111. *The Properties of the Chlorides of Sulphur. Part VII. Changes of Density on Heating or Irradiation.*

By A. Herbert Spong.

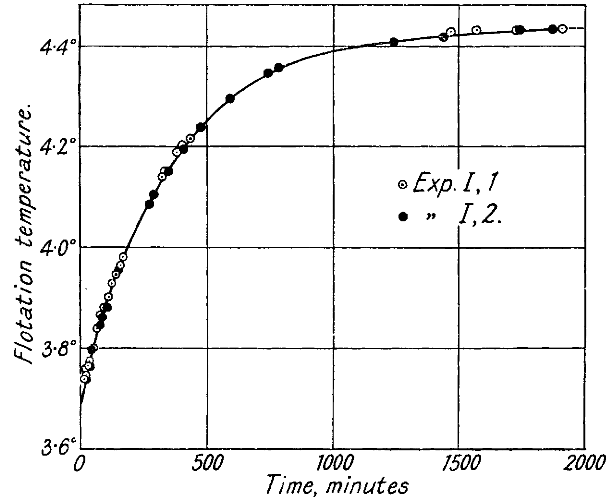
It has already been shown (Part V; J., 1931, 323) that the density of a mixture having the composition of sulphur dichloride undergoes a definite change when the liquid is heated at a given temperature for an hour or more and then rapidly cooled. This change depends only on the temperature and not on the time of heating, and can therefore be used to determine the extent to which the dissociation of the sulphur dichloride varies with the temperature. Preliminary observations also indicated the possibility of employing changes of density in order to follow the slow re-establishment of equilibrium at the lower temperature, in accordance with a method proposed, but not used, by Robinson and Smith (J., 1926, 1262). This method has therefore been applied to determine the velocity coefficients of the slow reactions which follow the heating and irradiation of both the di- and the mono-chloride.

(I) *Sulphur Dichloride.*—For this chloride, a mixture containing 66·5 atoms % of chlorine, and provided with a suitable float, was (i) heated in a sealed tube for one hour at 100° and then rapidly cooled to 0°, or (ii) exposed for some hours at room temperature to the light of a mercury-vapour lamp and then cooled to 0°. Flotation temperatures were then determined until steady values were again obtained.

Examination of the results showed that the course of the reaction could be represented by a first-order equation. Velocity coefficients were calculated directly from the observed flotation temperatures, since the relative values of these were more accurate than the densities or concentrations deduced from them; for instance, it was possible to detect a change of 0·002° in flotation temperature, corresponding to a change of density less than 5×10^{-6}, whereas the floats were calibrated with an accuracy of only 10×10^{-6}. The final values were extrapolated arithmetically (in many experiments such values agree exactly with the observed readings), and the initial values were obtained from the graph of $\log (T_\infty - T_t)$ against time, T_∞ and T_t being the flotation temperatures as extrapolated and at time t respectively. The average velocity coefficients were calculated, wherever possible, for the range 50—80% of the change, since Rice, Fryling, and Wesolowski (*J. Amer. Chem. Soc.*, 1924, **46**, 2405) have shown that errors are least in this region. The coefficients thus deduced agree very closely with the values obtained from the slope of the graph of log $(T_\infty - T_t)$ against time, and are also less affected by small errors in the extrapolations of the initial and final values than when results obtained outside that range are taken into account.

The reproducibility of the method was tested by duplicate runs with the same tube. The values of $k \times 10^3$ found were : (i) 2·73 (mean of 18 values ranging from 2·63 to 2·87) ; (ii) 2·74 (mean of 19 values ranging from 2·55 to 2·82). The two series of flotation temperatures are plotted together in Fig. 1, and must obviously be represented by the same curve.

Fig. 1.



Re-establishment of equilibrium in sulphur dichloride after displacement by heat showing reproducibility of the flotation method of determining reaction velocity.

The results obtained when equilibrium in the same mixture was displaced by heating, by irradiation, and again by heating some days after irradiation, are summarised in the table below.

