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# LXXXVII.—The Chemical Changes induced in Gases submitted to the Action of Ultraviolet Light.

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THE investigation which forms the subject of the present paper was suggested by the work of Burgess and Chapman on the interaction of chlorine and hydrogen, and it was started shortly after the inhibitive effect of compounds of ammonia on the above reaction was discovered. The circumstance that traces of such impurities completely prevented the interaction of chlorine and hydrogen submitted to the action of light could in the opinion of Burgess and Chapman be best explained on the supposition that the inhibitor altered the character of the vibrations set up by the light in the various species of molecules of which the system was composed; that, in fact, the presence of a trace of a suitable catalyst so materially altered the whole mode of degradation of the highly efficient light energy that the relative number of pairs of chlorine and hydrogen molecules in such states of vibration as to be capable of interacting was very considerably reduced.\*

Now there is no reason why the accelerating effect of a positive catalyst such as moisture should not be ascribed to a similar cause, and therefore the present authors determined to search for evidence for or against this view. The typical example of a reaction influenced by moisture, namely, the interaction of carbon monoxide and oxygen (Dixon, *Brit. Assoc. Report*, 1880, 503) was selected as being for several reasons the most suitable for investigation. Some means had

<sup>\*</sup> The results of a recent investigation on the retardation of the rate of combination of chlorine and hydrogen by oxygen (which it is hoped to publish shortly) lend some support to this view concerning the cause of inhibition by impurities.

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to be found whereby these two gases could be caused to interact slowly out of the presence of any other catalyst except moisture. The only possible method of accomplishing this object was by the gases being subjected to the influence of some form of radiant energy such as the cathode rays, ultraviolet light, or the silent or disruptive electric discharge.\* Of these ultraviolet light was to be preferred because of the complexity of the electric discharge and of the circumstance that the cathode rays in their passage through gases give rise to other forms of energy. A few cases in which the cathode rays and ultraviolet light induce chemical changes had been discovered already.

Ph. Lenard (Ann. Physik., 1894, 51, 225) had shown that cathode rays which had penetrated an aluminium window in a vacuum tube produced ozone in the air through which they passed. Whether the formation of ozone was due directly to the cathode rays or indirectly to the ultraviolet light produced by the passage of the cathode rays through air is doubtful. Lenard was unable to detect any other chemical changes induced by the action of this form of energy; electrolytic gas did not explode, carbon disulphide did not burn, hydrogen sulphide was unchanged, and nitrogen and hydrogen did not combine in the presence of the rays.

Lenard (Ann. Physik., 1900, 70, 486) also investigated somewhat exhaustively the effects of ultraviolet light on gases. He showed, firstly, that under the influence of light gases became conducting; secondly, that condensation nuclei were produced, and, thirdly, that in the case of oxygen ozone was formed. These effects were brought about in air by light of wave-length 0.00014 mm. to 0.00019 mm., that is, only by the rays of highest refrangibility to which air is comparatively opaque. Hydrogen was more transparent to ultraviolet light than air, and was accordingly unaffected by light of greater wave-length than 0.00016 mm. To the most chemically active rays, air at atmospheric pressure was more opaque than rock salt, fluorspar, or quartz. It is important that this relative opacity of air should be borne in mind in the construction of any apparatus to be used in the examination of the chemical effects of rays, and that air-spaces in the path of the rays should be avoided.

Closely connected with the subject is an interesting research by E. Warburg (*Sitzungsber. K. Akad. Wiss.*, *Berlin*, 1903, 1011), in which the discharge of electricity through oxygen from a point was investigated. Under different conditions the amount of ozone produced was from 1000 to 93 times greater than the amount which

<sup>\*</sup> There are various reasons for thinking that the chemical effects brought about by the electric discharge are mainly due either to the cathode rays or to ultraviolet light, or to both combined.

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would have been found had its production been due entirely to electrolysis. From this fact the necessary conclusion was drawn that ozone produced in the path of the electric discharge results from the action of ultraviolet light and cathode rays on oxygen, a view which received further support from the circumstance that the amount of ozone formed in a given time was roughly proportional to the intensity of the light.

