The accuracy of the method which is here described for measuring the electrolytic dissociation of water depends primarily on the accuracy with which the difference $k_w - A$ can be measured. For glucose this difference is only ten per cent. of the separate quantities, and consequently the accuracy of the method is not great, probably about twenty per cent., but from recent measurements which I have made on the rate of mutarotation of the related sugar fructose in pure water and acid solutions,[1] it appears that the above difference for this sugar is far larger than for glucose, being over forty per cent. of the separate quantities. Measurements on fructose will therefore, in all probability, give with closer accuracy the electrolytic dissociation of water.

LIQUID CHLORINE.

By F. M. G. Johnson and D. McIntosh.

Received August 24, 1909.

Among the liquefied gases which have been studied chlorine has received comparatively little attention. Knietsch[2] has measured its vapor pressure, and its density at various temperatures, while Grumach[3] has made a measurement of its molecular surface energy.

We thought it of interest to repeat their work and make a further study of this substance. We have measured:

1. The vapor pressure;
2. The density and its variation with temperature;
3. The molecular surface energy;
4. Chlorine as a conducting solvent.

The apparatus employed can be understood from the accompanying figures. Fig. 1 shows the method used for obtaining constant temperatures, and consists of a Dewar flask containing ether. This is closed by a rubber stopper through which passes the bulb of a constant-volume hydrogen thermometer, a modified form of Ramsay and Shields' apparatus for measuring capillary rise, which was also connected to the pressure apparatus, and the tubes necessary to keep the temperature constant. This is effected by blowing liquefied air into bulb A. The ether was kept stirred by a vigorous air current.

The chlorine was prepared by dropping hydrochloric acid on solid potassium permanganate. The gas was purified by washing with water, passing through a tube containing copper sulphate, and was dried with phosphorus pentoxide. It was then liquefied with solid carbon dioxide and ether, and fractionally distilled three times, the middle portion being retained. It was finally liquefied in the capillary apparatus and density bulb,

[1] This Journal, 30, 1578 (1908).

[2] *Ann.*, 259, 124 (1890).

[3] Landolt and Börnstein.

and the latter sealed. The chlorine during its preparation did not come into contact with rubber, and as it was distilled so many times we believe it to have been practically free from all impurities.

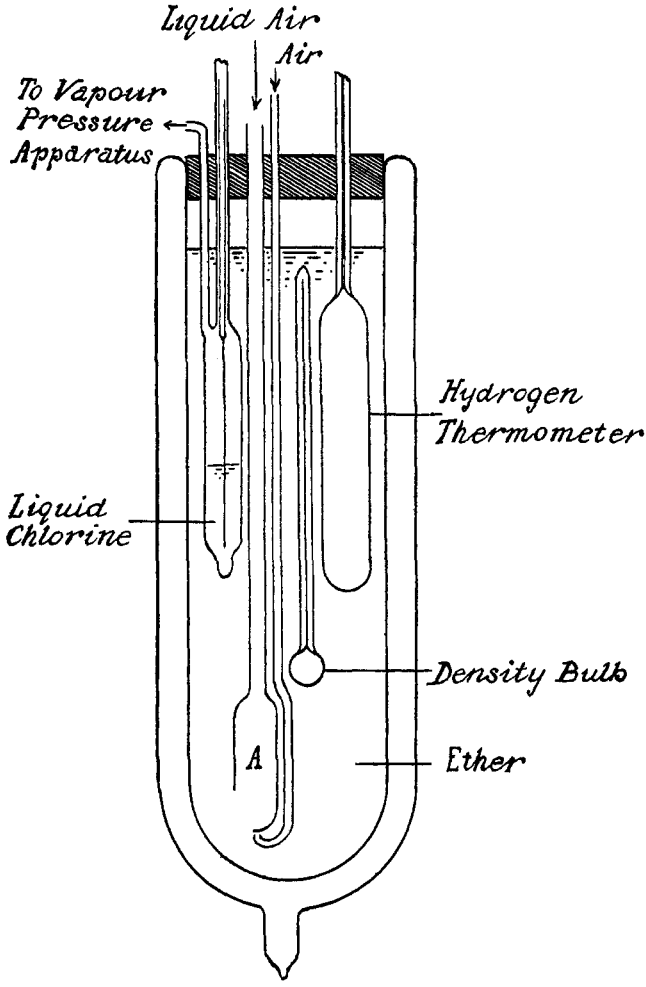

Fig. 1.

