IV. An Analysis of several Varieties of British and Foreign Salt, (Muriate of Soda) with a View to explain their Fitness for different economical Purposes. By William Henry, M.D. F. R. S. Vice-Pres. of the Literary and Philosophical Society, and Physician to the Infirmary, at Manchester.

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SECT. I. GENERAL OBSERVATIONS.

In undertaking the series of experiments, described in the following pages, I had not so much in view the discovery of novelties in science, as the determination, by the careful employment of known processes, and by the improvement of methods of analysis, of a number of facts, the establishment of which (it appeared to me probable) might have an influence on an important branch of national revenue and industry.

An opinion has for some time past existed, and I believe has been pretty general both in this and other countries, to the disadvantage of British salt as a preserver of animal food; and a decided preference has been given to the salt procured from France, Spain, Portugal, and other warm climates, where it is prepared by the spontaneous evaporation of sea water. In conformity with this opinion, large sums of money are annually paid to foreign nations, for the supply of an article, which Great Britain possesses, beyond almost any other MDCCCX.

country in Europe, the means of drawing from her own internal resources. It becomes, therefore, of much consequence to ascertain, whether this preference of foreign salt be founded on accurate experience, or be merely a matter of prejudice; and, in the former case, whether any chemical difference can be discovered, that may explain the superiority of the one to the other.

The comparative fitness of these varieties of salt for the curing of provisions, which has been a subject of much controversy among the parties who are interested, can be decided, it is obvious, in no other way, than by a careful examination of the evidence on both sides. Where evidence, however, is doubtful, and where there exists, as in this case, much contrariety of testimony, it cannot be unfair to yield our belief to that, which best accords with the chemical and physical qualities of the substances in question. Again, if salt of British production, should be proved to be really inferior in chemical purity to foreign salt, it would be important to ascertain, as the basis of all attempts towards its improvement, in what. precisely, this inferiority consists. It seemed desirable, also, to examine whether any differences of chemical composition exist among the several varieties of home-made salt, which can explain their variable fitness for economical purposes.

Such were the considerations that induced me to undertake an enquiry, which has occupied, for several months past, a large share of my leisure and attention. I began the investigation, wholly uninfluenced by any preconceived opinions on the subject; and I had no motive to see the facts in any other than their true light, since I have no personal interest, either directly or remotely, in the decision of the question. The principal sources of the salt, which is manufactured in this country, are rock salt, brine springs, and sea water. The first material is confined entirely, and the second chiefly, though not wholly, to a particular district of Cheshire. Of the extent and boundaries of this district, the process of manufacture, and other circumstances interesting to the mineralogist as well as to the chemist, an ample and excellent history has been given by Mr. Henry Holland, in the Agricultural Report of the county of Chester.* From his account, I shall extract, in order to render some parts of this memoir more intelligible, a very brief statement of the characteristic differences of the several varieties of salt, which are prepared in Northwich, and its neighbourhood.

In making the stoved or lump salt, the brine is brought to a boiling heat, which, in brine fully saturated, is 226° of Fah-Renheit. This temperature is continued during the whole process; and as the evaporation proceeds, small flakey crystals continue to form themselves, and to fall to the bottom of the boiler. At the end of from eight to twelve hours, the greatest part of the water of solution is found to be evaporated; so much only being left, as barely to cover the salt and the bottom of the pan. The salt is then removed into conical wicker baskets, termed barrows; and, after being well drained, is dried in stoves, where it sustains a loss of about one seventh of its weight.

On the first application of heat to the brine, a quantity of carbonate of lime, and sometimes a little oxide of iron, both of which had been held in solution by an excess of carbonic acid, are separated; and are either removed by skimming, or are

allowed to subside to the bottom of the pan, along with the salt first formed, and with some sulphate of lime; and are afterwards raked out. These two operations are called clearing the pan. Some brines scarcely require them at all, and others only occasionally. The whole of the impurities, however, are not thus removed; for a part, subsiding to the bottom, forms a solid incrustation, termed by the workmen pan-scale. The portion of this, which is lowest, acquires so much induration and adhesion to the pan, that it is necessary to remove it, once every three or four weeks, by heavy blows with a pick-axe. These sediments are formed, also, in making the other varieties of salt.

In preparing common salt, the brine is first raised to a boiling heat, with the double view of bringing it as quickly as possible to the point of saturation, and of clearing it from its earthy contents. The fires are then slackened, and the evaporation is carried on for 24 hours, with the brine heated to 160° or 170° Fahrenheit. The salt, thus formed, is in quadrangular pyramids or hoppers, which are close and hard in their texture. The remainder of the process is similar to that of making stoved salt, except that after being drained, it is carried immediately to the store house, and not afterwards exposed to heat, an operation confined to the stoved salt.

The large grained flakey salt is made with an evaporation conducted at the heat of 130 or 140 degrees. The salt thus formed, is somewhat harder than common salt, and approaches more nearly to the cubic shape of the crystals of muriate of soda.

Large grained or fishery salt, is prepared from brine heated only to 100° or 110° FAHRENHEIT. No perceptible agitation,

therefore, is produced in the brine, and the slowness of the process, which lasts from 7 or 8 to 10 days, allows the muriate of soda to form in large, and nearly cubical crystals, seldom however quite perfect in their shape.*

For ordinary domestic uses, stoved salt is perfectly sufficient. Common salt is adapted to the *striking* and salting of provisions, which are not intended for sea voyages or warm climates. For the latter purposes, the large grained or fishery salt is peculiarly fitted.

On the eastern and western coasts of Scotland, and especially on the shores of the Firth of Forth, large quantities of salt are made by the evaporation of sea water. In consequence of the cheapness of fuel, the process is carried on, from first to last, by artificial heat, at a temperature, I believe, equal or nearly so to the boiling point, and varying, therefore, according to the concentration of the brine. The kind of salt, chiefly formed in Scotland, approaches most nearly to the character of stoved salt. In some places a salt is prepared, termed Sunday salt; so called, in consequence of the fires being slackened between Saturday and Monday, which increases considerably the size of the crystals.

