; it is rather increased in bulk: and if the addition be repeated until it is no longer accompanied with effervescence, the liquor loses all taste of the alum, and yields only a very light cloud upon the admixture of an alkali.

FROM this experiment we learn, that acids attract the

calcarious earths more strongly than they do the earth of alum; and as the acid in this salt is exactly the same with the vitriolic, it composes with the calcarious earth a neutral substance, which is very difficultly soluble in water, and therefore falls down to the bottom of the vessel along with the earth of alum which is deprived of its acid. The light cloud formed by the alkali proceeds from the minute portion of the calcarious compound which saturates the water.

THE earth of animal bones, when reduced to a fine powder and thrown into a diluted vitriolic acid, gradually absorbs the acid in the same manner as the calcarious earths, but without any remarkable effervescence. When it is added to the nitrous or to the muriatic acid, it is slowly dissolved. The compound liquor thence produced is extremely acrid, and still changes the colour of the juice of violets to a red, even after it is fully saturated with the absorbent. Distilled vinegar has little or no effect upon this earth; for after a long digestion it still retains its sour taste, and gives only a light cloud upon the addition of an alkali.

By dropping a dissolved fixed alkali into a warm solution of alum, I obtained the earth of this salt, which, after being well washed and dried, was found to have the following properties.

It is dissolved in every acid but very slowly, unless assisted by heat. The several solutions, when thoroughly saturated, are all astringent with a slight degree of an acid taste, and they also agree with a solution of alum in this, that they give a red colour to the infusion of turnsol.

NEITHER this earth, nor that of animal bones, can be converted into quick-lime by the strongest fire, nor do they suffer any change worth notice. Both of them seem to attract acids but weakly, and to alter their properties less when united to them than the other absorbents.

PART II.

IN reflecting afterwards upon these experiments, an explication of the nature of lime offered itself, which seemed to account, in an easy manner, for most of the properties of that substance.

It is sufficiently clear, that the calcarious earths in their native state, and that the alkalis and magnesia in their ordinary condition, contain a large quantity of fixed air, and this air certainly adheres to them with considerable force, since a strong fire is necessary to separate it from magnesia, and the strongest is not sufficient to expell it entirely from fixed alkalis, or take away their power of effervescing with acid salts.

THESE considerations led me to conclude, that the relations between fixed air and alkaline substances was somewhat similar to the relation between these and acids; that as the calcarious earths and alkalis attract acids strongly and can be saturated with them, so they also attract fixed air, and are in their ordinary state saturated with it: and when we mix an acid with an alkali or with an absorbent earth, that the air is then set at liberty, and breaks out with violence; because the alkaline body attracts it more weakly than it does the acid, and because the acid and air cannot both be joined to the same body at the same time.

I also imagined, that, when the calcarious earths are exposed to the action of a violent fire, and are thereby converted into quick-lime, they suffer no other change in their composition than the loss of a small quantity of water and of their fixed air. The remarkable acrimony which we perceive in them after this process, was not supposed to proceed from any additional matter received in the fire, but seemed to be an essential property of the pure earth, de-

pending on an attraction for those several substances which it then became capable of corroding or dissolving, which attraction had been insensible as long as the air adhered to the earth, but discovered itself upon the separation.

THIS supposition was founded upon an observation of the most frequent consequences of combining bodies in chemistry. Commonly when we join two bodies together, their acrimony or attraction for other substances becomes immediately either less perceivable or entirely insensible; altho' it was sufficiently strong and remarkable before their union, and may be rendered evident again by disjoining them. A neutral salt, which is composed of an acid and alkali, does not possess the acrimony of either of its constituent parts. It can easily be separated from water, has little or no effect upon metals, is incapable of being joined to inflammable bodies, and of corroding and dissolving animals and vegetables; so that the attraction both of the acid and alkali for these several substances seems to be suspended till they are again separated from one another.

CRUDE lime was therefore considered as a peculiar acrid earth rendered mild by its union with fixed air: and quick-lime as the same earth, in which, by having separated the air, we discover that acrimony or attraction for water, for animal, vegetable, and for inflammable substances.

THAT the calcarious earths really lose a large quantity of air when they are burnt to quick-lime, seems sufficiently proved by an experiment of Mr. *Margraaf*,* an exceedingly accurate and judicious Chemist. He subjected eight ounces of *osteocolla* to distillation in an earthen retort, finishing his process with the most violent fire of a reverberatory, and caught in the receiver only two drams of water, which by its smell and properties shewed itself

* Mem. de l'Acad. de Berlin. an. 1748, p. 57.

to be slightly alkaline. He does not tell us the weight of the *osteocolla* remaining in the retort, and only says, that it was converted into quick-lime; but as no calcarious earth can be converted into quick-lime, or bear the heat which he applied without losing above a third of its weight, we may safely conclude, that the loss in his experiment was proportional, and proceeded chiefly from the dissipation of fixed air.

