CXXV.—*The Properties of the Chlorides of Sulphur. Part IV. Density and Surface Tension, with an Appendix on the Parachors of Mixtures.*

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THE experiments described below were undertaken with the idea that measurements of density and surface tension, followed by calculations of values of the parachor, might afford a sensitive method for the detection of sulphur tetrachloride, in view of the regular way in which "pervalent" compounds, such as PCl_5, $POCl_3$, $SOCl_2$, etc., exhibit a deficiency of about 26 units as compared with the values deduced from compounds of normal valency. From this point of view, the results were once more negative, since the densities, surface tensions, and parachors all provided evidence of the presence of the dichloride, without giving any indication of the presence of the tetrachloride. Interesting results were obtained, however, by comparing the parachor values of mixtures of sulphur monochloride and chlorine before and after chemical combination had taken place.

EXPERIMENTAL.

Density.—Methods. Since the sulphur chlorides are decomposed by moisture, and may have a vapour pressure as high as 6 atm. at room temperature, the densities were determined by flotation in sealed tubes. Silica floats were used, partly because the densities of glass floats were altered when the liquid in which they were suspended was heated to bring it to equilibrium, and partly because their small coefficient of expansion was an additional advantage. The floats were hollow, about 15 mm. long and of 3 mm. diameter. A series, ranging from 1·42 to 1·76 at intervals of 0·02, was made, the desired density being attained first by adjusting approximately the amount of silica in the solid tip of the float, and then by grinding the tip and rounding it off in the oxyhydrogen flame. They were calibrated in mixtures of bromoform and toluene, the densities of which were measured with a pyknometer with vertical arms, specially designed to avoid loss by creeping after adjustment.

The samples of sulphur chloride were sealed up in thick-walled tubes, about 12 mm. in bore and 15 cm. long, together with two or three floats of suitable densities and the capillaries for measurements of surface tension, and were heated to 100° to bring about a condition of equilibrium. The tube was then clamped upright in a large water-bath, the temperature of which was maintained for 10 minutes within 0·02° of the temperature of flotation of each float, since a difference of 0·01° was sufficient to make a float rise or sink slowly.

Results. The densities of 35 samples, of chlorine contents ranging from 36·9 to 100 atoms %, were measured at two or three temperatures by the method just described. The coefficients of expansion were then calculated and the densities at 15° and 0° were deduced. Measurements were also made of four mixtures of sulphur monochloride and chlorine, which had not yet interacted to form the red dichloride and were therefore still pale yellow. The results are given in Table I.

TABLE I.

(a) *Densities of equilibrium mixtures.*

At. % Cl.	Temp.	$d^{t^\circ}_{4^\circ}$.	$d^{15^\circ}_{4^\circ}$.	$d^{0^\circ}_{4^\circ}$.	At. vol.† at 15°.
36·90	28·25°	1·72191	1·7389	1·758	
	33·40	1·72191*			
42·03	13·3	1·72191	1·71942	1·74140	
	−1·05	1·74294			
	18·3	1·72191*			
	3·8	1·74294*			
43·68	18·5	1·70780	1·71285	1·73449	
	8·72	1·72191			
	21·50	1·70780*	1·71718	1·73882	
45·30	12·90	1·70780*	1·70465	1·7272	
45·60	15·70	1·70780*	1·70895	1·73158	
	30·26	1·68592*			
48·50	5·18	1·70780	1·6928	1·7156	
50·0	15·98	1·68592	1·68744		20·01
50·0	1·8	1·70780	1·68721	1·71064	20·01
	15·83	1·68592			
52·07	11·6	1·68592	1·68063		20·14
54·34	6·92	1·68592	1·67264	1·69728	20·27
	21·78	1·66152			
58·20	−0·38	1·68592	1·65950	1·68532	20·51
	13·83	1·66152			
58·37	17·40	1·65578	1·66003		20·50
	24·85	1·64260			
59·73	−2·90	1·68592	1·65410	1·68080	20·60
	10·90	1·66152			
60·09	−3·60	1·68592	1·65286	1·67956	20·62
	10·20	1·66152			
61·87	17·60	1·64260	1·64725		20·74
	26·68	1·62638			
62·38	16·45	1·64260	1·64521		20·78
62·75	7·85	1·65578	1·64262		20·82
	15·10	1·64260			
64·28	4·85	1·65578	1·63685	1·66490	20·91
	11·92	1·64260			
66·13	17·93	1·62638	1·63192		
66·43	7·52	1·64260	1·62866	1·65662	21·08
	16·20	1·62638			
66·82	7·45	1·64260	1·62839	1·65668	21·08
	16·05	1·62638			
	23·00	1·61283			
67·04	−0·40	1·65578	1·62663	1·65502	21·11
	15·13	1·63638			
	22·11	1·61283			
69·23	16·16	1·61283	1·61543		21·30
	21·98	1·60128			
71·14	4·83	1·62638	1·60625		21·47
	11·68	1·61283			
73·31	0·58	1·62638		1·62755	
	7·30	1·61283			
74·16	9·25	1·60128	1·58926		21·75
	18·33	1·58230			
76·47	−1·45	1·61283		1·60988	
	4·22	1·60128			
81·20	17·62	1·54264	1·54856		22·49
	26·10	1·52351			
81·37	0·20	1·58230	1·55014	1·58273	22·47
	18·45	1·54264			

