

CLXXXII.—*The Properties of the Chlorides of Sulphur.*
Part II. Molecular Extinction Coefficients.

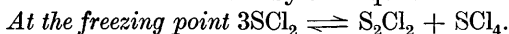
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IN the preceding paper (J., 1927, 746) on the freezing points of the chlorides of sulphur it was shown that sulphur dichloride, SCl_2 , has a definite range of stability in the equilibrium diagram and can be frozen out as a crystalline solid from a melt of suitable composition. In this respect, therefore, it resembles the monochloride and the tetrachloride, S_2Cl_2 and SCl_4 , which (with elementary sulphur and chlorine) had occupied the whole range from 0 to 100%

in all previous equilibrium diagrams. In our new diagram, on the other hand, the dichloride is shown as the stable solid phase over the range from 59 to 65 atoms % of chlorine, and a new chloride, S_3Cl_4 , appears as a stable phase over the narrow range from 57 to 59 atoms % of chlorine. There is no maximum at the composition of the dichloride, since this compound dissociates when it melts, and can only be frozen out from solutions containing an excess of sulphur monochloride; the tetrachloride is therefore the first solid to separate from a liquid having the theoretical composition of the dichloride.

This behaviour could be explained, on lines already suggested by Aten, if we were to assume: (i) that the dichloride is readily converted into monochloride and tetrachloride according to the reversible equation $3S_2Cl_2 \rightleftharpoons S_2Cl_2 + SCl_4$; (ii) that this change has a large temperature coefficient, the equilibrium being displaced in the direction of the dichloride at high temperatures, and of the monochloride and tetrachloride at low temperatures; (iii) that, as a result of this displacement of equilibrium, a liquid having the empirical composition of the dichloride, when cooled to a temperature near to its freezing point, consists mainly of the monochloride and the tetrachloride.

The fact that the vapour-pressure curves at higher temperatures give clear evidence of the presence of the dichloride, and only doubtful indications of the tetrachloride, could be reconciled with this view by supposing that, as the temperature is raised, the tetrachloride breaks down into the dichloride and free chlorine according to the equation $SCl_4 \rightleftharpoons SCl_2 + Cl_2$. The dissociation of the dichloride would then be controlled by two equations as follows:

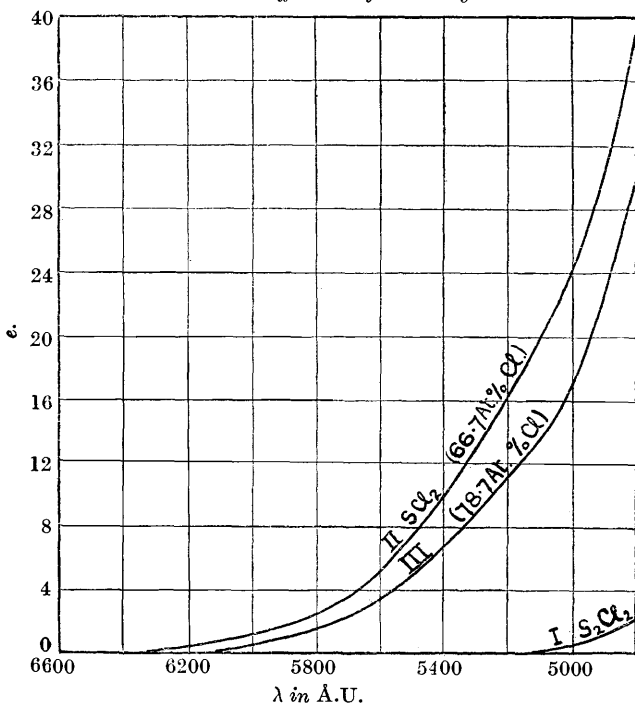


The experiments described in the present paper have led to the unexpected conclusion that, although the tetrachloride is the stable solid phase from 65 to nearly 100 atoms % of chlorine, it is almost non-existent in the liquid state. This deduction is of far-reaching importance, since, if the tetrachloride can be ignored in the study of the liquid chlorides of sulphur, the system is so simplified that a quantitative application of the laws of mass action to the equilibrium should for the first time become practicable. The conditions which prevail in samples in which equilibrium has not been attained are, however, still almost entirely unknown.

