CVI.—*The Properties of the Chlorides of Sulphur. Part III. Dielectric Constants.*

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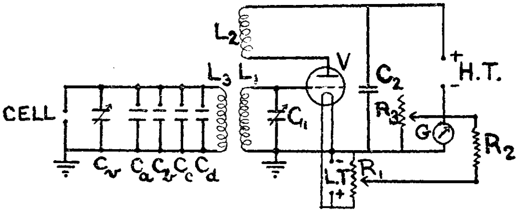
IN the two preceding papers of this series (J., 1927, 746; 1929, 1421), it has been shown (i) that sulphur dichloride, SCl_2, crystallises as a stable phase from a liquid chloride of sulphur containing from 59 to 65 atoms % of chlorine, and a new chloride, S_3Cl_4, separates in the range 57—59 atoms %; (ii) that sulphur dichloride in the liquid state is dissociated at atmospheric temperatures to the extent of about 16% according to the equation $2SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2$; (iii) that sulphur tetrachloride, SCl_4, which is the stable solid phase over a wide range of compositions above 65 atoms % of chlorine, cannot be detected in the liquid phase; and (iv) that a liquid chloride of sulphur therefore behaves as a ternary mixture of mono- and di-chlorides and chlorine only. In the present paper these results have been confirmed by measurements of the dielectric constants of a series of samples ranging from sulphur monochloride to pure chlorine, which show that sulphur tetrachloride is stable in the solid phase, but cannot be detected in the liquid phase.

EXPERIMENTAL.

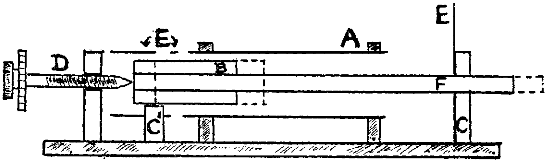
Methods.—The apparatus used for the measurement of dielectric constants (compare Sayce and Briscoe, J., 1925, **127**, 315) is shown in Fig. 1. It employs a valve generating circuit, but does not appear to be open to the objections which have been raised by many authors to such circuits. The stress applied to the dielectric must be small and of sine-wave form, without the harmonics of considerable amplitude which are found in most valve-operated circuits; and the apparent value of the capacity must not vary when the liquid shows a small conductivity. In the present apparatus these conditions are fulfilled in view of the fact that the circuit which contains the dielectric is not coupled directly to the valve; and experimental tests have shown that the introduction of a high resistance in parallel with the condenser merely reduces the accuracy of the measurement, without altering the absolute value of the constant. The main difficulties were (i) to construct a condenser of large capacity (150 cm.) which could be adjusted with great accuracy (within 0·01 cm.), and (ii) to construct a cell, which would hold only a small volume (5—10 c.c.) of a corrosive liquid, but could withstand an internal pressure of 1—2 atm., and be used at any temperature from — 100° to 25°.

FIG. 1.



Apparatus for measuring dielectric constants.

FIG. 2.

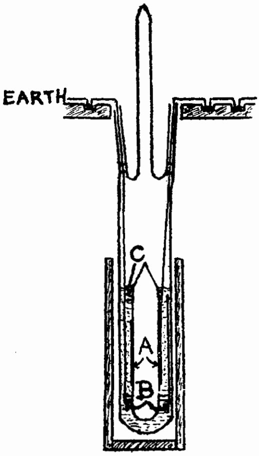


Variable condenser.

(a) *Condensers.* The condenser of variable capacity and wide range included four fixed condensers, C_a to C_d, having capacities of about 10, 20, 40, and 80 cm. respectively, and a variable condenser, C_v, with a capacity of about 15 cm. The fixed condensers were made from air-spaced aluminium plates mounted on ebonite. One set of plates was connected to the earthed lining of the box containing the apparatus, and the other to small mercury cups which could be connected to the "live" side of the circuit by means of wire bridges operated from the outside of this box. The variable condenser, C_v, was cylindrical, as shown in Fig. 2, whereas Sayce and

Briscoe used a rotating-plate condenser. The " live " side was a fixed brass tube, A, mounted on ebonite blocks. The earthed plate was formed by an accurately turned brass cylinder, B, attached to a rod F, and was mounted on two rigid bearings, C and C′, the latter, carrying the tube B, being V-shaped. The air gap between A and B was about 1 mm. The capacity of the condenser was varied with the help of a fine screw, D, against the point of which the end of the inner cylinder was pressed by a spring, which is not shown in the diagram. " End effects " were prevented by means of earthed guards, E. The condenser, which was used over a small range only, as shown by the dotted lines, was calibrated against a small fixed condenser, and it was found that the variation of capacity was proportional to the rotation of the divided head of the screw D over the entire working range.