E. Warburg and E. Regener (Sitzungsber. K. Akad. Wiss., Berlin, 1904, 1228) were the first to demonstrate that ultraviolet light could induce other chemical changes besides the conversion of oxygen into ozone. As a source of ultraviolet light they employed an electric spark between aluminium electrodes. With their apparatus  $2\cdot2*$  per cent. of oxygen at atmospheric pressure could be converted into ozone. They found that ammonia, nitric oxide, and nitrous oxide were readily decomposed by the light.

As a source of ultraviolet light we have used a quartz mercury lamp, the light from which has been shown by A. Pfluger (Physikal. Zeitsch., 1904, 5, 414) and Ladenburg (Physikal. Zeitsch., 1904, 5, 525) to be rich in ultraviolet rays. The formation of ozone from oxygen submitted to the action of the light from a quartz mercury lamp specially constructed for the purpose has been investigated already by Franz Fischer and Fritz Braehmer (Ber., 1905, 38, 2633). The maximum percentage of oxygen converted into ozone when a current of the gas was passed through the apparatus was only 0.26. Their primary object, however, was not to obtain a large percentage of ozone, but to estimate the yield for a given expenditure of energy under various For our purpose, the apparatus used by Fischer and conditions. Braehmer would have been unsuitable, particularly as the gases under investigation came into contact with an organic cement. Impurities in the gases would have rendered our results valueless.

The gases to be acted on were enclosed in a bulb of fused quartz through which ultraviolet light was caused to pass from the outside. Ultraviolet light partly owes its exceptional photochemical efficiency to the circumstance that it is absorbed with relative ease by most substances, including the colourless gases; but this characteristic is also the cause of most of the difficulties which arise in an experimental investigation of the effects produced by it. To obtain the best results the apparatus should, as a general rule, be constructed so that the light has to pass only through a vacuum or vitreous quartz. As the wave-length of the effective light decreases, the necessity of observing this precaution becomes greater. At first an iron arc placed at a few centimetres from the quartz vessel which contained

<sup>\*</sup> The low percentage of ozone was attributed to the property which some of the rays were supposed to possess of destroying the ozone formed.

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the gases to be acted on was used, but the chemical effects induced by the light capable of penetrating the layer of intervening air were too small to be accurately measured. Then the quartz vessel was illuminated by the rays from a mercury arc, the arc being in the same evacuated space as the quartz vessel, but at a short distance from it. This arrangement was also ineffective, owing no doubt to the most chemically active rays having been absorbed by the layer of non-luminous mercury vapour surrounding the arc. Finally, the quartz bulb was placed within the mercury arc, proper precautions being taken to prevent the temperature of the gases contained in it from rising more than a few degrees. The accompanying figure is a diagram of the apparatus in its final form.



The gases which we desired to submit to the action of ultraviolet light were contained within the cylindrical quartz vessel, A. This vessel was enclosed within a glass mercury lamp, B, of which the cathode was a pool of mercury, e, and the anode, a short cylinder of iron, d. Whenever the current passed between e and d the quartz vessel was completely surrounded with the arc, and the light had only to pass through  $l\frac{1}{2}$  mm. of vitreous quartz to reach the gas contained within it. The distance between the inner surface of the mercury lamp and the outer surface of the quartz cylinder was 2 mm. The mercury lamp was exhausted with a Sprengel pump. The method of making electrical connexion with the electrodes e and d can be seen from the figure. The neck of the quartz vessel, A, after passing through the VOL. XCI. 3 R

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stopper, a, which closed the lower end of the mercury lamp, was connected with the tube, f, by means of the ground-glass mercury joint, b. The mercury lamp was contained in a bath, C, through which a rapid current of cold water was caused to flow continuously. The bath was supported on blocks of paraffin wax.

