278. *The Properties of the Chlorides of Sulphur. Part VIII. The Reaction of Sulphur Monochloride with Chlorine.*

By A. HERBERT SPONG.

THE combination of sulphur monochloride with chlorine was held by Aten (*Z. physikal. Chem.*, 1906, **54**, 55) to be an autocatalytic reaction, both sulphur dichloride and sulphur tetrachloride being considered active in catalysing the process. The incorrectness of this view with regard to the catalysts was apparent, however, when Beckmann (*ibid.*, 1909, **65**, 289) demonstrated that sulphur tetrachloride is very rapidly formed from the dichloride and chlorine, so these two compounds should be indistinguishable under the conditions of Aten's experiments, and Lowry and Jessop (J., 1931, 323), accepting the first of Aten's conclusions, considered that the active catalysts were more probably S_3Cl_4 and SCl_4, both of which are regarded as polar.

Closer examination reveals the fact that Aten's experiments provide no convincing evidence of the existence of *two* autocatalysts, for the following reasons: (i) the conclusions are based solely on differences in the length of the induction period when reaction mixtures are made up in different ways, no regard being paid to the velocity of the reaction during its actual progress; (ii) it is by no means certain that equilibrium was attained during the first stage of Aten's preparations of reaction mixtures; (iii) in view of other observations recorded in Aten's paper, it is not certain that moisture was rigorously excluded, and it has been found in the course of the present work that this is necessary if comparable results are to be obtained.

A fresh investigation of this reaction, which may be represented as $S_2Cl_2 + Cl_2 \longrightarrow 2SCl_2$, therefore appeared desirable, and the experiments described in Part VII (this vol., p. 485) suggested a means by which this might be made, since if sulphur chloride mixtures of various compositions were heated at 100° for one hour and then rapidly cooled, the active intermediate compounds should be present in concentration depending only on the composition of the mixture, and the variation in the velocity with which the low-temperature equilibrium is re-established should yield definite information as to their character.

FIG. 1.

Retarded reaction in impure mixture.

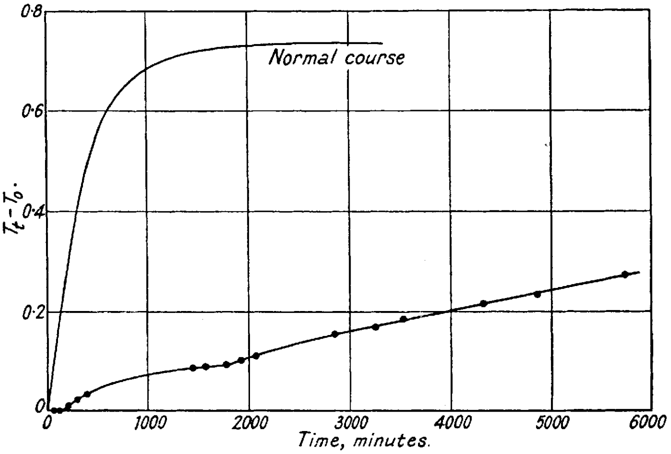
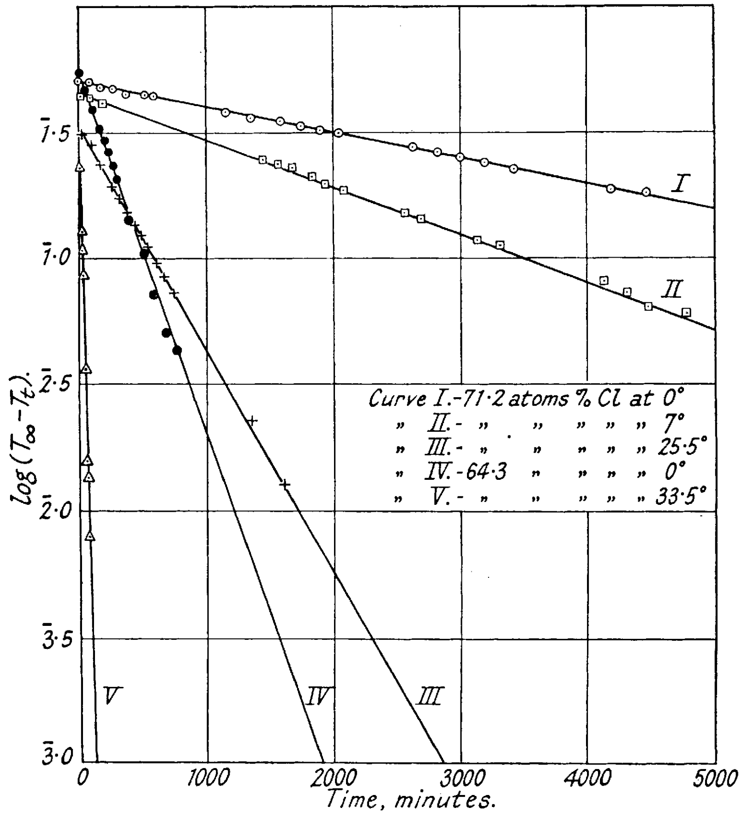


FIG. 2.