The Vapor Pressure.—Knietsch's measurements were made by means of a manometer in which the mercury was protected by a layer of oil. We have used an apparatus in which the chlorine comes in contact only with glass, the principle of which has been previously described.[3] The apparatus as modified for our purpose is shown in Fig. 2.

After introducing the liquid chlorine into the capillary apparatus it was frozen by means of liquid air, while it and the pressure apparatus

[1] *Z. physik. Chem.*, **61**, 457 (1908).

were completely exhausted through C with a mercury pump protected by a tube containing solid potassium hydroxide. Tap B was then closed, the liquid air was removed, and the Dewar flask with cooled ether substituted. The bath was then brought to the lowest required temperature, and kept constant by blowing small amounts of liquid air into bulb A.

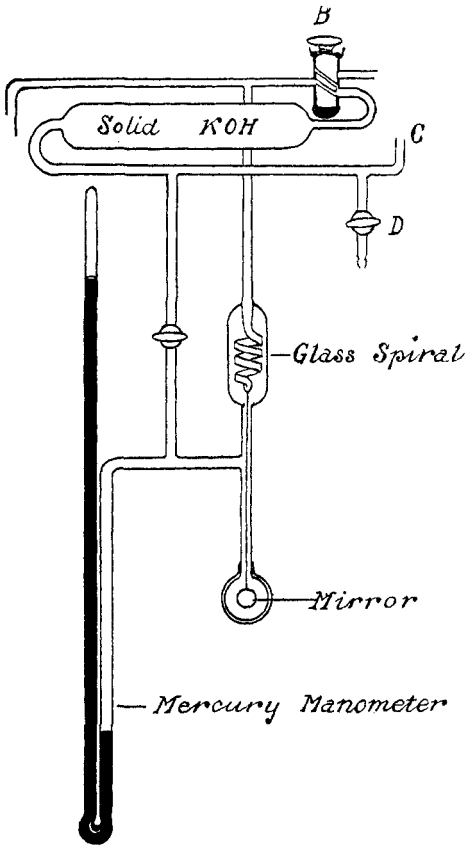

Fig. 2.

The pressure of chlorine vapor causes the glass spiral to twist, thus turning the mirror which hangs from it by a glass thread.

By admitting air through D into the outer chamber surrounding the spiral, the mirror is made to resume its original position. The pressure of air admitted, necessary to bring the mirror back to this position, is equal to the vapor pressure of the chlorine, and is read on the mercury manometer. The glass spiral used was sensitive to 0.3 mm. pressure.

The following results were obtained:

Temperature.	Pressure in mm.
—105.7°	8.0
—101.5	9.2
—96.3	16.5
—89.8	24.4
—84.3	39.6
—75.3	76.1
—65.9	141.5
—56.8	240.6
—47.3	399.5
—39.3	592.0
—32.0	820.5

These results, shown by the curve in Fig. 3, are almost identical with those obtained by Knietsch. He found the boiling point under atmospheric pressure to be —33.6°; our curve gives the temperature as —33.7°.

At the freezing point the vapor pressure of 9.2 mm. shows the temperature to be —101.5°.

By means of the Clausius formula, $d \log p/dT = W/RT^2$ the heat of vaporization at 760 mm. pressure for one gram molecule we find to be

21.1×10^{10} ergs. We are unable to find any direct determinations of this constant.

