

for  $K_f$  at infinite dilution. In any case, such a value would be of no practical importance in the determination of molecular weights.

To verify the results obtained by the Rast method cooling curves were obtained for pure *d*-camphor and for solutions of naphthalene in camphor. Comparatively large quantities of camphor (29 g.) were used. The camphor or the solution was melted in a small cylindrical Dewar flask by an electrically heated platinum coil immersed in it and its freezing point was found by the conventional time-temperature curve method. In order to obtain a sharp break it was found necessary to insulate the Dewar flask by suitable packing. The freezing point of the pure *d*-camphor found by this method, 178.4°, checked closely with that obtained by the Rast method, 178.6°. Naphthalene solutions of molal concentrations 0.031, 0.11 and 0.21, gave freezing point depressions of 1.25, 4.45 and 8.55°, respectively. The values of  $K_f$  calculated from these depressions are 46.4, 41.3 and 39.7, corresponding closely with the values for the same concentrations as determined by the Rast method. The results obtained with the Rast method are probably more accurate.

From these results it is obvious that in order to determine the molecular weight of an *unknown* substance with camphor as solvent, care must be taken to use solutions of concentrations sufficiently high to justify the use of the constant 39.7. A lower limit in concentration of 0.2 *m* is indicated. In order to ascertain what constitutes a 0.2 *m* solution a rough determination of

the molecular weight must first be carried out.

The change in  $K_f$  over the low concentration range presents a paradoxical situation. The expression relating  $K_f$  with the heat of fusion,  $L_f$ , of the solvent, *viz.*

$$K_f = RT^2/1000L_f$$

is presumed to apply most accurately to solutions of *low* concentrations. But applying this equation to the experimentally determined heat of fusion of camphor,  $1630 \pm 60 \text{ cal.} \times \text{mole}^{-1}$ , Frandsen<sup>10</sup> found  $K_f$  to be  $37.7 \pm 1.4 \text{ deg., mole}^{-1}, \text{ kg.}$ , a value very close to that found experimentally for the *higher* concentration range.

No satisfactory explanation for the variation of  $K_f$  with concentration has been conceived. Pirsch<sup>8</sup> suggests the possibility of cleavage of the solute but the close concordance of the  $K_f$  values for different solutes at low concentrations militates against this view. The results would also be explained by assuming a partial association of the solvent in low solute concentrations.

### Summary

It has been shown that the uncertainty regarding the value of the molal depression constant for camphor has been caused by the fact that the constant changes with changing concentration. The value of the constant 39.7 deg., mole<sup>-1</sup>, kg. holds for concentrations above 0.2 *m*; below this concentration the constant increases with decreasing concentration to a maximum of about 50.

(10) Frandsen, *B. S. Jour. of Res.*, **7**, 477 (1931).

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## An Electron Diffraction Study of Hydrogen Peroxide and Hydrazine

BY PAUL A. GIGUÈRE<sup>1</sup> AND VERNER SCHOMAKER

### Introduction

We undertook the investigation of the hydrogen peroxide and hydrazine molecules in order to determine the lengths of the oxygen-oxygen and nitrogen-nitrogen covalent single bonds which they contain, and so directly to fix the values of the corresponding single-bond covalent radii which had previously been estimated only by indirect methods.<sup>2</sup> Because of the relatively

low scattering power of hydrogen atoms nothing could be learned about the other interatomic distances in hydrogen peroxide, and only rough values were found for hydrazine. We wanted also to study hydroxylamine, but its instability was even more troublesome than that of hydrogen peroxide and we gave up our efforts to photograph it after a few unsuccessful attempts.

The covalent radii of oxygen and nitrogen (and

(1) Present address: Laval University, Quebec, Canada.

