CIX.—*The Properties of the Chlorides of Sulphur. Part I. Freezing Points.*

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THE fact that the chlorination of sulphur takes place in two stages, giving rise first to an orange and then to a red product, was recorded by Berthollet in 1807. It was confirmed in 1832 by Dumas, who analysed the two products and showed that the composition and vapour density of liquids which were saturated with sulphur and with chlorine respectively agreed with those calculated for compounds of the formulæ S_2Cl_2 and SCl_2. The view has, however, been held persistently (*e.g.*, by Rose in 1831, on account of the variable composition of the red product, by Isambert in 1878, on account of its variable vapour pressure, and by Ogier in 1883, on account of its small heat of formation) that the " dichloride " does not exist as a definite chemical compound, but is merely a solution of chlorine in the monochloride. In recent years, the existence of a higher chloride of sulphur has been generally admitted; but it has been agreed almost universally that this higher chloride (which Dumas had shown to behave towards indigo quite differently from free chlorine) must be regarded as a tetrachloride, the so-called " dichloride " being merely a mixture of sulphur tetrachloride with monochloride. This conclusion is based upon cryoscopic experiments of Ruff and Fischer (*Ber.*, 1903, **36**, 418) and of Aten (*Z. physikal. Chem.*, 1906, **54**, 55, where a full bibliography is given), which showed a sharp maximum in the melting-point curve at −80°, corresponding with the crystallisation of the *monochloride*, and a rounded maximum at −30°, corresponding with the crystallisation of the *tetrachloride*, but no discontinuity which would indicate the crystallisation of a *dichloride*, although Beckmann subsequently froze out a product of this composition (*Z. physikal. Chem.*, 1909, **65**, 289).

Aten found this result particularly puzzling, since his observations of vapour pressure and boiling point proved clearly that the composition of the liquid and vapour phases, which became almost identical at the composition of the *monochloride* (but diverged widely on either side of this composition as a result of the very unequal vapour pressures of Cl_2 and S_2Cl_2, on the one hand, and of S_8 and S_2Cl_2, on the other), definitely approached one another again at the composition of the *dichloride*, provided that opportunity was given for the monochloride and chlorine to enter into chemical combination with one another; under the same conditions, however, there were only very feeble indications of any similar approach at the composition of the *tetrachloride*. Aten was therefore obliged to postulate that the equilibrium $3SCl_2 \rightleftharpoons S_2Cl_2 + SCl_4$ had a temperature coefficient which was so large that a product which was almost all SCl_2 at 0° nevertheless deposited SCl_4 at −30°.

In view of the contradictory character of the evidence, and especially of the fact that the introduction of precise physicochemical methods of examination had made the problem of the real existence of sulphur dichloride even more contentious than before, we thought it important (in spite of the obstinately negative character of the results recorded by Ruff and Fischer, and by Aten) to open up this question again, and in particular to find out whether the freezing points did in fact afford a decisive proof of the non-existence of the dichloride at low temperatures. In the present paper, therefore, we describe the results of a careful redetermination of the freezing-point curve of the chlorides of sulphur over the range from 16 to 70% Cl. This redetermination has revealed, in addition to the main sections corresponding to the separation of the *monochloride* and the *tetrachloride*, a substantial section corresponding to the crystallisation of the *dichloride*, as well as a small loop near the eutectic point, which is attributed to the crystallisation of a *trisulphur tetrachloride* of the formula S_3Cl_4, which has not been prepared before.

EXPERIMENTAL.

General Principles.—The plotting of an accurate equilibrium diagram is only possible if attention is paid to the three conditions discussed below :

(*a*) Ruff and Fischer determined the *final melting points* in sealed tubes of samples containing 51·5—92·4% Cl. In view of the tedious disturbances of equilibrium which may result from partial or complete solidification in such a complex system, we regarded it as essential to determine in every case the *initial freezing point* of the unfrozen sample. Since Beckmann's values for the m. p. and f. p. of his samples differed in some cases by as much as 40°, in spite of their theoretical identity under ideal conditions, this choice is of some importance.