Comparison of the Effects of Heat Treatment and of Irradiation on Sulphur Dichloride.

Float 1·65578.

	Flotation temps.		
Treatment.	Initial.	Final.	$k \times 10^3$.
Heated 1 hour	— 0·094°	0·637°	2·74
Irradiated 5 hours	— 0·126	0·645	2·86
Irradiated 5 hours, kept for several days, then heated 2 hours	— 0·097	0·641	2·81

The reaction now under examination is represented by the equation $S_2Cl_2 + Cl_2 \rightleftharpoons 2SCl_2$, and would appear to be bimolecular. It has, however, long been known that the combination of sulphur monochloride with chlorine is autocatalytic (Aten, *Z. physikal. Chem.*, 1906, **54**, 55), and may therefore be expected to proceed by a complex mechanism. The observation here recorded that the change follows a first-order course is thus not surprising.

More important is the discovery that the velocity of reversion after irradiation is higher than after displacement by heat. The density to which the mixture reverts is also higher. These effects persist for several days and apparently decay gradually. They can be explained by supposing that the concentration of Aten's autocatalyst is increased by the action of light on the sulphur monochloride present in the mixture.

Evidence of the photochemical decomposition of this compound is given below, but indications that irradiation produces a secondary change (which is not brought about by heat) may be found in a very small decrease in flotation temperature at the end of the irradiation experiments, which was ascribed at the time to experimental error.

(II) *Sulphur Monochloride.*—Similar experiments with sulphur monochloride disclosed much slower changes. It was therefore possible to follow both the forward and the reverse reaction, since the heating and irradiation can be interrupted from time to time and the flotation temperature determined without the occurrence of any perceptible change in the mixture during the time required to complete an observation.

(1) *The effects of heat.* A tube containing sulphur monochloride and a float for measurements of density at or near 0° was prepared, and the flotation temperature corresponding to equilibrium at room temperature measured. The tube was then heated to 100° for seven periods totalling 8 hours; after each period of heating it was rapidly cooled to 0°, and the new flotation temperature determined. The tube was then kept for 6 weeks in a Dewar vessel containing crushed ice, the flotation temperature being read at suitable intervals during this period. The results are recorded in Table I (the temperatures being those on a Beckmann thermometer, and therefore arbitrary) and the changes are represented graphically by Curves I of Figs. 2 and 3.

The reaction is substantially of the first order. Consecutive reactions appear to be taking place, but no complete analysis of the course of the reaction was attempted on account of the extreme smallness of the observed changes of density.

TABLE I.

(a) *The Effect of Heat on Sulphur Monochloride.*

Float 1·71291.

Duration of heating, hrs.	0	1	2	3	4	5	6·5	8	∞
Flotation temp.*	2·836°	2·865°	2·883°	2·892°	2·895°	2·897°	2·898°	2·896°	2·899°
100 k.	—	62	68	73	69	69	69	—	—

(b) *The Re-establishment of Equilibrium at* 0° *in Sulphur Monochloride after Heat Treatment.*

Time, hrs.	Flotation temp.*	Time, hrs.	Flotation temp.*	Time, hrs.	Flotation temp.*	Time, hrs.	Flotation temp.*
0	2·896°	158	2·878°	354	2·854°	615	2·836°
13	2·905	257	2·866	398	2·850	718	2·825
61	2·894	305	2·860	446	2·844	815	2·820
113	2·885	329	2·856	494	2·841	1027	2·820

* Beckmann thermometer (see above).

(2) *The effects of irradiation.* For preliminary and qualitative purposes, redistilled sulphur monochloride was irradiated in a water-jacketed tube with the full light from a vertical mercury-vapour lamp, reflectors being employed to give very intense illumination. After exposure, the liquid was found to have darkened to a reddish-brown or deep red colour according to the duration of irradiation. When the tube was removed, and stored either in the dark or in diffused daylight, the colour gradually reverted to the original yellow. The observations are recorded in Table II.