FIG. 3.



Dielectric-constant cell.

FIG. 4.

Conductivity cell.

(b) *Cell.* The type generally used is shown in Fig. 3. The inner plate of the condenser consisted of a cylinder, A, of platinum foil, which was kept in shape by being mounted on a short closed glass tube. Surrounding this, and separated from it by a gap of about 1 mm., was a stout platinum cylinder, B, which formed the outer plate of the condenser. The inner tube and outer cylinder were held rigidly apart by means of small glass bridges, C. The condenser fitted loosely into a glass tube, closed at the bottom and provided at the top with a delivery tube, which could be sealed. Platinum wires from the condenser plates were led out near the top of the wide tube. Connexion with the "live" side of the circuit was made by means of a small wire bridge in mercury cups. The outer cylinder was permanently earthed.

The lower part of the cell was surrounded by a stout copper cylinder, which was earthed, and round which a Dewar flask containing liquid air could be placed. This served to hold the cell, to act as an earthed sheath, and to maintain a uniform temperature in the liquid. Temperature was measured by means of a single-junction copper–constantan thermocouple, with one junction inside the copper sheath and the other in a Dewar flask containing ice and water. The current from it was measured on a microgalvanometer which could be switched out of the valve circuit into the thermocouple circuit.

(c) *Arrangement of circuits.* Oscillatory currents were maintained in circuit L_1C_1 by means of the valve V, connected as shown. The magnitude of the direct component of the current in the anode circuit is a function of the oscillating currents in L_1C_1. If a second circuit, L_3C_3, is now coupled loosely to this, energy is withdrawn when the natural frequency of L_3C_3 is very nearly the same as that in L_1C_1. If the coupling is adjusted correctly, and the value of L_3C_3 is then altered, the anode current first falls gradually to a well-defined minimum and afterwards rises gradually again; this minimum is very sensitive to change of capacity in L_3C_3, and could be determined within about 0·02 cm. variation in the capacity of C_3.

The whole assembly of the apparatus is shown diagrammatically in Fig. 1. The cell and the battery of condensers, denoted by C_3, were connected in parallel with the inductance, L_3, which consisted of 12 well-spaced turns of No. 20 copper wire wound on an ebonite former, giving a wave-length of about 200 m. L_1 and L_2 were ordinary wireless inductances, No. 30. The variable condenser, C_1, had a maximum value of 0·0025 microfarad, and the by-pass condenser, C_2, had a value of 0·01 microfarad. G was a microgalvanometer of sensitivity about 0·5 microamp. per scale division. R_1 was a 300-ohm potentiometer, and R_2 a resistance of about 100 ohms. R_1 and R_2 were adjusted so as to neutralise the greater part of the anode current through the galvanometer. A galvanometer shunt, R_3, was added for convenience of working. The fixed condensers, C_{a-d}, were calibrated in terms of scale readings on the divided head of C_v. All the "live" parts of the apparatus, except the experimental cell, were housed in a wooden box with an earthed lining of sheet metal. In order to prevent sudden fluctuations of anode current the valve was wrapped in cotton wool, and a 6-microfarad condenser put across the terminals of the high-tension battery.

Before any measurements were made, C_1 was adjusted so that, with C_{a-d} in circuit, resonance was obtained with C_v at about the middle of its range. It then remained unaltered throughout the series of experiments. In an experiment, the resonance point was determined roughly with shunt R_3 partly in, and R_1 adjusted so that the galvanometer needle was about in the centre of the scale at the minimum point. R_3 was then taken out and the minimum found by altering C_v in each direction three times. The mean of these six readings gave the true resonance point. The experimental cell was then put in circuit and capacity removed from C_3 until resonance was again obtained as before. The capacity of the cell was equal to the capacity removed from C_3. Another set of readings was then taken to see that the zero had not altered. The change in zero was not usually more than 0·02 unit, whereas the capacity of the cell in air was of the order of 20 units.