(*b*) Owing to the slowness with which interaction takes place between sulphur monochloride and chlorine, Aten was able to plot b.-p. and f.-p. curves for these mixtures *before and after combination ;* but it appears to have been assumed that mixtures of ready-made chlorides of sulphur come to equilibrium immediately. In our experience, this is not the case, since the f. p. of a freshly prepared mixture of sulphur monochloride and sulphur dichloride may differ by 20° from the value recorded finally. The precaution was therefore taken of heating each sample to 100° in a sealed tube in order to establish a definite condition of equilibrium before determining its f. p. It was found that identical f. p.'s were given by unheated samples to which a trace (0·02%) of iodine had been added, but not by samples which had merely been made up in presence of charcoal.

(*c*) Although both Ruff and Fischer and Aten plotted enough points to show the two maxima in the m.-p. curve, their measurements were neither numerous nor accurate enough to reveal the minor breaks in the curve. The discontinuities due to the crystallisation of sulphur dichloride and of trisulphur tetrachloride were only discovered (i) by using a triple thermo-junction, in place of pentane and toluene thermometers, and so reducing the errors of observation to less than 1°; and (ii) by plotting 15 points in a region which contained only one observation, by Ruff and Fischer, of the eutectic temperature of a sample which was not, in fact, of the eutectic composition. The m.-p. curves which had been used to prove the non-existence of the dichloride were thus shown to be wholly imaginary in the region in which this compound actually crystallises out from the melt.

Materials.—Sulphur monochloride was purified by redistillation under 30 mm. pressure from 1% each of dry charcoal and of sulphur. Liquids richer in chlorine were prepared by adding 1% of dry ignited charcoal to the purified monochloride, cooling in ice, and passing in a current of chlorine which had been dried with sulphuric acid and phosphoric oxide. Some samples were prepared by direct chlorination of the monochloride, others by mixing sulphur monochloride with an over-chlorinated sample of " dichloride " containing 70·4% of chlorine, which was kept in a stoppered bottle and analysed from time to time. The analyses were made by weighing out 0·2 g. in a stoppered glass tube, dropping the tube into a flask containing 50 c.c. of distilled water and 5 c.c. of ammonia (*d* 0·880), and boiling for 5 minutes; 10 c.c. of nitric acid (*d* 1·42) were added to the cold solution, which was boiled to remove oxides of nitrogen. After adding 50 c.c. of *N*/10-silver nitrate, and filtering off the precipitated silver chloride, the excess of silver was titrated with *N*/10-potassium thiocyanate with ferric alum as indicator. This method, which gave results agreeing within 0·1%, was found to be much more convenient than Carius's method, and at least equally accurate.

Measurement of Temperature.—The f. p.'s were measured with a triple thermo-couple made from sleeved and silk-covered copper and constantan wire, gauge 32. The junctions were silver-soldered, filed down as much as possible, and enclosed in drawn-out glass tubes; the leads were protected with shellac. The thermo-couples were calibrated at the f. p.'s of water, mercury, chlorine, and ethylene; but the parabolic relation between *E.M.F.* and temperature, which was deduced from these four readings, was checked by observing also the f. p. of hydrogen chloride, and the b. p.'s of chlorine, hydrogen chloride, and ethylene. The temperatures thus recorded were consistent within 0·5°.

Determination of Freezing Points.—The f. p.'s were determined by cooling the sample over liquid air in a test-tube; this was provided with a glass stirrer passing through a closely-fitting glass tube mounted in a cork, which also carried the thermo-couple.

The voltage did not vary with the position of the thermo-couple in the liquid, but this was kept constant in order to secure as much uniformity as possible. The liquid was cooled rapidly to within a few degrees of the expected f. p., and then by half-degrees at intervals of about a minute until solid began to separate. Samples containing *more* than the eutectic proportion of chlorine gave, within 1° from the first separation of solid, an opaque turbidity; the temperature at which this turbidity first appeared was taken as the initial f. p. of the sample; the observation was repeated twice after allowing the turbidity to clear. The turbidity in samples containing *less* than the eutectic proportion of chlorine appeared very irregularly, apparently by reason of the separation of a second liquid phase; concordant f. p.'s were observed, however, when crystallisation was induced by inoculation with a glass rod dipped alternately into the sample and into liquid air. Since there was much overcooling, the temperature at which this crystallisation could be induced *without producing a rise of temperature* was taken as the initial f. p. of the sample.

