CCCLXIV.—*The Vapour Pressure of Chlorine Monoxide.*

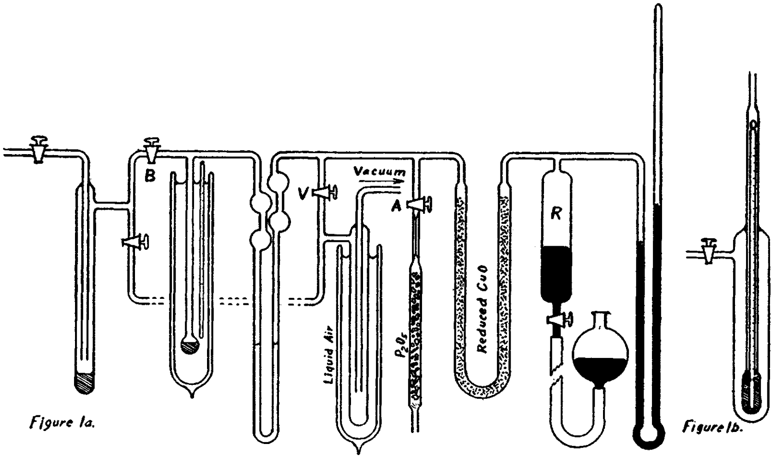
By Charles Frederick Goodeve.

During the photochemical and spectroscopic investigations of chlorine monoxide in these laboratories (Goodeve and Stein, *Trans. Faraday Soc.*, 1929, **25**, 738; Goodeve and Wallace, *ibid.*, 1930, **26**, 254), it was necessary to obtain accurate data as to vapour pressure over a wide range of temperatures which would serve as a guide to the purity of the gas and facilitate the filling of absorption and reaction vessels to a desired pressure. Apparently the only information on record is that by Goldschmidt (*Ber.*, 1919, **52**, 753), who found the b. p. to be 3·8°/766 mm.

EXPERIMENTAL.

Chlorine monoxide was prepared by a slight modification of the method used by Bodenstein and Kistiakowsky (*Z. physikal. Chem.*, 1925, **116**, 371). Chlorine, from a gas holder in which it was stored over saturated sodium chloride solution, was mixed with air and passed through bulbs containing mercuric oxide (previously heated to 250°). The chlorine monoxide was condensed in a trap cooled with solid carbon dioxide–alcohol, at a pressure below the vapour pressure of chlorine, so that most of the latter was carried on with the air stream. The monoxide was further purified by passage over phosphoric oxide to remove water and by fractionation to remove chlorine.

FIG. 1.



The experimental results, from which the accompanying data have been derived, were obtained over a period of several years and by means of several slightly varied arrangements of apparatus. In general, however, the chlorine monoxide was distilled into a vessel of small volume, which was maintained at the desired temperature by a jacket of carbon dioxide–alcohol or ice–salt mixtures, liquid ammonia, or alcohol–ether cooled by the addition of liquid air. The temperatures were read on an N.P.L. standard pentane thermometer, placed either in the cooling agent or in the chlorine monoxide itself. To this vessel was attached (see Fig. 1*a*) a U-tube filled with metaphosphoric acid, which, in turn, was connected to the mercury manometer system by a tube filled with air. Chlorine monoxide dissolves very slowly in metaphosphoric acid, owing to its low solubility and the high viscosity of the liquid.

The vapour pressure of chlorine monoxide was measured by adjusting the air pressure in the manometer system, until the levels of the liquid in the two arms of the U-tube were nearly the same. Corrections for the difference of level were then applied from the density of the liquid. Coarse adjustment of the air pressure was obtained by adding dried air through tap *A* or withdrawing it through tap *V*, and fine adjustment by changing the volume in the reservoir *R*.

The mercury manometer was made by spraying carefully purified mercury through an exceedingly fine jet into a highly evacuated and previously baked-out U-tube. Manometers made by this " cold process " have shown no signs of adhesion of the mercury on the walls of the tube even after several years. Stray chlorine was effectively prevented from coming in contact with the mercury surfaces by a tube of freshly reduced copper oxide wire.

In each determination, successive quantities of the gas were fractionated away until there was no further change in the vapour pressure of the liquid. Readings were taken with the temperature slowly increasing and decreasing, and consistent values obtained. At temperatures below −10° decomposition of the liquid monoxide was negligible except over long periods, but near the boiling point decomposition was rapid and accurate values could not be obtained. Moderately consistent results were obtained, however, in the following manner. Part of the gas in contact with the liquid was withdrawn as rapidly as possible through tap *B*, thus removing most of the products of decomposition. The tap was then closed and the gas and liquid were allowed to approach equilibrium. At the same time, the temperature was caused to decrease slowly, with the result that the pressure rose to a maximum and then decreased. The temperature and pressure were read at the moment this maximum occurred, which was generally less than $\frac{1}{2}$ minute from the time of turning off the tap. A true equilibrium point was thus reached before the concentration of the decomposition products seriously affected the results.