I am indebted to Dr. Thomson of Edinburgh, (who gave me his assistance with great zeal and alacrity) for an opportunity of examining upwards of twenty specimens of Scotch salt, prepared by different manufacturers. That distinguished chemist, it appears from a letter which he addressed to me on the subject, was some time ago engaged in experiments on Cheshire salt. The particulars he has lost; and he retains only a general recollection of the facts, which confirms, I am

^{*} Cheshire Reports, p. 53, &c.

happy to state, the accuracy of the results obtained by my own experiments.

At Lymington in Hampshire, advantage is taken of the greater heat of the climate, to concentrate the sea water by spontaneous evaporation to about one sixth its bulk, before admitting it into the boilers. One kind of salt is chiefly prepared there, which most nearly resembles in grain the stoved salt of Cheshire. The process varies a little, in some respects, from that which has been already described. The salt is not fished (as it is termed) out of the boiler, and drained in baskets; but the water is entirely evaporated, and the whole mass of salt taken out at once, every eight hours, and removed into troughs with holes in the bottom. Through these it drains into pits made under ground, which receive the liquor called bittern or bitter liquor. Under the troughs, and in a line with the holes, are fixed upright stakes, on which a portion of salt that would otherwise have escaped, crystallizes and forms, in the course of ten or twelve days, on each stake, a mass of sixty or eighty pounds. These lumps are called salt cats. They bear the proportion to the common salt, made from the same brine, of 1 ton to 100.

From the mother brine or bitter liquor, which has drained into the pits, the sulphate of magnesia is made during the winter season, when the manufacture of salt is suspended, in consequence of the want of the temperature required, for the spontaneous evaporation of the sea water. The process is a very simple one.* The bitter liquor from the pits is boiled

I am indebted for an account of this process, as well as of the method of making common salt at Lymington, to the liberal communication of CHARLES ST. BARBE, Esq. of that place. Though not strictly connected with the subject, I give his descrip-

for some hours in the pans, which are used in summer to prepare common salt; and the impurities, which rise to the surface, are removed by skimming. During the evaporation, a portion of common salt separates; and this, as it is too impure for use, is reserved for the purpose of concentrating the brine in summer. The evaporated bitter liquor is then removed into wooden coolers 8 feet long, 5 feet wide, and 1 foot deep. In these it remains twenty four hours, during which time, if the weather prove clear and cold, the sulphate of magnesia, or Epsom salt crystallizes at the bottom of the coolers, in quantity equal to about one eighth of the boiled liquor. The uncrystallizable fluid is then let off through plugholes at the bottom of the coolers; and the Epsom salt, after being drained in baskets, is deposited in the store-house. This is termed single Epsom salts, and after solution and a second crystallization, it acquires the name of double Epsom salts. Four or five tons of sulphate of magnesia are produced from a quantity of brine, which has yielded 100 tons of common, and 1 ton of cat salt.

On the banks of the Mersey, near its junction with the Irish Channel, the water of that river before evaporation is brought to the state of a saturated brine, by the addition of rock salt. The advantage of this method of proceeding, will be obvious when it is stated, that 100 tons of this brine yield at least 23 tons of common salt, whereas from the same quantity of sea

tion of the mode of making Epsom salt, because no correct statement of the process has, I believe, been hitherto published. The analysis of sea water, indeed, by a justly distinguished chemist (Bergman), excludes, erroneously, the sulphate of magnesia from its composition; and his results have led to the opinion, that to manufacture this salt on the large scale, requires the addition either of sulphuric acid, or of some sulphate to the bitter liquor. (See Aikin's Chemical Dictionary, II. 388.)

water, with an equal expenditure of fuel, only 2 tons 17 cwt of salt can be produced.*

Within the few past years, an attempt has been made to apply rock salt itself to the packing of provisions. For this purpose it is crushed to the proper size between iron rollers. The trials which have been made, I am informed, are but few, and the results hitherto are not perfectly known.

The bay salt imported from foreign countries is well known to be prepared by the spontaneous evaporation of sea water, which, for this purpose, is confined in shallow pits, and exposed to the full influence of the sun and air. I have no addition to make to the account of its manufacture, which have already been given by various writers.

As the results of the investigation, which forms the subject of this memoir, may be acceptable to many persons who can scarcely be expected to take an interest in a long detail of analytical processes, I shall present, in the following section, a general view of the experiments, and of the conclusions that may be deduced from them. In the last place, in order that other chemists may be enabled to repeat the analyses under similar circumstances, I shall describe minutely, the methods that were adopted, some of which are new, and others reduced to greater precision. If, however, in the future progress of science, it should appear that any of these processes are imperfect, it may still be admitted that, for all useful purposes,

^{*} See the Earl of Dundonald's "Thoughts on the Manufacture and Trade of Salt." London, 1785.

[†] Encyclop. Method. Art. Salins. (Des Marais Salans) Aikin's Dictionary of Chemistry, II. 224. Watson's Chemistry, Vol. II. p. 52. It is necessary to remark, that a great proportion of what is sold in London as bay-salt, is Cheshire large grained fishery salt.

they afford a fair comparison of the composition of the several varieties of culinary salt; since the sources of fallacy, that may hereafter be discovered, must have been the same in every case, and have produced in each an error of nearly the same amount.

SECTION II. GENERAL STATEMENT OF THE RESULTS OF THE EXPERIMENTS, AND CONCLUSIONS THAT MAY BE DEDUCED FROM THEM.

A comparison of the component parts of British and foreign salts, and of different varieties of British salt with each other. will best be made by an examination of the following table, which comprehends the results of the analysis of equal weights of each variety.

