IV. The Bakerian Lecture: on some new Electro-chemical Phenomena. By William Thomas Brande, Esq. F. R. S. Prof. Chem. R. I.

Read November 25, 1813.

§. I.

It has been ascertained by Sir H. Davy, that when compound bodies capable of transmitting electricity are submitted to the operation of the Voltaic pile, their proximate and ultimate elements are separated with uniform phenomena; that acids are attracted towards the positively electrified surface, and that alkaline and inflammable substances take an opposite direction and collect at the negative pole.

Of the *ultimate* chemical elements of bodies, the greater number exhibit the last mentioned character, and a few only appear to be attracted towards the positive extremity of the Voltaic instrument; and as bodies possessed of dissimilar electrical powers *attract* each other, it has been concluded, that the inherent electrical state of the former is positive, that of the latter negative.

These chemical effects were at first regarded as peculiar to the Voltaic pile, and were considered to depend upon the operation of a new agent, termed the Galvanic fluid, until Dr. Wollaston, in the year 1801,* succeeded in imitating the effects by means of the electrical machine, and thus

* Phil. Trans. 1801, p. 435.

H 2

experimentally demonstrated the identity of common and Voltaic electricity.

More recent investigations, and especially the admirable researches of Sir H. Davy, have fully established the correctness of these views, and have shewn that the different action of the Voltaic pile and the electrical machine, depends chiefly upon the quantity of electricity in the former being great, while its intensity is inconsiderable, and vice versâ.

In the following Lecture I shall have the honour of presenting the Royal Society with some new inquiries connected with these objects of research, and have much pleasure in adducing facts which throw further light upon this interesting department of chemical science, and which harmonize with the opinions of the able philosophers alluded to.

§. II.

When the flame of a candle is placed between two surfaces in opposite electrical states, the negative surface becomes most heated: this circumstance was considered by Mr. Cuthbertson as indicating the passage of electric fluid from the positive to the negative surface.*

Mr. Erman + has shewn that certain substances are unipolar in regard to the electricity of the Voltaic pile; that is, that they are only susceptible of transmitting one kind of electricity. The insulated flames of wax, of oil, of spirit of wine, and of hydrogen gas, only conduct positive electricity; dry soap, on the contrary, and the flame of phosphorus, under the same circumstances, only transmit negative electricity.

^{*} Practical Electricity.

[†] Annales de Chimie, 1807, Tom. LXI. p. 113.

Sir H. Davy * considers the result of Mr. Cuthbertson's experiment to depend upon the *unipolarity* of the flame, which would render it positive, and cause it to be attracted towards the negative pole.

On perusing these statements, it occurred to me that they admitted of another explanation, and that the appearances might be connected with the chemical nature of the substances employed. I repeated Mr. Cuthbertson's experiment, and found that when the electrical machine was in weak action, the negative surface not only became hot sooner than the positive, but that the smoke and flame of the candle were visibly attracted towards it. I now removed the candle, and substituted the flame of phosphorus, when the appearances were exactly reversed: the positive surface now became considerably warmer than the negative, and the flame and smoke of the phosphorus were powerfully directed upon it. I conceived, therefore, that the flame of the candle was attracted by the negative pole, in consequence of the carbon and hydrogen in which it abounds, and that the rapid formation of acid matter during the combustion of the phosphorus, was the cause of its attraction towards the positive pole: in short, that the appearances were consistent with the known laws of electro-chemical attraction.

To ascertain the correctness of this idea, it became necessary to examine the phenomena with greater precision, and to institute the more extended series of experiments, which, with their results, I shall proceed to detail.

The apparatus employed consisted of two insulated brass balls capable of being brought near to, or removed from each

^{*} Elements of Chem. Philos. Vol. I. p. 177.

other, with a small table between them, as represented in the annexed drawing. (Pl. II.)

When it was necessary to ascertain the relative temperatures of the balls with accuracy, I made use of the instrument, fig. 2, devised by Mr. Pepys, in which a a represent two thin spheres of brass containing delicate thermometers, the bulbs of which, as well as the interior of the spheres, were coated with lamp black, to render the increase of temperature more evident. One of the balls was connected with the negative, the other with the positive conductor of a small electrical machine of Mr. Nairne's construction, as represented in fig. 1, so that the apparatus was perfectly insulated.

§. III.

- Exp. 1. A small stream of olefiant gas was burned between the balls. The flame was evidently attracted towards the negative side. The combustion was continued for one minute. At the commencement of the experiment, the mercury in the thermometers stood at 60° Fahrenheit; at its termination the positive thermometer indicated 62°, the negative 72°.
- 2. The experiment was repeated with sulphuretted hydrogen: the flame was now only slightly attracted by the negative ball, but the sulphureous acid vapour passed off towards the positive surface.

