60. *Dichlorine Hexoxide.*

By Charles F. Goodeve and Frederick D. Richardson.

Although dichlorine hexoxide (Cl_2O_6) and chlorine trioxide (ClO_3) have been postulated as intermediates in a number of reactions involving the oxides of chlorine, little has been recorded of their physical and chemical properties.

It appears that the hexoxide was first obtained by Millon (*Annalen*, 1843, **46**, 311) by the action of sunlight on chlorine dioxide (ClO_2) cooled to below 20°. The oxide, which formed on the walls of the preparation vessel as a red liquid, decomposed even in the dark, but did not explode on heating. Eighty years later it was again prepared similarly (Bowen, J., 1923, **123**, 2328), and then Booth and Bowen (J., 1925, **127**, 510) found that on continued illumination the red oily liquid was converted into colourless dichlorine heptoxide. They showed that the liquid did not consist of the dioxide dissolved in anhydrous perchloric acid, and that its existence could not be explained on the basis of the then recognised oxides, *viz.*, Cl_2O, ClO_2, and Cl_2O_7. By analysis of the red liquid, Bodenstein, Harteck, and Padelt (*Z. anorg. Chem.*, 1925, **147**, 233) showed the oxygen : chlorine ratio to be 3 : 1; they also showed, by depression of the freezing point of carbon tetrachloride, that the molecular weight was of the order 153—156, a value approximately in agreement with the formula Cl_2O_6 ($M = 166{\cdot}9$).

The results of Goodeve and Todd (*Nature*, 1933, **132**, 514) indicated that the oxide existed as ClO_3 in the vapour phase, and the magnetic measurements of Farquharson, Goodeve, and Richardson (*Trans. Faraday Soc.*, 1936, **32**, 790) showed that, in the solid and the liquid phase, an equilibrium existed between the two forms ClO_3 and Cl_2O_6.

In this work, the main physical properties of the oxide have been determined, and the heat of activation for the decomposition of the liquid measured.

Experimental.

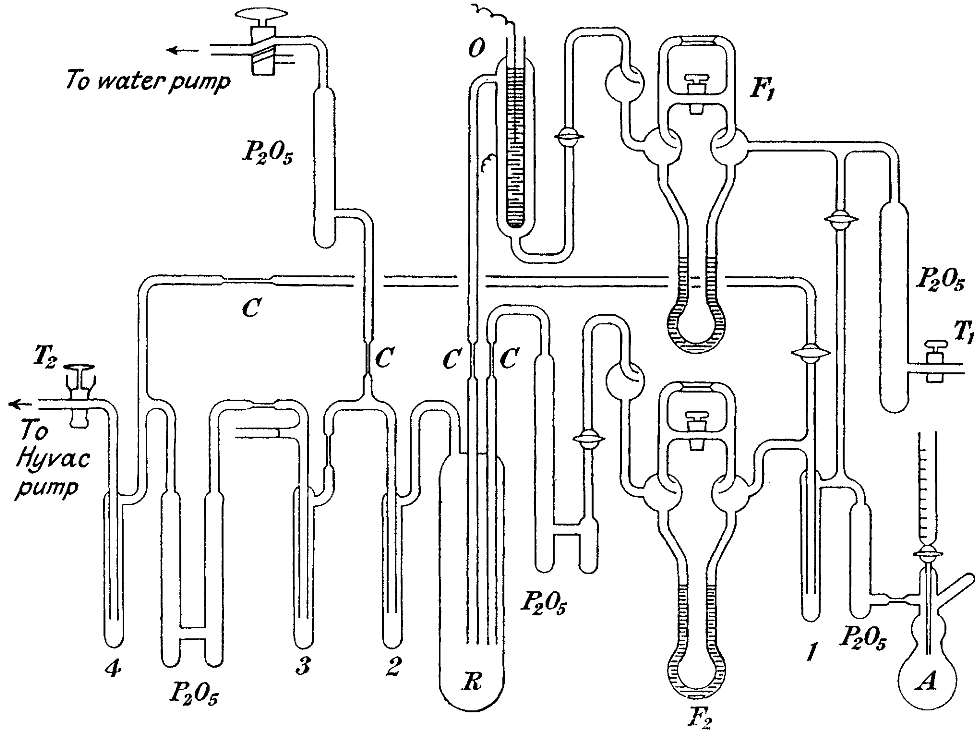
Preparation.—The dichlorine hexoxide was prepared (cf. Schumacher and Stieger, *Z. anorg. Chem.*, 1929, **184**, 272) by mixing a stream of ozonised oxygen with a stream of oxygen containing chlorine dioxide. The apparatus, which consisted entirely of soda glass, is shown in Fig. 1. Taps which were not open to attack from chlorine dioxide were lubricated with Apiezon L grease. The others were lubricated with pure metaphosphoric acid of a suitably viscous consistency. Since the hexoxide reacts with all known lubricants and dissolves very readily in phosphoric acid (thereby being itself decomposed), no taps were placed beyond the mixing vessel *R* in which the hexoxide was formed.