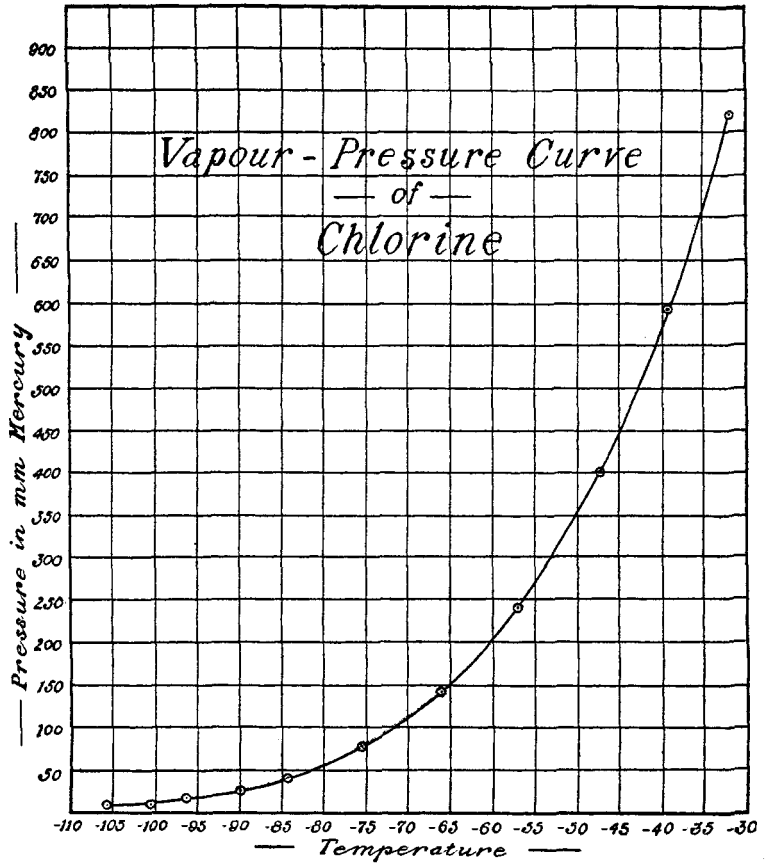

Fig. 3.

Density.—This value was determined by liquefying the chlorine in a calibrated tube of stout glass, which was then sealed, brought to constant temperature, and the volume read. A deep scratch was made on the glass, the tube brought to room temperature, and weighed. It was again cooled, opened, the chlorine allowed to escape, and then reweighed. Two determinations gave at —78.6° a density of 1.6725 and 1.6720. At —80° Knietsch found the value 1.6602 The change of density with temperature was observed by means of the density bulb with graduated capillary, shown in Fig. 1. The temperature and the height of the liquid chlorine in the capillary were noted. The following values were obtained:

Temperature.	Density.	Temperature.	Density.
—93.7°	1.7106	—57.5°	1.6245
—86.8	1.6957	—48.3	1.6000
—78.8	1.6740	—37.8	1.5778
—66.3	1.6463	—29.4	1.5574