Muriate Sulph. Total Pure of Total Sulph. ofTotal immuri Kind of Salt. Muriate Magneearthy magof. sulpuriate of matter. of lime. sia. muriates. lime. nesia. phates. ties. soda St. Ube's a trace 23 1/2 9 960 St. Martin's $3\frac{1}{2}$ do. 12 19 $40\frac{1}{2}959\frac{1}{2}$ $35\frac{3}{4}964\frac{1}{4}$ $3\frac{1}{2}$ 25 ж Oleron 10 do. 47515 4 23 3 $19\frac{1}{2}$ 28 or * Scotch (common) 28 or * $32\frac{1}{2}$ $16\frac{1}{2}$ 15 64 1 935 4 17 Scotch (Sunday) 1 113 1 I 1/2 12 29 Lymington (common) 2 II or * 11 15 35 50 63 Do. (cat) I 0. $\frac{3}{16}$ 0. $\frac{3}{16}$ 0. $\frac{3}{4}$ Crushed rock $6\frac{1}{2}$ 16 3 9834 10 0. 1 Cheshire $\begin{array}{c}
4 & 9 & 3 & 4 \\
1 & 3 & 4 & 9 & 8 & 6 & 3 \\
1 & 6 & 2 & 9 & 8 & 3 & 1 \\
1 & 7 & 1 & 2 & 9 & 8 & 2 & 1 \\
1 & 7 & 1 & 2 & 9 & 8 & 2 & 1 \\
\end{array}$

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Toco parts by weight consist of

 $II\frac{\tilde{1}}{4}$

 $14\frac{1}{2}$

I

11 4

 $14\frac{1}{2}$

I. The total amount of impurities, and the quantity of real muriate of soda, contained in each variety of common salt, may be learned by inspecting the two last columns of the table. From these it appears, that the foreign bay salt is purer.

Fishery

Stoved

Common

^{*} See page 95.

generally speaking, than salt which is prepared by the rapid evaporation of sea water; but that it is contaminated with about three times the amount of impurities, discoverable in an equal weight of the Cheshire *large-grained* salt, and with more than twice that of those, that are found in the *stoved* and *common* salt of the same district.

II. The insoluble matter in the foreign salt, after the action of boiling water, appears to be chiefly argillaceous earth coloured by oxide of iron, and is probably derived in part from the pits in which the sea water is submitted to evaporation. We may, perhaps, assign the same origin to the very minute portion of muriate of lime, which is not found in the salt prepared by evaporating sea water in metallic vessels, nor even in the mother liquor, or uncrystallizable residue. In sea salt prepared by rapid evaporation, the insoluble portion is a mixture of carbonate of lime with carbonate of magnesia, and a fine silicious sand; and in the salt prepared from Cheshire brine, it is almost entirely carbonate of lime. The insoluble part of the less pure pieces of rock salt is chiefly a marly earth, with some sulphate of lime. The quantity of this impurity, as it is stated in the table, is considerably below the average, which in my experiments has varied from 10 to 45 parts in 1000. Some estimate of its general proportion, when ascertained on a larger scale, may be formed from the fact, that government, in levying the duties, allows 65 lb. to the bushel, of rock salt, instead of 56lb. the usual weight of a bushel of salt.

III. The earthy muriates, and especially that with base of magnesia, abound most in salt which is prepared by the rapid evaporation of sea water. Now since common salt, in all its

forms, contains as will afterwards appear, very little water of crystallization, it is probable that the muriate of magnesia, discovered by the analysis of sea salt, is derived entirely from that portion of the mother liquor, which adheres to the salt after being drained, and which amounts to about $\frac{1}{2}$ of its weight. The larger the size of the grain, the less is the quantity of this solution which the salt holds suspended, and hence the salt prepared at a lower degree of heat, being in larger crystals, is less debased by the magnesian muriate, than the salt formed at a boiling temperature. It is probable, also, that when the salt is drawn at intervals from the boiler, the proportion of the earthy muriate will vary with the period of the evaporation, at which it is removed. For it may readily be conceived, that as the proportion of the earthy muriates in any brine is increased by the separation of muriate of soda, the greater will be the quantity of the muriates which the crystals of common salt, formed in the midst of the brine, will retain; thence it follows, that, so far as the earthy muriates only are concerned, salt must diminish in purity as the process of evaporation advances.

In the several varieties of Cheshire salt, the earthy muriates do not exceed one thousandth part of this weight, and they are precisely, (or so nearly so, that the difference is not ascertainable) the same in all. This will cease to be matter of surprise, when it is considered that the salt obtained by evaporating to dryness the whole of a portion of Cheshire brine, does not give more than 5 parts of earthy muriates in 1000. In the entire salt of sea water, according to Bergman, the earthy muriates form no less than 213 parts in the same quantity.

According to the proportion in which the earthy muriates are present in any kind of salt, will be its power of deliquescence, or of attracting moisture from the atmosphere. It is not entirely, however, from the salts with earthy base, that common salt derives this quality; for the most transparent specimens of rock salt, which I find to consist of absolutely pure muriate of soda, attract much moisture from a humid atmosphere.

IV. The sulphate of magnesia and the sulphate of lime, both enter into the composition of all the varieties of salt prepared from sea water; but the sulphate of lime alone is found in Cheshire salt. The proportion of sulphate of magnesia is greatest in that variety of sea salt, which has been formed by rapid evaporation. In foreign bay salt, its quantity is very insignificant.

From the table it may be seen, that the proportion of sulphate of lime is greater in foreign bay salt, than in any variety of British salt, even than in those which are prepared from sea water with a boiling heat. The only explanation of this fact, that occurs to me, is, that during the rapid evaporation of sea water, a considerable part of the calcareous sulphate is precipitated at an early stage of the process, and is partly removed in *clearing* the boiler, a process, which can scarcely be performed during the formation of bay salt, in pits whose sides are composed of moist clay. The remainder of the selenite, thus precipitated by the rapid evaporation of sea water, enters into the composition of the pan-scale.

In the course of this inquiry, I was induced to repeat the same experiments several times, on various specimens of salt bearing the same designation; and was surprised to find, that

the results by no means corresponded. In one instance, for example, fishery salt was found in 1000 parts to contain no less then 16 parts of sulphate of lime; while another specimen, nominally the same, contained only $11\frac{1}{4}$ parts of selenite in the same quantity; and a third only $5\frac{3}{4}$. At length it occurred to me, that these differences were probably owing to the circumstance of the salt having been taken from the boiler at different periods of the evaporation. I requested, therefore, to be furnished with specimens of salt, drawn at different stages of the process, from a given portion of brine, evaporated in the same boiler. These were submitted to analysis; and the results are shewn in the following table.

