

**On the manufacture of chlorine : a lecture, delivered, at the request of the Council of the Society of Arts, before the Chemical Section of that Society, May 22nd, 1874, A.W. Williamson ... in the chair / by Walter Weldon.**

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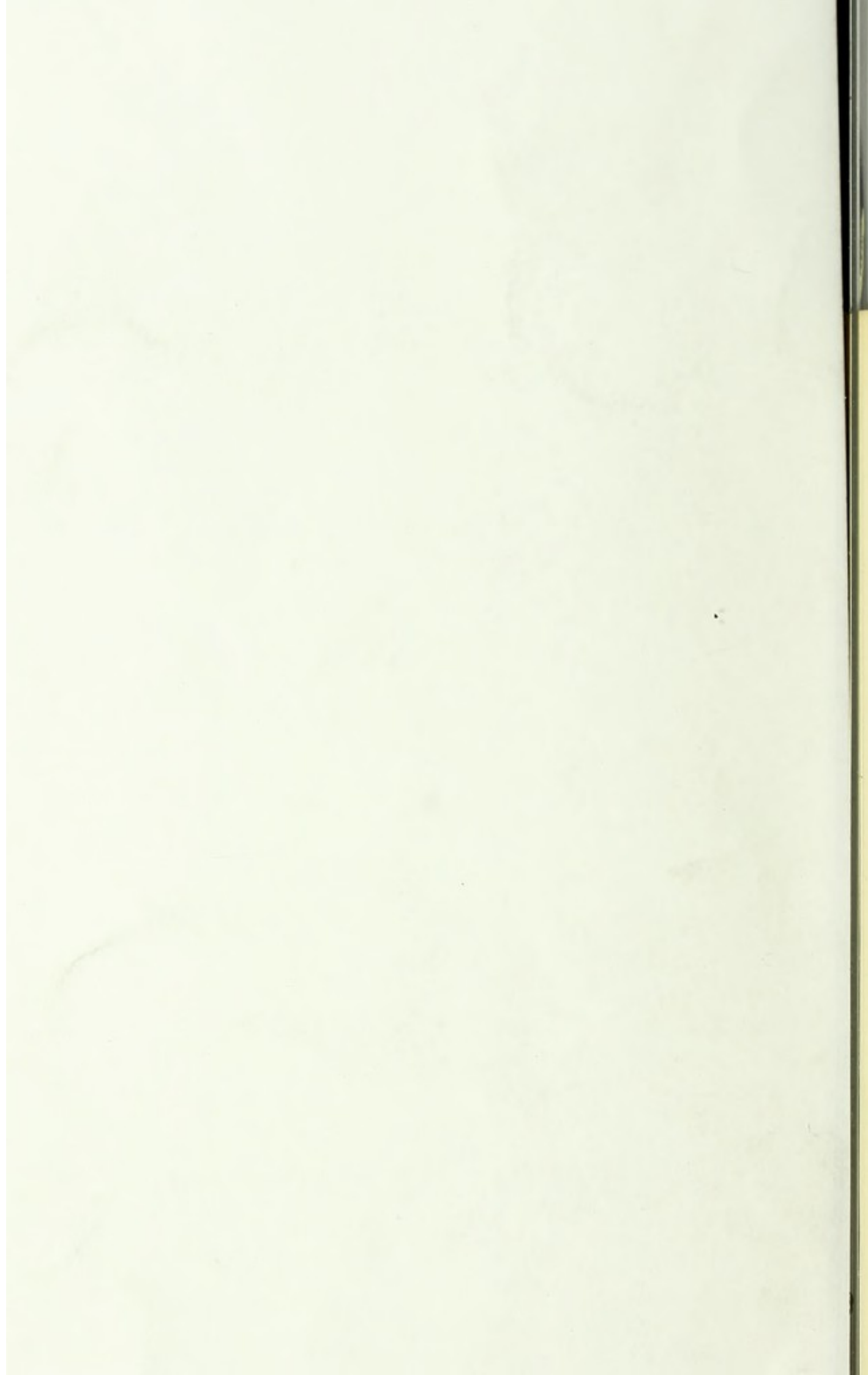
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ON THE

MANUFACTURE OF CHLORINE :

A Lecture,

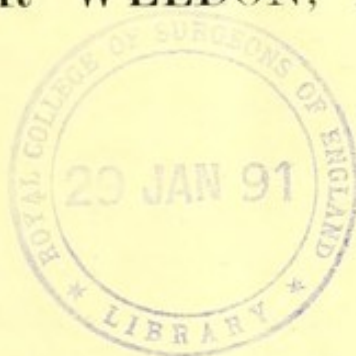
*Delivered, at the request of the Council of the Society of Arts, before the  
Chemical Section of that Society, May 22nd, 1874,*

A. W. WILLIAMSON, Esq., F.R.S.,

PRESIDENT OF THE BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE,  
CORRESPONDING MEMBER OF THE ACADEMY OF SCIENCES OF PARIS,  
ETC., ETC., ETC., IN THE CHAIR,

BY

WALTER WELDON, F.C.S.



PRINTED FOR PRIVATE CIRCULATION BY  
THOMAS SCOTT, WARWICK COURT, HOLBORN, LONDON,  
1874.



OF THE

# MANUFACTURE OF CHLORINE

MANUFACTURE OF CHLORINE  
A TREATISE

By the author of the report on the progress of the  
chemical industry of the United States, 1877

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IS A BRANCH OF THE  
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PROFESSOR WILLIAMSON, AND LADIES AND GENTLEMEN,

There are two kinds of research which contribute to the progress of the industrial arts: that which we call purely scientific, and which has for its sole object the extension of our knowledge of natural phenomena; and that which is directed to the end of what is termed invention, and which aims at increasing the material well-being of mankind by providing new appliances for the comfort or convenience of life, by producing new commodities useful or pleasant to man, or by the cheaper or otherwise more advantageous production of commodities already known and used. The industry of chlorine differs from all the other great chemical industries, excepting only the most recent of them, that of the coal-tar dyes, in having sprung directly from the first of these two kinds of enquiry; and I could not speak to you on the subject of the chlorine manufacture, in this centenary year of the triple discovery to which that manufacture is entirely due,—the discovery, namely, of the existence of the body called chlorine, of the most effective method yet known for obtaining it, and of that one of its properties for which it is now so largely employed in the service of man,—without commencing by reminding you of how much of the difference between the England of to-day and the England of a century ago is due to this result of the earnest pursuit of pure



scientific truth by that then assistant to a provincial Swedish apothecary who has rendered for ever illustrious the name of SCHEELÉ. Within the hundred years which have now elapsed since this discovery, the annual value of the cotton goods manufactured in Great Britain has risen from something less than two hundred thousand pounds to close upon one hundred millions sterling. To this stupendous growth of what is now our greatest industry, we owe, in very large part, the vast development of all other of our industries, and the enormous increase in the numbers, wealth, and comfort of our population, which have accompanied it; and although the largest part towards this result has no doubt been contributed by mechanical invention, not even the steam-engine, the carding-machine, the spinning-jenny, and the power-loom could have produced our modern Manchester, and all that it represents, without the aid of that discovery in pure science which rendered it possible to perform in a few hours, in a workshop in a town, at any season, and in any climate, that operation of bleaching which forms an essential part of the preparation for sale of most kinds of cotton goods, and which previously occupied at least four months, could be carried on only in the open country, could be well performed only at certain seasons, and could be best performed, for reasons of climate, only in certain countries, of which England is *not* one, and which moreover required an enormous expanse of green field, which it withdrew entirely from agricultural service. The discovery of chlorine, and of its property of destroying vegetable colours, is thus to be counted as not the least among the causes of the marvellous industrial progress of the last hundred years; and we have also to claim for it whatever influence upon the incalculably beneficent activity of the printing-press may have been due to our command of a practically unlimited supply of white paper. Notwithstanding the continually increasing production of bleached vegetable textile fabrics, and consequently