(d) *Calibration.* Since the air between the live plate and earth is not replaced completely by liquid, the dielectric constant could not be obtained directly by measuring the ratio of the capacity of the cell when filled and when empty. The cell was therefore calibrated with carbon tetrachloride and chloroform. These liquids were carefully purified and dried; their respective dielectric constants at 25° were taken as 2·20 and 4·79 (Sayce and Briscoe, J., 1926, 2623). The observed capacities were: Air, 30·19; CCl_4, 57·62; $CHCl_3$, 120·31. These were made the basis of a calibration curve for the cell over the range of dielectric constants covered by the experiments.

Results.

The dielectric constants of sulphur chloride mixtures were measured over the range of compositions from sulphur monochloride to pure chlorine, and at temperatures from that of the room down to that at which solidification was complete. Samples containing less chlorine than the dichloride were put into the cell as equilibrium mixtures; mixtures containing more chlorine were made in the cell and left over-night to reach equilibrium. The observed values for the dielectric constants of 13 different samples at different temperatures are recorded in Table I.

Discussion of Dielectric Constants.

(*a*) The dielectric constants of the liquids, which are plotted for 5 typical compositions in Fig. 5, fall as the temperature rises, the relationship being linear in each case. The temperature coefficient, as well as the magnitude of the dielectric constant, rises progressively from chlorine to sulphur monochloride. In accordance with Debye's analysis, this implies that there is a progressive increase in

TABLE I.

Dielectric Constants at Various Temperatures.

50·0 at. % Cl.

Temp.	15·0°	−23°	−41°	−28°	−1°	10·5°	(Solid) *
ε	4·79	5·41	5·81	5·54	5·05	4·88	3·2

	53·18 at. % Cl.		54·8 at. % Cl.				
Temp.	14·0°	10·4°	11·0°	−20°	−35·5°	−15·5°	19°
ε	4·39	4·45	4·23	4·65	4·93	4·63	4·14

	58·5 at. % Cl.					63·08 at. % Cl.		
Temp.	11·0°	−16·5°	−42·5°	−12·5°	1·6°	15·9°	12·7°	15·9°
ε	3·80	4·09	4·49	4·06	3·92	3·28	3·31	3·28

	S_2Cl_2–Cl_2 mixtures after combination. 61·39 at. % Cl.	61·84 at. % Cl.	65·24 at. % Cl.				
Temp.	0°	0°	12·5°	−15°	−39·5°	−51°	0°
ε	3·61	3·55	3·13	3·34	3·53	3·69	3·27

67·35 at. % Cl.

Temp.	17°	−1°	−46°	−95°	−93°	−79°	−75°	
ε	2·96	3·04	3·41	4·58	4·60	4·41	4·36	
Temp.	−58·5°	−50°	−32·5°	−25°	−42·5°	−48°	−54°	1°
ε	3·64	3·57	3·34	3·25	3·36	3·45	3·52	3·05

71·53 at. % Cl.

Temp.	−25°	−42·5°	15·2°	13·1°	−16·8°	−46°	−11·8°	8·6°
ε	3·02	3·13	2·83	2·83	2·96	3·17	2·96	2·86

76·32 at. % Cl.

Temp.	−7°	−2·3°	8·5°	17·5°	−17°	−30°	−46°
ε	2·77	2·74	2·69	2·64	2·83	2·91	2·99
Temp.	−53·5°	−63·5°	−63°	−62°	−57°	−48°	−40°
ε	3·05	4·23	4·90	5·85	5·99	5·98	5·51
Temp.	−33°	−33°	−33°	−17°	0·4°	21·5°	
ε	4·51	4·01	3·81	2·92	2·72	2·61	

85·4 at. % Cl.

	(Solid)*	(Liquid)†
ε	5·41	2·44

Chlorine.

