CXXXII.—*The Decomposition of Water Vapour by the Electric Spark.*

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THE hypotheses relating to the electrical aspect of chemical changes in solution have proved so fruitful in modern chemistry that it seems desirable that every effort should be made to extend them to the other states of matter, and in particular to the gaseous state. The most convincing evidence for the ionic theory of solution is the explanation which it affords of phenomena, such as electrolysis, which admit of simultaneous electrical and chemical measurements being made. It is therefore unfortunate that our knowledge concerning the chemical changes which accompany the passage of an electric spark through compound gases is not at present sufficiently wide to admit

of its being accepted as evidence for any theory correlating the chemical and electrical aspects of the phenomena. It was with the object of extending our knowledge in this direction that the present investigation was undertaken.

Several researches on the passage of electricity through compound gases have shown that, not only are the compounds decomposed, but an actual separation of the constituents occurs, and the attempts which have been made to compare the separation with the quantity of electricity which passes through the gas cannot be said to have excluded the possibility of a law connecting them similar to Faraday's law for solutions.

Perrot (*Ann. Chim. Phys.*, 1861, [iii], 61, 161) has shown that when an electric spark passes through steam the decomposition which occurs is not limited to the electrodes, but takes place throughout the length of the spark; that it varies with the length of the spark, and can, under favourable conditions, exceed by twenty times the decomposition in a voltameter placed in the same circuit, so that if any relation is to be discovered between the gases liberated and the current passed, only the excesses of oxygen and hydrogen which make their appearance at the anode and cathode respectively must be considered. Experiments were performed by Perrot for the purpose of testing this point. He found that the gases liberated at the anode contained an excess of oxygen, and those at the cathode an excess of hydrogen, their amounts being equivalent to the copper deposited in a voltameter in the same circuit. The experiments proved that the current is conveyed through water vapour in the same manner as through water.

Perrot's experiments were repeated by J. J. Thomson ("Recent Researches in Electricity and Magnetism," Appendix), who found that the separation was not independent of the length of the spark. With a *short* spark, the excesses of oxygen and hydrogen collected at the two electrodes were equal to the oxygen and hydrogen collected in a voltameter in the same circuit. The hydrogen, however, appeared at the positive electrode instead of, as in ordinary electrolysis, at the negative. With *medium* sparks, the separation of the oxygen and hydrogen in the steam was greater than in the water voltameter. The hydrogen was still liberated at the positive electrode as with the short sparks. With *long* sparks (provided they were not too long otherwise the results became irregular), the hydrogen appeared at the same electrode both in the voltameter and in the spark, their volumes being approximately equal. Thomson regards the separation of oxygen and hydrogen, which results from the passage of a spark through water vapour, as due to the movement of charged oxygen to one electrode, and oppositely charged hydrogen to the other electrode, the difference noticed with the short and long sparks being due to the fact that the hydrogen has

a negative charge when the discharge resembles an arc, whereas it is positively charged when the discharge is long and takes place as a series of separate sparks through the unmodified vapour.

E. Wiedemann and G. C. Schmidt (*Ann. Phys. Chem.*, 1897, [iii], 61, 737) concluded after a series of experiments on hydrogen chloride and the vapours of the halogen compounds of mercury that Faraday's law does not apply to gases, since the separated halogen was much less in amount than that required by the law.

Besides the quantitative investigations mentioned above, spectroscopic evidence of the separation of the constituents of compound gases by the passage through them of the electric spark has been obtained by several investigators.

In our experiments, a discharge from an induction coil was passed between the anode, *A*, and cathode, *C*, of a vacuum tube containing water vapour. The supply of water vapour was continually renewed by withdrawing it, together with the gases produced, in approximately equal quantities, through the tubes *E* and *F* situated near the electrodes, and

FIG. 1.

allowing a fresh quantity to enter through *D*. The quantity of electricity which passed between *A* and *C* was measured by means of a voltmeter placed in the same circuit. The gases withdrawn from *E* and *F* were analysed. The rate at which the water vapour passed through the tube could be regulated.

The gases withdrawn from *E* and *F* consisted of mixtures in different proportions of oxygen and hydrogen. They were separately collected, exploded to remove the excess of electrolytic gas, and the residue, consisting of oxygen or hydrogen, analysed. The conditions of the experiment were altered in two particulars, (1) the rate at which the water vapour passed through the tube was varied, (2) the position of the tube *D* at which it entered was altered.