of white rags, the demand for paper for printing has long outstepped the supply of it from that source; and if it were not for chlorine enabling us to make white paper, not only from coloured rags, but also from straw, Esparto grass, wood, refuse jute, and many at first blush still less promising materials, while it is perhaps conceivable,—for my own part I cannot think it is,—that books and newspapers would nevertheless have been as cheap and as abundant as they actually are, they must at least have been printed on a material which at best could have been only whitey-brown, and so must have been far inferior, both in convenience and in attractiveness, to the books and newspapers we actually have. They certainly could not have been such that those who ran might read them. The history of science abounds with instances of practical benefit to mankind resulting from single-minded enquiry into the facts of nature, by enquirers who neither sought nor received any reward but the satisfaction of extending human knowledge of the phenomena of the marvellous universe amid which we are placed; but it seems to me that of all such instances which have yet arisen, by far the most striking, and the most worthy to be held in remembrance,—although it is certainly not the one which is most generally recognized,—is that which is afforded by the results of the discovery upon which is founded the important industry of the latest phase of which it is my duty this evening to offer you some account.

This discovery Scheele arrived at in the course of a research with respect to the nature and properties of a black mineral substance, a sample of which you see upon the table. This substance is now known commercially as “manganese,” and contains a large proportion of the body which chemists call manganic peroxide. Scheele treated this substance with every reagent that was known to him. In the course of his investigation, he thus came to boil it with hydrochloric acid. We will repeat this experiment, in the hope of showing you,



at least in substance, what Scheele then found to happen. In one of the flasks on the table below is some manganic peroxide, the essential constituent of the mineral upon which Scheele's experiments were made, and Mr. Bunker will pour upon it some hydrochloric acid, and then apply to the flask the heat of a gas-flame. As it will take him a minute or two to obtain our desired result, I will call your attention, in the meantime, to the commencement of another experiment, which will require nearly an hour to complete, and which it is therefore desirable that we should commence as soon as possible. We have here three jars containing a pink solution, the nature of which I will explain to you by and bye. To the contents of one of the jars I add a certain quantity of milk of lime, to the contents of the second jar a smaller quantity of milk of lime, and to those of the third jar a quantity of solution of caustic soda, equivalent to the quantity of milk of lime which I have put into the first jar. In each of the three jars we have now a white precipitate, suspended in a colourless solution. We shall now begin to send a current of air through the contents of all the jars, and by and bye I shall have to call your attention to the results which I expect it will have produced. I will now only ask you to observe from time to time the changes which I expect will take place in the *colour* of the contents of the jars.

Coming back now to this experiment of Scheele's, he found that on boiling his mineral with hydrochloric acid, a gas was given off which had a green colour and a most penetrating odour, and which produced very painful effects when respired, powerfully attacked all the metals, and completely destroyed the colour alike of flowers and of green leaves. He called this gas "dephlogisticated muriatic acid;" but Sir Humphry Davy afterwards gave it the better name of chlorine. The two jars which we have connected with our flask are now pretty well filled with it, and by daylight you would have seen the green colour of the gas in them; but by gas-



light I fear it will be barely, if at all, perceptible. Its odour, and its effect upon the organs of respiration, we hope to avoid giving you experience of; I can assure you, with some authority, that they are not agreeable. Mr. Bunker, however, will show you that he has chlorine in the jars, and at the same time illustrate that property of attacking the metals which Scheele observed, by admitting into one of them a little powdered antimony. The attack is so rapid and energetic that as the antimony falls through the chlorine contained in the jar you observe there is actual incandescence. Into the other jar containing chlorine I will ask Mr. Bunker to introduce a piece of dyed calico, and I think you will see that its colour will be immediately discharged.

The idea of the practical application of this bleaching property did not occur to Scheele himself, but was the result of Berthollet's repetition of Scheele's experiments, some ten or twelve years later. Berthollet was then director of the Gobelins, and in that capacity had charge of dyeing and bleaching operations; and having found that a solution of chlorine in water bleached as readily as the gas itself, it occurred to him that a brief immersion in such a solution might be substituted for that long exposure to sun and air which up to that time had been the only known means of bleaching vegetable textile fabrics. In each of these jars I have some solution of chlorine in water, and to show you Berthollet's method of bleaching, I will introduce into one of them a piece of brown calico, and into the other a piece of calico which has been dyed. After a little time, both pieces of calico will have become perfectly white.

Curiously enough, considering how much assistance chlorine was destined to render in the development of the application of the steam-engine, this idea of Berthollet's was brought to this country by James Watt; and the first piece of goods ever bleached by chlorine in Great Britain was bleached under Watt's personal superintendence, at the bleach-field of



his father-in-law, near Glasgow, in the year 1787, being the year of Scheele's death. The process soon spread into nearly all the bleach-works of Great Britain; but it was attended by two serious inconveniences. Owing to chlorine-water being practically incapable of transport, each bleacher had to manufacture his own chlorine; and owing to its tendency to give off its dissolved gas, its use was all but intolerable to the workmen. Many attempts were made to remedy these disadvantages, and they finally resulted, in 1798, in the discovery, by Mr. Charles Tennant, of Glasgow, that dry slaked lime would absorb more than half its weight of chlorine gas, giving a product,—since become so well known as “bleaching-powder,” or chloride of lime,—which could be both stored and transported with the utmost facility, and which would yield, on treatment with water, a bleaching solution, having all the advantages of chlorine-water, without either of its disadvantages. I am not sure that our time will permit our doing so, but we propose to try to make a little of this product. At the bottom of the glass trough on the table there is some dry slaked lime, and Mr. Bunker will put a cover on the trough, and then send into it a little chlorine: which he will generate, this time, by means of a product similar to that which we hope to produce in two of the jars into which we are blowing air. I will ask him, however, first to take out a little of the lime, in order that, if our time permits us to complete the experiment, you may see the difference between the body which we put into the trough and the product which we hope to take out of it.

When Mr. Tennant first manufactured bleaching-powder, he sold it at one-and-sixpence per pound. Its present price is about £10 per ton, or very little over one penny per pound. Of it and its equivalent in chlorate of potash we now make in Great Britain one hundred thousand tons per annum, so that the annual value of the British chlorine manufacture is just about a million sterling. We manu-



facture in Great Britain rather more than two-thirds of the total chlorine made in the world.

The ultimate raw material of this manufacture is the universally familiar substance, common salt. We are fortunate in possessing in Great Britain enormous mineral deposits of this substance, those in some parts of Cheshire, for example, being more than two hundred feet thick, and this over an area of many miles. The salt exists in these deposits as a compact crystalline rock, of a reddish colour, due to the presence in it of small quantities of oxide of iron. A sample of it lies upon the table. Comparatively little of it is brought to the surface in that state, the greater portion of our output of salt,—which reaches the enormous amount of one and three-quarter millions of tons per annum,—being pumped up in the state of “brine,” formed by the action on the rock-salt of the water which infiltrates down to it through the superincumbent soil, and this is pumped up by the landowners or their lessees, and supplied by them to the salt manufacturers at a price sometimes as low as twopence, and I believe never exceeding sixpence, not per quantity of brine containing a ton of salt, but, so as to allow for any amount of loss in the process, per ton of salt actually turned out by the manufacturer. All that the salt-manufacturer has to do is to concentrate the brine by evaporation, and fish out from time to time the crystals which then form, and which collect at the bottom of the evaporating pan. According to the temperature at which he performs this evaporation, he produces either salt of such fine grain as we are familiar with in table salt, or such very coarse-grained salt as is used for curing fish, or salt in the state of the still larger and most exquisitely beautiful crystals known as “Diamond Bay Salt,” or salt in crystals of an intermediate size. Samples of all these kinds of salt, kindly supplied to me by Messrs. Fletcher and Rigby, of Northwich, are on the table. The intermediate grain being cheaper to



produce than either the very small or the very large, is preferred for that reason by the manufacturers of alkali and chlorine; and salt of that grain is hence known in the trade as "chemical salt." To produce a ton of salt of this kind requires about half a ton of coal; but the manufacturer can nevertheless sell it, even with fuel at its present price, at twelve shillings per ton, and for the ten years preceding the recent rise in the price of coal, its average selling-price did not exceed seven and sixpence per ton. One of the causes of our pre-eminence in the chlorine-manufacture is thus cheaper salt than is as yet at the command of any other people in the world.

