**202.** *Molecular Association of Aromatic Hydrocarbons with Thionyl Chloride, Sulphuryl Chloride, and Sulphur Dioxide.*

By GEORGE HAZLEWOOD LOCKET.

ATTENTION has frequently been drawn to the exceptionally high solubility of sulphur dioxide in aromatic hydrocarbons, and to the interaction of these components to give solid products (see, *e.g.*, Seyer and others, *Trans. Roy. Soc. Canada*, 1922, **16**, [iii], 307; 1924, **18**, [iii], 209; 1926, **20**, [iii], 343; *J. Amer. Chem. Soc.*, 1930, **52**, 14; de Carli, *Gazzetta*, 1926, **56**, 34; 1927, **57**, 347; *Atti R. Accad. Lincei*, 1926, [vi], **4**, 460, 523). Further, the viscosity–composition curves for mixtures of various organic liquids, as shown by Lewis (*J. Amer. Chem. Soc.*, 1925, **47**, 626), indicate that the tendency to such combination increases with progressive methylation of the benzene nucleus. The occurrence of similar association between sulphuryl chloride and aromatic hydrocarbons is suggested by the fact that addition of the chloride to xylene and mesitylene causes a yellow colour to develop, which, however, disappears when the sulphuryl chloride is distilled off.

The viscosities of a number of mixtures of one of the foregoing sulphur compounds with an aromatic hydrocarbon have now been determined, as well as the heats of mixing, with the object of throwing further light on the associations. Comparative determinations have also been made with a few liquids other than hydrocarbons. All measurements were carried out at 25°.

EXPERIMENTAL.

*Materials.—Thionyl chloride.* The commercial product was purified according to the directions of Meyer and Schlegel (*Monatsh.*, 1913, **34**, 569). The colourless liquid obtained was fractionated with an 18″ column, and the fraction used (about two-thirds) had b. p. 76·05°/760 mm., $d_4^{25°}$ 1·6284, $\eta^{25°}$ 0·006194.

*Sulphuryl chloride.* This was purified by fractionation, the early yellow fractions being rejected; b. p. 69·60—69·69°/774 mm., $d_4^{25°}$ 1·6573, $\eta^{25°}$ 0·006850.

*Benzene.* Purified as usual, this had f. p. 5·46° (corr.).

*Xylene.* The sulphur-free material was fractionated, and the portion of b. p. 140°/759 mm. was used; $d_4^{25°}$ 0·8521, $\eta^{25°}$ 0·006067.

*Toluene.* The sulphur-free liquid was fractionated; b. p. 110·35—110·55°/762 mm.

*Mesitylene.* The sulphonate, prepared from a specimen of b. p. 163—167°, was dissolved in a little water, salted out with con-

3 c 2

centrated hydrochloric acid, filtered off, decomposed again by refluxing with dilute hydrochloric acid, and the mesitylene dried over phosphoric oxide; b. p. 164·5—165·0°/761 mm., $d_{4°}^{25°}$ 0·8611, $\eta^{25°}$ 0·006518.

cycloHexane. This was refluxed with potassium permanganate for 24 hours, shaken with concentrated sulphuric acid until it gave only a light yellow coloration, washed with alkali, and then many times with water. After drying over phosphoric oxide, a fraction of b. p. 80·05—80·25°/773 mm. was frozen four times and then melted at 4·8°. Pure cyclohexane melts at 6·48° (Jones and Amstell, J., 1930, 1318), but as the impurity is probably a paraffin (compare Young, Proc. Roy. Soc. Dublin, 1910, 12, 384) and is not removed by repetition of the purification, this liquid was used in the experiments; $d_{4°}^{25°}$ 0·7759, $\eta^{25°}$ 0·008824.

Ethyl acetate. The ester was purified by the method of Wade (J., 1905, 87, 1668); b. p. 76·9—77·1°/755 mm. (after drying over phosphoric oxide), $\eta^{25°}$ 0·004269.