The chlorine dioxide was prepared by dropping concentrated sulphuric acid on powdered potassium chlorate cooled to − 78° in the vessel *A*. When all the acid had been added, the apparatus was evacuated with a Hyvac pump. The mixture was allowed to warm slowly, the temperature being so adjusted that the reaction proceeded gently. The dioxide was collected in trap 1, cooled in liquid air. The preparation vessel *A* was then sealed off at its constriction.

The Pyrex ozoniser *O* was of the vertical Siemens type; the inner tube was filled with copper sulphate solution, and the outer one coated on the outside with colloidal graphite. The discharge was produced by A.C. of 10,000 volts and 350 cycles.

A stream of cylinder oxygen was passed at atmospheric pressure into the apparatus at T_1, and was divided into two parts, one passing through the ozoniser, and the other over the chlorine dioxide in trap 1, now cooled in melting ice. The ozone and chlorine dioxide concentrations were about 7% and 20% by volume, respectively. The flow speeds were measured by the flow-meters F_1 and F_2, and regulated so that they were roughly 20 l./hr. for the ozone stream and 2 l./hr. for the dioxide. The streams were mixed in the reaction chamber R, cooled in melting ice. A brown liquid condensed on the sides of the vessel, and to some extent in the tubes beyond. The waste gases passed to the water pump, tap T_2 being closed.

FIG. 1.



In one preparation three separate charges of potassium chlorate were used, since it was not considered safe to prepare more than about 5 c.c. of chlorine dioxide at a time. When the liquid hexoxide was allowed to drain completely from the walls of the reaction chamber after the initial preparation, crystalline hexoxide was subsequently deposited at 0°. When the preparations had been completed, the reaction vessel and the traps for distillation were isolated from the rest of the apparatus by sealing off all the constrictions marked C in the figure. The preparation did not yield a pure product, chlorine dioxide and heptoxide being found amongst the impurities.

Purification.—Pure samples of the hexoxide could not be obtained merely by distilling away the top fractions and keeping the oxide in the preparation vessel—a method apparently used by previous workers. This was due largely to the presence of a white involatile solid residue which remained in R after all the oxides had been distilled away. A similar residue has been obtained by other workers with chlorine dioxide—the formation being especially marked in glass vessels. Schumacher and Stieger (*loc. cit.*) suggested that the white deposit resulted from attack of the dioxide on the glass and consisted of Si_6Cl_{14}. No detailed analysis has yet been carried out.

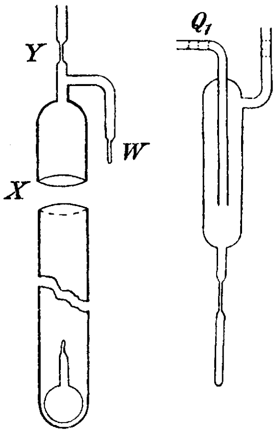
The oxide was, therefore, purified by fractional distillation. The reservoir R was kept at 6°, and the pure hexoxide was collected at $-$ 20° in trap 3, the more volatile impurities passing over to a liquid-air trap 4. Trap 3 was sealed off and attached to any desired apparatus by means of the septum, thereby avoiding exposure of the oxide to the atmosphere.

Analysis.—The hexoxide was analysed by sealing about 0·1 c.c. in a small, thin-walled bulb. This was introduced into the Pyrex tube (Fig. 2*a*), which was in two portions as shown. These were sealed together at *X*. The tube was connected to a Hyvac pump and dried by heating with a yellow flame. (The bulb was moved to a cool part of the tube during this process.) The tube was then sealed off at the constriction *Y*. The small bulb was broken by shaking the tube, which was then heated with a blow-lamp flame, at first gently and finally strongly, in order to decompose the sample into oxygen and chlorine. After being heated for about 20 minutes, the tube was allowed to cool. The constriction *W* was opened under potassium iodide solution, which was drawn up into the tube. The chlorine was absorbed, and the iodine liberated was subsequently determined with sodium thiosulphate; the volume of the oxygen was measured directly. The chlorine : oxygen ratios obtained in this manner were 1 : 3·00 ± 0·03.

