Studies in Catalysis.

By James H. Ransom.

In 1902 there was presented to this Academy by Mr. E. G. Mahin, working in my laboratory, a paper dealing with the action of heat on mixtures of manganese dioxide and potassium chlorate. In this paper it was shown that the nature of the reaction as well as the temperature of decomposition depended on the purity of the oxide, in that the purer and drier the material the higher the temperature of rapid decomposition and the smaller the amount of chlorine and chlorine oxides. The study of this action has been continued by the writer, and some new data accumulated.

Instead of using the purified commercial article, manganese dioxide was prepared in the laboratory by heating chemically pure manganous nitrate to a high temperature as long as decomposition occurred, and then washing out all soluble material. After this treatment the residue was dried for some hours at a high temperature in vacuo. It was then preserved in glass-stoppered bottles in a desiccator. Prepared in this way the oxide is not hygroscopic.

One to two grams of potassium chlorate, free from chlorides, was mixed with about the same weight of the manganese dioxide and the mixture heated in an air-bath, the temperature being controlled with a gas regulator. With the purified material there was observed little or no decomposition at 170° (as Mahin found), and only at 245° to 260° was the action at all perceptible. At 300° to 310° the action completed itself in a few minutes. It was observed that while little oxygen was evolved below 245° the residue gave a test for chlorides, though the tests made before heating gave wholly negative results. Some of the experiments showed less loss in weight during heating than that corresponding to the chloride found by titration against standard silver nitrate. Occasionally, however, the loss was even greater than that calculated so that it was felt that great reliance could not be placed in the difference in weight, especially as the tubes were often heated continuously for some days. The evidence of decomposition rests, therefore, on the formation of chloride.

After these facts were established twenty experiments were performed to find the amount of chloride produced at different tempera-

tures; and to determine, if possible, the lowest temperature at which any chloride would be formed. The temperatures varied in the different experiments between 90° and 200°, and the time of heating from one hour to 21 days. Chlorides were found in each of the 20 experiments, and the amount varied somewhat regularly with the increase of temperature and the time of heating. At 90°-93°, the lowest temperature used, the amount of chloride formed in 14 days was .22 per cent. of that theoretically possible.

In order to show whether the pure chlorate would decompose at all under these conditions some of it was heated in the same manner as that described above. The heating was continued for nine days at 106°-109°. But not a trace of a chloride was produced.

It is interesting to note that decomposition begins 200° below that at which it is sufficiently rapid to be easily observed. But this is in line with the modern idea that the velocity of an action is a function of the temperature. And this observation has its parallel in the fact that 200° below its ignition point hydrogen combines with oxygen in quantities sufficient to be determined.

It has been found also that mixtures of manganese dioxide and potassium perchlorate produce oxygen at a temperature much lower than that necessary to decompose the perchlorate alone. The amount of oxygen is quite appreciable at 310°, but does not become rapid at 360°—a temperature below that at which the perchlorate begins to evolve oxygen.

In order to compare the action of other catalytic agents at low temperatures mixtures of potassium chlorate and platinum black were heated at two temperatures; one sample for 6 days at 145°-150°, the other for 7 days at 95°-100°. Both tubes lost in weight and both gave evidence of considerable amounts of chloride produced. I hope soon to get results at higher temperatures. But at these temperatures manganese dioxide and platinum black are almost identical in their effect on the decomposition of potassium chlorate.

In the near future the study of the action of other oxides at low temperatures will be undertaken in order to get comparative results.

At the beginning of the investigation on catalysis it was believed that many of the actions would prove to be of a purely chemical nature. At the present time there is no evidence that such is the case; but rather that we are dealing with cases of true contact action.