It is remarkable that this substance, which forms so essential a constituent of the food of man and of all animals, is a compound of two bodies either of which, in the free state, would prove utterly destructive to any animal organism: namely, chlorine, the most energetic of known gases, and the metal sodium, one of the most energetic of known solids. I have here a sample of the latter constituent of our salt. It is immersed in naphtha, to protect it from the action of the air, from which it would instantly absorb oxygen, as indeed the lumps constituting our sample have already done on the surface; but if I take a piece of it out of the naphtha and cut it with a knife,—it is nearly as soft as cheese,—you will be able to see its metallic lustre, although only for a moment. It is a metal so light that it floats on water, and possessed of so much chemical energy that it instantly decomposes water, forming a solution of caustic soda and liberating hydrogen gas. Mr. Bunker will put a little piece of it into a dish of warm water under a bell-glass on the table below. The action, you see, is so violent, and produces so much heat, that both the hydrogen which it liberates and a portion of the sodium itself, take fire.

The proportions in which the salt contains these constituents are those of thirty-five and a half parts by weight of



chlorine to twenty-three parts by weight of sodium. Of the total weight of pure salt, therefore, between sixty and sixty-one per cent. consists of chlorine. A cubic foot of it contains the quantity of the metal which in the free state would occupy about five-sixths of a cubic foot, and, in addition, a quantity of the gas which would occupy, in the free state, at the average pressure of the atmosphere, not less than 450 cubic feet.

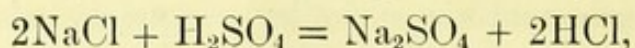
In the manufacture of chlorine as at present conducted, free chlorine is obtained from the salt, not directly, but by two successive operations; the first of which consists in the decomposition of the salt by sulphuric acid. We have some salt in a flask on the table, and if Mr. Bunker pours upon it some sulphuric acid there will be given off an acid vapour, which I hope we shall be able to condense in this little glass tower. This tower is packed with small pieces of coke, down which water from the little cistern above is kept trickling, and if we are successful in our experiment the acid vapour given off from the flask and conveyed first through a cooling jar and then into our little tower, close to the bottom, will dissolve in the water with which the coke is kept moistened, and an aqueous solution of the acid vapour will eventually run from the bottom of the tower into the beaker which you see placed to receive it. In the beaker is a little solution of blue litmus, and you will see when an acid solution begins to run from the tower by the blue colour of the litmus being changed to red.

What takes place when salt is treated by sulphuric acid is shown upon one of the diagrams on the wall, on which our compound of sodium and chlorine is represented by  $\text{NaCl}$ , sulphuric acid being similarly represented by  $\text{H}_2\text{SO}_4$ . When two equivalents of  $\text{NaCl}$ , or common salt, are treated with one equivalent of sulphuric acid, the sodium of the salt leaves its chlorine and unites with the  $\text{SO}_4$  of the sulphuric acid, taking the place of the hydrogen of that com-

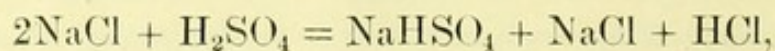


pound, and the hydrogen thus removed from the sulphuric acid unites with the chlorine of the salt, taking the place which the sodium has forsaken. The two original compounds cease to exist, and instead of them we get two new compounds. Instead of  $\text{H}_2\text{SO}_4$  we get  $\text{Na}_2\text{SO}_4$ , and instead of  $2\text{NaCl}$  we get  $2\text{HCl}$ . Perhaps the middle part of the diagram, in which one of the constituents of the salt and one of the constituents of the sulphuric acid are marked in red letters, and the other constituent of each in black letters, will make these transpositions clearer. The constituents marked in red go together, and the constituents marked in black go together. The product marked in black,  $\text{Na}_2\text{SO}_4$ , or sodic sulphate, is what the manufacturers call "salt-cake." It contains all the sodium of the salt, and by fusion with limestone and coal is made to yield carbonate of soda. The product marked in red contains all the chlorine of the salt, and is the compound now known as hydrochloric acid, and formerly called muriatic acid, or "spirits of salt."

Of the apparatus employed for the decomposition of salt by sulphuric acid on the large scale, I have here a diagram. At one end of it is a shallow circular vessel, or "pot," as it is called, from seven to ten feet in diameter, and made of very thick cast-iron. This vessel has a fire under it, and is domed over with brick. The salt is put into this pot in charges of from five to ten hundred-weight each, hot sulphuric acid is then poured in, the fire is kept up, and the charge is occasionally stirred by the workman with a long iron rabble. Now, although the ultimate result of the action of sulphuric acid upon salt is that represented by the equation:

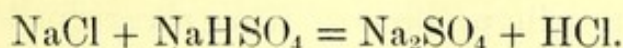


this result has really to be attained by two stages, during the first of which, represented by





only half the salt is decomposed, the second half of the salt being afterwards decomposed in accordance with the equation



The second stage of the reaction requires a temperature much higher than the first stage of it requires, and much higher than could be used with safety in the iron pot; therefore, as soon as the charge in the pot, which the sulphuric acid at first renders quite liquid, has become pasty, so that there is no risk of its running through a brick bed, which is usually at the end of a little less than an hour, the workman pushes it out of the pot, through an aperture arranged for the purpose, on to the bed of a furnace built of refractory brick, on which it is exposed to nearly a red-heat. Of the two successive reactions which have to be effected before the salt is completely decomposed, there takes place in the pot the whole of the first and so much of the second that about two-thirds of the salt is decomposed in the pot, the proportion which has to be decomposed in the furnace rarely exceeding one-third. The furnace shown in the diagram is a muffle-furnace, such as is used throughout the Lancashire district, and in Glasgow; but in the Newcastle-on-Tyne district reverberatory furnaces are usually employed. Where reverberatory furnaces are used, the condensing apparatus employed for the hydrochloric acid gas generated in the furnace is distinct from that employed for the hydrochloric gas generated in the pot; but where muffle-furnaces are employed, the gas from both pot and furnace go to the same condensing apparatus, as represented in the diagram. The gas is first conveyed either through cooling cisterns, or through some arrangement of cooling pipes, and then enters a condensing-tower, such as we have a model of now at work on the table below. These towers are usually about six feet square, and vary in height from thirty feet to sixty, seventy, or even a hundred feet. They are usually built of stone flags, clamped



together by iron tie-rods, and are packed with small pieces of coke, down which water is kept trickling. The gas enters at the bottom, and in passing upwards through the interstices between the pieces of continually moistened coke comes into contact with an enormous surface of water; and as it is a gas which is extremely soluble in water, if the tower is properly constructed, and properly proportioned to the quantity of hydrochloric acid gas which it is to receive, none of the acid ever reaches the top of the tower, all that enters it at the bottom as gas becoming converted into aqueous solution before any of it can get to the top. It is common, however, to have a second tower so connected with the first that any gas which may escape condensation in the first tower shall pass from the top of it to the bottom of the second tower, and be condensed in that. I need hardly remind you that this method of condensing hydrochloric acid is one of the many important inventions of Mr. William Gossage.