TABLE II.

Colour Changes in Irradiated Sulphur Monochloride.

Expt.	Time of exposure, hrs.	Colour at end of exposure.	Time of reversion.
1	10	Reddish-brown.	Completely reverted in 13 days.
2	20	Deep red (colour approx. that of mixture containing 60 atoms % of Cl).	Noticeably brown after 3 days; completely reverted in 5—6 weeks.
3	15	Deep red.	Slightly brown after 10 weeks.

For quantitative purposes, the changes of density after definite periods of irradiation were determined in the same way as those after heating. The lamp used in the qualitative experiments was placed behind a screen in which a slit was cut, and the intensity of the light was varied by altering the distance of the tube from the lamp. The results are set out in Table III and represented by Curves II and III of Figs. 2 and 3.

TABLE III.

The Effect of Light on Sulphur Monochloride.

(Displacement and re-establishment of equilibrium.)

Sulphur monochloride in water-jacketed tube. Float 1·70780. Lamp current, 3·5 amps. Terminal voltage, 140 volts.

(a) *Distance of tube from lamp,* 3·5 *ins.*

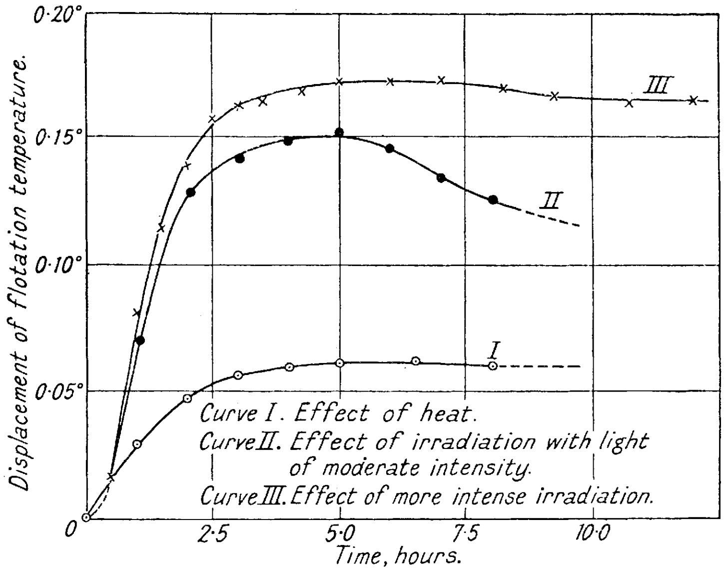
Displacement.				Re-establishment.			
Time, hrs.	Flotation temp.	Time, hrs.	Flotation temp.	Time, hrs.	Flotation temp.	Time, hrs.	Flotation temp.
0	5·522°	5	5·674°	0	5·648°	108·5	5·497°
1	5·592	6	5·668	12	5·522	136·5	5·498
2	5·651	7	5·656	60	5·489	157	5·500
3	5·663	8	5·648	84	5·493	180	5·501
4	5·670			90	5·495	228	5·500

(b) *Distance of tube from lamp,* 3 *ins.*

Displacement.						Re-establishment.	
Time, hrs.	Flotation temp.	Time, hrs.	Flotation temp.	Time, hrs.	Flotation temp.	Time, hrs.	Flotation temp.
0	5·522°	3·0	5·684°	7·0	5·697°	0	5·687°
0·5	5·538	3·5	5·686	8·25	5·692	14·5	5·514
1·0	5·603	4·25	5·690	9·5	5·688	33·5	5·496
1·5	5·636	5·0	5·694	10·75	5·686	79·25	5·501
2·0	5·660	6·0	5·694	12·0	5·687	128·25	5·499
2·5	5·680					234·25	5·502
						445·0	5·502

The changes in density produced in the monochloride by heating and by irradiation are similar and can therefore be discussed together. The fall of density after the maximum is reached (see Fig. 2) is, however, much greater in the irradiation experiments than during heat treatment, and the course of the reactions by which the equilibrium is restored (see Fig. 3) is markedly different in the two cases.