Hence it appears, that there was a gradually increasing purity in the salt from sulphate of lime, as the process of evaporation advanced; the greatest part of this earthy compound being deposited at an early stage of the process. Different specimens of the same kind of salt may, therefore, differ in chemical purity as much from each other, as from other varieties. But when the impurities, contained in a solution of muriate of soda, are of a different species, from those of Cheshire brine, and consist chiefly of the earthy muriates, the order will be reversed, and the purest salt, as I have already suggested, will be that which is first deposited; the contamination with the muriate of lime or of magnesia, continuing to increase, as the process advances to a conclusion.*

* I cannot on any other principle explain the considerable differences, as to the

At an early period of the enquiry, it appeared to me probable that the differences between the several varieties of culinary salt might depend, in some degree, on their containing variable proportions of water of crystallization. It was found, however, by experiment, that the proportion of water in any variety of common salt, after being dried at 212° FAHRENHEIT, is not much greater or less than that which is contained in any other variety. Pure transparent rock-salt, calcined for half an hour in a low red heat, (= 4° or 5° of Wedgwood's pyrometer) lost absolutely nothing of its weight. It is remarkable, also, that the pure native salt, if free from adventitious moisture, may be suddenly and strongly heated. with scarcely any of that sound called decrepitation,* which is produced by the similar treatment of all the varieties of artificial salt. Even these varieties, however, exposed during equal times to a low red heat, do not lose more than from half a grain to three grains in one hundred. This comparison cannot be extended to the salt prepared at a boiling temperature from sea water; because the muriate of magnesia, which

proportion of muriate of magnesia, that were discovered in the several varieties of Scotch salt, sent to me by Dr. Thomson. For this reason, in stating the analysis of Scotch salt, I have given, in the table, that result which was most frequently obtained; and have withheld the names of the manufacturers, because the differences were probably in a great measure accidental, and not the result of greater or less skill in the preparation. One specimen of Lymington salt, which I examined, contained fully as much muriate of magnesia as any of the Scotch samples. The cat salt of that place, however, contrary to my expectation, proved to possess a very extraordinary degree of purity; a fact of which I satisfied myself by repeated experiments.

* Decrepitation is occasioned by the sudden conversion into vapour of the water contained in salts, when its quantity is insufficient to effect the watery fusion. It is a property peculiar to salts which hold only a very small proportion of water in combination, as muriate of soda, nitrate of lead, and sulphate of potash.

these varieties contain, is decomposed at a red heat, and deprived of its acid.

The following table shews the quantity of water contained in several kinds of salt, inferred from the loss which they sustain by ignition during equal times, after being first dried at 212°.

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100 parts of large grained fishery salt contain of water 3

100 - foreign bay salt (St. Martin's) - - 3

100 - - do. - (Oleron) - - 2\frac{1}{2}

100 - - do. Cheshire common salt - - 1\frac{1}{2}

100 - - do. - stoved salt - - 0\frac{1}{2}
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The loudness and violence of the decrepitation was, as nearly as could be judged, in the same order, and was most remarkable in the large grained varieties.

To determine the proportions of real muriate of soda in those varieties of artificial salt which are nearly free from earthy muriates, I employed also the process of decomposition by nitrate of silver. The following are the quantities of fused luna cornea, obtained from 100 grains of each of three varieties dried, previously to solution, at the temperature of 212° FAHRENHEIT.

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100 gr. pure transparent rock salt gave of luna cornea 242
100 stoved salt, remarkably pure - 239
100 fishery salt. do. - - - 237*
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* From 100 grains of pure artificial muriate of soda, previously heated to redness, Dr. Marcet has since informed me, that he obtained 24.16 grains of fused luna cornea. The weights of the precipitates thrown down in my experiments by nitrate of silver, are not, I am aware, exactly those which might have been expected from the table of the comparative proportions of water given in the text. Each experiment, however, was twice repeated with every precaution I could adopt, and with the same results. That different kinds of salt give different proportions of luna cornea, is

The proportion of ingredients in the several kinds of muriate of soda (setting apart the impurities) appears, therefore, to be nearly the same in all. And as the very minute quantity of water, discovered by analysis, is not constant in the several varieties, it may be inferred to be rather an accidental than a necessary ingredient; for in the latter case, an invariable proportion might be expected, conformably to the important law, establishing an uniformity in the proportions of chemical compounds, which has been explained by Mr. Dalton, and confirmed by Drs. Thomson and Wollaston.

What then, it may be enquired, is the cause of those differences which are acknowledged, on all hands, to exist among the several species of muriate of soda, so far as respects their fitness for economical purposes. If I were to hazard an opinion, on a subject about which there must still be some uncertainty, it would be that the differences of chemical composition, discovered by the preceding train of experiments, in the several varieties of culinary salt, are scarcely sufficient to account for those properties, which are imputed to them on the ground of experience. The stoved and fishery salt, for example, though differing in a very trivial degree as to the kind or proportion of their ingredients, are adapted to widely different uses. Thus the large grained salt is peculiarly fitted for the packing of fish and other provisions, a purpose to which the small grained salts are much less suitable. different powers, then, of preserving food must depend on some mechanical property; and the only obvious one is the

proved also by comparing the experiment of Dr. Marcet, with the results of Dr. Black and Klaproth, both of whom found the fused muriate of silver, from 100 parts of common salt, to weigh 235 grains.

magnitude of the crystals, and their degree of compactness and hardness. Quickness of solution, it is well known, is pretty nearly proportional, all other circumstances being equal to the quantity of surface exposed. And since the surfaces of cubes are as the squares of their sides, it should follow that a salt whose crystals are of a given magnitude will dissolve four times more slowly than one whose cubes have only half the size.

That kind of salt, then, which possesses most eminently the combined properties of hardness, compactness, and perfection of crystals, will be best adapted to the purpose of packing fish and other provisions, because it will remain permanently, between the different layers, or will be very gradually dissolved by the fluids that exude from the provisions; thus furnishing a slow, but constant supply of saturated brine. On the other hand, for the purpose of preparing the pickle, or of striking the meat, which is done by immersion in a saturated solution of salt, the smaller grained varieties answer equally well; or, on account of their greater solubility, even better.

With the hardness or strong aggregation of the several varieties of salt, it seemed to me not improbable that their specific gravity might, in some degree, be connected. The exact determination of this property in saline substances is, however, a problem of considerable difficulty, as will sufficiently appear from the various results which have been given, with respect to the same salts, by different experimentalists. Thus Muschenbroek makes the specific gravity of artificial muriate of soda to vary from 1918 to 2148, the mean of which is 2033. Sir Isaac Newton states it at 2143, and Hassenfratz at 2200.*

^{*} Annales de Chimie, Vol. XXVIII. p. 13.

