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THE EFFECT OF PRESSURE ON THE DECOMPOSITION OF POTASSIUM CHLORATE IN THE PRESENCE OF MANGANESE DIOXIDE.

by

Henry Max McLaughlin.

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In charge of Major Work

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INTRODUCTION.

Although the results obtained by different experimenters on the decomposition of potassium chlorate differ widely and are often contradictory, these facts seem to have been fairly well established: (1) Potassium chlorate is an endothermic compound. Considerable heat is evolved during its decomposition. (2) When heated in a platinum vessel to 450° and above, the pure salt decomposes completely into potassium chloride and oxygen. (3) When the temperature is not raised too high and too rapidly potassium perchlorate is formed by auto-oxidation. (4) Many oxides cause the decomposition to take place at a lower temperature --- often 100° below that required to decompose the pure salt. When mixed with manganese dioxide the initial decomposition has been reported at 200°. The decomposition of the pure salt is exceedingly slow at 400°, when heated at atmospheric pressure. (5) No perchlorate is formed when a mixture of potassium chlorate and manganese dioxide is heated. (6) When potassium chlorate is heated with many of the oxides, a small amount of chlorine is given off. The amount of chlorine produced seems to increase slightly with the proportion of oxide used. Ozone has been reported in the gas evolved. However the evidences on which the presence of ozone was based would also be produced by chlorine. (7) An explosion may result from heating potassium chlorate alone.

Warren(1) introduced an intimate mixture of manganese dioxide and potassium chlorate into a wrought iron tube closed at one end and provided with a stopcock at the other. The tube was heated to just below redness. He observed that the rate of decomposition was much retarded by the pressure and that when the stopcock was opened the gas escaped with great violence carrying with it a relatively large quantity of chlorine. Warren reports that the water extract of the residue was alkaline.

From a consideration of the effect of a rapid rise of temperature in increasing the amount of chlorine obtained and the effect of pressure in retarding the decomposition, Fowler and Grant(2) suggested the possibility of a reversible reaction. The original plan of the present work was to establish such a reversibility. However, for reasons which will be pointed out in the data and discussion to be given later, the point of equilibrium for any given set of conditions has not been definitely established.

Sodeau(3) states that when calcium chlorate is heated

1. H. N. Warren. Chem. News 58, 247, (1888).
2. G. J. Fowler and J. Grant. J. Chem. Soc. 57, 272 (1890).
   Chem. News 61, 117 (1890).
3. W. H. Sodeau. J. Chem. Soc. T. 81, 1066 (1902).

slowly, 0.6% of its total chlorine is evolved whether the pressure is 760 mm. or 4 mm. In a discussion of the results of a study of lead chlorate, he remarks that "it seems remarkable that decrease of pressure should markedly impede the decomposition of the chlorate." He used pressures as low as 2 mm.

Cook(4) has studied the effect of temperature and pressure on potassium iodate and bromate. He maintained a pressure of 30-50 mm. and reports absolutely no difference in the results from those obtained at normal pressure. The residues gave the same analysis and the decomposition took place at the same temperature. When using pure potassium chlorate he reports 0.03% of the total chlorine given off during the short time elapsing between the first melting and its complete fusion. He does not make a statement concerning the effect of pressure on the decomposition of the potassium chlorate. The presence of chlorine in the gas evolved may have been caused by the glass in which the materials were heated. Stas and others(5) report absolutely no chlorine when pure potassium chlorate is heated in platinum vessels. We have also confirmed this result.

4. E. H. Cook. J. Chem. Soc. 65, 802-14 (1893).
5. J. S. Stas. Chem. News. 73, 15 (1896).

Veley(6) used a Sprengel pump with the usual gauge and a tube for the collection of gaseous products. The rate of evolution of gas was compared at 765.4 mm. and at 20 mm. The potassium chlorate was heated in a glass tube by means of a bath filled with molten potassium nitrate. He found a temporary slight increase in the rate of evolution at the lower pressure followed by little or no difference in the rate of decomposition at the two pressures.

Lewis and Randall(7) report that they heated potassium chlorate in a closed steel bomb at about 400°. The bomb was one and a half inches in diameter and had a three-eighth inch hole in the center. After about an hour the pressure became so great that the bottom of the bomb began to flow gradually into a bulb. They concluded that the equilibrium pressure would be too high to measure. Consequently under their direction Olson(8) determined the equilibrium constant for the reaction.

$$3H_2O + 3Cl_2 + HClO_3 + 5HCl.$$

On the assumption that the difference in free energy between

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6. V. H. Veley. Phil. Trans. (A) 179, 257-95 (1888).

7. G. N. Lewis and M. Randall. Thermodynamics and the free energy of chemical substances. P 508-11 (1924).

8. A. R. Olson. J. Am. Chem. Soc. 42, 896 (1920).
   C. A. 14, 1777 (1920).

solid potassium chloride and potassium chlorate is approximately the same as that between the chloride and chlorate ion, they calculated that the decomposition pressure of potassium chlorate would be of order of 10^{15} atmospheres at room temperature and would increase rapidly with rise of the temperature.

Before Lewis and Randall(7) had published their calculations we had made preliminary tests and found that the pressure developed by the decomposition of potassium chlorate would be very great. It was finally determined that potassium chlorate could be safely heated for days at a temperature of 300--400° in a piece of soft steel shafting two and a half inches in diameter with a three-quarter inch hole in the center.

APPARATUS.

The bomb used in this work is shown in Fig. 1. When in use the mixture of potassium chlorate and manganese dioxide contained in a hard glass test tube filled the space AB. Asbestos wool was packed tightly in the top of the test tube to prevent the charge from coming in contact with the inside walls of the bomb. The top of the test tube rested on the bottom of the bomb. This was necessary because the bomb was heated in an inverted position. The space BC was filled with a piece of steel rod, E, which fitted snugly in the bore of the bomb and rested on a narrow shoulder at B.

To hold the oxygen formed during the decomposition at the high pressures developed and at the temperatures necessary for decomposition was very difficult. The most carefully cut threads leaked even when tapered. A narrow shoulder with thin copper gaskets was tried with little success. When the threaded plugs clossing the bomb were heated for a long period and at the same time subjected to the high pressure developed it was found that the threads were usually stuck so tightly that the bomb was ruined by removing the plug. To prevent this the bomb was made eighteen inches long, fastened in a frame in an inverted position and heated only for a distance of ten inches from the bottom while cold water was kept running over the threaded end of the bomb. When closing the bomb for a run, after introducing the charge and the rod, E, a leather washer was placed on the sharp edge, C. A silver washer was then placed on the leather washer. The pressure applied by turning in the plug caused the sharp edge, C, to cut through the leather and cut a narrow groove in the silver. At the same time a ring of the leather was forced down into the groove, D, with as much force as could be applied in turning in the plug with a two foot wrench. The plug F was threaded at both ends, one of which fitted the