* After heating. † See p. 1011.

Table I (*contd.*).

(a) *Densities of equilibrium mixtures.*

At. % Cl.	Temp.	$d_{4^\circ}^{t^\circ}$.	$d_{4^\circ}^{15^\circ}$.	$d_{4^\circ}^{0^\circ}$.	At. vol.† at 15°.
83·71	18·39	1·52351	1·53137		22·79
	28·60	1·49980			
90·05	2·15	1·52351	1·49249	1·52863	23·53
	12·09	1·49980			
	20·05	1·47977			
93·83	2·70	1·49980	1·46730	1·50693	24·02
	10·28	1·47977			
100	2·30	1·45980	1·42391	1·46630	24·90
	11·80	1·43296			
100	2·60	1·45980	1·4247	1·46715	24·89
100	2·62	1·45980	1·4247	1·46717	24.89

(b) *Mixtures of sulphur monochloride and chlorine.*

At. % Cl.	Temp.	$d_{4^\circ}^{t^\circ}$.	$d_{4^\circ}^{15^\circ}$.	$d_{4^\circ}^{0^\circ}$.
57·68	−5·0	1·68592		1·67714
	8·9	1·66152		
66·43	−0·80	1·64260		1·64404
	8·2	1·62638		
71·14	−3·95	1·62638		1·61933
	3·65	1·61283		
83·01	15·1	1·52351		1·5583

† See p. 1011.

The following data are added for comparison :

Density of sulphur monochloride.

	At 0°.	At 10°.	At 15°.	At 20°.
Popp (1855)	1·7055			
Hagen (1867)				1·6828
Thorpe	1·7094			
Trautz (1929)	1·709	1·6950		1·6790
Lowry and Jessop (1930)	1·7106		1·6872	

Density of liquid chlorine.

Marchand (1913)	1·468 at 0°; 1·434 at 12°.
Lowry and Jessop (1930)	$1{\cdot}4671_5$ at 0°; 1·4247 at 15°.

Surface Tension.—Methods. Since the measurements of surface tension had to be made in a sealed tube, the only method which could be used was that of capillary rise. On account of the difficulty of measuring accurately the position of the lower meniscus when using a single capillary tube, the double capillary method described by Sugden (J., 1921, **119**, 1483) was finally adopted. Two capillaries, about 6 cm. long, with internal diameters of approx. 0·6 and 0·9 mm., were held together by glass bridges at the top and bottom. Glass projections were used in order to keep the capillaries upright and close to one side of the outer tube holding the liquid, so as to leave room for the silica floats which were also enclosed in the tube. Since the measurements were required primarily in order to calculate the parachor, which involves only the fourth root of the surface tension, no attempt was made to secure the highest order of accuracy, nor was it considered necessary to procure capillaries which were accurately circular in cross section.

