

XXV. *Observations respecting the natural production of Saltpetre on the walls of subterraneous and other Buildings.* By John Kidd, M. D. Professor of Chemistry at Oxford. Communicated by William Hyde Wollaston, M. D. Sec. R. S.

Read June 16, 1814.

ALTHOUGH the following observations afford no positive evidence of the source of that saline efflorescence, which is so frequently seen on the walls of subterraneous and other buildings, and which, as consisting principally if not entirely of common nitre, long since gave rise to the name* by which that salt is most commonly known; yet as tending to throw some light on a very obscure part of natural history, they will not, perhaps, be unacceptable to this honourable and learned Society.

There can be no doubt that the production of saltpetre or nitre, in the situations above alluded to, had been observed long before there existed any general inducement to collect it from those sources; but after the invention and subsequent extensive employment of gunpowder, it became an object not only to search out every natural source of the principal ingredient of that important compound, but also to investigate the circumstances of its production; for the purpose either of accelerating the natural process, or of imitating it by artificial means.

* Saltpetre (Sal Petræ).

The usual and almost exclusive occurrence of saltpetre on walls constructed of limestone, and in situations exposed to animal and vegetable effluvia, in all probability led to the empirical practice of heaping together the mortar and refuse of old buildings with putrescent animal and vegetable matter; from a mixture of which kind, after exposure for a sufficient length of time to the action of the air, a quantity of nitre may usually be obtained by lixiviation: but it would be a question of mere curiosity, on this occasion at least, to investigate the origin of the practice. The intention of the present Paper is to state the result of a series of observations made during the last year, on the connexion that exists between the natural production of nitre and the state of the atmosphere. In detailing these observations, it will be convenient to give previously a description of the laboratory of the Ashmole Museum, in which building they were principally made: nor shall I be afraid of being thought too minute in this description, or in any other part of the following detail, by those at least who know the precision that is requisite in every induction, which like the present rests on phenomena of an obscure and equivocal nature.

The Ashmole Museum, which was built by Sir C. WREN in the reign of Charles the Second, is an insulated building, constructed entirely of calcareous freestone, and consisting of three stories. The lowermost of these stories was originally designed for, and has constantly been used as, a chemical laboratory.

The pavement of the laboratory, on its eastern, northern, and western sides, is about nine feet below the level of the street in which the Museum stands: on its southern side it is

on the same level with an area, about ten feet in breadth, which in part occupies the site of the ditch of the old town and insulates a quadrangular projecting part of the whole building of the Museum. The laboratory itself is a single room sixty feet in length from east to west, and twenty-five in breadth; having an arched stone ceiling, the centre of which is seventeen feet above the level of the pavement. The walls of this room, which are nearly three feet in thickness, are constructed of squared calcareous freestone, which I have reason to believe was dug from a quarry near Burford, and is technically called Windrush stone, from the river of the same name. There are four windows in the upper part of the north side of the laboratory, formed in the curve of the arched ceiling; the dimensions of each of which are five feet by four and a half.

There is no window either on the eastern or western side of the laboratory.

On the south side there are two windows, one at each extremity, looking into the area above described; and these windows are placed at the usual distance from the ground, that is, about three feet: and all that part of the south side intermediate to these two windows separates the laboratory from the quadrangular projecting part of the whole building of the Museum already mentioned.

The saline efflorescence takes place most copiously on the north wall, and it occurs on various parts of it from nearly the level of the pavement to within three or four feet of the centre of the arched ceiling. It takes place also, though not so abundantly, on the east and west walls; and also at the eastern and western extremity of the south wall; but it is

worth noticing, that I have never seen it on that part of the south wall which is common to the laboratory and the attached projecting building of the Museum. It is true that there are chimneys in this wall connected with fires that are lighted daily; but this circumstance does not seem sufficient to account for the absence of the nitre, because its formation takes place in another part of the laboratory equally near a chimney, and in which, from being inclosed, the temperature of the air is always considerably higher.

It is also worth noticing, that between the highest and lowest points of its appearance in every part of the building there are intercepted spaces entirely and always free from the least deposition.

