

VIII. *Observations on the Sulphur Wells at Harrogate, made in July and August, 1785. By the Right Reverend Richard Lord Bishop of Landaff, F. R. S.*

Read February 2, 1786.

IN 1733, when Doctor SHORT first published his Treatise on Mineral Waters, there were only three sulphur wells at Harrogate; there are now four. I made some inquiry respecting the time and occasion of making the fourth well, and received the following account from an old man, who was himself principally concerned in the transaction. About forty years ago, a person who, by lease from the Earl of BURLINGTON, had acquired a right of searching for minerals in the forest of Knaresborough, made a shew as if he had a real intention of digging for coal, on the very spot where the three sulphur wells were situated. This attempt alarmed the apprehensions of the inn-keepers and others at Harrogate, who were interested in the preservation of the wells: they gave him what legal opposition they could, and all the illegal that they durst. At length, for the sum of one hundred pounds, which they raised amongst themselves, the dispute was compromised, and the design real or pretended of digging for coal was abandoned. Sulphur water, however, had risen up where he had begun to dig. They inclosed the place with a little stone edifice, and putting down a basin, made a fourth well. By a clause in the act of parliament for inclosing Knaresborough Forest, passed

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in 1770, it is rendered unlawful for any person whatever to sink any pit, or dig any quarry or mine, whereby the medicinal springs or waters at Harrogate may be damaged or polluted; so that no attempts of the kind above-mentioned need be apprehended in future.

This fourth well is that which is neareft to one of the barns of the Crown-Inn, being about ten yards diftant from it. In digging, a few years fince, the foundation of that barn, they met with fulphur water in feveral places. At a very little diftance from the four wells there are two others of the fame kind; one in the yard of the Half-Moon-Inn, difcovered in digging for common water in 1783, and another which breaks out on the fide of the rivulet below that Inn. On the banks of that rivulet I faw feveral other fulphureous fprings: they are eafily diftinguifhed by the blacknefs of the earth over which they flow.

On the declivity of a hill, about a quarter of a mile to the weft of the fulphur wells at Harrogate, there is a bog which has been formed by the rotting of wood: the earth of the rotten wood is in fome places four feet in thicknefs, and there is a ftratum confifting of clay, and finall loofe decaying fand-ftones, every where under it. The hill above is of grit-ftone. In this bog there are four more fulphur wells; one at the top, near the rails which feparate the bog from the Common; and three at the bottom, though one of thefe, ftrictly fpeaking, is not in the bog but at the fide of it in the ftratum on which the bog is fituated, and at the diftance of a yard or two from a rivulet of frefh water, which runs from thence to Low Harrogate, paffing clofe to the fide but above the level of the fulphur wells of that place. On the other fide of the hill, above the bog, and to the weft of it, there is another fulphur well on the fide of a brook; and it has been thought that the wells both at Harrogate and in the bog

bog are supplied from this well. In a low ground, between High Harrogate and Knaresborough, there is a sulphur well; another to the north of it in Bilton Park, at about the distance of a mile; and another to the south of it, at a less distance, was discovered this year in digging for common water by a person of the name of RICHARDSON; and, lastly, there is another at a place called Hookstone Crag: none of these last mentioned wells are above two miles distant from High Harrogate; and by an accurate search a great many more might, probably, be discovered in the neighbourhood.

It is not unusual to dig within a few yards of any of these sulphur wells, and to meet with water which is not sulphureous. I ordered a well to be dug in the fore-mentioned bog, sixteen yards to the south of the sulphur well which is near the rails, and to the same depth with it; the water with which it was presently filled was chalybeate, but in no degree sulphureous. I had another well dug, at about thirty yards distance from the three sulphur wells which are situated at the lower extremity of the bog; this well, by the declivity of the ground, was ten or twelve feet below their level, but its water was not sulphureous. From the first well which I dug, it is evident, that every part of the bog does not yield sulphur water; and from the second, which was sunk into the clay, it is clear that every part of the stratum on which the bog is placed does not yield it, though one of the wells is situated in it.

