Chemical Source of Oxygen

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Abstract. An investigation was made on the thermal decomposition of the alkali metal chlorates and perchlorates of sodium, potassium and lithium, and mixtures of these. The effects of various catalysts in promoting and controlling the decomposition with the production of minimum reaction temperature and maximum oxygen yield were studied. Experimental results are presented for potassium chlorate and perchlorate.

In recent years the military has advocated the development of a solid chemical oxygen source to the point where it may be used in an aircraft oxygen system. The need exists for a reliable oxygen source that is efficient on a weight and volume basis, and sufficiently developed for immediate availability for military use.

It has been known for a number of years that when chlorates and perchlorates are heated to a sufficiently high temperature, oxygen is evolved. A classical method for the production of oxygen in the laboratory is the heating of potassium chlorate. The reaction is known to proceed exothermally at high temperatures to produce potassium chloride and oxygen. Many potential chemicals exist that could be used as an oxygen source. Some of these are well known; others have only been made in the laboratory in small quantities and have not been evaluated as oxygen sources. A list of oxygen sources would include the nitrates, permanganates, chelate compounds, oxides, chlorates and perchlorates.

Several investigations have been conducted on the possibility of using the alkali metal chlorates and perchlorates as a source of oxygen. One of the first to generate oxygen from molded compositions of potassium chlorate and perchlorate was A. Hloch (1938, 1939). The Germans performed research on the securing of oxygen from solid chemical sources during World War II. Oxygen producing cartridges were developed after a long period of investigation. However, the cartridges had a fundamental defect, the origin of which could not be found; these cartridges were likely to explode. This defect was the only reason that the chemical oxygen generator was not adopted for aircraft, despite its high level of development (Surgeon General, USAF, 1950).

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Late in 1943 a development program was initiated by the United States government to acquire a solid oxygen source. This resulted in the utilization of sodium and potassium chlorates, in the form of candles, which would slowly "burn" with the evolution of heat and a large share of their combined oxygen (Schechter, 1950).

Bovard and Morse (1957), in their feasibility study report on oxygen generation from solids, state that although solid chemicals will produce oxygen, an adequate system to provide oxygen for aircraft has not been developed. The Pioneer-Central Division of the Bendix Aviation Corporation has conducted an investigation on the development of such a system. In this paper are presented the results of an investigation of chlorates and perchlorates as a source of oxygen for use in an aircraft artificial atmosphere system.

**Experimental**

The chemicals used were purchased as certified grade reagents. Those materials which were obtained as large crystals were pulverized with a mortar and pestle to obtain approximately uniform particle size. A decomposition apparatus was constructed that would permit measurement of the temperature and pressure developed as well as the amount of gas evolved. A cylindrical steel rod (3 x 5 inches) was bored to a wall thickness of a quarter of an inch. This was fitted with a cap secured by means of a sleeve, a seal being obtained with an "O" ring. Thermocouple and ignition wells, and a gas outlet were installed in this cap. An illustration of the solid oxygen system is shown in Figure 1.

Ignition was achieved by inserting a nichrome heating wire into the chemical mixture. The sample temperature was obtained as a function of time on a Wheelco Recorder (Model No. 800) at a chart speed of three inches per minute. The volume of oxygen evolved was measured by a Sprague gas meter.

**Chromatography Analysis of Gas**

A Beckman Gas Chromatograph (Model No. 178) was employed for the analysis of the evolved gas. Oxygen, nitrogen and carbon monoxide were tested for by use of a 5 ft. molecular sieve column. A 4 ft. column of silica gel was used for detection of any carbon dioxide formed. Chlorine was tested for by employing a 1.5 ft. column of silica gel material coated with "Aroclor". The oxygen obtained was ascertained to be of sufficient purity for physiological use, as evidenced by negative tests for carbon dioxide, carbon monoxide, and chlorine.

**Results and Discussion**

In the present work an attempt was made to obtain a solid oxygen chemical mixture which would give a maximum yield of oxygen per
weight of reactant in a minimum amount of time. The effect of various catalysts on the rate of decomposition of chlorates and perchlorates was tested.

The oxygen-evolving mixture developed consists of a mixture of alkali metal chlorates and perchlorates compounded with a material (such as iron powder) that undergoes oxidation with liberation of heat, and a substance to fix any elemental chlorine that may be formed, plus a catalytic material. A typical composition is, by weight, 90 percent oxygen-evolving chemical, 5 percent iron powder (reduced), 4 percent catalyst, and 1 percent barium peroxide (BaO₂) to fix chlorine, if any is formed.

A considerable number of catalysts, known for their ability to favor the decomposition of chlorates and perchlorates, were investigated. A new catalyst (cobaltous chloride) was found which gave a minimum reaction temperature and time. A comparison, on the basis of reaction rates, of a few of the catalysts tested is shown in Figure 2. It can readily be seen that Pioneer-Central’s catalyst gave a minimum overall reaction time.
The higher yield of oxygen per unit weight of reactant favored the use of perchlorate over chlorate. Various mixtures of chlorates and perchlorates were investigated to determine which would give a minimum overall reaction time with a maximum yield of oxygen. However, due to the endothermic nature of the perchlorate, the overall reaction time increased. The thermal decomposition curves of potassium chlorate, perchlorate, and mixtures of the same are shown in Figure 3. The composition by weight of the samples decomposed is as follows: 150 grams of perchlorate and/or chlorate, 20 grams of iron powder, 20 grams of catalyst, and 10 grams of barium peroxide.
The chemical oxygen source system developed at Pioneer-Central provides a controlled reaction with a reduction in the reaction time. The system itself is capable of providing up to 150 liters of gaseous oxygen per minute.

Because of the reduction in weight and volume over conventional equipment, the solid oxygen system is to be advocated for emergency use on aircraft. The solid oxygen system offers the additional advantage of being simple and fool proof, as well as having excellent storage characteristics.

In the present paper only the experimental results for potassium chlorate and perchlorate are presented. However, the catalyst was found to be equally effective for the decomposition of the chlorate and perchlorate of sodium. Due to the deliquescent nature of lithium chlorate, insufficient thermal decomposition data were obtained for presentation.
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Literature Cited


SENeca, ILLINOIS