II. *Supplementary Paper on certain Phenomena of Voltaic Ignition, and the Decomposition of Water into its Constituent Gases by Heat.* *By* W. R. Grove, *Esq.*

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In selecting the above title, I endeavoured to give as clear an enunciation of the phenomena to be described in the paper as was consistent with the brevity usual in a title.

An exception has, however, been taken to it, that as the effects of decomposition are produced by ignited platinum, the phenomena may result from that obscure mode of action called catalysis. That I did not intend to exclude from consideration any possible action of the substance employed, will be evident from the paper itself, in which I have called attention to the general production of catalytic effects by solid bodies.

Whatever value or novelty there may be in the facts I have communicated, is the same whether they be regarded as resulting from catalytic or from thermic actions. If the action be catalytic, it is one absolutely the reverse of that usually produced by platinum, and therefore just as much at variance with received experience as decomposition of water by heat would be; the effect of platinum, like that of heat, on the elements of water having been hitherto known only as combining them. With regard to any theoretic views I may have advanced, I by no means attach the same importance to them as I do to the facts themselves, though I consider it necessary for the collation of facts, and desirable for the progress of science, that an author pretending to communicate new results should give with them the impressions which led to their discovery, and the inferences which he regards as immediately deducible from them. No expression can be given to facts which does not involve some theory, and admitting the difficulty (perhaps insuperable) of correctly enunciating new phenomena, and the probability of future discoveries entirely changing our views regarding them, I cannot at present see that the title of my paper could be altered without being open to greater objections. I am of this opinion, not so much because other bodies than platinum will produce the effect, as I shall presently show, nor from the fact that the electrical spark will decompose aqueous vapour, though these are arguments in its favour; but from the following considerations. The catalytic action of platinum will induce or enable combination to take place where there is already a strong affinity or tendency to combine, as with mixed oxygen and hydrogen gases; it will also induce decomposition where the affinities are extremely weak, or in a state of unstable equilibrium, as in Thenard's peroxide of hydrogen; again, where there are nicely-balanced compound affinities, it may change the chemical arrangement of the constituents of a compound, but I do not know of any case in which a powerful chemical affinity can be overcome by catalytic action; to effect this we require some natural force of greater intensity than that to be overcome. We might as well say that the platinum electrodes of a voltaic battery decompose water, as to say that platinum decomposes it in the case in question; there, the force of electricity acts only by means of matter, and matter of a peculiar description; its action also is only perceptible at the surface of this matter. I seek to use the expression in my title with reference to heat in a similar sense to that in which we use similar terms with reference to electricity, *i. e.* to regard heat as the immediate dynamic force which overcomes the affinity; thus, as we say when employing the voltaic battery, that we decompose water by electricity, so here we should say that we decompose it by heat.

If it be said that heat so weakens or antagonizes the affinity of the elements of water as to enable catalytic action to separate them, this amounts to the same theory, as heat is then regarded as the antagonizing force, and in this case the action, both thermic and catalytic, is the reverse of the normal action. I have thought it desirable shortly to discuss this question as likely to lead to further investigation, though I have been somewhat embarrassed by the want of definite meaning in the term catalysis; I must plead guilty to have frequently used the term, but notwithstanding, or perhaps on account of, its convenience, it has I fear had an injurious effect on scientific perspicuity.

The following experiments were made to ascertain whether platinum was the only substance by which the effect could be produced. A knob or button of the native alloy of iridium and osmium of the size of a small pea was formed by the voltaic battery; to this was attached by fusion another smaller knob of the same metal one-fourth the size of the former, and to this smaller one was attached a stout platinum wire; the object of the second knob was both to prevent the fusion of the platinum wire and also to avoid the possibility of any surface of platinum being exposed to the recipient tube or alloyed with the metal to be heated. The preparation of this simple instrument was very troublesome, but when made it answered the purpose well; the larger button could be fully ignited to an intense glow, while on account of the narrow neck which united them, the smaller was barely red-hot, and the platinum wire not perceptibly ignited. An experiment having been made with this metallic button and prepared water, similar to that previously made with platinum, gas was given off which averaged 0·3 of mixed gas; the residue was nitrogen mixed with varying small quantities of oxygen. The effect, upon the whole, was decidedly inferior to that of the platinum. Indeed as platinum is the most dense and unalterable of all known substances, it would be likely, upon any received theory of heat, to produce the greatest effects.

I tried palladium in the same manner; the gas yielded was hydrogen with small quantities of oxygen, and the water was stained with the oxide o the metal.

I now tried silica and other oxides, but the results were not very satisfactory. A spheroid of silica was formed by fusing pulverized silica on to a platinum wire, so as to cover it for the length of 0·4 of an inch; when this was plunged into the hot water and again fused in the oxyhydrogen blowpipe, it constantly became frothed with small bubbles of vapour, and after a few experiments generally separated in fissures; in the experiment which was continued for the longest time without disintegration, the gas given off contained 0·15 of oxyhydrogen gas; from the whole result I believe there is an action of the water on the silica (probably forming a hydrate decomposable by heat) which is a bar to satisfactory results. With other oxides, at least such as would bear an intense heat, the difficulties were still more insuperable. PRIESTLEY has shown that water will corrode glass, and if I mistake not, others have shown the same effect produced on silica.

