

CXXIX.—*The Vapour Pressures of Chlorine Dioxide.*

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A CONNECTED series of measurements of the vapour pressures of chlorine dioxide from the melting point to the boiling point of the substance does not appear to have been recorded. A few isolated measurements, in poor agreement, are given in the literature. Millon (*Ann. Chim. Phys.*, 1843, **7**, 314; *Annalen*, 1843, **46**, 281) gives  $+20^{\circ}$  or  $+32^{\circ}$  as the boiling point, but does not describe the method used. He correctly states that chlorine dioxide attacks mercury, and dissolves in concentrated sulphuric acid to a bright yellow solution, but his assertion that the latter decomposes at  $10^{\circ}$  with evolution of chlorine, oxygen, chlorine dioxide, and "chlorine trioxide" we do not confirm. Millon also correctly described the colour of liquid chlorine dioxide as red, "like the brightly-coloured sulphur chloride," *i.e.*, the monochloride containing excess of chlorine, but he overestimated the explosive properties of the liquid. Brandau (*Annalen*, 1869, **151**, 340) gives the boiling point of what he calls chlorine trioxide as  $8-9^{\circ}$  at 745 mm.: the substance must have been the dioxide. Pebal (*ibid.*, 1875, **177**, 1) determined the boiling point by a rather crude method as  $8.7^{\circ}$  at 725.7 mm. Schacherl (*ibid.*, 1881, **206**, 68) attempted to determine the vapour pressure by means of a mercury manometer in direct communication with a water manometer, the metal being protected from the gas

by a long column of water. Schacherl first noticed that liquid chlorine dioxide, although exploding violently when the process is initiated, is not liable to spontaneous, erratic detonation, as asserted by Millon, provided that all traces of organic matter are excluded and the substance is manipulated entirely in glass. Schacherl gives the following pressures, which are really those over a saturated solution, although he remarks that the yellow colour of the solution had not passed round the water limb of the manometer before the conclusion of the measurements.

$t^{\circ}$ .....	10.6	7.6	9.6	14.0	14.1	16.9	10.3	7.6
$p$ (mm.) .....	767.8	728.8	784.4	961.9	983.9	1162.7	1335.6	1329.1

It is quite clear, as Schacherl himself admits, that these values are completely vitiated by decomposition of the gas at the higher temperatures, and that the first value only can be taken into account. He concluded that the vapour-pressure method must be abandoned as unsuitable for the determination of the boiling point. This was really an incorrect conclusion, since, if he had taken care not to raise the temperature too far above the boiling point, there would probably have been very little decomposition. Schacherl then made a direct estimation of the boiling point with a mercury thermometer bulb immersed in the liquid contained in a small open bulb in a water-bath. The temperature rose slowly to  $9.9^{\circ}$ , remained constant for a short time, then varied between  $9.9^{\circ}$  and  $10.1^{\circ}$ , then returned to  $9.9^{\circ}$ , and remained constant until practically all the liquid had evaporated. The pressure was 730.9 mm. The liquid, it was found, could be boiled rapidly at  $+30^{\circ}$  without explosion, and the vapour recondensed by cooling at  $8.9^{\circ}$ . During the boiling-point determination, care was taken to avoid superheating, and the liquid during the whole series of measurements boiled steadily without bumping.

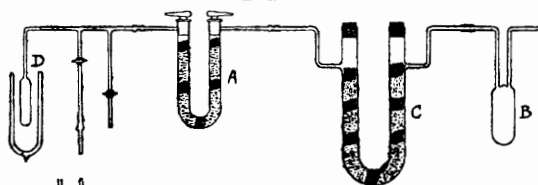
#### EXPERIMENTAL.