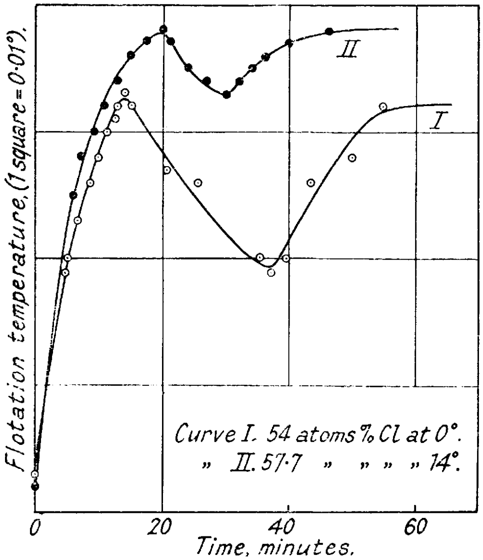
First-order course of reaction in mixtures of high chlorine content.



Preliminary experiments with a series of mixtures prepared according to the methods employed in earlier work (*e.g.*, Part I, J., 1927, 746) gave reaction rates which, although consistent amongst themselves, were much lower than the rate found for the corresponding reaction in Part VII (*loc. cit.*). It was suspected that this second series might have been exposed to moist air during preparation, and a new technique for the preparation of mixtures was therefore developed. When, with the new apparatus, moist air was admitted during the preparation of a mixture, the results shown in Fig. 1 were obtained, the reaction showing an induction period, although the autocatalyst must have been originally present. Other examples of negative catalysis by moisture, although rare, are not unknown (cf. Moelwyn-Hughes and Hinshelwood, *Proc. Roy. Soc.*, 1931, *A*, **131**, 177). Results obtained with pure mixtures have been found to be completely compatible with that of Part VII, which has been included with them in Table I.

FIG. 3.

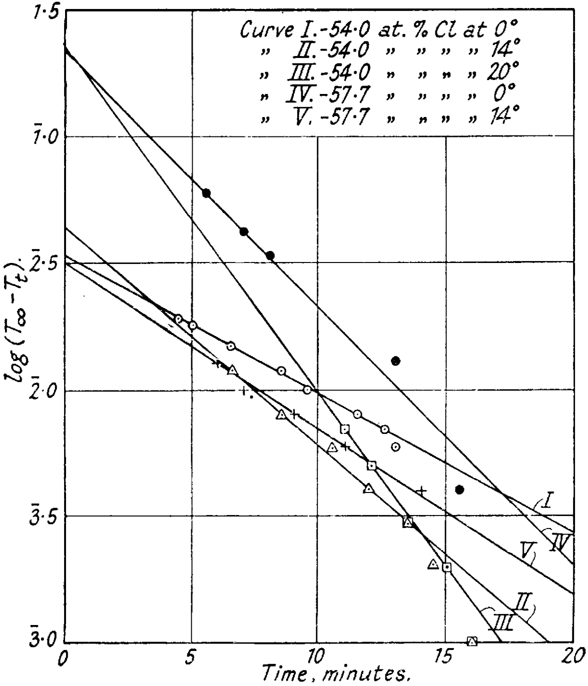
Course of density changes in mixtures of low chlorine content.



The course of the reaction in mixtures rich in chlorine is exactly similar to that represented in Fig. 1 of Part VII. The first-order nature of this reaction is demonstrated by the straight lines shown in Fig. 2, where log$(T_\infty - T_t)$ is plotted against time (T_∞ = extrapolated final flotation temperature, and T_t = flotation temperature at time t). When, however, the chlorine content is low, and the mixture therefore contains much free sulphur monochloride, the more complex density changes represented in Fig. 3 are observed. These can be recognised as due to the normal re-establishment of the dichloride equilibrium (Part VII, Fig. 1) proceeding simultaneously with the "catalysed" restoration of equilibrium in the free monochloride present (Part VII, Fig. 3, Curves II and III), and a slight fall of velocity coefficient often found near the end of experiments on chlorine-rich mixtures is probably to be ascribed to the same cause. The two reactions thus vary in rate in a similar manner, and the same catalyst must therefore be active in both. It has not been found possible to analyse these density changes completely, probably on account of experimental errors during the later stages of the reaction, but since the fall in density due to the monochloride reaction alone would be very nearly linear with time over the

FIG. 4.