ACCORDING to our theory, the relation of the calcarious earth to air and water appeared to agree with the relation of the same earth to the vitriolic and vegetable acids. As chalk for instance has a stronger attraction for the vitriolic than for the vegetable acid, and is dissolved with more difficulty when combined with the first, than when joined to the second: so it also attracts air more strongly than water, and is dissolved with more difficulty when saturated with air than when compounded with water only.

A calcarious earth deprived of its air, or in the state of quick-lime, greedily absorbs a considerable quantity of water, becomes soluble in that fluid, and is then said to be slaked; but as soon as it meets with fixed air, it is supposed to quit the water and join itself to the air, for which it has a superior attraction, and is therefore restored to its first state of mildness and insolubility in water.

WHEN slaked lime is mixed with water, the fixed air in the water is attracted by the lime, and saturates a small portion of it, which then becomes again incapable of dissolution, but part of the remaining slaked lime is dissolved and composes lime-water.

IF this fluid be exposed to the open air, the particles of quick-lime which are nearest the surface gradually attract the particles of fixed air which float in the atmosphere. But at the same time that a particle of lime is thus saturated with air, it is also restored to its native state of mildness

and insolubility; and as the whole of this change must happen at the surface, the whole of the lime is successively collected there under its original form of an insipid calcareous earth, called the cream or crusts of lime-water.

WHEN quick-lime itself is exposed to the open air, it absorbs the particles of water and of fixed air which come within its sphere of attraction, as it meets with the first of these in greatest plenty, the greatest part of it assumes the form of slaked lime; the rest is restored to its original state; and if it be exposed for a sufficient length of time, the whole of it is gradually saturated with air, to which the water as gradually yields its place.

WE have already shewn by experiment, that magnesia alba is a compound of a peculiar earth and fixed air. When this substance is mixed with lime-water, the lime shews a stronger attraction for fixed air than that of the earth of magnesia; the air leaves this powder to join itself to the lime. And as neither the lime when saturated with air, nor the magnesia when deprived of it, are soluble in water, the lime-water becomes perfectly pure and insipid, the lime which it contained being mixed with the magnesia. But if the magnesia be deprived of air by calcination before it is mixed with the lime-water, this fluid suffers no alteration.

IF quick-lime be mixed with a dissolved alkali, it likewise shews an attraction for fixed air superior to that of the alkali. It robs this salt of its air, and thereby becomes mild itself, while the alkali is consequently rendered more corrosive, or discovers its natural degree of acrimony or strong attraction for water, and for bodies of the inflammable, and of the animal and vegetable kind; which attraction was less perceivable as long as it was saturated with air. And the volatile alkali when deprived of its air, besides this attraction for various bodies, discovers likewise its natural degree of volatility,

which was formerly somewhat repressed by the air adhering to it, in the same manner as it is repressed by the addition of an acid.

THIS account of lime and alkalis recommended itself by its simplicity, and by affording an easy solution of many *phenomena*, but appeared upon a nearer view to be attended with consequences that were so very new and extraordinary, as to render suspicious the principles from which they were drawn.

I resolved however to examine, in a particular manner, such of these consequences as were the most unavoidable, and found the greatest number of them might be reduced to the following propositions :

I. IF we only separate a quantity of air from lime and alkalis, when we render them caustic they will be found to lose part of their weight in the operation, but will saturate the same quantity of acid as before, and the saturation will be performed without effervescence.

II. IF quick-lime be no other than a calcarious earth deprived of its air, and whose attraction for fixed air is stronger than that of alkalis, it follows, that, by adding to it a sufficient quantity of alkali saturated with air, the lime will recover the whole of its air, and be entirely restored to its original weight and condition : and it also follows, that the earth separated from lime-water by an alkali, is the lime which was dissolved in the water now restored to its original mild and insoluble state.

III. IF it be supposed that slaked lime does not contain any parts which are more firey, active or subtile than others, and by which chiefly it communicates its virtues to water ; but that it is an uniform compound of lime and water : it follows, that, as part of it can be dissolved in water, the whole of it is also capable of being dissolved.

IV. IF the acrimony of the caustic alkali does not depend on any part of the lime adhering to it, a caustic

or soap-ley will consequently be found to contain no lime, unless the quantity of lime employed in making it were greater than what is just sufficient to extract the whole air of the alkali; for then as much of the superfluous quick-lime might possibly be dissolved by the ley as would be dissolved by pure water, or the ley would contain as much lime as lime-water does.

V. WE have shewn in the former experiments, that absorbent earths lose their air when they are joined to an acid; but recover it, if separated again from that acid, by means of an ordinary alkali: the air passing from the alkali to the earth, at the same time that the acid passes from the earth to the alkali.

IF the caustic alkali therefore be destitute of air, it will separate magnesia from an acid under the form of a magnesia free of air, or which will not effervesce with acids; and the same caustic alkali will also separate a calcareous earth from acids under the form of a calcareous earth destitute of air, but saturated with water, or under the form of slaked lime.