The chlorine dioxide was prepared by a method stated by Spring (*Bull. Acad. roy. Belg.*, 1875, **39**, 882) to yield chlorine trioxide, a substance up to the present unknown. The method involved the action of chlorine on dry silver chlorate. We have convinced ourselves that the only gaseous products of this reaction are chlorine dioxide and oxygen, so that it probably proceeds according to the equation  $2\text{AgClO}_3 + \text{Cl}_2 = 2\text{AgCl} + 2\text{ClO}_2 + \text{O}_2$ . The chlorine dioxide is easily liquefied out of the gas by cooling and can be obtained pure and dry.\*

\* Garzarolli Thurnlackh (*Annalen*, 1881, **209**, 184) refers to Spring's work at the end of his paper and suggests that the gas may have been a mixture of the composition  $\text{Cl}_2\text{O} + 4\text{ClO}_2$ , rather than  $\text{Cl}_2\text{O}_3$ . He promised to investigate the matter further, but does not appear to have done so.

According to Spring, the reaction begins in the cold, but we have found that it is quite inappreciable below about  $80^{\circ}$  and occurs regularly and smoothly at about  $90^{\circ}$ . The silver chlorate was prepared from chloric acid and silver oxide, dried in a desiccator over phosphorus pentoxide, and then about 10 g. were filled into a U-tube with ground stopcocks (A, Fig. 1), with alternate plugs of dry glass wool. Ramsay lubricant proved to be efficient for the ground joints and stopcocks; it was only very slightly attacked, if at all, during the few hours necessary for actual measurements. Pure dry chlorine, liberated by warming liquid chlorine (from potassium permanganate and hydrochloric acid) in a bulb, B, and dried by passing over phosphorus pentoxide in the tube C, was passed slowly over the chlorate, the tube A being maintained at  $85$ – $95^{\circ}$  in an electrically heated air-bath. With fresh chlorate, the reaction was slow at

FIG. 1.



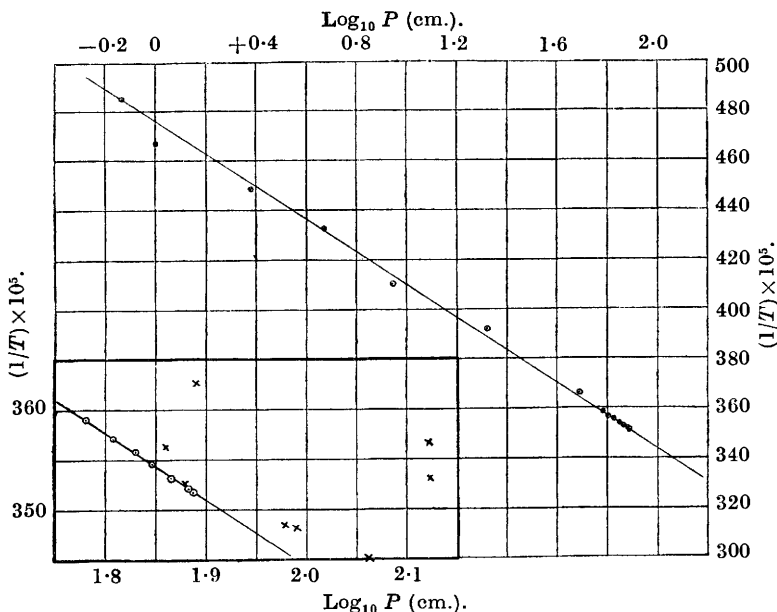
first and some free chlorine tended to pass over. The issuing gas was then passed to a small bulb, D, immersed in solid carbon dioxide and ether, communicating with a pump and two manometers. These contained mercury covered with concentrated sulphuric acid. The first (not shown) served to indicate the pressure after exhaustion and during filling; the second, which was closed by a tap until the actual measurements were begun, served to measure the pressures. By working in this way, excessive attack of the mercury surface used for measurement was avoided. The columns of acid were of the same length in each limb so as to compensate each other. We satisfied ourselves that, although mercury is attacked with the deposition of a white powder, no permanent gas is evolved from the sulphuric acid, which slowly becomes bright yellow in colour. The oxygen accumulating was removed from time to time by pumping.

