XLIV.—*The Properties of the Chlorides of Sulphur. Part V. Metastable States.*

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THE most striking evidence of metastable states in the chlorides of sulphur is to be found in the fact that Aten (*Z. physikal. Chem.*, 1905, **54**, 55) was able to plot a complete freezing-point curve for uncombined mixtures of sulphur monochloride and chlorine, and that in a preceding paper (J., 1930, 1005) we were able to record similar measurements of the densities, surface tensions, and parachors of yellow mixtures in which the red colour of the dichloride had not yet begun to appear.

The interaction of sulphur monochloride with chlorine in these metastable systems can be accelerated by the use of catalysts, such as charcoal (Pope and Heycock, B.P. 142879; *A.*, 1920, ii, 484), antimony pentachloride (Bothamley, *Trans. Faraday Soc.*, 1928, **24**, 47), and iodine, all of which have been proposed for use in the preparation of sulphur dichloride; but these are not essential, since in practice the autocatalysis of the action by the products appears to be sufficient. Thus, in Aten's dilatometric experiments it appeared that the period of induction in glass vessels, which could normally be prolonged to about 3 hours, was reduced to a few minutes when a little chlorine had been added in advance to the sulphur monochloride, and disappeared altogether when some of the sulphur monochloride was added in advance to the liquid chlorine.

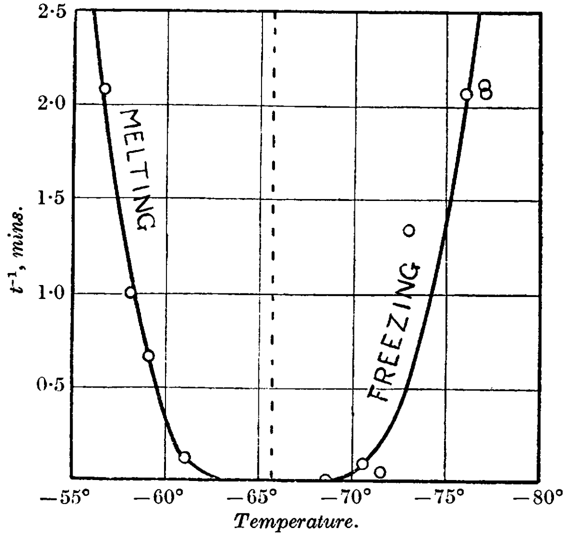
Aten attributed the milder catalysis to sulphur dichloride and the stronger catalysis to sulphur tetrachloride. The experiments described in the preceding papers of this series have disclosed, however, the presence of only *one* intermediate chloride in the liquid state, *viz.*, sulphur dichloride. On this basis it would be difficult to account for the difference between the catalytic activities of the products formed in the presence of an excess of sulphur monochloride and of chlorine respectively. We are, however, by no means convinced that the liquid chlorides of sulphur may not contain *traces* of *all* the compounds which can be frozen out from them in the solid state. If this be admitted, the observations on autocatalysis can be interpreted by supposing that the non-polar dichloro-compounds, Cl·Cl, Cl·S·Cl, Cl·S·S·Cl, are all inert (like ethylene and chlorine, Norrish, J., 1926, 55) except when placed in a polar environment, and that this can be provided by the two tetrachlorides, SCl_4 and S_3Cl_4, to both of which a polar structure may be assigned, *viz.*, $[\mathrm{Cl{\cdot}\overset{+}{S}Cl{\cdot}Cl}]\overset{-}{\mathrm{Cl}}$ and $[\mathrm{ClS{\cdot}\overset{+}{S}Cl{\cdot}SCl}]\overset{-}{\mathrm{Cl}}$.

In striking contrast to the reluctant interaction of sulphur monochloride and chlorine is the instantaneous separation of solid sulphur tetrachloride when liquid sulphur dichloride and liquid chlorine are mixed even at temperatures as low as — 75°, as observed by Beckmann (*Z. physikal. Chem.*, 1909, **65**, 289) and confirmed by the experiments described below. This interaction (which does not involve the rupture of a bond between two sulphur atoms or between a sulphur and a chlorine atom) is perhaps adequately catalysed by traces of the two tetrachlorides, formed as minor products of dissociation of liquid sulphur dichloride, $4SCl_2 \rightleftharpoons S_3Cl_4 + SCl_4$.