Calibration of the apparatus was carried out with benzene and checked with water, Sugden's values for the surface tension of these two liquids being used. The benzene was purified by fractional crystallisation and then distilled in an all-glass apparatus. The water was distilled from dilute permanganate in an all-glass apparatus, which had been thoroughly freed from grease, directly into the tube containing the capillary apparatus. The two calibrations agreed closely.

TABLE II.

Surface Tension and Parachor.

(a) *Equilibrium mixtures.*

				$[P_A]$ calc. − $[P_A]$ obs.* for 100 atoms :	
At. % Cl.	Temp.	γ_{t°.	γ_{0°.	t°.	0°.
50·0	16·3°	43·43	45·66	−7	7
52·07	20·2	41·6	—	2	—
54·34	15·0	40·48	42·70	33	39
58·20	17·1	38·10	40·61	47	53
58·37	18·2	38·18	—	39	—
59·73	14·6	37·70	39·79	53	64
60·09	15·2	37·56	39·75	52	61
61·87	15·7	36·84	—	49	—
64·28	—	—	37·63	—	69
66·82	15·0	34·39	—	58	—
67·04	14·5	32·24	36·58	53	59
69·23	20·1	31·87	—	65	—
73·31	—	—	33·03	—	80
74·16	16·0	29·47	32·53	83	69
76·47	—	—	30·84	—	99
81·20	19·0	24·91	—	99	—
81·37	—	—	28·20	—	103
83·71	13·0	24·81	26·81	94	98
90·05	15·9	21·79	24·31	75	81
93·83	16·4	20·44	23·31	44	44
100	12·9	18·87	21·10	2	5
100	—	—	21·21	—	−4
100	—	—	21·24	—	−3

(b) *Mixtures of monochloride and chlorine.*

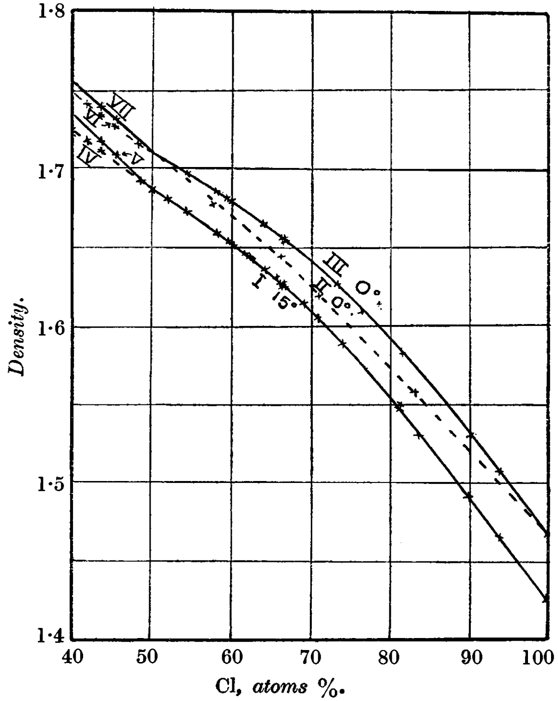
57·68	—	—	38·63	—	90
71·14	—	—	30·29	—	167
83·01	—	—	25·43	—	146

* For definition of $[P_A]$, see p. 1014.

If h is the difference in the heights of the liquid in the two tubes, measured from the base of one meniscus to the base of the other, and h_1 and h_2 are the respective heights of each meniscus, the corrected difference in rise, H, is given by $H = h + \frac{1}{3}h_1 - \frac{1}{3}h_2$, since Richards and Carver (*J. Amer. Chem. Soc.*, 1921, **43**, 827) found that $\frac{1}{3}h$ is a sufficiently accurate meniscus correction for most purposes. If D is the density of the liquid, and d that of the gas above the liquid, the surface tension is given by the equation $\gamma = H(D - d)/k$, where k is found from the calibrations. Values of d were estimated from the density of air together with Aten's values for the vapour pressure of sulphur chlorides of different compositions.

