

II. *On Bleaching Salts.* By M. DETMER, Esq.

Read April 27, 1841.

A SHORT time ago a notice was published by M. Millon on the Bleaching Salts of Chlorine, in which a new view was offered of the constitution of these compounds. They have for some time past generally been considered as compounds or mixtures of a metallic chloride with a hypochlorite of a metallic oxide; bleaching powder or the chloride of lime, for instance, as consisting of chloride of calcium and hypochlorite of lime, in single equivalents, the acid of the last salt containing one atom of oxygen to one atom of chlorine. The reaction of chlorine upon lime supposed, may be very simply stated: two atoms of lime take up two of chlorine; one atom

* *Ann. de Chim. et de Phys.*, t. lxiii. 118.† *Ibid.*, t. lxvi. 172.

only of the lime is decomposed, of which the calcium and oxygen respectively unite with an atom each of chlorine, forming chloride of calcium and hypochlorous acid. The hypochlorous acid combines with the other atom of lime.

Starting from the composition of chlorochromic and chlorosulphuric acids, which are represented by Walter and Regnault as chromic and sulphuric acids in which the third proportion of oxygen is replaced by chlorine ($\text{Cr O}_2 + \text{Cl}$ and $\text{S O}_2 + \text{Cl}$), Millon supposes that the bleaching chlorides have a similar relation to the peroxides of their metals. The peroxide of calcium being Ca O_2 , or $\text{Ca O} + \text{O}$, bleaching powder is $\text{Ca O} + \text{Cl}$, or the peroxide of calcium, with chlorine substituted for its second proportion of oxygen. In support of this view Millon adduces observations of his own on the composition of the bleaching compounds of chlorine with different metallic oxides, such as oxides of lead and protoxide of iron, as well as potash, soda and lime, in which the proportion of chlorine was found to vary, but to correspond with the excess of oxygen above one equivalent in the peroxides of the same metals. In particular, potash was found to absorb two equivalents of chlorine, and soda only one, the peroxide of potassium being $\text{K O} + 2 \text{O}$, while the peroxide of sodium is $\text{Na O} + \text{O}$.

The attention of the author was particularly directed to ascertain the accuracy of the latter statement. A solution of carbonate of soda was charged with chlorine gas till it acquired a yellow colour and retained not a trace of carbonic acid. The solution was then briskly agitated with air, by which the excess of free chlorine escaped. In analyzing the solution afterwards, one portion of it was treated with a few drops of ammonia, and the chlorine afterwards precipitated by nitrate of silver; another portion was evaporated to dryness for the sodium, which was obtained in the state of chloride of sodium.

In four experiments the liquids charged with chlorine contained chlorine and sodium in the following proportions, in 100 parts : —

Sodium..... 47·88 45·26 46·81 44·76

Chlorine... 52·12 54·74 53·19 55·24,

while, if the bleaching chloride of soda contained 1 eq. of chlorine to 1 eq. of soda, its composition would be

1 eq. sodium..... 46·91

1 eq. chlorine. 53·09

—————100·00

The results correspond as closely as could be expected with this theoretical statement. There can be no doubt then that the chloride of soda contains one of chlorine to one of

soda. This is the result required by Millon's theory, the peroxide of sodium containing, according to him, one of oxygen and one of soda; but it is equally consistent with Balard's theory that the salt is a mixture of single equivalents of chloride of sodium and hypochlorite of soda. To determine the quantity of chlorine which water dissolves, a stream of the gas was sent through water at 59° for five hours. One hundred grammes of water were found to take up 0.663 gramme of chlorine; or 200 cubic inches of water dissolved 207 cubic inches of gas. The chlorine was estimated by converting it into hydrochloric acid by the addition of a few drops of ammonia, slightly acidulating afterwards by nitric acid, and precipitating by nitrate of silver. A solution of 2.58 chloride of potassium in 38.96 water was found to dissolve less chlorine than pure water, in the proportion of 180 to 257. Chlorine gas being allowed to stream through a solution of 9.245 grammes carbonate of potash in 96.495 grammes of water, till saturation, the solution lost all its carbonic acid and took up 6.631 grammes of chlorine. Here 1 eq. of potash = 590 has taken up 656 chlorine, which is very nearly $1\frac{1}{2}$ eq. of chlorine = 663. But when the quantity of free chlorine in the liquid is deducted, the latter is found to contain only 1.34 equivalents of chlorine to 1 eq. of potash. In two other experiments, in which the liquid was agitated with air after being saturated with chlorine, to allow the excess of gas to escape, there were found to 1 eq. of potash 1.44 and 1.43 equivalents of chlorine. The carbonate of potash, therefore, without doubt, takes up more than a single equivalent of chlorine. But the quantity of chlorine combined with the potash is still greatly short of two equivalents, the proportion required by M. Millon's theory; the peroxide of potassium containing two oxygen to one potash, or K_2O_2 . The conclusion therefore is inadmissible, that the chloride of potash is analogous in constitution to the peroxide of potassium.

It remains to account for the property which potash is found to possess of taking up more chlorine than is necessary to convert it into chloride of potassium and hypochlorite of potash. On transmitting chlorine through carbonate of potash, a stage in the absorption is very observable, at which the liquid becomes all at once of a yellow colour. This happens when what remains of the potash is entirely converted into bicarbonate of potash. The suddenness of the appearance of the yellow colour appears to be due to a reaction of the carbonic acid upon the hypochlorite of potash in solution, by which hypochlorous acid is set free and tinges the liquid. By the continued application of chlorine to the bicarbonate of

potash, it is converted into a mixture of chloride of potassium, hypochlorite of potash, and free hypochlorous acid. By the ultimate action of the chlorine all the bicarbonate of potash is decomposed, the carbonic acid entirely expelled, and a portion of hypochlorous acid remains free in solution.

This formation of free hypochlorous acid does not occur with carbonate of soda, owing to the much weaker affinity which that base has for carbonic acid, and its forming a much less stable bicarbonate than potash does. The free carbonic acid cannot therefore react upon the hypochlorite of soda, and liberate hypochlorous acid as the free carbonic acid does upon the hypochlorite of potash. The same formation of free hypochlorous acid occurs in a more striking degree when chlorine is sent through a solution of acetate of potash; that solution, it is well known, absorbs a large quantity of gas, and acquires the strong yellow colour, the odour, and all the other properties of free hypochlorous acid. It is here evident, that by the action of chlorine upon acetate of potash, chloride of potassium is formed, with the binacetate of potash, free hypochlorous acid, and the hypochlorite of potash. If the large absorption of chlorine by carbonate of potash is due to carbonic acid, it follows that caustic potash should not absorb any excess of chlorine, but that the property should be confined to the carbonate. Accordingly, in two experiments, the proportion of chlorine absorbed by caustic potash was found to be as nearly as possible a single equivalent. In one experiment 449.1 chlorine, in the other 424.8 chlorine were taken up, instead of 442.6 chlorine, by a single equivalent or 589.9 of potash. Caustic potash, therefore, dissolves no more chlorine than caustic soda. There appears therefore to be no reason to abandon the old theory, that the bleaching solutions of chlorine in alkalies and alkaline earths contain a chloride and hypochlorite, for these bleaching compounds certainly do not correspond with metallic peroxides, as has been lately maintained.