Absorption Spectra of the Chlorides of Sulphur.—The most striking property of sulphur dichloride is its deep garnet-red colour, which first led to the recognition that two compounds of sulphur and chlorine exist. It is therefore remarkable that the opinion should have been held almost universally, over a period of more than 20

years, that the dichloride is a mere mixture of the monochloride and tetrachloride, since rough qualitative observations suffice to show that the colour of the mixtures reaches a maximum at the approximate composition of the dichloride and not of the tetrachloride. The deep red colour of the dichloride is indeed unique, since sulphur monochloride and liquid chlorine are both clear yellow liquids with no red tinge, and are actually indistinguishable in colour, although the high viscosity of the monochloride makes it easy to tell one

FIG. 1.
Extinction coefficients of 1-cm. layers.



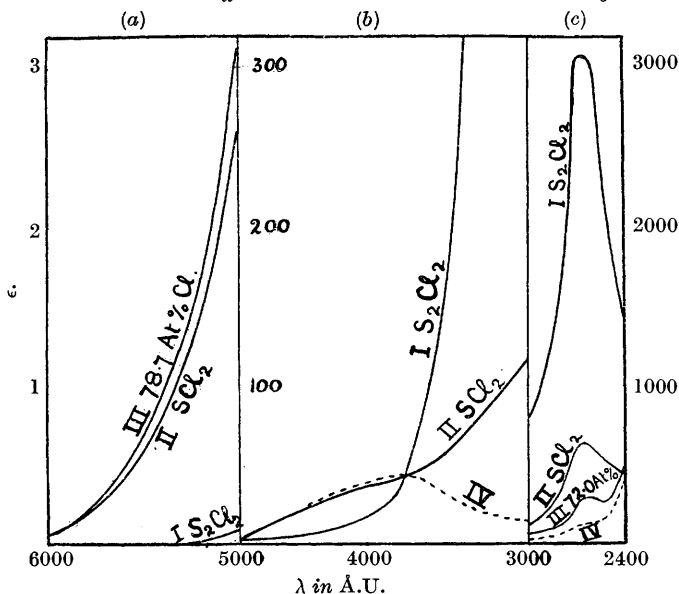
liquid from the other. We can also infer that the tetrachloride, which is only known with certainty as an almost white solid, with much less colour than the monochloride or than free chlorine, would give rise to an almost colourless liquid, if it could be melted without decomposition; actually the melt has the reddish-orange colour which we should expect to find if the tetrachloride were dissociated into the dichloride and free chlorine.

The present paper contains an account of quantitative observations of the extinction coefficients of chlorides of sulphur containing

from 50 to 80 atoms % of chlorine, *i.e.*, of compositions between that of the monochloride and that of the tetrachloride. Mixtures containing a larger proportion of chlorine were not examined on account of difficulties arising from their high vapour pressures at atmospheric temperature. Observations were made both in the visible spectrum, where the dichloride exhibits a unique intensity of colour, and in the ultra-violet spectrum, where an even more remarkable absorptive power is shown uniquely by the monochloride.

In order to make use of the colour of the dichloride as a quantitative measure of its concentration in a mixture of given composition, it

FIG. 2.
Atomic extinction coefficients in the visible and ultra-violet regions.



was necessary to select for observation one or more wave-lengths at which the colour of the other possible components of the mixture is so small as to be either negligible, or capable of being covered by a minor correction. The results of the tests which were made for this purpose are shown in Fig. 1, where data are given for the extinction coefficients of 1-cm. columns of sulphur monochloride, sulphur dichloride (or its dissociation products), and of a liquid approximating in composition to the tetrachloride. The corresponding extinction coefficients per atom of sulphur are shown in Fig. 2 (a). These figures show that the monochloride is transparent through the red and yellow regions of the spectrum, down to a wave-length of about

5200 Å.U., and only shows an appreciable absorption below about 5000 Å.U.; the absorption then increases rapidly to a strong maximum in the ultra-violet at 2660 Å.U., which is shown in Fig. 2 (c). Chlorine also begins to absorb at about 5000 Å.U., but the absorption is nowhere very strong. Liquid sulphur dichloride, on the other hand, is only transparent in the region of the spectrum down to about 6400 Å.U. (Fig. 1, II) and shows a marked absorption at all wave-lengths less than 6200 Å.U. This absorption also increases to a maximum in the ultra-violet region at about 2660 Å.U. [Fig. 2 (c), Curve II]; but, since the wave-length of the maximum is the same as for the monochloride, and there is ample evidence from other sources to show that the dichloride dissociates to form the monochloride, we have no hesitation in ascribing this maximum to the presence of the monochloride.