The use of an iron vessel for an operation in which sulphuric acid is employed, and hydrochloric acid generated, at a high temperature, is so contrary to laboratory ideas that it may be interesting to mention that when a "salt cake pot" is permitted to fairly wear out, and is not broken by sheer carelessness or neglect on the part of the workman, as is unhappily nowadays too often the case, as much as three thousand tons of salt may be decomposed in one. The average life of a salt cake pot is barely fifteen hundred tons of salt decomposed in it; but this is because so many pots get broken, either by the workmen neglecting to properly stir the charges in them, or by their charging heated pots with too cold materials. The wear of the pot is chiefly due to the action of the hydrochloric acid generated in it, and this action is also one of the causes of the yellow colour of commercial hydrochloric acid. Pure aqueous hydrochloric acid is quite colourless, but commercial hydrochloric acid has the yellow colour you see in this sample of it, owing to the presence in



it of a small quantity of ferric chloride, due partly to the action of the aqueous acid on the coke in the condensing towers, but partly also to the action of the acid gas on the inner surface of the salt cake pot. A little ferric chloride is formed in the pot, and flies over with the hydrochloric acid gas, and is condensed with it.

Another interesting point about salt-cake pots is that, within certain limits, like certain other good things, the older they are, the better they seem to be. There are some manufacturers who always keep their pots two or three years before using them, insisting that pots thus "seasoned," as they call it, are far less liable to breakage than pots more recently made. I believe it is really the fact that pots which have been long kept are much more durable in use than new pots; although, seeing that the pots are masses of cast iron, five or six inches thick at the bottom, tapering to one or two inches thick at the top, why this should be so is not at first blush quite intelligible.

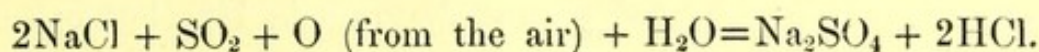
The operation in which salt-cake pots are used, and which I have endeavoured to describe, being the first step, not only in the manufacture of chlorine, but also in a still more important manufacture, that of soda, it is one of such moment that I cannot pass without mention a most important attempt which is now in progress, and which bids fair to be most successfully realised, to perform this operation in another and a very much simpler manner. Before salt can be decomposed by the method at present in universal use, sulphuric acid has to be manufactured. This is done by burning off into sulphurous acid gas, or  $\text{SO}_2$ , the sulphur contained in that native compound of sulphur and iron which is known as pyrites, and of all the properties and uses of which Dr. Wright gave us in this room so extremely clear and complete an account a month ago, and then sending this  $\text{SO}_2$ , mixed with air, steam, and vapour of nitrous acid, into vast leaden chambers, in which, by the aid of the carrying action of the



nitrous acid, the  $\text{SO}_2$ , unites with a third equivalent of oxygen, derived from the air which enters the chamber with it, and thus becomes converted into  $\text{SO}_3$ , which unites with the steam present to form sulphuric acid, or  $\text{H}_2\text{SO}_4$ . This  $\text{H}_2\text{SO}_4$  collects at the bottom of the chamber, diluted with a considerable quantity of water, and before it can be used for the decomposition of salt much of this surplus water has to be evaporated off from it. To produce the quantity of sulphuric acid required to decompose one hundred tons of salt per week, requires leaden chambers of the enormous capacity of somewhere about 200,000 cubic feet. My friend Mr. James Hargreaves, working in conjunction with Mr. Thomas Robinson of Widnes, has for some years been sedulously endeavouring to realize the idea of avoiding the necessity for this preliminary manufacture of sulphuric acid, and of obtaining salt-cake on the one hand, and hydrochloric acid on the other, by the direct reaction upon salt of a mixture of sulphurous acid gas, air, and steam, being the same mixture that at present goes into the sulphuric acid chambers, except that it does not contain that very costly element of the latter mixture, nitrous acid. To illustrate his mode of proceeding, Mr. Hargreaves has been so good as to supply me with some samples. His first step is to moisten his salt with water, and spread it upon iron plates, heated from below, but only to a low temperature, so as to dry the moistened salt very slowly. He thus obtains the salt in hard but very porous masses, a piece of one of which lies on the table. He breaks these up by machinery into smaller pieces of uniform size, and these he charges into vertical cast-iron cylinders, from ten to fifteen feet in diameter and from ten to twelve feet high. Arrangements are made for applying heat to the cylinders externally, and when the salt in them has attained a temperature of about  $800^\circ \text{F}$ . he sends into the cylinders the gases from pyrites burners, mixed with air and steam. He employs a series of from six to ten cylinders and



so arranges them that the gases pass in at the top of the first cylinder, then pass from the bottom of the first cylinder to the top of the second cylinder, then down through the contents of the second cylinder, out at the bottom of it, and in at the top of the third cylinder, and so on. The mixture of gases will not act on the salt below a temperature of about 800° F., but when that has been attained by the salt the external heating is discontinued, the heat of the gases themselves, together with that generated by their reaction upon the salt, being afterwards quite sufficient to keep up the required temperature. When the salt in the first cylinder is completely converted into salt-cake, the charge is withdrawn from it, fresh salt is put in, and what was the second cylinder of the series now becomes the first, while that which was the first, and is now newly charged with salt, becomes the last of the series. It takes from a fortnight to three weeks to completely convert the salt into salt-cake, but after that period from the commencement of the process has once elapsed, a cylinder, containing from fifteen to forty tons of salt-cake, becomes ready to be discharged every day, or every few days, according to the number of cylinders employed. The reaction which goes on in the cylinders may be represented by the equation :

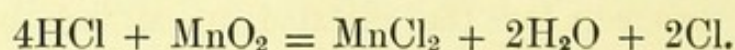


The hydrochloric acid passes off as gas and is condensed in coke towers in the usual way, and the salt-cake comes out of the cylinders in the state in which you see it in the sample on the table, in exactly such lumps as the salt went into them. For nearly a year past Mr. Hargreaves has been making from thirty to forty tons of salt-cake per week by this process, with such success that five large manufacturers are now building plant for it on a very extensive scale; and there seems every reason to expect that by and bye Mr. Hargreaves will find himself rewarded for many years of



most patient and persevering labour on this process by seeing it, if not universally adopted, which can hardly be hoped for in a single lifetime, at least invariably preferred to the process in use now whenever new plant has to be erected, or old plant to be replaced. He will thus have been the first to effect any essential change in what is unquestionably the most important of all the operations conducted by industrial chemists.

The chlorine of our salt having been driven off from it as hydrochloric acid gas, and this gas having been dissolved in water, the next step in the manufacture of chlorine is to treat this aqueous hydrochloric acid with manganic peroxide. The reaction which then takes place is that represented by the equation :



The manganic peroxide, or  $\text{MnO}_2$ , is a compound of the metal manganese with two equivalents of oxygen, and its oxygen combines with the hydrogen of the hydrochloric acid to form water, one half of the chlorine of the hydrochloric acid,—say the part which is represented on the diagram on the wall in red letters,—combining with the manganese to form  $\text{MnCl}_2$ , or manganous chloride, and the other half,—represented on the diagram in blue letters,—being set free. Six years ago, all the chlorine made in the world—except a certain portion of that manufactured at Glasgow, by Messrs. Charles Tennant and Co., the firm founded by the inventor of bleaching-powder—was obtained by digesting hydrochloric acid with native manganese ore: by exactly the method, in fact, by which chlorine was originally obtained by Scheele. In this country, the process was performed in square or oblong stills, built of silicious flags, and each provided with a false bottom, also of flags. One of these stills is shown in section on one of our diagrams. The manganese ore having been charged in lumps on the



false bottom, through a man-hole in the top, hydrochloric acid was admitted, and then, the man-hole having been first closed, steam was injected by means of a tube made by boring a hole through a block of stone. Chlorine went off slowly, the operation usually lasting from forty-eight to ninety-six hours; and there at length remained in the still only the silicious and other insoluble portions of the manganese ore, and a liquid residue familiar to the manufacturers as "still-liquor."

