29. *Freezing Points of the System Hydrogen Chloride–Sulphur Monochloride.*

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THE chlorides of many elements, including sulphur, give complex compounds with metallic chlorides. Most of the known sulphur chloride complexes are derived from the dichloride and tetrachloride, but Ruff and Golla (*Z. anorg. Chem.*, 1924, **138**, 17) have described a compound, $AlCl_3,2S_2Cl_2$, derived from the monochloride.

Since in the case of many elements these compounds possess the character of complex salts, and in several cases the corresponding acids are also known, it appeared to be of interest to investigate the possibility of compound formation between hydrogen chloride and sulphur monochloride.

EXPERIMENTAL.

Materials.—Sulphur monochloride, supplied by Hopkin and Williams, was redistilled three times from 1% of freshly ignited charcoal in an all-glass apparatus under a pressure of 20—25 mm. Lowry, McHatton, and Jones (J., 1927, 746) recommend the addition of 1% of sulphur, but this was found to result in deposition of sulphur in the condenser, the deposit being washed down into the receiver by later portions of the distillate. This procedure was therefore abandoned, but it may be remarked that the sample of sulphur chloride appeared already to contain excess of sulphur. The sulphur chloride was again redistilled during the course of the work either when its colour indicated that it was becoming rich in sulphur or when it was found that sulphur was deposited in the tubes in the course of a freezing-point determination.

The redistilled substance was analysed by taking two samples of about 1—1·5 g. by means of Lunge–Rey pipettes, the caps of which were enlarged to form small flasks in which 10 c.c. of a 35% solution of pure sodium hydroxide (prepared from sodium) were placed. This allowed the hydrolysis of the sulphur chloride to be carried out before the weighing. Chlorine was determined in one sample by the Volhard method, and sulphur as barium sulphate in the other (Found: S, 48·04; Cl, 51·94; total, 99·98. Calc.: S, 47·49; Cl, 52·51%). It appears to be impossible to remove the whole of the excess sulphur by redistillation.

The freezing point of the sulphur chloride so purified was found to be − 76·5°. That of pure sulphur chloride is stated by Beckmann, Junker, and Klopfer (*Z. physikal. Chem.*, 1909, **65**, 289) to be − 75° to − 76°. Aten (*ibid.*, 1906, **54**, 55) gives − 80°, and Lowry, McHatton, and Jones (*loc. cit.*) find − 79°.

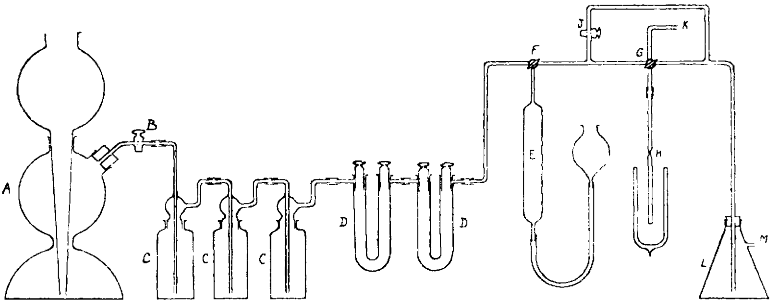
Hydrogen chloride was generated in the Kipp's apparatus (*A*, Fig. 1) by the action of sulphuric acid on fused ammonium chloride, and dried by passing through three spiral wash-bottles (*C*) containing concentrated sulphuric acid, and then over a layer of phosphoric oxide in the U-tubes (*D*), which were clamped in a horizontal position.

The freezing point of the hydrogen chloride thus dried was − 110°; Rupert (*J. Amer. Chem. Soc.*, 1909, **31**, 851) gives − 111°, and states that the presence of 0·5% of moisture is sufficient to cause separation into two layers, both of which are solid below − 15·5°.

Preparation of Mixtures.—The method of preparing mixtures and of determining their freezing points was based on that used by Rupert (*loc. cit.*). Tubes of Durosil, of 2 mm. bore, 2 mm. walls, and 20 cm. length, were sealed at one end and constricted about 5 cm. from the other. These were dried by heating for 30 hours at 170—180°, air dried by sulphuric acid and phosphoric oxide being blown into them throughout.

The tube to be filled was weighed, a small quantity of sulphur chloride introduced through a capillary funnel, and the whole rapidly weighed again. The tube was then immediately connected to the hydrogen chloride apparatus and immersed in liquid air. After introduction of hydrogen chloride and sealing, the tube was weighed a third time together with the piece sealed off, and the composition calculated from the weighings.