(2) (a) L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934);

(b) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y.

fluorine) were of particular interest because of the positive deviations from the additivity rule<sup>2</sup> which are found for many bonds involving two highly electronegative atoms when the radius values assigned by Pauling and Huggins are used. Some of the examples of this situation were provided by fluorine<sup>3</sup> itself, the fluorine and chlorine monoxides,<sup>4a</sup> and the methyl chloramines.<sup>4b</sup> The values found in this investigation for the O-O and N-N bonds are considerably greater than the corresponding sums of the Pauling-Huggins radii, as was anticipated. In a discussion<sup>5</sup> based in part on preliminary results of this study, it was shown that these positive deviations from additivity can be avoided by taking as twice the covalent radii for the nitrogen, oxygen and fluorine atoms the bond lengths found respectively in hydrazine, hydrogen peroxide and fluorine. Satisfactory quantitative agreement was then obtained for most bonds by use of a correction for the difference in electronegativity of the atoms involved.

Since our final values,  $r_{\text{N-N}} = 1.47 \pm 0.02 \text{ \AA.}$ , and  $r_{\text{O-O}} = 1.47 \pm 0.02 \text{ \AA.}$ , confirm our preliminary results (1.47 and 1.48  $\text{\AA.}$ ), nothing needs to be added to this discussion now. It is not clear whether the irregularity of the sequence of reported values for ethane, hydrazine, hydrogen peroxide, and fluorine (1.54, 1.47, 1.47, 1.43) is significant; perhaps the correct value for hydrogen peroxide is somewhat smaller as is suggested by the crystal structure of "hyperol" (see below). It is possible, therefore, that the oxygen radius suggested by Schomaker and Stevenson<sup>5</sup> should be reduced (by 0.01  $\text{\AA.}$ ) to 0.73  $\text{\AA.}$

A value of about 1.45  $\text{\AA.}$  for the O-O bond was suggested by the approximate results<sup>6</sup> obtained from crystal structure investigations of the peroxydisulfates. (The value  $1.31 \pm 0.03 \text{ \AA.}$  reported for the peroxide ion by Bernal and co-workers<sup>7</sup> on the basis of packing considerations and the positions found for the heavy atoms in powders of strontium peroxide and barium peroxide is undoubtedly greatly in error.) The third-harmonic O-H bands<sup>8</sup> of hydrogen peroxide and

the crystal structure<sup>9</sup> of "hyperol" ( $\text{H}_2\text{O}_2 \cdot (\text{NH}_3)_2 \cdot \text{CO}$ ) provide considerable information about the O-H distance, the bond angles, and the question of internal rotation in the hydrogen peroxide molecule, justifying the model assumed in the interpretation of our photographs; moreover, the former investigation confirms the long O-O bond, and the latter leads to a precise value  $1.46 \pm 0.03 \text{ \AA.}$ , which agrees well with that here reported.

The only other nitrogen-nitrogen single bond distance known to us is that found in hydrazinium difluoride, 1.42  $\text{\AA.}$ <sup>10</sup> The difference between this value and that for hydrazine no doubt arises from the widely different situations of the nitrogen atoms in the two cases; probably the formal charge effect<sup>1b,10,11</sup> plays an important role in the hydrazinium difluoride crystal, where each nitrogen atom bears a positive formal charge and has essentially five, rather than three, close neighbors.

Badger's rule,<sup>12</sup> with the bond force constants estimated from the observed vibrational frequencies of hydrogen peroxide and hydrazine, suggests values of about 1.5  $\text{\AA.}$  for both the O-O and N-N bonds.

### Experimental

Hydrogen peroxide was prepared from commercial 30% Perhydrol solution by fractional distillation under reduced pressure in an all-Pyrex apparatus. The sample used for the final photographs was found by titration with potassium permanganate to be 99.6% pure, and showed no tendency to decompose at room temperature. In order to obtain sufficiently dense electron diffraction photographs, however, it was necessary to heat the liquid nearly to the boiling point (about 150°) where after a short induction period hydrogen peroxide ordinarily decomposes rapidly. Using the glass high temperature nozzle illustrated in Fig. 1, and adding sodium metaphosphate solution as an inhibitor, however, we ultimately succeeded in suppressing this high temperature decomposition and obtaining satisfactory photographs.

