

NO_2 will on collision undergo reaction rather than thermal degradation increases rapidly as its excitation increases in the neighborhood of 70,000 calories per mole (corresponding to violet light).

Summary

Experiments are described which are in confirmation of Norrish's view that gaseous NO_2 is decomposed by light into NO and O_2 . By employing a technique permitting experimentation at sufficiently low partial pressures of NO and O_2 , recombination of these gases could be made slow enough to neglect. This permitted quantum yield determinations to be made treating the reaction simply as a decomposition rather than as a photochemical equilibrium. For the quantum yields, expressed as molecules of oxygen produced per quantum absorbed, the following mean values were obtained: λ 4350Å., 0.0046; λ 4050Å., 0.36; λ 3660Å., 0.77. These yields were found to be not markedly dependent on the pressure in the range studied.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF IOWA STATE COLLEGE]
THE DECOMPOSITION OF POTASSIUM CHLORATE. III. THE EFFECT OF PRESSURE ON THE DECOMPOSITION OF POTASSIUM CHLORATE-MANGANESE DIOXIDE MIXTURES¹

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The decomposition of potassium chlorate is considered irreversible under any attainable conditions. Lewis and Randall^{1a} report that they heated potassium chlorate in a closed steel bomb 1.5 inches in external diameter in which a 0.75 inch hole was bored. After 0.5 hour at 400° the bomb had become bulb shaped. By an indirect method (the comparison of free energies) they calculated that potassium chlorate decomposing at room temperature would be in equilibrium with oxygen under a pressure of about 10^{15} atmospheres and that the equilibrium pressure of the oxygen would rise rapidly with rise in temperature. These results and conclusions are in accord with most of the data on the effect of pressure on the decomposition of potassium chlorate.²

Fowler and Grant,³ however, suggested that the decomposition might be reversible; and Sodeau⁴ says of lead chlorate, "It seems remarkable

¹ A preliminary version of this article was received February 14, 1927.

^{1a} Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., 1923, pp. 508-511.

² (a) Veley, *Phil. Trans.*, **179A**, 257-295 (1888); (b) Warren, *Chem. News*, **58**, 247 (1888).

³ Fowler and Grant, *J. Chem. Soc.*, **57**, 272 (1890).

⁴ Sodeau, *J. Chem. Soc.*, **81**, 1066 (1902).

that decrease of pressure should markedly impede the decomposition of the chlorate." He used pressures as low as 2 millimeters.

It has been shown⁵ that potassium chlorate-manganese dioxide mixtures undergo spontaneous decomposition at quite definite temperatures for definite compositions of the mixture when under atmospheric pressure. As early as 1920 it was known in our Laboratory that mixtures whose spontaneous decomposition temperatures were below 300°, when under atmospheric pressure, could be heated for hours above 325° in sealed steel bombs without complete decomposition of the chlorate.⁶ It seemed worth while to make a more thorough investigation of the effect of pressure on the decomposition of potassium chlorate and to include pressures below atmospheric pressure. If high pressures retard this decomposition, even atmospheric pressure might have some retarding effect, and decomposition of potassium chlorate-manganese dioxide mixtures might be produced below 200°.⁷

Apparatus

For pressures below 5 atmospheres the apparatus was made of Pyrex glass. All joints were sealed and no stopcocks were used. When gas was collected at low pressures, the Toepler pump as modified by McLaughlin and Brown⁸ was used. Pressures were measured by means of a mercury manometer and a cathetometer.

For work at higher pressures the apparatus consisted of bombs, a connecting block, a pump capable of producing a pressure of 1000 kg. per sq. cm. and connecting tubing and pressure gages such as are used for hydraulic presses. The bombs were made of eighteen-inch sections of steel shafting 2.5 inches in diameter. A three-quarter inch hole was bored to a depth of seventeen inches. The open end was threaded and closed by means of a perforated plug. The outer end of the plug was threaded to fit the hydraulic press connections. The connecting block had four connections and a needle valve so arranged that oxygen could be introduced from a tank, water pumped into the block and connections including the plug of the bomb, and the needle valve closed to cut off the oxygen tank and the pump from the bomb and pressure gage. When no preliminary oxygen pressure was imposed, the pressure gages were connected directly to the bomb. All furnaces were electric resistance furnaces made in our Laboratory to fit the object to be heated. The temperature was regulated by means of a thermo-regulator consisting of a silver rod mounted in an invar steel frame in such a way that the differential elongation was magnified nearly fifty-fold by means of a lever. The contact points on the long arm of the lever completed a circuit which controlled a shunt around the external resistance in the heating circuit.

