[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, THE CALIFORNIA INSTITUTE OF TECHNOLOGY, NUMBER 638]

The Molecular Structure of Selenium Dioxide Vapor

BY K. J. PALMER AND NORMAN ELLIOTT

Electron diffraction photographs of selenium dioxide vapor were taken and interpreted in the way already described in the literature.[1] The photographs showed five well-defined but rather broad maxima, whose relative positions and intensities were approximately those to be expected for a diatomic molecule. This is due to the relative unimportance of the oxygen–oxygen scattering as compared to the selenium–oxygen scattering. The values of s_0 $[=(4\pi \sin \theta/2)/\lambda]$, the visually measured intensities (I_v), and C $(=I_v s_0^2 e^{-as(0)^2})$ are given in Table I. The values of C and s_0 were used in calculating a radial distribution curve as recently suggested,[2] and the resulting curve is reproduced in Fig. 1. The well-defined peak at 1.61 Å. corresponds to the selenium–oxygen distance; the other peaks lying farther out are too unreliable to be of any importance in determining the oxygen–oxygen distance.

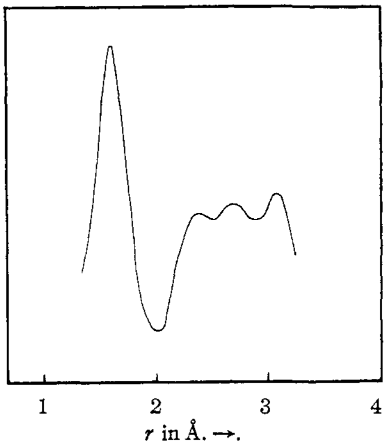

Fig. 1.—Radial distribution curve for selenium dioxide.

Two simplified intensity curves were calculated, one for a linear model and the other for a model having an O–Se–O angle of 120°. The latter is reproduced in Fig. 2. The two curves are so nearly identical, both with regard to shape and position of the maxima, that it is impossible from a qualitative comparison with the photographs to make a choice between them. The quantitative comparison of s_c and s_0 given in Table I leads to the selenium–oxygen distance 1.61 ± 0.03 Å. in exact agreement with the radial distribution curve. In analogy with sulfur dioxide, the O–Se–O angle is probably close to 125°. Using this value for the angle the oxygen–oxygen distance is 2.86 Å.

TABLE I

Max.	Min.	I_v	C	s_0	s_c[a]	s_c/s_0
1		10	33	5.185	4.32	(0.833)[b]
	2			6.800	6.00	.882
2		7	50	8.771	7.88	.898
	3			10.700	9.55	.893
3		4	38	12.404	11.28	.909
	4			14.690	13.15	.895
4		2	17	16.652	14.75	.886
	5			18.458	16.50	.894
5		1	6	20.391	18.37	.901
				Average		0.895
				Average deviation		.006

Se–O = (1.80)(0.895) = 1.61 ± 0.03 Å.

[a] Calculated for the model with Se–O = 1.80 Å. and the angle O–Se–O = 120°.

[b] Not included in the average.

Discussion.—The value 1.61 Å. is considerably lower than the sum of the double bond radii of selenium and oxygen. Assuming a double bond factor of 0.93 for the third row elements, the selenium–oxygen double bond distance is 1.66 Å. On correction for the formal charge effect as suggested by Elliott,[3] this is reduced to the value 1.64 Å. If one considers only the electronic structures representing resonance between a selenium–oxy-

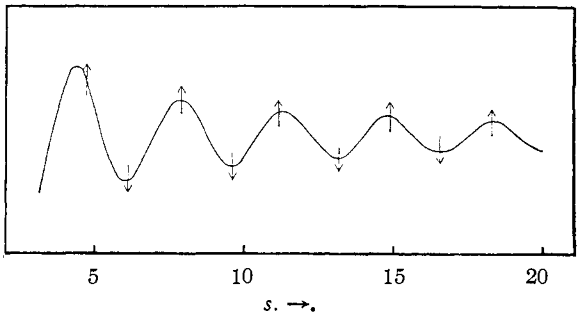

Fig. 2.—Intensity curve for selenium dioxide, calculated for Se–O = 1.80 Å. and O–Se–O angle = 120°. The positions of the arrows, indicating measured maxima and minima, have been decreased by 8.9% to indicate the quantitative agreement with the final model with Se–O = 1.61 Å.

