An Attempt to Determine the Electrode Potential and Raman Spectrum of Fluorine. The Entropy of Fluorine

By Clifford S. Garner and Don M. Yost

The Electrode Potential of Fluorine

Although the normal electrode potential of fluorine has been estimated to have the value −2.88 v.,[1] the thermodynamic constants of aqueous hydrogen fluoride are not known accurately. Consequently, investigations were undertaken in which cells of two types were measured

F_2 (p atm.), $KF(c$ f in $HF(l))$, $PbF_2(s) + Pb(s)$

H_2 (1 atm.), $HF(c$ f), $KF(c'$ f in $HF(c$ f)), $PbF_2(s) + Pb(s)$

for which the cell reactions (neglecting liquid-junction effects) presumably would be

$$Pb(s) + F_2(p \text{ atm.}) = PbF_2(s)$$

and

$$H_2 \text{ (1 atm.)} + PbF_2(s) = Pb(s) + 2HF(c \text{ f})$$

respectively. From the electromotive forces and temperature coefficients of these cells, together with data on the partial pressures of hydrogen fluoride above solutions of potassium fluoride in liquid hydrogen fluoride at the temperatures of interest[2] (needed in order to calculate the partial pressure of fluorine in the first cell), the thermodynamic constants of solid lead fluoride[3] and of aqueous hydrogen fluoride, as well as the normal electrode potential of fluorine, could be obtained. In this note only measurements of the first cell are treated.

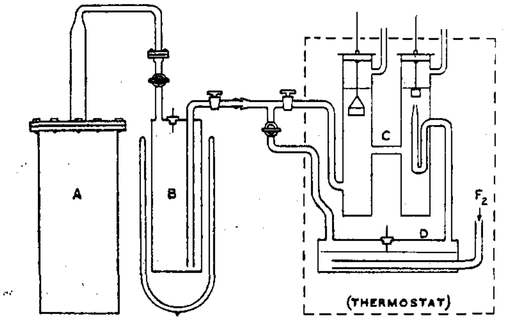

Fig. 1.—Apparatus.

Experimental Procedure.—All chemicals used were of a high grade of purity. The fluorine was generated by the electrolysis of molten anhydrous potassium hydrofluoride. The liquid hydrogen fluoride was prepared by heating anhydrous potassium hydrofluoride to 600° in a copper still (A) and condensing the distillate in a tared silver trap (B). The trap and contents were weighed and a known amount of dried potassium hydrofluoride added, after which the mixture was well shaken at 0° and then forced by a current of dry nitrogen into the platinum cell (C) and the silver saturator (D) which were thermostated at 0°. While the solution was being mixed, the platinum electrode was blacked, and the lead–lead fluoride electrode prepared and put in place. Fluorine was bubbled into the cell from the saturator, and potential readings were taken over a period of four to eight hours.

Results and Discussion.—In the four runs made, the potentials fluctuated irregularly from about 0.5 to 3 v. The rate of flow of fluorine was reasonably constant during each run, but varied from run to run. The amount of potassium fluoride added was changed and also the extent of stirring of the solution in the cell without any large effect. At the end of each run the container was found to be corroded and the black removed from the platinum electrode; in one case the electrode was not blacked, but the results were no better. No conditions were found which would give constant readings. In a somewhat different cell Simons and Hildebrand[4] were also unable to get reproducible and constant e. m. fs. This is probably because of the reaction of the fluorine with the electrode and container in the presence of liquid hydrogen fluoride.

The Raman Spectrum of Fluorine

Spectroscopic data for fluorine in the normal electronic state do not exist,[5] and consequently no accurate value for the entropy of fluorine is available. To obtain this information it was decided to determine the Raman spectrum of liquid fluorine.

Experimental Procedure.—The fluorine was prepared as previously, and was purified by being

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[1] Latimer, This Journal, **48**, 2868 (1926); Yost and Hatcher, *J. Chem. Ed.*, **10**, 330 (1933).

[2] Cady, This Journal, **56**, 1431 (1934).

[3] ΔH^0 for PbF_2 (s) has been determined to be −156,000 cal. and −155,600 cal., respectively, by v. Wartenberg and Fitzner, *Z. anorg. allgem. Chem.*, **151**, 313 (1926), and Jellinek and Rudat, *ibid.*, **175**, 281 (1928). Since the present work was completed a value of −147,300 cal. for ΔF^0 has been estimated by Jahn-Held and Jellinek, *Z. Elektrochem.*, **42**, 401 (1936), from measurements on certain cells.

[4] Simons and Hildebrand, This Journal, **46**, 2223 (1924). They reported that platinum, iridium, gold, nickel and graphite all react with fluorine at room temperature in the presence of liquid hydrogen fluoride; they did not state the extent of such reaction.