First-order course of reaction in mixtures of low chlorine content.



period during which density rise is actually observed, the velocity coefficients for the dichloride reaction were calculated by treating this density rise as an uncomplicated first-order reaction and extrapolating the end value in the usual way. That this procedure was justified is shown by the straight lines in Fig. 4, obtained by plotting logarithms as in the less complicated reactions.

The results of all these experiments are summarised in Table I, and the first-order velocity coefficients observed at or near 0° are plotted in Fig. 5, where the broken line shows on an arbitrary scale the variation of the product $[SCl_2][S_2Cl_2]$, which must be a measure of the concentration of S_3Cl_4 in the mixture, since the equilibrium $S_3Cl_4 \rightleftharpoons S_2Cl_2 + SCl_2$ must be obeyed.

TABLE I.

Reaction velocities in sulphur chloride mixtures.

Cl, atoms %.	$d_{4°}^{0°}$ of mixture at equil. at 15°.	Temp. of reaction.	Density of float.	10^3k, min.$^{-1}$.
54·0	1·70073	−2·15°	1·70400	127
		14·5	1·67702	203
		19·8	1·66762	283
57·9	1·68576	−0·05	1·68592	205
		14·0	1·66258	172
59·8	1·68077	−3·0	1·68592	156
63·3	1·66870	0·8	1·66762	6·00
64·3	1·66511	0·0°	1·66672	3·41
		33·5	1·60128	51·7
67·0	1·65671	0·0	1·65578	2·74
71·2	1·63386	0·0	1·64260	0·24
		7·0	1·62027	0·43
		25·5	1·58230	2·04

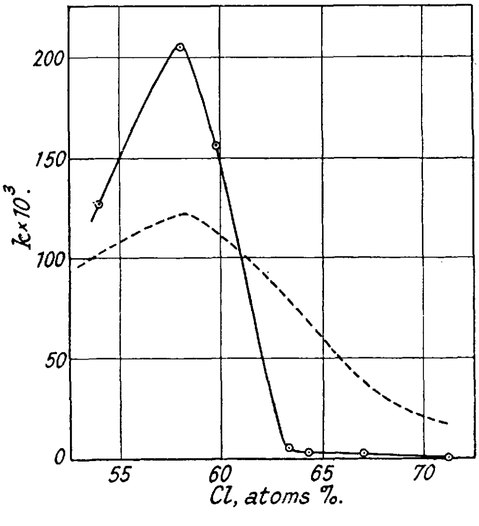
The identity of the position of the two maxima in Fig. 5 shows clearly that S_3Cl_4 alone is active in promoting the reaction, and the main course of the change is therefore to be regarded as proceeding by means of consecutive reactions

(1) $S_2Cl_2 + S_3Cl_4 \longrightarrow 2SCl_2 + S_3Cl_2$

(2) $S_3Cl_2 + Cl_2 \longrightarrow S_3Cl_4$

FIG. 5.

First-order velocity coefficients at 0°.



Evidence was presented in Part VI (J., 1933, 1547) indicating that reaction (2) must be rapid, and reaction (1) is therefore the slow process which controls the rate. It follows that

$$-d[S_2Cl_2]/dt = k[S_2Cl_2][S_3Cl_4].$$

The reaction has, however, been shown to be of the first order. This might be due to surface effects, although these are not usually important in reactions in liquid systems. The experiments recorded include measurements made in tubes of different glasses and of different diameters, and since no discontinuities are found in the series, this explanation can be excluded. A second possibility is that the rate is controlled by dissolution of chlorine from the gas phase, which would be a unimolecular process, but if this were the case, the high reaction rates observed in mixtures of low chlorine content would be impossible. It is therefore necessary to assume that the S_3Cl_4 concentration is kept constant by reaction (2) and that the first-order velocity coefficients recorded in Table I are given by $k' = k[S_3Cl_4]$.

