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THE ABSORPTION SPECTRUM OF SULPHUR TRIOXIDE.

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No measurements of the absorption spectrum of pure SO_3 have been recorded. Dutt¹ studied the absorption of SO_2 - SO_3 mixtures and claimed to be able to eliminate the effect of the former. "Continuous absorption" from 3300 to 2600 Å and from 2300 Å downwards was found and attributed to SO_3 . The present investigation in which the SO_2 content is reduced to a very low value, has not confirmed these conclusions.

Experimental.

The absorption spectrum of SO_3 was examined by means of a small Hilger quartz spectrograph, E. 370, and later by a medium Hilger quartz, E. 3. Wave-lengths were determined by comparison with a copper arc. A hydrogen discharge tube was used as a source of continuous ultra-violet

¹ A. K. Dutt, Proc. Roy. Soc., 1932, 137A, 366.

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light. Absorption tubes of 54 cm. and 346 cm. lengths were used. Joints between quartz and glass were sealed with sodium silicate and aged by leaving in contact with gaseous SO_3 for some days. As SO_3 attacks mercury even when dry, pressures were measured by means of a calibrated quartz Bodenstein gauge.²

The SO_3 was prepared by distilling *in vacuo* pure fuming sulphuric acid and fractionating between traps cooled in liquid air. The first and last fractions were rejected by sealing off the requisite traps. Removal





FIG. 1.—The absorption curve of sulphur trioxide (full line) and of sulphur dioxide (dotted line—approximate curve).

of the dioxide by fractionation is insufficient as it is reproduced rapidly during a measurement by photodecomposition of the SO_3 . Complete elimination of the absorption bands of SO_2 down to 2200 Å. was obtained by streaming the purified gas rapidly through the absorption tubes between traps at the ends.

The first photographic exposure was taken with liquid air on the traps and the intensity of the light reduced a definite amount by means of a rotating sector. The liquid air was then removed and the desired pressure

² J. W. Goodeve, Trans. Faraday Soc., 1934, 30, 501.

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and velocity of flow of SO₃ obtained by careful regulation of the temperatures of the end traps. With the sector open a second exposure through the gas was taken in an adjacent position on the photographic plate. A third adjacent spectrum was taken identical to the first, to test the constancy of the light source. The extinction coefficient α was obtained for the wave-length of the "match point," by the equation

$$\alpha = \frac{\mathbf{I}}{p \cdot l} \cdot \log_{10} \frac{I_o}{I_r} = \frac{\mathbf{I}}{p \cdot l} \cdot \log S,$$

where p is the pressure in mm. of Hg, l the length of the tube in cm., and S the sector angle. The molecular extinction ϵ was calculated by the equation,

$$\epsilon = \frac{\mathbf{I}}{cl} \cdot \log_{10} S,$$

where c is the concentration in gram molecules per litre, calculated assuming the temperature to be 18° C. Pressures in the range of 1 to 160 mm. were obtained and could be kept constant to within 5 per cent., except below 10 mm.

Results.

The absorption spectrum of sulphur trioxide was observed between 3000 and 2200 Å. and found to consist of weak diffuse bands superimposed on a continuous background. The logarithms of the extinction coefficients



FIG. 2.—The absorption in the region of the diffuse bands.

obtained as described above are shown in Fig. 1, plotted against frequency. It was found impossible to obtain reliable measurements below 2200 Å. owing to the very strong SO₂ absorption in this region.

The observed diffuse bands were of an unusual type. The maxima of absorption were flat and the minima sharp as indicated diagrammatically in Fig. 2. The distance between the minima was found to be approximately constant and equal to 430 W.N. It may be possible at some time to correlate this with a fundamental frequency of the molecule. The diffuse bands appear to extend to about 2700 A. but above 2500 Å. they could not be measured with certainty. These bands cannot be attributed to SO₂ as they occur at the position of minimum absorption of the latter. It is unlikely that they are due to other impurities as they always appeared with the same intensity under the same conditions. They are probably predissociation bands.

Discussion.

The observations recorded here indicate that the absorption of SO_3 is of a different character and in a different position from that found

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by Dutt. He claims that "it is possible to eliminate the SO_2 bands from the plate by putting an excess of oxygen in the absorption chamber and then filling it up with SO_3 vapour. According to the law of mass action the partial pressure of SO_2 is very considerably reduced by the addition of O_2 ." It is well known that even in the presence of a catalyst SO_2 does not react with oxygen at room temperature.

Approximate values of the extinction coefficients of SO_2 have been calculated from the results of Garret ³ and from a photometric curve of Kornfeld and Weegmann.⁴ These are indicated by the broken line in Fig. 1. It is seen that at some wave-lengths one part in one thousand of SO_2 is sufficient completely to mask the absorption of SO_3 . The coincidence between the limits of absorption found by Dutt and those for SO_2 , coupled with the above argument, leads to the conclusion that his observations were due to the presence of the dioxide.

The decomposition of SO₃ into SO₂ and normal O atoms requires $81\cdot3$ K cal. (Landolt-Börnstein). This corresponds to a wave-length of 3500 Å. It is probable that this is the primary photochemical process in most of the ultra-violet range. Coehn and Becker ⁵ found that SO₃ decomposes photochemically by light transmitted through "Uviol-glass" (transparent ⁶ to about 2500 Å). At wave-lengths below 2500 Å, it is possible for excited D oxygen atoms to be produced.

Our thanks are due to Professor Donnan for his interest and encouragement in this work.

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- ³ C. S. Garret, Phil. Mag., 1916, 31, 505.
- ⁴ Kornfeld and Weegmann, Z. Elektrochemie, 1930, 36, 789.
- ⁵ Coehn and Becker, Z. Elektr., 1907, 13, 545; Z. physik. Chem., 1910, 70, 88.
 - ⁶ Weigert, Opt. Methoden d. Chemie, p. 54.