The Diffraction of XRays by Liquid Oxygen

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reactions (1) and (2) require a third molecule of the hydrazine for ultimate decomposition giving over-all

$$2R + CH_3NHNHCH_3 = CH_4 + N_2 + NH_3$$
$$+ CH_3NH_2 + (CH_3N : CH_2)_2,$$

or

$$2R' + CH_3NHNHCH_3 = H_2 + N_2 + NH_3$$
$$+ CH_3NH_2 + (CH_3N : CH_2)_2.$$
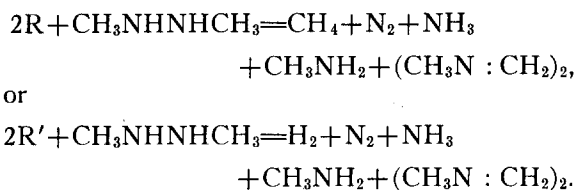
The observed quantum yield of 0.3 as opposed to the analytical yield of 3 is probably due to a reversal of (1a) or its equivalent. Henkin and Taylor[2] in the study of the addition of hydrogen atoms to azomethane found complete conversion of the azomethane to dimethylhydrazine even when the ratio of atomic hydrogen to azomethane was much less than 0.5 whereas, had the addition occurred entirely by steps involving atomic hydrogen, the ratio would have to have been at least two. It was obvious that some of the hydrogenation was occurring through hydrogen molecules and the reaction of the radical formed by addition of one hydrogen atom to azomethane, with hydrogen:

$$H_2 + CH_3NHNCH_3 \rightarrow CH_3NHNHCH_3 + H,$$
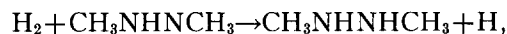
appeared very plausible as a Walden inversion type reaction. This reaction is equivalent to a reversal of (1a) and, since the maximum energy of activation of addition of hydrogen to azomethane was found to be 3-4 kcal., will occur quite readily reducing the quantum yield as found.

The recent observation of Birse and Melville[15] that the efficiency of the primary process in ammonia photolysis is 0.58 rather than one indicates, since no fluorescence has been detected in ammonia and the pressure dependence of the quantum yield is less than would be expected for any collisional process, that there is some mechanism for internal degradation of the energy. This might also be present in the hydrazine molecule.

[15] E. A. B. Birse and H. W. Melville, Proc. Roy. Soc. A175, 164 (1940).

The Diffraction of X-Rays by Liquid Oxygen*

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The x-ray diffraction pattern of liquid oxygen at 89°K shows an intense peak at $\sin \theta/\lambda = 0.157$, and very weak peaks at 0.35 and at 0.5; that at 62°K shows an intense peak at 0.159, and weak peaks at 0.35 and at 0.5. The atomic distribution curves have peaks at 1.3A, 2.2A, 3.4A, and 4.2A for 89°K, and at 1.25A, 2.15A, 3.2A, and 4.1A for 62°K. The first peaks are due to the interatomic distance in the diatomic molecule, the second may be due to triatomic oxygen, and the others may be due to higher molecular aggregates.

INTRODUCTION

A STUDY of the diffraction of x-rays by liquid oxygen is of interest not only for its contribution to the field of x-ray diffraction, but also for the information it may supply to our knowledge of molecular aggregates in liquid oxygen. The present work was undertaken to obtain as complete a diffraction pattern of liquid oxygen as possible and to analyze this pattern for the atomic distribution curve. This has been done for liquid oxygen at 89°K and at 62°K.

One of the earliest studies in the field of x-ray diffraction by liquids was done with liquid oxygen by Keesom and de Smedt. In their first work,[1] copper radiation filtered through nickel was used in an evacuated camera of 2.75-cm radius. Two peaks in the intensity curve were reported, the main peak at $\sin \theta/\lambda = 0.151$ and a weak second-

* A preliminary report of this work was presented at the December, 1940 meeting of the American Physical Society.