Melting Point.—Bodenstein, Harteck, and Padelt (*loc. cit.*) found the m. p. to be about − 1°, but Rollefson and Byrns (*J. Amer. Chem. Soc.*, **1934**, **56**, 364) have prepared samples of hexoxide melting just above 0°. These were liquid at 0° in the presence of a few mm. of chlorine.

A quartz tube was constructed as shown in Fig. 2*b*, and connected to the apparatus by quartz-to-soda glass, graded joints, Q_1 and Q_2. It was heated with a blow-lamp flame under a vacuum to remove the last traces of moisture adsorbed on the walls, and a small quantity of hexoxide was condensed in it at − 20°. The oxide was then melted and allowed to run into the thin-walled, narrow-bore tube attached by the constriction to the bottom of the trap. As described below, dichlorine hexoxide decomposes into oxygen, chlorine, and the di- and hept-oxide at temperatures above − 20°. It was, therefore, necessary to carry out the above process under a high vacuum, and, when the oxide had drained into the thin tube, to cool in stages in order to allow evaporation of the volatile impurities from the crystals. When the temperature had reached − 78°, the tube was sealed off at the constriction. The m. p. was determined in the usual way, three values per sample being obtained with different rates of warming.

FIG. 2.



(*a*) (*b*)

Three different samples gave m. p.'s 3·50°, 3·52°, and 3·50°; the true m. p. is, therefore, 3·50°, with a maximum error of 0·05°.

On keeping one sample at 5·5° for 15 minutes, the m. p. fell by 0·2°; on keeping at 17° for 7 minutes there was a further fall of 0·45°. This indicates the ease with which thermal decomposition takes place.

It was not possible to obtain reproducible results for different samples when glass was employed instead of quartz. When the hexoxide was run into glass m. p. tubes and then distilled away, there remained on the walls a white deposit similar to that referred to above.

The colour of the hexoxide, as well as the m. p., was markedly affected by small quantities of impurity. When the oxide was pure it possessed a bright orange-red colour at − 78° and was pale yellow at − 180°. At low temperatures the colour of an impure sample was dark brown.

Vapour Pressure.—A measurement of the vapour pressure was first attempted by Bodenstein, Harteck, and Padelt (*loc. cit.*), who obtained a value of about 1 mm. of mercury at room temperature. Schumacher and Stieger (*loc. cit.*) obtained the rough values 1 mm. at 20° and 5—10 mm. at 40°, and Norrish and Neville (*Nature*, **1933**, **131**, 544) found a value somewhat less than 1 mm. at 0°. Rollefson and Byrns (*loc. cit.*) made two measurements with an accuracy of about 10% : their results are indicated in Fig. 4 by " R. and B."

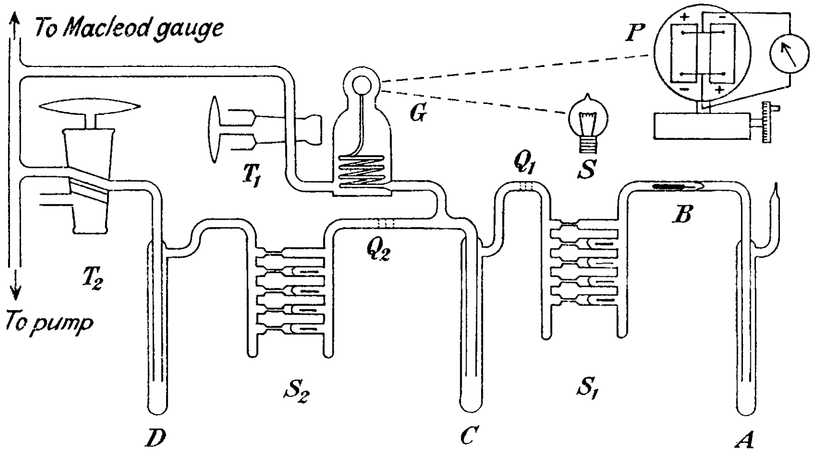
Measurement. The pressure-measuring apparatus was constructed as shown diagrammatically in Fig. 3. This consisted of a quartz spiral Bodenstein (Bourdon) gauge *G*, fitted with a mirror which reflected light from a source *S* about 1 m. distant into a photo-cell device *P*, a similar distance away. The lenses and slit of the optical system are not shown. The Bodenstein gauge was used with its outer jacket evacuated; the pressure in the spiral was determined by measuring the position of the reflected light beam with the photo-cell arrangement. The light source was a 15-c.p. filament lamp connected to a constant-voltage supply. The photo-cell device consisted of two separate selenium cells set up side by side and opposed in parallel as recommended by Hill (*Nature*, **1934**, **134**, 289) and by Wood (*Rev. Sci. Instr.*, **1934**, **5**, 295). The cells were connected to a Zernicke galvanometer, and screened from all light other than that reflected from the gauge mirror. They were further protected from local variations of temperature, to which they were susceptible, by means of suitable screens. The pair of cells was mounted on the carriage of a Hilger travelling micrometer, graduated in 0·01 mm. divisions and readable to 0·1 division. Readings of the micrometer were taken when, on illumination of the cells, there was no deflection of the galvanometer, *i.e.*, when the cells were equally illuminated. Their position, therefore, marked the centre of the reflected light spot. The gauge was calibrated against a wide-bore mercury manometer and a Macleod gauge. A pressure equivalent to 1 mm. of mercury in the spiral of the gauge caused a deflection of the light spot of 0·412 mm.