I may here mention that the occasional formation of nitre is observable in many other buildings and parts of Oxford, besides the laboratory of the Ashmole Museum; as on the wall, called Long Wall, which bounds the park of Magdalene College to the west—on the exterior surface of the south wall of the Theatre—on the exterior surface of the three walls of the quadrangular projecting part of the Ashmole Museum—very abundantly on the inclined base of the windows of the Examination School, looking to the north—and also very abundantly on the west side of the wall, which separates the square of the Schools from the arched way leading from thence to the Theatre and Convocation House.

It has been observed repeatedly, that the presence of lime is necessary to the natural production of saltpetre; and in all the foregoing instances the stone on which the saline efflorescence takes place is the common limestone of Oxfordshire. I have only once observed its formation on the surface of a

brick wall : but in that instance the substance of those bricks on which the nitre appeared had crumbled away to some depth ; and if this destruction of their texture be owing to the presence of an unusual proportion of lime in the clay of which they are made (a supposition not improbable, since many parts of the stratum of clay from which bricks in this neighbourhood are made do contain an unusual proportion of lime) the reason of the exception in the case of this brick wall will correspond with the truth of the general observation above stated.

The following circumstance is particularly deserving of notice. A part of the north wall of the laboratory, on which saltpetre usually effloresced, having been covered with wainscot some months since, and the wainscot having been painted with common white paint, I was surprised after a time in observing an efflorescence on particular parts of the paint, similar to what might have been expected on the wall itself. Where this efflorescence had taken place the paint was loosened from the wainscot, and might be readily peeled off in small flakes. The saline particles of which this efflorescence consisted I at first supposed to be nitrate of lead ; but upon examination in various ways no trace of lead could be found in them, and they exhibited the principal characters of common nitre : they deflagrated, for instance, with charcoal, leaving a deliquescent alkaline residuum. Many weeks have elapsed since that saline efflorescence was brushed off, but I have not yet observed any renewal of it.

Though the production of saltpetre had been pointed out to me in the laboratory of the Ashmole Museum as long since as the year 1802, I was prevented by many circumstances from observing with any degree of regularity or precision

the phenomena of this natural process previously to the commencement of last year: about which time having carefully brushed away the whole of the saline efflorescence from a part of the north wall situated below the level of the street, and very imperfectly exposed to the light, I was surprised by the fact of its quick reappearance. It was brushed away at the end of January, but within three days it had again effloresced in sufficient quantity to present that appearance of hoar frost, or down, or mould, which is very characteristic of the manner in which naturally formed saltpetre is often accumulated; and which a person, utterly incapable of judging of the real nature of the substance, described at the time by the term "damp."

I was still more surprised, however, in observing after a few days, that the quantity of the saltpetre was apparently very much diminished; and that at the end of eight or ten days there was scarcely any appearance of it remaining: though there was no reason to suppose a particle had either accidentally fallen to the ground or been intentionally removed.

The same part of the wall was again brushed perfectly clean, and I continued to make daily observations in expectation of a renewal of the process; but no new collection was perceptible, excepting in the form of a very few detached and minute capillary crystals, till the 16th of March: on which day, having been absent during the whole of the 14th and 15th, I found a more abundant accumulation than in the preceding instances.

It was an obvious supposition that the reproduction of the nitre was connected with some change in the state of the atmosphere: and it is to be remarked, that its first mentioned

appearance took place in frosty weather, and that its reappearance about the 16th of March had been preceded by a frost of a few days; whereas during the intervals, in which it disappeared and was not again produced, the weather had been mild. The wall was again brushed quite clean on the 16th of March; between which day and the 4th of April, a considerable quantity had again collected on the same part; the process having been more rapid during the last four or five days, which were cold.

On April the 12th the front of this part of the wall was renewed by scraping, for the purpose of observing what would be the effect of a fresh surface, and before the 25th of April, nitre had formed on many parts of this new surface; but having first increased and then continued stationary for some days, it began to diminish about the beginning of May, the state of the air having been very moist during the two or three preceding days.