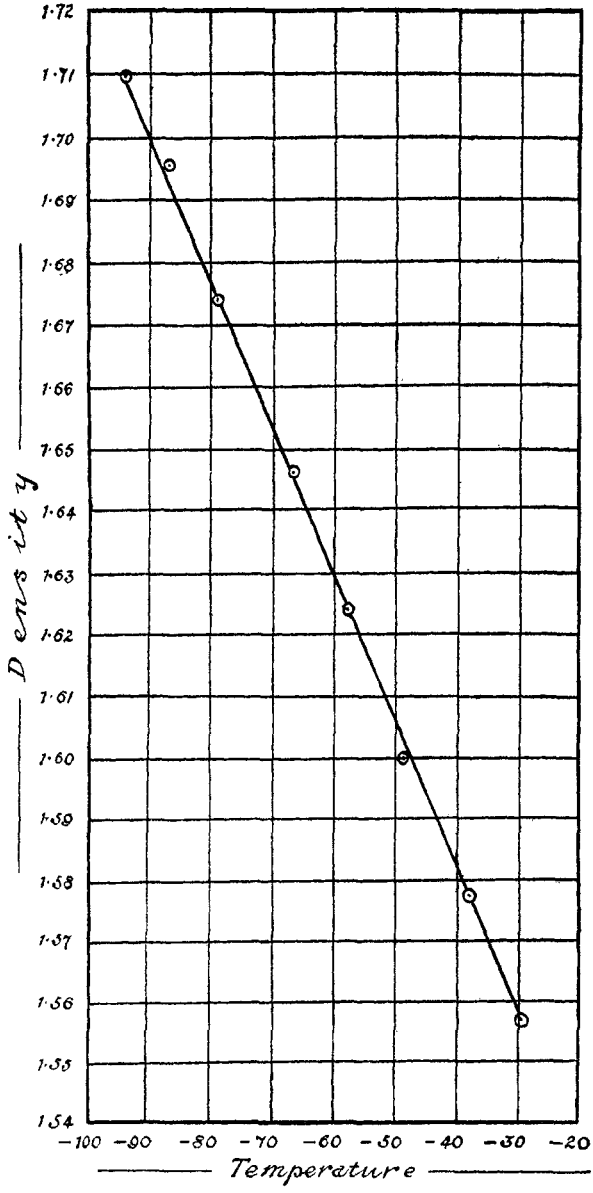

Fig. 4.

These values are shown by the curve in Fig. 4. The density at any temperature may be calculated by the formula $1.725 - 0.00243\ (100 + t)$, where t is the temperature on the centigrade scale.

Knietsch, by means of a hydrometer, found the expansion between —80° and —33.6° to be 0.00149 per degree.

At the boiling point, —33.7°, the density is 1.568. The molecular volume is therefore 22.6, which is in good agreement with Kopp's value obtained from organic compounds.

We may remark that the ratio of the boiling point to critical temperature, 0.57, is much lower than the value for the majority of substances, *viz.*, 0.66.

Molecular Surface Energy.—The apparatus employed was a modified form of that of Ramsay and Shields. The capil-

lary tube was calibrated with ether, and its radius found to be 0.01918 cm.

We obtained the following values, where h is rise in cms. of the chlorine in the capillary, D the density of the liquid chlorine, σ the calculated density of chlorine vapor, r the radius of capillary, γ = surface tension in dynes, g = 981 dynes, $\gamma(MV)2/3$ = molecular surface energy in ergs.

Temp.	h.	D from curve.	σ.	$r\frac{1}{2}rhgD$.	$\gamma(MV)^{\frac{2}{3}}$.
—28.7°	1.735	1.550	0.0041	25.23	322.7
—35.3	1.805	1.568	0.0034	26.55	337.0
—44.5	1.900	1.590	0.0025	28.38	356.8
—49.5	1.945	1.602	0.0021	29.28	366.3
—56.9	2.010	1.621	0.0012	30.63	380.1
—61.5	2.060	1.633	0.0008	31.61	390.6

The variation of molecular surface energy with temperature is shown by the curve in Fig. 5.

Between —65° and —30° $\frac{d(MV)^{\frac{2}{3}}}{dT} = 2.04$, and therefore liquid chlorine has the formula Cl_2. It is of interest to note that bromine has probably the formula Br_2.[1] From the curve, the molecular surface energy is zero at 129.4°, some 10° or 15° below the critical temperature.