THESE were all necessary conclusions from the above suppositions. Many of them appeared too improbable to deserve any further attention: some however, I found upon reflection, were already seconded by experience. Thus *Hoffman* has observed, that quicklime does not effervesce with spirit of vitriol;* and it is well known that the caustic spirit of urine, or of salt ammoniac, does not emit air, when mixed with acids. This consideration excited my curiosity, and determined me to inquire into the truth of them all by way of experiment. I therefore engaged myself in a set of trials; the history of which is here subjoined. Some new facts are likewise occasionally mentioned; and here it will be proper

* Hoff. Op. T. iv. p. 480.

to inform the reader, that I have never mentioned any without satisfying myself of their truth by experiment, tho' I have sometimes taken the liberty to neglect describing the experiments when they seemed sufficiently obvious.

DESIRING to know how much of an acid a calcareous earth will absorb, and what quantity of air is expelled during the dissolution, I saturated two drams of chalk with diluted spirit of salt, and used the Florentine flask, as related in a similar experiment upon magnesia. Seven drams and one grain of the acid finished the dissolution, and the chalk lost two scruples and eight grains of air.

THIS experiment was necessary before the following, by which I proposed to inquire into the truth of the first proposition so far as it relates to quick-lime.

Two drams of chalk were converted into a perfect quick-lime, and lost two scruples and twelve grains in the fire. This quick-lime was slaked or reduced to a milky liquor with an ounce of water, and then dissolved in the same manner, and with the same acid, as the two drams of chalk in the preceding experiment. Six drams, two scruples and fourteen grains of the acid finished the saturation without any sensible effervescence or loss of weight.

It therefore appears from these experiments, that no air is separated from quick-lime by an acid, and that chalk saturates nearly the same quantity of acid after it is converted into quick-lime as before.

WITH respect to the second proposition, I tried the following experiments.

A piece of perfect quick-lime made from two drams of chalk, and which weighed one dram and eight grains, was reduced to a very fine powder, and thrown into a filtrated mixture of an ounce of a fixed alkaline salt and two ounces of water. After a slight digestion, the powder being well washed and dried, weighed one dram and fifty eight grains. It was similar in every trial to a

fine powder of ordinary chalk, and was therefore saturated with air which must have been furnished by the alkali.

A dram of pure salt of tartar was dissolved in fourteen pounds of lime-water, and the powder thereby precipitated, being carefully collected and dried, weighed one and fifty grains. When exposed to a violent fire, it was converted into a true quick-lime, and had every other quality of a calcarious earth.

THIS experiment was repeated with the volatile alkali, and also with the fossil or alkali of sea-salt, and exactly with the same event.

THE third proposition had less appearance of probability than the foregoing; but, as an accurate experiment was the only test of its truth, I reduced eight grains of perfect quick-lime made of chalk, to an exceedingly subtile powder, by slaking it in two drams of distilled water boiling hot, and immediately threw the mixture into eighteen ounces of distilled water in a flask. After shaking it, a light sediment, which floated thro' the liquor, was allowed to subside; and this, when collected with the greatest care, and dried, weighed, as nearly as I could guess, one third of a grain. The water tasted strongly of the lime, had all the qualities of lime-water, and yielded twelve grains of precipitate, upon the addition of salt of tartar. In repeating this experiment, the quantity of sediment was sometimes less than the above, and sometimes amounted to half a grain. It consisted partly of an earth which effervesced violently with *aqua fortis*, and partly of an ochry powder, which would not dissolve in that acid. The ochry powder, as it usually appears in chalk to the eye, in the form of veins running thro' its substance, must be considered only as an accidental or foreign admixture; and, with respect to the minute portion of alkaline earth which composed the remainder of the sediment, it cannot be supposed to have

been originally different from the rest, and incapable, from its nature, of being converted into quick-lime, or of being dissolved in water; it seems rather to have consisted of a small part of the chalk in its mild state, or saturated with air, which had either remained, for want of a sufficient fire to drive it out entirely, or had been furnished by the distilled water.

I indeed expected to see a much larger quantity of sediment produced from the lime, on account of the air which water constantly contains, and with a view to know whether water retains its air when fully saturated with lime, a lime-water was made as strong as possible; four ounces of which were placed under the receiver of an air-pump, together with four ounces of common water in a vial of the same size; and, upon exhausting the receiver, without heating the vials, the air arose from each in nearly the same quantity: from whence it is evident, that the air, which quick-lime attracts, is of a different kind from that which is mixed with water. And that it is also different from common elastic air, is sufficiently proved by daily experience; for lime-water, which soon attracts air, and forms a crust when exposed in open and shallow vessels, may be preserved, for any time, in bottles which are but slightly corked, or closed in such a manner as would allow free access to elastic air, were a vacuum formed in the bottle. Quick-lime therefore does not attract air when in its most ordinary form, but is capable of being joined to one particular species only, which is dispersed thro' the atmosphere, either in the shape of an exceedingly subtile powder, or more probably in that of an elastic fluid. To this I have given the name of fixed air, and perhaps very improperly; but I thought it better to use a word already familiar in philosophy, than to invent a new name, before we be more fully acquainted with the nature and properties of this sub-

stance, which will probably be the subject of my further inquiry.

