



XXX. Observations on ozone as compared to chlorine

Professor Schœnbein

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me in the life of Mr. Watt in the Edinburgh Encyclopædia, and upon that statement I made the following observations:—

“We have copied the preceding statement as that of Mr. Watt’s friends, but a regard for the reputation of Mr. Cavendish, independent of higher motives, compels us to acknowledge that the statement is partial, and the argument not well-founded. We are not able, at present, to refer to the original documents, but we had occasion, some years ago, along with a distinguished chemist (Dr. Hope), to examine them with minute attention; and it was then our decided conviction, *that the merit of the discovery of the composition of water belonged to Mr. Cavendish.*”—Edin. Encycl., vol. xviii. p. 786.

These observations will, I trust, convince every candid reader that the reviewer’s charges against me are utterly groundless. Although Mr. Watt was my countryman, and my personal friend and correspondent; although I cherished for him the warmest affection, and admired him as one of the greatest and best men of his age, I have at three different times of my life come to the decision that he was not, and that Cavendish was the discoverer of the composition of water. Had I been disposed to sacrifice truth, under the influence of national and personal feelings, I might have found a safe shelter behind the broad shield of M. Arago and Lord Brougham’s authority, and would thus have avoided the annoyance of rebutting the calumnies of the British Quarterly reviewer.

I am, my dear Sir,

Ever most faithfully yours,

St. Leonard’s College, St. Andrews,
August 8, 1845.

D. BREWSTER.

XXX. *Observations on Ozone as compared to Chlorine.*

By Professor SCHœNBEIN of Basle.

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN,

MANY properties, and the most essential ones belonging to ozone, are so similar to those possessed by chlorine, that I was led to suspect ozone to be a simple halogenous body like chlorine*. My more recent researches having rendered it highly probable, if not altogether certain, that ozone is a peculiar compound of hydrogen and oxygen, I can no longer maintain my former view, and we must place ozone far away from chlorine, in case we regard, according to the established

* The nature and properties of ozone have been described in vol. xvii. p. 293, vol. xx. p. 64, and vol. xxiv. p. 466 of the present series.—ED.

theory of the day, the latter body as an elementary one. The elementary nature of chlorine having, however, by no means been proved by any decisive fact, and it being well known that all the reactions produced by that body can be accounted for by the theory of Berthollet, just as well as by the hypothesis set up by your illustrious countryman, it seems to me that the existence of ozone ought to induce chemists to reconsider the two once-rival theories, and make them the subject of a very close examination.

It was chiefly from reasons of theoretical simplicity and analogies, that chemists were determined to give up the old theory and adopt the new one, cyanogen forming with mercury a compound similar to that produced by chlorine with the same metal; cyanogen constituting with oxygen and hydrogen two acids bearing some analogy to the chloric and hydrochloric acids, the readily oxidable carbon remaining, even at the highest temperature, inactive towards chlorine, the muriatic acid of Berthollet having never been isolated, and the views of Davy offering a very great facility in explaining the reactions of chlorine; these were the reasons which induced chemists to abandon the old theory and admit the present one. In doing so they sacrificed a sum of analogies much larger than that on account of which the new hypothesis was adopted. The numerous class of muriatic salts that bear so close an analogy to what we call oxy-salts, could no longer be paralleled to the latter; nay, on account of the striking resemblance existing between those two classes of salts, chemists saw themselves, as it were, forced to change the views they had formerly taken of the oxy-salts and oxy-acids, and imagine a great number of compound halogenous bodies being, as to their chemical character, similar to chlorine and cyanogen. But up to this present moment not one of those imagined halogenous bodies has yet been produced in an isolated state, any more than the anhydrous muriatic acid of Berthollet. It appears, therefore, that there are at least as many arbitrary and hypothetical notions mixed up with the modern views as there were in the old theory, and that in this respect Davy's idea does not offer peculiar advantages over that of Berthollet.