All that was necessary for my purpose, was an approximation to the truth; and the introduction of a small error could be of no importance, provided it were the same in every case, since the comparison would still hold good.

The specific gravity of rock salt, there can be little difficulty in determining with precision. A piece of this salt,* of such perfect transparency, that I had reserved it as a cabinet specimen, weighed in the air 513 grains, and lost, when weighed in alcohol, 194 grains. The alcohol, at the temperature of 56° Fahrenheit, had the specific gravity of 820, and hence that of the salt may be estimated at 2170. Another specimen considerably less pure, and more approaching to a fibrous fracture, had the specific gravity of 2125 only.

For ascertaining the specific weights of artificial varieties of salts, I used a very simple contrivance. It consisted of a glass globe about $3\frac{1}{3}$ diameter, having a stem or neck 10 inches long. Sixteen cubic inches of water (each $252\frac{1}{2}$ grains at 60° Fahrenheit,) filled the whole of the globe, and about half an inch of the lower part of the neck; and from the line where the water stood in the instrument, it was accurately graduated upwards into hundredth parts of a cubical inch. Into this vessel I poured exactly sixteen cubic inches of a perfectly saturated solution of common salt; and then added 400 grains of the salt under examination, washing down the particles that adhered to the neck by a portion of the liquid, which had been previously taken out of the globe for the purpose. As much as possible of the air which adhered to the salt, was dislodged by agitation; and the increase of bulk was then observed.

Care was taken that the salts were all of equal temperature,

^{*} Foliated rock salt of JAMESON. See his Mineralogy, Vol. II. p. 10.

and dryness, and that no change of temperature happened during the experiment.

~	-	0	s of the les ken down	-					ndredths cub. in.	Hence its specific grav.was*
	fi	lled th	ie space of	-	-	AP4	-		75	2112
<	400	grain	s of stoved	salt -				-	75	2112
	400	do.	(another	sample) -		_	me	76	2084
	400	do.	common	salt	-	-	~		76	2084
	400	large	grained fis	shery s	alt ·	•	-	-	83	1909
<	400	do.	(another	sample	:) -		-	_	83	1909
	4,00		St. Ube's	-	-	•	-	-	82	1932

If the above mode of determination at all approach to correctness, it would appear that the specific gravity of rock salt is diminished, by being broken into small fragments, from 2125 to 2112, probably in consequence of the quantity of air which the fragments envelope, and which cannot be entirely separated by agitation. From the numbers given in the last column, it is evident, that the smaller grained salts are specifically heavier than those which are composed of larger and more perfect crystals. A difference of only one or two hundredth parts of a cubic inch, is perhaps entitled, in a process of this kind, to little reliance; and I do not therefore regard it as indicating any material difference in the specific gravity of the first four, or last three salts submitted to experiment. But when the difference amounts to eight hundredths, as between the small and large grained salt, it may safely be imputed to an inferior specific gravity in that species, which occupies so much greater a proportional bulk.*

^{*} Distilled water at 1000 being taken as the standard,

[†] M. HASSENFRATZ seems to have suspected that a difference in the specific

The last series of experiments proves decisively, that in an important quality, (viz. that of specific gravity,) which is probably connected with the mechanical property of hardness and compactness of crystals, little or no difference is discoverable between the large grained salt of British, and that of foreign manufacture. If no superiority, then, be claimed for British salt as applicable to economical purposes, on account of the greater degree of chemical purity which unquestionably belongs to it, it may safely, I believe, be asserted that the larger grained varieties are, as to their mechanical properties, fully equal to the foreign bay salt. And the period, it may be hoped, is not far distant, when a prejudice (for such, from the result of this investigation, it appears to be,) will be done away, which has long proved injurious to the interests and prosperity of an important branch of British manufacture.

SECTION III. ACCOUNT OF THE METHODS OF ANALYZING THE SEVERAL VARIETIES OF MURIATE OF SODA.

The method of analysis which I adopted, in examining the several varieties of muriate of soda, was as follows.

When the salt was in a state of solution, a measured quantity was evaporated to dryness in a sand heat, which was carefully regulated, to avoid the decomposition of the muriate of magnesia, if any of that salt were present in the solution.*

gravity of the same salt may be occasioned by a variation in its state of crystallization. De la Pesanteur spécifique des Sels, Ann. de Chem. XXVIII. p. 17.

* Muriate of magnesia, according to Dr. Marcet, begins to part with its acid at a temperature a few degrees above that of boiling water. This fact explains the observation of Mr. Kirwan, that too great a heat, employed in the desiccation of muriate of magnesia, decreases considerably its solubility in alcohol. (Kirwan on Mineral Waters, p. 275.)

Each specimen of salt was reduced to a fine powder, and was dried, in the temperature of 180° of Fahrenheit, during the space of two hours. This was done in order that the different experiments might be made on precisely equal quantities of salt.

I. To separate the earthy Muriates.

- (A) On 1000 grains of the dried and pulverized salt, (except in the case of the foreign salts, when only 500 grains were used,) four ounce measures of alcohol were poured, of a specific gravity, varying from 815 to 820, and at nearly a boiling temperature. To insure the access of the fluid to every part of the salt, they were ground together for some time in a mortar, and then transferred into a glass mattras, where they were digested for some hours, and frequently agitated. The alcohol was next separated by filtration, and the undissolved part was washed, as it lay on the filtre, with 4 ounce measures of fresh alcohol.
- (B.) The united washings were evaporated to dryness,* and to the dry mass a small portion of fresh alcohol was added, to separate the earthy muriates from a little common salt, which had been dissolved along with them. This solution might, however, still contain a minute portion of muriate of soda. It was therefore again evaporated, redissolved in hot water, and mixed with a solution of carbonate of soda. By boiling for some minutes, the whole of the earths were precipitated, and after being well washed, were re-dissolved in muriatic acid. This solution, being evaporated to dryness, gave the

^{*} In this and all similar cases, the heat was very cautiously regulated towards the close of the process.

