

It would follow that the production of nitric and nitrous oxides with nitrogen, in proportions varying according to the conditions, is due to subsequent changes occurring between nitrous acid and cupric or cuprous nitrate or nitrite in presence of nitric acid.

I propose to continue these researches, substituting other metals for copper, especially those which are supposed to yield primarily nitrous acid.

In conclusion, I would express my thanks to Mr. Vernon Harcourt for the suggestion which proved of so much value, and to the authorities of the University for affording me facilities for this investigation.

[*Postscript*.—Since the above was written experiments have been made in which the reaction between the copper and dilute nitric acid (sp. gr. = 1.1723), heated to 27° C., was successfully prevented for some time, even in absence of urea, by substituting a current of air for that of carbonic acid.—*May 22nd*, 1889.]

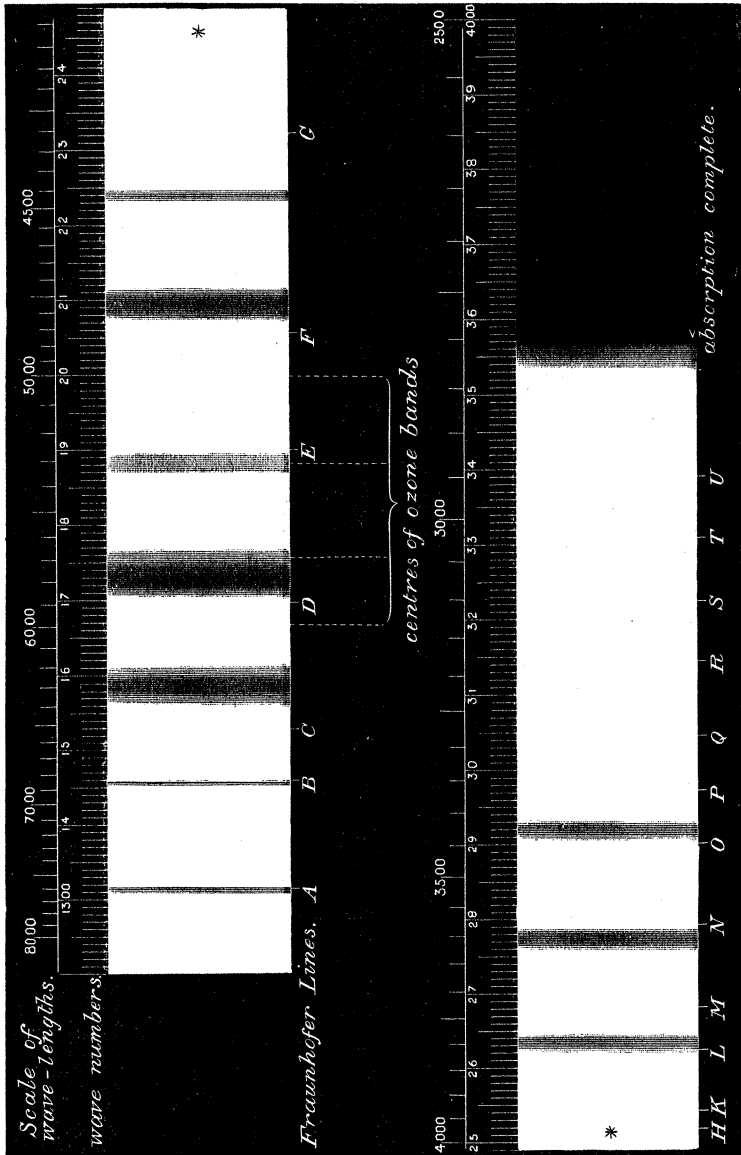
VI. "Notes on the Absorption-Spectra of Oxygen and some of its Compounds." By G. D. LIVEING, M.A., F.R.S., Professor of Chemistry, and J. DEWAR, M.A., F.R.S., Jacksonian Professor, University of Cambridge. Received May 23, 1889.

The absorption-spectrum of oxygen has engaged attention not only on account of the important part which that element plays in the world, but because of the remarkable character of that absorption, so strongly marked, exhibiting bands of two essentially different classes, and extremely variable under varying circumstances of condensation and combination.

It may be expected that the study of it will reveal something new as to the nature of the molecular changes brought about by different circumstances, physical and chemical.