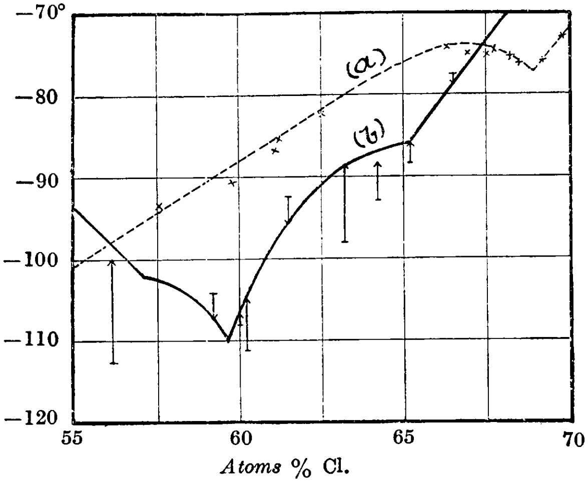
Experimental Results.

(a) *Freezing Points of Freshly Prepared Mixtures of Sulphur Monochloride and Sulphur Dichloride.*—The broken curve of Fig. 1 (*a*) shows the initial f. p.'s of a series of freshly prepared mixtures of sulphur monochloride with an over-chlorinated sample of sulphur dichloride, which had been prepared in presence of charcoal as described above, and contained 68·2 atoms % Cl; three points are also plotted for the same sample of dichloride after further addition of chlorine. Since all these f. p.'s fell to lower values after the mixture had been "aged" for a month in a sealed tube, and still more after heating to 100°, the curve has been drawn through the highest points, lower values being attributed to an approach towards the f. p.'s of the true equilibrium-mixtures.

The curve thus plotted differed from all others hitherto recorded in showing a pronounced maximum at the composition of sulphur dichloride, the real existence of which was thus fully established for the first time by means of f.-p. data. In spite of its very definite character, however, we do not wish to attach any undue value to this curve, since it represents only a particular series of "false equilibria," in which the interaction between the various components of the mixtures is still far from complete. The lower portion of the curve, where the f. p.'s fell below −100°, was regarded as untrustworthy, on account of a tendency for a second liquid phase to separate from the melt in this region, and has therefore been omitted.

(b) *Effect of Preliminary Heating on the Freezing Point of Freshly Prepared Samples.*—The samples used for plotting the f.-p. curve of Fig. 1 (*a*) did not give satisfactory values for the f. p.'s of the final equilibrium-mixtures, perhaps because the repeated manipulation of the samples had allowed too many opportunities for access of moisture. An attempt was therefore made to plot this curve by observing the f. p.'s of mixtures that had been freshly prepared *in presence of charcoal* by the direct chlorination of a sample of sulphur monochloride, under conditions which precluded the access of moisture. The f. p.'s were, however, still quite irregular, until these mixtures also had been heated to 100° in sealed tubes. The way in which the f. p.'s of the freshly prepared samples were displaced towards a smooth equilibrium curve by a preliminary heating is shown by the arrows of Fig. 1 (*b*). Although the equilibrium curve is not quite identical with that which was finally plotted, it will be seen that all the f. p.'s approach this curve, whether they were initially above it or below it, although they do not quite reach it in every case. Heating the mixtures *alone* to 100° is therefore far more efficient in producing a condition of equilibrium than mere contact *with charcoal* at atmospheric temperature.

FIG. 1.



(a) *Freezing points of freshly prepared mixtures of sulphur monochloride with sulphur "dichloride" containing* 70·4% *Cl (broken curve).* (b) *Effect of heating to* 100° *on sulphur monochloride chlorinated in presence of charcoal (full curve and arrows).*

(c) *Influence of Iodine as a Catalyst.*—Since 0·2% of iodine can be used instead of 1% of charcoal as a catalyst to promote the addition of chlorine to sulphur monochloride, experiments were made on the f. p.'s of heated mixtures to which a trace of iodine (0·02%) had been added, the proportion used being sufficiently minute to avoid the deposition of iodine trichloride on cooling. The results were as follows :

Cl =	68·4	63·1	67·3	68·0	62·2	67·6%.
=	66·1	60·7	65·0	65·7	59·8	65·3 atoms%.
F.p. =	−79·0°	−99·0°	−83·0°	−84·5°	−103·0°	−83·0° (without iodine).
=	−79·0	−98·0	−82·5	−83·5	−103·5	−83·0 (with 0·02% iodine).