In making measurements of surface tension, the outer tube, with the apparatus enclosed, was clamped upright inside a small tank with a plate-glass front and back. It was illuminated from behind, through a water tank, to absorb heat rays, and a ground-glass screen. The heights were read with a travelling microscope, reading to 0·001 mm. Comparative measurements on the same sample of liquid show a probable error of about 0·2 dyne per cm.

FIG. 1.



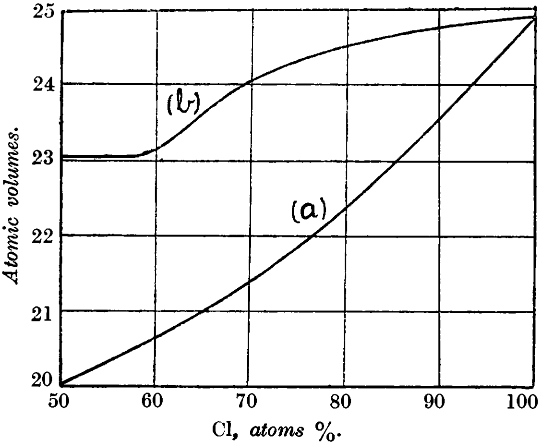
Results. The surface tensions, at room temperature or at 0° or both, of 23 equilibrium mixtures containing 50—100 atoms % of chlorine are set out in Table II, together with values for three mixtures of uncombined sulphur monochloride and chlorine.

Marchand (*J. Chim. physique*, 1913, **11**, 574) gives for the surface tension of liquid chlorine the values 21·90 at 0° and 19·47 at 12·7°, as compared with our values, 21·22 at 0° and 18·87 at 12·9°.

Discussion of Results.

(*a*) The densities at 15° and at 0° of mixtures of sulphur monochloride and chlorine at equilibrium are plotted in Fig. 1, I and III. The curves are nearly linear from S_2Cl_2 to SCl_2, after which the densities decrease more rapidly towards that of pure chlorine, but without giving any indication of a change of direction at the composition of the tetrachloride. The densities at 0° of uncombined mixtures of sulphur monochloride and chlorine, which are plotted in Curve II, are lower throughout, since chemical combination (which is revealed by a red coloration) is accompanied by a contraction, which reaches a maximum at or near the composition of the dichloride. Mixtures containing less than 50 atoms % of chlorine also become more dense after being heated, as may be seen by comparing curves IV and VI (unheated) with V and VII (heated). This contraction is attributed to the formation of polysulphides :

FIG. 2.



(a) *Mean atomic volumes.* (b) *Partial atomic volumes of chlorine.*

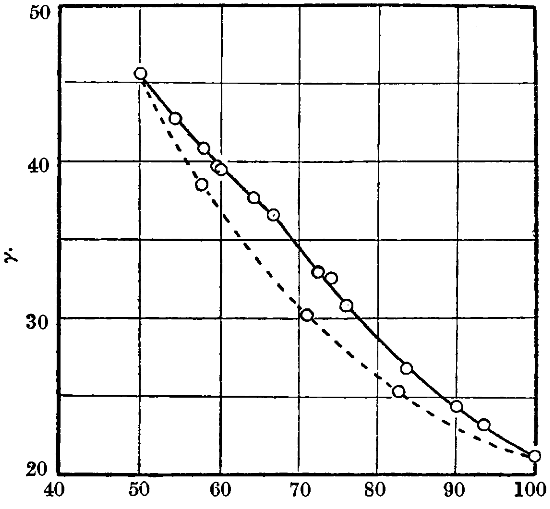
$$Cl{\cdot}S{\cdot}S{\cdot}Cl \longrightarrow Cl{\cdot}S{\cdot}S{\cdot}S{\cdot}Cl \longrightarrow Cl{\cdot}S{\cdot}S{\cdot}S{\cdot}S{\cdot}Cl$$

(compare Angeli and Magnani, *Gazzetta*, 1893, **23**, ii, 415; 1894, **24**, i, 349; Henrique, *Ber.*, 1894, **27**, 2993; Beckmann and Geib, *Z. anorg. Chem.*, 1906, **51**, 96; Bruni and Amadori, *Atti R. Accad. Lincei*, 1919, **28**, i, 217; Hammick and Zvegintzov, J., 1928, 1785; Trautz, *Z. Elektrochem.*, 1929, **35**, 110).