We have already published notes of some of our experiments on this subject ('Phil. Mag.,' September, 1888), and these confirm generally the observations of Egoroff, Janssen, and Olszewski.

The accompanying diagram represents the absorption of 18 metres of ordinary oxygen gas at a pressure of about 97 atmospheres, that is, of a mass of oxygen rather greater than is contained in a vertical column of equal section of the earth's atmosphere. Under the circumstances of the experiment the absorptions A and B are very black, and the lines of which they are composed appear much broader than in the ordinary solar spectrum. The other bands are all diffuse at their edges, and, so far as we have observed, unresolvable into lines. It will be noted that the complete absorption of the



ultra-violet rays does not extend quite so far down as the limit of the solar spectrum, though it approaches that limit. There is a diffuse edge of gradually diminishing absorption succeeding the complete absorption, and this fact, together with the rapid diminution of the extent of the complete absorption with decrease of pressure, lead us to class this absorption of the extreme rays with the diffuse bands, which, according to Janssen, increase in intensity as the square of the density of the gas. If that be so, it is unlikely that the limit of the solar spectrum is due to the absorption of ordinary oxygen. For though we may suppose interplanetary space to be pervaded by materials similar to our atmosphere, yet they must be in such a state of tenuity that, although they may to some extent reinforce A and B, they will not add sensibly to the strength of the diffuse bands. Moreover, these bands, though identical in position, so far as the blue and less refrangible part of the spectrum is concerned, with bands observed by Brewster and others in the solar spectrum, are seen much more strongly through our tubes of compressed oxygen than they appear in the solar spectrum with a low sun. The ultra-violet bands, of which the one near N appears in our photographs nearly as strong as the band just above F, and that in the indigo, have not, so far as we are aware, been noticed in the solar spectrum. Probably they would appear if photographs were taken with small dispersion when the sun was low.

As the pressure in the tube diminished, the bands rapidly faded; that in the indigo, with an oscillation-frequency or wave-number about 2240, was the first to disappear, then those near L and O and that near E. At the same time the limit of the transmitted ultra-violet light advanced from an oscillation-frequency of about 3575 at 97 atmospheres, to 3710 at 50 atmospheres and 3848 at 23 atmospheres. At 20 atmospheres the three bands above C, D, and F, respectively, were still visible, though faint. B remained visible until the pressure was reduced to 2 atmospheres, and A could still be seen, but with difficulty, when the pressure of the 18 metres of oxygen was reduced to 1 atmosphere.

When atmospheric air was substituted for oxygen we found that 7 atmospheres was the limit of pressure at which we could certainly distinguish A, and 18 atmospheres the limit at which we could see B. It is a difficult matter to say exactly when an absorption becomes invisible, but the observations on air were made under the same circumstances as those on oxygen, and the two sets of observations were fairly comparable. With air at 75 atmospheres the three bands above C, D, and F, respectively, could all be seen, but that near C only with difficulty. The mass of oxygen and its *partial* pressure in the tube was in this case less by about one quarter than that which was required to bring out the bands when oxygen alone was used. The

cause of this may be that the development of the diffuse bands depends in some degree on the total pressure of the air, and not only on the partial pressure of the oxygen in it.

The mass of oxygen which when unmixed with nitrogen made A visible would correspond to that in the tube filled with air at 5 atmospheres, and that which made B visible would correspond to air at 10 atmospheres. The differences between these pressures and those which are actually needed to render A and B visible seem too great to be ascribed to errors of observation, and seem to indicate that the addition of the nitrogen has some effect on the absorptive action of the oxygen. On the other hand, Egoroff found that he could still distinguish A when the thickness of air at ordinary pressure was reduced to 80 metres ('Compt. Rend.,' vol. 101, p. 1144). This amount of air corresponds to rather less oxygen than our tube would hold at a pressure of 1 atmosphere. Differences in the sources of light, in the spectroscope, and the observers, would, however, count for a good deal in observations of this kind.

In order to try the influence of temperature on the absorption, the shorter of our experimental tubes, 165 cm. long, was surrounded by a jacket filled with a mixture of solid carbonic anhydride and ether, which was rapidly evaporated by means of a large air-pump. By this means the temperature would be reduced to -100° . The absorption of oxygen at several different pressures up to 104 atmospheres was observed through the cooled tube. We were not, however, able to detect any increase of intensity, or other change, in the absorptions which could be ascribed to the cooling. To try the effect of an increase of temperature, the 18-metre tube was surrounded by a jacket and heated up to 100° by steam. Heating appeared to render the diffuse bands rather more diffuse and less distinct. On the whole the influence of a change of temperature of 100° either way is slight.