These velocity coefficients are the net coefficients for a reversible reaction, and it has been shown that for a process such as $A \underset{k_1}{\overset{k_2}{\rightleftharpoons}} B$ the observed constant calculated in a similar way to those here discussed is given by $k_{obs.} = k_1 + k_2$. But from previous work (Part II, J., 1929, 1421; Part VI, *loc. cit.*) it is known that for the sulphur chloride reaction

k_2/k_1 is not greater than 0·02, which is of the same order as the experimental error. Hence $k_{\text{obs.}} = k_1$ approx., and no correction for the reversibility of the reaction has been thought necessary.

The true bimolecular velocity coefficients can thus be obtained by dividing the observed constants by the concentration of S_3Cl_4. Unfortunately, there is so far no independent method of estimating the equilibrium constant of the reaction $S_3Cl_4 \rightleftharpoons S_2Cl_2 + SCl_2$ which has been used in Fig. 5 to indicate the variation of the S_3Cl_4 content of the mixtures. There is, however, an alternative method by which an *approximate* estimate of its concentration can be obtained. The results of Part VI (*loc. cit.*) indicate that normal sulphur monochloride is dissociated into S_3Cl_4 and S_3Cl_2 to the extent of about 2 mols. %, while the results of Part VII, together with the approximate density calculations there referred to, show that this dissociation is increased on heating, while at the same time some of the S_3Cl_4 is decomposed into monochloride and dichloride, and further they permit a rough calculation of the extent to which both these changes will proceed in the course of one hour at 100°. Finally, some of the S_3Cl_2 produced will react with the chlorine present in the mixtures, and it may be supposed that in presence of a large excess of chlorine, practically all the S_3Cl_2 will be converted into S_3Cl_4 at all temperatures, but that in mixtures of relatively low chlorine content the combination will proceed to a less extent varying with temperature in a way which cannot be determined. An estimate of the extent of combination in such mixtures may be made by comparing the values of the product $[S_2Cl_2][SCl_2]$ in them with those for mixtures where combination is regarded as complete. The results are :

Cl, atoms, %	54·0	57·9	59·8	63·3	64·3	67·0	71·2
Mol.-fraction of S_3Cl_4	0·005	0·0065	0·006	0·0035	0·003	0·0016	0·0007
$[S_2Cl_2][SCl_2]$	0·202	0·240	0·223	0·157	0·136	0·076	0·033

The bimolecular velocity coefficients can now be deduced by means of the expression

$$k = k'/[S_3Cl_4] = k'\overline{M}/m_{S_3Cl_4}\rho$$

where $m_{S_3Cl_4}$ = mol.-fraction of S_3Cl_4; ρ = density of mixture in g. per litre; $\overline{M}$ = mean molecular weight of the mixture $= m_{S_2Cl_2}M_{S_2Cl_2} + m_{SCl_2}M_{SCl_2} + m_{Cl_2}M_{Cl_2}$. The results are shown in col. 3 of Table II.

TABLE II.

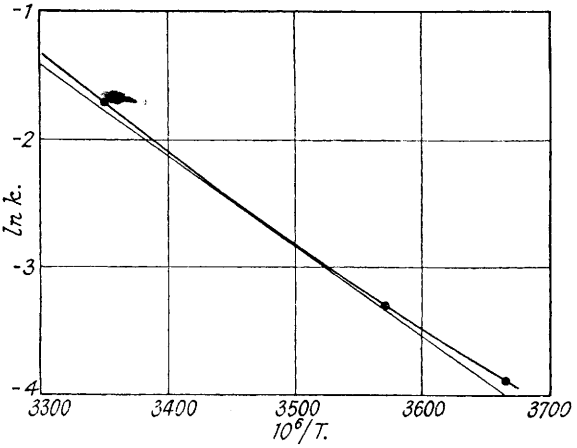
Bimolecular velocity coefficients.

		Velocity coefficients, litres/g.-mol./min.				
		Obs.	Calculated.			
		$k_{\text{exptl.}}$.	Formula (3).		Formula (4).	
Cl, atoms %.	Temp. of eaction, ° *K*.		$k_{\text{calc.}}$.	$\dfrac{k_{\text{calc.}}}{k_{\text{exptl.}}}$.	$k_{\text{calc.}}$.	$\dfrac{k_{\text{calc.}}}{k_{\text{exptl.}}}$.
54·0	270·85	1·87	23	12	57	31
	287·5	3·04	78	26	210	69
	292·8	4·26	114	27	310	73
57·9	272·95	2·20	11	5·0	34	15
	287	1·88	33	18	110	58
59·8	270	1·76	5·6	3·2	21	12
63·3	273·8	0·11	3·8	35	16	150
64·3	273	0·073	2·9	40	12	160
	306·5	1·15	44	38	200	170
67·0	273	0·107	1·8	17	8·9	83
71·2	273	0·020	1·2	60	6·8	340
	280	0·037	2·1	57	12	320
	298·5	0·178	10	56	58	330

