ON THE USE OF MANGANESE DIOXIDE IN THE GENERATION OF OXYGEN FROM POTASSIUM CHLORATE.

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The statement is sometimes made in texts on chemistry that the part played by manganese dioxide in the generation of oxygen from potassium chlorate is one of conduction only, that any other oxide, or ordinary saud, which would come in intimate contact with the potassium chlorate, would do as well. Since the black oxide, although not expensive, is more expensive than sand, the use of sand would to some extent diminish the cost of oxygen when generated from potassium chlorate.

To test this point Prof. Foley and the writer, at the suggestion of the former, made the experiments as described below.

The potassium chlorate, mixed with a definite proportion of black oxide or other material, was placed in an ordinary sheet-iron generating retort which was heated with a large Bunsen burner. The oxygen was led through a lead pipe coiled inside a calorimeter. From the calorimeter it passed through an experimental gas meter' reading to 10 c.c. By this means the total volume of oxygen generated and the generating rate could be determined directly, and from the rise of temperature of the contents of the calorimeter the approximate temperature of the gas could be determined. Experiments were made with manganese dioxide, powdered silica, sand, and Venetian red.* In no case except with the manganese dioxide, did the amount of gas given off compare with that computed from the chemical formula. In fact the rate of generating, when using substances other than manganese dioxide, was so slow that calorimetric determinations could not be made. The following table will give a general view of the results:

^{*}Equal parts iron oxide and calcium sulphate.

	Substance.	KClo ₃	Generating Time.	Volume. Observed. Calculated.	t	
1	50 gms. MnO ₂	250 gms.	8 min.	73 Liters. 74.4	2 2°	
2	200 ** **	1000 ''	18.5 "	257 " 296.5	18	Gas lost.
3	186 " Silica	930 "	24 ''	56 " 273	19	Exploded.
4	500 " Sand	500 "	20 ''	16.7 " 147.5	21	
5	120 " MnO _z	600 **	11 "	137.5 ** 177.5	21	Gas lost.
6	65 Venetian red	325 ''	25 "	21.9 " 97.6	25	

The first column gives the amount and name of substance used; 2d, amount of potassium chlorate; 3d, duration of the experiment in minutes; 4th, the volume of gas liberated as shown by the gas meter; 5th, volume of gas as calculated from mass of potassium chlorate and temperature and pressure of gas in the meter; 6th, temperature of gas in neter.

In the third experiment with powdered silica heat was applied steadily for twenty-four minutes until suddenly the delivery tube connecting the retort to the calorimeter was blown off and a stream of blazing molten silica was shot a distance of fifteen feet across the room. Upon cleaning the retort it was found that the mass of chlorate and silica had been in a foaming semi-fluid condition filling the entire retort and forcing itself through the delivery tube. In the case of sand (from the shore of Lake Michigan) heat was applied for twenty minutes with a very small amount of oxygen given off. In every case with manganese dioxide the gas had been entirely driven off in a shorter time with a flame greatly reduced from the normal. In fact a considerable amount of gas bubbled through the meter owing to the rapid rate of generation. With Venetian red a very small amount of oxygen was obtained, although the temperature was raised to the point where the entire mass was fused. Subsequent experiments performed in a test tube showed the temperature of fusion to exceed 360° C., while the temperature at which oxygen is liberated from the manganese dioxide mixture as shown by Mahin [Proc. Ind. Acad. Sci., P. 170, 1902] does not exceed 180° C. Calorimetric computations and direct observation in test tubes show the temperature of the gas to be from 65° to 100° C. It would seem that there is a lowering of temperature at liberation analagous

to the fall of temperature when water vapor is driven from a salt solution.

In conclusion, it seems that manganese dioxide serves for more than a distributer of heat, that it has a catalytic effect upon the potassium chlorate, permitting the oxygen to be liberated at a much lower temperature than when potassium chlorate is used alone. Powdered silica, sand, and Venetian red do not produce this effect, at least not to the same extent, at low temperatures, as black oxide of manganese. .