Now, if manganese ores consisted solely of  $\text{MnO}_2$ , and if it were possible to make an equivalent of  $\text{MnO}_2$  react on four equivalents of hydrochloric acid without using an excess of the acid, the liquid residue of this operation would be simply a solution in water of manganous chloride: the only products of the reaction upon each other of  $\text{MnO}_2$  and  $\text{HCl}$  being, as shown on our diagram, free chlorine, water, and manganous chloride, or  $\text{MnCl}_2$ . To utilize all the  $\text{MnO}_2$ , however, in substances so hard and compact as manganese ore, requires a very large excess of hydrochloric acid; and these ores moreover contain many bodies besides  $\text{MnO}_2$ , and especially considerable quantities of peroxide of iron. Instead, therefore, of being a practically neutral, wholly inodorous, and bright pink solution of manganous chloride, such as that of which I have a sample here, the residue of the treatment together of hydrochloric acid and manganese ores is a strongly acid, dark yellow, and ill-smelling liquid, containing a large quantity of that strongly acid salt, ferric chloride, and a still larger quantity of free hydrochloric acid. Of the total chlorine in it, one-half is very frequently in the state of free  $\text{HCl}$ . Except in Messrs. Tennant's case, this product, down to six years ago, was simply poured into the nearest stream; and a product more unfit to go into an inland river it would be difficult to conceive. It is utterly destructive to fish, rapidly injures both the iron-work and the masonry of bridges and the



like, and renders the water of the river poisonous to the land when carried on to it by floods, and entirely unfit for either manufacturing or domestic use. Being produced only in districts in which soda is manufactured, it had the still worse fault of being a prime agent of atmospheric contamination, seeing that it encountered in the streams the drainings from the tank-waste heaps, and reacted upon them with evolution of enormous volumes of sulphuretted hydrogen.

At the time I speak of, the extremely offensive nature of this product had already led to countless attempts to dispose of it otherwise than by sending it into the water-courses; and the fact that native manganese is not an abundant substance, and is therefore a costly one, had caused nearly all these attempts to take the direction of the regeneration from this product of manganic peroxide, for use over again. Of all the processes proposed to this end, the only one which had attained practical success was one which was invented by the late Mr. Charles Dunlop, of Glasgow, and the successive operations of which are represented on another of our diagrams. In Mr. Dunlop's process, the still-liquor is first treated with carbonate of lime, to neutralize its free acid and decompose its ferric chloride; the resulting ferric oxide is then separated by subsidence and decantation; and the clear liquor is then a second time treated with carbonate of lime, this time at a high temperature and under considerable pressure. In the first treatment with carbonate of lime, the manganous chloride in the liquor was not in the least acted upon; but in this second treatment with carbonate of lime, in closed boilers, under a pressure of several atmospheres, and at the temperature corresponding to the pressure employed, the manganous chloride is entirely decomposed; and whereas what went into the boilers was solid calcic carbonate suspended in solution of manganous chloride, what comes out of the boilers is solid manganous carbonate suspended in solution of calcic chloride. The manganous



carbonate is then separated from the calcic chloride by subsidence, decantation, and thorough washing; and is then dried and charged into little waggons which are passed slowly through an oven in such wise as to expose the manganous carbonate for forty-eight hours to a current of hot air. The carbonic acid of the carbonate is thereby completely expelled; oxygen is absorbed; and the white carbonate is converted into a soot-like product, containing about 72 per cent. of  $\text{MnO}_2$ . A sample of this product, and one of the carbonate from which it is made, you observe upon the table.

This very ingenious and extremely beautiful process was adopted, in 1857, for the larger part of their enormous production of chlorine, by Messrs. Charles Tennant and Company, who have kindly supplied the samples I am enabled to show you, and who were not only the first, but have always been, and are still, the largest makers of bleaching-powder in the world; and hence the exception which I made a little time ago in saying that six years since, all the chlorine manufactured, a portion of theirs only excepted, was obtained by means of native manganese. Mr. Dunlop's process, however, has never extended beyond Messrs. Tennant's great work at Glasgow; and although they are still using it there, Messrs. Tennant themselves, in their almost equally great new work near Newcastle-on-Tyne, have adopted instead of it another process, which has now become nearly universal, which is known by the name of the present lecturer, and which I shall now proceed to describe to you as briefly as I can.

This process is performed in an apparatus of which we have here a diagram. The vessels comprised in it are arranged, you see, at five successive elevations. The lowest of them is a well, sunk in the ground, and furnished with a mechanical agitator. The residual product of the manufacture of chlorine by means of native manganese,—such as



you see it in this sample, only hot, and reeking with acid vapour,—is run into this well, the agitator is put in motion, crushed limestone is thrown into the well, and in the course of half-an-hour the free acid at first contained in the liquor has become completely neutralized, and the ferric chloride which accompanied it completely decomposed. The liquor now consists of a perfectly neutral mixed solution of manganous chloride and calcic chloride, holding in suspension some ferric oxide, and, in smaller quantities, a few other solid bodies. This is pumped up into settling-tanks placed at the top of the apparatus; and here in a short time the suspended matters settle out, and we have above them a beautifully clear faintly rose-coloured solution, of which I have a sample in this beaker. This clear solution is run off into a tall cylindrical vessel, made of wrought-iron, and placed immediately below the vessels in which the liquor has settled. This vessel, called the "Oxidizer," is usually eleven feet in diameter, and thirty feet deep. A pipe for conveying a current of air from a blowing-engine, not shown on the diagram, goes down the centre of it; and terminates at the bottom in an arrangement of distributing pipes. The liquor from the settlers usually goes into the oxidizer at a temperature of about  $140^{\circ}$  F.; and if it has fallen below that temperature it is heated up to it, in the oxidizer itself, by injection of steam. The liquor being or having been made hot enough, the injection of air is commenced, and there is then rapidly added, in the state of very fine milk, 1.6 times the quantity of lime equivalent to the manganese in the liquor. This converts the charge into a thin white mud, such as I produce by adding milk of lime to the sample of the liquor in this beaker. This thin white mud consists of solution of calcic chloride holding in suspension an oxide of manganese, known as manganous oxide, or  $\text{MnO}$ , which contains only half as much oxygen as is contained in manganic peroxide, or  $\text{MnO}_2$ , and also holding, partly in suspension, but partly in solution,



six-tenths of an equivalent,—reckoned on the manganese present,—of free lime. When a little of this white mud is thrown on to a filter, the clear filtrate is naturally found, owing to the quantity of free lime present, and to the powerfully solvent action upon lime of hot solution of calcic chloride, to possess a strongly alkaline reaction. As the injection of air goes on, the mud becomes gradually darker and darker in colour, owing to the white hydrated  $\text{MnO}$  becoming converted into black  $\text{MnO}_2$  by absorption of oxygen from the injected air, what was originally a thin white mud being at length converted into a thin black mud, such as we have a sample of in another of these beakers. During the progress of this conversion of the originally white mud into a black mud, it is found that the alkaline reaction of the filtrate from the mud gradually diminishes in intensity, until at length it entirely disappears; and it is also found that when this alkaline reaction ceases, the absorption of oxygen from the injected air ceases also. When this stage is reached, which is at the end of two, three, four, or five hours, according to the relation between the size of the oxidizer and the size of the blowing-engine employed, a little more liquor is run into the oxidizer from the settlers above, the injection of air is continued for a few minutes longer and the charge is then run off from the oxidizer into one or other of a range of settlers placed below it. In these it separates, in the course of a few hours, into rather more than half perfectly clear solution of calcic chloride, of which we have here a sample, and a little less than half black mud of rather more than twice the density of that which left the oxidizer. The solution of calcic chloride is now decanted, and the settled mud is then ready for use for the liberation of chlorine from hydrochloric acid. To this end it is employed in stills which are very much larger than those used for the generation of chlorine by means of native manganese, but which are constructed of the same material, and in the