Fig. 1.



The hydrogen chloride, dried as already described, was introduced by means of the apparatus shown in Fig. 1. The three-way tap *F* allowed the gas reservoir *E* to be connected to the generator for filling or to the tube *H* into which it was desired to pass the gas, and also allowed connection to be made straight through when it was necessary to remove air from the whole apparatus. *G* was a four-way tap by means of which the tube *H* could be connected to the gas supply or to the pump, or through which dry air could be admitted to the apparatus, the side tube *K* being connected to a Drechsel bottle containing sulphuric acid for this purpose. The tap *J* and the side tube containing it were provided in order that the whole apparatus could be evacuated back to the tap *B*. *L* was a trap-flask containing sulphuric acid to prevent the entry of vapour from the water pump, which was connected to the tube *M*. All rubber joints were made of thick-walled tubing specially made from pure sheet rubber, bound with tape and wired. The ends of the glass tubes were in each case brought as nearly as possible butt to butt.

Before each day's work, the whole apparatus was evacuated and allowed to fill slowly with hydrogen chloride. This was repeated twice in order, as far as possible, to remove all the air before the weighed tube was connected to the apparatus. When the tube was in position, the level of the Dewar vessel was adjusted so that the sulphur chloride was just below the surface of the liquid air. After allowing time for the sulphur chloride to freeze, the tap *G* was turned so as to connect the tube to the pump, whereby the air was rapidly removed from it. The tube was then connected to the gas reservoir *E*, and by raising the mercury reservoir and very gradually raising the liquid air bath, hydrogen chloride could then be easily condensed in the tube to the solid form, the gas reservoir providing a means of estimating roughly the amount introduced. The presence of air in any quantity interfered with this process and might even interrupt it completely. When this occurred, the tube *H* was momentarily connected to the pump and then reconnected to the gas reservoir, after which condensation would again proceed smoothly.

When sufficient hydrogen chloride had been introduced, the tube was connected to the pump and sealed at the constriction. It was then removed from the apparatus and allowed to attain room temperature before the final weighing.

Determination of Freezing Points.—Two series of observations were made, the procedure being improved before the second set was commenced. In both series the prepared tubes were immersed in a bath of alcohol (95%) contained in a clear glass Dewar vessel and stirred electrically, the temperature being observed by means of a pentane thermometer. The bath was cooled by spraying liquid air directly into the alcohol, and this was continued as rapidly as possible until the neighbourhood of the expected freezing point was reached, and then more slowly until crystals appeared.

With the tubes of experiments in series A, the temperature was then regulated so that, with only a small quantity of solid in the tube, the crystals could be kept for five minutes without either increasing in size or becoming rounded at the edges and decreasing. In some cases a tendency to supercooling was noticed; in these, crystallisation could be started by removing the tube from the bath, shaking it vigorously, and dipping the end in liquid air. The tube was then held above the vessel until the solid produced had almost completely melted, whereupon it was returned to the bath at a temperature near the freezing point expected, and the adjustment of the temperature carried out as already described.

The tubes in series D were provided with an internal stirring device, consisting of a small piece of iron wire sealed in capillary tubing, which was introduced into the tubes before drying. This device was kept in motion during a determination by means of a small solenoid which surrounded the tube and was moved up and down by means of a crank. This was generally sufficient to prevent supercooling, and it was found that, provided the cooling of the bath was slow, the crystals appeared sharply at a reproducible temperature, which was taken as the freezing point. It will be seen that results obtained by the two methods are in fair agreement.