[1] W. H. Keesom and J. de Smedt, Proc. Amst. Akad. Sci. 25, 118 (1922).

ary peak at sin $\theta/\lambda = 0.254$. In their second work,[2] molybdenum radiation filtered through zirconium was used, enabling them to include larger values of sin θ/λ. They reported, in this case, the main peak at sin $\theta/\lambda = 0.154$, a weak second peak at sin $\theta/\lambda = 0.239$ on six out of nine films, and a somewhat questionable peak at sin $\theta/\lambda = 0.35$. Using Ehrenfest's relation,[3] $a = 7.72\lambda/4\pi \sin \theta$, and the angle θ corresponding to the main peak, they calculated "a" and correlated this with the distance between molecules in a close-packed system. The primary result of this work was that it indicated that the intense peak was probably due to interference of x-rays diffracted by neighboring molecules.

In view of the recent advances in both experimental technique and theoretical interpretation in this field, a repetition and extension of the early work of Keesom and de Smedt is clearly desirable. This attempt at an application of these newer techniques and interpretation has been made in the present work.

EXPERIMENTAL

Two types of system were used to obtain a sample of liquid oxygen, one which will be referred to as an open system, and one which will be referred to as a closed system. In using the open system, a large amount of liquid oxygen was prepared from tank oxygen with no further purification, and from pressure and temperature measurements, assuming it to have nitrogen as an impurity, its purity was found to be better than 96 percent. This liquid was transferred to a Dewar flask fitted at the bottom with a very thin-walled Pyrex glass tube 7.7-mm diameter in an evacuated camera of 9.53-cm radius, as shown in Fig. 1. As the oxygen evaporated, more was added, and for the low temperature work, a pump reduced the pressure over the oxygen. In using the closed system, which was nearly the same as that used for argon,[4] tank oxygen was given some further purification and introduced into the liquid air-cooled capillary at approximately one atmosphere. In this case, the reduced tempera-
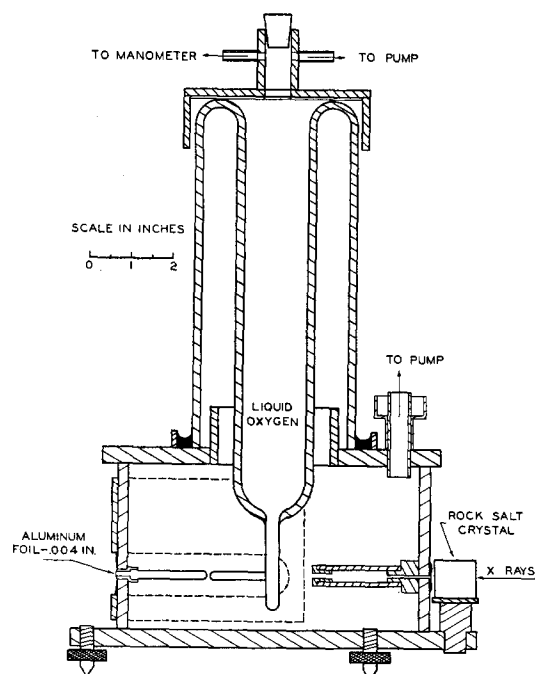

FIG. 1. A diagram of the evacuated camera using the "open system."

ture was attained by pumping on the liquid air in the Dewar flask.

Mo $K\alpha$ radiation reflected from a rocksalt crystal was collimated in part by the crystal, and in part by two slits and the width of the beam at the sample was about 1.5 mm. A photographic film recorded the diffracted x-rays and exposures of 20 to 30 hours gave adequate densities on the films. A Leeds and Northrup recording microphotometer was used to convert film densities to relative intensities, in the usual manner.

The relative intensity curves were corrected for polarization[5] and for absorption. The absorption correction used was that for a cylindrical sample completely bathed in a parallel beam of x-rays, as discussed by Blake.[6] In the present case, the sample was only partially irradiated, and hence this correction is approximate. However, it has been shown[7] that for sodium, with cylindrical samples having diameters of from one to five times the width of the beam, there is little difference in the ratio of the intensity of scatter-

[2] W. H. Keesom and J. de Smedt, Proc. Amst. Akad. Sci. **26**, 112 (1923).