same manner, as native manganese stills, except that they are usually octagonal, instead of square, like the latter; and instead of being charged, like native manganese stills, first with manganese, and then with acid, the acid is put into them first, the mud being then run in upon the acid, through a luted opening, in a gentle stream, regulated at will by a cock. Steam being gently injected at the same time, the mud dissolves almost immediately on reaching the acid, and chlorine comes off in an even current, the force and flow of which can be regulated with the utmost nicety by regulating the admission of the mud. When all the acid has been decomposed and neutralized except to the extent of from six to eight ounces of HCl per cubic foot, which at some works is at the end of two hours, and at others at the end of from four to six hours, the contents of the still are run off into the well placed below it, and there the round of operations which I have described is recommenced. Except to the extent of a certain mechanical loss, the cause of which I fear I shall not have time to explain, the same manganese is thus made to serve for the generation of chlorine over and over again, being successively transformed from the state of  $\text{MnO}_2$  to that of  $\text{MnCl}_2$ , from that of  $\text{MnCl}_2$  to that of  $\text{MnO}$ , and from that of  $\text{MnO}$  again to that of  $\text{MnO}_2$ , time after time, indefinitely. The manganese in the black mud I exhibit has already undergone all these transformations, at least eight or nine successive times, in the course of practical operations, at the great works of the Newcastle Chemical Works Company, who make 230 tons of bleaching-powder per week by this process; the manganese in this white mud and in these liquors has done the same, at the works of Messrs. Hugh Lee Pattinson & Co.; and the manganese in all of them is capable of undergoing the same transformations again, any required number of times. At some works the entire stock of manganese undergoes all these transformations every twenty-four hours.

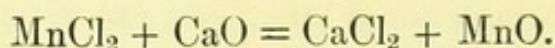


I will not occupy your time with any statement of those commercial advantages of this process, owing to which, of the 100,000 tons of bleaching-powder made annually in Great Britain, about 60,000 are now being made by it,—we have not yet actually made 60,000 tons in any one year, but I believe that the production by it has now attained that rate,—while plant for the greater portion of the remainder is now in course of construction; but for the information of any one who may be interested in that matter I have hung on the wall a tabular statement setting side by side the various items of the cost of a ton of bleaching-powder made by this process and the corresponding items of cost of a ton of bleaching-powder made by means of native manganese. Those of its advantages which to myself individually afford the greatest satisfaction are: firstly, that it enables the manufacture of chlorine to be carried on entirely without offence to the neighbourhood, its only residual product,—this perfectly clear, perfectly neutral, and indeed chemically pure, solution of calcic chloride,—being one which is entirely innocuous, and which, to quote one of the Reports of the Rivers' Pollution Commission, “can be sent into the rivers with no other effect than that of rendering the water a little harder;” secondly, that it does away to a very great extent with an operation which to the workmen employed in it was of a most offensive kind, that of charging and cleaning out native manganese stills; thirdly, that if it does not effect the proverbial benefit of making two blades of grass to grow where only one blade grew before, it at least enables four tons of bleaching-powder to be made from the quantity of acid formerly employed on an average for three; and, lastly, if I may be allowed to put the matter in the way in which the utilization of previously waste substances always presents itself to my mind, by turning to continual account a valuable substance which was formerly used only once and then thrown away, it adds another to the instances, which of

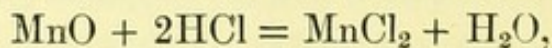


late years have begun to be so numerous, of industrial obedience to the Divine injunction: "Gather ye up the fragments, that nothing be lost."

I should much like to explain to you what takes place in the fundamental operation of this process, that which is performed in the oxidizer, because it results in the formation of compounds which were not known until they were produced in this process; but as I have already occupied you so long, the explanation must be a very brief one. We saw some time ago that when manganic peroxide, or  $\text{MnO}_2$ , is employed to liberate chlorine from  $\text{HCl}$ , the manganese of the manganic peroxide passes into the state of manganous chloride, or  $\text{MnCl}_2$ . By treating this manganous chloride with lime, we instantly transform it into manganous oxide, or  $\text{MnO}$ , in accordance with the equation:



This  $\text{MnO}$ , however, cannot liberate chlorine from hydrochloric acid; its reaction with  $\text{HCl}$ ,



simply reproducing manganous chloride, and producing water. A glance at one of the diagrams to which I have already drawn your attention will show that that part of the oxygen in  $\text{MnO}_2$  which liberates chlorine from hydrochloric acid is in fact only the portion which it contains in excess of the quantity contained in  $\text{MnO}$ . Therefore, to get into the state in which it can be used again in the manufacture of chlorine the manganese which was originally in the state of  $\text{MnO}_2$ , but which has been converted in the chlorine stills into  $\text{MnCl}_2$ , and then, by treatment of this compound with lime, has been made to pass into the state of  $\text{MnO}$ , we have to make this  $\text{MnO}$  absorb more oxygen. And for the process by which we do this to be practically available, it must be one which secures the absorption of a very large quantity of oxygen in a very little time.



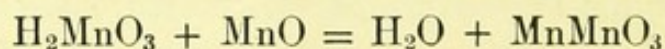
Now, it is well known that hydrated  $\text{MnO}$ , such as you produce by adding lime to a solution of manganous chloride, absorbs oxygen, on exposure to the air, apparently with extreme readiness. On this filter, just before the commencement of the lecture, I placed some pure white hydrated  $\text{MnO}$ , and you see that on the surface it has already become of a deep brown colour, by absorption of oxygen from the atmosphere of this room. The action, however, has been confined to the thinnest possible film on the surface, and if I cut into it with a knife you will see that all below the immediate surface remains perfectly white. Nevertheless, the rapidity of the action on the surface would seem to suggest that if the oxide on the filter were suspended in water, and a current of air were passed through the resulting mixture, the conversion of all the  $\text{MnO}$  into the compound we have here on the surface would take place extremely rapidly. The actual fact, however, is altogether otherwise. This conversion takes place only extremely slowly, its completion requiring not less than several days at the rate of blowing at which, in the process I have described to you, the corresponding operation can be completed in one hour.

Moreover, the compound which has been formed on the surface of the  $\text{MnO}$  is not  $\text{MnO}_2$ , or manganic peroxide; it is simply manganic oxide, or  $\text{Mn}_2\text{O}_3$ . Instead of containing, as  $\text{MnO}_2$  does, twice the quantity of oxygen contained in  $\text{MnO}$ , it contains only one-and-a-half times that quantity of oxygen; and the remarkable thing is that if hydrated  $\text{MnO}$  be exposed to air, in however intimate a manner, and for whatever length of time, it never, even in the course of years, absorbs more oxygen than just half the quantity necessary to raise it from the state of  $\text{MnO}$  to that of  $\text{MnO}_2$ , the ultimate result being just the same as though one half of the  $\text{MnO}$  were converted into  $\text{MnO}_2$  and the other half remained as  $\text{MnO}$ .