[5] Gale and Monk, *Astrophys. J.*, **59**, 125 (1924); **69**, 77 (1929), have analyzed a band spectrum of fluorine, amd they give a value of 1130.1 cm.$^{-1}$ for the fundamental frequency of vibration of the molecule in the normal state. It is not certain, however, that their spectra arise from transitions involving the normal state of the F_2 molecule.

passed through a tube filled with sodium fluoride (to remove hydrogen fluoride) and condensed in a Pyrex trap surrounded by fresh liquid air. A portion of the condensate was allowed to escape and about one-half of the remainder was distilled into an evacuated Raman tube which previously had been well heated while evacuated to remove any moisture. The Raman tube held about 25 cc. of liquid and was closed by means of a brass and steel needle valve joined to the tube with a thin layer of sealing wax or by a copper–Pyrex seal. While being filled, and during the exposure to radiation, the Raman tube was surrounded by a Dewar flask (silvered except for one portion where light was admitted to the tube) filled with fresh liquid air. The liquid air was filtered to remove any ice crystals; the Dewar flask was closed off from the atmosphere by a cork which supported the Raman tube, and it was provided with means for adding liquid air during the exposure. As exciting radiation the 5461 Å. line of mercury was used. The light was concentrated on the Raman tube by a cylindrical aluminum reflector, and radiation below 3700 Å. was removed by a filter of sodium dichromate solution.[6] In addition a filter of neodymium nitrate solution was used to cut down the intensity of the "yellow" lines of mercury, since it was expected from the evidence at hand that the Raman line would fall in the region adjacent. The plates used were Eastman, type I-C.

Results and Discussion.—In the first attempt a Pyrex Raman tube was used, and after about fifteen minutes of illumination a white precipitate began to form in the fluorine. The tube was later found to be etched, and following this a quartz Raman tube was used. Two photographs were taken with the quartz tube, one of one hour and one of four hours' exposure. Longer exposures seemed impractical because of the gradual attack of the container by the fluorine, and because of the formation of ice crystals in the liquid air with resulting optical difficulties. No Raman lines could be found on either plate. The absence of a Raman line may be attributed to poor scattering ability of liquid fluorine, or to the possibility of the line falling near or on a mercury line and being thus obscured.

The Entropy of Fluorine

Recently, Brockway[7] has taken electron-diffraction photographs of gaseous fluorine, and a value of 1.46 Å. has been obtained for the internuclear distance of the fluorine molecule in its normal electronic state. If one assumes that Badger's rule[8] holds here, the value 836 cm.$^{-1}$ is obtained for the fundamental frequency of vibration. Making use of these two data, a calculation gives 48.6 cal./deg. for the standard entropy, S^0_{298}, of fluorine at 25° and one atmosphere.

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[6] According to v. Wartenberg and Taylor, *Nach. Ges. Wiss. Göttingen, Math.-Phys. Klasse*, 119 (1930), fluorine gas at 1 atm. absorbs radiation below about 4500 Å. We found that if the dichromate filter was removed at the end of an exposure, a white precipitate appeared in the liquid fluorine in two to three minutes when the container was of Pyrex, and fifteen minutes when of quartz.

[7] Private communication from Dr. L. O. Brockway. The internuclear distance given is, for experimental reasons, regarded as provisional.

[8] Badger, *J. Chem. Phys.*, **2**, 128 (1934); **3**, 710 (1935).

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Refractive Indices at Low Temperatures[1]

BY ARISTID V. GROSSE

As is well known the refractive indices are usually determined at room temperature. Although a large number of substances have been measured above room temperature, the number of determinations below 0° is extremely scarce. A literature search has revealed that reliable data were available only on the three elements—oxygen,[2] nitrogen[3] and hydrogen,[4] at their respective boiling points.[4a]

The following simple self-explanatory device, Fig. 1, using dry ice as a cooling agent, but not limited thereto, shows how the well-known Abbé refractometer can be used for low temperature measurements, the lowest used so far being −50°. Efficient cooling to any desired temperature is accomplished by boiling an appropriate liquid, such as isobutane for −10°, methyl ether for −25° and propane for −42°. Finer temperature adjustments may be made easily by changing the total pressure of the system (by means of C and D).

Once the apparatus is available the cooling

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[1] Presented before the Petroleum Section of the American Chemical Society, Rochester Meeting, September, 1937.

[2] Liveing and J. Dewar, *Phil. Mag.*, [5] **40**, 268 (1895).

[3] Liveing and J. Dewar, *ibid.*, [5] **36**, 330 (1893).

[4] W. Meissner, *Verhand. Deut. phys. Ges.*, **14**, 540 (1913).

[4a] These values have quite recently been checked by E. F. Burton, see Abstracts, 94th Meeting Am. Chem. Soc., Div. of Phys. Chem., 1937, p. 15.