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).

advantage. The cuprous iodide or thiocyanate is white instead of the usual fawn color, giving a very sharp end-point.

Experimental

The standards obtained by copper were in all cases compared with those obtained by iodine. The latter before use was sublimed twice, the first time from a mixture with potassium iodide. It was dried over calcium chloride. Metallic copper was the same sample used in previous work[1] containing 99.955% of the metal. The impurity consisted chiefly of oxygen. $CuSO_4 \cdot 5H_2O$ was a twice recrystallized product which was crushed and air dried. The copper content was determined electrolytically, correcting for a trace of copper remaining in solution which was precipitated as sulfide and weighed as oxide. Four samples of somewhat over 2 g. each gave the following percentages of copper: 25.42, 25.42, 25.41, 25.41 (calculated 25.46). The value 25.42 was adopted in calculating normalities. A sample approximating $CuSO_4 \cdot 1H_2O$ in composition also was used. It was obtained by heating the pentahydrate at 105–110° for twenty-four hours. Two analyses as above gave 35.67 and 35.66% copper (calculated 35.78). It was considered possible that this material might be a convenient source of copper whose composition could be calculated with sufficient accuracy to use as a standard but it is evident that a slight excess of water is present, perhaps adsorbed by the exceedingly fine particles of salt.

The thiosulfate solution used was approximately 0.104 *N*. Its strength decreased slightly during the work and was therefore determined at frequent intervals by means of iodine. The difficulty of weighing iodine for this purpose on account of its volatility is well known and often commented on. For our purpose, it was weighed between two small watch glasses which were then introduced with the iodine into a concentrated solution of potassium iodide. The latter was prepared immediately before use and was markedly cooled by the negative heat of solution of the iodide. Under these conditions, it is believed that the loss of iodine by volatilization is negligible.

The buret, holding 50 cc., had been calibrated. Volumes of thiosulfate between 40 and 50 cc. were used in all titrations.

The standard by means of copper sulfate was determined as follows. Suitable amounts of salt were dissolved in about 25 cc. of water containing 2 cc. of concentrated hydrochloric acid, and 3 g. of potassium iodide added. The liberated iodine was titrated in the usual manner nearly to the end-point as shown by starch solution. Approximately 2 g. of ammonium thiocyanate was then added to liberate adsorbed iodine. The end-point is sharp, the precipitate turning white. When using copper instead of the sulfate, the metal was dissolved in nitric acid and evaporated with 5 cc. of 6 *N* sulfuric acid. It is necessary to remove all nitric acid. To accomplish this, it was found convenient, after nearly all nitric acid is removed, to add a little hydrochloric acid and evaporate again. After dissolving in water the titration proceeded as before without, however, adding more hydrochloric acid.

Our experience indicates that all commercial samples of potassium iodide contain a trace of iodate. This requires a slight correction, usually 0.01 to 0.02 cc. per gram of iodide in copper titrations, due to their acidity.

Below are given all the results obtained by the method outlined above. In a few cases, 6 g. of iodide was used in place of 3 g. but the larger amount is unnecessary. The figures represent the difference between the normality determined by copper and that determined by iodine, expressed in hundred thousandths. Thus, +7 means that the normality by copper is 0.00007 greater than by iodine.

$CuSO_4 \cdot 5H_2O$ (% Cu = 25.42)
+7, +14, +9, +11, −5, −13, −7, +6, +3, +15

$CuSO_4 \cdot 1H_2O$ (% Cu = 35.67)
−10, −4, +4, −7, −3, −16

Copper (% Cu = 99.955)
+13, +11, +9, +2, −10, +4, −2, −15, +2

Considering the twenty-five results as a whole, the mean deviation from the standard as determined by iodine is 0.00008 and the maximum deviation is 0.00016, corresponding to 1 part in 1300 and one part in 650, respectively. The average of all results happens to agree almost exactly (less than 1 part in 10,000) with the standard by means of iodine, which merely indicates that there is no marked tendency to give either higher or lower results than those obtained by iodine.

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Summary

1. The strength of a thiosulfate solution has been determined by means of copper or cupric sulfate (using a modified iodometric method) and compared with that determined by iodine.

2. Twenty-five such determinations show a mean deviation from the iodine standard amounting to 1 part in 1300; and a maximum deviation of 1 part in 650. The average of all results by means of copper shows no marked positive or negative trend compared with the iodine standard.

3. The advantages of copper and its sulfate are (1) that the purity of the material can be determined easily and with great accuracy, (2) that the equivalent weights, particularly of the sulfate, are relatively high, which decreases the error in weighing, (3) that the precipitate at the end-point is white which gives a very sharp end-point.

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