The sulphur wells at Harrogate are a great many feet below the level of those in the bog; but they communicate with them, if we may rely on what Doctor SHORT has told us—
“That about the beginning of this century, when the course of people was very great to the Spaw at Harrogate, one ROBERT WARD, an old man, made a basin in the clay under
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the moss of a bog where the strongest and briskest of these sulphur springs rise, and gathered half an hoghead of water at a time for the use of the poor; but when he laded this he almost dried the three sulphur wells at the village, whence it is evident, that all have the same origin and communicate with one another." By conversing with some of the oldest and most intelligent people at Harrogate, I could not find that they entertained any opinion of the water at the bog having a communication with that at the spaw. This circumstance might easily be ascertained; and, if the fact should be contrary to what Doctor SHORT supposed, the wells at the bog ought to be covered from the weather as those at the village are; they would by this mean yield great plenty of water for the baths which are wanted by invalids, and which are often very scantily supplied by the wells at Harrogate, notwithstanding the attention which is used in preserving the water which springs at the four wells, by emptying them as often as they become full during both the day and night time. And indeed it is surprising, that the well on the side of the rivulet below the Half-Moon-Inn, which is so well situated for the purpose, has never been inclosed for the furnishing sulphureous water for the baths. The present mode of carrying the water in casks to the several houses where the persons lodge who want to bathe in it, is very troublesome, and the water thereby loses of its virtue. Some of the wells about the village, that for instance which has been discovered at the Half-Moon-Inn, the water of which, I believe, springs from a different source from that which supplies the four sulphur wells, should be either enlarged to a greater horizontal breadth, or sunk to a greater depth, in order to try, by one or both of these ways, whether the quantity and strength of the water might not be increased;

and if that should, as it probably would be the case, one or more baths might be erected after the manner of those at Buxton and other places; or, by proper additional buildings, warm bathing in sulphureous water might be practised, as is done in common water in the bagnios in London. The saltness of the sulphureous water, if that should be thought useful, might easily be made even greater than that of sea water, by adding a quarter of a pound of common salt to every gallon of the water used in forming a bath. The waters at Harrogate, though they have long been very beneficial, have not yet been rendered so useful to mankind, as an intelligent and enterprising person might make them. The alternate strata of sand, stone, and shale, which compose the lower hills near the wells at Harrogate, dip very much, as may be seen in a stone quarry about two hundred yards from the wells; and the same circumstance may be observed in dry weather, in following the bottom of the brook from the village up to the bog; and hence, if there be a communication between the waters of the bog and of the village, as Doctor SHORT asserts, it is probable, that the same stratum of shale which is seen at the bottom of the wells at the village, breaks out again at the bog above the village, and that the water finds its way from the bog to the village through the crevices of that stratum.

After having observed, as carefully as I could, the number and situation of the sulphur wells about Harrogate, I took notice of the temperature of the four at the village. In the month of June, 1780, when the thermometer in the shade was 72° , and the pump water at the Granby-Inn, the well of which is fifty feet deep, was 48° , the strongest of the sulphur wells, being that of which invalids usually drink, was 50° . On the 29th of July in this year, after the earth had been parched with

with drought for many months, the heat of the strongest well was 54° ; the water of the Granby pump was on the same day 48° , and the heat of the air in the shade 76° . Doctor WALKER, who has lately written a treatise on Harrogate water, says, that the heat of this spring was 48° , when that of an adjoining rivulet was 53° . And I have little doubt in believing, that if the experiment was made in cold weather, the temperature of the same well would be found to be several degrees below 48° . This variation of temperature in the sulphur water indicates its springing from no great depth below the surface of the earth; or at least it indicates its having run for a considerable distance in a channel so near to the surface of the earth, as to participate of the changes of temperature, to which that is liable from the action of the sun. But the heat of the sulphur water is not only variable in the same well, at different times, but it is not the same in all the wells at the same time. If we call the strongest well the first, and reckon the rest in order, going to the right, the third well, which is reckoned the next strongest, was 57° hot when the first well was 54° . In support of the conjecture that the sulphur water of the strongest well would in a cold season make the thermometer sink below 48° , which is the constant temperature of springs situated at a great depth in the earth in this country, it may be observed, that though the first and the third well are never frozen, yet the second and the fourth well are frozen in severe weather. When the second and the fourth well are covered with ice, it is probable, that the first and the third have a temperature far below 48° ; but that the sea salt, which is more abundant in them than in the other two wells, and which of all salts resists most powerfully the congelation of the water in which

it is dissolved, preserves them from being frozen in the coldest seasons incident to our climate.

