

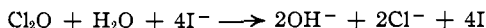
which may be compared with the experimental $\Delta F_{298.1}^{\circ} = -3910$ given by Lewis and Randall.⁸ If the previously accepted value⁹ of 29.6 for the entropy of hydrogen be used instead of that later recommended by Giauque,¹ $\Delta F_{298.1}^{\circ} = -4900$ is obtained. It is obvious that Giauque's value gives the better agreement with experiment.

Villars¹⁰ has calculated the molecular entropy of ammonia from spectroscopic data. His figure, 44.0 E. U., is not given on the same basis as the above value. When Villars' result is made comparable with the entropy of hydrogen used here (31.23), his value becomes 46.5, in close agreement with the 46.7 given above.

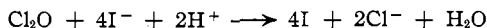
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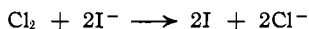
The Analysis of Chlorine Monoxide-Chlorine Mixtures.—Chlorine monoxide may be determined by absorption in potassium iodide solution and titration of the iodine liberated.



It is necessary to acidify the solution before titrating with thiosulfate.¹



The liberation of OH^- provides a further means for the determination of chlorine monoxide and indicates a method for the analysis of chlorine monoxide-chlorine mixtures.



Excess of standard sulfuric acid is added and after titration of the total iodine with thiosulfate the excess acid is found by back titration with standard alkali. Bowen² used methyl orange as indicator, while Hinshelwood³ used *N*/10 baryta and phenolphthalein. If x cc. of thiosulfate is used and then y cc. of sulfuric acid is required to neutralize the OH^- ; $\text{Cl}_2\text{O} \propto y$ and $\text{Cl}_2 \propto x - 2y$. Acid, base and thiosulfate must all be of the same normality or correcting factors are necessary.

The analysis can be simplified by an adaptation of the method used by Bodenstein⁴ for the analysis of chlorine-ozone mixtures.

As before, the gases are absorbed in potassium iodide solution and excess standard *N*/10 sulfuric acid added and the total iodine found.

⁹ Giauque and Wiebe, *THIS JOURNAL*, **50**, 121 (1928).

¹⁰ Villars, *ibid.*, **53**, 2006 (1931).

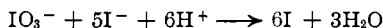
¹ Kistiakowsky, *Z. physik. Chem.*, **116**, 371 (1925).

² Bowen, *J. Chem. Soc.*, **123**, 1203 (1923).

³ Hinshelwood, *Proc. Roy. Soc. (London)*, **A131**, 177 (1931).

⁴ Bodenstein, Schumacher and Padelt, *Z. physik. Chem.*, **5B**, 209 (1929).

The excess sulfuric acid is estimated by addition of a slight excess of *N*/10 potassium iodate solution and titration of the iodine liberated.



The acid may be standardized by addition of potassium iodide and a slight excess of *N*/10 potassium iodate solution, the results agreeing very well with those by other methods.

The agreement between this method and that used by Hinshelwood³ may be seen by comparing the amounts of standard *N*/10 sulfuric acid used to neutralize the OH^- liberated by the chlorine monoxide contained in 5 cc. of a solution of chlorine monoxide-chlorine in carbon tetrachloride.

	Solution A	Solution B	Solution C
H_2SO_4 estimated by KIO_3 method, cc.	7.40	5.67	7.88
H_2SO_4 estimated by baryta method, cc.	7.42	5.74	7.89

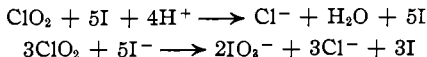
Doing duplicate experiments showed an agreement to about one-half of one per cent. but the method could be brought up to the usual accuracy of iodine titrations using calibrated apparatus and greater care than in these preliminary experiments. The concentrations of chlorine monoxide and chlorine were between 0.05 and 0.30 g. moles per liter in these experiments.

This method would appear to have the advantage of speed, simplicity and a convenient end-point. Since the acid can be standardized in terms of the thiosulfate, only the latter need be determined absolutely and, furthermore, the ratio of chlorine to chlorine monoxide can be found without a knowledge of the actual normality of the thiosulfate.

The method could also be used for the analysis of chlorine dioxide-chlorine mixtures, the excess acid being determined as above by addition of potassium iodate solution.



Bowen² analyzed chlorine dioxide-chlorine mixtures by absorption in potassium iodate solution, followed by thiosulfate titration in acid and in neutral solution according to Bray's⁵ method.



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⁵ Bray, *Z. physik. Chem.*, **54**, 731 (1906).