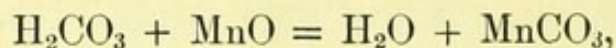
I have no doubt whatever that this is what actually



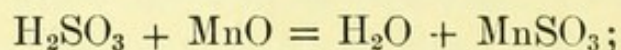
happens, and that the  $\text{Mn}_2\text{O}_3$  into which  $\text{MnO}$  is slowly converted by long exposure to the air is really a compound of  $\text{MnO}$  with  $\text{MnO}_2$ , exactly as manganous carbonate is a compound of  $\text{MnO}$  with  $\text{CO}_2$ , and manganous sulphite of  $\text{MnO}$  with  $\text{SO}_2$ . There seems no doubt that hydrated  $\text{MnO}_2$ , or  $\text{H}_2\text{MnO}_3$ , must be regarded as manganous acid, and that it reacts upon  $\text{MnO}$  in a manner exactly similar to that of the reaction upon  $\text{MnO}$  of carbonic and sulphurous acids. The reaction



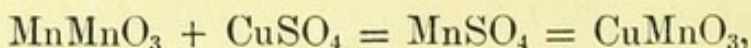
can be effected just as readily as the reaction



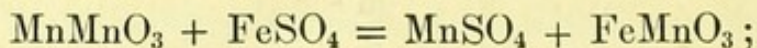
or the reaction



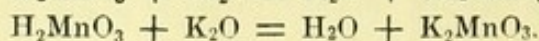
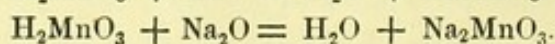
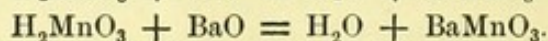
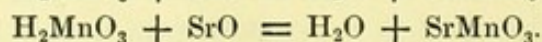
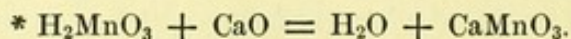
and you see that all three reactions are represented by precisely similar equations. And that the product of this reaction is really a salt, and not merely an oxide, is proved by its reacting with other salts according to the manner in which salts ordinarily react on each other, as in the examples—



and



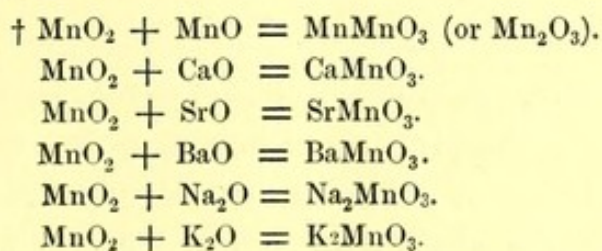
and moreover by the fact that hydrated  $\text{MnO}_2$  reacts on other protoxides in a precisely similar way, giving products which are unquestionably salts. It does this in especial with all the alkalies and alkaline earths, in accordance with the equations \* which you see written on our diagram, the





products all being  $\text{Mn}_2\text{O}_3$ , regarded as  $\text{MnMnO}_3$ , with its first Mn replaced by another metal. On another† diagram I have represented these compounds as produced by the direct union of  $\text{MnO}_2$  with lime, strontia, baryta, soda, and potash respectively. It is on the existence of these and other compounds of  $\text{MnO}_2$  with the alkalies and alkaline earths, and especially on that of compounds of  $\text{MnO}_2$  with  $\text{CaO}$ , and on the fact that these compounds can be produced with much greater facility than the corresponding compounds of  $\text{MnO}_2$  with  $\text{MnO}$ , that the process which I have described to you entirely depends.

I will now call your attention to what has taken place in the three jars into which, as long as we could endure the noise of it, we sent a current of air. At the commencement of the experiment, all the jars contained solution of manganous chloride. To the contents of the jar at this end I added a quantity of lime in excess of the quantity required to decompose the manganous chloride in it; to the contents of the jar at the further end I added a quantity of caustic soda in excess of the quantity required to decompose the manganous chloride in it; but to the contents of the middle jar I added a quantity of milk of lime insufficient to completely decompose the manganous chloride in it. The colour of the contents of the jars is an index to the quantities of oxygen absorbed by them respectively; and you see that those of the jar in which at the commencement of the blowing we had manganous oxide in presence of free soda are darkest in colour; that those of the jar in which we had manganous oxide in presence of free lime are nearly as dark, but not quite; and





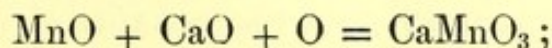
that those of the middle jar, in which we had manganous oxide only, are darkened in a very much less degree. If we were to continue blowing into these jars until their contents would absorb no more oxygen, we should find at the end of the experiment that the whole of the manganous oxide originally contained in the furthest jar was converted into  $\text{MnO}_2$ , this  $\text{MnO}_2$  being combined with soda; that the whole of the manganous oxide originally contained in the nearest jar was converted into  $\text{MnO}_2$ , this  $\text{MnO}_2$  being combined with lime; but that of the manganous oxide originally contained in the middle jar only half was converted into  $\text{MnO}_2$ , the half thus converted into  $\text{MnO}_2$  being combined with the half remaining as  $\text{MnO}$ . At the rate at which we injected air in carrying the experiment as far as we have done, the whole of the manganous oxide in the furthest jar would be converted into  $\text{MnO}_2$  in about an hour, and the whole of that in the nearest jar in about an hour and a half; while the conversion into  $\text{MnO}_2$  of only half the manganous oxide originally contained in the middle jar would require between two and three days.

The fact seems to be that the production of  $\text{MnO}_2$  by direct absorption of atmospheric oxygen by hydrated  $\text{MnO}$  absolutely requires the presence of some base with which the  $\text{MnO}_2$  can combine as it forms. If the  $\text{MnO}$  has no other basic body in contact with it, a part of the  $\text{MnO}$  itself has to act as the required base, and only the other part of it can become peroxidized; but if any more powerfully basic body be present also, the  $\text{MnO}_2$ , as it is formed, combines with *that*, instead of with  $\text{MnO}$ , and so the whole of the  $\text{MnO}$  can become peroxidized. The more intimate the contact between the  $\text{MnO}$  which is to be converted into  $\text{MnO}_2$  and the body with which the  $\text{MnO}_2$  is to combine, the more rapid the absorption of oxygen by the  $\text{MnO}$ ; and hence, owing to the extremely slight solubility of  $\text{MnO}$  in neutral menstrua, the extreme slowness of the absorption of oxygen when  $\text{MnO}$  alone is

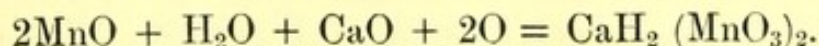


operated upon. Hence, also, owing to caustic soda being so much more soluble in water than lime is in cold solution of calcic chloride, the more rapid blackening of the contents of the jar in which we had free soda than of the contents of the jar in which we had free lime. When, however, as in working on the large scale, the solution of calcic chloride containing the MnO and free lime is at a temperature not below 140°F., owing to lime being so much more soluble in solution of calcic chloride hot than cold the operation goes on quite as rapidly as if soda were used. We are thus enabled to absorb and solidify, in practical operations, as much as two hundred weight of oxygen per hour.

One fact more, and I can pass from this process. When I first attempted to press this process upon the attention of the manufacturers, I was always met by the objection that as yet I had only performed it in the laboratory, and that many things are possible in the laboratory which on the large scale are utterly impracticable. No doubt that is so; but in this process we have an instance of results being readily obtainable on the large scale which cannot be obtained in the laboratory at all. I have never obtained in the laboratory, by this process, and for some time we never obtained in manufacturing operations, a product containing less than a full equivalent of basic oxide per equivalent of MnO<sub>2</sub> in it, being the product obtained, as represented on the upper part of our final diagram, according to the equation—

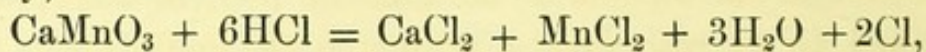


but each time that the scale of our operations has been increased, the chemical quality of our product has improved, until we are now enabled to make regularly a product containing only one equivalent of base per two equivalents of MnO<sub>2</sub> in it, as represented on the lower part of the diagram:

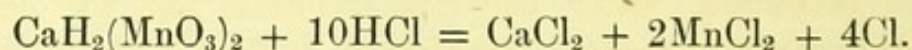




The first product may be compared with calcic carbonate,  $\text{CaCO}_3$ , and the second with hydrocalcic carbonate,  $\text{CaH}_2(\text{CO}_3)_2$ . The one is a normal manganite, and the other an acid manganite. The greater value of the latter than of the former is due, firstly, to its requiring less lime to produce it, and, secondly, to its liberating more chlorine from a given quantity of hydrochloric acid. The first yields an equivalent of chlorine per three equivalents of hydrochloric acid, and the second an equivalent of chlorine per two-and-a-half equivalents of hydrochloric acid; the reactions being, respectively,—



and



The conditions which determine the formation of this acid manganite are still somewhat obscure, and we have not time to discuss them; but I could not help suggesting to any chemical inventor here to whose proposals manufacturers may be raising the objection to which I have referred, the answer that there is at least one case of a new process in which the results regularly obtained in manufacturing operations are far superior to the very best that have yet been obtained with it in the laboratory.

