acetic anhydride upon the acidity of the solution. Since it has been shown that it is possible to use the hydrogen electrode in the presence of anhydride, it should be possible to correlate the velocity of acetylations with the hydrogen-ion activity of the solution with considerable success.

Summary

1. A technique is described for making measurements with the hydrogen electrode in acetic acid–acetic anhydride solutions.
2. Sulfuric acid, perchloric acid, and certain sulfonic acids show increased acidities in the presence of acetic anhydride which cannot be accounted for by dehydration of the solution.
3. In the case of sulfuric acid, the effect is concluded to be due to the formation of a mixed anhydride of sulfuric and acetic acid which rearranges on standing into sulfo-acetic acid which does not exhibit ultra-acidic behavior.
4. This effect of acetic anhydride upon the acidity of such solutions must be considered when investigations of the effect of hydrogen-ion activity upon rate of acetylation reactions are being made.

ROCHESTER, N. Y. RECEIVED FEBRUARY 17, 1938

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 645]

The Internuclear Distance in the Fluorine Molecule

BY L. O. BROCKWAY

The structure of the fluorine molecule in the ground state is still unknown in spite of the great interest which attaches to fluorine as a member of the halogen family. In the only spectroscopic investigation reported in the literature[1] several emission bands were observed for a transition $^1S \rightarrow {}^1P$. The internuclear distances for the initial and final states of this transition are 1.48 and 1.28 Å., but these results afford no information about the ground state. The electron diffraction investigation which has now been made on fluorine vapor is the subject of this report.

The gas was prepared by Professor D. M. Yost and Dr. C. S. Garner by means of the electrolysis of potassium bifluoride in a fluorine generator constructed largely of monel metal. The product was passed over potassium fluoride to remove hydrogen fluoride and condensed to a liquid. After a first fraction had been evaporated and rejected, a sample was collected in a Pyrex flask for the electron diffraction investigation. The flow of gas during the exposures was controlled by an all-metal valve sealed to the flask by a metal-to-glass joint.

Five rings were observed on the photographs, but the first three were dark and smudgy while the fourth and fifth were well resolved. In spite of the very short exposures (of the order of one-half second) the removal of the fluorine introduced into the apparatus was not rapid enough to prevent the gas from spreading through the camera during the exposure. The scattering of electrons by fluorine molecules at various points along the electron beam then gave rise to a heavy background in the photographs. The momentary rise in pressure also caused high voltage discharges through gas in the electron-accelerating tube, and the resulting unsteadiness in the operation of the tube contributed somewhat to a lack of sharpness in the diffraction pattern.

Four samples of fluorine prepared at different times were used. In order to eliminate the possibility of contamination by silicon tetrafluoride the last sample was handled in brass and copper vessels and kept from contact with glass at all stages. The diffraction photographs from this sample have the same appearance and give the same measured ring diameters as the photographs from the earlier samples, and there is no evidence of contamination of the fluorine.

The diffraction pattern of a diatomic molecule is represented by the simple $(\sin ls)/ls$ function. The visually measured diameters of the five maxima and the two outer minima given as s_0 values ($= 4\pi\ (\sin \theta/2)/\lambda$) are compared with the corresponding maxima and minima of the $(\sin ls)/ls$ function in Table I. The first of the internuclear distances in the last column is 12% smaller than the average of the remaining values. This difference is rather large. It suggests the possibility that the pattern is that of a mixture of

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(1) Gale and Monk, *Astrophys. J.*, **69**, 77 (1929).

TABLE I

Max.	Min.	s_0	s	F–F, Å.
1		6.08	7.73	(1.271)
2		9.96	14.06	1.413
3		13.70	20.37	1.486
	4	16.08	23.52	1.463
4		18.15	26.67	1.469
	5	20.69	29.81	1.443
5		22.84	32.96	1.442
			Average	1.453

fluorine and some unknown impurity at a considerable concentration, but this is improbable in view of the precautions taken in the preparation and manipulation of the fluorine samples. The discrepancy of the first ring is more likely due to the difficulty of making reliable measurements in the part of the photographs where the background is very heavy.

The average internuclear distance excluding the measurements on the first ring is 1.45 Å. It is improbable that this result is in error by more than about 0.05 Å. Half of this distance is 0.73 Å., whereas the fluorine atom covalent radius obtained by extrapolation of the carbon, nitrogen and oxygen radii and also obtained from the observed distance in methyl fluoride is only 0.64 Å. In each of the other three halogens the radius taken as half of the observed distance in the molecule of the element is supported by the observed distances in many halogen compounds. The discrepancy for fluorine indicates that the bond type in the F_2 molecule may be different from that in other fluorine compounds and may not be a normal single covalent bond.

It should be emphasized that the quality of the photographs on which this determination is based is not very satisfactory, and that the value determined for the interatomic distance is not so reliable as those given by other electron diffraction investigations. An apparatus can be designed which would provide more effective removal of the gas from the camera and which would probably give clearer photographs. It became necessary, however, to drop the investigation temporarily, and the present result is accordingly reported at this time.

Summary

The F–F distance in the F_2 molecule is assigned the value 1.45 ± 0.05 Å. by the electron diffraction method. This value is about 14% greater than that expected for a normal single covalent bond.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Standardization of Thiosulfate Solutions by Means of Copper and Cupric Sulfate

BY H. W. FOOTE

The use of copper or copper compounds in standardizing sodium thiosulfate solutions for iodometry has not been generally recommended except when the thiosulfate is to be used in the iodometric determination of copper. This is chiefly because the iodine liberated in the reaction

$$CuSO_4 + 2KI \longrightarrow CuI + I + K_2SO_4$$

is adsorbed somewhat by precipitated cuprous iodide and is not completely available to thiosulfate. The standard determined by means of copper is therefore higher than that from iodine. The difference in the two standards is of the order of 1 part in 300.

It has been shown recently[1] that the iodine adsorbed by cuprous iodide in the reaction mentioned above is liberated and made available to thiosulfate if a soluble thiocyanate is added to the solution just before the end-point is reached in the usual titration. Under these conditions, the total iodine liberated is closely equivalent to the copper. Assuming this equivalence, the use of copper or its compounds appears to have certain advantages over the materials commonly used in standardizing thiosulfate solutions—potassium iodate, dichromate and permanganate, iodine and (by means of an iodine solution) arsenious oxide. The chief advantage is that the copper content of the material used as a standard can be determined very easily (by electrolysis) with a high degree of accuracy. None of the other substances used have this advantage to the same extent and their purity is usually assumed. The high equivalent weight of copper and particularly of the sulfate is also a well-known and obvious

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(1) H. W. Foote and John E. Vance, THIS JOURNAL, **57**, 845 (1935); *Ind. Eng. Chem., Anal. Ed.*, **8**, 119 (1936); **9**, 205 (1937).