It is, perhaps, needless to mention here, that the calcareous substances used in making the above experiments should be of the purest kind, and burnt with the utmost violence of heat, if we would be sure of converting them into perfect quick-lime. I therefore made use of chalk burnt in a small covered crucible with the fiercest fire of a Black-smith's forge, for half an hour, and found it necessary to employ, for this purpose, a crucible of the *Austrian* kind, which resemble black lead; for if any calcareous substance be heated to such a degree in an ordinary or *Hessian* crucible, the whole of it is melted down, together with part of the vessel, into glass.

I now prepared to inquire into the properties of the caustic alkali; in order to which, I made a caustic or soap ley in the following manner.

TWENTY six ounces of very strong quick-lime made of chalk, were slaked or reduced to a sort of fluid paste, with eleven pounds of boiling water, and then mixed in a glass vessel with eighteen ounces of a pure fixed alkaline salt, which had been first dissolved in two pounds and a half of water. This mixture was shaken frequently for two hours, when the action of the lime upon the alkali was supposed to be over, and nothing remained but to separate them again from one another. I therefore added 12 pounds of water, stirred up the lime, and, after allowing it to settle again, poured off as much of the clear ley as possible.

THE lime and alkali were mixed together under the form of a very thick milky liquor or fluid paste; because they are thus kept in perpetual contact and equal mixture until they have acted sufficiently upon one another: whereas in the common way of using a larger quantity of water, the lime lies for the most part at bottom, and, tho' stirred up ever so often, cannot exert its

influence so fully upon the alkali, which is uniformly diffused thro' every part of the liquor.

THE above ley was found upon trial to be saturated by acids without the least effervescence or diminution of weight.

IT was now proper to examine whether the alkali suffered any loss in becoming caustic, which I proposed to attempt by ascertaining the strength of the ley, or the quantity of salt which a given portion of it contained; from which by computation some imperfect knowledge might be obtained of the quantity of caustic produced from the eighteen ounces of mild salt.

I therefore evaporated some of my ley, but soon perceived that no certain judgment could be formed of its strength in this way, because it always absorbed a considerable quantity of air during the evaporation, and the dried salt made a pretty brisk effervescence with acids, so that the ley appeared stronger than it really was; and yet, upon proceeding in the estimate from this rude and unfair trial, it appeared that the salt had lost above a sixth in becoming caustic, and the quantity of acid saturated by two drams of it was to the quantity of acid saturated by two drams of salt of tartar, nearly as six to five.

THESE experiments are therefore agreeable to that part of the second proposition which relates to the caustic alkali.

UPON farther examining what changes the alkali had undergone, I found that the ley gave only an exceeding faint milky hue to lime-water; because the caustic alkali wants that air by which salt of tartar precipitates the lime. When a few ounces of it were exposed in an open shallow vessel for four and twenty hours, it imbibed a small quantity of air, and made a slight effervescence with acids. After a fortnight's exposure in the same manner, it became entirely mild, effervesced as violently with acids, and had the same effect upon lime-water as a solution of an ordinary alkali.

It likewise agrees with lime-water in this respect, that it may be kept in close vessels, or even in bottles which are but slightly covered, for a considerable time, without absorbing a sensible quantity of air.

IN order to know how much lime it contained, I evaporated ten ounces in a small silver dish over a lamp, and melted the salt, after having dissipated the water.*

THE caustic thus produced was dissolved again in a small quantity of water, and deposited a trifling portion of sediment, which I imagined at first to be lime; but finding that it could easily be dissolved in a little more water, concluded it to be a vitriolated tartar, which always accompanies the fixed alkali of vegetables.

I then saturated the solution of the caustic salt with spirit of vitriol, expecting thus to detect the lime; because that acid precipitates a calcareous earth from its ordinary solutions. During the saturation, a large quantity of white powder was formed; but this likewise turned out to be a vitriolated tartar, which had appeared in the form of a powder, because there was not enough of water in the mixture to dissolve it.

LASTLY, I exposed a few ounces of the ley in an open shallow vessel so long, that the alkali lost the whole of its causticity, and seemed entirely restored to the state of an ordinary fixed alkali; but it did not however deposite a single atom of lime. And to assure myself that my caustic ley was not of a singular kind, I repeated the same experiments with an ordinary soap-ley, and with one made by mixing one part of a pure fixed alkaline salt

* This evaporation was performed in a silver dish, on account of the acrimony of the salt; which is so very great, that, having once evaporated a part of the same ley in a bowl of English earthen or stone ware, and melted the caustic with a gentle heat, it corroded and dissolved a part of the bowl, and left the inside of it pitted with small holes.

with three parts of common stone lime fresh slaked and sifted; nor could I discover any lime in either. The first of these contained a small quantity of brimstone, and was far from being perfectly caustic, for it made a pretty brisk effervescence with acids; but the last was so entirely deprived of its air, that it did not diminish in the least the transparency of lime-water.