About the middle of May, 1813, I selected several distinct parts on which the spontaneous formation of nitre usually takes place, some within and some without the building of the Museum, and began to make daily observations on the phenomena of that process, which I noted down at the time: but as a register of this kind would be unnecessarily tedious in its recital, I shall beg leave to give the following general results of those observations; requesting it may be kept in mind that I do not presume to lay a greater stress on them than is proportional to the short period of time, and the circumscribed space in which they were made.

It appears then from the observations I have hitherto been able to make, that the spontaneous formation of saltpetre is,

generally speaking, much more extensive and rapid in winter than in summer, whether it take place on the interior or exterior of a building: thus during the period of the cold weather in January, 1814, it became visible not only on parts of the walls where I had never before observed it, but even on the pavement of the laboratory. The part of the pavement on which it appeared is adjacent to the north wall; but as the greater part of the pavement is covered by a flooring of wood, it is impossible to say whether or not it took place on other parts also. The stone forming the pavement, is the same kind of limestone as that of which the walls are built.

Again, whereas in summer its reproduction is most rapid and extensive in proportion to the degree of light present, the reverse of this (though not universally) takes place in winter. Wherever the saline efflorescence in question occurs, the surface of the stone becomes permanently discoloured, as if from the effect of damp; but this discoloration is merely superficial. If these discoloured parts be whitewashed, the process still goes on; and the whitewash is gradually detached in flakes: but it is difficult to ascertain whether the nitre is formed on the whitewash, or on the wall which it covers; though probably the latter.

When the spontaneous formation of nitre takes place slowly and in a sheltered situation, it is at first visible in the form of minute prismatic crystals, which usually project from the surface of the wall nearly at right angles; but sometimes they are scattered in different directions, lying upon its surface so lightly as scarcely to appear in contact with it. In general, however, the saline efflorescence makes its appearance in extremely minute capillary crystals, either accumulated

in groups, which resemble recently fallen flakes of snow, or investing the wall like a fine down.

During the severely cold weather of January, 1814, it appeared in some places in the form of minute dense grains closely aggregated; while in others it still continued to wear the appearance of down or wool: and the local circumstances most obviously connected with this difference in the manner of crystallization, were the presence of a greater degree of light, where the granular deposition took place, and a less degree of shelter from the influence of cold air.

In some instances the production of the saltpetre is accompanied with a disintegration of the substance of the stone on which it is formed: but this circumstance is only observable on stones of a loose texture.

The shortest interval I have observed between the time of its having been brushed away and its reappearance, is four hours: but it was then in full efflorescence, and would probably have been visible much earlier. The observation was made on November the 17th, about midnight: there had been snow in the middle of the day, and the night was frosty.

The spontaneous formation of nitre takes place indifferently on the surface of the stones composing a wall, and of the mortar by which those stones are cemented: and near the close of the late frost, I observed it for the first time on the surface of a partition, consisting entirely of laths plastered over with the mortar or stucco commonly used for that purpose.

It accumulates in greater quantity on some parts of a given surface than on others; and this difference in the degree of its accumulation, is probably connected with some slight difference in the texture or composition of the stone on which it is formed:

for I have repeatedly observed that after a careful removal of it, its reproduction takes place to the same proportional extent in the same parts : and this difference in the degree of the efflorescence often takes place not by a gradual transition, but as abruptly as if the line of separation had been marked by a graver ; so that the part of the surface on one side of the line shall be almost totally devoid of any efflorescence, while on the other side it shall resemble the accumulation of hoar-frost on the small branches of a tree.

The saltpetre formed in summer scarcely appears to contain a particle of any calcareous salt : that formed in winter contains most evident traces of such a salt, though probably even in winter the amount of this is not much above one part in two hundred of the whole mass.

A frosty, clear, and dry state of the atmosphere, is particularly favourable to the natural production of nitre : but there seems to be a limit to its formation, on the same spot, even under the most favourable circumstances ; the quantity of the nitre not continuing to increase after it has proceeded to a certain extent.