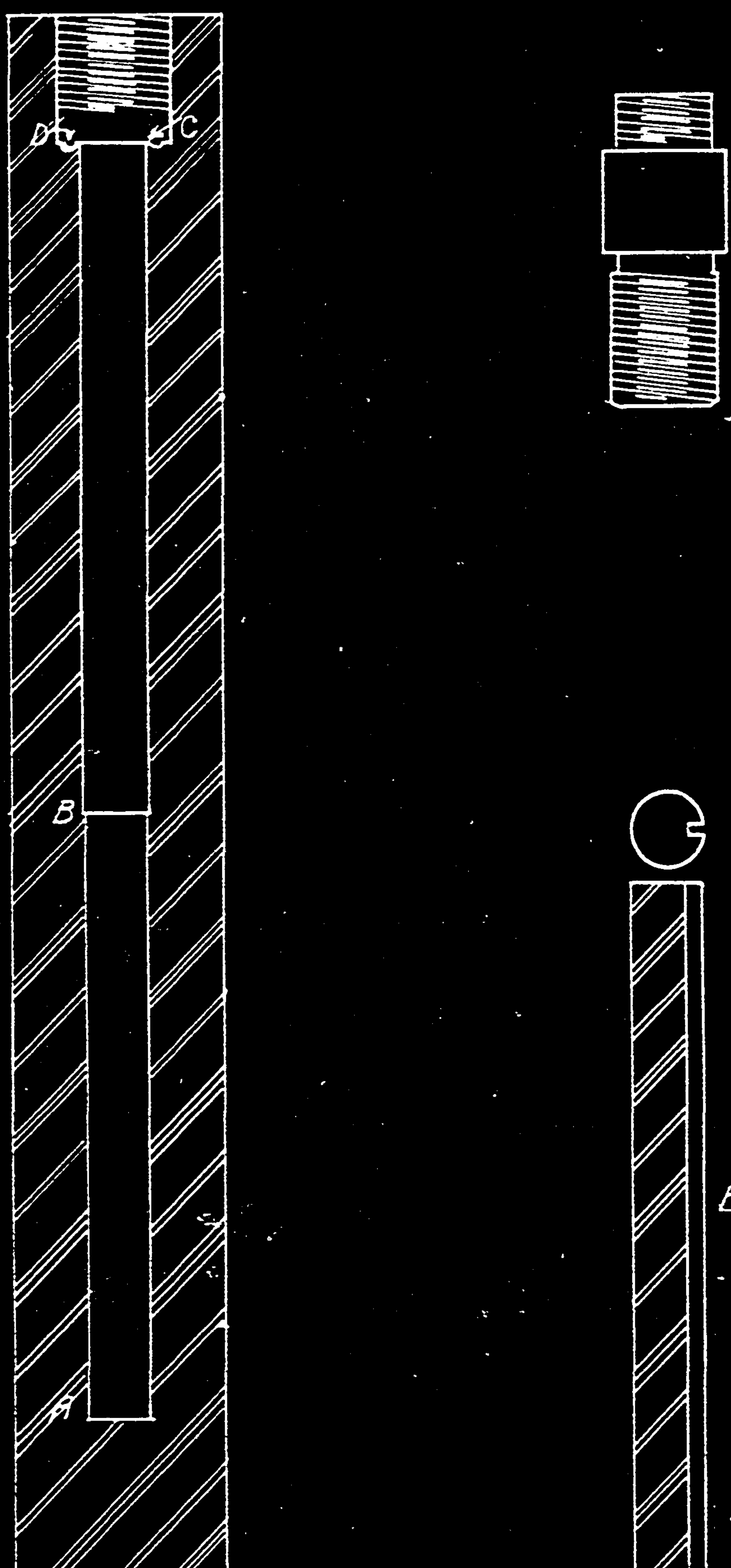


Fig. 1

bomb while the other made the connection through the connecting block, Fig. 2 and Fig. 3, C, to the pressure gauge. The end which fitted the bomb was threaded for a distance of one and a half inches, thirteen threads to the inch.

The connecting block, Fig. 2 and Fig. 3, C, was made of soft steel. The block was one and three-fourth inches square with a three-sixteenth inch hole through the center and to all connections. The threaded connections were used as follows: (1) The bomb was attached directly to A by means of flexible copper tubing with bronze couplings as furnished by the Watson-Stillman Co. (2) A pressure gauge was attached to B. (3) The high pressure pump, Fig. 3, was attached to C. (4) When filling for a run an oxygen tank was attached to D. At other times D was closed with a blind nut. The needle valve E was made of rolled brass. The point was covered with hard solder and tapered to an angle of 59° and fitted into a seat having an angle of 60°. To prevent leak when the valve was open, threads were cut in the block to fit corresponding threads on the rod at G for a distance of one inch. The rod for the distance between the two oppositely tapered metal washers, F and F, was wrapped with an asbestos cord which had been rubbed with a mixture of graphite in a heavy, non-volatile oil. The washer F rested on a narrow shoulder. When the nut H was turned down the pressure on F forced the packing into the space between F and F with sufficient force to prevent a leak at five hundred atmospheres or above. When the oxygen tank was attached to D the valve E was opened. The oxygen was allowed to fill the bomb and connections to a pressure equal to that furnished by the oxygen tank or to some lower pressure as desired. The valve E was then closed, the oxygen tank disconnected and D closed with a blind nut. The valve E was then opened and by means of the high pressure pump, Fig. 3, a quantity of water was forced into the connections. The amount of water required to fill the connecting block and all connections up to the bomb was determined by previous trial. No water was allowed to enter the bomb. When thus filled the valve E was closed. The pressure gauge, Fig. 3, A, on the high pressure pump was used as the standard for comparison of the readings on the gauge attached to B. (See also Fig. 3 B.). The latter gauge gave the pressure in the bomb at all times during the run. This arrangement enabled us to maintain a relatively small decrease of pressure across the valve E. For by means of the high pressure pump water was forced into the apparatus until the pump gauge read only a very few atmospheres less, never more, than that of the gauge indicating the pressure in the bomb. Also in this way the pressure in the bomb could be raised to the desired value before the heat was applied.

The high pressure pump, Fig. 3, was made by the Geneva Society for the construction of instruments for physics and mechanics. It was capable of producing a pressure of 1000 kgs. per cm^2. The gauge was graduated in steps of 10 kgs. per $cm.^2$ A variation of about 2 kgs. per cm^2. could be estimated. This probably exceeded the accuracy of the gauge.

The bomb was heated in a circular resistance furnace, Fig. 4 A, made of nichrome wire wound on a hard asbestos frame. The wire was covered with a paste of alundum cement and baked till thoroughly dried. The furnace which was ten inches high was open at the top and the bottom so that it could be set in a frame and the bomb introduced from the bottom. Or the furnace could be set on any suitable heat insulating material and the tubes for heating could be introduced at the top.