When the stream of water vapour is slow, the separation of oxygen and hydrogen in the tube is small, but *ceteris paribus* increases rapidly as the stream becomes faster, so that in order to obtain the maximum effect a rapid and continuous current of water vapour must be passed through the tube.

The result of varying the position of the tube *D* is very interesting. When it was near the cathode, the gases collected at *F* contained an excess of hydrogen, as in ordinary electrolysis, but this excess of hydrogen was found in several cases to be *five or six times* as great as that collected in the voltameter. The fact that this large difference can exist in the volume of hydrogen separated by the same current in water vapour and in liquid water points to the conclusion that the separation in the vapour cannot be *entirely* due to electrolysis.* † The large difference in the hydrogen obtained from the two sources was, however, not maintained when the water vapour entered the tube at a greater distance from the cathode. When the tube *D* was midway between the anode and cathode, the excess of hydrogen passing out of the cathode exit tube was not more than double that collected in the voltameter, and the ratio continued to decrease as the tube *D* was moved nearer the anode. If the inlet tube is brought very near to the anode, the electrodes at which the excesses of oxygen and hydrogen appear are reversed, that is, the oxygen appears at the cathode and the hydrogen at the anode, a result which recalls that obtained by J. J. Thomson with short sparks. Now during all the experiments an effort was made to maintain a uniform discharge, so that the reversal of the poles at which the oxygen and hydrogen make their appearance is not entirely due to a change in the character of the discharge. The position of the tube *D* through which the vapour enters has, obviously, a marked influence on the composition of the gases withdrawn at *E* and *F*.

With these facts before us, we can draw the following conclusions.

1. That when a series of electric sparks is passed through water vapour, decomposition of the water and recombination of the oxygen and hydrogen take place simultaneously until equilibrium is established.
2. The oxygen and hydrogen produced by the decomposition tend to separate and take up different positions in the tube. This separation does not proceed to an unlimited extent, and is prevented from doing so by a simultaneous mixing due to convection currents and to diffusion. The rate of mixing, of course, increases as the variation in the composition of the gases in different parts of the tube becomes greater.
3. The arrangement of the products of decomposition does not take place in such a manner that the hydrogen appears at one pole and the oxygen at the other, but hydrogen separates at both the anode and cathode, the oxygen being driven to the middle of the spark gap.

* The word electrolysis is used here and elsewhere to denote the process of conduction of electricity by the movement of charged ions.

† Disregarding, of course, the exceedingly improbable hypothesis that the ions are highly polymerised molecules.

It will be seen that conclusions 1 and 2 account for the fact that a more rapid stream of water vapour causes a greater separation of oxygen and hydrogen, and that with a slow current very little separation can be observed, for with a slow stream of vapour the gases are not driven out of the tube immediately they are separated, and they are thus given a greater chance of remixing. In connection with this point, it is perhaps well to observe that the small separation of hydrogen and chlorine obtained by Wiedemann and Schmidt with hydrogen chloride was probably due to the stream of gas being too slow to prevent a rapid mixing of the separated gases in the vacuum tube itself.

Conclusion 3 accounts for the nature of the results obtained by

FIG. 2.

varying the position of the tube D . For suppose that the tendency of the oxygen and hydrogen to collect in different parts of the tube is represented by the curve $D O Y F E$, where the points A and C correspond to the anode and cathode respectively, and an excess of hydrogen per unit length is measured by a line drawn upwards from $A C$ to the curve and an excess of oxygen by a line drawn downwards. These lines represent equivalents of oxygen and hydrogen respectively, so that the area $F E C$ together with the area $A O D$ must equal the area $O Y F$. If the water vapour enters at the point F , the stream which passes in the direction $F C$ will drive out the hydrogen represented by the area $F E C$, whereas the stream of water vapour which passes in the direction $F A$ will drive out an equivalent amount of oxygen. On the other hand, if the vapour enters the tube at the

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point O , hydrogen will be driven towards the anode and oxygen towards the cathode, that is, there will be a reversal of the electrodes at which the oxygen and hydrogen make their appearance. If a point X be chosen, such that the area $A O D$ is equal to the area $O X Y$, and the area $X Y F$ to the area $F E C$, then on allowing the water vapour to enter the tube at the point X we ought to find, on collecting the gases at the anode and cathode, that no separation had taken place. The point X is, however, not absolutely fixed in position, and moves backwards and forwards during the course of the experiment, so that if the inlet tube is near to this point, the pole at which the excess of hydrogen appears is continually reversed, but at the end of an experiment lasting for a long time the separation produced by the spark is only a small fraction of the gases collected in the voltameter.