Before entering into an appreciation of both rival theories, I shall take the liberty to point out once more the very great similarity existing between the properties of ozone and chlorine.

1. Though we are not yet acquainted with ozone in its pure condition, we nevertheless know that at the common temperature it exists in a gaseous state like chlorine.

2. Ozone when concentrated has an odour very similar to that of chlorine, bromine and iodine.

3. Ozone, like the three last-named bodies, enjoys the power of negatively polarizing gold and platinum.

4. Ozone, like chlorine, is absorbed at the common temperature by most metallic substances.

5. Ozone, like chlorine, is readily taken up by phosphorus at the common temperature, causing at the same time a disengagement of light and some heat.

6. Ozone, like chlorine, is absorbed by iodine.

7. Ozone, like chlorine, very easily unites with olefiant gas, producing a compound which seems to be analogous to the chloride of hydrocarbon.

8. Ozone, like chlorine, has the power of decomposing sulphuretted hydrogen, and other compounds of hydrogen similarly constituted.

9. Ozone, like chlorine, transforms sulphurous acid into sulphuric acid.

10. Ozone, like chlorine, decomposes the iodide of potassium and the ferro-cyanuret of the same metal.

11. Ozone, like chlorine, being placed in contact with the protoxides of a number of metals, converts them into the corresponding peroxides. The protoxides of lead, manganese and nickel, for instance, are transformed into the peroxides both by ozone and chlorine.

12. Ozone, like chlorine, discharges the colour of many sulphurets, for instance, that of the sulphurets of lead and antimony.

13. Ozone, like chlorine, destroys completely, and with great energy, all the vegetable colouring matters.

14. Ozone, like chlorine, is readily taken up by a variety of other organic substances, for instance, by the ligneous ones, albumen, fibrine, caseous matter, &c.

15. Ozone, to finish the comparison, being inhaled, causes catarrhal affections, very similar to those produced by chlorine.

Now, as there can be hardly any doubt that the reactions just mentioned are due to part of the oxygen contained in ozone, and as there is not one single fact known which is irreconcilable to Berthollet's theory, we must think it at least possible that the chemical effects produced by chlorine may also depend upon the oxygen supposed to be contained in oxy-muriatic acid.

In a theoretical point of view it is a most important, and, I may add, by far too little an appreciated fact, that free or isolated oxygen happens to be much less apt to unite with oxidable substances than oxygen in a certain state of combination. In proof of the correctness of my assertion, I need only call

to mind certain acids and peroxides. Half the oxygen contained in chromic acid exhibits such a high degree of chemical excitement, that at the common temperature it sets on fire, not only æther and alcohol, but also ligneous substances, as paper and wood; whilst under the same circumstances, free oxygen does not act at all, or at any rate very slowly upon the above substances. Nitric acid offers a similar instance; and the peroxides of lead and manganese being put in contact with a solution of indigo, destroy, like chlorine, that colouring matter; and the same peroxides, when brought into the presence of a solution of iodide of potassium, eliminate iodine. But the most striking instance of the exalted oxidifying power of latent oxygen we have in ozone itself. The affinities of free oxygen are generally called forth by the agency of heat, so that at the common temperature even potassium is not acted upon by oxygen, if the latter happens to be completely anhydrous.