A sample of liquid sulphur chloride containing substantially more chlorine (78·7 at. % Cl) than the dichloride gave in the visible spectrum an absorption curve (Fig. 1, III) of the same type as the dichloride, but with a smaller intensity throughout. This diminution of colour might be attributed to the formation of a colourless tetrachloride from a coloured dichloride, but a quantitative study of the data shows that it is merely due to dilution, and that the absorptive power per atom of sulphur is actually increased by the diminished dissociation of the dichloride in presence of an excess of chlorine. The ultra-violet absorption of an over-chlorinated sample again reaches a maximum at about 2660 Å.U. [Fig. 2 (c), III], but the intensity of the maximum is even less than in the case of the "dichloride." We can therefore infer that the visible colour of the "tetrachloride" is due to the dichloride, and that its ultra-violet absorption is due to the monochloride. There is thus no evidence of any strong selective absorption either in the visible or in the ultra-violet region which must be attributed to the undissociated tetrachloride. If, however, we accept the obvious deduction that the tetrachloride is virtually free from colour both in the visible and in the ultra-violet region, this purely negative result would serve as positive evidence of the absence of the tetrachloride from the solutions, since it is shown below that the colour of the "tetrachloride" is identical with that of an equimolecular mixture of sulphur dichloride and chlorine, and cannot be accounted for on the hypothesis of a colourless tetrachloride.

From the course of the curves in the visible region, where the dichloride is strongly coloured, and in the ultra-violet region, where the monochloride is most absorptive, it is clear that the absorption curves of these two chlorides must intersect at some point in the extreme violet or early ultra-violet region of the spectrum. The

actual crossing of the curves is shown in Fig. 2 (b) at about 3750 Å.U. We can also infer on general grounds that the absorptive power of the dichloride must rise to a maximum either in the accessible ultra-violet region (selective absorption) or at a wave-length beyond the range of experimental observation (general absorption). The position of this maximum could not be determined directly on account of the enormous absorptive power for ultra-violet light of the monochloride in the dissociated liquid. Curve II [Fig. 2 (b)], however, shows a flattening out which may be regarded as an indication of an incipient absorption band at about 4000 Å.U. This is not strong enough to develop a "step-out" in the curve, but, if a correction is made (by the methods described on p. 1433) for the known absorptive power of the known proportion of monochloride in the dissociated liquid, a curve is obtained [Fig. 2 (b), IV] which rises to a shallow maximum at about 3600 Å.U. The continuation of this curve in the ultra-violet shows a rapid increase of general absorption from about 2500 Å.U., but no second maximum. These observations indicate that the dichloride exhibits both a general and a selective absorption; but this conclusion is based, not very securely, only on a series of differences between an observed and a calculated curve.

Colorimetric Analysis of the Chlorides of Sulphur.—The two wave-lengths selected for colorimetric analysis in the visible spectrum were 5200 Å.U. and 5400 Å.U. At the shorter of these two wave-lengths the absorptive power of the monochloride can be detected, but is negligible under the conditions used in the present series of experiments; at the longer wave-length the liquid appears to be completely transparent when examined under the same conditions. The absorption of light of these two wave-lengths was also found to be negligible for a solution of chlorine in carbon tetrachloride. The extinction coefficients, e , for 1-cm. layers of samples of sulphur chloride containing from 50 to 78.7 atoms % of chlorine are set out in Table I and are shown graphically in Fig. 3. When plotted against the atomic percentage of chlorine, these coefficients increase according to an almost linear law from 50 to about 60 at. % Cl, and then less steeply to a well-defined maximum at the theoretical composition (66.7 at. % Cl) of the dichloride; they then fall again according to an almost linear law from 72 to 100 atoms % of chlorine.

