XLVII.—*On the Detonation of Chlorine Peroxide.*

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M. BERTHELOT (*Sur la Force des Matières Explosives*, 1, 109) discovered the fact that certain endothermic gaseous compounds, *e.g.*, acetylene, cyanogen, and nitric oxide, could be decomposed by the detonation of a small charge of fulminate. The sudden shock arising from the fulminate is communicated, according to M. Berthelot, to the gas immediately round it, breaking down the chemical compound with liberation of heat; the heated molecules so produced in turn act on their neighbours, and thus the decomposition is propagated from layer to layer with the violence and the velocity characteristic of the explosion-wave.

In 1889 Dr. Thorpe described to the Chemical Society the explosion of carbon bisulphide vapour, produced by means of a detonator. He adopted M. Berthelot's view, that the decomposition was of the nature of the explosion-wave.

According to this view, it would seem that the explosion, once initiated, should travel as far as the gas extends, and that the rate of the explosion should conform to the laws governing the propagation of the explosion-wave in gaseous mixtures. It appeared of interest, therefore, to determine whether the explosion, set up by the shock of the fulminate, was propagated along a tube filled with one of these endothermic gases; and, if so, to measure the rate at which the flame was propagated.

In 1891 we made experiments on acetylene and carbon bisulphide. In neither case could we succeed in setting up a true explosion-wave in a tube filled with these gases. Our explosion apparatus consisted of a steel bomb, holding 400 c.c., connected with a strong glass or a steel tube of 15 mm. internal diameter. A copper detonator holding 1 gram of fulminate was fired in the middle of the bomb. With acetylene, although the gas was completely decomposed in the bomb, the decomposition never extended more than 15 cm. down the tube. With the vapour of carbon bisulphide, on the other hand, the flame was more intense, and it travelled from 2 to $2\frac{1}{2}$ metres along the tube. The deposit of carbon and sulphur along the tube became gradually thinner until the explosion died out. A true explosion-wave was not set up (*Manchester. Memoirs*, 1892). Last year M. Maquenne published in the *Comptes Rendus* some similar results with nitrous oxide and acetylene.

With chlorinel peroxide, however, even when diluted with other gases, we have found that the explosion is propagated through a long tube.

The chlorine peroxide mixed with oxygen (and a trace of chlorine) was evolved by warming sulphuric acid and chlorate of potassium in a glass flask by means of a water bath; the gas was washed in a small bulb, and, passing through a sampling vessel, was conveyed by flexible glass tubing to the lower end of a long and stout glass tube, AB, 9.9 metres long, inclined at an angle of 30° . The two ends of

the long tube (made for us by Messrs. Molyneux and Webbe) were fitted with steel flanges, so that they could be readily clamped up to the two "bridge pieces." These bridge pieces, EF, CD, were steel tubes with taps at one end and flanges at the other. In both, an insulated bridge of silver foil was stretched across the tube close to the flange, by which an electric current was carried to the electromagnetic stylus on the chronograph. The silver bridge was coated, for protection, with paraffin. The lower bridge piece CD was bent; it was a metre in length, and was fitted with firing wires near the tap.

The chlorine peroxide passed into the tube without coming into contact with the metal flange, or any material other than glass. The explosion-tube was inclined, because it was found that the heavy peroxide flowed along the bottom of the tube without pushing the air before it when the tube was horizontal. When the long tube was filled, the flow of gas was diverted. The upper bridge piece was first clamped on, and then the lower; both being previously filled with electrolytic gas. On passing a spark through the electrolytic gas, the explosion-wave was set up, and this was communicated in turn to the chlorine peroxide in the glass tube. The flame was seen to suddenly illuminate the whole glass tube, the passage of the flame being too rapid to be followed by the eye.

We had many premature explosions of the gas, usually set up in the long tube. Only once did the explosion appear to start in the generating flask. At first, we attempted to prepare pure chlorine peroxide, but found it was impossible for us to fill the long tube and clamp on the bridge pieces without firing it; even with the diluted mixtures we used, we made seven experiments running, all of which failed at the last moment. The analysis of the sample showed considerable variations in the proportion of chlorine peroxide present, and we cannot be sure that the samples were of exactly the same composition as the gas in the tube.

Two experiments, we think, gave fairly trustworthy results:—

	Composition of mixture.	Rate of explosion, in metres per sec
I. ClO_2	53·5	1065
O_2	46·5	
II. ClO_2	64·0	1126
O_2	36·0	

The rate of explosion of chlorine peroxide is thus of the same order as the rate of explosion in gaseous mixtures, in hydrogen and chlorine, for example. Unfortunately, the heat of formation of chlorine peroxide has not been determined, so that we cannot com-

pare the observed rate with the theoretical velocity calculated according to Berthelot's formula, or according to the "sound wave" hypothesis. Working backward from the latter, we should predict a heat of formation for ClO_2 of $-15,800$ cal. from the first experiment, and of $-16,800$ cal. from the second. It would be of interest to check this result by direct experiment.

From the density of the mixture and the velocity of the explosion, the pressure produced in the wave may be calculated by Riemann's equation.* According to this calculation, the faster explosion generated a pressure of 31 atmospheres in the wave.

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