Ether. Purified as usual and kept over sodium.

Stannic chloride. Chlorine was passed over A.R. tin, and the liquid was kept over tin until required. It was colourless and boiled at 114·07°/762 mm.; $d_{4°}^{25°}$ 2·2164, $\eta^{25°}$ 0·008145.

All liquids were distilled immediately before use from an all-glass still having a 12″ column ;· the hydrocarbons, ether, and ethyl acetate were distilled from phosphoric oxide.

Measurement of Viscosities.—The Scarpa method (Gazzetta, 1910, 40, 271) was used, since its independence of the volume of liquid (within reasonable limits) made it convenient where liquids had to be weighed free from moisture. Two viscometers of the ordinary form having a capillary about 10″ long were used. The larger had a bulb of about 5·5 c.c. capacity, which emptied of benzene in 117 secs.; the second was about $4\frac{1}{2}$ times as slow and was only used occasionally, since both instruments gave results agreeing to within $\pm$ 0·1%. The liquids were distilled into a small bottle, having a ground-in stopper for weighing, which was then fixed by a ground-in joint to the limb of the viscometer. An aspirator, in which the water level could be regulated continuously, sucked up the liquid under a constant pressure recorded on a gauge containing carbon tetrachloride placed in the thermostat. Turning a three-way tap disconnected the aspirator and allowed the liquid to fall back as usual. The error in the viscosity measurements was about $\pm$ 0·1%.

For the sulphur dioxide mixtures, air was first removed by bubbling nitrogen through the liquid in the viscometer, and a stream of sulphur dioxide was then passed through until sufficient had been absorbed (mesitylene and ethyl acetate absorb it very

rapidly); finally, nitrogen was bubbled through for a little while and the viscosity of the mixture measured. The reduced pressure during the upward flow did not make a detectable difference to the dioxide concentration, concordant results being obtained after long standing. Some of the mixture was now tipped back into the

FIG. 1.
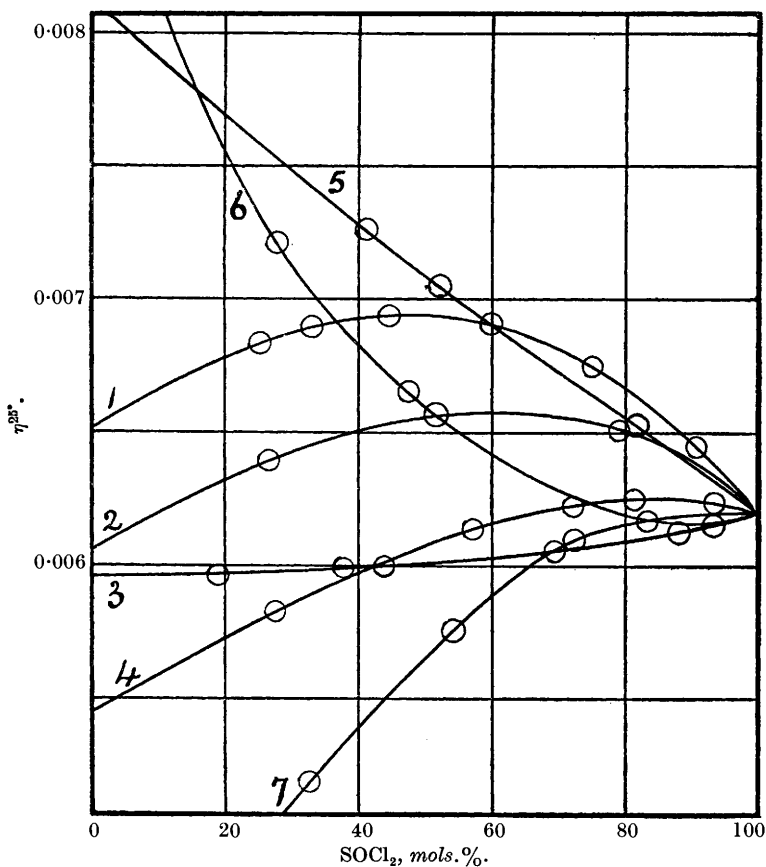


1. *Mesitylene.*  2. *Xylene.*  3. *Benzene.*
4. *Toluene.*  5. *Stannic chloride.*  6. cyclo*Hexane.*
7. *Ethyl acetate.*