An alternative way of displaying the densities is to plot the mean atomic volume, $V = (A_1n_1 + A_2n_2)/d$, where A_1 and A_2 are the atomic weights, and n_1 and n_2 the atom fractions. The resulting curve for equilibrium mixtures at 15° (Fig. 2*a*) is at first nearly linear, but rises more steeply as the composition of the dichloride is approached. A more sensitive method is to plot the partial atomic volume of the chlorine (Lewis and Randall, "Thermodynamics," New York, 1923), *i.e.*, the increase of volume when 1 g.-atom of chlorine is added to an infinite volume of the mixture and brought to equilibrium. The resulting curve (Fig. 2*b*) is at first horizontal, since monochloride is converted quantitatively into dichloride with a constant increment of volume, the mixture behaving in this respect as an "ideal solution." The curve then rises steeply through the composition of the dichloride; this rise corresponds with the range of dissociation of the dichloride, at the beginning of which the chlorine is all used to form dichloride whilst at the end it all remains free. Finally, the curve rises gently to the atomic volume of free chlorine, without any sign of discontinuity at the composition of the tetrachloride, although the slope of the line shows that the dichloride and chlorine do not form an ideal solution.

FIG. 3.

Surface tensions.



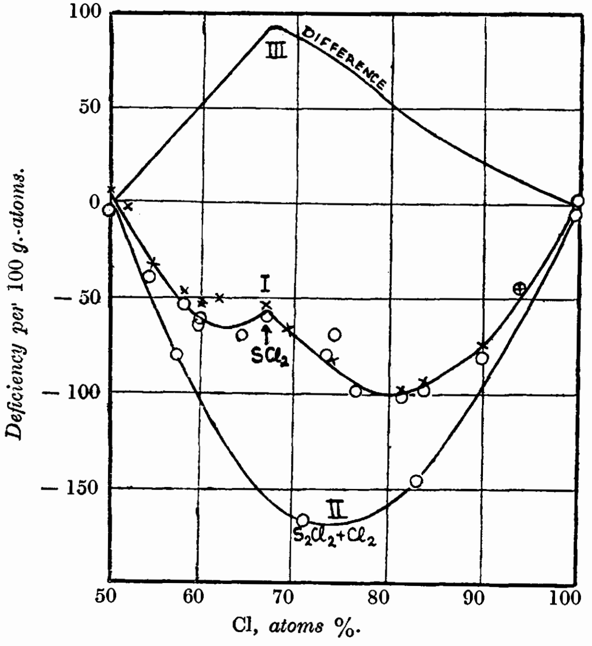
(*b*) The surface tensions, which are plotted in Fig. 3, increase progressively from 21·2 for chlorine to 45·7 for sulphur dichloride. The values for uncombined mixtures lie on a smooth curve; but those for equilibrium mixtures, which are higher throughout, cannot be represented by a simple curve. An attempt to represent the data by two curves unexpectedly revealed a discontinuity at

67 atoms % of chlorine, which is so close to the composition of the dichloride that the coincidence can scarcely be accidental. An even more striking discontinuity is seen in the "parachor deficiencies" (see below), but in neither case has any similar feature been observed at the composition of the tetrachloride.

Summary.

1. The densities and surface tensions of equilibrium mixtures of the chlorides of sulphur have been measured from 37 to 100 atoms % of chlorine, between − 4° and 30° and at 0° and room temperature respectively. The following constants have been determined:

FIG. 4.



Mean atomic parachors.