On account of the variation of the current during the

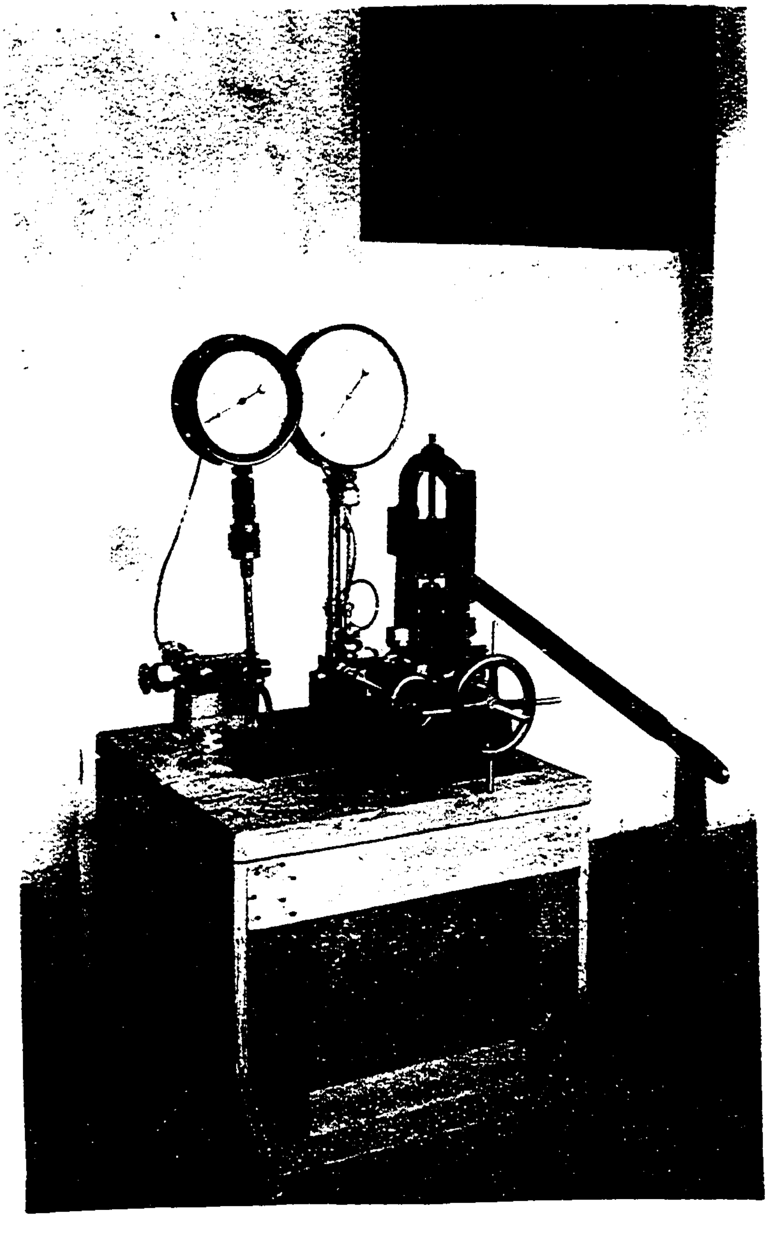


Fig. 3.

day much difficulty was encountered in the earlier experiments in regulating the temperature of the furnace for long periods of time. For this purpose a heat regulator was developed which could be set to regulate the temperature of the furnace within a range of about one degree over a period of days. The ordinary thermal regulators for thermostats could not be used for it was necessary at times to heat the furnace to 400° or above. The regulator with the system of wiring is shown in Fig. 4. The regulator was made from a single piece of invar steel, CH, bent at right angles. The lower end of C was turned at right angles to form the platform B. A portion of CH was cut so as to form the upright extension of C at K. The arm IJ was attached to CH at K by a pivot arrangement so that the ends I and J were free to move up and down. A silver rod, D, stood on the platform B. The extension of D was the invar steel rod E. Any rise in temperature would cause the silver rod to expand. This expansion would be multiplied by the ration of the lengths IK : KJ. In the apparatus used this factor was nearly 100. The wiring which can be readily followed on the Fig. 4 consisted of a primary heating circuit across the terminals of the furnace FG. A secondary circuit LM was wired in parallel with the primary circuit.

The secondary unit shunted a portion of the current around the resistances R and R. The magnet of the relay, O, was activated by the opening and closing of the contact N due to the expansion or contraction of the silver rod D. In this way the relay circuit threw in or out the secondary circuit as required to main an almost constant temperature in the furnace. The small variation in temperature is caused principally by the lag in the expansion and contraction of the silver rod.

In order to study the effect of low pressure on the rate of decomposition of potassium chlorate, it was necessary to collect, accurately measure and analyze the gas evolved. There are several vacuum pumps which permit the collection of the exhaust gas. None of these operates continuously and automatically, maintains a high vacuum, guards completely against the inclusion of air in the exhaust gas and is so simple in construction that an ordinary laboratory worker can construct it easily.

Without increasing the difficulties of construction, the Toepler pump has been modified so that it operates continuously and automatically. There is the further advantage that the exhaust mercury is returned to the reservoir after each stroke. The only auxiliary apparatus needed is a pump which will produce a pressure as low as five