Freezing Points of Metastable Systems.—In addition to Aten's freezing-point curve for uncombined mixtures of sulphur monochloride and chlorine, attention may be directed to the curve for metastable mixtures of sulphur monochloride with an over-chlorinated sample of sulphur dichloride, as recorded in Part I of the present series (J., 1927, 751 ; Fig. 1, curve *a*). This curve was remarkable in showing an initial separation of sulphur dichloride over a wide range of compositions, including that of the dichloride itself, whereas the equilibrium mixture only deposited the dichloride over a narrow range from 59 to 65 atoms %, and actually deposited the tetrachloride when the mixture had the exact composition of the dichloride.

During preparations for the repetition of these earlier observations, the more important discovery was made of a lag in the freezing and melting of an equilibrium mixture having the composition of sulphur dichloride. The curve, reproduced in Fig. 1, which shows the rate of melting and freezing at temperatures above and below the true melting or freezing point, is similar in form to the catalytic catenaries plotted by Dawson and his colleagues, but bears a more striking resemblance to the curve which shows the rate of reciprocal transformation of the two polymorphic forms of ammonium nitrate at temperatures above and below the transition point at 32° (Early and Lowry, J., 1919, **115**, 1399). In each case there is a considerable range of temperatures within which the transformation is either very slow or is entirely suspended. In the present instance this extends from — 63° to — 69°. Beyond these limits the transformation proceeds with rapidly increasing velocity; but, in spite of the widely different character of the processes of freezing and melting (one of which requires, for instance, the presence of nuclei and the other not), the curve is symmetrical, like the curve for the interconversion of the two solid forms of ammonium nitrate, where nuclei are obviously needed for both transformations. The true melting and freezing point of the system can therefore be deduced, like the transition point of ammonium nitrate, by drawing a rectilinear diameter to the curve, which cuts the axis of zero velocity at — 66°.

FIG. 1.



The phase-rule diagram shows that the solid which separates is not the dichloride but the tetrachloride, although this is not present in substantial quantities in the liquid phase at atmospheric temperatures. Since, however, it is precipitated instantly from a mixture of sulphur dichloride and chlorine at — 80°, it is unlikely that the chemical reaction involved in its formation can be responsible for the lag described above.

Changes of Density in Metastable Systems.—In order to detect a possible displacement of equilibrium with change of temperature, a liquid having the composition of sulphur dichloride was sealed up with a silica float having a flotation temperature near 0°. The liquid was heated at 100° for a period of 1—3 hours, and quenched quickly to 0°. Its density was then determined by means of its flotation temperature and was found in three experiments to be *less* by 0·00140, 0·00143, 0·00142 than the equilibrium density at 0°. The density at 0° of a sample which had been heated to 56° and quenched was 0·00083 less than its equilibrium density at 0° ; after storage at 15°, its density at 0° was 0·00015 less than the equilibrium density. It has, however, already been shown that the combination of sulphur monochloride and chlorine is accompanied by an increase of density from 1·64404 to 1·65662 (J., 1930, 1008), *i.e.*, of 0·01258 at 0°. If the liquid were brought to equilibrium at room temperature (15°) this increase of density at 0° would (as shown above) be 0·00015 less. Since the equilibrium concentration at room temperature is 84% SCl_2 (J., 1929, 1428), each 1% of combination must increase the density at 0° of the mixture by (0·01258 — 0·00015) ÷ 84 = 0·000148. From these results we can at once deduce the equilibrium proportions as 85% of SCl_2 at 0° and 75% at 100°.

Whilst no claim for precise accuracy can be made for these figures, they appear to be of real value as a first attempt at a numerical estimate of quantities that have hitherto been entirely unknown. The concordance of the three numbers deduced for the change of density at 0° after heating at 100° suggests, however, that the numbers now put forward may approximate to the correct values.

EXPERIMENTAL.