No further change of f. p. was produced by the addition of iodine to the heated samples; moreover, identical values were observed when the f. p.'s of unheated samples to which iodine had been added were compared with those of samples (containing no iodine) which had been heated to 100°. It therefore appears that the condition of equilibrium brought about by the addition of iodine at atmospheric temperature is substantially identical with that produced by heating to 100°.

(d) *Freezing-point Curve of Samples previously heated to* 100°.—When a precise method for measuring the f. p.'s had been established, and a satisfactory process had been devised for bringing the sample to a uniform condition, no difficulty was experienced in plotting a f -p. curve (Fig. 2) in which all the minor details were clearly displayed. The data from which this curve was plotted were as follows :

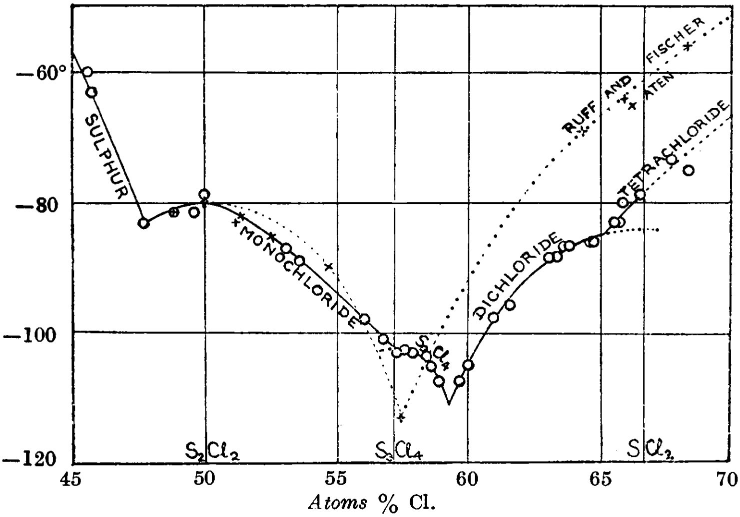
Cl %.	Atoms %.	F. p.	Cl %.	Atoms %.	F. p.	Cl %.	Atoms %.	F. p.
50·2	47·7	− 83·1°	60·9	58·4	−103·6°	66·3	63·9	−86·6°
51·6	49·1	− 81·5	61·0	58·6	−105·1	66·4	64·0	−87·2
52·1	49·6	− 81·3	61·3	58·9	−107·4	67·1	64·8	−85·9
52·5	50·0	− 79·0	62·1	59·7	−107·4	67·2	64·9	−86·1
55·6	53·1	− 87·0	62·4	60·0	−105·0	67·9	65·6	−82·9
56·1	53·6	− 89·0	63·4	61·0	− 97·6	68·2	65·9	−82·9
58·6	56·1	− 98·4	64·0	61·6	− 95·7	68·2	65·9	−80·0
59·3	56·8	−101·0	65·5	63·1	− 88·6	68·8	66·5	−78·8
59·8	57·3	−103·0	65·5	63·1	− 88·4	70·1	67·8	−73·5
60·1	57·6	−102·6	65·8	63·4	− 88·3	70·6	68·3	−75·0.
60·4	57·9	−103·0						

It will be seen that, whereas the broken curve of Fig. 1 (*a*) shows a maximum corresponding with the composition SCl_2, this is not reached in mixtures which had been brought to a condition of equilibrium by heating to 100°, since, after this treatment, *a mixture having the composition of sulphur dichloride deposits crystals of sulphur tetrachloride.*