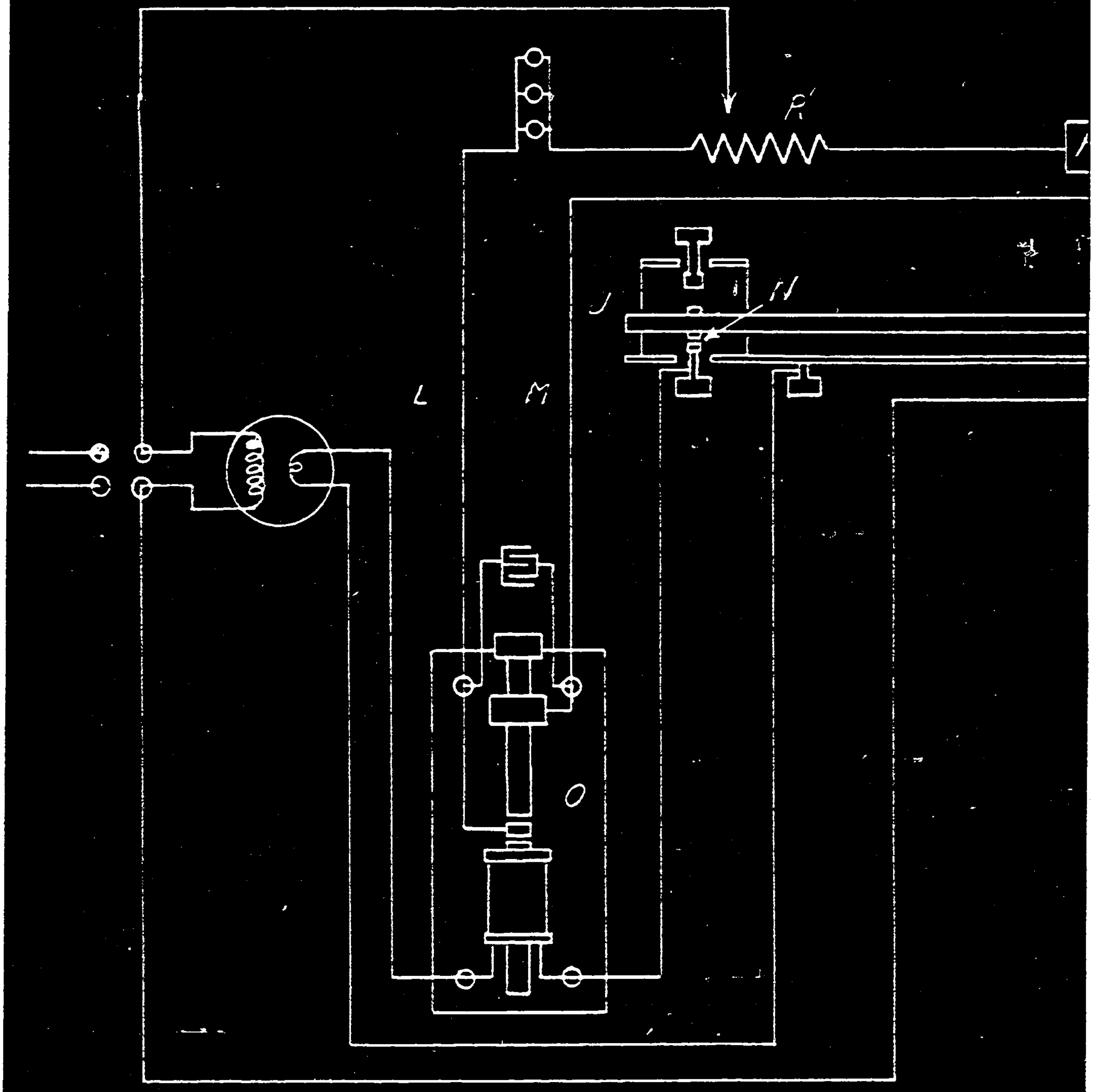


Fig. 4

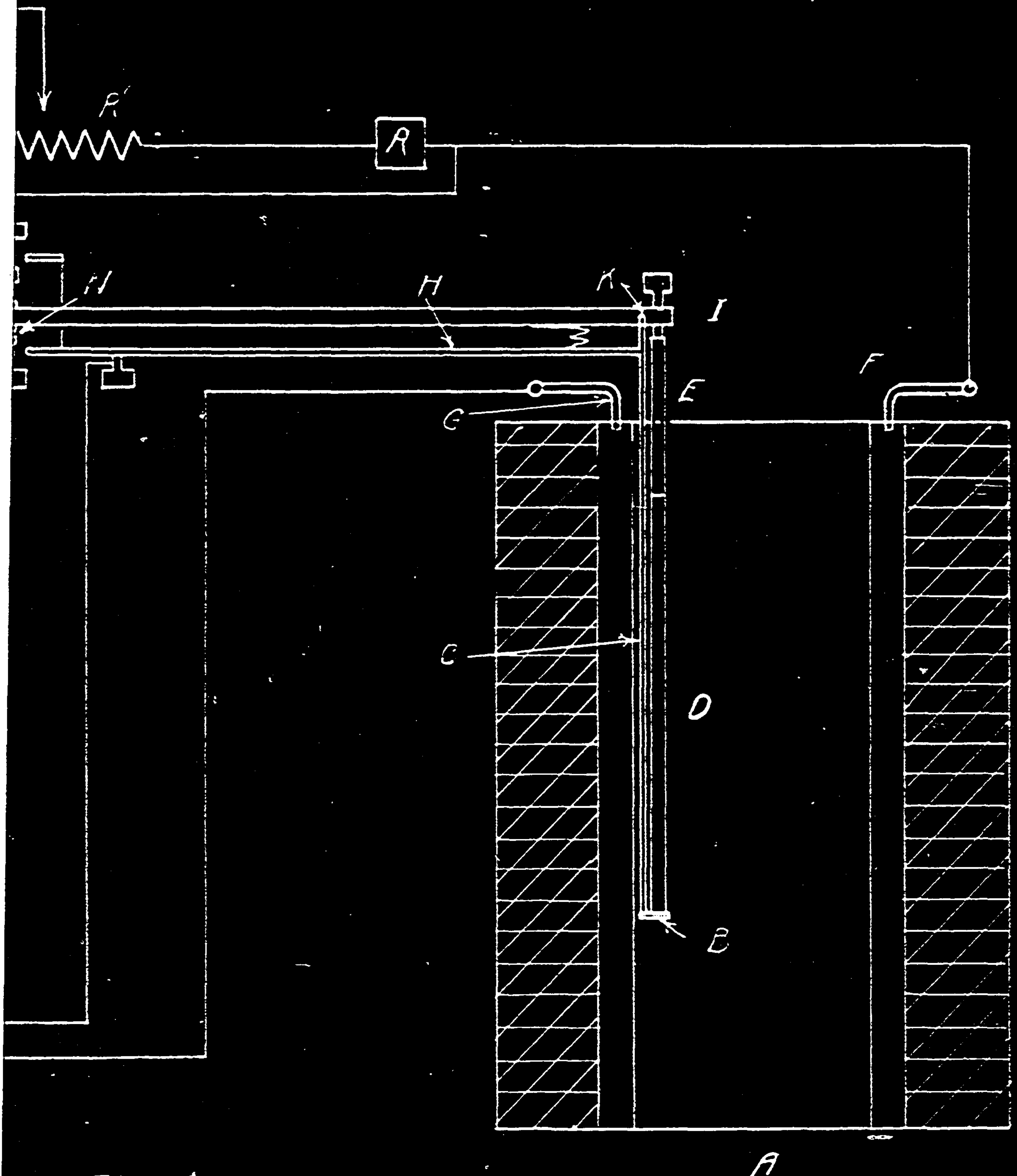


Fig. 4

centimeters of mercury. An ordinary water pump is satisfactory.

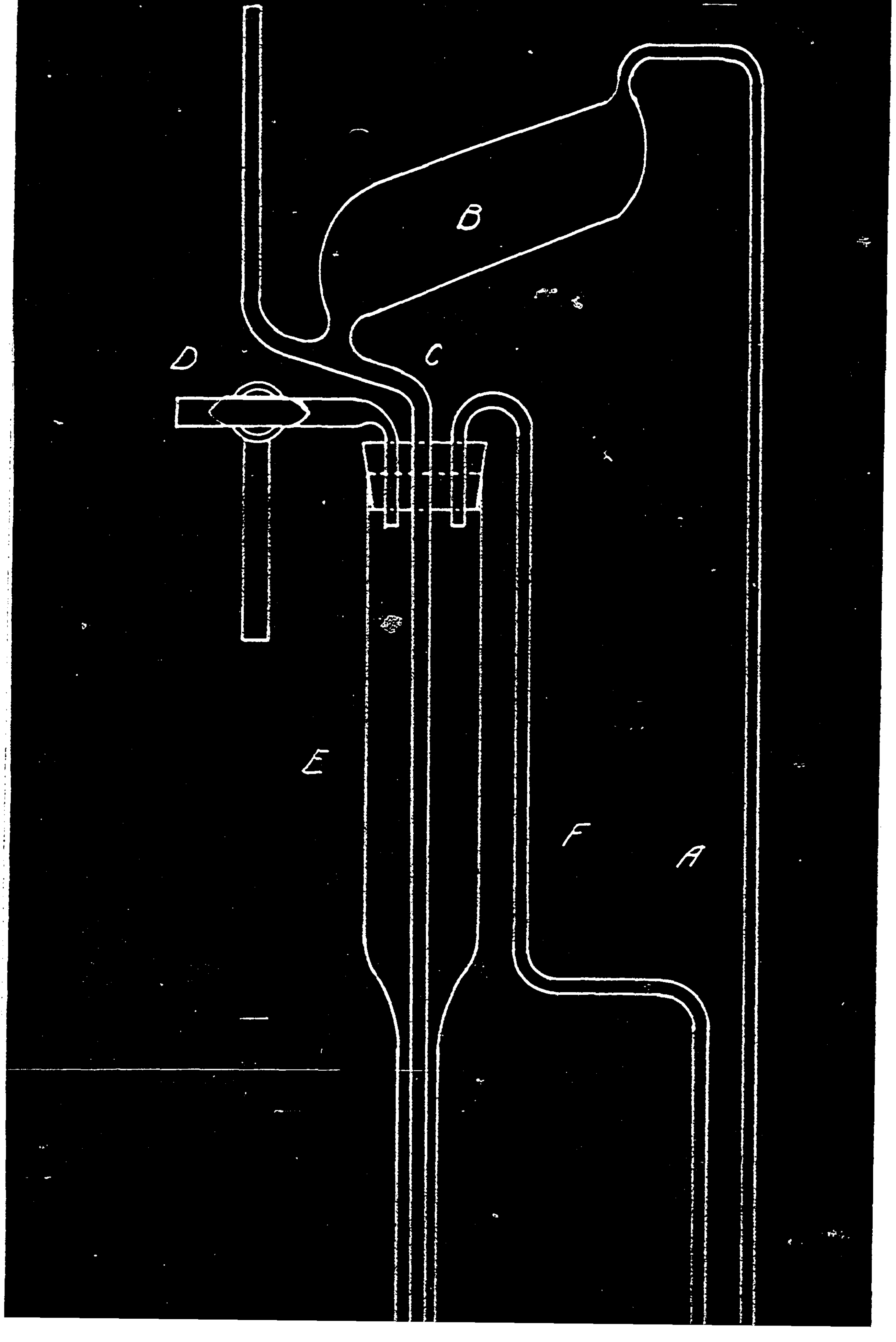
A, B, C (Fig. 5) is an ordinary Toepler pump without the moveable mercury reservoir and the rubber tube connections. The lower end of the downfall tube, A, is turned up and surrounded by the mercury cup, H, to facilitate the collection of the exhaust gas. Instead of the moveable reservoir, a fixed reservoir, E, surrounds C. The lower part of E is small to avoid the use of an unnecessarily large amount of mercury and the upper part is large so that the bulb B may be filled without too great a change in the level of the mercury in E. The lower end of E is sealed. The upper end is closed by a rubber stopper through which pass the tubes C and F which extends into the mercury cup H and the three-way cock D to one arm of which the auxilliary pump is connected. The tube F is fitted with a stopcock G and supported by the rubber stopper only, so that it will hang lower when filled with mercury than when empty. Its lower end should be between one and two centimeters above the upturned end of A.