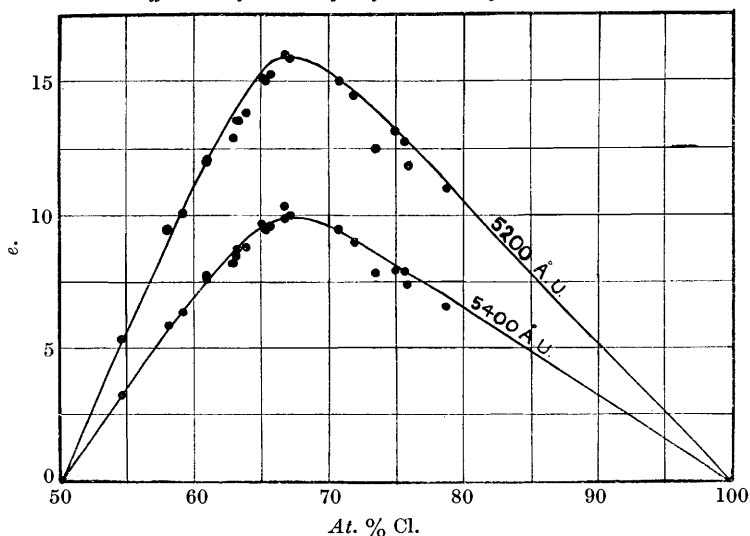
The well-marked maximum (which is here recorded for the first time) agrees closely with the composition of the dichloride and thus proves that the absorption of light of these two wave-lengths is due to this compound. Further, the absence of any other break or inflexion in the curve provides evidence that no other compound is

present in appreciable quantities. Thus, if a colourless chloride of the formula S_3Cl_4 or SCl_4 were sufficiently stable to persist as the main constituent of a melt of similar empirical composition, the molecular extinction coefficients should droop towards a zero value at 57 or at 80 atoms % of chlorine instead of at 50 or 100 atoms %.

If sulphur dichloride were sufficiently stable to be melted without decomposition, we should expect the maximum to be formed by the intersection of two straight lines (or flat curves) representing the extinction coefficients of mixtures of the dichloride with the monochloride and with free chlorine respectively. The rounding

FIG. 3.

Extinction coefficients of 1-cm. layers for wave-lengths 5200 and 5400 Å.U.

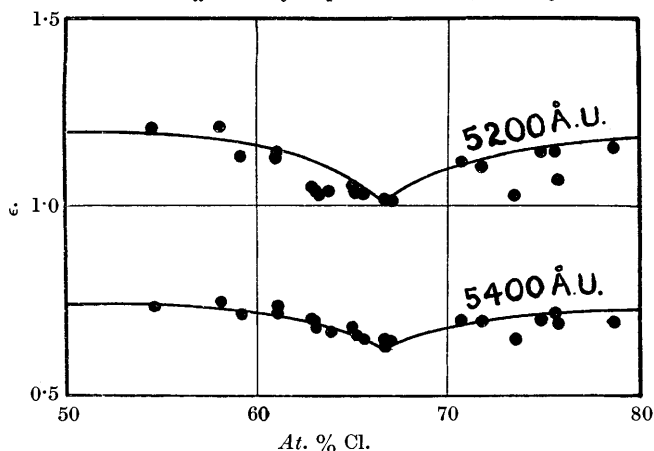


of the maximum, and the consequent curvature of these lines in the adjacent range of compositions, can therefore be attributed to dissociation, and (as in the case of a freezing-point diagram) this curvature can be used as a measure of the dissociation. The extent of this dissociation can be shown most effectively by plotting the data as in Fig. 4, where the ordinates show the molecular extinction coefficients, ϵ , of sulphur dichloride when calculated on the supposition that the whole of the *sulphur* in mixtures which are richer in *chlorine*, and the whole of the *chlorine* in mixtures which are richer in *sulphur* than sulphur dichloride, is present as the dichloride. This method of plotting shows the molecular extinction coefficient of the dichloride, *whether dissociated or not*, and so enables us to

determine the degree of dissociation, on the assumption that the intensity of absorption of the molecule of the dichloride is not affected by dilution with the monochloride or with chlorine. Thus, since the dissociation represented by the equation $2\text{SCl}_2 \rightleftharpoons \text{S}_2\text{Cl}_2 + \text{Cl}_2$ must be repressed by an excess of either of the products of dissociation, we should expect that the curve would rise to a maximum in solutions containing a little less than 100%, or a little more than 50%, of chlorine atoms. This maximum is actually reached in the latter case, where the molecular extinction coefficient rises to $\epsilon = 1.20$ at 5200 Å.U. and to $\epsilon = 0.74$ at 5400 Å.U. On the other side, this steady value is not quite reached, since the

FIG. 4.

Molecular extinction coefficients of sulphur dichloride, showing dissociation.



measurements were not carried beyond 79 atoms % of chlorine, on account of the high vapour pressures of the mixtures.