In a moist state of the atmosphere the formation either does not take place at all, or goes on slowly : and if that state of the atmosphere which is unfavourable to the production of nitre continue a sufficient length of time, the nitre already formed gradually disappears. At the commencement of these observations I attributed the occasional disappearance of the nitre to its mechanical removal from the wall, and supposed that it must have been by accident brushed off : but repeated observations convinced me this was not the case, its disappearance proceeding as gradually as its previous appearance ;

besides which, had it fallen from the wall, I should most probably have found it on the pavement beneath, which never happened to me. It afterwards appeared probable, although I have never met with any condensed moisture on the surfaces submitted to the foregoing observations, that the aqueous vapour precipitated from the atmosphere in the state of it above alluded to, might dissolve minute particles of the nitre, and be absorbed with them into the substance of the wall; but on this supposition nitre ought to be found in lixiviating a portion of the stone taken near the surface. I have however made the experiment without detecting any nitre in the stone so taken. But, in opposition to the idea of the absorption of the nitre into the substance of the stone, I found the efflorescence disappear in more places than one during the severe frost of the present year (1814), at a time, when from the temperature of the stone, if not of the air also, the absorption here supposed could not have taken place; since, that temperature being below the freezing point, the aqueous particles would by congelation have been rendered incapable of dissolving the nitre.

It is deserving of notice, that such a spontaneous disappearance of the nitre, as has been just mentioned, took place antecedently to, and during the late heavy fall of snow on January 18 and 19.

Wishing to ascertain whether the free presence of atmospheric air be necessary in the natural process under consideration, I selected a part of the wall on which the formation of saltpetre usually takes place to a considerable extent; and insulated about a square foot of its surface which had been previously brushed quite clean. It was insulated by means of a plate of

glass, the edges of the frame of which were covered with a cement, so as to exclude any access of air between the glass and the wall. As the depth of the frame was not more than the third of an inch, the inclosed space contained but an inconsiderable quantity of atmospheric air. On the following day, October 29, I observed that a formation of nitre had taken place on the part of the wall within the glass, but that it was not so extensively diffused nor so abundantly deposited, as had been usual before the application of the glass; and the crystals, which were distinctly prismatic, were much more accurately defined, and larger than I had ever before observed them; in consequence, probably, of the tranquil state of the medium in which they were formed. On the day following, October 30, the quantity was increased; but it remained stationary from that time to November 12, when it began to diminish; and on November 16, there was no longer any appearance of it: nor did it reappear in the interval between November 16 and 29. In the mean time the efflorescence had not only taken place on the adjacent parts of the wall in the usual manner, but had been more than once brushed off and again deposited, while no increase had taken place in that originally formed within the glass.

On Nov. 29, the exterior surface of the glass was, for a purpose to be mentioned presently, covered over with whitewash; which was not removed till January 8, 1814. No observation could of course be made on the appearance of the surface within the glass during the interval that the glass itself was covered with whitewash; but no nitre was visible on the removal of the whitewash on January 8. It had, however, reappeared before the morning of January 10, partly in separate

capillary prismatic crystals which were much larger than on the former occasion, and reached from the surface of the wall to the inner surface of the glass; and partly in small flocculent tufts: the whole quantity of the nitre formed being much greater than, and the manner of its formation being very different from, that formation which took place within the glass on October 29 and 30. Still the whole quantity was not nearly equal to that which was usually formed on the same surface when exposed to the free action of the atmosphere. The increased quantity however formed in January, compared with that formed in October, corresponds with the observation that the natural production of nitre is much influenced by temperature: but it is worth mentioning that while the nitre formed within the glass in January occurred either in distinctly prismatic crystals or in flocculent tufts, that which was formed on the adjacent parts of the wall was of the granular character above described. (pag. 516, lin. 3.)