FIG. 2.

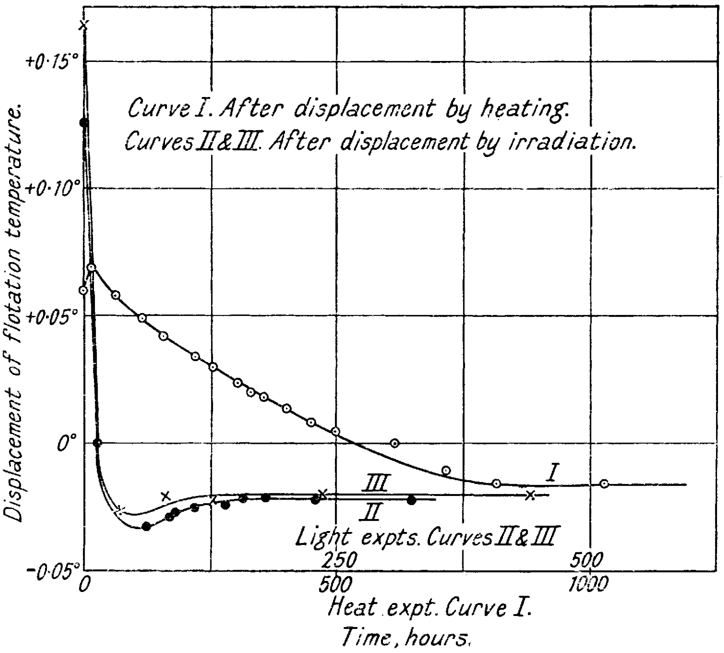


The effect of heat and light on sulphur monochloride.

The effect of varying the intensity of illumination brings out clearly the existence of photostationary states in the dissociation of sulphur monochloride, and it may well be that this fact accounts, in part at least, for the irregularity of the results recorded in the chemical analysis of sulphur chloride mixtures (J., 1933, 1547). Unfortunately, no definite knowledge of the products of dissociation is available, but certain inferences can be drawn with the help of the measurements of density described in Part IV of this series (J., 1930, 1005).

The colour produced in the qualitative observations shows that sulphur dichloride is one of the final products of the reaction, while the course of the density changes shows that the reaction proceeds in at least two stages. The scheme A, suggested in Part VI (J., 1933, 1547), satisfies these requirements, but there are also two other possibilities, B and C.

Fig. 3.



The re-establishment of equilibrium in sulphur monochloride

A. (i) $3S_2Cl_2 \rightleftharpoons S_3Cl_2 + S_3Cl_4$; (ii) $S_3Cl_4 \rightleftharpoons S_2Cl_2 + SCl_2$
B. (i) $3S_2Cl_2 \rightleftharpoons 2S_3Cl_2 + Cl_2$; (ii) $S_2Cl_2 + Cl_2 \rightleftharpoons 2SCl_2$
C. (i) $2S_2Cl_2 \rightleftharpoons S_4Cl_2 + Cl_2$; (ii) $S_2Cl_2 + Cl_2 \rightleftharpoons 2SCl_2$

By extrapolating the results of Part IV (*loc. cit.*; see also Part V, J., 1931, 323), it is possible to obtain approximate estimates of the densities at 0° of S_4Cl_2 (1·7812), S_3Cl_2 (1·7551), and SCl_2 (1·6589), while the densities of S_2Cl_2 and Cl_2 are given as 1·7106 and 1·4671 respectively. Calculations from these data show that, the validity of the mixture law being assumed, both stages of scheme C result in increases of density, while scheme B represents a decrease followed by an increase. Scheme A is thus the most probable of the three, since it is compatible with an increase of density followed by a decrease, although this increase cannot be proved to be due to the formation of S_3Cl_4, since no estimate of the density of this compound is yet available.