We are not prepared at present to offer any theory to account for the distribution of oxygen and hydrogen in a tube containing water vapour subjected to the action of a series of sparks from an induction coil, as we believe that, with the exceedingly limited number of facts at our disposal, more than one plausible hypothesis could be constructed. Our experiments, however, prove decidedly that the separation of the constituent elements of water is not entirely due to a process of electrolysis, because in that case oxygen should appear at one electrode and hydrogen at the other, whereas hydrogen collects at both electrodes; and, secondly, their quantities should not exceed the quantities of oxygen and hydrogen collected in a voltameter through which the same current passes.

EXPERIMENTAL.

The arrangement of the apparatus used is indicated by the accompanying diagram. The flask A contains water which is continually evaporating during the experiment. The vapour thus produced passes up the tube C into the vacuum tube, $E F$. On entering the vacuum tube, the current of water vapour divides, part going towards E and the other part towards F . The gases produced on each side of the inlet tube by the passage of the spark are driven forward by the water vapour along the tubes G and H into the condensers M and N , which are surrounded by freezing mixtures. The water vapour condenses in M and N , and the gases which are left behind are drawn out by the continuous Sprengel pumps P and Q . The pumps were constructed without rubber in order to avoid as far as possible the presence of sulphur and organic matter. The spark is produced by the induction coil X .* The quantity of electricity passing in one

* The induction coil was provided with a large condenser, and an air gap was always introduced into the circuit.

direction is measured by the gases collected in the voltameter *Y*. The gases produced in the spark are collected and measured in the apparatus *Z* and in a precisely similar apparatus (not shown in the diagram) attached to the other pump. The voltameter *Y* contained dilute potash solution. At the close of an experiment, the gases which it contained were measured by turning off the tap *a*, drying

FIG. 3.

the tube below the tap, and weighing the voltameter with the enclosed gases. Two other weighings are obtained, firstly, with the gas in one limb displaced by potash solution, and secondly, with both limbs full of potash solution. From the weight of potash displaced in both limbs, it is obvious that the volumes both of oxygen and hydrogen can be calculated when the necessary corrections for

density of potash solution, barometric pressure, heights of columns of potash, temperature, and vapour tension have been made.

The volumes of oxygen and hydrogen separated in the spark are measured by the weights of mercury displaced in the apparatus *Z*. During the experiment, the gas is collected in the compartment γ . When this is full, the taps α and β are opened and the gas passes into the compartment δ , where the admixed electrolytic gas is removed by explosion with α and β closed. This operation is repeated until a sufficient quantity of gas has been collected. The apparatus is weighed with the taps α and β closed, and the vessel γ and the tube below the tap β empty. All necessary measurements of columns of mercury are made in a mercury trough with a scale and telescope. The gases can, with the aid of this apparatus, be measured directly and also analysed by explosion.

Every precaution must be taken to exclude organic matter from the apparatus, as the oxygen produced by the spark appears to be in a particularly active form. The absence of rubber is imperative.

Method of Conducting an Experiment.—Distilled water is drawn into the flask *A* through the tube *B* by working the Sprengel pumps, and *B* is then closed before the blow-pipe. The air is next removed from the apparatus by setting the pumps in action. This operation is accelerated by surrounding *M* and *N* with freezing mixtures, which produce a rapid current of water vapour through the apparatus towards the pumps. As soon as *M* and *N* are full of water, the freezing mixtures are removed and the water distilled back into the flask *A* by surrounding it with ice. After repeating this process several times, the experiment is started. A series of sparks is sent from an induction coil through the voltameter *Y* and the vacuum tube *EF*. The flask *A* is placed in a water-bath which is kept approximately at a temperature of 15°, and *M* and *N* are surrounded with freezing mixtures of ice and salt. The pumps are kept in continuous action during the whole course of the experiment. The gases which collect in *Z* must be exploded from time to time as previously described. A fresh vacuum tube must be made and fused on to the apparatus whenever it is desired to vary the conditions.