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(1) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

(2) V. Schomaker and C. Degard, to be published soon.

(3) Norman Elliott, THIS JOURNAL, **59**, 1380 (1937).

gen double bond and a single bond, then each bond would possess 50% double bond character. The interatomic distance found by application of the usual resonance curve is 1.69 Å. The discrepancy between this value and that observed is probably due to the importance of electronic structures in which the oxygen is bonded to the selenium atom by a triple bond. A bond of this type is possible because selenium is not restricted rigorously by the octet rule.

The observed sulfur–oxygen distance in sulfur dioxide bears about the same relation to the radii as that found for selenium dioxide, and the two molecules are probably closely similar in electronic structure.

The selenium dioxide crystal[4] does not contain discrete SeO_2 molecules, but instead consists of infinite chains. The observed Se–O distances in the crystal, 1.78 Å. and 1.73 Å., have been discussed by McCullough.

We are indebted to Dr. James D. McCullough for furnishing us with the sample of selenium dioxide, and to Professor Linus Pauling for his aid and criticism during the course of this investigation.

Summary

Electron diffraction photographs of selenium dioxide vapor have been interpreted to lead to the value 1.61 ± 0.03 Å. for the Se–O distance. The value of the angle O–Se–O could not be determined.

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[4] James D. McCullough, THIS JOURNAL, **59**, 789 (1937).

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The Heat Capacities, Entropies, and Heats of Solution of Anhydrous Sodium Sulfate and of Sodium Sulfate Decahydrate. The Application of the Third Law of Thermodynamics to Hydrated Crystals

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It is known that true equilibrium is not attained when ice is cooled to very low temperatures, and that consequently the entropy of ice as calculated from low temperature heat capacity data in the usual manner is incorrect.[1] The reason for this behavior has been ascribed to a randomness in the position of the protons which form hydrogen bonds between the oxygen atoms.[2] The question then arises as to whether a similar situation may not exist in hydrated crystals, particularly those containing a relatively large number of loosely held molecules of water. In order to investigate this possibility, and in addition to obtain an accurate value for the entropy of sulfate ion, we have measured the heat capacity of both anhydrous sodium sulfate and its decahydrate from 14 to 300°K., and have determined the heat of solution in water for both substances.

Materials.—Samples of sodium sulfate decahydrate were prepared by recrystallization of the "C. P." salt, and were dried in a vacuum desiccator over anhydrous sodium sulfate. A slight "premelting" effect observed below the 32.38° "transition" can be explained on the basis of less than 0.1% of impurity which is soluble in the solution present above 32.38°. The sample of decahydrate used in the heat capacity measurements (wt. 58.715 g. *in vacuo*) contained a very small excess (0.02 g.) of water which was determined both by analysis and by the high heat capacity value obtained at the ice-point, the two results being concordant. Correction was made for its presence as ice below 0°C. and as water above. The samples of decahydrate used in heat of solution measurements were the same except that no appreciable excess of water was present.

The anhydrous sodium sulfate was prepared by dehydration of the decahydrate under vacuum at temperatures below 80°C. A sample of 115.52 g. (wt. *in vacuo*) was used in the heat capacity measurements. A high heat capacity measurement near 32.38°C. indicated the presence of a trace (less than 0.1%) of the decahydrate, for which suitable correction was made.

Apparatus.—The cryostat and block assembly which have been used for some time and have been described previously[3] were retained for this investigation. However, a new calorimeter containing a strain-free platinum resistance thermometer was constructed. The platinum thermometer serves the purposes of both the copper–constantan thermocouple and the gold resistance thermometer (non-strain-free) which were used previously, thus considerably simplifying both the measurements and calculations. Also it is hoped that a somewhat improved temperature scale may result, although to date only the initial steps have been taken in this direction. As yet the platinum

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[1] Giauque and Ashley, *Phys. Rev.*, **43**, 81 (1933); Giauque and Stout, THIS JOURNAL, **58**, 1144 (1936).

[2] Pauling, *ibid.*, **57**, 2680 (1935).

[3] Latimer and Greensfelder, *ibid.*, **50**, 2202 (1928); Brown Smith and Latimer, *ibid.*, **58**, 1758 (1936).