(e) *Solubility of Sulphur in Sulphur Monochloride.*—In order to carry the equilibrium diagram up to 100% S, measurements were made of the solubility of sulphur in sulphur monochloride. For this purpose sulphur, purified by recrystallisation from toluene, was added to the monochloride, and heated to a temperature just below the transition point at 96°. The temperatures at which solid sulphur began to separate on cooling the solutions are shown with sufficient exactness in Fig. 3, which covers a much wider range of temperatures than the preceding figures. The temperatures recorded by Aten *for complete dissolution* of sulphur in sulphur monochloride are also shown; as might perhaps be expected, these are considerably higher, since complete saturation is very difficult to attain in presence of a vanishing quantity of the solid phase. It should be noted that, after being heated to 170°, sulphur dissolves permanently in sulphur monochloride, perhaps as the result of the formation of sub-chlorides of sulphur (Ruff and Golla, *Z. anorg. Chem.*, 1924, **138**, 17, 33; Bruni and Amadori, *Atti R. Accad. Lincei*, 1919, [v], **28**, 217), but there is no reason to suppose that this takes place during a short heating at temperatures below 100°.

Fig. 2.

Freezing points of chlorides of sulphur after heating to 100°.



(f) *Appearance of the Solid Phase.*—The fact that several different compounds may separate in the range from S_2Cl_2 to SCl_4 was confirmed by noting the physical appearance of the solids. Thus :

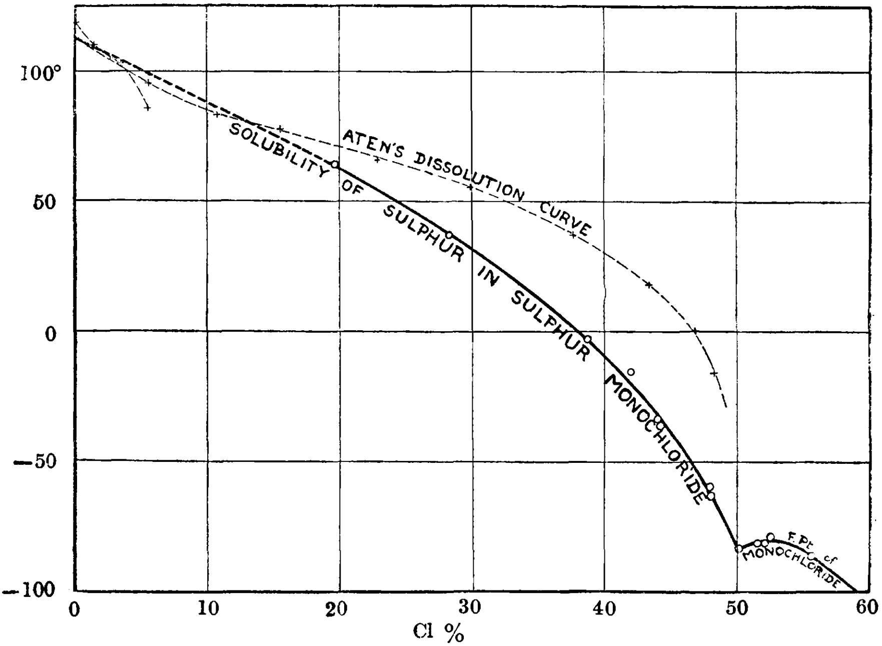
(i) *Sulphur tetrachloride* separated in a buttery form (without overcooling) from mixtures containing more than 67·2% Cl (64·9 atoms %).

(ii) *Sulphur dichloride* separated, again without overcooling, in the form of a finely divided, buff-yellow powder, from mixtures containing 61·6—67·2% Cl (59·2—64·9 atoms %).

(iii) The solid which separated over the narrow range 59·1—61·6% Cl (56·6—59·2 atoms %), after seeding with a sample cooled in liquid air in order to prevent the separation of a liquid phase, was of a flocculent nature, very different from the granular monochloride or the pasty dichloride; since this different appearance corresponded with the limits of a section of the broken f.-p. curve, it was regarded as evidence of the separation of a compound intermediate in composition between the monochloride and the dichloride.

FIG. 3.

Solubility of sulphur in sulphur monochloride.



(iv) Finally, *sulphur monochloride* separated in the usual granular form from mixtures containing less than 59·1% Cl (56·6 atoms %), although these liquids had still to be seeded in order to obtain the true f. p. of the sample.