In the absence of any excess of either product, the dissociation should rise to a maximum, and the extinction coefficient should therefore fall to a minimum, at the composition of the dichloride, and this is actually realised in Fig. 4, where the lowest values of the extinction coefficient are $\epsilon = 1.02$ at 5200 and 0.63 at 5400 Å.U. The ratio of these minimum values to the corresponding maxima gives the proportion of undissociated sulphur dichloride in the liquid as 0.85, but the general course of the curves can be expressed more accurately by using a slightly lower value 0.83. The dichloride therefore dissociates to the extent of about 16% when the melt is allowed to come to a condition of equilibrium at atmospheric temperature.

TABLE I.

Absorption in the visible spectrum.

Extinction coefficients per cm. of liquid, e , and molecular extinction coefficients, ϵ , of sulphur dichloride.

		5200 Å.U.		5400 Å.U.				5200 Å.U.		5400 Å.U.	
At. % Cl.	e .	ϵ .	e .	ϵ .	At. % Cl.	e .	ϵ .	e .	ϵ .	e .	ϵ .
50.0	0.06	—	0.0	—	65.60	15.30	1.031	9.60	0.648		
54.48	5.34	1.212	3.24	0.733	66.67	16.04	1.02	9.92	0.627		
58.05	9.54	1.213	5.88	0.748		16.04	1.020	10.36	0.644		
59.10	10.10	1.135	6.34	0.715	67.04	15.90	1.019	10.02	0.642		
60.85	12.00	1.135	7.58	0.718	70.7	15.06	1.120	9.50	0.695		
	12.06	1.145	7.74	0.735	71.76	14.50	1.107	9.06	0.691		
62.84	12.90	1.050	8.26	0.670	73.51	12.52	1.030	7.88	0.645		
63.08	13.54	1.080	8.50	0.678	74.9	13.20	1.145	8.00	0.695		
63.11	13.54	1.077	8.74	0.693	75.56	12.80	1.148	7.94	0.741		
63.78	13.82	1.040	8.82	0.663	75.80	11.90	1.070	7.44	0.682		
65.00	15.14	1.059	9.70	0.678	78.7	11.08	1.153	6.64	0.690		
65.24	15.05	1.036	9.50	0.653	100	0.0	—	0.0	—		

Photometric Analysis in the Ultra-violet Region.—The ultra-violet spectrum of the chlorides of sulphur is characterised by a maximum selective absorption at 2660 Å.U., which is so strong that measurements could not be made with the pure liquids, but had to be made with dilute solutions in *cyclohexane*. These were made up immediately before use from liquids which had been brought to equilibrium by heating at 100° for an hour and then storing for several days at atmospheric temperatures. The results of the measurements are in Table II, where the extinction coefficients per atom of sulphur are set out for different atomic percentages of chlorine. They are also shown graphically in Fig. 5. The maximum value of the atomic extinction coefficient at 2660 Å.U. rises to 3170 in a solution of pure sulphur monochloride, which has therefore a molecular extinction coefficient of 6340, on the assumption that it is not dissociated to any appreciable extent in solution at room temperature. As the atomic percentage of chlorine is increased, the atomic extinction coefficient diminishes rapidly. The fall is roughly linear in character, tending towards a zero value at about 70 atoms %; but, instead of cutting the axis of zero absorption, the curve flattens out from about 65 atoms % and approaches it tangentially. The general form of the curve is of the type that one would expect if the principal product of chlorination were a rather unstable dichloride, which is dissociated to such an extent that a complete conversion of monochloride into dichloride could only be effected in presence of a large excess of free chlorine.

Although the absorption of light of wave-length 2660 Å.U. increases progressively as the proportion of chlorine is reduced to 50 atoms %, this absorption cannot be used as a direct measure of the proportion of sulphur monochloride in a given sample of liquid,

since the absorption of the dichloride at this wave-length is too great to be ignored, although that of free chlorine appears to be negligible.

