290. *The Vapour Pressure of Chlorine Heptoxide.*

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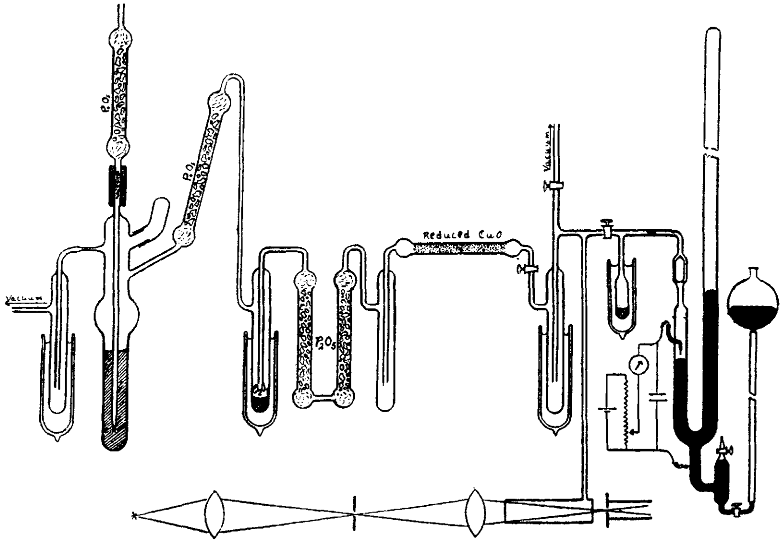
CHLORINE heptoxide was first isolated by Michael and Conn (*Amer. Chem. J.*, 1900, **23**, 444), who prepared it by adding anhydrous perchloric acid very slowly to phosphoric oxide cooled below −10°. The mixture was kept for a day and then distilled at 82°. They state that the apparatus may be virtually pulverised by an explosion and emphasise the necessity of adequate protection.

As a preliminary to further investigations of chlorine heptoxide it was necessary to measure its vapour pressure, for which data are lacking.

Cl_2O_7 was prepared by a modified method in which an endeavour was made to minimise the risk of explosion, and only very small quantities (0·5—1 c.c.) were prepared at a time. The prep. was always carried out at low pressure in order to avoid the use of high temps. A slow stream of air was passed through the reaction vessel by means of a high-resistance copper-plated graphite leak, its purpose being to carry the Cl_2O_7 through the P_2O_5 tubes into the collecting traps. It also helped to prevent superheating of the reaction mixture. A 60% solution of $HClO_4$ was first concentrated as far as possible by distilling off H_2O at low pressure into a side trap. The conc. acid was then surrounded with solid CO_2–EtOH, and P_2O_5 slowly added through a side tube The pressure was lowered with a Hyvac pump, and the mixture allowed to warm slowly to room temp. and finally warmed to about 40°, at which temp. Cl_2O_7 was freely evolved, being collected in the first trap surrounded by CO_2–EtOH. It was distilled several times through a second P_2O_5 tube, passed over freshly reduced CuO turnings to remove last traces of lower oxides and Cl, and fractionated until a pure colourless sample was obtained. Further samples were prepared as required, by adding more P_2O_5 to the $HClO_4$ and warming the mixture. All the taps were lubricated with graphite and HPO_3.

The pure Cl_2O_7 was distilled into a trap connected to the Hg manometer (a preliminary test had shown that pure Cl_2O_7 does not readily corrode Hg). The pressures were measured with a cathetometer reading to 0·01 cm. The zero level of the Hg meniscus was adjusted with the aid of an electrical circuit as shown in Fig. 1. As it was essential that there should be no arcing at the Pt–Hg contact, a current of 0·5 milliamp. at 0·01 volt was employed, and a milliammeter used as an indicating device. The contacts were shunted with a large condenser. Slight corrosion of the Hg did not affect the zero adjustment. The Cl_2O_7 was maintained at the required temp. by surrounding it with a jacket containing cooled EtOH, ice–salt mixture, or water. After each successive v.p. reading, quantities of the vapour were passed into a quartz cell and the absorption spectrum determined, a Hilger visual spectrograph being used. Any traces of ClO_2 present were clearly shown by its characteristic absorption bands. This was found to be a very sensitive test of purity, for Cl_2O_7 absorbs light only in the far ultra-violet region, whilst ClO_2 exhibits well-marked bands in the near ultra-violet at pressures as low as 0·01 mm. It was impossible to remove every trace of ClO_2, but v.p. readings of any fraction were rejected if the intensity of the ClO_2 bands appeared excessive. V.p. readings were taken both with the temp. slowly increasing and decreasing. Reliable results could not be obtained at temps. much above 30° owing to thermal decomp. of the Cl_2O_7 and subsequent corrosion of the Hg. Above room temp. measurements were made with the whole of the manometer system jacketed and heated to a temp. slightly greater than that of the liquid Cl_2O_7 in the trap.