As the temperature of these four wells is not the same in all of them at the same time, nor invariable in any of them, so neither does there seem to be any uniformity or constancy in them, with respect to the quantity of salt which they contain. The salt with which they are all impregnated is of the same kind in all, and it is almost wholly common salt; and though the quantity contained in a definite portion of any one of the wells is not, I think, precisely the same at all seasons of the year, yet the limits within which it varies are not, I apprehend, very great. A method is mentioned in the LXth volume of the Philosophical Transactions, of estimating the quantity of common salt dissolved in water, by taking the specific gravity of the water: this method is not to be relied on, when any considerable portion of any other kind of salt is dissolved along with the sea salt; but it is accurate enough to give a good notion of the quantity contained in the different wells at Harrogate. On the 13th of August, after several days of rainy weather, I took the specific gravities of the four sulphur wells at the village, the drinking well being the first.—Rain water 1.000; first well 1.009; second well 1.002; third well 1.007; fourth well 1.002. By comparing these specific gravities with the table which is given in the LXth volume of the Transactions, it may be gathered, that the water of the first well contained $\frac{1}{72}$ of its weight of common salt; that of the second and fourth, $\frac{1}{356}$; and that of the third, $\frac{1}{84}$. After four days more heavy rain I tried the strongest well again, and found its specific gravity to be 1.008. It is worthy of observation, that the water, as it springs into the first and third well, is quite transparent, but usually of a pearl colour in the second and

fourth, similar in appearance to the water of the first or third well after it has been exposed a few hours to the air; hence it is probable, that the external air has access to the water of the second and fourth well before it springs up into the basin. A great many authors have published accounts of the quantity of common salt contained in a gallon of the water of the strongest well; they differ somewhat from each other, some making it more, others less, than two ounces. These diversities proceed either from the different care and skill used in conducting the experiment; or from a real difference in the quantity of salt with which the water is impregnated at different seasons of the year. The medium quantity of salt contained in a gallon falls short of, I think, rather than exceeds two ounces. The sea water at Scarborough contains about twice as much salt as is found in the strongest sulphur well at Harrogate. The sulphur wells at the bog are commonly said to be sulphureous, but not saline. This, however, is a mistake; they contain salt, and salt of the same kind as the wells at the village. I could not distinguish the kind of salt by the method in which I had estimated the quantity contained in the sulphur wells; I therefore evaporated a gallon of the water of the well in the bog which is near the rails, and obtained a full ounce of common salt, of a brownish colour: the colour would have gone off by calcination. In what degree the medicinal powers of Harrogate water depend on its sulphureous, and in what degree on its saline impregnation, are questions which I meddle not with: I would only just observe on this head, that any strong sulphureous water, such as that of Keddlestone in Derbyshire, or of Shap in Westmoreland, which naturally contains little or no sea salt, may be rendered similar to Harrogate water, by dissolving in it a proper proportion of common salt. The four
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Sulphur wells at Harrogate are very near to each other; they might all be included within the circumference of a circle of seven or eight yards in diameter; yet, from what has been said it is evident, that they have not all either the same temperature, or the same quantity of saline impregnation. This diversity of quality, in wells which have a proximity of situation, is no uncommon phenomenon; and though at the first view it seems to be surprising, yet it ceases to be so on reflexion: for the waters which feed wells so circumstanced, may flow through strata of different qualities situated at different depths, though in the same direction; or through strata placed both at different depths, and in different directions; and that this is the case at Harrogate is probable enough, there being hills on every side of the hollow in which the village is placed.

With respect to the sulphureous impregnation of these waters, I made the following observations.