The tube C has an internal diameter of 0.4 cm. and extends 80 cm. below and 75 cm. above its junction with B. To the extension of C beyond the mercury trap at its upper end is attached a manometer and a second mercury trap and tube which extends down into a cup of mercury. The latter tube serves as a safety tube in case of a sudden evolution of gas and also as a means of letting in air at the close of an experiment. A McCleod gauge may be used instead of or with the manometer. The bulb B has a capacity of about 150 cm^3. and is so arranged that a rise of mercury in E will cut it off from the remainder of the system and force its contents out through the tube A. The tube A is 0.3 cm. in internal diameter and 84 cm. in length from its highest to the lowest point. The bottom of the cup I should be nearly 10 cm. above the bottom of E so that the tube ABC will not siphon all the mercury out of E as soon as the pump is stopped.

In order to start the pump a preliminary evacuation is necessary for all of the gas trapped in the bulb B must be compressed into the part of the downfall tube between its highest point and the top of the mercury contained in it just before the gas is driven out. The maximum preliminary pressure p_0 under which the pump will act automatically can be calculated by the equation: $p_0 V = (P - h)v$. Where V is the volume of air trapped, P is the atmospheric pressure, h is the difference in level between the mercury in E and the highest point in the downfall tube, and v is the volume of the gas as it is compressed in the upper part of the downfall tube just as the mercury sweeps past the highest point in the downfall tube. The bulb B can be made of such size that the auxiliary pump will give a sufficiently low preliminary pressure by direct evacuation.

If the bulb is small enough the pump may be started by connecting by means of pressure tubing the upturned end of A with E and to the auxiliary pump through the three-way stopcock D. E is filled by drawing through the tube F from the cup H. The mercury should stand in E as high as possible without danger of drawing it out through D. In H the mercury should just cover the lower end of F. The cock G is closed and the entire apparatus is evacuated. When the pressure p_0 is reached, D is turned so that the auxiliary pump is connected with E but not with A. The pressure tubing is removed and the cock G opened. When enough mercury has been transferred into E by suction through F so that the level of the mercury in H has fallen below the lower end of F, air rushes into E, forces the mercury down in E and up into the bulb B. The contents of B are forced out through A. Mercury flows into H until the lower end of F is covered. The auxiliary pump evacuates E. The mercury falls in B until a connection is again made through the upper part of C to the apparatus being evacuated. During this time mercury is drawn from H into E until the lower end of F is above the level of the mercury. The cycle is then repeated.

Since the capacity of the pump is directly proportional to the capacity of the bulb, B, it is often desirable to make this bulb so large that the auxiliary pump will not produce a pressure p_o on preliminary evacuation. In this case the pump may be started by the use of the apparatus Fig. 5, I, which consists of a side-neck test tube with the stopcock J. The entire apparatus, I, as shown is raised vertically into such a position that the lower end of the capillary tubing may be attached to the upturned end of A by means of a short piece of pressure tubing. I and D are connected with pressure tubing. After filling E to the desired height, the cock G is closed and the cocks J and D are turned so that the entire apparatus is evacuated through A and E as before. When the pressure is as low as the auxiliary pump will produce, J is closed and G opened. The air rushes into E through F, but will not force the mercury in C and B to the highest point of A. To draw out the air trapped in A, turn the cock D so that it will evacuate A but not E. Open cock J. When a little mercury has been drawn into the side neck test tube, close J. Now close G and keep J closed so as to evacuate E but not A. When the mercury in B has fallen below the junction between B and C,


