

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 (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 (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.

DEPARTMENT OF CHEMISTRY
CORNELL UNIVERSITY
ITHACA, NEW YORK
RECEIVED JANUARY 22, 1932
PUBLISHED FEBRUARY 5, 1932

L. M. DENNIS
E. G. ROCHOW

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°K . can be found, and by the use of empirical specific heat equations a good estimate of the free energy change at 838°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°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 N_2O and 10 mm. of N_2 . The rate of decomposition is of the order of

10^{13} molecules per cc. per sec. [Hinshelwood and Burk, *Proc. Roy. Soc.* (London), **A106**, 284 (1924)]. On the other hand, the number of collisions between N_2O molecules and oxygen atoms at the equilibrium concentration under these conditions proves to be of the order of 10^{24} collisions per cc. per sec., and thus the thermal decomposition is very small compared to this. We are thus forced to the conclusion that either the probability of reaction between N_2O and O is very small, or that the rate of thermal dissociation into N_2 and O is very small, never even approximately establishing equilibrium even for low rates of the thermal decomposition. Both statements may, of course, be true. The first is not at all surprising, rather, indeed, probable. However, the second statement, also, may very possibly be true. In this case, in contrast to the case of ozone (see first reference cited above), we are dealing with a molecule made up of the dissociation products O (normal state 3P) and N_2 (normal state $^1\Sigma$) and this, in addition to all chemical knowledge of the inertness of nitrogen, suggests that the two reactions represented by the equilibrium $N_2O \rightleftharpoons N_2 + O$, even at $838^\circ K.$, are very slow. In the case of the molecule O_3 the situation is different, the constituents being O (normal state 3P) and O_2 (normal state $^3\Sigma$). It should be noted that, with respect to the dissociation products, the energy content of the two molecules N_2O and O_3 is of the same order of magnitude, namely, about 41,500 calories and 24,000 calories, respectively. The author plans to discuss the above more fully in a later paper.

BUREAU OF CHEMISTRY AND SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

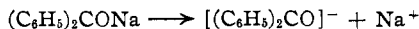
OLIVER R. WULF

RECEIVED JANUARY 26, 1932
PUBLISHED FEBRUARY 5, 1932

THE STRUCTURE OF METAL KETYLs

Sir:

The metal ketyl derived from benzophenone has been found to conduct the electric current in liquid ammonia solution [observations of Mr. Paul B. Bien in this Laboratory] and the results also suggest that this substance is ionized in accordance with the equation



The anion represents an interesting and unusual type of stable complex for it contains both an *odd* and an *extra* electron. Consequently, a careful study of such substances might be expected to throw some new light on fundamental valence problems.

It has already been shown [Wooster, *THIS JOURNAL*, **51**, 1856 (1929)] that the Schmidlin formula for the metal ketyl is incorrect and that the question of their constitution is still open. Several alternative hypotheses