The 2-cc. bulb A of the high temperature nozzle (Fig. 1) is connected by a standard taper ground joint to the three-way stopcock B which leads through the side arm C to an

(3) L. O. Brockway, *THIS JOURNAL*, **60**, 1348 (1938); M. T. Rogers, V. Schomaker and D. P. Stevenson, *ibid.*, **63**, 2610 (1941).

(4) (a) L. E. Sutton and L. O. Brockway, *ibid.*, **57**, 473 (1935); (b) D. P. Stevenson and V. Schomaker, *ibid.*, **62**, 1270 (1940).

(5) V. Schomaker and D. P. Stevenson, *ibid.*, **63**, 37 (1941).

(6)  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and  $\text{Cs}_2\text{S}_2\text{O}_8$  (1.46  $\pm$  0.15  $\text{\AA.}$ ), W. H. Zachariasen and R. C. L. Mooney, *Z. Krist.*, **88**, 63 (1934);  $\text{K}_2\text{S}_2\text{O}_8$  (1.40  $\text{\AA.}$ ), R. C. Keen, *ibid.*, **91**, 129 (1935).

(7) J. D. Bernal, E. Djalilowa, I. Kasarnowsky, S. Reichstein and A. G. Ward, *ibid.*, **92**, 344 (1935).

(8) L. R. Zumwalt and P. A. Giguère, *J. Chem. Phys.*, **9**, 458 (1941).

(9) Chia-Si Lu, E. W. Hughes and P. A. Giguère, *THIS JOURNAL*, **63**, 1507 (1941). This article contains a review of earlier work pertaining to the molecular structure of hydrogen peroxide.

(10) M. Kronberg and D. Harker, *J. Chem. Phys.*, **10**, 309 (1942).

(11) N. Elliott, *THIS JOURNAL*, **69**, 1382 (1937).

(12) R. M. Badger, *J. Chem. Phys.*, **3**, 710 (1935).

auxiliary vacuum pump, or through the thick-walled tube D to the diffraction chamber. The nozzle is attached to the diffraction chamber by the metal taper E which supports the tube D by means of a packing nut and lead gasket. This seal is convenient and sturdy, and under the conditions of our experiment remained adequately vacuum tight. To avoid condensation the ground joint, stopcock, and tube D were electrically heated with Nichrome windings. The stopcock and ground joint were sparingly lubricated with Apiezon grease.

The manipulation of the nozzle and sample involved in making the photographs will now be described. The sample bulbs A were very carefully cleaned with sulfuric acid, dichromate solution, washed in distilled water, and dried. One of these bulbs, containing about 0.5 cc. of hydrogen peroxide to which a very small amount of sodium metaphosphate solution had been added, was attached to the nozzle, evacuated through C, heated for about thirty seconds with an oil-bath (at 125–140°), and briefly evacuated again to remove any oxygen formed by decomposition of the hydrogen peroxide during the heating. Immediately thereafter an exposure (of about 0.2 second) was made by simultaneously raising the electron shutter and opening the stopcock to D. Successive exposures, each following evacuation through C, could be made at fifteen second intervals until the rate of decomposition became too great; sometimes the sample remained quiet even after five minutes at 140° and could be used for more than one photograph. Eight of the ten photographs made in this way are satisfactory, showing no obvious indication of oxygen admixture; our final report is based on them.