B
D
C
E
F
A

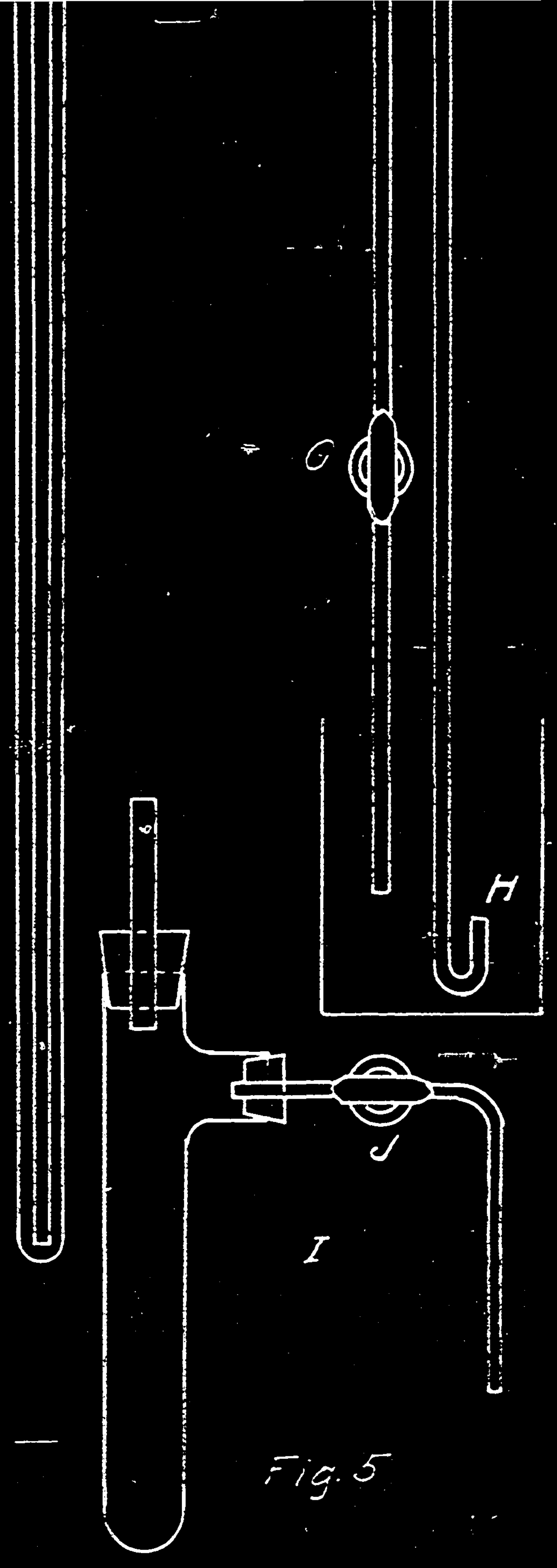


Fig. 5

open G. If the mercury does not rise to the highest point of A, the gas in A must again be drawn out through I by turning D so as to evacuate E but not A and opening J. This cycle must be repeated until the pressure in the apparatus is as low as p_0. The pump will now operate automatically without the use of I which is in no way necessary for the operation of the pump except for starting when the auxiliary pump can not evacuate the apparatus to the pressure p_0.

The value of p_0 for the pump as here described is about 1.2 cm. of mercury. When using a water pump for the auxiliary pump and evacuating a two liter flask, it was necessary to make nine strokes by the use of I before the operation became automatic. The pump makes one cycle or stroke per minute and has been run continuously for 96 hours without any attention whatever. In one preliminary trial when the pressure was read by a McCleod gauge on which a pressure of 2×10^{-5} mm. could be read, a pressure averaging 0.065 mm. was maintained for 30 hours.

Temperatures below 250° were measured by mercury thermometers which had been compared with a standard thermometer. Temperatures at 250° or above were measured by a chromel-alumel thermocouple using ice water as the cold juntion. The thermocouple was standarized against a Pt - Pt - Rh thermocouple which had been standardized by the Bureau of Standards. The temperature was read by means of a Leeds, Northup potentiometer. Some of the higher temperatures were read with a Hoskins pyrometer using a standardized chromel-alumel thermocouple. When heating the steel bomb, the thermocouple was placed near to, but not touching, the bomb at a position in the furnace opposite the middle of the charge in the bomb. When heating mixtures in hard glass tubes at the lower temperatures the bulb of the thermometer was placed against the part of the tube containing the material.

PREPARATION OF MATERIALS.

The potassium chlorate used in this work was Baker and Adamson C. P. grade. No further purification was made. Preliminary tests showed that a nearly saturated solution gave a very slight cloudiness with silver nitrate. No heavy metals, calcium, bromates, nitrates or sulfates were present. Weighed samples of the potassium chlorate were reduced by boiling with ferrous sulfate. The excess of ferrous sulfate was titrated with a standard potassium permanganate solution. Two determinations gave 98.15% and 98.22% pure potassium chlorate. Since the samples had not been heated to 110° immediately before weighing for analysis, it was considered that the slightly low values obtained was principally due to adsorbed moisture.

The manganese dioxide was prepared by reduction of potassium permanganate with manganese sulfate in a strong sulfuric acid solution. The quantities used and the method of procedure was essentially the same as described by Merrill and Scalione(9). The precipitated manganese dioxide was washed with distilled water until no test for sulfate could be obtained. The washing was continued until the precipitate became colloidal so that it would not settle out for several days. After filtering the precipitate was dried at 110°.

Before using, both the potassium chlorate and the manganese dioxide were ground in an agate mortar and run through a 200 mesh sieve. The materials were heated several hours at 110° just before the proportions were weighed out for the mixture which was made by sifting together repeatedly through a 150° mesh sieve until the mixture appeared entirely uniform. The proportions used were, expressed as molar concentrations, $2KClO_3 : MnO_2$. This mixture was found by Brown, Burrows and McLaughlin(10) to have the lowest spontaneous decomposition temperature. This mixture prepared in this way was kept in glass stop-

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9. D. R. Merrill and C. C. Scalione. J. Am. Chem. Soc. 43, 1986 (1924).

10. Brown, Burrows and McLaughlin. J. Am. Chem. Soc. 45, 1343-8 (1923).

pered bottle until needed for experimental work.

EXPERIMENTAL WORK AND RESULTS.

The same quantity of the mixture of potassium chlorate and manganese dioxide was placed in each of two hard glass tubes, sealed at the bottom. After sealing the top of each tube, the two were tied together with a copper wire and put into the top of the furnace, Fig. 4 A. The side neck of one of these tubes in which the material was to be heated at atmospheric pressure was connected by means of pressure tubing to a glass tube the other end of which was turned upward to facilitate the collection of gas and dipped into a cup of mercury.

The method of collecting and measuring the gas evolved was the same for both. The stopcock of a quantitative burette was cut off and sealed to the top. A leveling bulb was fastened to the bottom of the burette. The end of a capillary tube opposite a second stopcock was sealed into the side of the burette between the first cock and the graduation and bent down along the side. A tube of larger diameter for setting down over the upturned tube in the mercury cup was sealed to the lower end of the second cock. When in position for collecting gas the burette with the capillary tube was filled with mercury. When a volume of gas was read the mercury in the cup was drawn up to a graduation of the capillary by lowering the leveling bulb and the second cock closed. The mercury in the burette was adjusted to atmospheric pressure and the volume read.

A somewhat larger tube in the form of a boat was sealed to the side-neck of the other tube and to the mercury pump, Fig. 5. The boat was partly filled with phosphorus pentoxide and arranged so that the gas from the tube in the furnace had free passage over the pentoxide to the pump. The pump, Fig. 5, ABC, the boat and the tube containing the charge in the furnace was one glass tube. All connections were glass seals.

The material heated at atmospheric pressure was taken from the same mixture and subjected to the same temperature in the same furnace for the same length of time as that for which data are given in Table I.

TABLE I.

Part (a).--$KClO_3$-MnO_2 mixture contained 2 g. of $KClO_3$.

Temperature.	Pressure(&)	Time of heating.	Total Volume of gas.
Room.	0.045 cm.Hg.	19 hrs.	0.00 cc.*
100°	0.035 " "	2.4 hrs.	0.00 " *
Room	0.035 " "	13. "	0.00 " *
125°	0.010 " "	6. "	2.90 "
145°	0.010 " "	80. "	23.00 "

Part (b).--$KClO_3$=MnO_2 mixture contained 2 g. of $KClO_3$.

Temperature.	Pressure(&)	Time of heating.	Total Volume of gas.
Room.	0.06 cm.Hg.	14. hrs.	0.0 cc.*
90-100°	0.02 " "	1.5 "	0.0 " *
Room	0.07 " "	21. "	0.0 " *
90-100°	0.025 " "	1.5 "	0.0 " *
Room	0.055 " "	48. "	0.0 " *
175°	0.125 " "	3. "	35.5 "

Part (c).--$KClO_3$=MnO_2 mixture contained 1 g. of $KClO_3$.

Temperature.	Pressure(&)	Time of heating.	Total Volume of gas.
Room.	0.020 cm.Hg.	19. hrs.	0.0 cc.*
65-100°	0.010 " "	1.5 "	0.0 " *
Room	0.010 " "	17. "	0.0 " *
196-200°	0.01-0.24 " "	3. "	30.0 "

(&) -- Read on a manometer with a cathetometer.