The inside of the basin, into which the water of the strongest well rises, is covered with a whitish pellicle, which may be easily scraped off from the grit-stone of which the basin is made. I observed, in the year 1780, that this pellicle on a hot iron burned with the flame and smell of sulphur. I this year repeated the experiment with the same success; the substance should be gently dried before it is put on the iron. I would further observe, that the sulphur is but a small part of the substance which is scraped off. That I might be certain of the possibility of obtaining true palpable sulphur from what is scraped off from the basin, and at the same time give some guess at the quantity of sulphur contained in it, I took three or four ounces of it, and having washed it well, and dried it thoroughly by a gentle heat, I put two ounces into a clean glass retort, and sublimed from it about two or three grains of

yellow sulphur. This sulphur, which stuck to the neck of the retort, had an oily appearance; and the retort, when opened, had not only the smell of the volatile sulphureous acid, which usually accompanies the sublimation of sulphur, but it had also the strong empyreumatic smell which peculiarly appertains to burnt oils; and it retained this smell for several days. It has been remarked before, that the salt separable from the sulphur water was of a brownish colour; and others, who have analysed this water, have met with a brown substance, which they knew not what to make of; both which appearances may be attributed to the oil, the existence of which was rendered so manifest by the sublimation here mentioned. I will not trouble the Society with any conjectures concerning the origin of this oil, or the medium of its combination with water; the discovery of it gave me some pleasure, as it seemed to add a degree of probability to what I had said concerning the nature of the air with which, in one of my Chemical Essays, I had supposed Harrogate water to be impregnated. I will again take the liberty of repeating the query which I there proposed. "Does this air, and the inflammable air separable from some metallic substances, consist of *oleaginous* particles in an elastic state?" When I ventured to conjecture, in the Essay alluded to, that sulphureous waters received their impregnation from air of a particular kind, I did not know that Professor BERGMAN had advanced the same opinion, and denominated that species of air, Hepatic Air. I have since then seen his works, and very readily give up to him not only the priority of the discovery, but the merit of prosecuting it. And though what he has said concerning the manner of precipitating sulphur from these waters can leave no doubt in the mind of any chemist concerning the actual existence of sulphur

in them; yet I will proceed to the mention of some other obvious experiments on the Harrogate water, in support of the same doctrine.

Knowing that, in the baths of Aix-la-Chapelle, sulphur is found sticking to the sides and top of the channel in which the sulphureous water is conveyed, I examined with great attention the sides of the little stone building which is raised over the basin of the strongest well, and saw them in some places of a yellowish colour: this I thought proceeded from a species of yellow moss, commonly found on grit-stone: I collected, however, what I could of it by brushing the sides of the building, at the distance of three or four feet from the water in the basin: on putting what I had brushed off on a hot iron, I found that it consisted principally of particles of grit-stone, evidently however mixed with particles of sulphur.

Much of the sulphureous water is used for baths at Harrogate; and for that purpose all the four wells are frequently emptied into large tubs containing many gallons apiece; these constantly stand at the wells, and the casks, in which the water is carried to the several houses, are filled from them. On examining the insides of these tubs, I found them covered, as if painted, with a whitish pellicle. I scraped off a part of this pellicle: it was no longer soluble in water; but, being put on a hot iron, it appeared to consist almost wholly of sulphur. Some of these tubs have been in use many years, and the adhering crust is thick in proportion to the time they have been applied to the purpose; but the sulphur pellicle was sufficiently observable on one which was new in the beginning of this season. The water when it is first put into these tubs is transparent; when it has been exposed to the air for a few hours, it becomes milky; and, where the quantity is large, a white
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cloud may be seen slowly precipitating itself to the bottom. This white precipitate consists partly, I am not certain that it consists wholly, of sulphur; and the sulphur is as really contained in the waters denominated sulphureous, as iron is contained in certain sorts of chalybeate waters; in the one case the iron is rendered soluble in water by its being united to fixed air, or some other volatile principle; and in the other sulphur is rendered soluble in water by its being united to fixed air, or some other volatile principle: neither iron nor sulphur are of themselves soluble in water, but each of them, being reduced into the form of a salt by an union with some other substances, becomes soluble in water, and remains dissolved in it, till that other substance either escapes into the air, or becomes combined with some other body.