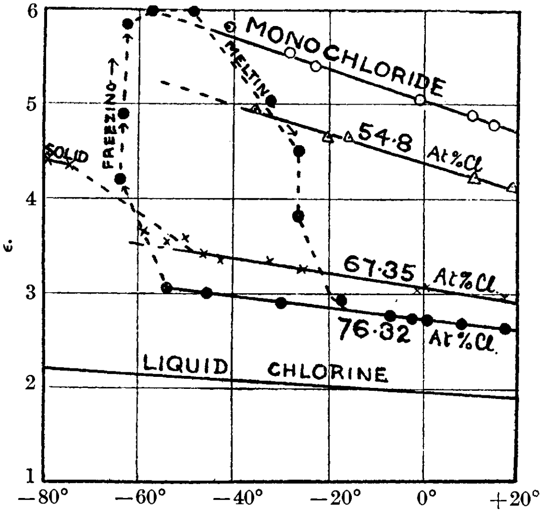
	(Solid)*	(Liquid)†	(Solid)*	(Liquid)†
ε	2·14	2·16	2·07	2·19

* Below the temperature of complete solidification.

† A few degrees above the melting point.

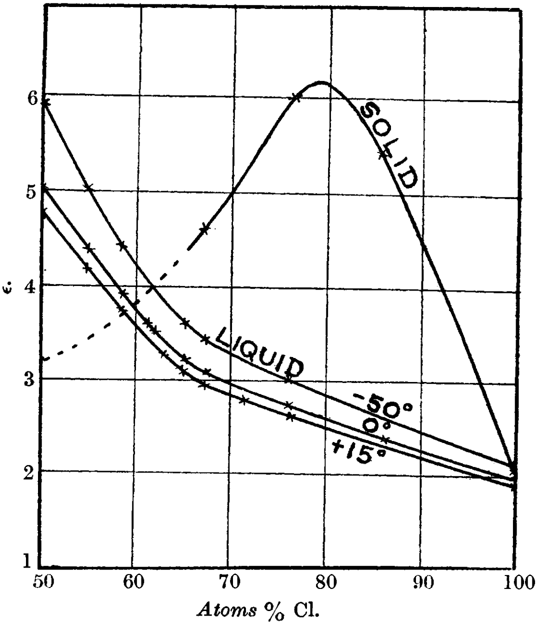
the dipole moments as well as in the polarisability of the molecule as atoms of sulphur are inserted between the chlorine atoms in the series Cl_2, SCl_2, S_2Cl_2. The curves obtained by plotting the dielectric constants against composition at three temperatures (Fig. 6) are approximately linear, but with a sharp bend at the composition of the dichloride; the absence of a complete discontinuity can be attributed, as in the case of other properties, to the dissociation of the dichloride into a ternary mixture containing also the monochloride and free chlorine. No indication was obtained, however,

Fig. 5.



Variation of dielectric constant with temperature.

Fig. 6.



Dielectric constants.

of any discontinuity or change of curvature at the composition of the tetrachloride.

(*b*) The dielectric constants of the solid, which are practically independent of the temperature, have been plotted in Fig. 6 and joined by an arbitrary curve. Three types of behaviour can be recognised.

(i) Solid chlorine, of which the dielectric constant is now recorded, apparently for the first time, has almost exactly the same dielectric constant as liquid chlorine, the average values above and below the m. p. being 2·17 and 2·10. This is interpreted as meaning that, whilst the molecules are polarisable, they have only a very small permanent dipole moment, a result in harmony with the small temperature coefficient recorded above and with other methods of estimating this quantity.

(ii) Sulphur monochloride, on the other hand, after a progressive rise from 4·7 to 5·8 as the liquid is cooled from 15° to – 50°, shows an abrupt fall from 6·4 to 3·2 when it finally solidifies. This behaviour is characteristic of liquids with a large permanent dipole moment, since water ($\varepsilon = 81$), alcohol ($\varepsilon = 62·7$), and nitrobenzene ($\varepsilon = 43·3$) show an abrupt fall on solidification to values (3·1, 2·7, and 4·1 respectively) which are comparable with those observed in non-polar liquids such as benzene (2·2) or carbon tetrachloride (2·2).