In this experiment the positive thermometer rose 3°, and the negative thermometer 6° in one minute.

3. A very small flame of phosphuretted hydrogen was slightly bent towards the positive pole. In one minute it produced an effect upon the positive thermometer $= 5^{\circ}$, upon the negative $= 3^{\circ}$. When a larger flame was used, it

appeared equally drawn towards the two electrical poles, but the acid vapour passed off in the direction of the positive ball.

- 4. The flame of arsenicated hydrogen was attracted by the negative surface: the fumes of white arsenic produced during the combustion were slightly attracted towards the positive pole.
- 5. The flame of hydrogen appeared weakly attracted by the negatively electrified ball, but on employing the apparatus with thermometers, the rise was nearly equal on both sides. In one experiment, made with much caution, the thermometers stood at its commencement at 56°. The gas was burned for two minutes: the negative thermometer rose to 62°, the positive to 61°.

In a second experiment, the combustion was continued for five minutes: the effect upon the negative thermometer was $= 4^{\circ}$, that upon the positive $= 2.5^{\circ}$.

6. With a very small stream of carbonic oxide, the results were still less distinct. The tip of the flame appeared in some cases to be slightly inclined towards the positive ball, but one thermometer was not more affected than the other.

On substituting a larger current of the gas, which produced a flame between three and four inches in length, it was much more evidently directed to the positive surface, but the rise in the positive thermometer was less than might have been expected. In several cases where the combustion was continued for two minutes, the rise in the positive thermometer did not exceed that of the negative more than 2,5 to 3 degrees.

7. Sulphur, in a state of combustion, was placed between the oppositely electrified balls. The flame being extremely small, its direction could not be observed, but the sulphureous acid vapour was attracted by the positive ball.

- 8. The flame of the sulphuret of carbon (sulphuretted liquor of Lampadius) was attracted by the negative surface: the acid fumes which it throws off took an opposite direction.
- 9. When phosphorus in a state of vivid combustion was introduced into the electrical circuit, the flame, and the phosphoric acid produced, were powerfully directed towards the positive surface.

The acid vapour which arises from phosphorus, during its slow combustion in a warm atmosphere, is also attracted by the positively electrified ball.

10. A small stream of muriatic acid gas was allowed to pass into the atmosphere between the electrified spheres; it was immediately attracted to the positive pole. This effect is rendered more evident by the diffusion of a small quantity of ammonia through the atmosphere of the room in which the experiment is made.

The attraction of the muriatic acid is strikingly exhibited by coating the conductors with litmus paper, placing them at a distance of about six inches asunder, and propelling a current of the gas through a small tube between them. If the electrical machine is not in too powerful action, the positive ball is instantly reddened, while the blue colour of the negative surface remains unaltered.

- 11. Nitrous acid gas exhibited the same appearances as muriatic acid.
- 12. Potassium in a state of combustion was placed between the electrified surfaces. Its flame, and the alkaline fumes it produces, were drawn to the negative conductor.

- 13. Ammonia afforded no very distinct results. I attempted to ascertain its electrical state by disengaging it through a small tube placed between the conductors, the atmosphere being slightly tainted with muriatic acid; but it was apparently equally attracted and repelled by the electrical surfaces. When the conductors were coated with turmeric paper, the negative appeared sooner reddened than the positive, but in a very short time the effect upon each became equal.
- 14. Benzoic acid evolved by gently heating benzoin between the electrical poles, was attracted to the positive side; but when the balsam took fire, the flame and carbonaceous matter were immediately drawn in an opposite direction.

I heated some pure benzoic acid placed upon a silver capsule, between the balls; as long as the temperature was only sufficient to raise it in vapour, it took the positive direction; but the moment that the acid was inflamed, the carbonaceous fumes passed to the negative side.

- 15. Camphor during its combustion throws off a large quantity of charcoal, and when burned between the opposite electrical surfaces, furnishes a good instance of the attraction of that substance by the negative pole, which soon becomes coated with it, the positive ball being much less soiled.
- 16. The resinous bodies in general exhibited the same appearances as camphor: when in a state of combustion, both the flame and smoke were repelled by the positive, and attracted by the negative pole.
- 17. Amber, on the contrary, presented phenomena nearly similar to those of benzoin. When brought into a state of fusion, its acid vapour was attracted by the positive ball, but when made to burn, an opposite effect was produced.

MDCCCXIV.

§. IV.

In the preceding detail of experiments, such only have been selected as were attended with marked results. The electrical energies of many other substances were examined and compared, but no new facts were ascertained, nor were any circumstances observed which interfere with the inferences suggested by the above statement.