As it was desirable that the temperature of the quartz vessel should not rise more than a few degrees, the electric current was passed through the mercury lamp for one second only at the end of every half minute, the heat developed in the arc during one second being thus allowed half a minute to escape. It was estimated that in an experiment conducted on this plan no portion of the gas under examination ever acquired a temperature of more than 40°. That part of the apparatus by which the arc was struck every half minute and maintained in action for one second only is represented in the figure diagrammatically. The terminals of the secondary coil of an induction coil were connected with the outside of the lamp, B, and the mercury electrode, e, by the fine wires m and n respectively. The current through the primary coil of the induction coil could be made and broken by the contact breaker, X. A current of 6 amperes regulated by means of a resistance, R, was supplied to the mercury lamp. A mercury contact breaker, Y, served to close the circuit. When X was closed a high tension discharge filled the mercury lamp, and this was sufficient to strike the arc on Y being closed. It was arranged that X and Y should remain closed for one second, but that the closing of X should take place a fraction of a second before that of Y, the apparatus being so adjusted that the above sequence of events should recur every half minute.

The currents were made and broken by a contrivance, not shown in the figure, which was regulated electrically by a clock. The other details connected with this part of the apparatus do not require description.

At q was a ground glass mercury joint by means of which connexion could be made with any apparatus intended for the preparation of one or other of the gases required in an experiment. Through the tube rgas could be withdrawn by a Sprengel mercury pump. The taps o and p were not lubricated and accordingly were not completely airtight. The tube on either side of each tap could, however, be sealed when necessary with mercury as shown in the figure, the prevention of the escape of gas in one direction (which was all that was required) being The flask F contained mercury which could be thereby achieved. raised by way of the tube S and trap t as far as the taps o and p by the forcing of air into the flask with a pump. By F being brought into communication with a water pump the mercury could be lowered The customary device of a movable mercury reservoir joined again.

to the apparatus by a rubber tube was not resorted to because mercury in flowing through a rubber tube always carries with it a small amount of organic impurity. The tube G was introduced for the purpose of containing phosphoric oxide. The gas was passed backwards and forwards many times through the phosphoric oxide and was thereby dried, the mercury in globe E being raised and lowered alternately for the purpose.

The oxygen used in the experiments was prepared by heating potassium permanganate; the carbon monoxide by the action of a mixture of equal volumes of sulphuric acid and water on sodium formate, the gas being washed with potash solution; and the carbon dioxide by the action of dilute sulphuric acid on sodium bicarbonate.

## Conversion of Oxygen into Ozone.

The experiments on the conversion of oxygen into ozone were performed mainly for the purpose of testing the efficiency of the apparatus. It was found that a mercury manometer could be used to estimate the pressure provided that the manometer was connected with the quartz vessel by a sufficient length of capillary glass tubing. The oxygen was imperfectly dried, having been passed only once through the tube Gcontaining phosphoric oxide. The temperature of the bath varied between 8° and 9°. As was to be expected, the rate of formation of ozone was comparatively rapid at first, but fell continuously until after the lapse of five hours—that is, after the oxygen had been exposed for ten minutes in all to the light of the lamp—equilibrium had almost been attained. 3.5 per cent. of oxygen had been converted into ozone. This is the largest percentage of ozone yet obtained by any means other than the silent discharge.

#### Interaction of Carbon Monoxide and Oxygen.

In these experiments oxygen in excess of that required to convert the carbon monoxide into carbon dioxide was taken, since it was anticipated that with such a mixture the relative rates of formation of ozone and of carbon dioxide could be more accurately studied.

Experiment I.—Carbon monoxide and oxygen, dried by being passed through strong sulphuric acid, were present in equal volumes. When the mixed gases had been exposed for six hours to the intermittent light, that is, to the light of the lamp for twelve minutes, the contraction was 15.54 per cent. of the total volume. After the experiment a sample of gas was withdrawn and the ratio of carbon monoxide to carbon dioxide contained in it was determined by analysis. The ratio of carbon monoxide to oxygen in the original mixture had previously been

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found. These two ratios together with the percentage contraction are sufficient data for calculating the composition of the final mixture.

The actual values found for the two ratios were :

 $\frac{CO_2}{CO}$  in the gases which had been submitted to the action of the light = 0.2979.

 $\frac{O_2}{CO}$  in the original mixture = 0.949.