(iii) An entirely different and novel behaviour was observed in solids of intermediate composition, where a large *increase* of dielectric constant was recorded on solidification. This striking abnormality is shown clearly in the broken curve of Fig. 5, where the dielectric constant is seen to turn sharply upwards as the liquid becomes solid, and to droop again as the solid gradually melts. If we were obliged to admit that the solid had the same chemical constitution as the liquid, we should conclude that the molecules had a negative dipole moment, which is absurd. It is, however, easy to see that this anomaly reaches a maximum *at or near the composition of sulphur tetrachloride*, and must therefore be attributed to the presence of this compound in the solid phase. The proportions in which it would be present in each case cannot yet be stated, and might vary widely with the conditions of crystallisation, but the position of the maximum fixes beyond question the chemical composition of the abnormal component of the mixture. Moreover, the complete dissociation of the tetrachloride on fusion is demonstrated once more by these observations, since, if it survived in any appreciable proportion, it could scarcely fail to reproduce in the curve for the *liquid* the maximum which is so conspicuous a feature of the curve for the *solid* sulphur chlorides. Finally, it may be pointed out that the high dielectric constant (6·2) of solid sulphur tetrachloride brings it into line with *salts* such as rock-salt (6·3), sylvine (4·9), fluorspar (6·9), and ammonium chloride (7·0), whereas the solid monochloride (3·2) resembles sulphur (3·9) and chlorine (2·1) in showing the low dielectric constants usually observed in solid molecular compounds.

Since no case appears to have been established previously of a large increase in the dielectric constant of a liquid on solidification,* it is of interest to record that we have discovered an analogous case in phosphorus pentachloride, m. p. 148°, where our own observations show an increase in the dielectric constant from 2·7 for the liquid at 165° to 4·1 for the solid at 130°. As is well known, Langmuir has attributed to both compounds a salt-like structure, which would explain the high dielectric constant of the solids, but at this stage we are content merely to point out that the abnormality to which we have directed attention suggests a change of structure during the passage from the liquid to the solid state, the precise nature of which awaits investigation with the help of *X*-ray analysis.

(*c*) The dielectric polarisation, in terms of the molecular weights (M_1 and M_2) and mole-fractions (n_1 and n_2) of a mixture, can be deduced from the formula

$$p = \frac{\varepsilon - 1}{\varepsilon + 2} \frac{M_1n_1 + M_2n_2}{d}$$

We have therefore calculated the values of this function in the first instance for mixtures of sulphur dichloride (i) with monochloride and (ii) with chlorine, in such large excess that the dissociation of the dichloride would be quite insignificant. Since, however, the formula is not restricted to gases or dilute solutions, we have extended the calculations to solutions containing much larger proportions of the dichloride, and obtained results which are entirely concordant with those given by the more dilute solutions. For this purpose, the dielectric constants were first reduced by interpolation to a temperature of 0°, and were then combined with the densities at this temperature to give the dielectric polarisation of the mixtures. When these numbers are plotted against the mole-fraction of sulphur (Fig. 7), two straight lines are obtained, which intersect accurately on the boundary of the diagram. These liquids therefore obey a simple mixture rule with $p = 12$, 27, and 46 for chlorine, dichloride, and monochloride, respectively.

This result might, perhaps, have been predicted if we were certain in advance that we were dealing with a simple ternary (pseudobinary) system containing only the components shown in the

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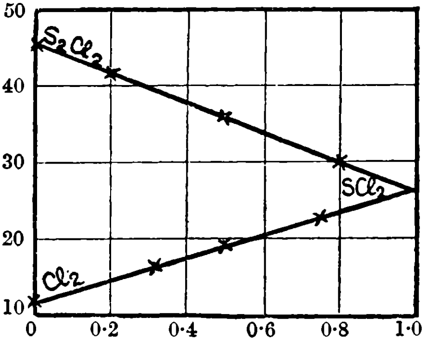
* Schlundt, *J. Physical Chem.*, 1904, **8**, 122, gives phosphorus (solid) 4·1, (supercooled liquid) 3·85 at 20°; Pirani, Diss., Berlin, 1903, gives sulphur (at f. p.) 3·98, solid (room temperature) 4·22.