(g) *Recrystallisation of Sulphur Dichloride.*—Although an equilibrium mixture having the composition of sulphur dichloride deposits crystals of the tetrachloride on cooling, the dichloride forms the solid phase when an over-chlorinated sample of sulphur dichloride is brought back to the correct composition by the addition of sulphur monochloride. Two samples prepared in this way were cooled over liquid air until about one-third frozen; the liquid was then decanted, and the solid remelted and again partly frozen. On analysis, the final products from a sample containing 69·4% Cl gave Cl = 68·4, 67·3 (calc., 68·9). These results are, of course, merely negative, since they only show that there was no marked change of composition on freezing; but they are of value in that they do not exhibit the striking changes of composition which would be expected if the solid phase were the tetrachloride and not the dichloride. More definite results were obtained by recrystallising the dichloride from light petroleum (b. p. 40°; f. p. −147°). The crystals which separated were drained on an asbestos filter, pressed down with the flattened end of a glass rod, and again drained from the melt. Since the solid always retained some of the solvent, the chlorine and sulphur were both estimated and the percentage composition calculated from the ratio [Found: Cl, (*a*) 68·5, (*b*) 68·0; S, (*a*) 31·5, (*b*) 32·0. SCl_2 requires Cl, 68·9; S, 31·1%].

Discussion.

The equilibrium of the chlorides of sulphur in the middle regions of concentration appears to be dominated by two simultaneous dissociations of sulphur dichloride, proceeding with very unequal speeds:

$$2SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2; \quad 3SCl_2 \rightleftharpoons S_2Cl_2 + SCl_4.$$

(i) Since the combination of sulphur monochloride and chlorine is extremely slow at atmospheric temperatures, the first dissociation is probably also slow; the chlorination is, however, known to be catalysed by sulphur tetrachloride, which must therefore also act as a catalyst for the dissociation.

(ii) On the other hand, since sulphur tetrachloride acts as a carrier of chlorine in the chlorination of sulphur monochloride, its interaction with that compound is probably very rapid even at low temperatures (compare $SCl_2 + Cl_2 \rightleftharpoons SCl_4$ which takes place immediately at −75°); moreover, since the dissociation of the dichloride proceeds so far that sulphur tetrachloride actually separates as the solid phase on freezing, this reverse process evidently proceeds with similar speed, so that the second dissociation must be quite rapid.

On this simple basis, we can explain the anomalies now recorded in the f. p.'s of the chlorides of sulphur. In particular, the fact that *sulphur dichloride* separates as the solid phase from a freshly prepared mixture of two liquids, which deposit *sulphur monochloride* and *sulphur tetrachloride* respectively when frozen, is a clear indication that a large yield of the dichloride must have been produced by a rapid interaction of these two compounds, thus:

$S_2Cl_2 + SCl_4 = 3SCl_2$. Moreover, since the f. p., after rising when the two chlorides are mixed, falls again after they have aged, it is clear that the *rapid* reaction by which sulphur dichloride is *produced*, is followed by a *slow* reaction by which it is *destroyed*. This destruction probably depends on a slow dissociation of the excess of sulphur dichloride into monochloride and chlorine according to the equation $2SCl_2 = S_2Cl_2 + Cl_2$; but we are not in a position to assert that this simple and very plausible explanation is in fact correct.

Summary.

(*a*) Samples of sulphur chloride, which have been heated to 100° in sealed tubes in order to bring about a condition of equilibrium, give a f.-p. curve which exhibits not only the familiar maxima due to the crystallisation of S_2Cl_2 and SCl_4, but also two well-defined breaks which are attributed to the crystallisation of SCl_2 and of a *trisulphur tetrachloride*, S_3Cl_4, which has not been prepared previously. The molecular structure of these compounds will be discussed in a subsequent paper.

(*b*) Although an equilibrium mixture having the composition of sulphur dichloride deposits sulphur tetrachloride on freezing, freshly prepared mixtures of sulphur monochloride with an over-chlorinated sample of sulphur dichloride exhibit a maximum f. p. at the composition SCl_2, which disappears when the mixture is brought to a condition of equilibrium. This is attributed to a rapid production of sulphur dichloride, followed by a slower process of destruction, perhaps $S_2Cl_2 + SCl_4 = 3SCl_2$ and $2SCl_2 = S_2Cl_2 + Cl_2$.

(*c*) Sulphur dichloride has been frozen out from mixtures freshly prepared as under (*b*), and has been recrystallised from light petroleum by cooling the solution with liquid air.

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