Having by the foregoing experiment satisfied myself with respect to the necessity of the free presence of atmospherical air for the full effect in the spontaneous production of nitre, I wished to ascertain the nature of the connexion between the nitre formed and the stone on which it is formed; and particularly whether carbonate of lime simply would be sufficient for its production. I therefore made a nearly liquid paste with distilled water and prepared chalk,* with which I covered the exterior surface of the glass that had been attached to the wall for the purpose already mentioned: but though nitre was

* As chalk sometimes contains magnesia, and almost always a small proportion of silex and alumine, I intend on a future occasion to repeat the experiment, using very finely pulverised crystallised calcareous spar, instead of chalk.

repeatedly formed in the neighbourhood of the glass, not a particle appeared on the whitewash during the space of nearly six weeks, from November 29 to January 8.

The foregoing statement contains the general results of all the observations I have hitherto been able to make on the present subject. I subjoin an imperfect analysis of the stone of which the laboratory of the Ashmole Museum is built, and of the saltpetre periodically formed on it; concluding with a few remarks on the local differences connected with a more or less extensive formation of that substance, and on its probable or rather possible source.

The stone, of which the laboratory is constructed, belongs to one of those alternating series of clay, and sand, and calcareous freestone, of which the varieties of Bath stone form nearly the lowermost strata; and the Headington stone, of which the greater part of Oxford is built, the uppermost. It is principally made up of the *debris* of small sea shells, but frequently contains organic vegetable remains, and always some proportion of sand and ochry clay.

Six portions of this stone taken from different parts of the laboratory, each weighing at least two hundred grains, were separately submitted to the action of a sufficient quantity of diluted muriatic acid. The undissolved residuum, which amounted in no instance to as much as four parts in a hundred, consisted of a yellowish brown ochry clay, mixed with a few particles of white sand, and small laminar fragments of a dirty white colour, very much resembling portions of the siliceous incrustation of the Geyser spring. Small flocculent

shreds slowly subsided in the muriatic solution, derived probably from the membranous part of the shelly matter of the limestone; for this insoluble residuum, when thrown into red-hot nitre, slightly deflagrated, and gave out an odour resembling burnt bones: and as this residuum had been collected without the use of a filter, the inflammable matter could not well have been derived from any other source than the stone itself.

The muriatic solution contained a small proportion of iron, and gave a very slight trace of magnesia. So that the composition of the stone may be thus stated.

Carbonate of lime	-	-	-	-	96
Oxide of iron, sand, ochry clay, and animal membrane					4
					<hr/>
					100

In offering the following imperfect analysis of the saltpetre produced in the situations above alluded to, it is necessary to state, that the quantities on which I have hitherto had it in my power to operate have been very small.

Some preliminary experiments made on a solution of saltpetre which had been formed during the summer, gave the following results.

The solution contained no disengaged acid or alkali; and upon the addition of oxalate of ammonia afforded the slightest possible evidence of the presence of lime. It contained minute portions of sulphuric and muriatic acid. A portion of it being evaporated left a mass of crystals which, in their form, as in all their other characters, exhibited the properties of nitrate of potash.

As it is usually stated by writers who speak of the subject,

that nitrate of lime is a principal constituent part of saltpetre formed by a natural process, I was much surprised by the very slight trace of lime evident in the present instance; though I had felt assured previously that but little would be found in the natural saltpetre which I have had an opportunity of examining; having never observed in it any tendency towards deliquescence. Having had frequent occasion to suppose that carbonate of lime is much more readily soluble in water than is commonly believed, and having never been able to detach the saline efflorescence in question from the walls of the laboratory, &c. without admixture of particles of the limestone, or of the whitewash, amounting to at least seven or eight parts in a hundred, it struck me that these particles might be the source of the lime rendered evident by the addition of the oxalate of ammonia in the solution of the saltpetre. I therefore pulverised small portions of calcareous spar, of the common limestone of this country, and of whitewash; and having agitated accurately distilled water, at the common temperature, with each of these portions, I then filtered the water, and tested it with oxalate of ammonia. In each instance there was fully as copious a precipitate as when the oxalate of ammonia had been added to an equal quantity of the solution of saltpetre.