We have observed repeatedly the absorption of liquid oxygen in thicknesses of 8 and 12 mm. Our observations confirm those of Olszewski. 8 mm. of liquid oxygen gives plainly the three diffuse bands above C, D, and F, respectively. With a thickness of 12 mm. we were not able to detect any more.

We observed the absorption produced by liquid oxygen on the one hand when it was cooled by its own evaporation until the tension of its vapour was only equal to that of the atmosphere, that is, to a temperature of -181° , according to Olszewski, and also when the temperature of the liquid was allowed to rise under pressure up to nearly the critical temperature. There appeared to be no appreciable difference in the absorption under these different circumstances when the oxygen was completely liquid, when it was near its critical temperature, and when it was completely gaseous; so far at least as

concerns the three principal bands, which were all that could be seen in the light transmitted by the liquid in a thickness of 12 mm.

It will be observed that taking the density of oxygen at -181.4° to be 1.124, as given by Olszewski, 12 mm. of the liquid would be equivalent to 9.37 metres of the gas at atmospheric pressure—hardly more than half the thickness required to make A visible. The experiments, therefore, point to the conclusion that gaseous and liquid oxygen have the same absorption-spectrum. This is a very noteworthy conclusion. For, considering that no compound of oxygen, so far as is known, gives the absorptions of oxygen, the persistency of the absorptions of oxygen through the stages of condensation to the state of complete liquidity implies a persistency of molecular constitution which we should hardly have expected.

In order to compare the absorption of ozone with that of oxygen we employed a tube 12 feet long, made of tinsplate fitted with glass ends and coated with paraffin on the inside. We could not use the 18 m. steel tube on account of the action of the ozone on the metal which rapidly reduced the proportion of ozone, and also because we could not conveniently cool it. Ozonised oxygen was passed into the tin tube for some time, while the ozoniser and the tube itself were cooled with ice and salt. The lime-light, viewed through the tube, looked very blue, and also the spot of light thrown from the tube on to a sheet of white paper was equally blue, indicating a considerable absorption of the less refrangible part of the spectrum. The absorption, so far as the visible rays are concerned, appeared to be of a general character, for the spectroscope revealed only four extremely faint absorption-bands. The centres of these bands were at about the wave-numbers 1662, 1752, 1880, and 1990, and their positions with reference to the bands of oxygen are indicated in the diagram. They were so faint as to be seen only with difficulty. When the hot carbon of an arc lamp was substituted for the lime-light they were rather more distinct, but the positions of the edges were undefinable. The light of a gas-lamp was insufficient to show them, and they were no better seen with a single-prism spectroscope of low dispersive power than with the spectroscope we employed for observing the oxygen. Only one of these bands, it will be seen from the diagram, is nearly coincident with an oxygen-band, namely, that near E, the faintest of the oxygen-bands. That at wave-number 1752 overlaps the strongest oxygen-band, but not at its strongest part, and has none of the peculiar character of its shading, abruptly increasing on the less refrangible side and slowly decreasing on the other side. Photographs of the spectrum (taken through a tube with quartz ends) showed that the ozone absorbed all the rays above the wave-number 3086—a point between Q and R—while partial absorption extended below Q. We may say, therefore, that we can

trace no identity between the absorptions of ozone and those of ordinary oxygen. There is no mere displacement of the bands, such as we sometimes get when a coloured substance is dissolved in different menstrua, nor any such a resemblance as we have between the absorption-bands of the different cobaltous salts derived from different acids.

The four bands which we see to be produced by ozonised oxygen correspond fairly with the 2nd, 3rd, 5th, and 6th of the bands described by Chappuis as due to ozone ('*Annales de l'École Normale*,' 2nd ser., vol. 11, May, 1882). These four bands, he says, are the first to be seen. We have failed to perceive any others with the 3.66 m. tube, though the oxygen was highly ozonised and maintained at a low temperature. None of the bands were of sufficient intensity to make themselves visible on our photographic plates.