⁵ (a) Brown, Burrows and McLaughlin, *THIS JOURNAL*, **45**, 1343-1348 (1923); (b) Brown and White, *Proc. Iowa Acad. Sci.*, **31**, 291-298 (1924); (c) Burrows with Brown, *THIS JOURNAL*, **48**, 1790 (1926).

⁶ Dr. Dwight L. Scoles and Dr. Victor G. Heller did some of the preliminary work on this problem in 1919.

⁷ Speaking of potassium chlorate, Mellor says, "The evolution of oxygen begins. . . with manganese dioxide between 200° and 205°."

Mellor "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. I, Longmans, Green and Co., 1922, p. 350.

⁸ McLaughlin with Brown, *THIS JOURNAL*, **47**, 613-615 (1925).

A variation of more than 2° from the mean temperature was unusual even in the experiment which was continued for 300 days. Temperatures were determined by means of mercury thermometers for the lower temperatures, and by means of chromel-alumel thermocouples for the higher temperatures.

Materials

The potassium chlorate used in this work was Baker and Adamson's c. p. grade. A saturated solution gave only a slight cloudiness with silver nitrate. Suitable tests showed the absence of heavy metals, calcium, bromates, nitrates and sulfates. Reduction with excess ferrous sulfate and back titration with potassium permanganate indicated 98.2% of potassium chlorate. Absorbed moisture was the impurity.

The manganese dioxide was prepared by the method of Merrill and Scalione⁹ from potassium permanganate and manganese sulfate in strong sulfuric acid. The washing of the precipitated manganese dioxide was continued until it became colloidal and remained in suspension several days after each decantation and addition of distilled water.

The potassium chlorate and manganese dioxide were ground and sifted separately through a 200-mesh sieve, dried at 110°, weighed out and sifted together through a 150-mesh sieve until the mixture was uniform. The composition of the mixture used was 2KClO₃·MnO₂, the composition which Brown, Burrows and McLaughlin^{5a} found to have the lowest spontaneous decomposition point.

Experimental Work

The Effect of Low Pressures at Temperatures below 200°.—Equal amounts of the mixture of potassium chlorate and manganese dioxide were carefully dried and placed in each of two hard glass test-tubes with side necks. After sealing the top of each tube, the two were tied together with a copper wire and put into a furnace. The side neck of one of these tubes, in which the material was to be heated at atmospheric pressure, was connected by means of heavy rubber tubing to one end of a glass tube, the other end of which was dipped into a cup of mercury and turned upward to facilitate the collection of gas.

The tube to be heated at reduced pressures was connected to the modified Toepler pump by sealing between them a glass tube containing an enlarged section nearly filled with phosphorus pentoxide.

The results of heating three different samples of the mixture under low pressures are reported in (a), (b) and (c) of Table I. The sample described in part (a) was heated to 100° for two and four-tenths hours and kept under pressures of less than 0.05 cm. for

TABLE I
LOW PRESSURE RESULTS

Sample, wt. of KClO ₃ , g.	Temp., °C.	Press., cm. of Hg	Duration of collection, hours	Volume of gas collected, cc.	Cc. of gas evolved per g. per hr.	Vol. of gas calcd. from chloride analysis
(a) 2	125	0.010	6	2.90	0.24	25.1
	145	.010	80	23.00	.15	...
(b) 2	175	.125	3	35.50	5.92	63.9
(c) 1	196-200	.01-.24	3	30.00	10.00	108.0
(d) 2	125	73-75	6	.0	.0	...
	145	73-75	80	.0	.0	...
	175	73-75	3	.0	.0	.0
	196-200	73-75	3	.0	.0	...

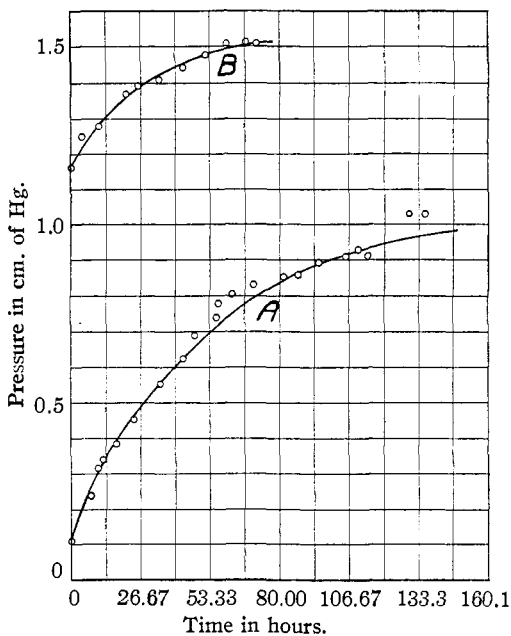
⁹ Merrill and Scalione, *THIS JOURNAL*, **43**, 1986 (1924).