Starting from the hypothesis of Berthollet, according to which chlorine is composed of muriatic acid and oxygen, we can easily conceive why chlorine at the common temperature acts upon so great a number of oxidable substances. The oxygen being latent in chlorine, is in a state of great chemical excitement, similar to that in which the same element exists in ozone, chromic acid, nitric acid, the metallic peroxides, &c.; and in which state oxygen is so very apt to unite, even at the common temperature, with most of the oxidable matters. If these substances happen to be of such a kind as to combine readily in their oxidized condition with the muriatic acid of the older chemists, which is the case with hydrogen, phosphorus, sulphur, and the greater part of the metals, that circumstance must prove an additional reason why, in most instances, oxymuriatic acid acts at the common temperature upon those bodies. There are two facts that have, as already observed, much contributed to set aside Berthollet's views, and gain to oxymuriatic acid the reputation of being a simple body. Those facts are, the chemical inactivity exhibited by chlorine towards carbon, and the discovery of cyanogen. As to the difficulty arising out of the first fact, it is easily removed by admitting that anhydrous muriatic acid unites only in one proportion with carbonic acid to form what Davy called phosgene gas, and that there does not exist a compound consisting of muriatic acid and carbonic oxide. These suppositions, taken together with Berthollet's view, according to which muriatic acid cannot be obtained in an isolated state, satisfactorily account for the inactivity alluded to. Giving anhydrous muriatic acid the sign \overline{M} , we must consider

chlorine as $\overline{M} + O$. Now C with $\overline{M} + O$ might possibly produce $CO + \overline{M}$, but no such compound existing, according to our supposition, chlorine does not act upon carbon. C with $2\overline{M} + O$ could form $CO_2 + 2\overline{M}$, but no such compound likewise existing, only $CO_2 + \overline{M}$ could be produced; but we easily see that in such a case \overline{M} would consequently be set at liberty, that \overline{M} , however, not being able to exist in an isolated state, chlorine must prove chemically inactive towards carbon.

As to cyanogen, it certainly cannot be denied, that with regard to some of its chemical bearings, that compound exhibits a close analogy to chlorine; and we can easily conceive how such a fact could induce Berzelius to adopt the new doctrine, after having so ably, and with so much tenacity, defended the old theory.

But in paralleling cyanogen to chlorine, chemists were forced to admit, that in some cases a compound body is capable of acting the part of an elementary substance; and indeed a very extensive use has lately been made of such an admission to account for a great number of facts belonging to organic chemistry, though not one single organic element has been produced in an isolated state, for as far as I know, nobody has as yet seen either ethyle, formyle, benzyle, or any other yle*. In order to establish an analogy between cyanogen and chlorine, according to the principles of Berthollet's theory, we must admit that the former contains oxygen; but cyanogen yielding nothing but nitrogen and carbon, from whence shall we take oxygen? Starting from Berzelius's hypothesis, according to which nitrogen consists of one equivalent of an elementary substance called Nitricum and one equivalent of oxygen, we can conceive how cyanogen might be a compound similar to oxymuriatic acid. C_2N (by N we note the nitricum of Berzelius) is to be considered as a body analogous to \overline{M} , and as $\overline{M} + O = Cl$, so is $C_2N + O = Cy$. In combining cyanogen with potassium, the latter takes up the oxygen of the cyanogen, and C_2N combines with the oxide just in the same way as, agreeably to the old theory, the oxygen of the oxymuriatic acid unites with the metal, and the muriatic acid with the oxide. In decomposing cyanide of mercury, the oxygen of the oxide of that metal unites with C_2N to form $C_2N + O = Cy$. In exposing cyanogen to the action of intense heat, it is resolved into carbon and $N + O$ or nitrogen. I need not say, that on this hypothesis what is called anhydrous hydrocyanic acid must be considered as $C_2N + HO$, as, according to the old doctrine, anhydrous hydrochloric acid

* Prof. Schœnbein forgets that kakodyle has been isolated.—Ed.

must be taken for $\overline{M} + \text{HO}$. This view of the nature of cyanogen offers, in my opinion, the advantage of assigning a similar constitution to two bodies, being, as to their chemical bearings, so very like each other, whilst the established theory is forced, in spite of that similarity, to consider one of those bodies as an elementary substance, and the other as a compound consisting of principles which differ from chlorine as much as night from day.