weight of the earthy muriates, which had been extracted by alcohol.*

- (B.a.) The dry mass thus obtained might consist either of muriate of magnesia, of muriate of lime, or of both. An aliquot part, therefore, was dissolved, separately, for the purpose of assaying it by the usual tests. Sometimes, as in the case of the earthy muriates procured from sea salt, muriate of magnesia alone was indicated, and any further process was rendered unnecessary. Muriate of lime was in no instance found uncombined; but in the majority of cases (as in the earthy muriates obtained from Cheshire salt) was mixed with muriate of magnesia.
- (B.b.) To the solution of two earthy muriates was added fully saturated carbonate of ammonia, which has the property of throwing down lime in combination with carbonic acid, but has no effect on the muriate of magnesia at ordinary temperatures. The solution of the latter salt, along with that of the excess of carbonate of ammonia, was therefore separated by filtration; and to the filtred liquor a solution of phosphate of soda was added, according to the formula of Dr. Wollaston.†
- *By the analysis of artificial mixtures of pure muriate of soda with the earthy muriates in known quantities, I afterwards found that the full amount of the earthy muriates was not ascertained in this way of proceeding. The deficiency of the latter salts was about one sixth; but as the error must necessarily have been the same in all, it does not affect the comparison of different varieties of salt, as to their proportion of this ingredient. If the numbers in the 5th column of the table (indicating the total earthy muriates) be increased in the proportion of six to five, we shall then obtain the true quantities in each variety of salt.

[†] See Dr. Marcer's analysis of the Brighton Chalybeate, published in the last edition of Saunders on Mineral Waters.

- (B.c.) By direct experiments I had learned that 100 grains of muriate of magnesia, when thus decomposed by carbonate of ammonia, conjoined with phosphate of soda, give 151 grains of an insoluble ammoniaco-magnesian phosphate dried at about 90° of Fahrenheit. Hence it was easy, from the weight of the precipitate, to calculate how much of the former salt was contained in the mixture of muriate of lime and muriate of magnesia. Thus, if 20 grains of a mixture of the two muriates yielded 15.1 of ammoniaco-magnesian phosphate, it is obvious that the mixture must have consisted of equal weights of muriate of lime and muriate of magnesia.
- (B. d.) The estimation of the proportion of muriate of lime, in a mixture of this salt with muriate of magnesia, was sometimes performed in a different way. To a cold solution of a known weight of the two salts, super-oxalate of potash was added; and the precipitate was collected, washed, and dried at about 160° Fahrenheit. Of this precipitate I had previously found that 116 grains are formed by the decomposition of 100 grains of dry muriate of lime. From the quantity of oxalate of lime it was easy, therefore, to infer that of the muriate, from whose decomposition it resulted; and this subtracted from the weight of the two salts, gave the weight of the muriate of magnesia.

II. To separate and estimate the earthy Sulphates.

(C.) The portion of salt which had resisted the action of alcohol, was dissolved by long boiling in sixteen ounce measures of distilled water, and the solution was filtered. On the filtre a small quantity of undissolved matter generally remained, which was washed with hot water, till it ceased to

have any action. The weight of the insoluble portion was then ascertained.

- (C. a.) By this operation were dissolved, not only the muriate of soda, but all the other salts, insoluble in alcohol, which might be mingled with it. To the solution, carbonate of soda was added; and the liquid, which in most cases gave, on this addition, an abundant precipitate, was boiled briskly for several minutes, in order that none of the earthy carbonates, which were separated, might remain dissolved by an excess of carbonic acid.
- (C. b.) The precipitated earths were allowed to subside, and were well edulcorated with boiling water, the washing being added to the liquor first decanted from the precipitate. To these united liquids, (after the addition of more muriatic acid than was required for saturation) muriate of barytes was added, till it ceased to occasion any further precipitate. The sulphate of barytes was then washed sufficiently; dried; ignited; and its amount ascertained.

To the earthy carbonates, an excess of sulphuric acid was added in a platina dish, and the mixture was triturated, till all effervescence ceased. It was then evaporated to dryness, calcined in a low red heat, and the weight of the earthy sulphates was ascertained.

- (D. a.) The dry sulphates were washed with a small quantity of lukewarm water. In several instances, the loss of weight, thus sustained, was extremely trifling, nothing being dissolved but a very minute portion of sulphate of lime, of which earthy salt, solely, the residue was presumed to be composed.
 - (D. b.) But in other cases, a considerable loss of weight

ensued; and in these, to the watery solution was added a mixture of equal parts of saturated solutions of carbonate of ammonia, and phosphate of soda. A precipitate more or less copious was produced, which was collected, dried at 90° FAH-RENHEIT, and weighed.

- (D. c.) By direct experiments I had determined, that 90 grains of this precipitate result from the decomposition of 100 grains of sulphate of magnesia, of such a degree of dryness, as to lose 44 grains out of 100, by exposure to a low red heat. Hence 100 grains of ammoniaco-magnesian phosphate indicate 111 grains of crystallized, on 62.2 of desiccated, sulphate of magnesia.* From the weight of the ammoniaco-magnesian phosphate, it is easy, therefore, to infer the proportion of sulphate of magnesia in any mixture of the two earthy sulphates.
- (D. d.) It was possible, however, that in addition to the sulphates of lime and of magnesia, the quantity of which had been determined by the foregoing process, the specimen of salt under examination might contain also an alkaline sulphate. To decide this point, it was necessary to compare the amount of the acid, deducible from the weight of the sulphate of barytes (C. b.), with that which ought to exist in the sulphate of lime, and sulphate of magnesia actually found by experiment. But to make this comparison, some collateral experiments were previously necessary.
- (D. e.) By these experiments, I found that sulphate of lime prepared by double decomposition, then calcined in a low

^{*} The assumption that crystallized sulphate of magnesia contains only 44 per cent, of water, though it was correctly true with the specimen on which I operated, is below the average, which, I find from several experiments, is about one half the weight of the salt. Mr. Kirwan states the water of crystallization to be 53.6 in 100 grains; but this, I believe, a little exceeds the truth.

red heat, and afterwards dissolved in a large quantity of boiling distilled water, yields, when precipitated by a barytic salt, in the proportion of 175.9 grains of sulphate of barytes from 100 of the calcareous sulphate.* The same quantity of ignited sulphate of lime (= 128 grains dried at 160° FAHRENHEIT,) precipitated by super-oxalate of potash, gives 102.5 of oxalate of lime; or, precipitated by sub-carbonate of potash at a boiling heat, 74.3 grains of carbonate of lime.† One hundred grains of crystallized sulphate of magnesia (= 56 desiccated) afford when precipitated by muriate of barytes, 111 or 112 of the barytic sulphate.