THESE experiments seem therefore to support the fourth proposition, and to shew that the caustic alkali does not contain any lime.

As it seems probable, from the quickness and ease wherewith the alkali was rendered caustic, that more lime had been employed than what was just sufficient to extract the whole of its air, we are surprised to find that little or none of the superfluous quick-lime was dissolved by the water. But this *phænomenon* will become less surprizing, by comparing it with some similar instances in chemistry. Water may be made to deposite a salt, by the admixture of a substance which it attracts more strongly than it does that salt; such as spirit of wine; and quick-lime itself may be separated from water upon the same principle; for if that spirit is added to an equal quantity of lime-water, the mixture becomes turbid and deposite a sediment, which, when separated and dissolved again in distilled water, composes lime-water. We may therefore refer the above *phænomenon*, with respect to the ley, to the same cause with these, and say, that the water did not dissolve the lime, because it already contained a caustic alkali, for which it has a superior attraction.

I also rendered the volatile alkali caustic, in order to examine what change it suffered in the operation, and obtained an exceedingly volatile and acrid spirit, which neither effervesced with acids, nor altered in the least the transparency of lime-water; and, altho' very strong, was lighter than water, and floated upon it like spirit of wine.

I next inquired into the truth of the fifth proposition, in the following manner.

Two drams of epsom-salt were dissolved in a small quantity of water, and thrown into two ounces of the caustic-ley; the mixture instantly became thick, like a decoction of starch or barley, by the magnesia, which was precipitated. I then added spirit of vitriol by degrees, until the mixture became perfectly clear, or the whole of the magnesia was again dissolved; which happened without any effervescence or emission of air.

HALF an ounce of chalk was dissolved in spirit of salt, the quantity of which was so adjusted, that the mixture was not acid in the least degree; and the solution was thrown into twelve ounces of the caustic ley; which quantity I found, by experiment, to be sufficient for precipitating almost the whole of the chalk. I now filtrated this turbid liquor, and laid the powder remaining in the paper upon a chalk-stone, in order to draw as much of the water from it as possible, and thereby reduce it to the form of a more dense and heavy powder, that it might subside the more perfectly in the following part of the experiment. I then mixed it with about twenty ounces of pure water in a flask, and, after allowing the powder to subside, poured off the water, which had all the qualities of lime-water. And I successively converted eight waters more into lime-water, seven of these in the same quantity, and with the same management, as the first. The eighth was likewise in the same quantity; but I allowed it to remain with the chalk, and shook it frequently, for two days. This, after being filtrated, formed a cream or crust upon its surface when exposed to the air; changed the colour of the juice of violets into green; separated an orange-coloured powder from a solution of corrosive sublimate; became turbid upon the addition of an alkali; was entirely sweetened by magnesia;

and appeared so strong to the taste, that I could not have distinguished it from ordinary lime-water. And when I threw some salt ammoniac into the lime which remained, the vapour of the volatile alkali immediately arose from the mixture.

IN this experiment therefore the air is first driven out of the chalk by an acid, and then, in order to separate this acid from it, we add an alkali which has been previously deprived of its air; by which means, the chalk itself is also obtained free of air, and in an acrid form, or in the form of slaked lime.

WE have also several processes for obtaining the volatile alkali in a caustic form, which seem to be only so many methods of obtaining it in its pure state, and free of fixed air. The first of these is the separation of the alkali from an acid, merely by heat; an instance of which we have from Mr. *Margraaf*.* He prepared from urine an ammoniacal salt, the acid of which is the basis of the phosphorus, and is of such a peculiar nature, that it endures a red heat without being dissipated. Sixteen ounces of the neutral salt were subjected by him to distillation. The acid remained in the retort, and he found in the receiver eight ounces of an alkaline spirit, which, he tells us, was extremely volatile, very much resembling the spirit of salt ammoniac distilled with quick-lime; and no crystals were formed in it, when exposed to the cold air.

A caustic volatile alkali may also be obtained, by mixing salt ammoniac with half its weight of a caustic fixed alkali, or of magnesia which has been previously deprived of its air by fire; and then submitting these mixtures to distillation: Or merely by adding any ordinary volatile alkali to a proper quantity of a caustic ley; for

* Mem. de l'Acad. de Berlin. an. 1746, p. 87.

in this case the air passes from the volatile to the fixed alkali, by a superior attraction for the last, and, by a gentle heat, the compound yields a spirit similar to that prepared from salt ammoniac and quick-lime.