bottle and weighed, the dioxide being determined gravimetrically as barium sulphate after absorption in alkali and oxidation with hydrogen peroxide.

Densities were measured with a 7-c.c. pyknometer having ground-on caps. The thermostat was kept at 25° ($\pm$ 0·015°).

*Heats of Mixing.*—These were measured by means of an apparatus

similar to that of Drucker and Weissbach (*Z. physikal. Chem.*, 1925, **117**, 220).   A weighed quantity of the first liquid was placed in an unsilvered Dewar vessel fitted with a Beckmann thermometer, a heating coil of platinum wire, and a stirrer of an up-and-down type shaped like a Witt stirrer (preliminary experiments having

FIG. 2.



$\eta^{25°}$

SO$_2$Cl$_2$, *mols.*%.
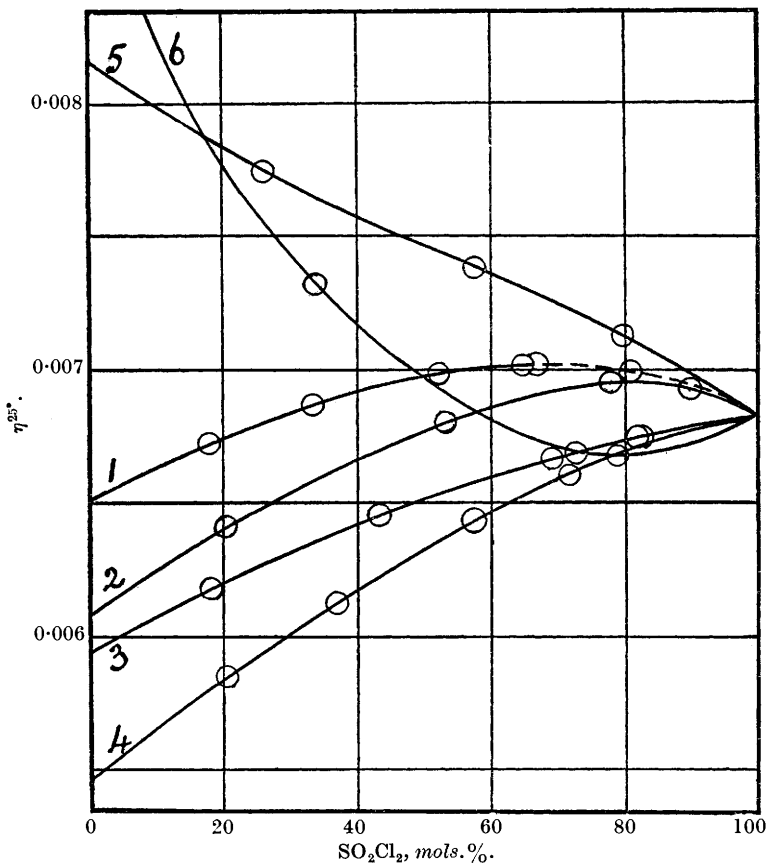
1. *Mesitylene.*          2. *Xylene.*          3. *Benzene.*
4. *Toluene.*            5. *Stannic chloride.*      6. cyclo*Hexane.*

shown that this was a great improvement on a rotary stirrer for this purpose).   The second liquid was blown in from a pipette (graduated by weight) immersed in the first liquid.   The pipette could be refilled out of contact with moist air, and so the heat of mixing of a fresh quantity of liquid with the mixture already formed could be measured, and from the sum of the effects the heat evolved or absorbed per 100 g. or per g.-mol. of mixture was

calculated. The heat capacity of the system after each mixing was found by running a known current (about 0·4 amp.) under a known $E.M.F.$ (2—2·5 volts) through the platinum coil for exactly 5 minutes. The temperature rises were obtained from curves made from readings taken every half minute. The errors were approximately as found by Drucker and Weissbach, $viz.$, $\pm\,3\%$ (those for