[3] P. Ehrenfest, Proc. Amst. Akad. Sci. **17**, 1184 (1915).

[4] A. Eisenstein and N. S. Gingrich, Phys. Rev. **58**, 307 (1940).

[5] S. Katzoff, J. Chem. Phys. **2**, 841 (1934).

[6] F. C. Blake, Rev. Mod. Phys. **5**, 180 (1933).

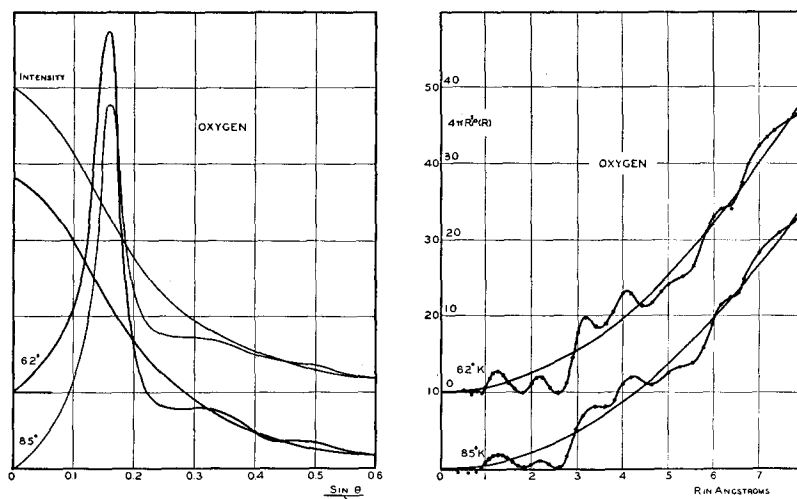[7] G. A. Mitchell, unpublished work.

FIG. 2(a). (Left.) The x-ray diffraction patterns of liquid oxygen at 89°K and at 62°K. (b). (Right.) The atomic distribution curves for liquid oxygen at 89°K and at 62°K.

ing at the main peak to that at angles as large as were used here. It is believed, therefore, that this approximation has introduced no serious error. The curve corrected in this way and for incoherent radiation was fitted to the independent coherent scattering curve for making an analysis of the pattern.

Seven exposures were made with the oxygen at 89°K, and six were made at 62°K, this lower temperature being attained by pumping on the liquid oxygen or on the liquid air. Some of the films were heavily over-exposed in order to disclose features of the pattern at large angle where the intensity is normally very low. Typical curves are reproduced in Fig. 2(a). At each temperature, the pattern consists of one intense peak and two secondary prominences more in the nature of plateaus than of peaks. At 89°K, these occur at values of $\sin \theta/\lambda$ of 0.157, 0.35, and 0.5, while in the 62°K case, they occur at 0.159, 0.35, and 0.5. The position of the main peak at 89°K, 0.157, is slightly higher than the two values given by Keesom and de Smedt, 0.151[1] and 0.154,[2] but it is believed that with the larger camera here used, the present value is likely to be more nearly correct. Their second peak at 0.254 or 0.239 could not be found and it is believed that there is no peak near this position. Their third peak[2] at 0.35, however, does check well with a prominence found in the present work.

ANALYSIS OF PATTERNS

Fourier analyses of the patterns were made according to the method of Debye and Menke[8] giving the atomic distribution of atoms about any atom in the liquid. The expression used is derived elsewhere[9] and is

$$4\pi R^2 \rho(R) = 4\pi R^2 \rho_0 + 2R/\pi \int_0^\infty Si(S) \sin Rs\, ds,$$

where $i(s)$ is a function obtained from the experimental data, $S = 4\pi \sin \theta/\lambda$, θ is half the scattering angle, ρ_1 is the average density of atoms, $\rho(R)$ is the actual density of atoms, and R is the distance in angstroms from the origin atom. Four analyses were made for 89°K oxygen and five for 62°K oxygen. These various analyses were made for different patterns and for different fittings on a given pattern. In about half the cases, the integral was evaluated by plotting $Si(S) \sin Rs$ against S and integrating graphically, and for the remaining ones, the integral expression was evaluated by the method of trigonometric interpolation.[10] As is to be expected, the two methods gave very closely the same result for a given curve and fitting. The large number of analyses was made because of the unusual appearance of

