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THE DECOMPOSITION OF POTASSIUM CHLORATE. I. SPONTANEOUS DECOMPOSITION TEMPERATURES OF MIXTURES OF POTASSIUM CHLORATE AND MANGANESE DIOXIDE

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The decomposition of potassium chlorate has been the subject of many investigations. Rapid decomposition and even explosibility have been ascribed to it.

Neumark,[1] and Gartenmeister,[2] have discussed the dangers of potassium chlorate explosions. Baudrimont,[3] McLeod,[4] Fowler and Grant,[5] Hodgkinson and Lowndes,[6] and Neumark[1] have mentioned a violent evolution of oxygen when potassium chlorate is heated in the presence of a catalyst. Neumark ascribes this violent action to incomplete mixing which allows the potassium chlorate to melt before it comes in contact with the catalyst. Fowler and Grant believe that the rapid rise of temperature reported by Baudrimont is due to the decomposition of some substance formed during the heating. Bertholet[7] called attention to the fact that the decomposition of potassium chlorate is exothermal, but says that no explosion occurs under the influence of progressive heating.

In the course of some experiments with mixtures of potassium chlorate and manganese dioxide it was noticed that some of the mixtures abruptly began to evolve oxygen violently. The temperature at which violent evolution began differed for mixtures of different composition, but for mixtures of the same composition this temperature was nearly constant.

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[1] Neumark, *Met. Chem. Eng.*, **9**, 641 (1911).

[2] Gartenmeister, *Chem.-Ztg.*, **31**, 174 (1907).

[3] Baudrimont, *J. Chem. Soc.*, **24**, 1151 (1871).

[4] McLeod, *ibid.*, **55**, 184 (1889).

[5] Fowler and Grant, *ibid.*, **57**, 278 (1890).

[6] Hodgkinson and Lowndes, *Chem. News*, **58**, 309 (1888).

[7] Bertholet, *Compt. rend.*, **129**, 926 (1899); *Ann. chim. phys.*, [7] **20**, 11 (1900).

This temperature was called the "spontaneous decomposition temperature," and a series of experiments was conducted to determine the relation between the composition of the mixture of potassium chlorate and manganese dioxide and its spontaneous decomposition temperature.

Materials and Apparatus

The potassium chlorate and manganese dioxide were the best quality furnished by dealers in chemical supplies. Each substance was ground, separately, until it passed through a 200-mesh sieve, dried at 140° and stored in a glass-stoppered bottle. Each mixture was made by sifting the powdered materials through a 150-mesh sieve until it appeared homogeneous.

Preliminary experiments proved that 2 g. of potassium chlorate may be heated to 400° in a hard glass tube without an evolution of more than 1 cc. of oxygen per minute. This justified heating the samples in a glass container. The apparatus consisted of a hard glass, side-neck test-tube connected with a system of bottles in a manner such that the volume of gas evolved could be measured by water displacement at any desired intervals of time. The tubes were heated by indirect radiation in either a gas furnace or an electric furnace. The temperature could be maintained within 2° of any desired point. The temperatures were determined by mercury thermometers which had been compared with a standard thermometer. One thermometer had its bulb embedded in the reacting mixture and a second thermometer was suspended in the heating chamber near the tube containing the decomposing mixture.

Experimental Work

All mixtures were made on the basis of molecular equivalents, not grams. One molecular equivalent of potassium chlorate was mixed with as little as 0.0001 and with as much as 16 of manganese dioxide.

For each experiment a quantity of the chosen mixture containing 2 g. of potassium chlorate was weighed, transferred to the hard glass tube and the latter placed in the furnace. The temperature was raised rapidly, until the volume of gas evolved indicated that the decomposition was complete. The rate of evolution of gas always increased with increasing temperature. In the cases of mixtures containing between $^1/_{16}$ and 5 molecular equivalents of manganese dioxide to 1 of potassium chlorate, a violent evolution of oxygen occurred at a temperature characteristic for each mixture. A rapid rise in temperature always accompanied this violent evolution of oxygen. After the spontaneous decomposition temperature had been determined approximately in this way, several other similar charges were heated. In all tests after the preliminary one, the furnace was heated almost to the temperature of spontaneous decomposition before the introduction of the charged tube, and kept near that temperature during the entire time of the reaction.

Experimental Results

The first graph shows the progress of 5 individual experiments. Curve I represents the results for a mixture containing 2 molecular equivalents of manganese dioxide to 1 of potassium chlorate; Curve II represents the results for a mixture whose molecular proportion was $MnO_2 : KClO_3 :: 1 : 1$; the proportion for Curve III was $MnO_2 : KClO_3 :: 1 : 6$; the proportion for Curve IV was $MnO_2 : KClO_3 :: 1 : 16$. The points located by circles unconnected by a curve represent the behavior of pure potassium chlorate. The ordinates represent the number of cubic centimeters of oxygen evolved per minute. The abscissas represent the temperature at the close of the minute, and the spaces between successive open circles on a curve represent an interval of 1 minute. Those preceding inked-in circles represent 5 minutes.