A fourth possible mechanism (D), *viz.*, (i) $2S_2Cl_2 \rightleftharpoons S_3Cl_2 + SCl_2$; (ii) $S_2Cl_2 + SCl_2 \rightleftharpoons S_3Cl_4$, is improbable, since (i) it will not account so satisfactorily as scheme A for the facts recorded in Part VI (*loc. cit.*), and (ii) in the preliminary experiments on irradiation, when much sulphur dichloride was produced, the rate of reversion to equilibrium was much slower than in the quantitative experiments after exposure to less intense light, suggesting that the production of dichloride is related with the destruction of a catalyst by the light, and the most probable catalyst is S_3Cl_4 on account of its polar character. Direct evidence of the catalytic activity of S_3Cl_4 will be given in a later paper.

The difference between the effects of heating and irradiation can be most satisfactorily accounted for by the hypothesis that at 100° the decomposition of S_3Cl_4 is much more rapid than it is in the illuminated mixture at lower temperatures. This would account both for the smallness of the decrease of density after the maximum in Curve I of Fig. 2 and also for the slow re-establishment of equilibrium at 0°, corresponding to a small concentration of catalyst. The small rise in density after cooling to 0° is also in agreement with this view, since it represents the production, by the reversal of A (ii), of a small amount of S_3Cl_4 necessary to catalyse the dissociation of the dichloride.

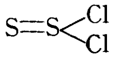
The actual mechanism of the changes must, however, be still more complex, since the thermal reaction has been shown to be of the first order and the photochemical reaction shows a short induction period. Some such scheme as the following therefore appears to be necessary, reaction (1) being slower than (2) and hence characterising the rate.

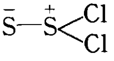
$$(1)\ S_2Cl_2 \longrightarrow SCl_2 + S \qquad (3)\ S_2Cl_2 + S \longrightarrow S_3Cl_2$$
$$(2)\ S_2Cl_2 + SCl_2 \longrightarrow S_3Cl_4 \qquad (4)\ S_3Cl_4 \longrightarrow S_2Cl_2 + SCl_2$$

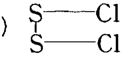
It might be thought that the production of sulphur dichloride was satisfactorily explained by reaction (1) above, but since there is reason to believe that sulphur atoms are incapable of free existence in solution, this must be followed either by reaction (3) of this scheme or by $2S \longrightarrow S_2$. The former alternative is kinetically the more probable, and moreover, it has been shown in Part IV (*loc. cit.*) that molecular sulphur combines with the monochloride on heating. Reactions (1) and (3) together reduce to stage (i) of scheme D which has already been rejected, and it appears to be impossible to account both for the results here recorded and for the apparent presence of free chlorine in normal sulphur monochloride (Part VI, *loc. cit.*) without postulating the formation at some stage of the dissociation process of S_3Cl_4, which can be isolated by freezing mixtures of suitable composition (Part I; J., 1927, 746).

The Structure of Sulphur Monochloride.

Measurements of the Raman spectra of various sulphur compounds, including the monochloride, were made by Matossi and Aderhold (*Z. Physik*, 1931, **68**, 683; see also Meyer, *Z. anorg. Chem.*, 1931, **203**, 146), and the formula (I) deduced therefrom. This is

(I.)


(II.)


(III.)


improbable, since it involves a 10-electron shell round the central atom of sulphur, and for this reason formula (II) with a semipolar double bond is to be preferred. Matossi and Aderhold found, however, that the restoring force at mean amplitude for the vibration of the two sulphur atoms was 2·4 times that for the sulphur–chlorine linkage, and cited this as evidence in favour of formula (I), since Dadieu and Kohlrausch (*Ber.*, 1930, **63**, 251) had concluded that this property should have approximately double the value in a double bond that it has in a single link, and further, that the semipolar double bond behaves as a single linkage in this respect. This Y-shaped structure is not in conformity with views which have been held in this laboratory for some years (*e.g.*, see J., 1930, 782) and it has therefore been thought desirable to review the whole of the available evidence.