If the photo-cells had been perfectly uniform and matched, vibration of the pressure-gauge mirror, being of a very much higher frequency than the period of the galvanometer, would not have affected the zero position. As this was not altogether the case, it was necessary to set the entire apparatus on a special bench mounted on six old tennis balls. Under favourable conditions pressures could be measured to within 0·01 mm. of mercury.

The trap A, containing the hexoxide, was sealed to the rest of the apparatus at B. S_1 and S_2 are banks of septa, and Q_1 and Q_2 graded quartz-to-soda glass seals. The septa were broken with magnetically operated hammers. C is a quartz trap, and D a waste trap cooled in liquid air. The taps T_1 and T_2 did not come into contact with the hexoxide, and were lubricated with Apiezon L grease.

About 0·05 c.c. of hexoxide was distilled into C after the septum at B had been opened. Both traps were then cooled to − 78°, and S_1 closed by sealing a constriction. The entire apparatus was evacuated to 0·003 mm., and the bank of septa S_2 and the tap T_1 closed. Measurements of the vapour pressure of the sample in C were then made. The temperature was adjusted by immersing C in cooled alcohol, the temperature of which was measured with a calibrated thermometer. Below 0° the rate of decomposition of the sample was negligible, and the vapour pressure was measured directly. At temperatures where the liquid was decomposing, pressure readings were taken every 2 minutes until the pressure increased uniformly with time. The true vapour pressure was determined by plotting the results and extrapolating the pressure–time curve to zero time.

Fig. 3.



It was not possible to obtain reproducible values of the vapour pressure when large quantities of hexoxide (1 c.c.) were used. This was due to the impossibility of removing the last traces of volatile impurity (formed by thermal decomposition of the liquid, see p. 296), which was entangled in the bulk of the hexoxide when it was solidified. At temperatures above − 180° these impurities diffused slowly into the gas phase where they registered a small variable pressure. When a small crystal of hexoxide was used, the error due to this effect was negligible in comparison with the vapour pressure of the oxide, and the results were reproducible for different samples. The use of a small crystal at the higher temperature was also an advantage, as the effect of thermal decomposition was very much reduced. At temperatures below 0° the values for the vapour pressure were probably accurate to 0·02 mm. At temperatures above this the limit of error increased with the rate of decomposition of the hexoxide. Below 0° the error in absolute temperature was about 0·5°; above 0°, 0·2°.

Results. The results for three different samples are shown plotted on the usual logarithmic scale in Fig. 4. The values for the liquid and for the solid lie on two straight lines, the equations for which are :

$$\text{Liquid, } \log_{10} p_{\text{mm.}} = -2070/T + 7{\cdot}1 \quad (1)$$

$$\text{Solid, } \log_{10} p_{\text{mm.}} = -2690/T + 9{\cdot}3 \quad (2)$$

These lead to values for the latent heat of evaporation and of sublimation of 9·5 ± 1 and 12·3 ± 0·5 kg.-cals. per g.-mol. respectively. It is seen that, in spite of the association to hexoxide in the liquid phase, the constant in equation (1) has the normal value of about 7·5 (Trouton's rule). This may be due to the small heat of dissociation (cf. Farquharson, Goodeve, and Richardson, *loc. cit.*) for the hexoxide molecule :

$$Cl_2O_6 \text{ (liquid)} \longrightarrow 2ClO_3 \text{ (liquid)}; \ \Delta U = +\ 1{,}700 \pm 500 \text{ cals.}$$

FIG. 4.