I will now ask Mr. Bunker to take the lime out of our little bleaching powder chamber on the table below, and to mix it with water, so that we may be able to see if it has absorbed any chlorine. While he is doing that, I will say a word upon a process for the manufacture of chlorine which the title of my lecture obliges me to mention, but which, for reasons which will be obvious, apart from that of my having already detained you so long, I shall touch upon only very briefly. I refer, of course, to the process which we know as Mr. Deacon's, and in connexion with which we ought not to forget the name of Dr. Ferdinand Hurter. In the year 1845, Mr. Robert Oxland, of Plymouth, patented the

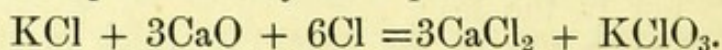


manufacture of chlorine by passing a mixture of hydrochloric acid gas and air through chambers filled with pieces of pumice-stone kept at a red heat. Mr. Deacon's process substitutes for the fragments of pumice-stone either fragments of fire-brick, or, preferably, clay marbles steeped in solution of cupric sulphate, and then dried. A sample of the marbles which Mr. Deacon has latterly employed is in one of the bowls on the table below. Mr. Deacon originally supposed that the cupric sulphate on his fragments of fire-brick acted only catalytically, its mere presence causing a portion of the oxygen in the mixture of hydrochloric acid gas and air to react upon a portion of the hydrochloric acid in it, producing water and free chlorine, and the cupric sulphate itself remaining unchanged. That I should offer you any statement of how far this theory has been justified by the practical trials which have been made of the process, or of what have been otherwise the results of these trials, would be obviously improper. I will only say of the process that I am not in the least surprised at the great attention which it excited, nor at the extent to which most chemists fell in love with it forthwith, for a simpler process, theoretically, for obtaining chlorine from hydrochloric acid, is of course impossible, seeing that it involves only one chemical reaction; while a more brilliant method of effecting that reaction has certainly never yet been suggested, and, indeed, probably never can be. For a considerable time I was obliged to anticipate, a little,—or, rather, not a little—sadly, that it would render of no avail the results of the years of incessant labour, accompanied by the expenditure of large sums of other people's money, which I had devoted to the realization of my own process; but what has actually happened is that Mr. Deacon's own firm have all along made the greater portion of their bleaching-powder by my process; and that there is now scarcely a manufacturer of chlorine in Great Britain, making



any appreciable quantity of chlorine, who is not, either actually making it by my process, or building plant to enable him to do so.

I must not occupy you further except just to say that the greater portion of the chlorine manufactured is sold as bleaching-powder, which is made by simply sending the chlorine gas into great chambers, sometimes constructed of lead, sometimes of stone, and sometimes of cast-iron plates, upon the floor of which is spread a layer of slaked lime, from three inches to five or six inches thick. This lime remains in the chamber until the product contains from 35 per cent. to 38 per cent. of chlorine, which is at the end of from three days to a week, according to the thickness of the layer of lime, and other circumstances. About a tenth, however, of the total chlorine manufactured is not sold as such at all, but is employed in the manufacture of potassic chlorate, in which its function is simply to transfer oxygen from lime, employed as milk, to potassic chloride, in the manner represented by the equation :



The lime which we have exposed to the action of chlorine in the glass trough on the table below will hardly have absorbed as much chlorine as is contained in commercial bleaching-powder, which takes, as I have said, from three days to a week to make ; but that it will at least have absorbed some chlorine I think I shall be able to show you. Mr. Bunker has mixed it with water in this beaker, and he has also mixed with water in this other beaker a portion of the lime as it was before it was exposed to the action of the chlorine. If I pour the latter mixture into a solution of manganous chloride, there is produced, as I have shown you before, a white precipitate of hydrated manganous oxide ; but if I pour the other mixture into a similar solution we obtain, as you see, a dark brown precipitate, which consists essentially of manganic peroxide, formed by the reaction on the



manganous chloride of the hypochlorite produced by the action of the chlorine on the lime.

We have now shown you, however imperfectly, all the operations involved in the commercial production of chlorine: the decomposition of salt by sulphuric acid, the decomposition of the resulting hydrochloric acid by manganic peroxide, the regeneration of manganic peroxide from the resulting manganous chloride, and the absorption of chlorine by lime. Here, then, I ought to cease to detain you; but if I might ask you to allow me just one minute more, I should like, with your permission, to conclude with a plea, founded on the existence, as a realized manufacturing operation, of the process with which I have occupied so much of your time, in favour of the policy of a Patent Law. I want to illustrate by it the proposition that, in many cases,—I believe in most cases,—without patents, inventions would be impossible. My illustration consists simply in the fact that the realization of the process which has been the main subject of my lecture has required, not only years of incessant work, but a very large money expenditure, as utterly beyond my personal means as the payment of the National Debt; and that its existence as anything beyond a mere crude idea is therefore entirely owing to the operation of the Patent Laws. Those persons who propose that the patent system should be abolished and a system of State rewards to inventors substituted in its stead, certainly suggest that the inventor should be paid when he has done his work; but they propose no means of enabling him to do his work, and that, I take it, is the matter of most moment. It is not important, except to themselves personally, that inventors should make money, but it is important to the community that they should make inventions; and those who fancy that there would be as many inventions without patents as with them, fail to recognise that an industrial invention, instead of being a mere idea, demanding for its realization nothing more than the effort



which a poet expends in embodying his conceptions in verse, is a result which is usually only attainable by the expenditure upon an idea, or upon a set of ideas, not only of immense labour, but also of an amount of money frequently equal to the value of a very large real estate. Inventors are usually poor men, and I am not concerned that they should be enabled to clothe themselves in fine raiment and fare sumptuously every day; but it is surely of the utmost importance that there should continue to exist some means of enabling them to do their special work; and it is obvious that nothing which has as yet been proposed instead of it could be so effective to that end as the system which gives to the inventor a temporary property in his ideas, and thus enables him to tempt the capitalist to supply him with the means of endeavouring to carry them into practice. If the endeavour is successful, the capitalist of course takes the lion's share of that portion of the profits which ought to constitute the inventor's reward; but he at least enables the result to be achieved, and that is the main thing. In the case of a process like my own, too, even if it had been invented by a rich manufacturer, he would not have worked it out if he could not have patented it; because by so doing he would simply have placed himself at a disadvantage as compared with his competitors in the trade, all of whom would have shared with him the advantages of his invention,—seeing that he could not possibly have kept it secret,—while the cost of its realization would have had to be borne by himself alone. This illustration of the influence of the patent system in promoting industrial invention seemed to arise so naturally out of the subject of this lecture that I could not forbear submitting it to you; and I have now only to apologize for having occupied you so long, and to express my regret that I have not been able to make my subject more interesting to you.