1. *The Parachor.*—The parachor of sulphur monochloride is given by Sugden (J., 1925, **127**, 1525) as 205·1, by Mumford and Phillips (J., 1929, 2112) as 204·3, and by Lowry and Jessop (J., 1930, 1005) as 205·5. The calculated values for the three formulæ according to Sugden's system of parachor equivalents ("The Parachor and Valency," London, 1930) are (I) 228·2, or if allowance is made for covalency increase (Sidgwick and Bayliss, J., 1930, 2027) 202·6; (II) 203·4; (III) 205·0; the values according to the Mumford and

Phillips system (*loc. cit.*) are (I) 223·0, (II) 204·0, (III) 210·0. Formula (I) thus appears to be completely inadmissible, but it is not easy to decide between (II) and (III), though the balance of evidence is perhaps slightly in favour of the latter.

2. *Dielectric Properties.*—The dielectric constants of sulphur chloride mixtures were measured at various temperatures by Lowry and Jessop (J., 1930, 782), but under conditions which did not admit of accurate evaluation of the dipole moments of the compounds. Nevertheless, approximate values can be calculated, and such calculations were, in fact, made by Dr. Jessop but not published on account of their uncertainty. The results are for SCl_2 $\mu = 0·55$ and for S_2Cl_2 $\mu = 0·78$ (in terms of 10^{-18} e.s.u.).

Now if sulphur monochloride has the structure (I), its moment should differ only slightly from that of the dichloride, while if it has the structure (II), which will be pyramidal, the positively charged sulphur atom being at the apex, its moment should be comparable with or possibly greater than the value 1·38 for thionyl chloride (Smith, *Proc. Roy. Soc.*, 1932, *A*, **138**, 154) since the group moment of $>\overset{+}{S}-\overset{-}{S}$ would be expected to be of the same order as, or possibly greater than, that of $>\overset{+}{S}-\overset{-}{O}$. The structure (III), since the molecule must be capable of free rotation about the sulphur–sulphur linkage, would have a smaller moment than the *cis*-form represented above. If we assume that the sulphur valency angle is 90°, the moment of this *cis*-form is seen to be $\sqrt{2} \times \mu_{SCl_2} = 0·78$.

It thus appears that the observed moment is too high to be explained by formula (III) and too low for (II), but in view of the uncertainty attaching to the experimental value, further mathematical analysis is scarcely warranted. It does appear justifiable, however, to suggest that normal sulphur monochloride actually contains a mixture of the forms (II) and (III). It is of interest that evidence has recently been obtained of a somewhat similar isomerism in hydrogen peroxide (Geib and Harteck, *Ber.*, 1932, **65**, 1551).

The difficulty of reconciling this view with the results of Matossi and Aderhold (*loc. cit.*) disappears when the photo-decomposition of sulphur monochloride is taken into account. It is true that these authors made use of a Zeiss " Monochromator Filter B," but since they record Raman lines excited by the mercury lines at 5769 Å.U. and 5790 Å.U., which [according to the specification supplied by Messrs. Carl Zeiss (London) Ltd.] are transmitted by the filter with about the same intensity as the lines at 4077 Å.U. and 4047 Å.U. (which are almost certainly chemically active), it seems probable that their monochloride underwent some decomposition during the exposure, and in view of the complexity of the resulting mixture, a correct assignment of vibrations is extremely difficult.

It is quite possible, however, that the structure (II) corresponds to a higher energy state than (III) and may therefore be one of the first products of heating or irradiating sulphur monochloride. The isomeric change (III) $\longrightarrow$ (II) may thus represent the unimolecular change which governs the rate of the thermal reaction and also the change which takes place during the photochemical induction period. The Y-shaped molecule on account of its semipolar linkage, would be expected to be more reactive than the simple chain.

EXPERIMENTAL.