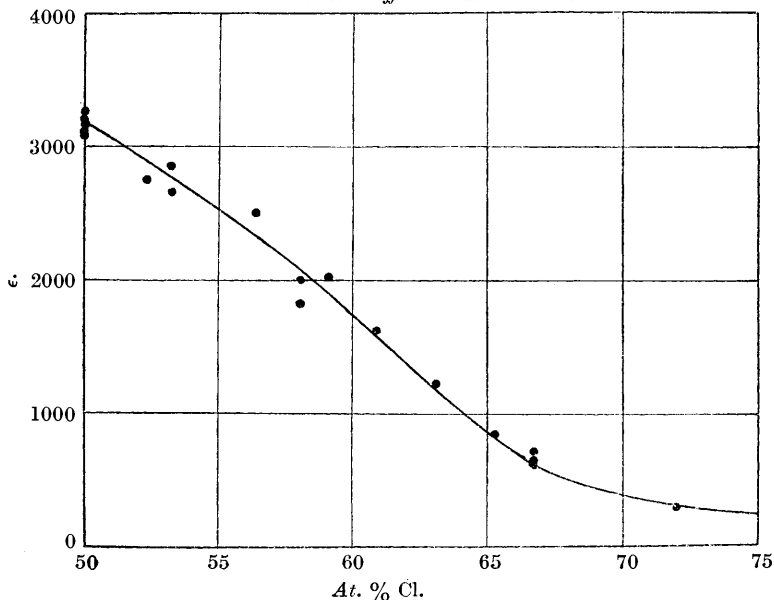
TABLE II.

Absorption in the ultra-violet spectrum.

Extinction coefficients per gram-atom of sulphur at 2660 Å.U.

At. % Cl.	50.0	52.3	53.26	54.48	56.37	58.05
ϵ	3250, 3070, 3150, 3200	2750	2850, 2650	2600	2500	2000, 1820
At. % Cl ...	59.09	60.85	63.08	65.24	66.7	72.04
ϵ	2020	1620	1220	840	650, 640, 710, 640, 630	290, 300 <10

FIG. 5.

Atomic extinction coefficients at 2660 Å.U.

Experimental Methods.—Measurements of absorption in the visible spectrum were made with a Nutting spectrophotometer and a Hilger constant-deviation spectrometer. The ultra-violet measurements were made with a Bellingham and Stanley ultra-violet spectrophotometer mounted on a large Hilger quartz spectrograph.

On account of the high absorption of sulphur dichloride in the visible region, the various liquids had to be examined in layers of less than 1 mm. thickness; and, since mixtures containing more than about 70 atoms % of chlorine have a vapour pressure at room temperature which is greater than an atmosphere, it was necessary that the cells should be sealed and should then be capable of

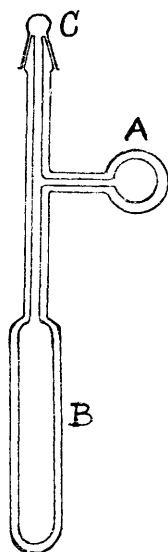
holding an internal pressure of about 3 atmospheres. After several unsuccessful attempts to construct such a cell by cementing glass parts together, a cell was constructed in fused silica without cement, as shown in Fig. 6. A reaction bulb, B, of clear silica with walls about 1 mm. in thickness, was formed at the end of a tube which could be closed by a stopper, C, and fastened by filling the joint with solidified paraffin wax. A side tube carried an observation cell, A, made from optically-plane discs of fused silica about 3 mm. thick; the thickness of the film was deduced from the weight of mercury required to fill the parallel portion of the cell, and was found to be 0.0526 cm.

For measurements in the visual region, mixtures containing less than 67 atoms % of chlorine were stored in sealed tubes and transferred by a pipette to the absorption cell. Mixtures containing more chlorine could only be transferred without loss of chlorine when cooled below 0° , and even then were liable to contamination by atmospheric moisture. These mixtures were therefore prepared by putting about 3 g. of sulphur dichloride into the weighed reaction bulb, weighing again, cooling over liquid air, and then passing dried chlorine into the cell until the desired quantity had been condensed. The stopper was then fastened down, and the bulb weighed again at room temperature in order to determine the composition of the mixture. The mixture was left over-night at room temperature in order to bring about a condition of equilibrium. The apparatus had been tested to withstand an internal pressure of 3 atmospheres, but it was not considered safe to work with mixtures containing more than about 79 atoms % of chlorine.

The ultra-violet measurements were made with 1-cm. or 2-cm. columns of solutions in *cyclohexane*, freshly prepared from mixtures which had been brought to equilibrium by storing for several days at room temperature after heating for an hour at 100° ; they were not carried beyond 72 atoms %, on account of the increasing vapour pressure of chlorine.