	Densities.		Mol. volumes.		Surface tensions.	
	0°.	15°.	0°.	15°.	0°.	15°.
S_2Cl_2	1·7106	1·6892	78·86	80·04	45·7	43·6
SCl_2 (equilm.)	1·6567	1·6285	62·10	63·2	36·6	34·4
Cl_2	1·4671	1·4247	48·33	49·78	21·2	—

Well-marked discontinuities occur at the composition of the dichloride, but not of the tetrachloride. The densities and surface tensions of uncombined mixtures are lower than after combination has taken place.

2. The values found for the molecular parachors, *viz.*, Cl_2 = 104·6, S_2Cl_2 = 205·5, lead to atomic parachors S = 50·48, Cl = 52·28. The mean atomic parachors of intermediate mixtures are lower than those required by a linear law of mixing, but the deficiencies are smaller after combination (see Fig. 4 and Appendix). The single loop from S_2Cl_2 to Cl_2 is then replaced by a double loop from S_2Cl_2 to SCl_2 and from SCl_2 to Cl_2, but with no indications of a break at SCl_4.

APPENDIX.

The Parachor of Mixtures.—Hammick and Andrew (J., 1929, 754) recorded the existence of deviations from a linear relation in the parachors of mixtures, and suggested "that the deviation is connected with the Gibbs surface-adsorption effect," since it appeared to be associated with a *difference* in surface tension between the two components. Our experiments (which were completed nearly two years before, but had been circulated only in the form of a thesis) had already established the existence of similar deviations from the linear law, not only in mixtures of sulphur monochloride and chlorine, but also in mixtures of partly dissociated sulphur dichloride with sulphur monochloride and with chlorine; but, since the parachor is fundamentally a volume relationship, we do not regard the difference in surface tensions, nor the Gibbs surface-adsorption effect, as the only factor in producing these deviations. Thus, apart from the relative inaccuracy of all measurements of surface tension, there is no obvious reason why small changes of volume, produced by mixing a pair of optically isomeric compounds, should be exactly balanced by changes in the fourth root of the surface tension.

The methods and formulæ of Hammick and Andrew imply a knowledge of molecular constitution which we did not possess in this case. Our analysis of the problem was therefore carried out with the help of the mean atomic parachor, which we define by the equation $[P_{\mathrm{A}}] = (A_1n_1 + A_2n_2)\gamma^{\frac{1}{4}}/(D - d)$, where A_1, A_2, n_1 and n_2 have the same significance as before (p. 1011). If there were no change in the parachors of the components, either on admixture or on chemical combination, the value of this function would be $[P_{\mathrm{A}}] = P_1n_1 + P_2n_2$, where P_1 and P_2 are the atomic parachors of the two elements *as deduced from the molecular parachors of the limiting components of the system.* Our measurements give for the molecular parachors, S_2Cl_2 = 205·5, Cl_2 = 104·6, whence S = 50·5, Cl = 52·3; whereas Sugden (J., 1925, **127**, 1533) gives S_2Cl_2 = 205·1, and deduces (J., 1924, **125**, 1188) Cl_2 = 111·5 from the data of Marchand (*loc. cit.*), finally adopting for the atomic parachors the values S = 48·2, Cl = 54·2.

The *atomic parachor deficiencies* plotted in Fig. 4, I and II, represent the differences (× 100) between the values of $[P_A]$ derived from the two preceding equations (i) for equilibrium mixtures and (ii) for uncombined mixtures of sulphur monochloride and chlorine. It is therefore possible for the first time to make a direct comparison of the deviations from the linear law which are produced by chemical and by physical interaction between the components, in liquids of identical composition. The uncombined mixtures show the largest deviations, rising to a maximum of about 3% at about 75 atoms % of chlorine. When chemical combination takes place, this deviation is reduced, *e.g.*, to about 1% at the composition of the dichloride; but secondary maxima are then developed in mixtures of this compound with the two components from which it was formed. The curve III, which shows the change in the mean atomic parachor on chemical combination, rises to a maximum at or near the composition of the dichloride, but shows no analogous singularity at the composition of the tetrachloride.

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