FIG. 3.
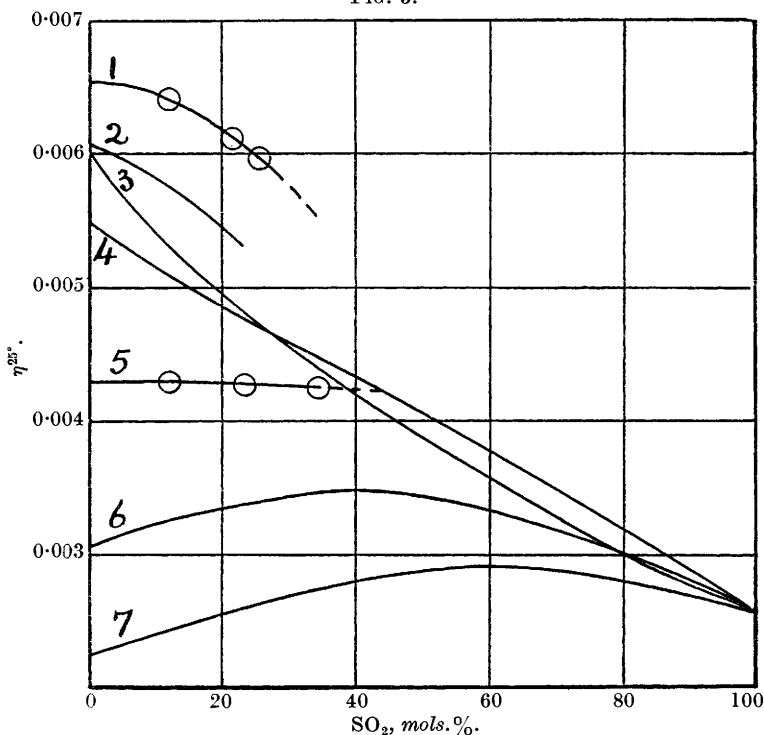


1. *Mesitylene.*     2. *Xylene.**     3. *Benzene.**
4. *Toluene.**     5. *Ethyl acetate.*     6. *Acetone.**
7. *Ether.**       * *From Lewis's results.*

sulphuryl chloride with benzene and toluene are probably rather larger).

*Results.*—The viscosities of the mixtures are given in Table I. Figs. 1 and 2 show the viscosity isotherms for thionyl and sulphuryl chloride respectively; Fig. 3 shows those for mesitylene and ethyl acetate with sulphur dioxide, together with some of Lewis's results (recalculated to give molecular percentages) for comparison. The heats of mixing are given in Table II in cals. per mol. (i) and per 100 g. of mixture (ii).