The wide variation in the experimental velocity coefficients indicates that there is still another factor influencing the reaction, and the difference in the shapes of the two curves in Fig. 5 also points to the same conclusion. Moreover, if an attempt is made to determine the energy of activation by plotting ln k against $1/T$, the three values for the mixture containing 71·2 atoms % of chlorine lie, not on a straight line, but on a curve as shown in Fig. 6. (A similar curve is given by the three values for 54 atoms % chlorine.) The apparent energy of activation thus changes with temperature, and its value under given conditions must be obtained by drawing the appropriate tangent to the curve. If a similar process is carried out for other mixtures, it appears that the apparent energy of activation for any one temperature decreases as the chlorine content of the mixture is reduced.

FIG. 6.

Relation between velocity coefficient and temperature. (The radius of the dots is roughly equal to the probable error.)



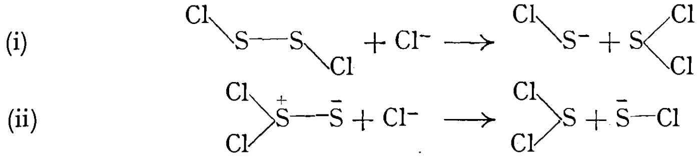
The explanation of this phenomenon is found in the fact that S_3Cl_4 is to be regarded as ionic, and is probably completely dissociated, or almost so, under the conditions of these experiments. Reaction (1) of p. 1286 then proceeds in two stages:

$$(a)\ S_2Cl_2 + Cl^- \longrightarrow SCl_2 + SCl^-$$
$$(b)\ SCl^- + S_3Cl_3^+ \longrightarrow SCl_2 + S_3Cl_2.$$

It is obvious that (*b*) will be much more rapid than (*a*), which is therefore the actual rate-controlling step.

Now, it has been tacitly assumed in much of the previous work on reactions in liquids that a reaction between an ion and a neutral molecule is not affected by electrostatic factors, and this view appears to be implicit in the treatment of such reactions by Moelwyn-Hughes (" Kinetics of Reactions in Solution," Oxford, 1933, pp. 181, 199). Although this may be true of symmetrical molecules or in a medium of high dielectric constant such as water, yet it will probably not be so when the reacting molecule is unsymmetrical and the dielectric constant of the medium relatively low.

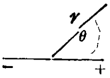
It was shown in Part VII that sulphur monochloride is probably a mixture of two different structural forms, and there are therefore two possible modes of attack by chlorine ions:



In (i) the positive end of the dipole is being attacked, and in (ii) the negative. In the latter case the bond may be regarded as being ruptured by the chlorine ion repelling the two electrons forming the link towards the central sulphur atom; the energy required to bring this about would then be equal to the electrostatic energy of the bond.

The distribution of ions round such dipoles will not be uniform, and by applying the methods of Debye and Hückel (*Physikal. Z.*, 1923, **24**, 185, 334; cf. A. A. Noyes, *J. Amer. Chem. Soc.*, 1924, **46**, 1080) to such a system, it is found that the concentration n' of negative ions in an element of volume near a dipole is given by $n' = ne^{\epsilon V/kT}$, where n is the average concentration of the ion in the bulk of the liquid, ε the electronic charge, k the Boltzmann constant, T the absolute temperature, and V the average potential in the element of volume considered, which is given by

$$V = [(\mu \cos \theta)/Dr^2](1 + Br)e^{-Br}$$



where μ is the moment of the dipole, θ the angle of orientation of the element of volume to the dipole (see inset), D the dielectric constant of the medium, r the mean distance of the element of volume from the centre of the dipole, and B the familiar Debye–Hückel term defined by

$$B^2 = 4\pi\varepsilon^2\Sigma(cz^2)/DkT$$

where c is the concentration of an ionic species in single ions per c.c., and z its valency.

(The expression for V here given cannot be regarded as entirely satisfactory, but having regard to the difficulty of representing the field round a free dipole, the particular solution of the Poisson equation employed appears to be the most suitable.)