Experiments on the Combination of Sulphur Monochloride with Chlorine.—The velocity of combination of sulphur monochloride and chlorine, with and without a catalyst, was studied with the help of a glass apparatus in which a known quantity of sulphur monochloride was shaken with the gas, and the volume of chlorine absorbed was shown by displacement from a graduated tube in which it was stored over concentrated sulphuric acid. It was found that, when the flask containing the monochloride was surrounded with a bath of iced water, saturation was reached when the mixture contained 53·3 atoms % of chlorine. No further absorption then took place during a " period of induction " of above 2 hours. The absorption then became rapid and the yellow liquid became red.

When iodine was added to the sulphur monochloride at a concentration of 0·1 mg. per c.c., it eliminated the period of induction completely and caused an immediate rapid absorption of chlorine at 0°. Antimony pentachloride at a concentration of 1·4 mg. per c.c. only reduced the period of induction to 10 minutes, but the subsequent absorption of chlorine was similar to that observed with iodine at a concentration of 0·1 mg. per c.c.

Qualitative observations were made of the length of the period of induction which elapsed before the red colour of the dichloride began to appear at different temperatures in yellow mixtures of sulphur monochloride and chlorine, which had been enclosed in sealed tubes and kept in the dark. Observations were also made of the time then required for the red colour to develop to about one-half of its maximum intensity. The times thus observed were roughly as follows:

Temp.	15°	50°	80°
Period of induction	150 mins.	Few mins.	None.
Half-change period	45 mins.	15 mins.	80 mins.

These results can be explained if we suppose that temperature has a two-fold effect, *viz.*, (i) to increase the velocity of interaction and (ii) to decrease the stability of the autocatalyst.

Experiments on the Instantaneous Equilibrium between Sulphur Tetrachloride and its Products of Dissociation.—Chlorine was condensed with the help of liquid air on to solid dull-yellow sulphur dichloride. A thin layer of whitish solid was formed immediately at the interface, and was identified as sulphur tetrachloride by the fact that it only melted completely at − 30° to − 40°. A white precipitate was also formed immediately when chlorine was passed into a solution of sulphur dichloride in hydrogen chloride at a temperature just below its boiling point at − 83°. The combination of sulphur dichloride and chlorine, $SCl_2 + Cl_2 \longrightarrow SCl_4$ (solid), is therefore instantaneous even at temperatures as low as − 80°.

In order to obtain information as to the velocity of the reverse change, $SCl_4 \longrightarrow SCl_2 + Cl_2$, the density of an equilibrium mixture, containing about 90 atoms % of chlorine, was determined by the flotation method. The liquid was then frozen with liquid air, giving rise (as the freezing-point diagram shows) to a mixture of solid sulphur tetrachloride and solid chlorine. After freezing, the mixture was warmed to about − 20°, and its density again determined. The flotation temperature was the same, within less than the recognised experimental error at these low temperatures, *i.e.*, 0·1°. The tetrachloride formed on freezing had therefore dissociated again to the same equilibrium mixture as before, although the temperature had not been allowed to rise above − 20°.

Experiments on the Melting Points and Freezing Points of Metastable Systems.—The experiments were made with a liquid having the composition of sulphur dichloride. This was cooled to a temperature a little below its true freezing point, at − 66°, as deduced by the method described below. After inoculation with a little of the solid, the liquid was maintained at constant temperature and stirred vigorously. As a measure of the rate of freezing, the time was noted which elapsed before one of the thermocouple junctions in the liquid became invisible. Conversely, the rate of melting, at temperatures above — 66°, was measured by the time which elapsed between the first visibility of this junction and the final clearing of the liquid. The results of a typical series of observations are set out in Fig. 1, in which the reciprocal of the time interval is plotted against the temperature of melting or freezing.

The quantity of solid which separated or melted in these experiments was small. Since the liberation of latent heat is insufficient to develop an inflexion in a cooling curve, even when the quantity of solid which separates is large, the problem of heat transference was evidently unimportant in the well-stirred liquid; and the presence of finely divided solid was sufficient to guard against supersaturation.

Flotation temperatures.

Sample 1. Made with charcoal catalyst and filtered.