Twenty photographs were made according to this procedure in August, 1939, using, however, no inhibitor, or an organic inhibitor. Hydroquinone, the best of these tried, was inadequate under the then prevailing conditions. Most of the exposures involved excessive decomposition of the hydrogen peroxide as was indicated by ebullition of the sample, by breakdown of the high voltage (caused by oxygen, which could not be condensed in the liquid-air traps but passed through the diffusion pumps into the electron tube), or by the resulting diffraction pattern. Indeed, some of the photographs showed essentially the oxygen pattern, as was verified by measurement of the ring diameters. Only three of the twenty photographs showed what we now recognize as the hydrogen peroxide pattern; our preliminary report<sup>6,8,9</sup> was based on them.

Hydrazine is stable at high temperatures and our metal high temperature nozzle<sup>13</sup> could be used. The samples used for the ten photographs on which this report is based were prepared by repeated fractional distillation in an atmosphere of hydrogen, starting with an 85% water solution of the hydrate (Eastman Kodak Co.), and were found by titration with iodine to be 99% hydrazine. Some photographs were made with 89% hydrazine; they were not sensibly different from the others.

The electron diffraction apparatus and general method of interpretation of the photographs have been described

(13) L. O. Brockway and K. J. Palmer, *THIS JOURNAL*, **59**, 218 (1937).

by Brockway.<sup>14</sup> The camera distance was about 11 cm. and the electron wave length (for Au,  $a_0 = 4.070 \text{ \AA}$ .) 0.06 Å. The film expansions of the calibration and gas photographs were measured and the required small corrections applied to the measured ring diameters.

### Interpretation and Results

Only the correlation procedure<sup>14</sup> was used in the interpretation of the photographs of hydrogen peroxide and hydrazine because we felt that for these very simple molecules little could be gained by the preliminary application of the radial distribution method. The X–H (N–H, O–H) distances and the X–X–H bond angles assumed for the calculation of the simplified theoretical intensity functions shown plotted in Fig. 2 were suggested by the known structures<sup>1b</sup> of water and ammonia and their derivatives, while the dominating X–X distance was estimated in both cases by correlating the observed ring diameters with the extrema of  $\sin x/x$ . In the calculation of these functions the hydrogen, nitrogen and oxygen atoms were assigned the effective relative scattering factors 1.25, 7, and 8, respectively, and temperature factors  $e^{-as^2}$  with  $a$  equal to 0.0018 and 0.0036 (as roughly estimated from spectroscopic data) were used respectively for the bonded and non-bonded X–H terms. The H–H terms were neglected.

**Hydrogen Peroxide.**—The hydrogen peroxide pictures were compared with intensity curves drawn for several mixtures of hydrogen peroxide, water and oxygen in order to take account of the effect of the oxygen and water which may have been present in the diffracting gas because of decomposition of the hydrogen peroxide. The molecular proportions H—O—O—H:H—O—H:O—O: for curve A, 1:O:O; B, 1:1/2:O; C, 1:1/2:1/4; D, 1:1/2:1/2; and, E, 1:1/2:1. The assumed parameter values are 1.20 Å. for  $r_{O-O}$  in oxygen, 1.48 Å. for  $r_{O-O}$  in hydrogen per-

(14) L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

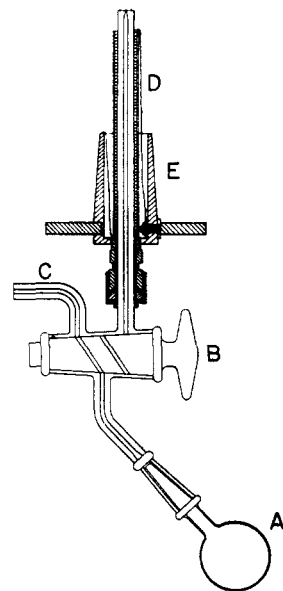


Fig. 1.—Diagram of high temperature nozzle used for hydrogen peroxide.