## TABLE I.

### (a) Mixtures with thionyl chloride.

| SOCl$_2$, mols.%. | $\eta^{25°}$ ×10$^6$. | $d_{4°}^{25°}$. | SOCl$_2$, mols.%. | $\eta^{25°}$ ×10$^6$. | $d_{4°}^{25°}$. | SOCl$_2$, mols.%. | $\eta^{25°}$ ×10$^6$. | $d_{4°}^{25°}$. |
|---|---|---|---|---|---|---|---|---|
| | *Benzene.* | | | *Toluene.* | | | *Mesitylene.* | |
| 0·0 | 5961 | — | 0·0 | 5460 | — | 0·0 | 6518 | 0·8611 |
| 18·1 | 5962 | 0·9895 | 26·1 | 5832 | 1·0116 | 23·4 | 6850 | 0·9674 |
| 36·6 | 5999 | 1·1161 | 42·6 | 6019 | 1·1214 | 31·4 | 6908 | 1·0099 |
| 48·1 | 6020 | 1·2011 | 55·9 | 6139 | 1·2206 | 43·2 | 6952 | 1·0811 |
| 68·6 | 6068 | 1·3585 | 72·0 | 6223 | 1·3544 | 57·1 | 6939 | 1·1751 |
| 87·7 | 6165 | 1·5172 | 80·2 | 6250 | 1·4278 | 74·3 | 6770 | 1·3236 |
| 100·0 | 6194 | 1·6284 | 92·3 | 6236 | 1·5460 | 90·0 | 6495 | 1·4925 |
| | *Xylene.* | | | *Ether.* | | | *Stannic chloride.* | |
| 0·0 | 6067 | — | 33·4 | 3365 | 0·9148 | 0·0 | 8145 | 2·2164 |
| 25·8 | 6419 | 0·9859 | 84·5 | 5480 | 1·4430 | 40·2 | 7259 | 2·0451 |
| 51·1 | 6572 | 1·1500 | | | | 51·7 | 7057 | — |
| 78·9 | 6515 | 1·3891 | | | | 80·3 | 6524 | 1·7942 |

| SOCl$_2$, mols.%. | $\eta^{25°}$ ×10$^6$. | $d_{4°}^{25°}$. | SOCl$_2$, mols.%. | $\eta^{25°}$ ×10$^6$. | $d_{4°}^{25°}$. |
|---|---|---|---|---|---|
| | *Ethyl acetate.* | | | *cycloHexane.* | |
| 0·0 | 4268 | — | 0·0 | 8824 | 0·7739 |
| 22·5 | 4911 | 1·0283 | 27·2 | 7201 | 0·9410 |
| 31·6 | 5174 | 1·0854 | 46·6 | 6634 | 1·0832 |
| 53·4 | 5759 | 1·2346 | 80·6 | 6183 | 1·4018 |
| 70·0 | 6117 | 1·3615 | 93·7 | 6156 | 1·5452 |
| 83·0 | 6177 | 1·4719 | | | |

### (b) Mixtures with sulphuryl chloride.

| SO$_2$Cl$_2$, mols.%. | $\eta^{25°}$ ×10$^6$. | $d_{4°}^{25°}$. | SO$_2$Cl$_2$, mols.%. | $\eta^{25°}$ ×10$^6$. | $d_{4°}^{25°}$. | SO$_2$Cl$_2$, mols.%. | $\eta^{25°}$ ×10$^6$. | $d_{4°}^{25°}$. |
|---|---|---|---|---|---|---|---|---|
| | *Benzene.* | | | *Toluene.* | | | *Mesitylene.* | |
| 17·6 | 6172 | 1·0002 | 20·7 | 5841 | 0·9910 | 17·2* | 6735* | — |
| 43·0 | 6463 | 1·1917 | 37·3 | 6144 | 1·1073 | 32·3 | 6885* | — |
| 69·9 | 6673 | 1·4042 | 57·2 | 6457 | 1·2615 | 51·5 | 6997* | — |
| 73·4 | 6691* | 1·4326 | 71·3 | 6642 | 1·3805 | 64·5 | 7028 | 1·3388 |
| 84·5 | 6757 | 1·5247 | 82·6 | 6759 | 1·4844 | 66·9 | 7025 | — |
| 100·0 | 6850 | 1·6573 | | | | 80·4 | 6976* | — |
| | | | | | | 34·1 | — | 1·0758 |
| | *Xylene.* | | | *cycloHexane.* | | | *Stannic chloride.* | |
| 20·9 | 6413 | 0·9727 | 0·0 | 8824 | 0·7739 | 26·8 | 7739 | 2·1054 |
| 52·5 | 6805 | 1·1891 | 32·1 | 7303 | 0·9956 | 56·3 | 7396 | 1·9580 |
| 77·9 | 6963 | 1·4153 | 64·7 | 6770 | 1·2717 | 79·5 | 7144 | 1·8170 |
| 90·7 | 6937 | 1·5477 | 79·7 | 6695 | 1·4113 | | | |