It is therefore probable, that, had we also a method of separating the fixed alkali from an acid, without, at the same time, saturating it with air, we should then obtain it in a caustic form; but I am not acquainted with an instance of this separation in chemistry. There are two indeed which, at first sight, appear to be of this kind; these are the separation of the fixed alkali from the nitrous acid by means of inflamed charcoal, in the process for making *nitrum fixatum*, and of the same alkali, from vegetable acids merely by heat; but, upon examining the product of each process, we find the alkali either fully or nearly saturated with air. In the first, either the charcoal or the acid, or both together, are almost wholly converted into air; a part of which is probably joined to the alkali. In the second, the acid is not properly separated, but rather destroyed by the fire: a considerable portion of it is converted into an inflammable substance; and we learn from Dr. *Hales*, that the bodies of this class contain a large quantity of fixed air.

WHEN we consider that the attraction of alkalis for fixed air is weaker than that of the calcareous earths, and reflect upon the effects of heat in chemistry, we are led to imagine, that alkalis might be entirely deprived of their air, or rendered perfectly caustic, by a fire somewhat weaker than that which is sufficient to produce the same change upon lime; but this opinion does not seem agreeable to experience.

THE alkalis do, however, acquire some degree of causticity in a strong fire, as appears from their being more easily united with spirit of wine after having been kept in fusion for some time. For that fluid, which

cannot be tintured by a mild salt of tartar, will soon take a very deep colour from a few drops of a strong caustic ley. The circumstances which hinder us from rendering these salts perfectly caustic by heat, are their propensity to dissipation in the utmost violence of the fire, their extreme acrimony, and the imperfection of our common vessels. For before the heat becomes very intense, the alkalis either evaporate, or dissolve a part of the crucibles in which they are contained, and often escape thro' their pores; which happens, especially as soon as they have already acquired some degree of additional acrimony, by the loss of part of their air.

THE fusion also, which they so readily undergo, is well known by Chemists, as a strong obstacle to the separation of the volatile from the fixed parts of a compound by fire; accordingly, in several processes, we are directed to add to the fusible compound some porous substance which is incapable of fusion, and will retain the whole in a spongy form, thereby to facilitate the dissipation of the volatile parts.

IN order to know whether an alkali would lose a part of its air, and acquire a degree of causticity, when exposed, with this precaution, to the action of a strong fire, I mixed an ounce and a half of salt of tartar with three ounces of black-lead, a substance of any the most unchangeable by chemical operations. This mixture I exposed, for several hours, in a covered crucible, to a fire somewhat stronger than what is necessary to keep salt of tartar in fusion. When allowed to cool, I found it still in the form of a loose powder; and taking out one half, I diluted it with water, and by filtration obtained a ley, which, when poured into a solution of white marble in *aqua fortis*, precipitated the marble under the form of a weak quick-lime: for the turbid mixture gave a green colour to the juice of violets, and threw up a crust like

that of lime-water ; and the precipitated powder collected and mixed with salt ammoniac immediately yielded the scent of the volatile alkali.

LEST it should here be suspected, that the alkaline qualities of this mixture, and of the precipitated marble, were not owing to a lime into which the marble was converted, but to the alkali itself which was added, it is proper to observe, that I mixed so small a proportion of the ley with the solution of marble as made me sure, from certain experiments, that the whole of the alkali was spent in performing the precipitation, and was consequently converted into a neutral salt by attracting the acid. The properties therefore of the mixture can only be referred to a lime, as is indeed sufficiently evident from the crust which is peculiar to lime-water.

I was therefore assured by this experiment, that an alkali does really lose a part of its air, and acquire a degree of causticity, by the proper application of heat ; but finding by several trials, that the degree of causticity which it had thus acquired was but weak, and that the quick-lime produced in this experiment was exhausted and rendered mild by a small quantity of water, I exposed the crucible together with that half of the alkali which remained in it to a stronger fire, in order to expel a larger quantity of air, and render it more remarkably caustic ; but the whole of it was dissipated by the force of the heat, and the black lead, which still retained the form of a loose and subtile powder, yielded little or nothing to water.

WE learn then from the above experiment the reason why the alkali newly obtained from the ashes of vegetables is generally of the more acrid kinds of that salt. It never appears until the subject be converted into ashes, and is supposed to be formed by the fire, and to be the result of a particular combination of some of the principles of the vegetable ; one of which principles is air, which is

contained in large quantity in all vegetable matters whatever. But as soon as the smallest part of a vegetable is converted into ashes, and an alkali is thus formed, this salt necessarily suffers a calcination, during which it is kept in a spongy form by the ashes, and shews a very considerable degree of acrimony if immediately applied to the body of an animal; but if the ashes are for any time exposed to the air, or if we separate the alkali from them by the addition of a large quantity of water and subsequent evaporation, the salt imbibes fixed air from the atmosphere, and becomes nearly saturated with it: tho' even in this condition it is generally more acrid than salt of tartar, when this is prepared with a gentle heat.