In several experiments made at the beginning of the investigation, it was noticed that the volume of the oxygen collected at the anode was less than half that of the hydrogen collected at the cathode, pointing to a disappearance of oxygen. This we believe was due to the formation of ozone in the spark, which subsequently acted on the mercury of the pumps, a supposition which is rendered more probable by the fact that this source of error may be considerably reduced by introducing silver gauze into the horizontal tubes leading

from the condensers to the pumps, and warming the gauze during the experiment. This precaution was taken in all the later experiments.

The Results Obtained.

I. In a large number of earlier experiments, the water vapour was conducted into the vacuum tube at a point near to the middle of the spark, and the current of water vapour through the tube was slow owing to the fact that the temperature of the condensers was only three or four degrees lower than that of the reservoir. Under these circumstances, the amount of hydrogen coming from the cathode of the spark varied between one-half and one-fourth of the volume of the same gas collected at the cathode of the voltameter. One example will suffice to illustrate this :

Hydrogen from spark = 3.1 c.c.

Hydrogen from voltameter = 6.6 „

II. *Experiments with the Inlet Tube near the Middle of the Spark Gap.*—The condensers were made larger and kept at a lower temperature by means of a freezing mixture of ice and salt. The water vapour entered the tube near the middle of the spark. The ratio of hydrogen from the spark to hydrogen from the voltameter varied from 1 to 2 :

Number of experiment.	H ₂ from voltameter.	2 × O ₂ from anode.		H ₂ from cathode.	
		A.	B.	A.	B.
1	1.088 c.c.	1.084 c.c.	—	—	1.163 c.c.
2	1.108 „	0.952 „	—	1.101 c.c.	1.08 „
3	1.338 „	1.133 „	—	—	1.155 „
4	0.889 „	1.982 „	—	2.32 „	2.14 „
5	0.696 „	—	—	0.837 „	0.827 „
6	1.76 „	3.05 „	—	3.80 „	3.63 „
7	1.57 „	—	1.36 c.c.	1.95 „	1.76 „

The numbers in column A were obtained by direct measurement, and those in B by explosion.

It will be observed that, in spite of the silver gauze, the oxygen was always less than half the hydrogen, and that the hydrogen was mixed with a small proportion of inert gas.

III. *Experiments with the Inlet Tube near to the Cathode.*—The length of the spark varied from about 100 to 110 mm., and the inlet

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tube was about 10 mm. from the bulb containing the cathode. The electrodes were made of thick platinum wire and varied in length from 25 to 30 mm. The tube through which the spark passed was 8 mm. in diameter, and the inlet tube 5 mm. :

Number of experiment.	H ₂ from voltmeter.	2 × O ₂ from anode.		H ₂ from cathode.	
		A.	B.	A.	B.
1	1·23 c.c.	4·22 c.c.	4·40 c.c.	4·19 c.c.	4·15 c.c.
2	0·992 "	5·74 "	—	5·95 "	—
3	0·376 "	2·60 "	—	2·75 "	—
Sum	2·598 "	12·56 "	—	12·89 "	—
$\frac{\text{Hydrogen from spark}}{\text{Hydrogen from voltmeter}} = \frac{12·89}{2·598} = 4·9 \text{ (nearly).}$					

IV. *Experiments with the Inlet Tube near to the Anode.*—These experiments were much more difficult to perform on account of the residues of oxygen and hydrogen collected at the two pumps being much smaller than in the previous series. In three experiments, we showed that the hydrogen appeared at the anode and the oxygen at the cathode by applying qualitative tests, and in one case a complete analysis of the gases was made with the following results :

H ₂ from voltmeter.	2 × O ₂ from cathode.		H ₂ from anode.	
	A.	B.	A.	B.
1·545 c.c.	0·33 c.c.	0·33 c.c.	0·86 c.c.	0·78 c.c.

The percentage error due to the absorption of the oxygen by the mercury of the pumps and the contamination of the hydrogen by inert gases becomes more pronounced, since the actual quantities of gases obtained in the same time is much less than in all the previous experiments.

Conclusion.

The separation of oxygen and hydrogen produced by the passage of an electric spark through water vapour cannot receive a complete explanation from a hypothesis based exclusively on the unmodified theory of electrolysis of liquids.

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