Now since Br is very small, we may neglect all terms involving higher powers than the first, and

$$\begin{aligned} V &\doteq \mu \cos \theta(1 + Br)(1 - Br)/Dr^2 \\ &= \mu \cos \theta[1 - (Br)^2]/Dr^2 \\ &\doteq (\mu \cos \theta)/Dr^2 \end{aligned}$$

It follows that if Z is the collision number calculated by one or other of the ordinary formulæ (Moelwyn-Hughes, *op. cit.*, p. 28) without regard to the unsymmetrical nature of the distribution, the velocity coefficient of the reaction will be given by

$$\begin{aligned} k &= Ze^{\epsilon V/kT}e^{-E/RT} \\ &= Ze^{-(E-N_0\epsilon V)/RT} \qquad \qquad (1) \end{aligned}$$

where N_0 is Avogadro's number and E the true energy of activation of the reaction (*idem, ibid.*, p. 195). Now the experimental results of Lowry and Jessop (Part III, J., 1930, 782) show that over a wide range of temperatures the dielectric constants of sulphur chloride mixtures are represented by $D = Ae^{-mT}$, where A and m are constants characteristic of the particular mixture. The apparent energy of activation of the reaction is therefore given by

$$\begin{aligned} E_{\text{app.}} &= RT^2 d \ln k/dt \\ &= N_0\varepsilon V(mT - 1) + E \qquad \qquad (2) \end{aligned}$$

The values of the constants for the different mixtures studied are such that the observed variation of the apparent energy of activation with composition (see p. 1288) can only be realised if the term $N_0\varepsilon V(mT - 1)$ is positive, while under the conditions of the experiments here described, the factor $(mT - 1)$ is always negative. Hence the values of V concerned must also be negative, *i.e.*, $\cos \theta$ must be negative and θ must lie between $\frac{1}{2}\pi$ and π. The average value of $\cos \theta$ for this range is $-0{\cdot}637$. It follows that it must be the negative end of the dipole which is attacked, and the primary mechanism is therefore according to scheme (ii) of p. 1288. This fact, which at first sight seems improbable, is possibly due to the rupture of the bond between the sulphur atoms requiring less energy in this mechanism than in any other; it can, in fact, be easily shown that the electrostatic energy is probably least in this case.

In order to make further calculations, it is necessary to know the values of μ and r. The former is seen to be, for the mechanism proposed, the effective moment of the semipolar double bond between the two sulphur atoms, which cannot, at present, be estimated. It will probably not be very different from the moment of the link $>\overset{+}{\mathrm{S}} - \overset{-}{\mathrm{O}}$ which has been stated by Hampson, Farmer, and Sutton (*Proc. Roy. Soc.*, 1933, *A*, **143**, 147) to be $2{\cdot}63D$. This value has therefore been used in the calculations.

The value of r must vary with θ, since the molecule is not spherical. It has been taken, as a first approximation, to be $a \cos \theta + b$, where a is the diameter of the sulphur atom and b the radius of the chlorine ion (Sidgwick, *Ann. Reports*, 1933, **30**, 117). This gives a mean value of 3·16 Å.U.

When these values, together with the appropriate values of D, m, and T and two values of the apparent energy of activation obtained from curves similar to that of Fig. 6, are substituted in equation (2) above, the true energy of activation is found to be (i) 13,100, 13,500, mean 13,300 cals./g.-mol., (ii) 11,600, 12,100, mean 11,850 cals./g.-mol., according as allowance is or is not made for the variation of free space with temperature. These are possible values for the electrostatic energy of the semipolar double bond given the moment assumed, the former requiring the plausible bond polarisability $3{\cdot}75 \times 10^{-24}$ c.c., the latter $4{\cdot}21 \times 10^{-24}$ c.c. (cf. Waters, J., 1933, 1551). These values of E may now be substituted in equation (1).

The values of Z may be calculated in two ways, either from an expression deduced by a treatment similar to that given by Moelwyn-Hughes for the catalysed inversion of cane sugar (*Phil. Mag.*, 1932, **14**, 112), which leads to

$$Z = 60 \times 2{\cdot}9 \times 10^{24} \sigma_{\mathrm{Cl'}} \eta / \overline{N} M_{\mathrm{Cl'}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which allowance is made for the variation of free space with temperature, or from the ordinary formula for bimolecular gas reactions

$$Z = 60 \times 5{\cdot}71 \times 10^{25} T^{\frac{1}{2}} \left(\frac{M_{\mathrm{S_2Cl_2}} + M_{\mathrm{Cl'}}}{M_{\mathrm{S_2Cl_2}} \cdot M_{\mathrm{Cl'}}} \right)^{\frac{1}{2}} \left(\frac{\sigma_{\mathrm{S_2Cl_2}} + \sigma_{\mathrm{Cl'}}}{2} \right)^2 \quad . \quad . \quad . \quad (4)$$