BORAX has sometimes been referred to the class of alkalis, on account of some resemblance it bears to those salts: but it has been demonstrated by accurate experiments, that we should rather consider it as a neutral salt; that it is composed of an alkali and of a particular saline substance called the sedative salt, which adheres to the alkali in the same manner as an acid, but can be separated by the addition of any acid whatever, the added acid joining itself to the alkali in the place of the sedative salt. As this conjunction of an acid with the alkali of borax happens without the least effervescence, our principles lay us under a necessity of allowing that alkali to be perfectly free of air, which must proceed from its being incapable of union with fixed air and with the sedative salt at the same time: whence it follows, that, were we to mix the sedative salt with an alkali saturated with air, the air would immediately be expelled, or the two salts in joining would produce an effervescence. This I found to be really the case upon making the trial, by mixing a small quantity of the sedative salt with an equal quantity of each of the three alkalis, rubbing the mixtures well in a mortar, and adding a little water. It is however proper

in this place to observe, that, if the experiments be made in a different manner, they are attended with a singular circumstance. If a small quantity of the sedative salt be thrown into a large proportion of a dissolved fixed alkali, the sedative salt gradually disappears, and is united to the alkali without any effervescence; but if the addition be repeated several times, it will at last be accompanied with a brisk effervescence, which will become more and more remarkable, until the alkali be entirely saturated with the sedative salt.

THIS *phænomenon* may be explained by considering the fixed alkalis as not perfectly saturated with air: and the supposition will appear very reasonable, when we recollect, that those salts are never produced without a considerable degree of heat, which may easily be imagined to dissipate a small portion of so volatile a body as air. Now, if a small quantity of the sedative salt be thrown into an alkaline liquor, as it is very slowly dissolved by water, its particles are very gradually mixed with the atoms of the alkali. They are most strongly attracted by such of these atoms as are destitute of air, and therefore join with them without producing an effervescence; or, if they expel a small quantity of air from some of the salt, this air is at the same time absorbed by such of the contiguous particles as are destitute of it, and no effervescence appears until that part of the alkali, which was in a caustic form or destitute of air, be nearly saturated with the sedative salt. But if, on the other hand, a large proportion of the sedative salt be perfectly and suddenly mixed with the alkali, the whole, or a large part, of the air is as suddenly expelled.

IN the same manner may we also explain a similar *phænomenon*, which often presents itself in saturating an alkali with the different acids: the effervescence is less considerable in the first additions of acid, and becomes more violent as the mixture approaches the point of

saturation. This appears most evidently in making the *sal diureticus* or regenerated tartar: The particles of the vegetable acid here employed being always diffused thro' a large quantity of water, are more gradually applied to those of the alkali, and during the first additions are chiefly united to those that are freest of air.*

THAT the fixed alkali, in its ordinary state, is seldom entirely saturated with air, seems to be confirmed by the following experiment.

I exposed a small quantity of a pure vegetable fixed alkali to the air, in a broad and shallow vessel, for the space of two months; after which I found a number of solid crystals, which resembled a neutral salt so much as to retain their form pretty well in the air, and to produce a considerable degree of cold when dissolved in water. Their taste was much milder than that of ordinary salt of tartar; and yet they seemed to be composed only of the alkali, and of a larger quantity of air than is usually contained in that salt, and which had been attracted from the atmosphere: for they still joined very readily with any acid, but with a more violent effervescence than ordinary; and they could not be mixed with the smallest portion of vinegar, or of the sedative salt, without emitting a sensible quantity of air.

As it now appeared that several alkaline substances have an attraction for fixed air, I tried a few experiments to learn the relative strength of their several attractions.

TWENTY four grains of magnesia in fine powder were mixed with five ounces of the caustic ley in a small vial, which was immediately corked and shaken frequently for four hours. The ley was then poured off, and the magnesia washed with repeated affusions of water, and dried. It had lost about the half of its weight, and when reduced to a fine powder was readily dissolved by acids

* Boerh. Operat. Chem. process. LXXVI.

with an effervescence which was hardly perceivable: the alkali had therefore extracted its air. I also threw some fresh magnesia into the ley which had been poured off, and thereby rendered it perfectly mild and similar to a solution of salt of tartar; so that it effervesced briskly with acids.

WITH an ounce of the mild spirit of salt ammoniac, I mixed a dram of magnesia in very fine powder which had been previously deprived of its air by fire; and observing that the magnesia had a tendency to concrete into a solid mass, I shook the vial very frequently. After some days the powder was increased to more than double its former bulk; and when the vial was opened, the alkaline spirit emitted a most intolerably pungent smell. It likewise floated upon water, but was not perfectly caustic; for it still yielded some air when mixed with acids, and also rendered lime-water turbid: neither of which would probably have happened if I had used a greater quantity of magnesia, or had allowed the mixture to remain a longer time in the vial. I now washed out the whole of the mixture into a bowl, and dried the magnesia until it lost all smell of the alkali. It weighed a dram and fifty eight grains, effervesced violently with acids, and therefore contained a large quantity of air, which had been drawn from the alkali by a stronger attraction.