Light passing through the cell is lost by reflexion at the interfaces as well as by absorption. Since the refractive indices of the sulphur chlorides are nearly the same as that of silica, there would be very little loss by reflexion at the inner surfaces, and the zero of the

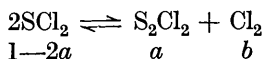
FIG. 6.
Absorption cell for
visual measurements.



instrument was therefore determined with a single silica plate in front of the cell. Since densities can be treated additively, the density thus found was subtracted from the total density, as defined by the equation $d = \log I_0/I$, where I_0 and I are the intensities of the incident and the transmitted light. The extinction coefficient e was calculated from the equation $e = 1/l \cdot \log I_0/I$ and the atomic extinction coefficient ε from the equation $\varepsilon = 1/cl \cdot \log I_0/I$, in which l is the length of the column and c the concentration in gram-atoms per litre of the element under consideration.

Application of the Law of Mass Action.—The experiments now described lead to the conclusion that the only compound which is formed in substantial quantities at room temperature by the interaction of sulphur monochloride and chlorine is the dichloride. This conclusion makes it possible to carry out a quantitative analysis of the extinction coefficients by a simple application of the laws of mass action.

(a) *Visible spectrum.* For the purpose of this analysis we may write :



In this equation the total atomic concentration of sulphur is taken as unity and the molecular concentration of free chlorine is taken as b . The degree of dissociation of the dichloride is $2a$, so that a is also the molecular concentration of S_2Cl_2 . The values of a and b can be deduced from the empirical composition of the sample and the dissociation constant of the dichloride. It is assumed throughout that a condition of equilibrium has been reached in all the mixtures.

The law of mass action cannot be expected to apply strictly to liquid mixtures, but since there are equal numbers of molecules on the two sides of the equation, the degree of dissociation should be almost independent of the volume, and the conditions are therefore favourable for a trial. The dissociation constant $K = ab/(1-2a)^2$ can be calculated most readily from the degree of dissociation of the dichloride, as deduced on p. 1428. It was there shown that for each gram-atom of sulphur there is 0.84 gram-molecule of SCl_2 , and therefore 0.08 gram-molecule each of S_2Cl_2 and Cl_2 . Putting $a = b = 0.08$, therefore, we find $K = 0.009$. We can now proceed to find the degree of dissociation of the dichloride in presence of an excess either of sulphur monochloride or of chlorine as follows. The total number of atoms of chlorine for each atom of sulphur is $2(1-a+b)$; the atomic percentage of chlorine is therefore $2(1-a+b)100/\{1+2(1-a+b)\}$. The ratio of the actual amount of dichloride in the mixture to the amount deduced from its empirical composition is $1-2a$ when there is an excess of chlorine,

and $(1 - 2a)/(1 - 2a + 2b)$ when sulphur monochloride is in excess. The values of this ratio, for a series of atomic percentages of chlorine, are set out in the fourth column of Table III, where the value of b has been calculated for a series of values of a on the assumption that $K = 0.009$. Assuming now that the molecular extinction coefficient of undissociated sulphur dichloride is $\epsilon = 1.20$ at 5200 \AA.U. and $\epsilon = 0.74$ at 5400 \AA.U. , we can calculate the atomic extinction coefficients of the preceding mixtures. These are set out in the last two columns of Table III, and are shown as full curves in Figs. 3 and 4. The concordance between these calculated curves and the experimental points is close enough to show that the method of calculation is fundamentally sound. In particular, the atomic extinction coefficient at the composition of the tetrachloride agrees with the value deduced from its content of dichloride so closely that we cannot find room for more than 1–2% of a colourless tetrachloride. The application of the laws of mass action therefore provides further support for the conclusion that the only important components of liquids containing from 50 to 100 atoms % of chlorine are the monochloride, the dichloride and free chlorine.

(b) *Ultra-violet spectrum.* The same methods of analysis can be applied to the ultra-violet absorptions as follows. Taking the total atomic concentration of sulphur as unity, and the degree of dissociation as $2a$, the molecular concentration of the monochloride is a and the absorption due to the monochloride at wave-length 2660 \AA.U. is $6340a$. By using the equilibrium constant, $K = 0.009$, which has already been deduced from the visual observations, we can calculate the values of a and of $6340a$ for different atomic percentages of chlorine, and thus obtain the numbers shown in the second and third columns of Table IV.