* -- No gas was collected.

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Part (a):

The pump was kept running during the time of heating the mixture but not while cooling to room temperature or during the time of standing at room temperature. At the close of the experiment the entire apparatus stood for 11 days without showing any leak which could be read on the manometer or the burette.

The gas was analyzed by the use of a slight modification of the Elliot apparatus. The collecting apparatus in this case was set at zero so that enough air was contained in the gas analyzed to fill the collecting apparatus above the graduation on the burette.

Volume of gas transferred - - - - - - - - 30.5 cc.
Volume of gas absorbed as oxygen - - - -23.1 "
Barometric pressure - - - - - - - - - - - -740 mm.
Temperature - - - - - - - - - - - - - - - - - 25°

By changing these volumes to dry gas at standard conditions and making correction for the 7.5 cc. of air, it is found that 95.1% of the original 23 cc. of gas collected was absorbed as oxygen.

A sample of the mixture which had been heated was analyzed for chlorides by the method of Votecek(11). The

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11. E. Votecek. Chem. Ztg. 42, 257, 271 (1918).

The amount of chlorides found corresponded to an evolution of 25.1 cc. of oxygen. The results of later experiments to be described showed that this difference might easily be accounted for by the loss of oxygen at 100° before the collecting apparatus was attached.

Part (b):

The procedure and methods of analysis were a duplicate of those described for Part (a) except (1) during the preliminary heating to 100°, the pump was kept running both while heating up to 100° and cooling down to room temperature; (2) the collection apparatus was completely filled with mercury before any gas was collected.

Volume of gas transferred - - - - - - - - - - 35.9 cc.
Volume of gas absorbed as oxygen - - - - - 35.0 "

Evidently the gas collected was all oxygen for the difference between the amount collected and the volume absorbed as oxygen was easily within the limits of experimental error. Analysis of the residue for chlorides indicated that 63.9 cc. of oxygen had been evolved from the mixture.

Part (c):

An amount of the mixture containing 1 g. of potassium chlorate was used because it was expected that the rate of evolution at 200° would be too great for the capacity of the pump. Even with 1 g. of potassium chlorate the pressure rose to 0.25 cm. of mercury, although the pump was working continuously. On account of an accident the gas could not be analyzed. The amount of chlorides in the residue corresponded to an evolution of 108 cc. of oxygen.

During the progress of the previous experiments it was noted that when the mixture was subjected to a pressure of 0.1 - 0.2 mm. and heated to 50--60° a small amount of moisture was given off. When the temperature was raised to temperatures 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 grams of the mixture of potassium chlorate and manganese dioxide was sealed in tubing and connected to the pump as previously described. The apparatus was evacuated to a pressure of 0.03 cm. The material was repeatedly heated to 72° and then cooled to room temperature for a period of three days. During this time the apparatus was occasionally pumped out for it proved impossible to get a constant pressure while the material was being heated and cooled. The pressure did remain constant at 0.05 cm. for a period of 24 hours when the temperature did not average more than 50°; but when the temperature was then raised to 60--70° the pressure increased to 0.110 cm. in 12 hours. The temperature was now kept as nearly constant as possible and the heating continued to determine what pressure would develop.

TABLE II.

Part (a): Average temperature was 68°.

Time.	Pressure.	Time.	Pressure.
0.0 hrs.	0.11 cm.	62.0 hrs.	0.80 cm.
7.5 "	0.24 "	70.0 "	0.83 "
10.0 "	0.31 "	81.5 "	0.85 "
12.0 "	0.34 "	87.0 "	0.86 "
17.0 "	0.38 "	94.5 "	0.89 "
24.0 "	0.45 "	105.5 "	0.91 "
34.0 "	0.55 "	109.5 "	0.93 "
43.0 "	0.62 "	114.0 "	0.91 "
47.5 "	0.69 "	130.0 "	1.03 "
56.0 "	0.74 "	138.0 "	1.03 "
57.0 "	0.78		

Part (b): Average temperature was 90°.

0.0 hrs.	1.16 cm.	43.0 hrs.	1.45 cm.
4.0 "	1.25 "	51.5 "	1.48 "
10.5 "	1.28 "	59.0 "	1.51 "