Although, as applied to the facts detailed, I attached no further meaning to the title of my paper than that which I have above stated, yet in one or two theoretical inferences I have certainly gone further; for instance, when I suppose the possibility or probability of mechanical rarefaction producing the same effects as heat, here (although I do not, indeed I cannot conceive the existence of heat without matter) I certainly abstract from the proposition any consideration of solid matter. In order to ascertain how far this view might be founded on truth, I had thought of making a few experiments on the effect of mechanical rarefaction on the tendency of gases to combine, but (in addition to the interference of necessary occupations) I find that M. DE GROTTHUS has already experimented on the point; his experiments, as far as they go, corroborate the views I have put forth.

He finds* that mixed gases, such as chlorine and hydrogen, or oxygen and hydrogen, when rarefied either by slow increments of heat or by the air-pump, do not take fire ("ne s'enflamment pas") by the electric spark. From the context, he evidently means that the gases will not detonate or unite in volumes, as he states that a partial combination ensues. GROTTHUS appears to have considered the combination of gases by the electric spark as an effect of sudden compression or molecular approximation, certain particles being brought within the range of their affinities by the sudden dilatation of others. Although he did not pursue the subject far enough to ascertain whether a degree of rarefaction could be reached which would be an actual bar to combination, still his experiments strengthen those views which assimilate mechanical and thermic molecular repulsion, and regard chemical affinity as being antagonized by physical repulsion.

Pursuing the series of analogies from the decomposition of euchlorine at a low temperature, that of ammonia at a higher, that of metallic oxides at a higher, and so on to oxide of hydrogen, there appears to be an extensive series of facts which afford strong hope of a generalized antagonism between thermic repulsion and chemical

* Annales de Chimie, vol. lxxxii.

affinity, and a consequent establishment of the law of continuity in reference to physical and chemical attraction.

The deposit from chlorine, to which I have alluded in my paper, I have since examined, and though it differs in colour from that described in books, I find it is a protochloride of platinum, formed at the expense of the platinum wire. The larger portion of the chlorine in the tube combines with the hydrogen of the aqueous vapour, and the muriatic acid is absorbed by the water; when the experiment terminates the gaseous volume is reduced to nearly one-half, and this residue is oxygen.

This effect induced me to try an ignited wire on other analogues of chlorine, and I tried bromine and chloride of iodine in the apparatus (fig. 5). The tube was filled with the liquid, and its extremity was in the first experiments immersed in another narrow tube of the same liquid as that which filled it. When the platinum wire was ignited, permanent gas was given off both from the bromine and from the chloride of iodine, which gas on examination proved, to my surprise, to be oxygen. In one experiment I collected half a cubic inch of gas from an equal volume of chloride of iodine. As the experiment in this form required too large a quantity of the liquid to enable me to observe any change which might take place in its character, I repeated it with a tube five feet long, bent in two angular curves. A small quantity of the liquid was placed in the extremity of the tube containing the wire, which was so arranged as to be the lowest point; the angles were placed in cold water and the experiment proceeded with; my object was to enable the dense vapour of the liquids to shelter them from the atmosphere, there being no satisfactory method of shutting them in and yet allowing room for the elimination of the liberated gas, or of absorbing the latter by combination without also absorbing the vapours.

I had hoped by the above means to proceed with the experiments until all the oxygen was liberated that could be driven off, and then to have examined the residua; but I found that after experimenting for a short time, both the platinum wire and the glass in proximity to it were attacked by the liquids; this difficulty, similar to those which have hitherto prevented the isolation of fluorine, I have not yet been able to conquer, though I hope to resume the experiments.

As chloride of iodine is decomposed by water, it cannot contain any notable quantity of the latter, but, until the experiments are carried further, it must remain a question whether the oxygen results from a small quantity of water contained in the liquid, the hydrogen combining with the liquid itself, or from a decomposition similar to that of the peroxides. The experiments certainly add a new and striking analogy to those already known to exist between the peroxides and the halogens, but they do not, as far as I have hitherto carried them, necessarily prove analogy of composition.

In conclusion, I would call attention to a point which I omitted to notice in my original paper, viz. the explanation afforded by the results contained in it of the hitherto mysterious phenomena of the non-polar decomposition of water by electrical discharges, as in the experiments of PEARSON and WOLLASTON. This class of decompositions may now be carried much further. With the exception of fused metals, I know of no liquid, which, when exposed to intense heat such as that given by the electric spark, the voltaic arc, or incandescent platinum, does not give off permanent gas; phosphorus, sulphur, acids, hydrocarbons, water, salts, bromine and chloride of iodine, all yield gaseous matter.

Viewing these effects simply as facts, and without entering on any theoretical explanations or speculations, I cannot but think that there is a remarkable generality pertaining to them worthy of the most careful attention.

The apparatus I have described, particularly that represented by fig. 5, and the numerous applications of voltaic ignition which will occur to those who duly consider the subject, promise, I venture to believe, new methods and powers of investigating the molecular constitution of matter, and will, I trust, lead to novel and important results.

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