Chlorine as a Conducting Solvent.— While several investigators have examined the conductivity of solutions of various substances in bromine and iodine, we are not aware that any such measurements have been made in

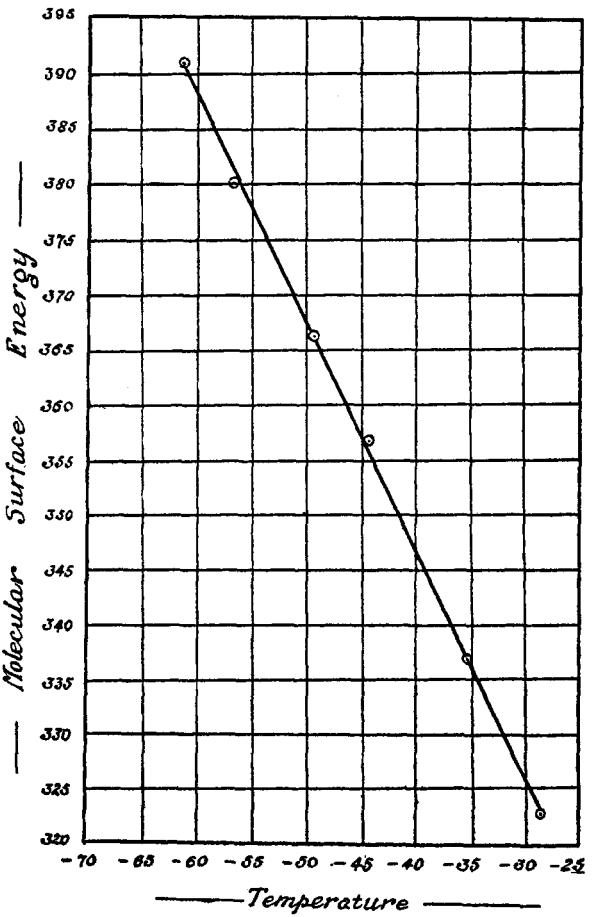

Fig. 5.

[1] Ramsay and Aston, *Z. physik. Chem.*, **15**, 89 (1894).

liquid chlorine. We have failed to find any inorganic substance which is ionized in this liquid. Bromine, hydrochloric acid, hydrobromic acid, water, and a number of salts may be cited as examples of substances which are not ionized. Ether, alcohol, ketones, esters, and other organic substances containing oxygen dissolve and give compounds of the general type, $\text{ether}_x\ Cl_y$, and these substances also fail to carry the current; but if a small amount of hydrochloric acid be added, the solution immediately conducts, and the appearance of the separated compound is altered. Ether dissolved in hydrochloric acid gives a compound, $C_4H_{10}O{-}{-}HCl$, which conducts well.

It seems probable therefore, that the conductivity produced in liquid chlorine by the addition of ether and HCl is due to the formation of this compound.

Plotnikov[1] has shown that ether dissolved in bromine gives a conducting solution. It is well known that this substance forms a compound, $C_4H_{10}O{-}{-}Br_3$, and to the ionization of this compound the conductivity is ascribed. Other oxygen compounds act in the same way. All these, however, are acted on by the bromine with the formation of HBr.

In the light of the experiment with chlorine, and the similarity in the organic complexes of chlorine and bromine, it is reasonable to suppose that the conductivity in the case of bromine is due to the ionization of a compound of the type of ether + HBr, rather than to the ionization of a compound of the Br + ether type.

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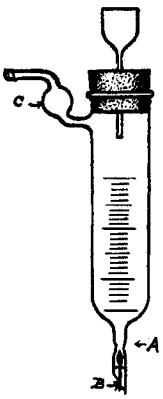
NOTES.

Automatic Filter Funnel.—The accompanying illustration shows a filter funnel with automatic discharge which has been found very convenient as a substitute for the ordinary filter flask, or bell-jar and beaker, usually employed in filtering with suction. The tube, which may be of any convenient size, terminates in a small glass stem constricted at point "A" and having a little plug "B" ground to fit against the lower surface of this constriction. Two or three small points on the inside of the stem just below the head of the valve serve to hold it in position and prevent its falling out of the tube when the vacuum is turned off, but allow it to drop down far enough, from the seat, so that the liquid above it can readily discharge. A small bulb "C," as a sort of safety trap, is blown in the side arm. In many cases it is desirable to wash



[1] *Z. physik. Chem.*, **57**, 502 (1906).