[CONTRIBUTION FROM THE ENGINEERING DIVISION, ARGONNE NATIONAL LABORATORY]

The Absorption Spectrum of Fluorine[1]

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The visible and ultraviolet absorption spectrum of fluorine gas was determined over the range 2100 to 8000 Å. A single broad absorption peak was observed with a maximum molar absorptivity of 6.00 liters per mole cm. at a wave length of 2845 Å. Beer's law was obeyed over a pressure range of 50 to 760 mm. Increasing the temperature to 100° caused only a slight decrease in the absorption which was within the experimental error arising from more rapid etching of the cell windows. This absorption appears to be consistent with the pale yellow color of fluorine, and it falls in place in the trend of the colors of the halogens in the periodic system.

Although Moissan[2] reported both liquid and gaseous fluorine to possess a pale yellow color, he did not observe an absorption spectrum for either state. More recently, attempts to obtain the dissociation energy of fluorine from the convergence of the band spectra have indicated continuous absorption with a maximum in the vicinity of 2800 Å.[3-6] Others have expressed doubt as to the existence of any absorption due to fluorine in the visible and ultraviolet regions.[7]

Experimental

Apparatus.—The measurements were made over the range 2100 to 8000 Å. with a Cary Model 11 double-beam recording spectrophotometer. The cells were machined from nickel pipe, 2.2 cm. in internal diameter, and were equipped with replaceable quartz windows which were held in position by brass ring nuts and sealed with Teflon gaskets. The optical path in the cells was 10.00 cm. in length. A $^1/_4$-inch nickel side tube for filling the cell was provided with a Hoke No. 1103 bellows valve and a flare connector.

To fill the cell, it was connected to a manifold which was provided with sources of fluorine, nitrogen and vacuum. The pressures were measured with a mercury manometer and cathetometer, using a McLeod gage as a standard. This system, which was exposed only to helium, was isolated from the fluorine manifold by a Taylor Model 204 RF-3 differential pressure multiplier, which was operated as a null-point indicator. This arrangement gave a precision of about ±0.05 mm. in determining the fluorine pressure in the cell.

Material.—The fluorine was acquired from the General Chemical Division of the Allied Chemical and Dye Corporation under a purity specification of 99%. Analyses by absorption in mercury[8] and by titration with bromine in a bromine trifluoride medium[9] indicated a purity of about 99.5%. This material was used without further purification.

Procedure.—The cell was attached to the fluorine manifold, evacuated, and leak tested. It was then conditioned with about 300 mm. of fluorine for two periods of approximately one hour each. After re-evacuation it was filled with a measured pressure of fluorine at room temperature. The valve on the cell was then closed, and the measurements were made in the spectrophotometer, using an identical evacuated cell as the standard. The total time required to fill the cell and obtain the spectrum was about 20 minutes.

The determinations at higher temperatures employed a similar cell equipped with electrical resistance heaters. The heat input was controlled with a Variac autotransformer and the temperature was measured with a copper-constantan thermocouple soldered to the cell wall.

In all the determinations, blanks were established by measurements on the evacuated cell before and after each series of observations.

The resulting molar absorbancy index values, in units of l. mole^{-1} cm.$^{-1}$, were calculated by means of the ideal gas law from the pressure and temperature when the cell was filled. Under these conditions fluorine behaves ideally within the experimental error as shown by the data of Doescher,[10] and by direct vapor density measurements using the Regnault method (observed: 38.00 ± 0.15 g. per G. M. V.; theoretical, 38.00).

Results

A series of runs at room temperature with various concentrations of fluorine resulted in the data shown in Table I. A rather broad peak was found with a maximum at 2845 ± 5 Å. Beer's law was obeyed over the pressure range 50 to 760 mm., giving a molar absorbancy index of 6.00 ± 0.05 l. mole^{-1} cm.$^{-1}$ at the maximum.

TABLE I

ABSORPTION SPECTRUM OF FLUORINE AT 25°

λ, Å.	aM, l. mole^{-1} cm.$^{-1}$	λ, Å.	aM, l. mole^{-1} cm.$^{-1}$
2100	1.10	3400	2.56
2200	1.60	3500	1.89
2300	2.18	3600	1.35
2400	3.02	3700	0.92
2500	3.98	3800	.63
2600	4.94	3900	.41
2700	5.63	4000	.30
2800	5.95	4100	.21
2845	6.00	4200	.14
2900	5.95	4300	.10
3000	5.59	4400	.07
3100	4.94	4500	.06
3200	4.14	5000	.00
3300	3.35		

Although chemical analysis had shown the purity of the fluorine to be about 99.5% a further confirmation by a physical method appeared desirable. A three-gram sample of the fluorine was condensed into a trap with liquid nitrogen, and twenty approximately equal fractions were removed successively at the equilibrium vapor pressure of about 285 mm. for spectrophotometric measurements. Low molar absorbancy indices in the first and last fractions indicated about 4 and 10 volume %, respectively, of non-absorbing impurity; the intervening fractions gave the normal value. This resulted in

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(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) H. Moissan, "Fluor et ses Composes," G. Steinheil, Paris, 1900.

(3) H. G. Gale and G. S. Monk, *Phys. Rev.*, **29**, 211 (1927).

(4) H. von Wartenberg and J. Taylor, *Nachr. Ges. Wiss. Göttingen Math.-physik Classe*, **1**, 119 (1930).

(5) H. von Wartenberg, G. Sprenger and J. Taylor, *Z. physik. Chem.* Bodenstein-Festband, 61 (1931).

(6) M. Bodenstein and H. Jockusch, *Z. anorg. allgem. Chem.*, **231**, 24 (1937).