more than thirty-four hours before any gas was collected. The sample described in part (b) was kept at pressures below 0.07 cm. for eighty-six hours before any gas was collected. On two different days the temperature was raised to 90–100° for one and one-half hour periods. The sample described in (c) was heated to 65–100° for one and one-half hours and kept at pressures below 0.02 cm. for 37.5 hours before any gas was collected. The sample described in (d) was taken from the same supply bottle as the samples referred to in (a), (b) and (c) and was in the furnace with them all of the time but it was subjected to atmospheric pressure during the entire period of the experiments.

At the close of the experiment the apparatus stood for eleven days without any change of reading of the manometer. The gas collected in parts (a) and (b) analyzed

95 and 100% oxygen, respectively, by absorption in alkaline pyrogallate. The gas collected in (c) was lost by an accident. Manganese dioxide absorbs carbon dioxide and the manganese dioxide was exposed to the atmosphere before it was introduced into the test-tube. Carbon dioxide would be absorbed by alkaline pyrogallate. However, the absorption and retention of more than 25–35 cc. of carbon dioxide through 34–86 hours of evacuation, some parts of which were carried out at 100°, on 0.5–1.0 g. of manganese dioxide is unlikely. The formation of chlorides could be due to no cause but the decomposition of some of the chlorate. There is always a close agreement between the amount of oxygen collected and the amount of chloride formed or an excess of chloride formed. The excess of chloride probably corresponds to the amount of oxygen evolved and pumped out before any gas was collected. There seems to be no reasonable doubt that the gas evolved and collected at these temperatures was oxygen.

During the progress of the experiments described in the preceding paragraphs, it was noticed that when the mixture was subjected to pressures less than 0.02 cm. of mercury and heated to 50–60° a small amount of moisture was given off. When the temperature was kept between 60 and 100°, there was evidence that a small amount of gas was being drawn out over the phosphorus pentoxide through the pump—evidently not moisture. In order to determine whether oxygen was given off at these lower temperatures and what pressures would be developed at different temperatures, 10 g. of the mixture, potassium chlorate and manganese dioxide, was sealed in a test-tube and connected to the pump as previously described. The apparatus was evacuated to a pressure of 0.03 cm. The material was heated to 72° and then cooled to room temperature repeatedly for a period of three days. During this time the apparatus was occasionally pumped out, for it proved impossible to keep a constant pressure while the material was being heated and cooled. The pressure did remain constant at 0.05 cm.



Temperatures 68 and 90°.

Fig. 1.

for a period of twenty-four hours when the temperature did not average above 50° ; but when the temperature was then raised to $60-70^{\circ}$ the pressure increased to 0.110 cm. in twelve hours. The temperature was then kept as nearly constant as possible at 68° and the heating continued to determine what pressure would develop. The results are plotted on curve A, Fig. 1. The ordinates are pressures and the abscissas are duration of heating. When the increase in pressure became very slow at 68° , the temperature was raised to 90° without in any way disturbing the apparatus. Curve B, Fig. 1, is a plot of pressure against time for this same charge at 90° . Before the temperature was