Whence the compositions of the original and final mixtures are found to be:

Original Mixture. $O_2 = 48.69$ volumes		Final Mixture. O <sub>3</sub> =19·30 volumes		
		CO = 39.53	,,	
100	"	$O_2 = 13.85$	,,	
		84.46	,,	

Now carbon monoxide is not appreciably affected by ultraviolet light, whereas oxygen is readily converted into ozone, so that it would appear reasonable to assume that the first chemical effect of the ultraviolet light is the decomposition of the oxygen molecules into atoms, and then the immediate combination of the latter either with oxygen molecules or with carbon monoxide molecules according to the equations:

$$O_2 = O + O$$
$$O_2 + O = O_3$$
$$CO + O = CO_2$$

These equations are not necessarily a complete expression of the truth, but they would appear to be the simplest representation of the facts known at present, so far, at any rate, as these facts can be represented by equations at all. It is conceivable, for example, that ozone and carbon dioxide might be formed without actual dissociation of the oxygen molecules being inevitably involved, but in this event the argument which follows would not be invalidated. The high percentage of ozone in comparison with that of carbon dioxide in the final mixture is significant, and points to the conclusion that the tendency of an atom of oxygen to combine with a molecule of oxygen must be somewhat greater than that of an atom of oxygen to combine with a molecule of carbon monoxide when the gases are dry.

The stability of the ozone formed under the conditions of the experiment is also remarkable and affords material for future speculation and research. Is ozone more stable in all circumstances in the presence of oxides of carbon, or do the oxides of carbon inhibit the decomposition of ozone by the decomising rays assumed by Warburg to be present in ultraviolet light? This problem is one which we hope at an early date to attack.

*Experiment* II.—This experiment was a repetition of the last, with one variation. The gases were dried with greater care, the desiccating agent being pure redistilled phosphoric oxide. The gases were submitted to the intermittent light for eight hours, and therefore the time during which they were exposed to the light of the lamp was in all sixteen minutes. The following results were obtained:

Contraction = 14.13 per cent. of original volume.

 $\frac{CO_2}{CO}$  in the gases which had been submitted to the light = 0.2419.

 $\frac{O_2}{CO}$  in the original mixture = 1.015.

Whence we deduce:

Original Mixture.	Final Mixture.	
$O_2 = 50.38$ volumes	$O_3 = 18.59$ volumes	
CO = 49.62 ,,	$CO_2 = 9.67$ ,	
	CO = 39.95 ,,	
100 "	$O_2 = 17.66$ ,,	
Contraction = $100 - 85.87$ volumes.	85.87	

A comparison of the results of the first experiment with those obtained in the one just quoted discloses the fact that the trace of moisture left after drying with sulphuric acid is only capable of raising the value of the ratio  $\frac{CO_2}{O_3}$  above that of the carefully dried gases by a small amount. The effect of a further increase in the percentage of moisture on the ratio in question is, however, very considerable, as the following experiment demonstrates.

*Experiment* III.—A mixture of approximately equal volumes of carbon monoxide and oxygen, saturated with water vapour at 16°, was submitted to the action of the intermittent light for ten hours. The rate of contraction was a little slower than in the two preceding experiments. The analysis of the resulting mixture showed that the contraction was in this case almost entirely due to the formation of carbon dioxide. The composition of the final mixture was as under :

O <sub>3</sub> .	CO <sub>2</sub> .	co.	0 <sub>2</sub> .	Contraction.
1.31	27.90	21.72	35.12	13.95 volumes

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On repeating this experiment we obtained a similar result.

One interesting fact is clearly brought to light by a comparison of the results of the three experiments. The rate of chemical change as measured by the contraction was practically the same in every case, for although the presence of moisture resulted in an increase in the amount of carbon dioxide formed in a given time, it reduced the yield of ozone by an equivalent amount. A simple explanation is afforded by the hypothesis that the dissociation of diatomic oxygen proceeds with equal facility in the absence and presence of moisture, and that the oxygen atoms resulting from the dissociation immediately enter into combination either with oxygen or with carbon monoxide molecules, the chances of a union taking place with the latter class of molecules being greater in the presence of moisture. It is conceivable that the moisture might increase the chances of combination of carbon monoxide molecules with oxygen atoms in two possible ways, but to which of these preference should be given in the case under discussion is not at present clear.