in which no such allowance is made. [$\sigma_{\mathrm{Cl'}}$ = diameter of chlorine ion, $\sigma_{\mathrm{S_2Cl_2}}$ = that (estimated) of sulphur monochloride molecule; $M_{\mathrm{Cl'}}$ = molecular weight of chlorine ion; $M_{\mathrm{S_2Cl_2}}$ = that of sulphur monochloride; $\overline{N}$ = total number of g.-mols. per litre; η = viscosity of reaction mixture. The viscosities of a few mixtures were measured at several temperatures, and the remainder have been interpolated; it is hoped to extend these measurements and to record them at a later date.] The factor 60 occurs in both formulæ since the unit of time employed is the minute.

The velocity coefficients thus calculated are recorded in cols. 4 and 6 of Table II, and cols. 5 and 7 give the ratios of the calculated to the experimental values. It will be seen that in the absence of excess chlorine, which would minimise the effect of temperature on the S_3Cl_4 concentration, neither formula is successful in representing the variation of the reaction velocity with temperature. If, however, in the mixtures of low chlorine content, attention is confined to velocity coefficients measured at temperatures near 15° (for which the estimated S_3Cl_4 concentrations are most likely to be correct) the values in col. 5 are all of similar order. The variation observed in these ratios is not unreasonable when it is borne in mind that no arbitrary constant has been employed in the calculations, but that the values of μ and r are necessarily subject to some uncertainty.

This result makes it highly probable that the mechanism here proposed is correct, and also indicates that, in this reaction, allowance must be made for the variation of free space with temperature, although neither reactant is considered to be present in any large concentration. The high values of the ratio recorded in col. 5 are consistent with the view that the active **Y**-shaped form is only a small portion of the total monochloride present.

No effect which can be ascribed to sulphur tetrachloride has been observed, and since this compound would also probably yield chlorine ions, this result supports the view previously expressed that it is not present in the liquid state.

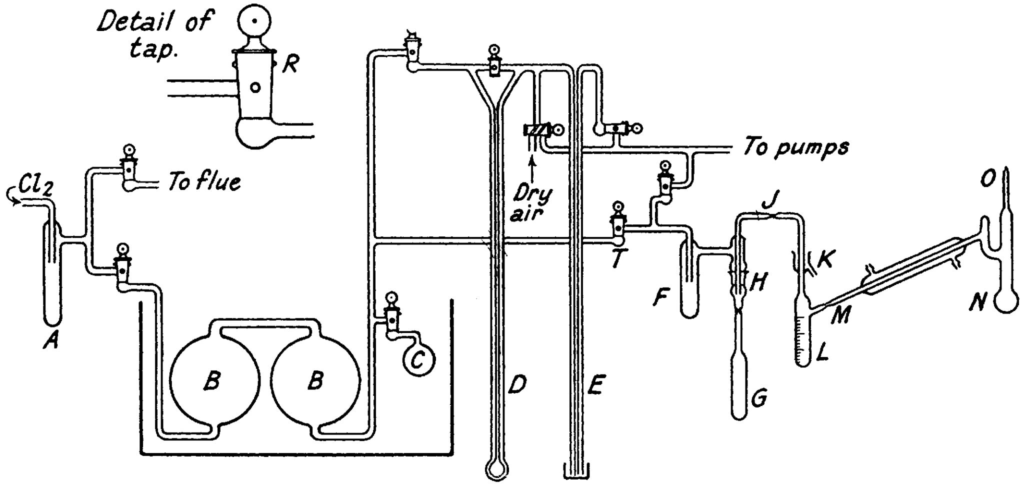
EXPERIMENTAL.

The reaction tubes were filled by means of the apparatus shown in Fig. 7, which is based on that of Maass (*e.g.*, Maass and Russell, *J. Amer. Chem. Soc.*, 1918, **40,** 1847). The tube G containing the floats, having been thoroughly cleaned and dried, was weighed and connected to the apparatus by means of the ground joint H. The whole was then exhausted completely by a mercury-diffusion pump. The right-hand side—the sulphur monochloride distillation section —was then filled with dry air, the tap *T* being closed. The flask *N* was opened at *O* and charged with sulphur monochloride to which had been added 1% of recrystallised sulphur and 1% of ignited charcoal. The flask was then again sealed at *O*, and the monochloride distilled into the graduated tube *L*. During this distillation, the apparatus was continually evacuated by the water-pump in order to remove gaseous products of hydrolysis of sulphur monochloride, but the vapour of the monochloride itself was condensed by means of solid carbon dioxide placed in the funnel *K*.