(E.) By a comparison of the above proportions with those obtained in the analysis of any specimen of common salt, we may learn whether it contain other sulphates beside those with earthy bases. For example, if the precipitate (D.) consist of carbonate of lime only, and bear to the sulphate of barytes (C.b.) the proportion of 74 to 175, or very nearly so, we may infer, that no other sulphate is present, but that of lime. The same conclusion will follow, if, after having decomposed one half of the watery solution (C.) by muriate of barytes, and another half by oxalate of potash, we find that the sulphate of barytes bears to the oxalate of lime, the proportion of 175.9 to 102.5.

^{*} This result corresponds, within a fraction of a grain, with one obtained in a somewhat different way by Dr. Marcer, and very nearly with an experiment of my friend Mr. James Thomson, who found the barytic sulphate, precipitated from 100 grains of sulphate of lime by nitrate of barytes, to weigh 173 grains.

[†] On reversing this experiment, I found that 100 grains of carbonate of lime, saturated with sulphuric acid, and calcined in a low red heat, afford 135 of sulphate of lime. A similar experiment of Mr. Thomson gave 134.6 grains. Dr. Marcet, also, informs me that from 93.55 grains of pure marble, he obtained 125.95 grains of sulphate of lime, proportions which exactly co-incide with those of Mr. Thomson,

Now these proportions were, as nearly as could be expected, obtained in the analysis of Northwich salt; from whence we may conclude, that the only sulphate which it contains, is gypsum, or the sulphate of lime.

It must be remembered, however, that the calcareous sulphate, contained in any variety of common salt, cannot be in a state of complete desiccation, but would lose 22 parts out of 100, by exposure to a red heat.* It becomes necessary, therefore, either to increase, in the proportion of 5 to 4, our estimate of the sulphate of lime obtained by the foregoing rule, or, more simply, to assume that 100 grains of sulphate of barytes, indicate 73 grains of sulphate of lime, dried at 160° FAHRENHEIT, = 57 ignited.

(F.) When sulphate of lime and sulphate of magnesia, were both ascertained, and other sulphates also might possibly be present, as in the varieties of salt from sea water, the calculation became a little more complicated. In this case, after determining the quantity of both sulphates, (by the processes D. &c.) I estimated how much sulphate of barytes they ought respectively to afford; and then compared the estimated quantity, with that which was actually obtained. The earthy carbonates, for example, precipitated from 1000 grains of Lymington salt, which had previously been digested with alcohol, were converted into 31 grains of calcined sulphates, consisting of 19 grains of dry sulphate of magnesia, and 12 grains of dry sulphate of lime. Now from the magnesian sulphate 38 grains of sulphate of barytes should result, and

^{*} This Lind to be the loss sustained by 100 grains of artificial selenite, dried at 160°, and then ignited. The same quantity of crystallized native selenite, I learn from Dr. Marcet, loses 20.7 grains, by being calcined in a strong red heat.

from the sulphate of lime, 21 grains, the sum of which is 59. But the quantity actually obtained was 59.8. There is only, therefore, an excess of 0.8 grain of the actual above the estimated quantity, a difference much too trivial to be admitted as an indication of any sulphate with an alkaline base; and arising, probably, from unavoidable errors in the experiment.

- (F. a.) If in any mixture of salts, free from the earthy muriates, we are certain that no other sulphates exist beside those of lime and magnesia, their estimation becomes extremely simple. Decompose two equal quantities of the salt in question, the one by muriate of barytes, the other by oxalate of potash. From the weight of the latter precipitate, we may calculate the quantity of sulphate of lime. Suppose, for example, the oxalate of lime (as was actually the case with the precipitate from 1000 grains of Lymington salt,) to weigh 12 grains; these denote 15 of sulphate of lime, dried at 160° FAHRENHEIT, which quantity, if decomposed, would give 201 of sulphate of barytes. The latter number $(20\frac{1}{2})$, subtracted from the weight of sulphate of barytes actually obtained (say 60), gives $39\frac{1}{2}$ grains for the sulphate of barytes, resulting from the decomposition of sulphate of magnesia. The quantity of the latter salt, it will be found, therefore, by applying the rule already given (D. e.), must be 35 grains.
- (F. b.) The same object may be accomplished by decomposing two equal quantities, the one by oxalate of potash, the other by the compound solution (D. c.). From the weights of the precipitates, it is easy to calculate from how much of the calcareous and magnesian sulphates they have resulted.
- (G.) When the salt left by alcohol was known to contain muriate of soda, and sulphate of magnesia, but no sulphate of

lime, the presence of alkaline sulphates was investigated in the following manner. The salt was dissolved in water, and the solution was divided into two equal portions. To the one muriate of barytes was added, and to the other, the compound precipitant of carbonate of ammonia, and phosphate of soda. If the sulphate of barytes, thus produced, bore to the ammoniaco-magnesian phosphate, the proportion of 112 to 90, it was concluded that no other sulphate had been decomposed, but that with base of magnesia.

(H.) At one time, I expected to have ascertained the quantity of sulphate of soda, in an artificial mixture of that salt with sulphate of magnesia and muriate of soda, by the following formula. To a solution of the three salts, heated to a boiling temperature, I added sub-carbonate of ammonia, which decomposes the sulphate of magnesia only. I had then a solution containing muriate and sulphate of soda, with sulphate of ammonia, and some carbonate of ammonia. This solution was evaporated to dryness, and the mass was sufficiently heated to expel the ammoniacal salts. I found, however, that at this temperature, the sulphate of ammonia acted upon the muriate of soda, and produced an additional, and not inconsiderable quantity of sulphate of soda.