In the first place, the reaction represented by the equation

# $CO + O \rightarrow CO_2$

is accompanied by change of potential energy into highly efficient kinetic energy. The absence of any means by which this kinetic energy might be degraded into a less efficient form would simply result in its reconversion into potential energy, that is, the reaction would not take place. So that if water could aid the kinetic energy to degrade into heat it would be able to accelerate the chemical change in question.

In the second place, for two substances to interact the molecules of each must first be brought into a suitable state of vibration, and the addition of a third substance, such as moisture, to the system might result in a change of distribution of the vibrational energy, the pairs of molecules in a state of vibration conducive to interaction being either increased or decreased in number thereby.

The conjecture that the distribution of energy is essentially different in two mixtures of carbon dioxide, carbon monoxide, and oxygen of the same composition, except in respect of their content of moisture, and illuminated by light of the same intensity, receives confirmation from the experimental results quoted below.

## Experiments on the Decomposition of Carbon Dioxide by Ultraviolet Light.

The method of working has already been sufficiently indicated; a description, therefore, of most of the details of these experiments can be omitted.

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Experiments at Atmospheric Pressure.\*—It was found that after long exposure to the intermittent light, dry carbon dioxide at atmospheric pressure was decomposed to an extent from 2.6 to 3 per cent. The amount of decomposition was in each case estimated by the ratio of carbon monoxide to carbon dioxide in the resulting gases. The oxygen was partially ozonised.

When the moist carbon dioxide was submitted to the action of ultraviolet light, no increase of pressure within the apparatus could be observed, and no carbon dioxide could be detected in the gases withdrawn after the experiment.

Experiments at Reduced Pressure.—Carbon dioxide nearly saturated with water vapour was admitted to the apparatus until the pressure was equal to that of the atmosphere. Gas was then withdrawn until the manometer indicated that the pressure within the apparatus was 30 mm. The pressure did not increase when the gas was submitted to the action of ultraviolet light, and the gas withdrawn at the end of the experiment did not contain either carbon monoxide or oxygen. When the alkaline pyrogallol was added, a slight change in its colour was noted, but no decrease in the volume of the gas could be detected.

Carefully dried carbon dioxide at a pressure of 36 mm. was next submitted to the action of the intermittent light for forty-five hours. The analysis of the gases withdrawn at the end of the experiment showed that 46 per cent. of the carbon dioxide had been decomposed.

The above experiments demonstrate that dry carbon dioxide is decomposed by ultraviolet light, the percentage decomposition being increased by a reduction of pressure, but that under the same conditions the moist gas at all pressures remains practically unchanged. Now it is well known that in a balanced reaction in a system kept at the same temperature as its surroundings the state of equilibrium is unaffected by a small amount of a catalyst. The extent, for example, to which carbon dioxide is decomposed when it is maintained at constant temperature in an opaque vessel is dependent only on the temperature and pressure, and is independent of the degree of desiccation. The reason for this well-established fact is that the distribution of energy amongst the various groups of molecules after equilibrium has been established is unaffected by the presence of a small amount of a foreign substance.

When, on the other hand, the reaction is photochemical, the position of equilibrium is not independent of the catalyst, as the above

<sup>\*</sup> H. Buff and A. W. Hofmann (Trans., 1860, 12, 282) decomposed carbon dioxide at atmospheric pressure by electric sparks. H. B. Dixon and Lowe (Trans., 1885, 47, 571) showed that dry carbon dioxide is decomposed by sparks between metal electrodes to an extent of from 20 to 43 per cent.

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experiments demonstrate, and this fact impels us to conclude that under such conditions the catalyst (moisture) exerts a marked influence in determining the mode of distribution of the energy amongst the molecules of the reacting substances (the two oxides of carbon and oxygen). The experiments on the decomposition of moist and dry carbon dioxide therefore appear to afford a simple means of demonstrating the truth of one of our principal assumptions.

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