### (c) Mixtures with sulphur dioxide.

| SO$_2$, mols.%. | $\eta^{25°}$ ×10$^6$. | $d_{4°}^{25°}$. | SO$_2$, mols.%. | $\eta^{25°}$ ×10$^6$. | $d_{4°}^{25°}$. |
|---|---|---|---|---|---|
| | *Mesitylene.* | | | *Ethyl acetate.* | |
| 13·7 | 6381* | 0·8841 | 11·5 | 4299 | — |
| 22·3 | 6062 | 0·9026 | 23·6 | 4289 | 0·9814 |
| 25·5 | 5926 | 0·9122 | 35·0 | 4239 | — |
| (100·0† | 2559 | 1·3667) | | | |

\* Results obtained with the slower viscometer.

† Lewis, *loc. cit.*

## TABLE II.

*Heats of Mixing :* (i) *cals. per mol.* ; (ii) *cals. per* 100 *g.*

### (a) *Mixtures with thionyl chloride.*

| SOCl₂, mols.% | (i). | (ii). | SOCl₂, mols.% | (i). | (ii). | SOCl₂, mols.% | (i). | (ii). |
|---|---|---|---|---|---|---|---|---|
| *Benzene.* | | | *Toluene.* | | | *Mesitylene.* | | |
| 10·4 | 34·0 | 41·3 | 12·6 | 65·7 | 68·8 | 16·5 | 121·6 | 98·7 |
| 19·0 | 55·5 | 64·8 | 22·4 | 110·4 | 112·5 | 28·2 | 180·0 | 146·9 |
| 26·0 | 70·6 | 79·7 | 30·2 | 135·2 | 134·9 | 37·4 | 208·0 | 170·2 |
| 32·0 | 81·2 | 89·1 | 36·6 | 151·3 | 148·4 | 44·4 | 220·0 | 180·6 |
| 37·3 | 87·7 | 94·3 | 41·9 | 159·0 | 154·0 | 49·8 | 222·5 | 182·9 |
| 71·9 | 78·2 | 72·9 | 75·6 | 118·6 | 105·6 | 79·7 | 159·0 | 133·4 |
| 76·3 | 70·7 | 64·6 | 79·4 | 104·9 | 92·5 | 83·1 | 136·9 | 115·1 |
| 81·0 | 60·5 | 54·3 | 83·7 | 87·1 | 76·0 | 86·7 | 111·3 | 93·6 |
| 86·7 | 45·5 | 40·4 | 88·5 | 65·2 | 56·3 | 90·8 | 79·9 | 67·0 |
| 92·9 | 26·2 | 22·6 | 94·0 | 37·2 | 31·7 | 95·3 | 43·3 | 36·4 |
| *Xylene.* | | | *cyclo*Hexane. | | | *Ethyl acetate.* | | |
| 14·2 | 94·8 | 87·9 | 12·1 | −117·0 | −132·6 | 11·3 | 132·1 | 144·3 |
| 24·8 | 142·3 | 130·4 | 21·6 | −182·6 | −199·7 | 20·3 | 207·0 | 219·6 |
| 33·1 | 175·7 | 159·4 | 29·3 | −214·1 | −228·3 | 27·5 | 255·6 | 259·2 |
| 39·7 | 192·0 | 172·9 | 35·5 | −235·4 | −244·2 | 33·6 | 288·0 | 292·6 |
| 45·2 | 201·5 | 180·0 | 40·8 | −244·6 | −249·3 | 38·7 | 308·1 | 308·0 |
| 77·7 | 140·8 | 121·2 | 75·6 | −178·1 | −161·4 | 74·1 | 249·0 | 224·0 |
| 81·3 | 123·6 | 105·9 | 79·3 | −157·2 | −146·1 | 78·1 | 220·9 | 196·8 |
| 85·3 | 101·1 | 86·4 | 83·7 | −131·1 | −115·8 | 82·7 | 184·7 | 162·6 |
| 89·7 | 73·8 | 62·7 | 88·7 | − 96·2 | − 83·5 | 87·8 | 139·6 | 121·2 |
| 94·6 | 40·5 | 34·3 | 94·1 | − 53·7 | − 45·9 | 93·6 | 78·5 | 67·1 |
| | | | *Ether.* | | | | | |
| 12·0 | 104·0 | 131·0 | 35·3 | 230·5 | 256·9 | 83·9 | 132·9 | 120·3 |
| 21·2 | 165·6 | 198·2 | 40·5 | 239·6 | 260·2 | 88·7 | 100·8 | 89·6 |
| 28·9 | 204·5 | 234·9 | 79·6 | 158·2 | 145·6 | 94·1 | 59·0 | 51·0 |

