Absorption Spectrum of Oxygen at High Pressures and the Existence of O_4 Molecules

AT high pressures gaseous oxygen exhibits a large number of absorption bands between 12610 and 2200 A., similar to those of the liquid[1]. In order to establish the nature of these bands one of us together with Finkelnburg[2] commenced about three years ago to measure the dependence of the intensity of absorption at high pressures on the oxygen concentration and on the presence of foreign gases. Some results have already been published[2,3]. We now wish to report briefly on the most important recent results, since *all* the bands have now been classified in the ways described below, and because the absorption spectrum of oxygen has been investigated by other workers[4,5]. The complete account of this work with the relevant data will appear shortly in *Zeitschrift für Physik*.

From the variation of the absorption with the concentration of oxygen and with the addition of foreign gases, conclusions may be drawn as to the carriers or processes which are involved in the production of the individual bands.

1. If the absorption varies *linearly* with the O_2-concentration and is *not* influenced by foreign gases, it must take place in an (almost) undisturbed O_2-molecule.

2. If the absorption varies with the *square* of the O_2-concentration and is *not* influenced by foreign gases, two O_2-molecules must take part in the act of absorption : that is, a collision pair O_2–O_2 or a loosely bound O_4 molecule.

3. If the absorption varies with the *square* of the O_2-concentration and its intensity *is* influenced by foreign gases without change of structure in the spectrum the absorption takes place during the collision in *one* O_2-molecule, in which the selection rules may be altered by the collision.

Corresponding to these considerations we actually find *three* groups of spectra :

Group 1. Intensity increases *linearly* with O_2-concentration ; no influence of foreign gases ; bands from 10320 to 6890 A. Attributed to forbidden transitions $^3\Sigma - {}^1\triangle$ and $^3\Sigma - {}^1\Sigma$ in the *normal* O_2-molecule.

Group 2. Intensity increases with the *square* of the O_2-concentration ; *no* influence of foreign gases ; bands from 6300 to 3289 A. Since *two* O_2-molecules are involved, and *only* two, these bands definitely correspond to absorption by an O_4-molecule. These bands coincide with those which were suggested by Ellis and Kneser[4], on the basis of their term values, to be electron-combination terms between two O_2-molecules. The present experiments confirm this suggestion, since the bands possess the *necessary* physical characteristics.

Group 3. Intensity increases with the *square* of the O_2-concentration, and, at constant O_2-concentration, *linearly* with the concentration of foreign gas. The intensity varies with the foreign gas, without alteration in the structure of the spectrum, the effect increasing, at constant partial pressure, in the order He, Ne, A, N_2, CO_2. Bands from 2859 to 2440 A. followed by continuous absorption. These bands have been attributed by Wulf[6] to the O_4-molecule. In a previous paper with Finkelnburg[2] it was shown that the vibration terms converge to the dissociation energy of the O_2-molecule in normal atoms, which led us to suggest that the absorption takes place in

one only of the colliding O_2-molecules. Evidence supplied by Warburg[7] on the influence of N_2 on the absorption led us to investigate the influence of other foreign gases with the above results, which confirm that suggestion. These bands therefore correspond to absorption by one O_2-molecule during the collision, by which it may be influenced, with either O_2 or a foreign gas molecule (or by loosely bound polarisation molecules O_2–X). A probable relationship of this system with the bands observed by Herzberg[8] in O_2 at 1 atm. will be decided by experiments now in progress.

Molar extinction coefficients for the various absorbing carriers can be calculated from these absorption measurements. The order of magnitude is 10^6 or 10^7 times smaller than the normal absorption (Schumann-Runge bands). The probability of the electron combination transition (group 2) must, on quantum mechanical grounds, be small compared with the probability of the normal transition. The values found for the molar extinction coefficients of group 2 therefore seem to us to be a further argument in favour of Ellis and Kneser's attempt to explain these spectra.

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Heavy Water and Water of Crystallisation

THE statement made by Prof. Erlenmeyer and Mr. Gärtner in NATURE of September 1, that, by crystallising sodium sulphate from solutions containing a few per cent of heavy water, the latter is divided practically equally between the water of crystallisation and solution, is in harmony with experiments I carried out some months ago. To ascertain if heavy water normally present in ordinary water could be concentrated by crystallisation, several litres of warm saturated solution of sodium sulphate were cooled. The crystals that separated were heated and the refractive index of the expelled water was determined with the Pulfrich refractometer as this was thought to afford a sensitive method of observing any change in the composition of small quantities of water. The dehydrated salt was added to the original solution and a fraction again crystallised out. This process was repeated many times until the original solution was reduced to small bulk. No change in the refractive index could be detected, however, between the initial and final fractions from either crystals or solution. It does not appear possible, therefore, to concentrate heavy water in this manner

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