About forty years ago, they took up the basin of the third well, and a credible person, who was himself present at the operation, informed me, that in all the crevices of the stone on which the basin rested, there were layers of pure yellow sulphur. This I can well believe, for I ordered a piece of shale to be broken off from the bottom of the fourth well; it was split, as shale generally is, into several thin pieces, and was covered with a whitish crust. Being laid on a hot iron, in a dark room, it cracked very much, and exhibited a blue flame and sulphureous smell.

If the water happens to stand a few days in any of the wells, without being disturbed, there is found at the bottom a black sediment; this black sediment also marks the course of the water which flows from the well, and it may be esteemed characteristic of a sulphur water. The surface of the water also, when it is not stirred for some time, is covered with a whitish scum. Doctor SHORT had long ago observed, that
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both the black sediment, and the white scum, gave clear indications, on a hot iron, of their containing sulphur: I know not whence it has come that his accuracy has been questioned in this point; certain I am, that on the repetition of his experiments I found them true. The white scum also, which is found sticking on the grafs over which the water flows, being gently dried, burns with the flame and smell of sulphur. From what has been said it is clear, that sulphur is found at Harrogate, sticking to the bason into which the water springs; sublimed upon the stones which compose the edifice surrounding the well; adhering to the sides of the tubs in which the water stands; subsiding to the bottom of the channel in which the water runs; and covering the surface of the earth, and of the blades of grafs, over which it flows. It is unnecessary to add another word on this subject; it remains that I risk a conjecture or two, on the primary cause of the sulphureous impregnation observable in these waters.

In the Chemical Essay before referred to, I have shewn, that the air separable from the lead ore of Derbyshire, or from Black-Jack, by solution in the acid of vitriol, impregnates common water with the sulphureous smell of Harrogate water; and I have also shewn that the bladder fucus or sea-wrack, by being calcined to a certain point, and put into water, not only gives the water a brackish taste, but communicates to it, without injuring its transparency, the smell, taste, and other properties of Harrogate water. Professor BERGMAN impregnated water with a sulphureous taste and smell, by means of air separated by the vitriolic acid from *hepar sulphuris*, made by fusion of equal weights of sulphur and pot-ashes, and from a mass made of three parts of iron filings melted with two of sulphur; and he found also, that Black-Jack and native Siberian

iron yielded hepatic air, by solution in acids. This, I believe, is the main of what is known by chemists on this subject; what I have to suggest, relative to the Harrogate waters in particular, may perhaps be of use to future inquirers.

I have been told, that on breaking into an old coal-work, in which a considerable quantity of wood had been left rotting for a long time, there issued out a great quantity of water smelling like Harrogate water, and leaving, as that water does, a white scum on the earth over which it passed. On opening a well of common water, in which there was found a log of rotten wood, an observant physician assured me, that he had perceived a strong and distinct smell of Harrogate water. Dr. DARWIN, in his ingenious Account of an artificial Spring of Water, published in the first part of the LXXVth volume of the Philosophical Transactions, mentions his having perceived a slight sulphureous smell and taste in the water of a well which had been sunk in a black, loose, moist earth, which appeared to have been very lately a morass, but which is now covered with houses built upon piles. In the bog or morass above-mentioned there is great plenty of sulphureous water, which seems to spring from the earth of the rotten wood of which that bog consists. These facts are not sufficient to make us certain, that rotten wood is efficacious in impregnating water with a sulphureous smell; because there are many bogs in every part of the world, in which no sulphureous water has ever been discovered. Nor, on the other hand, are they to be rejected as of no use in the inquiry; because wood, at a particular period of its putrefaction, or when situated at a particular depth, or when incumbent on a soil of a particular kind, may give an impregnation to water, which the same wood, under different circumstances, would not give.