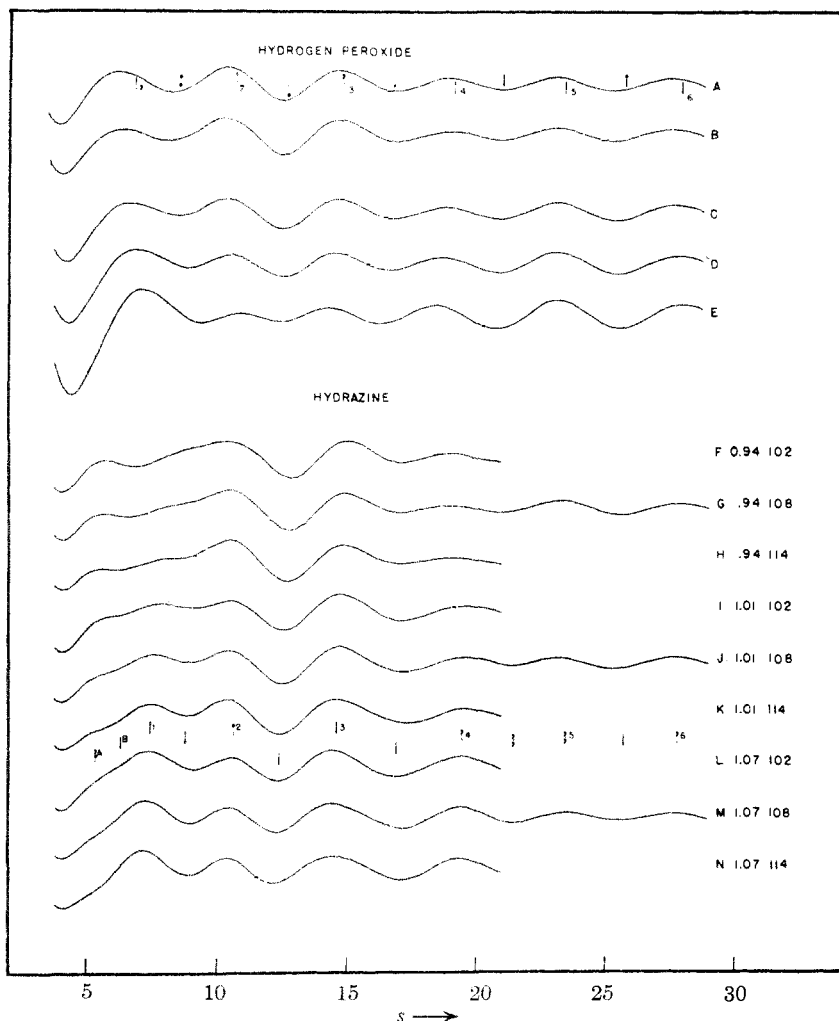


Fig. 2.—Simplified theoretical intensity curves for hydrogen peroxide and hydrazine. Following the alphabetical designation of each curve there is given first the N-H distance, then the H-N-N bond angle;  $r_{N-N} = 1.47 \text{ \AA}$ . See the text for other details. The arrows indicate the values of  $s_0$ , and are numbered according to the table.

oxide,  $0.97 \text{ \AA}$ , for  $r_{H-O}$  in both hydrogen peroxide and water, and  $105^\circ$  for the H—O— bond angle.<sup>15</sup>

Of the six rings which can be seen on the photographs in spite of a rather heavy background the first two are well represented by curves A, B and C, but not by D or E; the third minimum (min. 3) is deep, the third maximum (max. 3) is strong, max. 4 seems to be as strong as max. 5, and min. 5 is not deeper than min. 4 or min. 6. Curves B, D, and E may accordingly be ruled out, and A judged better than C.