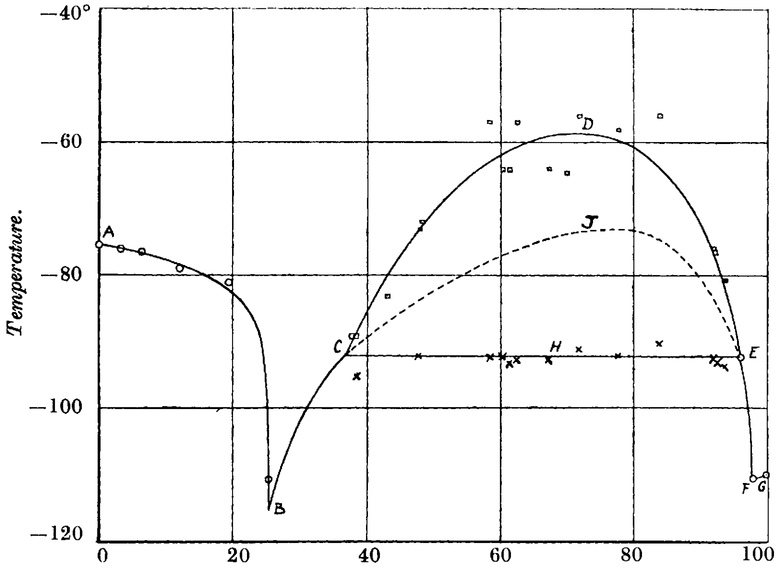
Over a considerable range of compositions, the mixtures separate at low temperatures into two layers, and on further cooling the amount of separation increases. Throughout this range the crystallisation of the upper layer commences at a constant temperature, and at the same time the walls of that part of the tube containing the lower layer are covered by an opaque deposit, but it is not possible to determine by inspection whether this consists of minute crystals or droplets of liquid. These freezing points are believed to be accurate within one degree, it being possible to keep the temperature constant and to obtain reproducible results well within that limit.

An attempt has also been made to determine the highest temperatures at which separation into two layers takes place. This, however, is a matter of some difficulty and considerable inaccuracies may arise. In series A, the method employed was to allow the bath to warm gradually and note the highest temperature at which a turbidity appeared after removing the tube from the bath and shaking it. In series D, the appearance of turbidity was noted as the bath was being cooled. As this phenomenon is not so sharp as crystallisation, and as, especially in the method used with series A, considerable differences in temperature may exist between the contents of the tube and the bath, too great reliance cannot be placed on these results. In fact, the same reproducibility was not found here as in the freezing points, and the temperatures given in the table are usually means of two or three observations.

Attempts were made to obtain the eutectic temperatures by finding the temperatures at which the contents of a few of the tubes became completely solid. It is very difficult to work the bath at temperatures below − 110°, as the alcohol becomes extremely viscous, preventing both efficient stirring and clear vision of the tube. No concordant values were therefore obtained. For the eutectic on the sulphur chloride side, values varying between − 110° and − 130° have been observed, but the most probable, on account of the relative ease with which it was obtained, is − 119°

obtained from tube D11. It is not claimed, however, that this is more than an approximation, but it is suggested that the results from this tube establish definitely the existence of a eutectic in this neighbourhood. The eutectic on the hydrogen chloride side was sought only in one of the tubes which froze without separation of layers, A28, and this gave the value − 112°. It is noteworthy that the upper layer of tube D8 became completely solid at the same temperature.

FIG. 2.



ABC, EFG.—*Freezing points of homogeneous mixtures.*
CDE.—*Temperature of separation into two layers.*
CHE.—*Freezing points of upper layers.*
CJE.—*Hypothetical curve showing results expected if no separation into layers occurred.*

The results are set out in Tables I and II and represented graphically in Fig. 2.

TABLE I.

Freezing points of mixtures which do not separate into two layers.

	Composition, mols. %.				Composition, mols. %.		
Tube.	S_2Cl_2.	HCl.	F. p.	Tube.	S_2Cl_2.	HCl.	F. p
A2	100·0	0·0	−76·5°	D11	74·6	25·4	−110·5°
A4	96·4	3·6	−77·0	A26	3·9	96·1	− 92·0
	93·7	6·3	−77·5	A28	2·2	97·8	−110·5
A8	88·2	11·8	−79·0	A1	0·0	100·0	−110·0
A3	80·6	19·4	−81·0				

TABLE II.

Observations on tubes in which separation into two liquid phases takes place.

Tube.	Composition, mols. %. S_2Cl_2.	HCl.	Temp. of septn.	F. p. of upper layer.
D15	62·4	37·6	−89·0°	(*a*)
D4	61·7	38·3	−89·0	−95·0°
A7	57·0	43·0	−83·0	(*a*)
D7	52·2	47·8	−73·0	−92·0
D5	52·0	48·0	−72·0	(*a*)
A18	41·7	58·3	−57·0	−92·0
D13	39·6	60·4	−64·0	−92·0
D10	38·6	61·4	−64·0	−93·0
A12	37·7	62·3	−57·0	−92·5
D8	32·6	67·4	−64·0°	−92·5°
D12	30·0	70·0	−64·5	−93·0
A16	28·3	71·7	−56·0	−91·0
A11	22·4	77·6	−58·0	−92·0
A17	14·1	83·9	−56·0	−90·0
A13	7·9	92·1	−76·0	−92·5
A27	7·6	92·4	−76·5	−93·0
A30	6·3	93·7	−80·5	−93·5

(*a*) Freezing points not determined owing to the small volume of the upper layer.