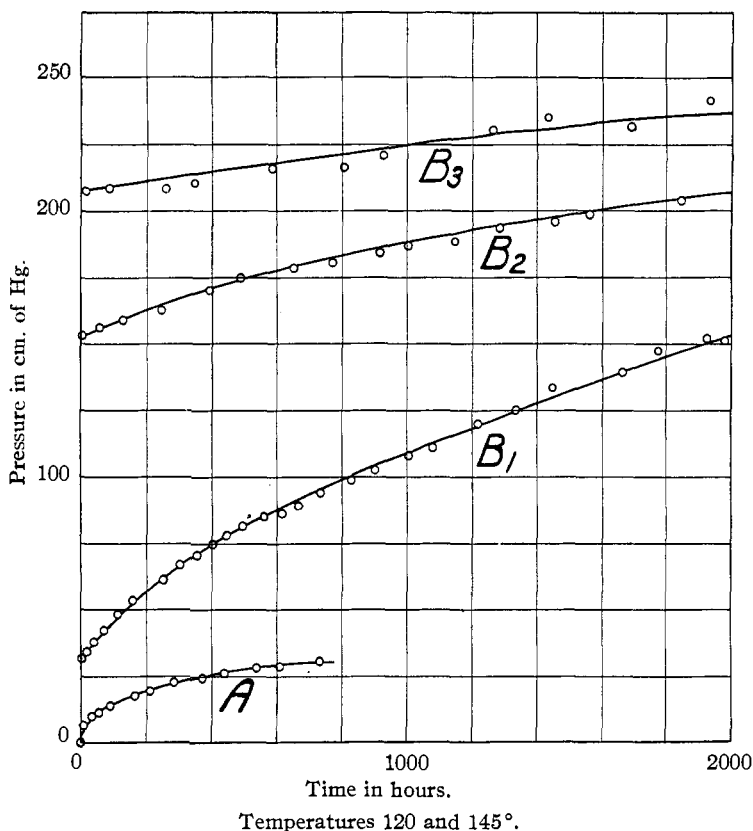


Fig. 2.

stabilized, the pressure had risen from 1.03 cm. to 1.16 cm.; so 1.16 cm. is taken as the pressure at zero time for 90° . Curve A on Fig. 2 is a similar plot for a second charge heated at 120° . Curves B_1 , B_2 , and B_3 on Fig. 2 are a similar representation of data secured at 145° with the same charge which was used at 120° . B_1 represents the first 2000 hours at 145° , B_2 the hours between 2000 and 4000 and B_3 the hours between 4000 and 6000 at 145° .

Two samples were heated at 200° in steel bombs without charging with oxygen. The lowest pressure which the gage recorded was 100 lbs. The curves on Fig. 3 represent the data at 200° . There is close agreement between the curves until a pressure of 40 atmospheres is reached, when the curve marked by crosses indicates a leak.

Many other experiments carried out in the study of the effect of high pressure on the decomposition of potassium chlorate have failed because of explosions or leaks in the apparatus. The following tables contain the results of those experiments in which there was no apparent leak of oxygen.

Before the high-pressure pump and gages were available for measuring the pressure during the progress of an experiment, two apparently successful runs were made. By measuring the volume of the bomb, using

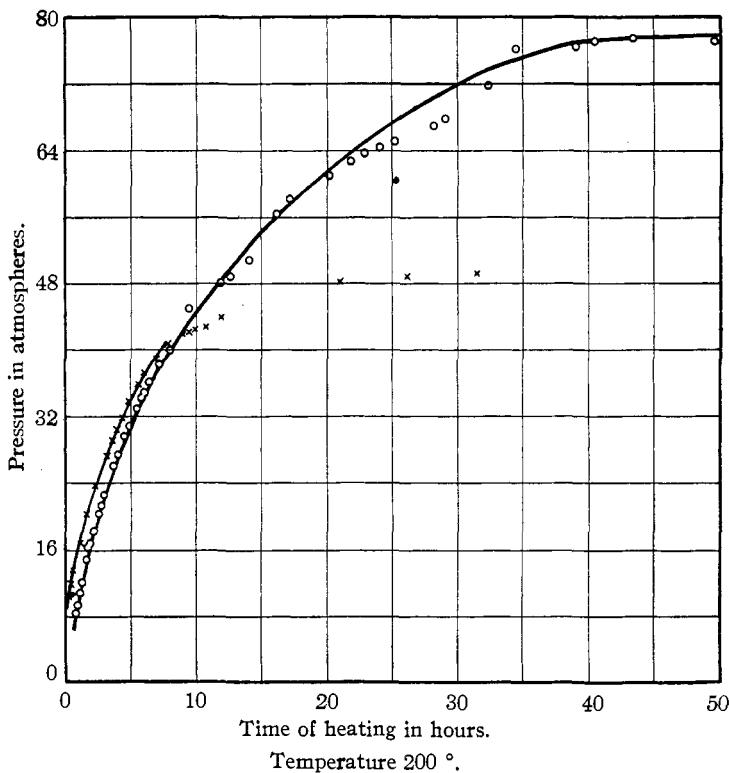


Fig. 3.

the density as found in tables, by weighing each substance in the bomb to determine its volume and by analyzing the residue for chlorides formed by the decomposition of the potassium chlorate, the highest pressure that could be produced by retaining all of the oxygen in the free space

TABLE II

RESULTS AT HIGH PRESSURES—CALCULATED BY THE AMOUNT OF DECOMPOSITION

No.	KClO ₃ , g.	Free space in bomb, cc.	Hours heated	Av. temp., °C.	Press. reached, calcd., atm.	Press. at 20°, calcd., atm.	Vol. of gas at stand. cond., cc.	Cc. of oxygen per g. (stand. cond.)	KClO ₃ left in bomb, %
1	28.39	14.6	1.0	335	236.7	99.35	1551.5	54.64	80.2
2	23.57	15.57	7.5	335	322.7	125.63	2230.5	12.62	66.6

of the bomb was calculated. The temperature of the furnace was measured by a mercury thermometer. The results are given in Table II.

