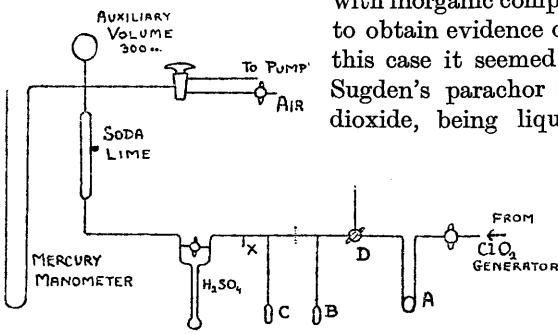
VIII.—*The Parachor of Chlorine Dioxide.*

By GEOFFREY HERBERT CHEESMAN.

THE structure of chlorine dioxide, ClO_2, has always been the subject of much speculation, and the electronic ideas of valency do not solve the difficulty, for the total electron content (19 outer-sheath electrons) is an odd number. As usual with inorganic compounds, it is difficult to obtain evidence of structure, but in this case it seemed reasonable to try Sugden's parachor method. Chlorine dioxide, being liquid between −59° and +10° under atmospheric pressure, is suitable for surface-tension and density measurements. Throughout this work the chlorine dioxide–carbon dioxide mixture produced by Bray's method was frozen out and fractionated.

FIG. 1.



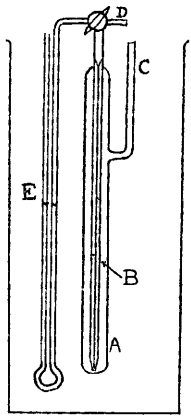


FIG. 2*a*.

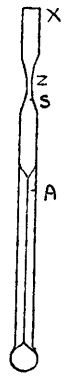


FIG. 2*b*.

Quantities of liquid up to about 1 c.c. were condensed and fractionated in the simple vacuum apparatus shown in Fig. 1. The material was condensed in A, and warmed to 0°, whereupon all the carbon dioxide passed off. About one-quarter of the liquid was allowed to evaporate away through tap D. The remainder was frozen out, the apparatus pumped out, and two-thirds of the remainder distilled into B by surrounding the latter with liquid air. From this, one-quarter was again rejected, and the middle portion distilled as before into C. All the material was then frozen in liquid air, and the apparatus evacuated and sealed between C and B. About 0·2—0·4 c.c. was thus obtained.

The purity of the material was followed by vapour-pressure determinations with the mercury manometer and sulphuric acid buffer on the left of the apparatus. Reproducible pressures were obtained

in good agreement with those of King and Partington (J., 1926, 925).

Two sets of density determinations were made, the first by a method of balancing columns, and the second by a pyknometer method. The first method is illustrated by Fig. 2*a*. The inner tube of the apparatus, B, was a uniform capillary, and the material was distilled into the lower portion of A through the side tube C. Suction was gently applied at D, and the heights of the liquid in the capillary and of the water in the U-tube E were measured with a sliding microscope. About 20 readings were taken, and the height of liquid plotted against the height of water. The points lay on a straight line, the gradient of which gave the relative density of the liquid at the temperature of the experiment (0°).

Two experiments on these lines gave rather different results, and hence the second method was tried. The actual pyknometer resembled a small thermometer (Fig. 2*b*) with a mark at A on the capillary stem, and a file scratch at S; it was sealed to the fractionation apparatus at X. Sufficient material was distilled in to fill it nearly to A when at 0°, and then frozen out. The apparatus was evacuated, sealed off at Z, and maintained at 0° till the meniscus remained steady, and the distance below A was measured with the sliding microscope. (Further readings at other temperatures gave the corresponding densities, which it is hoped to communicate later.) The instrument was then weighed, the contents frozen, and the apparatus carefully broken open at S, any small fragments (which were only produced on one occasion) being retained. The contents were allowed to evaporate, the apparatus dried in a vacuum, and reweighed. A previous calibration with mercury gave the volume to the mark A and the volume per mm. of stem below the mark. Hence the density of the liquid could be calculated. The densities (g./c.c. at 0°) obtained by the two methods were as follows, the mean of all five determinations being 1·642.

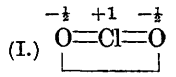
Balanced-column method: 1·622, 1·645. Pyknometer method: 1·661, 1·639, 1·644.

The surface tension was measured by capillary rise, the mean of seven consistent experiments in different apparatus giving $\gamma/D = 20{\cdot}1$. Combination of this with the density above gives the surface tension as 33·1 dynes/cm. at 0°, and hence the parachor is 98·7 units.

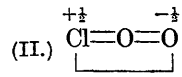
The data of King and Partington (*loc. cit.*) and cryoscopic measurements of Bray (*Z. physikal. Chem.*, 1906, **54**, 569) appear to indicate absence of association, and a determination in the present work of the Ramsay–Shields coefficient confirms this. (The experiments upon the surface tension, density, and other properties at lower temperatures will be published later.) The determined parachor

may therefore be compared with the sum of the atomic parachors of the elements, *viz.*, 94·3, leaving a structural parachor of +4·4 units.

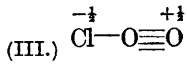
On the assumption that all octets are completed, there are eleven possible electron distributions for chlorine dioxide. Of these, three do not yield readily calculable parachors, but are improbable on account of large polarities accumulated on single atoms; five others are unlikely because they give large negative structural constants. The remaining three are shown below :



2 Semipolar double bonds	− 3·2
Non-polar singlet	− 11·6
3-Membered ring	+ 17·0
Structural const.	+ 2·2



Semipolar singlet	− 12·4
3-Membered ring	+ 17·0
Structural const.	+ 4·6



Semipolar singlet	− 12·4
Double bond	+ 23·2
Structural const.	+ 10·8

On the assumption that formula (I) contains only one integral dipole, the structural parachor amounts to + 3·6 units. Formulæ (I) and (II) therefore give the closest agreement with the observed value, and further work is now in hand to adduce other evidence for the structure of the dioxide and other halogen oxides. The structure (II) herein suggested appears somewhat novel, but accords quite well with the known reactions of the oxide.

The work was carried out in the laboratory of Professor Baker, and thanks are due to him for his interest in it.

ROYAL COLLEGE OF SCIENCE,
SOUTH KENSINGTON.

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