The comparison of the  $s_0$  values<sup>16</sup> (Table I) for maxima

(15) The small moment of inertia calculated for the H-O-O-H model with these parameters (for any relative angle of rotation of the O-H groups) agrees to within 2% with the value  $2.786 \times 10^{-40} \text{ g.cm.}^2$  reported by Zumwalt and Giguère.<sup>8</sup>

(16) The  $s_0$  values are based on two sets of measurements made with an intervening interval of six weeks. For the six features min.3—max.5 the two sets agreed with an average deviation of 0.4%.  $s = 4\pi/\lambda \sin \varphi/2$  where  $\varphi$  is the angle of scattering.

and minima with those of curves A and C leads to the value  $1.480 \times 0.991 = 1.467 \text{ \AA}$ . for the O-O distance. This value involves only the six consecutive features min. 3—max. 5 which we believe to be most susceptible to reliable measurement; equal weight is given to A and C in spite of the indications of the qualitative comparison because the internal consistency of the quantitative comparisons (for all but the usually unreliable extreme inner and outer rings max. 1, min. 6, and max. 6) favors C. In consideration of the satisfactorily small average deviations shown in the table, the mediocre quality of the photographs, and the remaining uncertainty regarding the amount of oxygen and water to be accounted for, we round our result to  $1.47 \text{ \AA}$ . and assign to it probable limits of error of  $\pm 0.02 \text{ \AA}$ .

**Hydrazine.**—Intensity curves were drawn for models ( $\text{H}_2\text{NNH}_2$ ) with  $r_{N-N}$  equal to  $1.47 \text{ \AA}$ . with the N-N-H bond angle  $\vartheta$  ranging from  $102$  to  $114^\circ$  and the ratio  $\rho = r_{N-H}/r_{N-N}$ , from  $0.97/1.47$  to  $1.09/1.47$ ; a representative selection of the curves is shown in Fig. 2. The correlation of the photographs with the curves

leads, as described below, to the values  $r_{N-N} = 1.47 \pm 0.02 \text{ \AA}$ .,  $r_{N-H} = 1.04 \pm 0.06 \text{ \AA}$ . and  $\angle \text{H-N-N} = 108 \pm 8^\circ$ . The range of acceptable  $\rho$  and  $\vartheta$  values (on a  $\rho$  vs.  $\vartheta$  plot) actually resembles a tilted ellipse. While the hydrogen parameter values agree within the indicated limits with those suggested by the ammonia molecule<sup>1b</sup> ( $r_{N-H} = 1.01 \text{ \AA}$ .  $\angle \text{H-N-H} = 108^\circ$ ), the interpretation does definitely favor the higher value for  $r_{N-H}$ .

Curves J, K, L and M are in good agreement with the photographs, which show a slight bulge at  $a$ , max. 1 stronger than max. 2, min. 2 strong but much shallower than min. 3, max. 3 strong and somewhat asymmetric, min. 4 deeper than min. 5, max. 4 appreciably stronger than max. 5, and min. 6 as deep or deeper than min. 5. Curves I and N are less satisfactory, while curves F, G, and H may be ruled out. The curve for  $\rho = 1.04/1.47$  and

TABLE I

Max.	Min.	No. of Readings	Sobs. H <sub>2</sub> O <sub>2</sub>	Scaled./Sobs.		Sobs. N <sub>2</sub> H <sub>4</sub>	Scaled./Sobs.					
				A	C		J	K	L	M		
a		<20				4.37						
	b	<20				5.32						
1		<20	5.93	(0.885) <sup>b</sup>	(0.978)	6.48	{1.034}	{1.000}	{0.994}	{0.972}		
	2	<20	7.64	{.958 <sup>b</sup> }	{1.008}	7.81	{1.024}	{1.011}	{1.039}	{1.024}		
2		20	9.74	{.975}	{0.968}	9.67	{0.982}	{0.982}	{0.995}	{0.982}		
	3	20	11.76	.992	.985	11.43	1.008	0.999	.997	.989		
3		20	13.88	.991	.988	13.63	1.005	1.000	.990	.989		
	4	20	15.85	1.003	.996	15.93	1.017	1.029	1.004	1.018		
4		20	18.19	0.984	.981	18.49	1.006	1.006	1.000	0.995		
	5	20	20.05	1.002	.994	20.48	1.001	1.001	1.001	1.001		
5		20	22.50	0.987	.988	22.51	0.991	0.991	0.991	0.999		
	6	<20	24.76	(.985)	(.989)	24.77	(.985)	(.985)	(.989)	(.989)		
6		<20	26.93	(.986)	(.991)	26.84	(.993)	(.993)	(.991)	(.991)		
		Av. b <sub>6</sub>		0.993	0.989	a <sub>6</sub>	1.005	1.004	0.999	0.998		
		Av. dev.		0.006	0.004	a.d.	0.006	0.009	0.005	0.008		
		Av. b <sub>8</sub>		0.986	0.988	a <sub>9</sub>	1.008	1.001	1.002	0.996		
		Av. dev.		0.011	0.008	a.d.	0.012	0.008	0.009	0.012		