The graduation of the tube *L* enabled an approximate estimate to be made of the amount collected, and when a sufficient quantity had been obtained, the distillation was stopped, and the flask and condenser sealed off at the constriction *M*. The distillate in *L* was now frozen in liquid air, and the mercury pump started. When evacuation was complete, the liquid air was removed from the tube *L* and placed below the reaction tube *G*, so that the monochloride distilled slowly into this tube. The tube *L* was then sealed off at the constriction *J*.

FIG. 7.

Apparatus for filling reaction tubes.



Meanwhile, chlorine from a purification train (Part VI, *loc. cit.*) was condensed in the trap *A* over liquid air. This chlorine was then fractionated, the head and tail portions being allowed to escape to the flue, and the bulbs *B* being filled from the middle fraction. The volume of the bulbs *B*, and also of the connecting tubing as far as the constriction *J*, had previously been determined by measuring the pressure produced when air at atmospheric pressure in the bulb *C* was allowed to expand into the evacuated apparatus. The volume of *C* was found by measuring with a gas burette the air required to fill it to atmospheric pressure.

The pressure of the chlorine was now measured by means of the bromonaphthalene gauge *D*, which was balanced by either exhausting or admitting dry air, the pressure of which could be read on the mercury manometers *E*. The tap *T* was now opened, and the chlorine admitted to the tube *G*. The trap *F* was cooled in solid carbon dioxide and ether in order to condense any volatile products of the action of chlorine on the tap-grease or on bromonaphthalene or any vapour of the latter itself. A faint film was observed in this trap after several weeks' working of the apparatus. The condensation of the chloride was followed by the change in pressure, and when the desired quantity had been withdrawn from the bulbs, the tap *T* was closed. After allowing time for all the chlorine in *F* to distil into *G*, this tube was sealed off and set aside to attain room temperature and reach equilibrium. It was then again weighed together with the part sealed off.

The ground joint and all taps were lubricated with Shell-Mex Apiezon Grease "L," the taps being made of the special form shown, a modification of those described by Trautz (*Z. Elektrochem.*, 1929, **35**, 110), in order that, the well *R* being full of grease, adequate lubrication would be ensured with only the thinnest possible film of grease in the barrel of the tap.

It should be possible to calculate the weight of chlorine added directly from the observed pressures and the known volumes. This was tested by several experiments on the condensation of chlorine alone in weighed tubes. The amount condensed was found to be about 98% of that calculated, and to vary slightly with differences in manipulation. The loss is believed to be due mainly to slow reaction with the grease or the bromonaphthalene. It is thus possible to calculate the composition of the mixture with a fair degree of certainty from the two weighings and the pressure readings.

SUMMARY.

1. The reaction between sulphur monochloride and chlorine has been studied in mixtures of diverse composition by methods previously described.

2. It is shown that the reaction velocity is markedly influenced by the concentration of S_3Cl_4.

3. The admission of moisture has a strong retarding effect.

4. The primary mechanism is probably ionic, the chlorine ion attacking the negatively charged sulphur atom in the **Y**-shaped form of the monochloride. The mechanism then becomes :

$$\text{(i)}\quad S_2Cl_2 + Cl^- \longrightarrow SCl_2 + \overset{-}{S}Cl$$

$$\text{(ii)}\quad \overset{+}{S}_3Cl_3 + \overset{-}{S}Cl \longrightarrow SCl_2 + S_3Cl_2$$

$$\text{(iii)}\quad S_3Cl_2 + Cl_2 \longrightarrow \overset{+}{S}_3Cl_3 + Cl^-$$

5. It is found necessary in calculating velocity coefficients to make allowance for the variation of free space with temperature.

6. The energy of activation is found to be of the same order as the electrostatic energy of the semipolar double bond which is ruptured in stage (i) of the process.

The author is indebted to the Council of Trinity College, Cambridge, for a grant from the Rouse Ball Research Fund, to Professor T. M. Lowry, C.B.E., F.R.S., for his interest in this work, to Professor J. E. Lennard-Jones, F.R.S., for advice in connexion with the theoretical treatment of the problem, and to Dr. E. A. Moelwyn-Hughes for helpful suggestions made while the paper was being prepared for publication.

LABORATORY OF PHYSICAL CHEMISTRY,
CAMBRIDGE UNIVERSITY.

[*Received, June* 27*th*, 1934.]