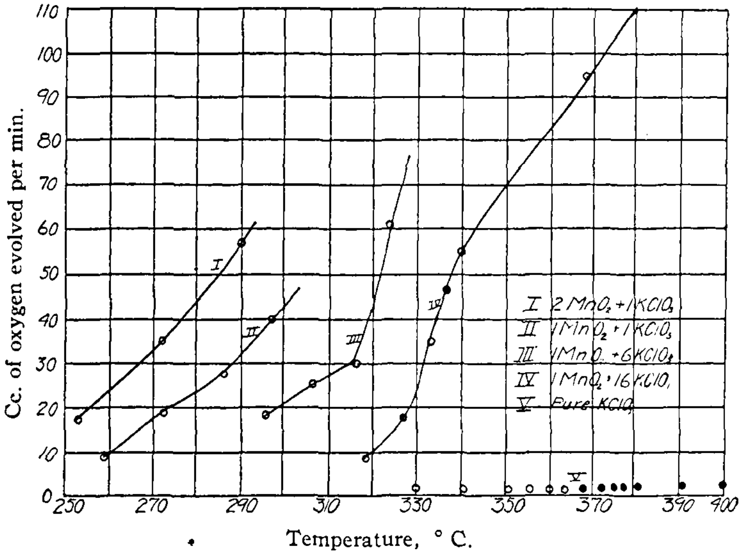

Fig. 1.—Rate of evolution of O_2 from 2 g. of $KClO_3$ mixed with various molecular proportions of MnO_2.

The second graph shows the relation between the compositions of the mixtures of potassium chlorate and manganese dioxide and their temperatures of spontaneous decomposition. The abscissas represent the molecular percentages of manganese dioxide and of potassium chlorate. The ordinates show the temperature of spontaneous decomposition for each mixture. Each small black circle represents the result of an individual experiment, and the center of the ring drawn on each abscissa is the average of all of the determinations made for the mixture whose composition is represented by that abscissa.

Mixtures richer or poorer in manganese dioxide than those shown on the second graph did not evolve oxygen at a rate too rapid to be measured; but many of them did evolve oxygen rapidly, and the thermometer embedded in the mixture rose as much as 15° above the temperature in the furnace. For manganese dioxide from any one bottle it was unusual to find a variation of more than 5° in the temperature of spontaneous decomposition; but samples of manganese dioxide from different bottles frequently showed much greater variation.

Experiments were conducted with a 500° thermometer, so that the maximum temperature reached could be recorded. To cover the bulb of this thermometer, it was necessary to use a charge containing 4 g. of potassium chlorate. When the temperature of the furnace was about 320°, the maximum temperature attained by 3 charges varied from 405° to 412°. The composition of the mixture was $KClO_3 : MnO_2 :: 2 : 1$.

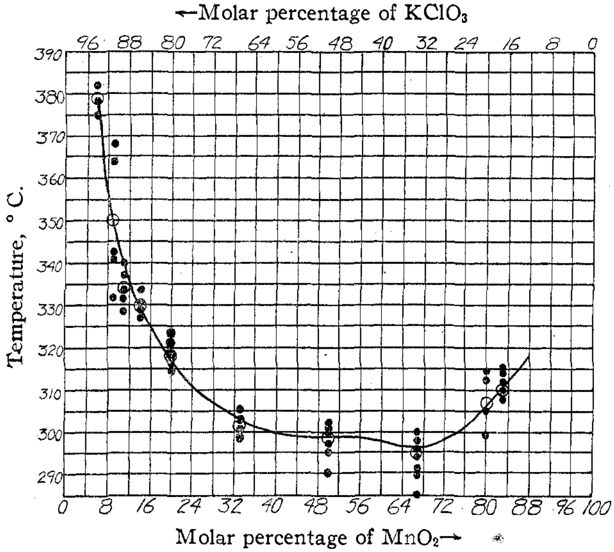

Fig. 2.—Spontaneous decomposition temperatures of mixtures of $KClO_3$ and MnO_2 of various molecular proportions.

Discussion of Results

Besides the variation in the quality of the manganese dioxide, lack of homogeneity, variations in the temperature of the furnace fraction of charge already decomposed, and inaccuracies in recording rapidly changing temperatures by means of a mercury thermometer contributed to produce differences between the different temperatures of spontaneous decomposition recorded for mixtures of the same composition.