<sup>a</sup> Models described in text and on Fig. 2. <sup>b</sup> Values included in the averages of 8 or 9 features but not those of 6 are enclosed in braces. Values not included in either average are shown in parentheses.

$\angle\text{H-N-N} = 108^\circ$  would be somewhat better than any of those shown. Accordingly, no values of  $\rho$  between 0.98/1.47 and 1.10/1.47 can be excluded, but those close to 1.04/1.47 are favored; values of the H-N-N angle between 100 and 116° are acceptable, the favored value being less than 108° for  $\rho > 1.04/1.47$ , and *vice versa*.

These indications are supported by the quantitative comparisons shown in Table I.<sup>17</sup> For example, it can be seen that the  $s_e/s_0$  averages involving the structure sensitive features max. 1, min. 2, and max. 2 would agree exactly with those not involving these features for intermediate curves between J and K, K and L, or L and M. Our final value for the N-N distance is for  $\rho = 1.04/1.47$  and is based on the six well-defined outer features min. 3—max. 5 whose theoretical positions, thanks to the severe temperature factor in the non-bonded N-H term, are not appreciably influenced by variation of the H-N-N angle. If the N-H distance be regarded as fixed between 1.01 Å. and 1.04 Å., the value for  $r_{\text{N-N}}$  becomes 1.474 Å. with a probable limit of error of only  $\pm 0.01$  Å.

In conclusion it may be mentioned that all of the hydrazine photographs were carefully examined for the presence of any fine-scale features such as would arise from the longer interatomic distances of any reasonably rigid dimeric molecule present in appreciable concentration. That no such features were found is in agreement with

(17) The  $s_0$  values are averages from two sets of measurements made a year apart; the average deviation for the six features min.3—max.5 is 0.5%.

the subsequent finding of Giguère and Rundle<sup>18</sup> that hydrazine vapor is not appreciably associated, but not with that of Eucken and Krome<sup>19</sup> who reported that hydrazine is largely associated even at moderately high temperatures and low pressures.

We are indebted to Professor Pauling for his continued interest and helpful discussion.

### Summary

A study of hydrogen peroxide and hydrazine by electron diffraction gives  $r_{\text{O-O}} = 1.47 \pm 0.02$  Å. and  $r_{\text{N-N}} = 1.47 \pm 0.02$  Å., respectively, together with the rough values  $r_{\text{N-H}} = 1.04 \pm 0.06$  Å., and H-N-N =  $108 \pm 10^\circ$  for hydrazine. The diffraction patterns from hydrazine vapor show no evidence for dimerization. Hydrogen peroxide was studied with the help of a new Pyrex-glass nozzle; the high-temperature ( $\sim 140^\circ$ ) decomposition of the liquid was found to be effectively inhibited by small additions of sodium metaphosphate solution.

PASADENA, CALIF.

RECEIVED JULY 6, 1943

(18) P. A. Giguère and R. E. Rundle, *THIS JOURNAL*, **63**, 1135 (1941).

(19) A. Eucken and H. Krome, *Z. physikal. Chem.*, **B45**, 175 (1940).