Similar preliminary experiments having been made on some saltpetre detached from the same part with that already submitted to examination, but formed during the winter instead of the summer, the same results were obtained with this single difference, that the precipitate obtained by the addition of oxalate of ammonia was much more copious: and I found this to be the case from whatever part of the laboratory or else-

where the saltpetre had been detached, provided it had been formed during the winter. I could not extend the experiment on the saltpetre formed during the summer, having only reserved a portion from one spot.

Judging from such experiments as I have made, it appears that the saltpetre formed in the situations described in this paper, consists of full 99 parts in 100 of nitrate of potash; with a very minute proportion of some calcareous salt, which is either not at all present in the saltpetre formed during summer, or is present in smaller quantity than in that formed during winter—though even in the latter instance it scarcely amounts to one part in 200.

The proportion of sulphuric and of muriatic acid, and the bases with which these acids are combined, I have not attempted to ascertain, on account of the minuteness of the proportion in which they evidently exist.

In considering the relative situations of the different parts of the laboratory, and the other buildings also, in which saltpetre is naturally formed, it is evident that the efflorescence takes place only where the exterior of the wall on which it is formed, is either exposed to the direct influence of the weather, or is in contact with the adjacent ground; not taking place at all in those instances in which the wall is neither exposed to the weather on either side, nor is in contact with the adjacent ground: from which it might be argued, that the effect depends upon the action of the external air, or of the moisture of the ground transmitted through the substance of the wall: but the result of that experiment in which, the action of the

air on the interior surface of the wall having been prevented by the intervention of a glass, the formation of nitre took place only to a very slight extent, is in a great measure at variance with such a supposition.

Again, though it is evident that the natural production of the saltpetre is closely connected with changes in the state of the atmosphere, those changes relating not only to its temperature but also to the degree of its moisture and barometrical pressure; yet a much longer series of observations, and these not partial like the present, but carried on in various parts of the world, is requisite, before even this part of the problem can be accurately solved. There still would remain a part of much more difficult solution, namely, the source of the metallic base of the alkali of the nitre.

With respect to this difficult question, if we compare the elements present in the composition of the saltpetre formed, with the elements of the substances present during its formation, it seems a reasonable conclusion that the potassium, or the metallic base of the potash of the saltpetre, is either a simple principle of some of the elements present, or that it results from the union of two or more of those principles, or of two or more of the elements themselves.*

The gross compounds present during the formation of saltpetre, in the instances mentioned in this paper, are atmospheric air and the limestone on which the saltpetre effloresces;

* The terms "element" and "principle" are here used in the same relation to each other as the early physical philosophers used the terms στοιχεῖα and Ἀρχαί. They supposed that the former, though incapable of decomposition by common means, were not necessarily to be considered as absolutely simple substances; those absolutely simple substances they expressed by the term Ἀρχαί.

and all the component parts of these may be ultimately resolved into the following elements—oxygen, nitrogen, hydrogen, and carbon, together with iron and the metallic bases of some of the earths,

The component parts of nitrate of potash, of which the saltpetre under consideration almost entirely consists, are nitric acid, water, and potash; which may be resolved into the following elements—oxygen, nitrogen, hydrogen, and potassium: and all these elements are experimentally known to be present in the situations where saltpetre is formed, with the exception of potassium.

In the supposition then that the saltpetre is a product and not an educt of the above process, since no potash can be detected either in the air or limestone, the potassium must either be contained in a free state in the atmosphere or in the limestone, which from its remarkable attraction for oxygen is inadmissible: or it must be a component principle of some one of the elements present; or lastly, it must be itself a compound of two or more of the principles of those elements, or of two or more of the elements themselves.

But I am aware that the saltpetre may be considered as an educt of the process, and that it may possibly exist already formed in the atmosphere in a state of minute division: yet, when we consider the comparatively fixed nature of that salt, and that no experiments have yet detected its presence in atmospherical air, or in the moisture precipitated from atmospherical air; and lastly, when we reflect on the probability that the metals, of which potassium is one, are compound bodies, the former supposition seems upon the whole preferable to the latter.

February, 1814.