Discussion.

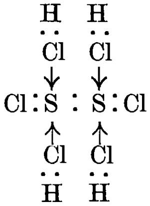
It is suggested as a probable explanation of these results that sulphur monochloride and hydrogen chloride form a compound which is miscible with its components to a limited extent only at low temperatures, and has therefore an incongruent melting point.

It will be seen from the diagram that addition of hydrogen chloride to sulphur chloride depresses the freezing point until the point *B* is reached. Beyond that point, the temperature of freezing rises until, at *C*, separation into two liquid phases commences. Beyond the point *E*, the freezing point again falls to a second eutectic at *F* and then rises to the freezing point of pure hydrogen chloride, *G*.

The occurrence of the two eutectics seems to be convincing evidence that the solid which separates from the upper layer is a compound of sulphur chloride and hydrogen chloride. Additional indications are to be found in the following facts : (1) The substance crystallised in long transparent pale yellow needles. These differ entirely in appearance from the crystals of sulphur monochloride and of hydrogen chloride. (2) Some of the tubes which were prepared burst during the warming to room temperature, and when this occurred a slightly sweetish odour was noticed, differing completely from that of hydrogen chloride or sulphur monochloride.

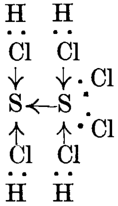
On these grounds, the dotted curve in Fig. 2 has been constructed as an indication of what might be expected if no separation of liquid phases took place. It is not possible from the experimental evidence to draw any conclusion as to the composition of the compound, but the maximum of this hypothetical curve has been placed at 80 mols. % of hydrogen chloride on account of the following valency considerations.

The formation of the compound would seem to depend on the power possessed by the sulphur atom to expand its valency octet to a twelve-membered ring. This can only take place by the sharing of lone pairs from the chlorine atoms of hydrogen chloride, *i.e.*, by co-ordination. In that case, each sulphur atom can receive only four more electrons, and can therefore co-ordinate only two molecules of hydrogen chloride, giving as the saturated compound $S_2Cl_2,4HCl$, which may be



$$\begin{array}{rcccl} & \mathrm{H} & & \mathrm{H} & \\ & \cdot\cdot & & \cdot\cdot & \\ & \mathrm{Cl} & & \mathrm{Cl} & \\ & \downarrow & & \downarrow & \\ \mathrm{Cl}{:} & \mathrm{S} & : & \mathrm{S} & {:}\mathrm{Cl} \\ & \uparrow & & \uparrow & \\ & \mathrm{Cl} & & \mathrm{Cl} & \\ & \cdot\cdot & & \cdot\cdot & \\ & \mathrm{H} & & \mathrm{H} & \end{array}$$

or



$$\begin{array}{cccl} \mathrm{H} & & \mathrm{H} & \\ \cdot\cdot & & \cdot\cdot & \\ \mathrm{Cl} & & \mathrm{Cl} & \\ \downarrow & & \downarrow & \cdot\,\mathrm{Cl} \\ \mathrm{S} & \leftarrow & \mathrm{S} & \vdots \\ \uparrow & & \uparrow & \cdot\,\mathrm{Cl} \\ \mathrm{Cl} & & \mathrm{Cl} & \\ \cdot\cdot & & \cdot\cdot & \\ \mathrm{H} & & \mathrm{H} & \end{array}$$

The possibility of the compound being less rich in hydrogen chloride cannot be excluded, but there seems to be a slight balance of probability in favour of the view that, in presence of sufficient hydrogen chloride, expansion of the octet would proceed to the limit.

Sulphur monochloride and hydrogen chloride are both generally regarded as covalent compounds. The separation of two liquid phases may therefore imply that a polar compound is produced. This polarity may arise simply from the co-ordination or may correspond to a definite ionisation $[S_2Cl_6]^{----}H_4^{++++}$.

Summary.

1. The freezing points of mixtures of sulphur monochloride and hydrogen chloride have been determined.
2. Mixtures containing between 35 and 95 mols. % of hydrogen chloride separate on cooling into two layers, of which the upper freezes at the same temperature (— 92·5°) whatever the total composition of the mixture.
3. It is suggested that the upper layer contains a compound of sulphur chloride and hydrogen chloride which is practically immiscible with its components at low temperatures.
4. This compound may be $H_4S_2Cl_6$, and is possibly polar.

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