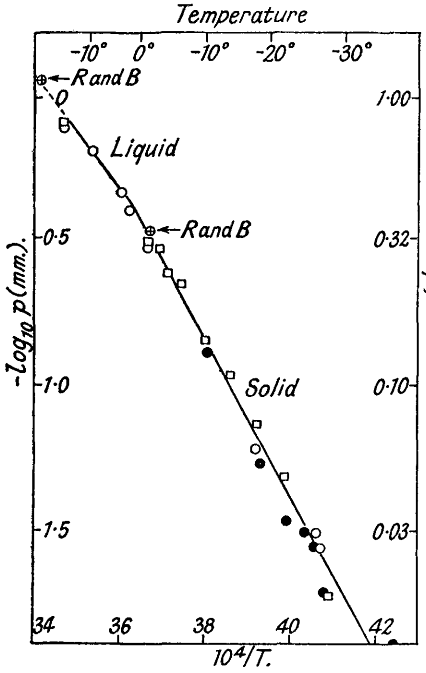
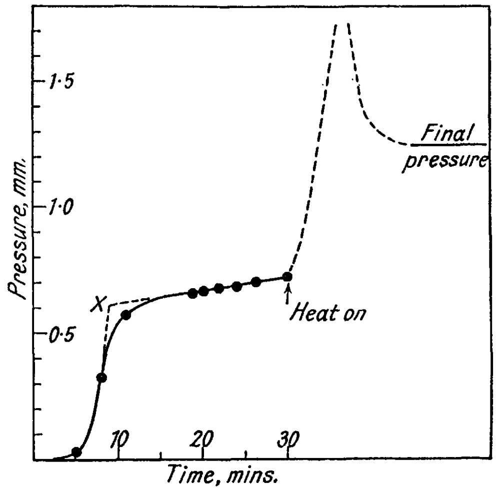


FIG. 5.



Decomposition of Liquid Hexoxide.—Norrish and Neville (*loc. cit.*) found a temperature coefficient of 2·34 per 10° for the thermal decomposition of the liquid oxide. Byrns and Rollefson (*J. Amer. Chem. Soc.*, 1934, **56**, 2245), from measurements of the temperature coefficient, have obtained a value of 21—26 kg.-cals. for the heat of activation.

A value for the heat of activation for the decomposition of the liquid can be calculated from the Arrhenius equation, the velocity constant for the reaction being taken as proportional to the rate of pressure increase. The pressure–time curves at 4·8°, 10·0°, and 14·8° lead to a value of 22 ± 2 kg.-cals., which corresponds to a temperature coefficient of 3·8 per 10°. This is in agreement with the value determined by Byrns and Rollefson (*loc. cit.*). They assumed that this value represents the heat of activation for the reaction $ClO_3 \longrightarrow ClO_2 + \frac{1}{2}O_2$. Since the liquid exists almost entirely as hexoxide, and since we have found that chlorine and dichlorine heptoxide, as well as chlorine dioxide and oxygen, are formed in the liquid decomposition, it is impossible to state exactly what the equation may be. The decomposition may, however, occur through the trioxide present in the equilibrium mixture.

Molecular Constitution and Decomposition in the Vapour Phase.—This investigation was carried out in order to verify the previous work of Goodeve and Todd (*loc. cit.*), who showed that the molecular weight in the vapour phase corresponded to the formula ClO_3; the pressures mentioned in their note are, however, greater than the vapour pressures at room temperature.

Measurement. Some chlorine hexoxide was sealed in a small trap, which was connected to a 54-cm. quartz tube with end windows, and to the Bodenstein pressure gauge used for the vapour-pressure measurements. About half of the oxide was distilled away, leaving only enough to fill the apparatus to about 1 mm. pressure or less. Thus no liquid remained unevaporated when the small trap was warmed to room temperature. Pressure readings were taken as soon as the cooling mixture (— 78°) was removed, and were continued until the rate of pressure increase became constant. The absorption spectrum was photographed through the tube at intervals. The tube was then heated with a hand blow-pipe to decompose the oxide vapour to oxygen and chlorine. The tube was heated and cooled alternately until the pressure in the system at room temperature reached a constant value and there was no evidence of oxides of chlorine in the absorption spectrum. The final pressure was then measured and assumed to be due to the oxygen and chlorine formed by decomposition.