The pressures given in Table III were measured on the pressure gage attached to the high pressure pump. The temperatures were measured by a thermocouple. The pressure shown at room temperature at the beginning of each experiment was produced by filling the bomb with oxygen from an oxygen tank through the connecting block as previously described. The charges referred to in Table III were not weighed.

TABLE III
RESULTS AT HIGH PRESSURES—MEASURED BY GAGES

No.	Time heated, hrs.	Average temp., °C.	Pressure, atms.	KClO ₃ undecomposed, %
1st Expt.	..	Room	200.0	..
	3.0	345	443.3	..
	12.0	Room	280.0	Present ^a
2d Expt.	..	Room	180.0	..
	12.0	Room	180.0	...
	7.0	320	463.3	..
	2.5	290	436.6	..
	3.5	325	480.0	..
	4.0	285	450.0	..
	6.0	320	483.3	..
	5.0	325	496.6	..
	14.0	Room	240.0	23.5

^a Not quantitatively determined.

The data under high pressures are not entirely comparable with those under low pressures; for at low pressures the materials were carefully dried while at high pressures the gas was enclosed by a water seal. We have evidence in later experiments that water is very important as a promoter of the catalytic effect of manganese dioxide on potassium chlorate. This promoter effect of water is under investigation in this Laboratory.

Discussion

It is evident that the decomposition of potassium chlorate-manganese dioxide mixtures begins at temperatures far below 200°. Probably there is some decomposition as low as 60°. Certainly at 68° the decomposition progresses continuously if the pressure is kept low enough. The rate of decomposition at a given pressure increases rather rapidly with rise in temperature. At all temperatures below 350° the rate of decomposition is very greatly affected by the pressure of oxygen on the decomposing mixture. This is shown by the experiments reported in Table I. In each of three experiments oxygen was collected from a tube at low pressure while a tube at atmospheric pressure wired to it in the same furnace and charged with the same amount of the same mixture evolved no measurable amounts of gas. Tables II and III show that under pressures of

from 200 to 500 atmospheres, potassium chlorate-manganese dioxide mixtures may contain undecomposed potassium chlorate after being held for hours at temperatures as much as 40° above their spontaneous decomposition temperatures at atmospheric pressure. The curves show that the rate of evolution of oxygen decreases faster than the amount of undecomposed chlorate decreases. That this decrease in rate of evolution of oxygen is not due to insufficient contact between catalyst and chlorate is shown by the large increase in rate of evolution when the undisturbed mixture is raised to a higher temperature.

The reaction is not stopped or retarded because of attaining or approaching an equilibrium pressure; for increases of pressure to many times that of the retarding pressure produced no potassium chlorate from oxygen and potassium chloride. Pressures as high as 100 atmospheres of oxygen on potassium chloride-manganese dioxide mixtures at 145° produced no detectable amounts of potassium chlorate in two days. Table III shows that when the temperature is lowered, as from 320°, and brought back to the same temperature again, the pressure is always higher at the return than at the first time that temperature was reached.

Summary

1. Pressure has a marked effect on the rate of decomposition of potassium chlorate in the presence of manganese dioxide within the range of 70 to 350°.
2. For each temperature there is a pressure above which decomposition is very slow or absent.
3. When this pressure has been reached for any temperature, a lowering of the temperature does not result in recombination of oxygen with the potassium chloride and the pressure decreases only as would be expected from the gas laws.
4. Equilibrium for the reaction $2\text{KClO}_3 = 2\text{KCl} + 3\text{O}_2$ has not been attained.
5. The decomposition of potassium chlorate in the presence of manganese dioxide has been effected at temperatures as low as 70°.
6. The decomposition of potassium chlorate in the presence of manganese dioxide is retarded by pressures of oxygen below 500 atmospheres when the mixture is heated for periods of several hours at temperatures 40° above its spontaneous decomposition temperature under atmospheric pressure.
7. Water is a promoter in the catalysis of the decomposition of potassium chlorate by manganese dioxide.