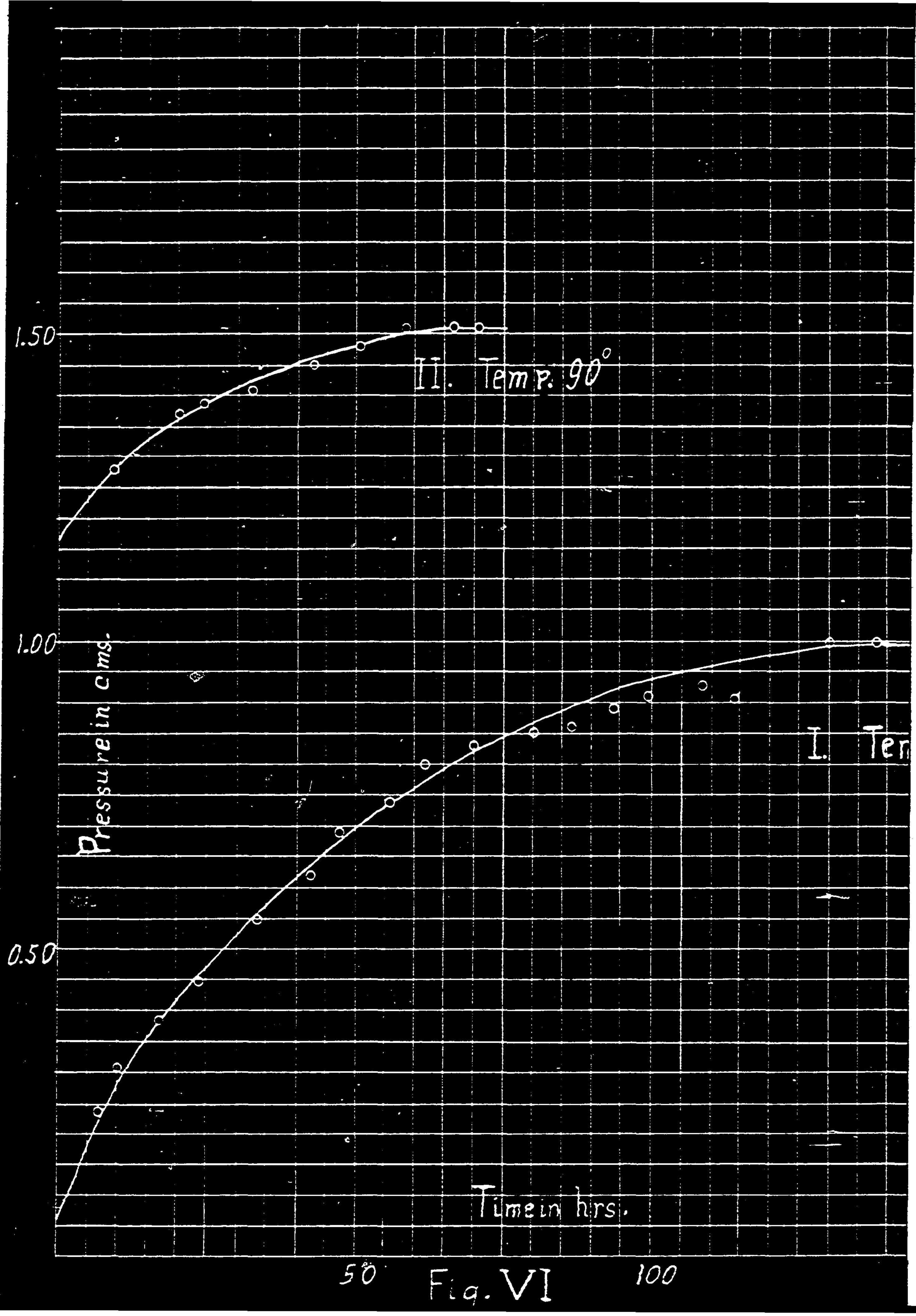
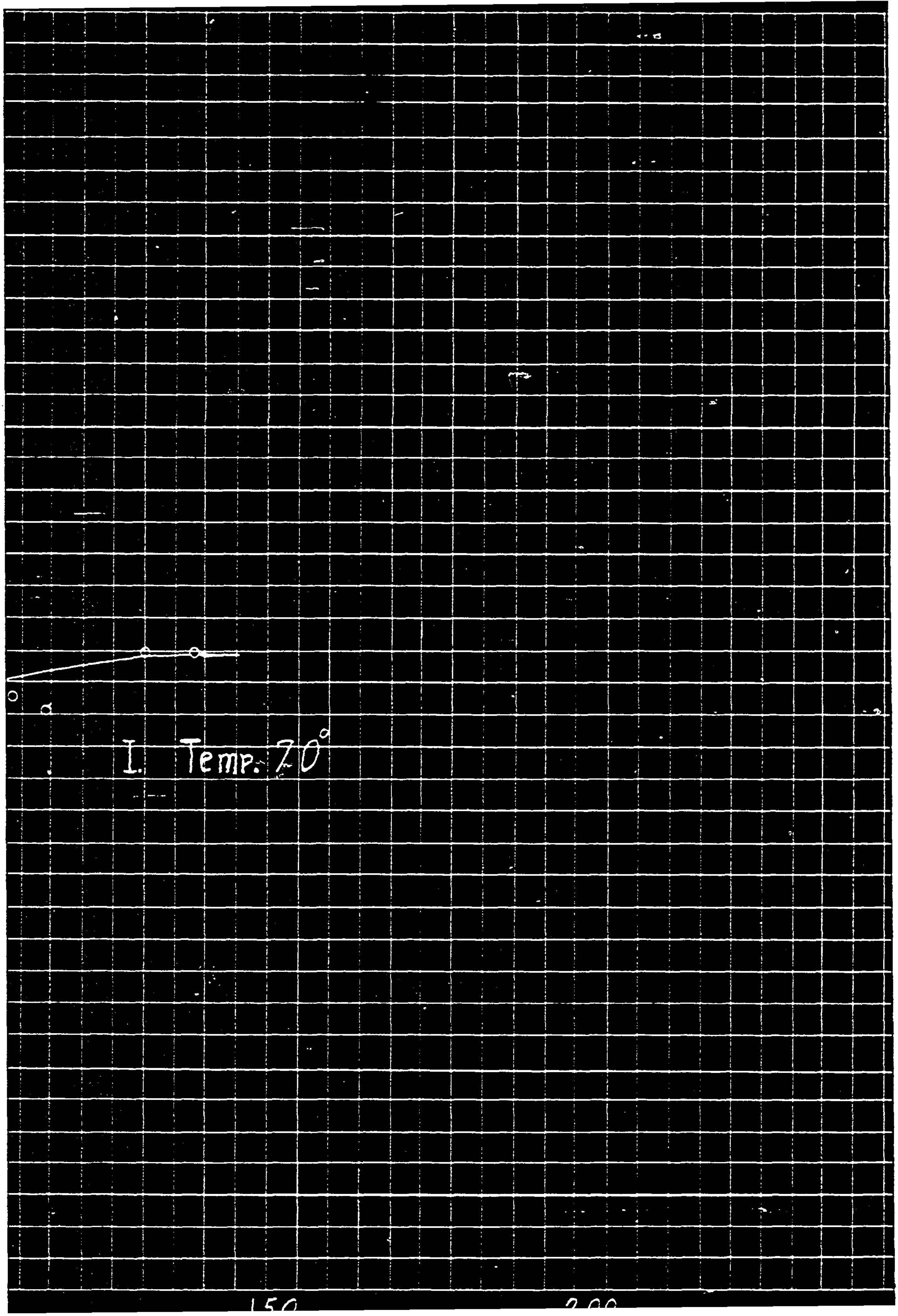


Fig. VI


I. Temp. 70°
150
200

21.0 hrs.	1.37 cm.	67.0 hrs.	1.51 cm.
25.5 "	1.39 "	71.0 "	1.51 "
33.5 "	1.41 "		

Many of the 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 Fig. 3 was available for measuring the pressure during the progress of the experiment two apparently successfully runs were made from which the pressure could be calculated. About forty grams of the potassium chlorate and manganese dioxide were used. The space in the bomb exclusive of that occupied by the substances introduced was about 38 cc. By measuring the volume of the bomb, using the density, as found in tables, and the weight of each substance in the bomb to determine its volume and analyzing the residue for chlorides formed by the decomposition of the potassium chlorate, the highest pressure that could be attained by compressing the volume of oxygen corresponding to the potassium chlorate decomposed into the free space of the bomb could be calculated. The temperature of the furnace was measured by a mercury thermometer.

TABLE III.

No.	Time heated.	Av. temperature.	Pressure.	%$KClO_3$ undecomposed.
1.	1.0 hr.	335°	236.7 atmos.	80.2%
2.	7.5 "	335°	322.7 "	66.6%

The pressures given in Table IV were measured on the pressure gauge attached to the high pressure pump Fig. 3. The temperatures were measured by a thermocouple. Pressure shown at room temperature at the beginning of the experiment was produced by filling the bomb with oxygen from an oxygen tank through the connecting block as previously described.

TABLE IV.

No.	Time heated.	Av. Temperature.	Pressure.	$KClO_3$ undecomposed.
1.	--- hrs.	Room	200.0 atmos.	
	3.0 "	345°	443.3 "	
	15.0 "	Room	280.0 "	----Present.x
2.	--- "	Room	180.0 "	
	12.0 "	Room	180.0 "	
	19.0 "	320°	463.3 "	
	21.5 "	290°	465.6 "	

25.0 hrs.	325°	480.0 atmos.	
29.0 "	285°	450.0 "	
34.0 "	320°	483.3 "	
39.0 "	325°	496.6 "	
53.0 "	Room	240.0 "	------23.5%

* Not quantitatively determined.

DISCUSSION.

The curves I and II, Fig. VI, show a rapid increase of pressure at first with a gradual slowing down as the decomposition continues. The pressure built up to a limiting value which remained constant for about 12 hours. A similar rapid rise of pressure with a gradual slowing down was also indicated at the higher pressures and temperatures.

The data for experiment 2 in table IV are typical. When the temperature was increased the pressure increased but when the material was cooled to the previous temperature the pressure stopped at a value higher than previously obtained at that temperature. This has occurred throughout the work at all temperatures and indicates that no equilibrium has been established.

SUMMARY.

1. Pressure has a marked effect on the 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 constant 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, $2KClO_3 = 2KCl + 3O_2$ 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 has been prevented by pressure when the mixture was heated for a period of 7 hours at a temperature 40° above its spontaneous decomposition temperature.