equation $Cl_2 + S_2Cl_2 \rightleftharpoons 2SCl_2$. If, however, we were to postulate, with Trautz (*Z. Elektrochem.*, 1929, **35**, 110), a series of equilibria in which the tetrachloride plays an essential part, no such simple relationship could be expected. The data plotted in Fig. 7 are therefore of real importance, since they prove that the compound formed by adding a small excess of chlorine to sulphur monochloride (which might have been S_3Cl_4) and the compound formed by adding a small amount of sulphur to pure liquid chlorine (generally supposed hitherto to be SCl_4) have in fact the same constant of dielectric polarisation, and in this respect, as in others, are identical.

FIG. 7.



Mole fractions of SCl_2.
Dielectric polarisations at 0°.

Conductivities.

It is generally agreed that sulphur mono- and di-chlorides and chlorine are covalent compounds, as represented by the formulæ Cl·S·S·Cl, Cl·S·Cl, and Cl·Cl; and this formulation is confirmed by the gradation in the dielectric polarisation of the three substances. Langmuir, however, has attributed to sulphur tetrachloride a polar formula $[SCl_3]^+Cl^-$, and the electronic theory of valency suggests that a similar polar formula should be assigned to trisulphur tetrachloride, which may be formulated as $[ClS{\cdot}\overset{+}{S}Cl{\cdot}SCl]Cl^-$. Evidence of the presence of sulphur tetrachloride and justification of Langmuir's polar formula would therefore be provided simultaneously if solutions could be prepared showing a substantial electrolytic conductivity. The apparatus used to test this is shown in Fig. 4. It had a cell constant of 0·17 and was specially designed for use at low temperatures with corrosive substances easily decomposed by water.

(i) A solution of sulphur tetrachloride (*sic*) in liquid chlorine was prepared by weighing the liquid dichloride into the cell, cooling it over liquid air, and passing in an excess of chlorine. When the liquid was cooled *to a temperature at which solid sulphur tetrachloride was beginning to separate*, the conductivity of the saturated solution was found to be only 0·18 × 10^{-6} mho, *i.e.*, of the same order as that of liquid chlorine.

(ii) A solution of sulphur dichloride in liquid hydrogen chloride was prepared by weighing the liquid dichloride into the cell and condensing hydrogen chloride by cooling over liquid air. The conductivity of the solution just below its boiling point was 0·7 × 10^{-6} mho. Chlorine was then passed in until the red colour of the dichloride had disappeared completely by precipitation of the tetrachloride as a colourless solid. The conductivity of the saturated solution was then 0·65 × 10^{-6}.

These observations show that no electrolytic conductivity is developed on attempting to prepare solutions of sulphur tetrachloride in chlorine or in hydrogen chloride. This result could be interpreted as showing either (i) that the tetrachloride is a non-electrolyte in these two solvents, or (ii) that it is insoluble in, or completely dissociated by, these two solvents and is therefore precipitated quantitatively as fast as it is formed. There is no method available for distinguishing sharply between these possibilities, although the first deduction is obviously unproven in view of the failure of all attempts to detect the presence of the tetrachloride in solution. The completeness with which the tetrachloride is removed from the solutions is, however, itself an indication of a wide difference in polarity from chlorine and the mono- and di-chloride, with which it should otherwise be freely miscible, as in the case of the non-polar chlorides of carbon. A similar argument can be applied to trisulphur tetrachloride which, at temperatures below − 100°, forms two liquid layers with its products of dissociation. We can therefore only return a negative reply to any questions as to the conductivity or other similar properties of sulphur tetrachloride, since we have been unable to find any evidence of the existence of this compound in the liquid state.

Summary.

(*a*) The dielectric constants of sulphur chloride mixtures have been measured over the range of composition from monochloride to chlorine and from room temperature down to the freezing points.

(*b*) The isothermals for the liquids confirm the existence of sulphur dichloride, but do not show any inflexion corresponding with the tetrachloride, even at − 50°.

(*c*) The dielectric constant of the solids shows a pronounced maximum at the composition of the tetrachloride.

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[*Received, December* 23*rd*, 1929.]