The preparation and calibration of the floats, and the preparation and sealing up of the mixtures have already been described (J., 1930, 1005). The equilibrium in the mixture was displaced either by heating for one hour at 100°, the tube being placed axially in a brass cylinder through which steam was blown under slight pressure, or by irradiation by the light of a mercury-vapour lamp, the tube being surrounded by a water jacket to prevent heating. After being cooled as rapidly as possible to the temperature of reaction, the tube was clamped upright in an observation bath consisting of a large cylindrical glass jar, fitted with a constant-level siphon and lagged with felt, of which a small panel was removed to form an observation window. When the temperatures to be observed were in the neighbourhood of 0°, a well-stirred bath of saturated brine was cooled by adding small pieces of ice or warmed by running in brine which had been pre-cooled to a temperature a little above that of the bath itself by passing through a coil immersed in ice and water. For temperatures above 10°, control was effected by varying the velocities of two streams of water, one a little cooler and the other slightly warmer than the bath itself. The temperatures were observed by means of Beckmann thermometers which were standardised from time to time, either by comparison with a standard thermometer or by immersion in pure ice and water. In order to avoid changes due to contraction or expansion of the bulbs, the thermometers were kept in Dewar vessels packed with ice or filled with water at a temperature as near as possible to that at which they were to be used.

When the tube was placed in the bath, the temperature was slowly lowered until the float just commenced to rise, and then raised gently so that the float rose to a position near the middle of the tube before beginning to sink. As soon as sinking was observed, the bath was again cooled, and the position of the float marked by an adjustable wire pointer outside the tube. These movements were continued until, after a few minutes, they could be limited to a few mm. in either direction. The time and temperature were then read at each change of direction and temperatures of rise and fall differing by as little as 0·006° have often been observed.

The static method of determining flotation temperatures was rendered impracticable by the fact that during the earlier stages of a reaction, when the density was changing rapidly, it was not possible to maintain the float in a stationary condition for long enough to ensure accuracy; moreover, the dynamic method has been commended by Robinson and Smith (*loc. cit.*), Richards and Shipley (*J. Amer. Chem. Soc.*, 1914, **36**, 1), and Richards and Harris (*ibid.*, 1916, **38**, 1000).

The averages of consecutive times and temperatures were calculated and these were then grouped and again averaged in order further to reduce the probable error. In the later stages of a reaction, when successive temperatures of rising and falling were often unchanged, the reaction tube was kept at constant temperature and only placed in the observation bath when readings were actually required.

Robinson and Smith and Richards and Harris (*locc. cit.*) found that vibration of the liquids caused the floats to acquire an electric charge, in consequence of which they adhered to the walls of the tubes. A somewhat similar but less pronounced effect was noticed in the present work, especially when the liquids were contained in narrow tubes. The adhesion of the float to the wall was usually disclosed by an abnormally large difference between the temperatures of rising and falling, but it has undoubtedly led to the recording of some incorrect flotation temperatures.

SUMMARY.

1. A method of determining the velocity of reactions taking place in liquids in sealed tubes has been developed from measurements of density by means of floats.
2. When the dissociation equilibrium of sulphur dichloride is displaced either by heat or by exposure to light, the re-establishment of equilibrium at low temperature is a first-order reaction.
3. This reaction proceeds more rapidly after irradiation than after heat treatment, probably as a result of the production of a catalyst by the action of light.
4. When sulphur monochloride is heated or exposed to light, the density first rises and then falls, the fall being greater on irradiation than on heating.
5. Sulphur dichloride is shown by colour changes to be one of the final products of the dissociation of the monochloride during the exposure to light.
6. The existence of photostationary states is observed
7. The most probable mechanism of the reactions of the monochloride is :

$$\text{(i) } 3S_2Cl_2 \rightleftharpoons S_3Cl_4 + S_3Cl_2; \quad \text{(ii) } S_3Cl_4 \rightleftharpoons S_2Cl_2 + SCl_2.$$

8. Normal sulphur monochloride is shown to be probably a mixture of a **Y**-shaped form with a chain form.

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