If we compare the compounds which oxygen forms with elementary bodies with the compounds which chlorine produces with the same substances, we cannot but be struck by the similarity existing between both series as regards the ratio in which the equivalents of their constituent parts are united. If we except the bromides, iodides, and, to a certain extent, the sulphurets, there are, to my knowledge, no other sets of compounds that bear, with respect to the relation alluded to, so close an analogy to each other as the oxides and chlorides do. That similarity loses, however, its peculiar character so soon as we admit the correctness of the old views. According to them, it is, as it were, a matter of course that chlorine unites, for instance, with iron in the same definite proportions as oxygen combines with that metal; for Cl being $\overline{M} + \text{O}$, protochloride of iron is $= \overline{M} + \text{FeO}$, and the perchloride $3\overline{M} + \text{Fe}_2\text{O}_3$.

It is a very remarkable exception to that rule according to which no elementary substance forms a real chemical compound with water, that chlorine and bromine produce hydrates. If we take chlorine and bromine for compound substances, their capability of chemically uniting with water loses its exceptional character and comes under the general rule.

Admitting with Berthollet that chlorine is muriatic acid united to oxygen, and considering ozone as a compound analogous to chlorine, we are obliged to parallel water to muriatic acid, and admit that with regard to oxygen, water acts the same part as muriatic acid does. Water uniting so intimately with the stronger bases that these compounds cannot be decomposed by any degree of heat, and the same substance combining so readily with many other basic oxides, water may be considered as a sort of acid; and that view has very often been taken of the chemical nature of the compound mentioned. We may therefore be allowed to consider water as an acid and arrange it beside muriatic acid. As to ozone, it appears not unlikely that it is an isomeric modification of peroxide of hydrogen, *i. e.* composed of one equivalent of water and one equivalent of oxygen. Now chlorine being considered as a compound consisting of one equivalent of muriatic acid and one equivalent

of oxygen, it is very easy to parallel to each other the reactions exerted both by ozone and chlorine upon metallic substances. Let us take potassium for an instance: ozone is readily taken up by that metal, hydrate of potash being produced, as potassium is transformed by chlorine into a muriate of potash; in one case the metal unites with the oxygen of ozone, in the other with that of chlorine; and in one instance water unites with the base, and in the other muriatic acid. The latter being a strong acid completely neutralizes the basic properties of potash, whilst water, on account of its being a feeble acid, is not able to do so. In a similar manner all the other chemical reactions exhibited by ozone and chlorine, may very easily be compared to each other. The greater energy of action exhibited by chlorine is not very difficult to be accounted for. Muriatic acid has a very powerful affinity for metallic oxides, whilst that of water for the same substances happens to be much weaker.

A fact which merits attention is the formation of ozone and chlorine being effected by electrical means. If electrical sparks are caused to pass through a mixture of aqueous vapour and oxygen, ozone is generated; and on making electrical sparks act upon a mixture of anhydrous hydrochloric acid and oxygen, chlorine is produced. As to the generation of chlorine effected by electrical means, the old theory accounts for it by admitting that electricity has the power of determining free oxygen to combine with muriatic acid and eliminate water. Regarding the formation of ozone under the circumstances above mentioned, we cannot explain it in any other way than by saying, that electricity causes the direct union between water and oxygen. The similarity existing between the before-mentioned ways of producing ozone and chlorine is at any rate a very remarkable fact, establishing another analogy between both bodies.

My experiments have shown, that in electrolysing water ozone is disengaged at the positive electrode as a secondary product. Now by subjecting hydrochloric acid to the action of a current, chlorine happens to be set free at the same electrode. According to the old theory this chlorine must also be considered as a secondary product of electrolysis; and in this respect another striking analogy is exhibited between chlorine and ozone.

The question is, whether phosphorus acts upon a mixture of muriatic acid gas and oxygen in the same way as that substance does upon a mixture of aqueous vapour and oxygen. I have not yet tried the experiment, though it is worth while to do so.