HAVING formerly shewn, that magnesia saturated with air separates an acid from a calcarious earth, which it is not able to do after being deprived of its air by fire; I now suspected that the air was the cause of this separation, because I found that it was joined to the calcarious earth at the same time that the acid was joined to the earth of magnesia; and imagined that a pure calcarious earth might possibly have a stronger attraction for acids than a earth of magnesia.

I therefore dissolved two drams of magnesia in the

marine acid, and thus obtained a compound of an acid and of the pure earth of this substance ; for the air which was at first attached to it, was expelled during the dissolution. I then added thirty grains of strong quick-lime in exceeding fine powder, shook the mixture well, and filtrated it. The powder remaining in the paper, after being well washed, was found to be a magnesia, which, as I expected, was destitute of air ; for it was dissolved by the vitriolic acid without effervescence. And the filtrated liquor contained the lime united to the acid ; for upon dropping spirit of vitriol into it, a white powder was immediately formed.

WE must therefore acknowledge a stronger attraction between the calcarious earths and acids than between these and magnesia : but how does it then happen, that, if magnesia saturated with air be mixed with a compound of acid and calcarious earth, these two last, which attract one another the most strongly, do not remain united ; but the acid is joined to the magnesia, and the calcarious earth to the air which it attracts much more weakly than it does the acid ? Is it because the sum of the forces which tend to join the magnesia to the acid and the calcarious earth to the air, is greater than the sum of the forces which tend to join the calcarious earth to the acid, and the magnesia to the air : and because there is a repulsion between the acid and air, and between the two earths ; or they are somehow kept asunder in such a manner as hinders any three of them from being united together ?

THE first part of this supposition is favoured by our experiments, which seem to shew a greater difference between the forces wherewith the calcarious earth and magnesia attract fixed air, than between those which dispose them to unite with the acid. The repulsions however hinted in the second are perhaps more doubtful, tho' they are suggested in many other instances of decom-

position ; but the bounds of my present purpose will not allow me to enter upon this subject, which is one of the most extensive in chemistry.

We meet also with a difficulty with respect to the volatile alkali similar to the above. Thus a calcareous earth that is pure or free of air has a much stronger attraction for acids than a pure volatile alkali, as is evident when we mix quick-lime with salt ammoniac ; for the alkali is then immediately detached from the acid : and agreeably to this I found, upon trial, that a pure or caustic volatile alkali does not separate a calcareous earth from an acid. Yet, if we mix a mild volatile alkali, which is a compound of alkali and air, with a compound of acid and calcareous earth, these two last, which attract one another most strongly, do not remain united ; but the acid is joined to the alkali and the earth to the air, as happens in the precipitation of a calcareous earth from an acid, by means of the common or mild volatile alkali.

I remember likewise a parallel instance with regard to quick-silver. This metal has an attraction for the vitriolic acid, and when joined to it appears under the form of turbith mineral : but this attraction is weaker than that of the fixed alkali for the same acid ; for if we mix a dissolved salt of tartar with turbith mineral, the turbith is converted into a brown powder, and the alkali into vitriolated tartar ; which change happens the sooner, if the pure or caustic alkali is used. Yet, if to a compound of quick-silver and the nitrous acid, we add a compound of the fixed alkali and the vitriolic acid, or a vitriolated tartar, and digest the mixture with a strong heat, the vitriolic acid does not remain with the alkali, but is joined to the quick-silver which it attracts more weakly, composing with it a turbith mineral ; while the alkali is joined to the nitrous acid which it likewise attracts more weakly than it does the vitriolic, and is converted into saltpetre.

From some of the above experiments, it appears, that a few alterations may be made in the column of acids in Mr. *Geoffroy's* table of elective attractions, and that a new column may be added to that table, according to the following scheme, where the alkaline substances are all considered as in their pure state and free of fixed air.

Acids.	Fixed air.
Fixed alkali,	Calcarious earth.
Calcarious earth,	Fixed alkali.
Volatile alkali and magnesia,	Magnesia.
* * * * *	Volatile alkali.
	* * * *

AT the foot of the first column several of the metals might follow, and after these the earth of alum; but as I don't know what number of the metals should precede that earth, I have left it to be determined by further experience.

THE volatile alkali and magnesia are placed in the same line of this column; because their force of attraction seems pretty equal. When we commit a mixture of magnesia and salt ammoniac to distillation, the alkali arises and leaves the acid with the magnesia; because this earth, by attracting the acid, represses its volatility, and it seems also to diminish the cohesion of the acid and alkali, and to render them separable by a gentle heat. If the magnesia be saturated with air, this likewise, on account of its volatile nature and attraction for the alkali, is driven up along with it, and makes it appear under a mild form, and in the same manner do the alkali and air arise from a mixture of salt ammoniac and of a crude calcarious earth.

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