(7) P. J. Elving, C. A. Horton and H. H. Willard, "Fluorine Chemistry," Vol. II, ed. J. H. Simons, Academic Press, Inc., New York, N. Y., 1954, p. 56.

(8) H. Schmitz and H. J. Schumacher, *Z. anorg. allgem. Chem.*, **245**, 221 (1940).

(9) I. Sheft, H. H. Hyman and J. J. Katz, *Anal. Chem.*, **25**, 1877 (1953).

(10) R. N. Doescher, *J. Chem. Phys.*, **20**, 330 (1952).

an over-all purity of 99.3% for the fluorine used in these measurements. All the data have been corrected by this factor.

The addition of nitrogen to the fluorine caused no observable effect on the absorption spectrum. In one case 600 mm. of nitrogen was added to 100 mm. of fluorine, and in a second experiment an equal pressure of nitrogen was added to 300 mm. of fluorine. In both cases a decrease of only 0.01 l. mole^{-1} cm.$^{-1}$ was found, which is well within the experimental uncertainty.

In order to determine the extent of the reaction between the fluorine and the cell, measurements were made over time periods much longer than the normal 20 minutes. These showed that the cell windows were very slowly etched at a rate generally less than 0.001 absorbance unit per hour, as indicated by blank measurements. In addition, the fluorine was consumed at a rate of about 0.7% per hour. For the usual observation period of 20 minutes, both effects were negligible.

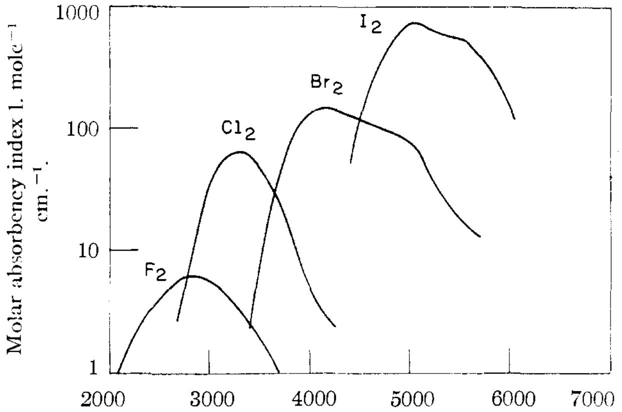

Fig. 1.—Absorption spectra of the halogens.

Higher temperature measurements at 50, 75 and 100° indicated no large differences in the absorption peak. Decreases of 2.1, 2.8 and 3.1%, respectively, were observed, but these values are subject to some uncertainty due to the appreciable etching of the cell windows at these temperatures.

Discussion

The continuous absorption peak height and location for fluorine are in agreement with those found by von Wartenberg[4,5] and Bodenstein,[6] falling between their results. There is little doubt as to the existence of this absorption of fluorine, but it is small in comparison with those of the other halogens.[11,12,13] The position of this peak, with its lower region extending into the violet part of the visible spectrum suggests the very pale yellow color frequently reported for gaseous fluorine. The relation of the absorption spectrum of fluorine to those of the other halogens is apparent in Fig. 1.

[11] G. E. Gibson and N. S. Bayliss, *Phys. Rev.*, **44**, 188 (1933).

[12] A. P. Acton, R. G. Aickin and N. S. Bayliss, *J. Chem. Phys.*, **4**, 474 (1936).

[13] E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 540 (1936).

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[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DIVISION, ARGONNE NATIONAL LABORATORY[1]]

Liquid-Vapor Equilibria in the System Bromine–Bromine Trifluoride

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The 75 and 100° isotherms of the system bromine–bromine trifluoride have been determined. At both temperatures the system exhibits azeotropes at pressures greater than the sum of the pressures of pure bromine and bromine trifluoride. This suggests another molecular species in the vapor phase coexistent with bromine and bromine trifluoride.

The presence of bromine monofluoride as a species in mixtures of bromine and bromine trifluoride was suggested by Ruff and Braida.[2] Fischer, Steunenberg and Vogel[3] showed that there is a marked positive deviation from ideality with the formation of a liquid immiscibility gap in the condensed system bromine-bromine trifluoride. There was no evidence for the formation of solid bromine monofluoride.

It had been observed at temperatures around −10° by Ruff and Braida that the pressures over mixtures of bromine and bromine fluorides were in excess of those predicted from the properties of the known pure compounds using reasonable assumptions. Similar excesses of pressure for liquid mixtures of bromine and bromine trifluoride at temperatures from 25 to 125° have been noted in this Laboratory. In order to obtain further information about the occurrence of bromine fluoride and to evaluate the feasibility of the bromine-bromine trifluoride separation, 75 and 100° isotherms of the bromine–bromine trifluoride system were studied. Apparent molecular weights calculated from vapor densities at 75 and 100° for the system bromine–bromine trifluoride were obtained.

Experimental

Materials.—Reagent grade bromine was purified by distilling off a large portion, about one-quarter of the original volume at room temperature to remove any chlorine present. The remainder was passed over phosphorus pentoxide in order to remove traces of water. The sample to be used was condensed in a Fluorothene trap cooled with liquid nitrogen. Approximately 15- to 20-ml. portions were collected in the trap at a time. Each portion was frozen, evacuated and thawed several times to remove non-condensable gases. A 3- to 4-ml. portion of the bromine in the trap was distilled off to remove any further impurities more volatile than bromine. The residual amount of bromine was then distilled into the equilibrium cell of the apparatus.

Reagent grade bromine trifluoride was purified by dis-

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] O. Ruff and A. Braida, *Z. anorg. allgem. Chem.*, **214**, 81 (1933).

[3] J. Fischer, R. K. Steunenberg and R. C. Vogel, THIS JOURNAL, **76**, 1497 (1954).