To insure accuracy, each of the experiments was several times repeated in the presence and with the assistance of some of my chemical friends, and the results were uniform when proper precautions were attended to. It is especially necessary to operate in a quiet atmosphere, and to employ a feeble electrical power, for if the machine is too strongly excited, the substances under examination are alternately attracted and repelled between the poles, especially if insulated, or non-conductors of electricity. The balls were usually withdrawn from each other to a distance of four inches, and the subject of experiment placed equidistant between them. The poles too were occasionally changed, by moving the connecting wires from one ball to the other, with a view to insure correctness by observing the change thus produced in the direction of the flame or vapour.

The experiments were sometimes varied, by using the Leyden jar with a sliding electrometer connected with its outer surface: the substance, the electricity of which was to be examined, was placed between the ball of the charged jar, and that of the electrometer.

Regarding these experiments, as connected with electrochemical theory, they appear to furnish a more evident proof than has hitherto been offered, of the inherent electrical states of matter, which are decidedly exhibited by the attractions and repulsions between the opposite poles; and when connected with Dr. Wollaston's researches, to which I have elsewhere alluded, they amply demonstrate the identity in chemical powers of common and Voltaic electricity.

The attraction of acids by the positively electrified surface, and of alkalies and inflammables by that which is negatively electrified, is thus easily exhibited; and the theory which regards their mutual attractive energies, as dependent upon their opposite electrical states, confirmed by experiments, not less decisive, than those in which the Voltaic instrument was employed.

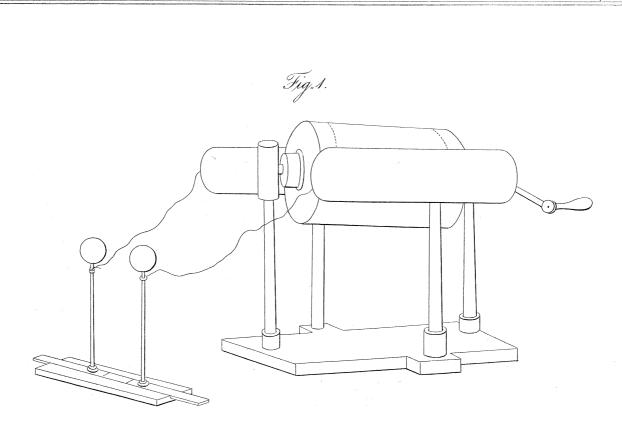
Of the former class phosphorus in slow, and in rapid combustion, and benzoic acid, furnish the most striking instances; and of the latter, the combustion of potassium and of camphor are excellent examples.

There are, however, some circumstances which appear difficult to explain, and which have not turned out as might have been expected a priori. The combustion, for instance, of carburetted hydrogen gives rise to the production of water and carbonic acid, but its flame is entirely and powerfully attracted by the negative surface; and carbonic oxide, which produces carbonic acid, is not very evidently attracted by either pole, unless the flame be of a very large size. It may, however, be conceived with regard to carburetted hydrogen, that the carbonic acid which is formed does actually pass off to the positive surface, and that the polarity of its flame is influenced rather by the combustible, than by the product of combustion: this idea is in some measure sanctioned by the appearances

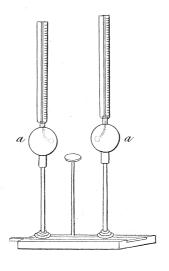
exhibited by the flame of the sulphuret of carbon, which is directed towards the negative ball, although the sulphureous acid visibly passes towards the positive side, and it is fair to infer, that the carbonic acid accompanies it.

An attempt was made to detect the carbonic acid by means of caustic potash: for this purpose a piece of linen, moistened with the alkaline solution, was applied to each conductor, and a current of carbonic acid, issuing from a small tube, was directed between them. The linen was then put into dilute muriatic acid, and it was expected that the effervescence would be greatest in that removed from the positive pole; this generally appeared to be the case, but I cannot say that the results were satisfactorily distinct, nor indeed does the method admit of the accuracy required.

The experiments related in the second section of this lecture, suggest an explanation of the phenomena alluded to, as observed by Mr. Erman, more consonant with the known laws of electricity than that which he has suggested. The flame, for instance, of oil, wax, &c. must be considered as consisting chiefly of those bodies in a state of vapour, and their natural electricities being positive, it is obvious, that, when connected with the positive pole of the battery, and with a gold leaf electrometer, the leaves will continue to diverge, but when applied to the negative pole, that electrical state will be annihilated by the inherent positive energy of the flame, and consequently the leaves of the negative electrometer will not diverge. On the other hand, the flame of phosphorus is negatively unipolar. Now it has been shewn, that this flame, (owing probably to the rapidity with which it is forming a powerful acid by combination with a large portion of oxygen,)







is attracted by the positively electrified surface, and consequently that it is itself negative, so that it would transmit negative electricity to the electrometer, but would annihilate the positive power, and thus appear as an insulator under the particular circumstances which Mr. Erman has described.