It will be noted that the absorption by ozone extends far below the limit of the solar spectrum. We found, however, that by diminishing the proportion of ozone to oxygen in the tube the limit of the transmitted light was continually advanced, as already described by Hartley. The limit of the solar spectrum may, therefore, very well be determined by the average amount of ozone in the atmosphere, as Hartley supposes. The known variations in the limit of the solar spectrum may be taken as confirmatory of this hypothesis, although the comparatively small amount of those variations is certainly less than we should have expected if they measure the changes in the proportion of ozone in the atmosphere.

The absorptions of the class to which A and B belong must be those which are most easily assumed by the diatomic molecules (O^2) of ordinary oxygen. Whether oxygen in more complex molecules, as in ozone (O^3), may be capable of taking up the corresponding vibrations cannot easily be determined because we cannot isolate ozone; but since none of the compounds of oxygen with nitrogen, hydrogen or carbon, or, so far as known, with any other element, exhibit these absorptions, it is very probable that they are peculiar to the molecule O^2 . From this point of view it will be interesting to determine—as we hope to do shortly—whether liquefied oxygen, which we suppose to have more complex molecules, produces these absorptions. The corresponding spectrum of emission has not as yet been observed, probably because the agency employed to render the gas luminous breaks up the molecules into single atoms of oxygen.

As for the other class of absorption, the diffuse bands, since they appear to have intensities proportional to the square of the density of the gas, they must depend on a change produced by compression. This may either be the formation of more complex molecules, as for example O^4 , corresponding to the deviation from Boyle's law exhibited by oxygen gas, or it may be the constraint to which the

molecules are subject during their encounters with one another. Increase of temperature would affect the former, tending to diminish the number of complex molecules formed at a given pressure, but would have no effect on the latter, for though the number of encounters of the molecules in a given interval of time would be greater the higher the temperature, yet so long as the volume was unaltered the ratio of the duration of an encounter to that of free motion would be sensibly unaltered. So far as any change due to temperature has been observed, it is that a rise of temperature slightly weakens the diffuse absorptions.

Reverting to the compounds of oxygen, none of them show the absorptions of oxygen, not even the general absorption of the ultra-violet rays. Some of them, such as water and carbon dioxide, appear quite transparent to ultra-violet rays, while in others, such as nitrous oxide, which show a general absorption of the ultra-violet rays, the limit of transparency is different from that of oxygen. In other respects we may say that there is no resemblance between the absorptions of the compounds of oxygen and those due to oxygen itself. Some of the former have very definite and characteristic absorptions, such as the well-known spectra of the peroxides of nitrogen and chlorine, and we must regard these as indicating the rates of vibration which the molecules NO^2 and ClO^2 respectively are capable of easily taking up. The absence of the absorptions due to oxygen from all compounds of oxygen seems to indicate either that chemical combination is not, as has been supposed by some chemists, a temporary relation in which the molecular groupings are continually breaking up, to be formed anew with ever-changing elementary atoms; or, that the periods of dissociation are very small compared with the periods of association. For otherwise we should expect that such compounds of oxygen as CO^2 and NO^2 must always have amongst their molecules some molecules identical with those of oxygen and capable of taking up vibrations of the same period. At least we must conclude that little, if any, of the oxygen of these and other compounds is ever out of the influence of the other components.

We have re-examined the absorption-spectrum of N^2O^4 at various temperatures, and agree to the conclusion of Bell ('Amer. Chem. Journ.,' vol. 7, p. 32) that N^2O^4 , whether liquid or gaseous, effects only a general absorption at either end of the spectrum, and that the selective absorptions observed with it are due to the presence of NO^2 .

In order to obtain pure N^2O^4 , the tube in which the liquid was sealed was placed in a freezing mixture, and a large part of the liquid frozen; the remaining liquid was then drained as completely as possible into the other end of the tube, and sealed off.

