

the limiting value of the ratio of  $-\log f$  to  $c^{1/2}$  is not 0.5 as required by the theory but something nearer to 0.38.

Since both Davies and Lange and Streeck discuss hydrochloric acid, and conclude that in this case the data are inadequate to decide the question, new evidence on this substance should be particularly welcome. Using the value of  $E^\circ$  given by Carmody in his recent paper [THIS JOURNAL, 54, 188 (1932)] a simple calculation yields as values of the ratio of  $-\log \gamma$  to  $m^{1/2}$ : 0.47, 0.45, 0.43, 0.45, 0.47, 0.47 and 0.47 for the seven lowest molalities studied by Carmody, ranging from 0.005 to 0.0003 molal. The mean value 0.46 is slightly lower than the Debye-Hückel value, as has been noted in many other cases, but is not inconsistent with it in view of the experimental uncertainty of the e. m. f. measurements. Carmody's careful investigation certainly lends no support to Davies' views.

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#### OXYACIDS OF FLUORINE

*Sir:*

When fluorine is passed into a 50% solution of potassium hydroxide cooled to  $-20^\circ$ , potassium fluoride separates and the supernatant liquid actively liberates iodine from a solution of potassium iodide. This liquid maintains its oxidizing power for several days at room temperature, even after air has been passed through it for some time, and even after being heated for three hours at  $60^\circ$ . These results seem to preclude the possibility of the oxidation being due to ozone.

To test this point still further, ozone was passed through a cold solution of lithium hydroxide for a considerable time. The liquid showed no oxidizing power. When, however, fluorine was passed into a solution of lithium hydroxide under identical conditions, the resulting liquid was strongly oxidizing, and when this solution was evaporated to dryness on a water-bath and the residue was dissolved in water, the solution still showed strong oxidizing power.

Similarly, a solution of calcium hydroxide was found to be unaffected by ozone, but to have a marked oxidizing action after treatment with fluorine.

These alkaline solutions retained their oxidizing character even after acidification with sulfuric acid, which indicated the presence of an oxyacid of fluorine.

To prepare a solution of the free oxyacids, fluorine was passed into a suspension of calcium carbonate in cold water, and the contents of the

flask was then subjected to distillation. The distillate had an acid reaction and actively oxidized a neutral solution of potassium iodide.

Approximate determinations of the ratio of hydrogen to oxygen in the distillate from three separate distillations gave 1:2.31, 1:2.22 and 1:2.80. These results indicate the presence of fluoric acid ( $\text{HFO}_3$ ) in the distillate; and a greater oxidizing power of the liquid in the reaction flask, before distillation from the calcium carbonate, indicates that a less stable oxy-acid of fluorine, probably hypofluorous acid ( $\text{HFO}$ ), is also formed. It may here be added that the distillate contained no trace of chlorine.

When fluorine was passed into a cold solution of cesium carbonate until the salt had been entirely converted into fluorine compounds, the resulting liquid was extremely reactive. It was evaporated to dryness on a water-bath, and a water solution of the residue showed strong oxidizing power. Fractional solution of this residue with successive small amounts of water indicated that the oxidizing power is greatest in the most soluble portions.

This investigation is being carried forward and detailed results will be published later.

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#### THE THERMAL DISSOCIATION OF NITROUS OXIDE

*Sir:*

From the known entropies of other triatomic molecules it is possible to determine a value for the entropy of nitrous oxide which is probably correct within a few entropy units. Following the procedure used in a recent article by the author [THIS JOURNAL, 54, 156 (1932)] the value  $S_{298}^{\circ}(\text{N}_2\text{O})_g = 51.9$  E. U. is obtained. This leads to interesting conclusions regarding the thermal dissociation of nitrous oxide into nitrogen molecule and oxygen atom, for the entropy change in this reaction can now be determined, and the change in heat content is known. Thus the free energy change at  $298^{\circ}\text{K}$ . can be found, and by the use of empirical specific heat equations a good estimate of the free energy change at  $838^{\circ}\text{K}$ . can be made and thus of the equilibrium constant  $K = p_{\text{N}_2} \cdot p_{\text{O}} / p_{\text{N}_2\text{O}}$ . An approximate value such as this is quite sufficient to show that the equilibrium pressure of oxygen atoms is surprisingly high, being of the order of  $10^{-4}$  atm. at this temperature.

At  $838^{\circ}\text{K}$ . the thermal rate of decomposition is low. For the purposes of a calculation to be made in a moment, let us consider simply as an example the thermal rate in a bulb at this temperature containing 190 mm. of  $\text{N}_2\text{O}$  and 10 mm. of  $\text{N}_2$ . The rate of decomposition is of the order of