Results. Fig. 5 shows a typical pressure–time curve. It is seeen that no constant initial pressure was reached, but that as soon as the oxide had evaporated the rate of increase of pressure became approximately constant. The pressure of the oxide vapour, corresponding to the amount of hexoxide initially present, was determined by extrapolation of the pressure–time curve to the point X in the graph. Four experiments were carried out. The results are given below :

Initial press. (mm.) extrapolated	1·13	0·73	0·62	0·25
Final pressure	2·29	1·45	1·25	0·48
Ratio	2·03	1·97	2·04	1·95

These results show conclusively that the oxide exists almost entirely, if not completely, as ClO_3 in the vapour phase, the total decomposition being represented by the equation :

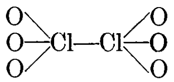
$$\begin{array}{l} ClO_3 \longrightarrow \tfrac{1}{2}Cl_2 + \tfrac{3}{2}O_2 \\ 1 \text{ vol.} \quad \rightarrow 2 \text{ vols.} \end{array}$$

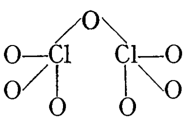
The higher pressures found in the previous work (Goodeve and Todd, *loc. cit.*) may have been due to a faulty calibration of the pressure gauge.

The photographs of the absorption spectrum showed that the continuous absorption due to ClO_3 decreased with time at room temperatures after the tube had been filled, whereas the band absorption due to the dioxide increased in intensity.

Discussion.

The physical properties of dichlorine hexoxide are compared with those of the other oxides in the table. It is of interest to note that this oxide has the highest melting point, the highest density, and the highest latent heat of evaporation (lowest vapour pressure). The contrast is particularly striking when it is compared with the heptoxide. A symmetrical structure for the hexoxide and an unsymmetrical one for the heptoxide would explain these differences. The symmetrical molecules could form crystals more easily, pack closer together, and thus have a larger latent heat of evaporation. They would, therefore, have a higher melting point, density, and latent heat than the unsymmetrical molecules. An exactly parallel relation is seen when these properties for the aliphatic alcohols are contrasted with the corresponding properties for the isomeric ethers. The latter are more


(non-planar).


(non-planar).

Oxide.	Cl_2O.	ClO_2.	Cl_2O_6.	Cl_2O_7.
Mol. wt.	87	67·5	167	183
M. p.	−116° *	−59° †	+3·5°	−91·5° ‖
B. p.	2° *	11·0° †	203° (calc.)	80° ‖
Latent heat of evaptn., kg.-cals.	6·20 *	6·52 †	9·50	8·29 ‖
Trouton's const.	22·5 *	23·0 †	21	23·4 ‖
Vap. press., mm. at 0°	699 *	490 †	0·31	23·7 ‖
Density	—	1·64, 0° ‡	2·02, 3·5° §	1·86, 0° ¶
G.-mol. vol., c.c.	—	41·1	82·7	98·4

* Goodeve, J., 1930, 2733. † King and Partington, J., 1926, 925. ‡ Cheesman, J., 1930, 36. § Farquharson, Goodeve, and Richardson, *loc. cit.* ‖ Goodeve and Powney, J., 1932, 2078. ¶ Private communication from Mr. A. E. L. Marsh.

unsymmetrical than the former (as they possess a central oxygen atom with a valency angle of about 126°) and they have very much lower melting points, densities, etc.

Dichlorine hexoxide has been found to be the least explosive of all the known oxides of chlorine. It does not explode with shock or sudden heat, although it may do so on contact with water or organic matter. It is, however, the least thermally stable of the oxides, and decomposes very readily in the liquid or the vapour phase at room temperature.

At the same time the authors' experiences with this and other oxides of chlorine have shown that *there are no safe conditions* under which they can be handled. Elaborate precautions against harm arising from explosions have only partly succeeded in preventing personal injuries.

SUMMARY.

The preparation of dichlorine hexoxide from chlorine dioxide and ozone, and its purification and analysis have been described.

The melting point has been determined as 3·50° ± 0·05°. The vapour pressure has been measured over a temperature range — 40° to + 20°. The values for the latent heats of evaporation and sublimation have been calculated from these results.

The heat of activation for the decomposition of the liquid has been found to be 22 ± 2 kg.-cals. The oxide has been shown to exist in the vapour phase as ClO_3, which decomposes readily into dioxide and oxygen.

The physical properties of the hexoxide have been contrasted with those of the other oxides of chlorine, and the structures of it and of the heptoxide have been discussed.

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