It should be observed that the crystals of N^2O^4 appear colourless,

and that when they are melted the liquid and superincumbent vapour are of a very pale yellow colour. As the temperature rises both liquid and vapour become, as is well known, of a deep orange, and finally of a dark, reddish-brown colour. We examined the spectra produced by two thicknesses of liquid and vapour—(1) by that contained in a narrow tube about 1 mm. in diameter, and (2) by that in a tube about 1 cm. in diameter. At 15° to 20° the vapour in the narrow as well as in the wider tube showed the well-known absorption-spectrum of fine, dark lines; no absorption by the liquid in the narrow tube could be detected, and the liquid in the wide tube showed no fine lines, but several faint, very diffuse bands, unresolvable into lines with a spectroscope of three prisms. These bands had their maxima in places where the fine lines of the vapour were most intense and most closely set, so that it might be inferred that they were due to similar molecules in both cases, but that in the liquid the vibrations of these molecules were no longer sharply defined but modified by the constraint arising from the liquid state. Some parts, however, of the spectrum of the vapour, where the lines were closely set, did not appear to be represented by any definite bands in the liquid. The liquid absorbed a good deal of blue light in a continuous manner, while the vapour only absorbed it selectively. At the red end the limit of the visible spectrum was lower for the liquid than for the gas, that is, there was more absorption of red light by the vapour than by the liquid, so much so that below a certain point the absorption by the vapour appeared continuous.

The narrow tube was next immersed in a wider tube full of glycerine, which was gradually heated. As the temperature rose, the colour of both liquid and vapour deepened, the absorptions of the vapour were stronger, and the liquid gave the same bands as had been before observed with the greater thickness. At still higher temperature the absorption of blue light, both by liquid and vapour, diminished sensibly, until at 85° the groups of lines in the blue had pretty well disappeared from the spectrum of the vapour. In fact, at 85° there was no sensible difference between the actions of liquid and vapour on blue light, it seemed only some continuous absorption. At the red end the difference between the liquid and vapour remained quite as strongly marked as at lower temperatures, if anything, more so; and the absorptions in the orange, yellow, and green were unaltered. At 90° the lines of the vapour in the green began to fade, and at 100° they were very faint; but those in the orange, as well as the corresponding diffuse bands in the liquid, were as strong as before. There was still considerably more absorption of red light by the vapour than by the liquid, as if there were a strong absorption-band in the red of the vapour which was absent in the liquid.

As the temperature rose to 110° all the lines in the vapour had become faint, and at 115° they were no longer discernible, and there

was no difference between the spectra of liquid and vapour except in the red, and even here the difference was less marked than at lower temperatures. At 130° no distinction was observable between the spectra of liquid and vapour, there were no lines or bands in either, but a good deal of general absorption. Liquid and vapour were dark, and appeared much of a colour, but the meniscus at the junction was quite evident. The tube was further heated to 155° , but no further change was noticed in the spectrum. On gradually cooling the tube, at 112° the least refrangible band in the orange was seen coming in both in vapour and liquid, diffuse in both. At 100° the usual lines were well seen in the orange, yellow, and citron of the vapour, faint lines in the green, and none in the blue; and subsequently the appearances presented on heating followed in the reverse order.

A solution of N^2O^4 in carbon bisulphide gave, in a thickness of 7 or 8 cm., diffuse absorption-bands in the green and citron, ill-defined as in liquid N^2O^4 and in corresponding positions. In a thickness of 1 cm. these bands were no longer visible.

These observations bear out the supposition that pure N^2O^4 is without selective absorption of the visible rays, and that the absorption observed is due to NO^2 , both in the vapour and liquid, this absorption being modified in the liquid by the state of solution in which the molecules have much less freedom. As the temperature rises the proportion of NO^2 increases, and at the same time the density of the vapour increases and the freedom of motion of the molecules is diminished, they are less able to assume the more rapid vibrations, and those which they do assume become less sharply defined, so that the lines fade into bands and ultimately into a general absorption.

Taking Willard Gibbs's expression ("Equilibrium of heterogeneous substances," 'Connecticut Acad. Trans.,' vol. 3, p. 239) for the density D , in terms of the pressure in atmospheres p , at temperature t°

$$D = 3.178 + \theta - \sqrt{\theta(3.178 + \theta)},$$

$$\text{where} \quad \log_{10}\theta = 9.47056 - \frac{3118.6}{t + 273} - \log_{10}p,$$

as deduced from Deville and Troost's experiments, we find the density of NO^2 at 140° and 50 atmospheres, equal to 2, *i.e.*, equal to the density of N^2O^4 vapour at 60° and 1 atmosphere.

Dewar and Ansdell found the critical temperature for N^2O^4 to be 156° .

Scale of
wave-lengths.

wave numbers.