Having determined, by the foregoing processes, the quantity and kind of the earthy muriates, the amount of the insoluble matter, and the proportion of sulphates, the weights of all these different impurities were added together, and the sum being deducted from the weight of the salt submitted to experiment, the remainder was assumed as the amount of the pure muriate of soda in the specimen under examination.*

^{*} I have deemed it unnecessary to state, in the table, the quantities of acid and

Though I purposely refrain from giving the details of the several analyses, which were made according to the foregoing plan, from the conviction that they would be both tedious and unnecessary, yet there are a few circumstances, which it may be proper to mention more fully, than can be done in the form of a table.

1. The brine which I examined was from Northwich, and was sent to me in the state in which it was taken from the spring.* At the temperature of 56° Fahrenheit, it had the specific gravity of 1205. It was perfectly limpid, but lost a little of its transparency when raised to a boiling heat, in consequence of the deposition of a very minute quantity of carbonate of lime, and oxide of iron. It was immediately precipitated by muriate of barytes, oxalate of ammonia, and alkaline solutions, both mild and caustic. Eight ounce measures, evaporated to dryness in a sand heat, gave 1230 grains of salt, which, for the sake of distinction, I term entire salt. It proved, on analysis, to contain in one thousand parts, †

base in the several varieties of muriate of soda. They may readily be estimated from the proportion, deduced by Dr. Marcet, of 46 acid, and 54 soda, in 100 of the pure muriate. In this determination he assumes, that 100 parts of luna cornea, after being melted and heated to redness, consist of 19 05 parts of acid, to 80.95 oxide of silver. This statement agrees very nearly with the recent one of Gar Lussac, who makes 100 parts of silver to combine with 7.60 oxygene, and this oxide to neutralize 25.71 parts of real muriatic acid.

- * I have lately been informed that this brine had been pumped out of a rock-salt mine, into which, from the impossibility of obtaining the salt in a solid form, it was allowed to flow. Hence it was fully saturated with muriate of soda.
- + The specific gravity and proportion of earthy sulphates in Cheshire brine appears to differ considerably in the brine of different springs. See HOLLAND's Cheshire Report, p. 45, &c.

Carbonate of lime and oxide of iron - - - 2

Muriate of lime, and muriate of magnesia, in nearly
equal proportions - - - - - 5

Sulphate of lime - - - - - 19

Muriate of soda - - - 974

2. The mother liquor, or brine that remains after separating all the common salt, which it is thought worth while to extract, had the specific gravity of 1208. The dry salt contained

Muriate of magnesia - - 35

lime - - - 32

Sulphate of lime - - - 6

Muriate of soda - - 927

3. The *clearings* of the brine, which are raked out of the pan when the salt first begins to granulate, contained in 1000 parts,

Muriate of soda - - - 800 Carbonate of lime - - 41 Sulphate of lime - - - 159

4. Of the substance called by the workmen pan-scale, two specimens were analysed, the one containing a large proportion of muriate of soda, the other very little. The first variety consisted of

Muriate of soda - 950
Carbonate of lime - 10
Sulphate of lime - 40

The second variety was composed of

Muriate of soda - - 100
Carbonate of lime - - 110
Sulphate of lime - - 790

Circumstances, however, are constantly occurring to vary the proportion of ingredients, both in the clearings and in the pan-scale. If, for example, the brine be short of the point of saturation with common salt, it acts, when admitted into the pan, upon the muriate of soda which the pan-scale contains, and we obtain the second variety. But if the brine be fully charged with salt, it effects no solution of the muriate of soda, carried down along with the gypsum; and then the first species of pan-scale results.

5. The salt oil, or mother liquor from sea water, a specimen of which I received from Dr. Thomson, had the specific gravity of 1277. It was abundantly precipitated by muriate of barytes: by pure ammonia, but not by the carbonate; and was not changed by oxalate of potash, either immediately or after an interval of some hours. One thousand parts of the dry salt consisted of

Muriate of magnesia - - 874
Sulphate of magnesia - - 70
Muriate of soda - - 56

6. The salt brine, or liquor which drains from the Scotch salt, had the specific gravity of only 1188. It was affected by the same tests as the salt oil, but less remarkably. The dry residue contained

Muriate of magnesia		-	-	205
Sulphate of magnesia	-	***	-	135
Muriate of soda -	-		-	66o
•				
				1000.

7. The mother liquor, or bittern pan Lymington, presented, on analysis, an unaccountable variation from the similar fluid sent from Scotland, and gave a much larger proportion of sulphate of magnesia. A considerable quantity of this salt had, moreover, crystallized in the bottle which contained the liquid. Its specific gravity was 1280. One thousand parts of the dry salt contained of

Muriate of magnesia - - - 640
Sulphate of magnesia - - - 260
Muriate of soda - - - 100

8. The pan-scale from Lymington contained

Muriate of magne	esia -			-	29
Desiccated sulpha	te of n	nagnesia			18
Carbonates of lime	e and 1	nagnesia*	***	-	127
Sulphate of lime	***	_			216
Muriate of soda	-				610
					Company of the Compan
•					1000.

From the very near approximation of the proportions between the sulphate of barytes and ammoniaco-magnesian phosphate, obtained in the analysis of all these products of sea water, to those which result from the decomposition of

^{*} The proportion of these carbonates I was prevented from determining by an accident.

two equal quantities of sulphate of magnesia, it may be inferred that they contain no sulphate of soda.* For example, to decide whether the Scotch salt contains an alkaline sulphate, or not, I dissolved 1500 grains in a pint of boiling water, and evaporated till fourteen drachm measures only remained, the common salt being removed as soon as it was formed. The residuary liquid was divided into two equal portions, one of which gave $18\frac{1}{2}$ grains of sulphate of barytes, and the other, 14 grains of ammoniaco-magnesian phosphate. The proportion between these numbers is so nearly that which has been already assigned, (viz. 112 to 90,) that we may safely infer the total absence of sulphate of soda. This salt, indeed, is considered as incompatible with muriate of magnesia; but after digesting, for two or three days, 100 grains of the former, with 20 of the latter, evaporating to dryness, and washing the residuum with repeated affusions of alcohol, I found that two grains of the muriate of magnesia had escaped decomposition.

Manchester, June 19, 1809.

^{*} I employed more attention in investigating the presence of sulphate of soda in the products of sea water; because this salt is stated to be one of its ingredients by the Bishop of LLANDAFF, (Chemistry vol. ii. p. 62,) and by other chemical writers.