The electro-chemical system, as established by Berzelius, places oxygen at the head of what are called the electro-negative elements, and puts chlorine in a positive relation to that body. It is however a well-known fact, that in a great number of cases, chlorine, with respect to its electro-negative activity, very much surpasses oxygen. Chlorine is capable of expelling oxygen from a great number of oxides; chlorine eliminates bromine and iodine from the bromides and iodides, whilst pure oxygen seems not to act upon those compounds. In spite of these exalted electro-negative powers possessed by chlorine, it is apt to produce with oxygen a series of acids in which chlorine is said to act the part of an electro-positive principle. I ask, how is it possible that in some cases chlorine proves to be a more electro-negative body, and in another instance a more positive one than oxygen? It seems to me that the facts alluded to are very little in accordance with the principles of the electro-chemical system; nay, that they imply a direct contradiction to them, provided chlorine be taken for a simple substance. But if we consider it as oxymuriatic acid, all the anomalies spoken of disappear, and we can easily account for the reactions produced by chlorine. The oxygen disengaged, for instance, during the reaction of chlorine upon potash, comes from the oxygenized muriatic acid, and not from the potash; and the decomposition of the former is effected by the strong affinity which potash has for muriatic acid. Those who maintain that there is some truth in the principles of the electro-chemical system, must, I think, be inclined to readopt the views of Berthollet, in order to save their endangered theory.

Before concluding, I shall take the liberty to add some general considerations regarding the subject I have treated of. By regarding chlorine as an elementary substance, one of the greatest theoretical changes that ever took place in the history of chemistry was effected. Indeed, by Davy's theory, oxygen lost, if I may say so, its royal dignity amongst the elements; and at any rate a very powerful rival was set up in chlorine. Oxygen was no more the body exclusively enjoying the privilege of being the generator of acids, the supporter of combustion, &c.; that privilege was also claimed for the upstart. But if there should be found good reasons for giving up Davy's hypothesis and readopting the old doctrine, we could hardly help restoring oxygen to its ancient dignities, and considering it again as an agent that has not its equal amongst the rest of the elementary bodies. To speak without metaphor, oxygen would become again one of the centres of chemistry, as it formerly was, and as most likely hydrogen

may be. Indeed both substances bear so much the stamp of simplicity, they exhibit so decided a chemical antagonism towards each other, both of them, conjointly with their remarkable product "water," act throughout the domain of our science so extensive and important a part, that we can hardly help suspecting them to be active in some way or other in most, if not in all chemical reactions, and seeing in oxygen and hydrogen the hinges upon which the whole chemical world turns. The theory of Davy, seducing and plausible as it appears at first sight, has possibly proved a check, rather than a spur, to the development of chemistry, on account of its having changed, perhaps, the true point of view from which oxygen ought to be looked at. For if oxygen should happen to act that all-important part which Lavoisier and the chemists of the last century assigned to that element, it is not difficult to see that the views of Davy are calculated to retard the progress of theoretical chemistry rather than to accelerate it.

I need not say, that the considerations I have taken the liberty to submit to you have been entered into with the view only of drawing the attention of philosophers towards a subject which seems to me to be of considerable theoretical importance, and worthy of our study.

C. F. SCHÖENBEIN.

XXXI. *On the Existence of an Equivalent Relation between Heat and the ordinary Forms of Mechanical Power.* By JAMES P. JOULE, Esq.

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN,

THE principal part of this letter was brought under the notice of the British Association at its last meeting at Cambridge. I have hitherto hesitated to give it further publication, not because I was in any degree doubtful of the conclusions at which I had arrived, but because I intended to make a slight alteration in the apparatus calculated to give still greater precision to the experiments. Being unable, however, just at present to spare the time necessary to fulfil this design, and being at the same time most anxious to convince the scientific world of the truth of the positions I have maintained, I hope you will do me the favour of publishing this letter in your excellent Magazine.

The apparatus exhibited before the Association consisted of a brass paddle-wheel working *horizontally* in a can of water. Motion could be communicated to this paddle by means of