[8] P. Debye and H. Menke, Physik. Zeits. 31, 797 (1930).
[9] B. E. Warren, J. App. Phys. 8, 645 (1937).
[10] C. Lanczos and G. C. Danielson, Phys. Rev. 55, 242 (1939).

the distribution curve with many prominent peaks. An averaged curve for each temperature is shown in Fig. 2(b). In all the curves obtained from these analyses, most of the essential features shown in the figure were reproducible up to a little over 5A, but beyond that distance the various analyses differed considerably, and hence, no confidence is placed in the curves beyond 5A. At less than this distance, the first four peaks appeared in all cases at approximately the same positions but with somewhat different heights. This feature appeared to be unusually dependent upon the fitting of the corrected experimental curve to the independent coherent curve for the peaks between 3A and 5A. The first peak was reproducible to within about 5 percent of the reported value for position and to within about 10 percent of the reported value for the area and the weak second peak persisted under all fittings with variations in position and area slightly greater than for the first peak.

DISCUSSION OF RESULTS

The positions of the peaks for the 89°K case are 1.3A, 2.2A, 3.4A, and 4.2A, and for the 62°K case they are 1.25A, 2.15A, 3.2A, and 4.1A The area under the first peak, for 89°K, is 1.08, and that for 62°K is 1.18, indicating that there is one nearest neighbor, or that liquid oxygen has a fundamental diatomic aggregate closely similar to the diatomic molecule in the gas, for which each atom has one nearest neighbor at about 1.22A.[11, 12] From this analysis, one cannot be sure that there is a significant difference between 89°K and 62°K, in the positions of this first peak, i.e., between 1.3A and 1.25A. The area under these peaks is slightly more than one, but it is believed that the precision and reproducibility of this peak is hardly great enough to give this difference much significance. Liquid oxygen is the only element thus far to show a second discrete peak, which occurs here at 2.2A and at 2.15A in the cases of 89°K and 62°K, respectively, and the interpretation of this second peak, if it is real,

is somewhat difficult. It is true that from the assigned structure of ozone,[13] O_3, the first interatomic distance is between 1.25A and 1.30A and that the second distance is about 2.2A, but the amount of O_3 present in liquid oxygen is normally very small. On the other hand, irradiation of liquid oxygen is known[14] to enhance the amount of O_3 present, which would contribute both to the presence of this peak and to an area under the first peak greater than one, since one atom of O_3 would have two neighbors at about 1.3A. Thus the distribution curves here obtained are consistent with the assumption that there was O_3 in the samples used, though the data are not considered sufficiently well known to warrant making quantitative deductions from this result.

The third and fourth peaks appear to be related to distances between oxygen atoms in larger aggregates of oxygen molecules. From studies of the magnetic susceptibility and of the absorption spectra of oxygen,[15] it appears probable that O_4 may exist in the liquid in a considerable amount. Vegard[16] has determined the crystal structure of the γ-form of crystalline oxygen, and he states that the x-ray diffraction pattern was typical of that for a cubic lattice with rotating molecules. The O_2 molecules are grouped into pairs along the trigonal axis and the distance between the two molecules of a pair is given as 3.48A. In the present work, two distances, about 3.4A and 4.2A, appear fairly predominantly, and it is not unlikely that the former may have some relation to Vegard's value, 3.48A, though an unambiguous interpretation of both these peaks appears somewhat difficult.

ACKNOWLEDGMENTS

[11] A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand Company, 1935), p. 161.
[12] G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice Hall, 1939), p. 491.

[13] W. G. Penney and G. B. B. M. Sutherland, Proc. Roy. Soc. **A156**, 672 (1936).
[14] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* (Longmans, Green and Company, 1922), p. 880.
[15] M. and B. Ruheman, *Low Temperature Physics* (Cambridge University Press, 1937), p. 228.
[16] L. Vegard, Nature **136**, 720 (1935).