Heat treatment.	Flotation temp.	Density.	Decrease of density.
Kept at 0° over-night	+0·950°	1·65749	0
Heated at 100° for 3 hours and quenched	[+0·17]*	1·65609	0·00140
0·5 hours at 0°	+0·22	1·65618	
1·0 ,, ,, ...	+0·27	1·65627	
2·0 ,, ,, ...	+0·36	1·65643	
2·5 ,, ,, ...	+0·405	1·65651	
22 ,, ,, ...	+0·905	1·65741	
Heated at 100° for 2 hours and quenched	[+0·17]*	1·65609	0·00140
0·25 hours at 0°......................	+0·18	1·65610	
0·5 ,, ,, ...	+0·21	1·65616	
1·0 ,, ,, ...	+0·27	1·65627	
1·5 ,, ,, ...	+0·315	1·65635	
Heated at 56° for 5 hours and quenched	[+0·49]	1·65666	0·00083
0·25 hours at 0°......................	+0·505	1·65669	
0·5 ,, ,, ...	+0·515	1·65671	
1·0 ,, ,, ...	+0·55	1·65677	
Sample 2. Made without a catalyst.			
Kept at room temperature (15°) ...	+0·515	1·65671	0·00015
Heated at 100° for 1 hour	[−0·19]*	1·65544	0·00142
0·25 hours at 0°......................	−0·16	1·65549	
0·5 ,, ,, ...	−0·125	1·65556	
1·0 ,, ,, ...	−0·075	1·65564	
1·5 ,, ,, ...	−0·030	1·65573	
1·7 ,, ,, ...	−0·015	1·65575	
2·3 ,, ,, ...	+0·035	1·65584	
2·8 ,, ,, ...	+0·055	1·65588	
3·5 ,, ,, ...	+0·125	1·65600	
Kept at 0° for several days	+0·600	1·65686	0

* By extrapolation.

Experiments on Changes of Density in Metastable Systems.—The experiments were made with two samples having the approximate composition of sulphur dichloride. The first was prepared with the help of charcoal as a catalyst and was filtered before use; and the second was prepared without the addition of a catalyst. The densities, before and after heat-treatment in a sealed tube, were determined at temperatures between — 0·2° and + 0·9° by means of a silica float having a density of 1·65578. The change of density of the liquid at equilibrium had already been found (J., 1930, 1005) to be 0·00180 per degree for temperatures near to 0°.

The experimental results are set out in the table, which shows the observed flotation temperatures and the densities deduced from them. It also shows the changes of density which were produced by heat-treatment at 0°, 15°, 56°, and 100°, as deduced from densities extrapolated to zero time. By combining these data with the value already deduced for the equilibrium concentration at 15°, values can be deduced for the equilibrium concentrations at 0°, 56°, and 100°. By plotting the densities against the time, information could also be obtained as to the velocity with which equilibrium is restored at 0° after heating to some higher temperature; but the time during which observations were made was too short to justify any deductions as to the form of the curve or the velocity coefficient at 0°.

Summary and Conclusions.

(*a*) The period of induction in the combination of sulphur monochloride with chlorine can be eliminated or reduced by catalysts such as iodine and antimony pentachloride or by autocatalysis. The fact that mixtures rich in chlorine are better autocatalysts than mixtures rich in sulphur monochloride can be explained by attributing the catalysis to traces of the two tetrachlorides SCl_4 and S_3Cl_4.

(*b*) The combination of sulphur dichloride and chlorine to form solid sulphur tetrachloride is instantaneous even at — 80°, and no lag can be detected in the restoration of equilibrium when the tetrachloride is melted at temperatures below — 20°.

(*c*) The freezing and melting of sulphur tetrachloride in a well-stirred sample of sulphur dichloride is accompanied by a lag, which varies with the temperature in the same way as the lag in the reciprocal transformation of two forms of ammonium nitrate on either side of the transition temperature at 32°.

(*d*) A displacement with temperature of the equilibrium concentrations in samples of sulphur dichloride has been established by observations of density by the flotation method. From these data it has been deduced that the degree of dissociation increases from about 15% at 0° to about 25% at 100°.

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