FIG. 1.



The Vapour Pressure and Boiling Point.—The values obtained for the v.p. of

Cl_2O_7 are given in Table I. When their logarithms are plotted against the reciprocals of the absolute temp., a straight line is obtained. The corresponding equation is $\log_{10} P \text{ (mm.)} = -1818/T + 8{\cdot}03$.

TABLE I.

T (Abs.).	P (mm.).	T (Abs.).	P (mm.).	T (Abs.).	P (mm.).
244·0°	4·0	265·0°	14·1	289·5°	55·1
252·0	7·0	273·0	23·7	293·3	72·0
253·5	6·7	281·0	36·7	301·5	93·6
259·5	9·1	287·0	48·9	303·0	108·0

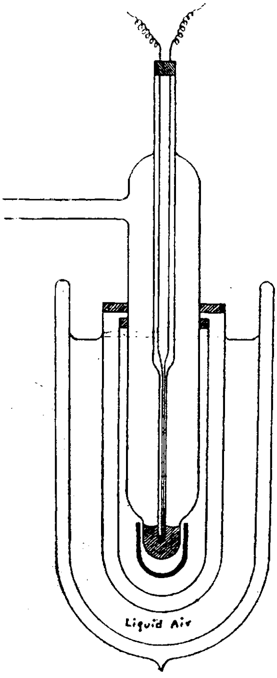


FIG. 2a.

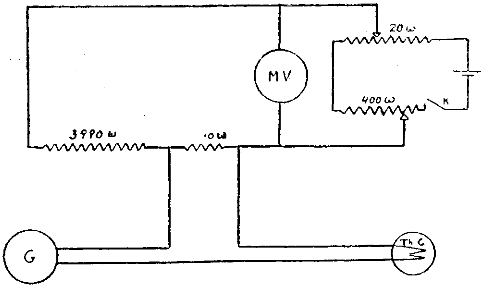


FIG. 2b.

By extrapolation of the v.p. curve, the b. p. of Cl_2O_7 is found to be 80° (± 1°). This value agrees closely with that (82°) directly observed by Michael and Conn. From the slope of the line, the latent heat of evaporation has been found to be 8290 cals. per g.-mol. The entropy change at the b. p. is $L_e/T = 23{\cdot}4$, and according to Trouton such a value indicates that the liquid is only slightly associated.

The Melting Point.—The m. p. of Cl_2O_7 has not previously been determined: Cl_2O_7 is still liquid at −78°, but freezes to a white solid at liquid-air temp.

A special apparatus was designed to measure the m. p. of the necessarily small quantity (see Fig. 2a). The lower bulb was made to hold about 0·5 c.c. of Cl_2O_7. A copper–constantan thermo-junction, contained in a fine glass capillary tube, was arranged so that its lower end was immersed in the liquid. A small piece of Wood's metal was placed round the end of the junction to ensure good thermal contact with the glass tube. A Cu cup was fitted loosely round the outside of the bulb in order to ensure uniform cooling, and to give a sharper transition point. The lower end of the main tube was surrounded by one or more air jackets to provide sufficient lagging. A simplified form of a special micro-potentiometer circuit devised by Guild (*J. Sci. Inst.*, 1930, **7**, 378) was used to measure the thermocouple *E.M.F.*'s (see Fig. 2*b*). A voltage step-up factor of 400 was employed, and readings made directly with a Weston standard 0—2000 mv. voltmeter. The whole of the lower end of the apparatus was surrounded with liquid air and Cl_2O_7 distilled over into the small bulb. The Cl_2O_7 was then completely frozen and the liquid air removed. Readings of *E.M.F.* were taken whilst the Cl_2O_7 was warming, and a time–*E.M.F.* curve plotted. A series of curves was obtained having definite breaks, due to the latent heat of fusion, corresponding to the m. p. A similar series of cooling curves was obtained having breaks close to those on the warming curves. Supercooling occurred to a considerable extent, and very careful adjustment of the degree of lagging was necessary in order not to miss the transition point.

The thermocouple had been previously calibrated under the conditions of the experiment, by distilling suitable pure liquids of known m. p.'s into the vessel, and obtaining warming and cooling curves in the manner previously indicated. Toluene (m. p. $-94{\cdot}5°$) and CS_2 (m. p. $-112°$) were used for two points, and a third was obtained by surrounding the bulb, containing one of the liquids, with solid CO_2–EtOH. The temperature of the freezing mixture was measured with a standard pentane thermometer and, after equilibrium had been reached, the corresponding *E.M.F.* was observed. From these measurements, the m. p. of Cl_2O_7 was found to be $-91{\cdot}5° \pm 2°$.

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