The bilge water, usually found at the bottom of ships which are foul, is said to smell like Harrogate water: I at first supposed, that it had acquired this smell in consequence of becoming putrid in contact with the timber on which it rested, and this circumstance I considered as a notable support to the conjecture I had formed of rotten wood being, under certain circumstances, instrumental in generating the smell of Harrogate water. But this notion is not well founded; for the bilge water is, I suppose, salt water; and Dr. SHORT says, that sea water, which had been kept in a stone bottle six weeks “stunk not much short of Harrogate sulphur water.” It has been remarked above, that calcined sea-wrack, which contains a great deal of sea salt, exhales an odour similar in all respects to that of Harrogate water; and in confirmation of the truth of this remark, I find that an author, quoted by Dr. SHORT, says, that “Bay salt thrice calcined, dissolved in water, gives exactly the odour of the sulphur Well at Harrogate.” From these experiments considered together, it may, perhaps, be inferred, that common salt communicates a sulphureous smell to water both by putrefaction and calcination. Hence some may think, that there is some probability in the supposition, that either a calcined stratum of common salt, or a putrescent salt spring, may contribute to the production of the sulphureous smell of Harrogate water; especially as these waters are largely impregnated with common salt. However, as neither the salt in sea water, nor that of calcined sea-wrack, nor calcined bay salt, are any of them absolutely free from the admixture of bodies containing the vitriolic acid, a doubt still remains, whether the sulphureous exhalation, here spoken of, can be generated from substances in which the vitriolic acid does not exist.

The shale from which alum is made, when it is first dug out of the earth, gives no impregnation to water; but by exposure to air and moisture its principles are loosened, it shivers into pieces, and finally moulders into a kind of clay, which has an aluminous taste. Alum is an earthy salt resulting from an union of the acid of sulphur with pure clay; and hence we are sure, that shale, when decomposed by the air, contains the acid of sulphur; and from its oily black appearance, and especially from its being inflammable, we are equally certain that it contains phlogiston, the other constituent part of sulphur. And indeed pyritous substances, or combinations of sulphur and iron, enter into the composition of many, probably of all sorts of shale, though the particles of the pyrites may not be large enough to be seen in some of them; and if this be admitted, then we need be at no loss to account for the bits of sulphur, which are sublimed to the top of the heaps of shale, when they calcine large quantities of it for the purpose of making alum: nor need we have any difficulty in admitting, that a phlogistic vapour must be discharged from shale, when it is decomposed by the air. Dr. SHORT says, that he burned a piece of aluminous shale for half an hour in an open fire; he then powdered and infused it in common water, and the water sent forth a most intolerable sulphureous smell, the very same with Harrogate water. He burned several other pieces of shale, but none of them stunk so strong as the first. This difference may be attributed, either to the different qualities of the different pieces of shale which he tried, or to the calcination of the first being pushed to a certain definite degree; for the combination of the principles on which the smell depends may be produced by one degree of heat, and destroyed by another. I have mentioned, briefly,

briefly, these properties of shale, because there is a stratum of shale extended over all the country in the neighbourhood of Harrogate; several beds of it may be seen in the stone quarry above the sulphur wells; many of the brooks about Harrogate run upon shale, and the sulphur wells spring out of it. They have bored to the depth of twenty yards into this shale, in different places, in search of coal, but have never penetrated through it. Its hardness is not the same at all depths. Some of it will strike fire, as a pyrites does, with steel; and other beds of it are soft, as if in a state of decomposition, and the sulphur water is thought to rise out of that shale which is in the softest state. But whatever impregnation shale when calcined, or otherwise decomposed to a particular degree, may give to the water which passes over it, it must not be concluded, that shale in general gives water a sulphureous impregnation; since there are many springs, in various parts of England, arising out of shale, in which no such impregnation is observed.

I forgot to mention, in its proper place, that having visited the bog, so often spoken of, after a long series of very dry weather, I found its surface, where there was no grass, quite covered over with a yellowish crust, of tolerable consistency, which had a strong aluminous taste, and the smell of honey. BERGMAN speaks of a turf found at Helsingberg in Scania, consisting of the roots of vegetables, which was often covered with a pyritous cuticle, which, when elixated, yielded alum; and I make no doubt, that the Harrogate morass is of the same kind.

Whether nature uses any of the methods which I have mentioned of producing the air by which sulphureous waters are impregnated, may be much questioned; it is of use, however, to record the experiments by which her productions may be

imitated; for though the line of human understanding will never fathom the depths of divine wisdom, displayed in the formation of this little globe which we inhabit; yet the impulse of attempting an investigation of the works of God is irresistible; and every physical truth which we discover, every little approach which we make towards a comprehension of the mode of his operation, gives to a mind of any piety the most pure and sublime satisfaction.