The rapid evolution of oxygen cannot be due to incomplete mixture of the components nor to melting before contact between them: for spontaneous decomposition occurs 70° below the melting point of potassium chlorate, (Carpenter[8] gives 357.1°) and in an apparently homogeneous mixture of particles all of which have passed through a 200-mesh sieve. The rapid decomposition is not due to the formation of an intermediate

[8] Carpenter, *Chem. Met. Eng.*, **24**, 569 (1922).

substance and its subsequent decomposition. A mixture of manganese dioxide and potassium chlorate, whose molecular ratio was $KClO_3 : MnO_2 :: 2 : 1$, was sealed in a steel bomb and held for more than 7 hours at a temperature between 331° and 347°. When the bomb was cooled and opened, 66% of the potassium chlorate was undecomposed. No other substances were found except potassium chloride and oxides of manganese insoluble in water.[9]

The explanation for the sudden evolution of oxygen and rise in temperature is simpler. The violent evolution of oxygen depends on the completeness of the contact with the catalyst, and on the temperature attained. The heat required to produce the necessary temperature comes from the exothermal decomposition of the potassium chlorate. Whenever the externally applied temperature is sufficient to cause a rate of decomposition rapid enough to produce heat faster than it is lost to the surroundings, the temperature of the mixture rises. This, in turn, accelerates decomposition, heat evolution and rise in temperature. The result is an extremely rapid decomposition of the potassium chlorate in contact with the catalyst. If a small proportion of catalyst is present, the lack of contact saves some potassium chlorate from immediate decomposition. If a great proportion of catalyst is present, much of the chlorate is decomposed at lower temperatures and not enough is left to produce a great increase in temperature. In the latter case, the heat capacity of the system is larger because of the large amount of manganese dioxide associated with a fixed amount of potassium chlorate.

The heat of decomposition of potassium chlorate as given in Landolt-Börnstein "Tabellen" is 10,000 calories. The heat associated with the evolution of 1 cc. of oxygen would be 0.3 calorie. During the spontaneous decomposition of the 4g. samples, an average of 800 cc. of oxygen was evolved after spontaneous decomposition started. This indicates that 240 calories of heat was developed, if all of the heat came from the decomposing potassium chlorate. The heat capacity of the oxygen evolved, the potassium chloride and manganese dioxide residue, and the thermometer bulb and the part of the heating tube in contact with the charge was 2.4. To raise this 90° would require 216 calories. The remaining 24 calories could have been lost easily by radiation and conduction to the cooler surroundings.

Summary

1. When homogeneous mixtures of potassium chlorate and manganese dioxide are heated rapidly, those containing more than $^1/_{16}$ and less than 5 molecular equivalents of manganese dioxide to 1 of potassium chlorate

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[9] Considerable data on the effect of the pressure of oxygen on the decomposition of potassium chlorate have been collected by two of the authors of this paper, and will soon be ready for publication.

suffer spontaneous decomposition accompanied by a rapid rise of temperature, at a temperature characteristic for each mixture.

2. This acceleration is due to the exothermal nature of the decomposition.

3. Pressure of oxygen exerts a marked effect on the decomposition of potassium chlorate.

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THE IONIZATION OF ALCOHOLS

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Since early in the history of organic chemistry, esterification has been compared to neutralization and alcohols have been said to play the role analogous to that of bases. Current statements can be found, however, to the effect that alcohols are not bases, and the analogy of esters and salts though used by many is probably accepted as satisfactory by few. The purpose of this work was to contribute to our knowledge of the extent of ionization of alcohol in either of the two ways, as a base into ethyl and hydroxyl ions or as an acid into hydrogen and ethylate (OC_2H_5) ions. In an article published since this work was completed, Danner and Hildebrand,[2] have measured the ionization of alcohol by two methods, considering the ionization as an acid as predominant and assuming the ionization of alcohol as a base to be negligible in comparison.

Approximate Measurement of the Degree of Ionization of Alcohol into Hydrogen and Ethylate Ions

An attempt was first made to determine the degree of ionization of ethyl alcohol into hydrogen and ethylate, by determination of the equilibrium point in the reaction, $C_2H_5OH + NaOH \rightleftharpoons C_2H_5ONa + H_2O$. At the time the work was started, knowledge of the equilibrium point in this reaction was exceedingly scant, so even approximate results were thought desirable. When sodium hydroxide is dissolved in absolute alcohol some water is formed by reaction. A dynamic method was devised, accurate to about 10%, for determining very small amounts of water in alcohol, in such a way that equilibrium would not be appreciably disturbed. This method was then applied to the determination of the amount of water formed by the addition of a known amount of solid sodium hydroxide of

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[1] The experimental work concerned with metallic nitrides and hydrides was done by R. W. Truesdail, and a report of this work was incorporated in a thesis submitted by him at the University of Oregon, in partial fulfilment of the requirements for the degree of Master of Science.

[2] Danner and Hildebrand, THIS JOURNAL, 44, 2824, 2832 (1922).