The Vapour Pressure and Boiling Point.—The values found for the vapour pressure of chlorine monoxide are indicated in Fig. 2*a*. A straight line is obtained when the logarithms of the vapour pressures (in mm.) are plotted against the reciprocals of the absolute temperatures. The corresponding equation is

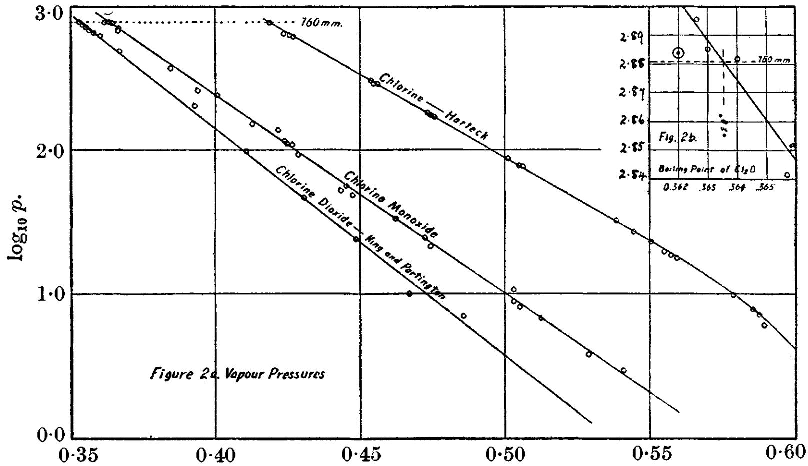
$$\log_{10} p = -1373/T + 7{\cdot}87.$$

The values, obtained from this line, for every 5° of temperature are tabulated below. The data for the vapour pressure of chlorine obtained by Harteck (*Z. physikal. Chem.*, 1928, **134**, 21) and of chlorine dioxide obtained by King and Partington (J., 1926, 925), have been calculated in the same manner and plotted for purposes of comparison in Fig. 2*a*. As seen from the figure, chlorine may be removed readily from chlorine monoxide by fractionation, whereas the dioxide can be removed only with difficulty.

Vapour pressure of chlorine monoxide.

T, Abs.	p, mm.	T, Abs.	p, mm.	T, Abs.	p, mm.	T, Abs.	p, mm.
288°	1227	258°	356	228°	71	198°	8·7
283	1052	253	280	223	52	193	5·7
278	860	248	217	218	37·6	188	3·7
275	760	243	167	213	26·7	183	2·4
273	699	238	127	208	18·7	178	1·44
268	563	233	96	203	12·8	173	0·86
263	450						

FIG. 2.



The vapour pressures given in the figure and shown on a larger scale in Fig. 2*b* indicate that the b. p. 2·0°/760 mm. is more correct than Goldschmidt's value, 3·8°. The higher value may have been due to superheating of the liquid, a phenomenon often observed with pure chlorine monoxide.

From the slope of the line, the latent heat of evaporation has been found to be 6200 cals. per g.-mol. The latent heat for chlorine, as calculated from Harteck's values of the vapour pressure, is 5300 cals., and for chlorine dioxide 6520 cals. The value of Trouton's coefficient, $L_e/T_{\text{b. p.}} = 22{\cdot}5$, indicates very little, if any, association of chlorine monoxide in the liquid state.

The Melting Point.—The International Critical Tables and other tables give the m. p. of chlorine monoxide as — 20°, but the source of this value is not recorded. Preliminary investigation showed this point to be below − 100°, and a determination was therefore made in the apparatus shown in Fig. 1*b*. The outer jacket was surrounded by liquid air, and chlorine monoxide was distilled into the inner chamber until the bulb of the standard pentane thermometer was completely covered by the liquid. The outer jacket was evacuated in order to reduce the rate of cooling. Temperatures were read at regular intervals until the liquid had completely solidified, and the readings were plotted. The curve showed the usual short break at the m. p. due to the latent heat of fusion. The curve of increasing temperature was obtained simply by removing the liquid air and allowing the outer jacket to warm, and again a break was found which commenced at the same temperature as in the cooling curve. The curves were repeated with successive fractionations of chlorine monoxide, and concordant results were obtained which indicated that the m. p. of chlorine monoxide is − 116° ± 1°.

Owing to the inaccessibility of this temperature, the m. p. is not convenient as a test of purity. It is of interest that, although the vapour-pressure curve of chlorine monoxide is intermediate between those of chlorine and the dioxide, its m. p. is below that of chlorine (*viz.*, − 101°), and some distance from that of chlorine dioxide (*i.e.*, − 59°).

In conclusion, the author wishes to thank Professor F. G. Donnan for suggesting the research on chlorine monoxide. He is also indebted to the Royal Commission for the Exhibition of 1851 for a Scholarship held while the work was carried out.

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