These absorptions are lower than those observed experimentally at 2660 \AA.U. , since we have ignored the ultra-violet absorption of the dichloride, which is not legitimate in view of the rapid increase of its absorptive power in the blue and violet regions of the spectrum. We can, however, calculate the magnitude of its molecular extinction coefficient from the excess of the observed above the calculated values. Thus, the observed extinction for a liquid having the composition of the dichloride is $\epsilon = 640$, whilst the calculated value is 510. If the difference of 130 units is attributed to the 84% of dichloride which it contains, the molecular extinction coefficient of the latter compound must be $130/0.84 = 158$ at 2660 \AA.U.

For all other mixtures the concentration of the dichloride is $(1 - 2a)$ and its contribution to the atomic extinction coefficient is $158(1 - 2a)$. These values are given in the fourth column of Table IV, and the total calculated absorption by the mono-

chloride and dichloride is shown in the last column. The theoretical curve for 16% dissociation is plotted in Fig. 5, and shows a very satisfactory concordance with the observed values.

The correctness of the value deduced for the molecular extinction coefficient of pure sulphur dichloride at 2660 Å.U. can also be checked by studying the extinction curve for a mixture containing 72 atoms % of chlorine (Fig. 2, III). This mixture should contain about 5.0% of its sulphur as monochloride and the rest as dichloride. We therefore subtract from the total atomic extinction coefficients at various wave-lengths a series of theoretical values deduced by multiplying the molecular extinction coefficients of the monochloride by the factor 0.025. The residual absorption, which should be equal throughout to that of sulphur dichloride, multiplied by the factor 0.950, is shown in Fig. 2 (c), curve IV. The fact that this curve shows neither a hump nor a depression at the wave-length of maximum absorption by the monochloride is clear evidence that the allowance made for the proportion of monochloride in the mixture is substantially correct.

TABLE III.

Calculated absorptions in the visible spectrum.

Molecular extinction coefficients of sulphur dichloride.

<i>a.</i>	<i>b.</i>	At. % Cl.	SCl ₂ ratio.	Calculated extinction coefficients.	
				5200 Å.U.	5400 Å.U.
0.4	0.00091	54.6	0.990	1.186	0.732
0.3	0.00484	58.6	0.978	1.171	0.723
0.2	0.01632	62.1	0.949	1.135	0.702
0.1	0.0580	65.8	0.873	1.046	0.646
0.08	0.0800	66.7	0.840	1.006	0.621
0.05	0.1469	68.8	0.900	1.079	0.665
0.02	0.418	73.7	0.960	1.150	0.710
0.01	0.870	78.8	0.980	1.174	0.725

TABLE IV.

Calculated absorptions in the ultra-violet.

Extinction coefficients per gram-atom of sulphur.

At. % Cl.	<i>a.</i>	Absorption by monochloride.	Absorption by dichloride.	Total absorption.
54.6	0.4	2540	32	2570
58.6	0.3	1900	63	1960
62.1	0.2	1270	95	1360
65.8	0.1	630	126	760
66.7	0.08	507	133	640
68.8	0.05	317	142	460
73.7	0.02	130	152	280
78.8	0.01	63	155	220

Finally, attention may again be directed to the fact that the complete omission of sulphur tetrachloride from the scheme of equilibrium at atmospheric temperature makes it possible to provide a satisfactory interpretation of all the data now recorded and that this would be spoiled if the highly absorbent monochloride and dichloride were diluted with a non-absorbent tetrachloride, and still more so if the tetrachloride possessed any marked absorptive power, since this would have led almost inevitably to its detection in the course of the present series of experiments.

Summary.

(a) The red component of the chlorides of sulphur is sulphur dichloride, SCl_2 ; this can be estimated by absorption of light of wavelength 5200 or 5400 Å.U., to which the monochloride and chlorine are completely transparent. Colorimetric analysis shows that the liquid dichloride is dissociated to the extent of about 16% at atmospheric temperature.

(b) Sulphur monochloride shows a strong maximum of selective absorption in the ultra-violet, $\log \epsilon = 3.8$ at 2660 Å.U., but cannot be estimated photometrically on account of the absorption of ultra-violet light by the dichloride.

(c) Sulphur tetrachloride is not formed in appreciable quantities in the liquid chlorides of sulphur, which behave as ternary equilibrium mixtures, to which the law of mass action can be applied in accordance with the equation $2\text{SCl}_2 \rightleftharpoons \text{S}_2\text{Cl}_2 + \text{Cl}_2$.

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