The chlorine dioxide condensed in the bulb as a crystalline solid of the colour of potassium dichromate. If any excess of chlorine had passed through, this either floated unchanged on the surface of the solid dioxide or condensed along with dioxide to a deep red liquid which did not solidify in the freezing mixture. In either case, the chlorine was easily removed by pumping for a few minutes with

the bulb immersed in the freezing mixture. The pressure finally fell suddenly and the red crystals remained. The vapour pressure of the solid at  $-80^{\circ}$  was negligible.

By adding ether to the freezing mixture until all the solid carbon dioxide had disappeared, it was possible to raise the temperature slowly in steps to  $-30^{\circ}$ . Melting occurred sharply at  $-59^{\circ}$ , both solid and liquid being at first present, and all the solid melted at this temperature. This result is in agreement with the only previous observation, that of Faraday (*Phil. Trans.*, 1845, 135, 155), who found the melting point  $-59^{\circ}$ .\*

FIG. 2.



By further addition of ether, the temperature was gradually raised, the temperatures being measured on a pentane thermometer. After  $-30^{\circ}$ , a mixture of ice and salt, pure ice, and water were used successively, with a mercury thermometer.

The gauge pressures were subtracted from the mercury column reading corresponding with the vacuum attained in the apparatus before admitting gas. After the measurements, the chlorine dioxide was resolidified by immersing the bulb in solid carbon dioxide and

\* Faraday's result is given in most works of reference as  $-76^{\circ}$ ; this, however, is the temperature on the Fahrenheit scale used by Faraday. The correct figure is given in Watts' Dictionary, 1890, vol. 2, p. 13.

ether, and the original vacuum recovered, showing that decomposition had not occurred during the measurements.

The logarithms of the pressures recorded in Table I are plotted against the reciprocals of the absolute temperatures in Fig. 2, and it will be seen that a fair approach to a straight line is obtained. The part near the boiling point is drawn on an enlarged scale to the left. It so happened that the barometric pressure corresponded exactly with 760 mm. when the boiling point was reached, so that the value of the latter, 11.0°, could be determined directly.

The isolated points observed by Pebal and Schacherl are also shown. The first measurement of the latter in the vapour pressure series, when corrected for the vapour pressure of water at 15°, lies almost on the curve, but the remaining measurements show great irregularity. The direct measurement of the boiling point made by Schacherl, *viz.*, 9.9°/730.9 mm., also lies on the curve.

TABLE I.

$T^\circ$ Abs. ....	193	206	214*	223	232.5	243.5	255	273
$p$ mm. obs. ...	†	7	10	24	47	88	201	490
$T^\circ$ Abs. ....	278.3	279.9	281	282	283	284†	284.2	
$p$ mm. obs. ...	608	642	674	700	732	760	769	
			† Boiling point.			‡ Not measurable.		

\* Melting point.

† Boiling point.

‡ Not measurable.

From the values of the vapour pressures at different temperatures, it is possible to calculate the latent heat of evaporation of liquid chlorine dioxide by means of the formula :

$$\lambda = 4.576\{\log(p_2/p_1)\}T_1T_2/(T_2 - T_1) \text{ cal. per mol.}$$

From data near the boiling point the value 6520 is obtained. From this, by division by the absolute boiling point  $T_0$ , we find the Trouton coefficient  $\lambda/T_0$  of 23. The values of this calculated by the two formulæ of Nernst are :

$$8.5 \log T_0 = 20.85 \text{ and } 9.5 \log T_0 - 0.007T_0 = 21.3,$$

and from Wartenberg's formula  $7.4 \log T_0 + 1.985 = 20.2$ .

The ratio of the absolute temperatures corresponding with vapour pressures of 760 mm. and 200 mm. (really 201 mm.) is 1.114, which is the value shown by Ramsay and Young to correspond with normal liquids (*Z. physikal. Chem.*, 1887, 1, 249). These considerations seem to point to very little, if any, association of chlorine dioxide in the liquid state, so that its formula in both the gaseous and the liquid state may be considered to be  $\text{ClO}_2$ . The colours of the solid, liquid, and gaseous forms would also point to the same conclusion.