### (b) *Mixtures with sulphuryl chloride.*

| SO₂Cl₂, mols.% | (i). | (ii). | SO₂Cl₂, mols.% | (i). | (ii). | SO₂Cl₂, mols.% | (i). | (ii). |
|---|---|---|---|---|---|---|---|---|
| *Benzene.* | | | *Toluene.* | | | *cyclo*Hexane. | | |
| 9·8 | 9·9 | 11·8 | 12·2 | 22·0 | 22·6 | 11·6 | −106·7 | −118·7 |
| 18·2 | 16·6 | 18·7 | 21·8 | 35·2 | 34·7 | 20·8 | −171·0 | −180·9 |
| 24·8 | 21·1 | 22·9 | 29·6 | 42·0 | 40·2 | 28·5 | −209·5 | −214·0 |
| 30·4 | 22·7 | 23·9 | 36·1 | 46·0 | 42·8 | 34·8 | −230·2 | −226·3 |
| | | | | | | 40·0 | −242·5 | −232·3 |
| 78·1 | 14·0 | 11·4 | 76·3 | 35·3 | 28·3 | 72·8 | −188·7 | −155·8 |
| 84·6 | 10·7 | 8·5 | 81·0 | 30·4 | 24·0 | 77·1 | −166·6 | −135·2 |
| 91·8 | 5·7 | 4·4 | 86·5 | 23·5 | 18·2 | 82·0 | −139·2 | −110·8 |
| | | | 92·7 | 13·6 | 10·3 | 87·3 | −104·0 | − 80·9 |
| | | | | | | 93·3 | − 59·3 | − 45·0 |

| SO₂Cl₂, mols.% | (i). | (ii). | SO₂Cl₂, mols.% | (i). | (ii). |
|---|---|---|---|---|---|
| *Xylene.* | | | *Mesitylene.* | | |
| 12·5 | 23·5 | 21·3 | 14·0 | 47·4 | 38·8 |
| 22·3 | 36·9 | 32·8 | 24·5 | 60·8 | 49·2 |
| 30·1 | 45·7 | 39·8 | 32·9 | 64·6 | 51·9 |
| 83·6 | 30·0 | 23·1 | 39·6 | 65·9 | 52·4 |
| 88·3 | 25·9 | 19·7 | 94·8 | 25·5 | 18·9 |
| 93·9 | 18·6 | 14·0 | | | |

Sulphuryl chloride has been shown to react with aromatic hydrocarbons usually in the presence of aluminium chloride (Tohl and Eberhard, *Ber.*, 1893, **26**, 2940; Silberrad, J., 1921, **119**, 2029; 1925, **127**, 1727), but at the temperature at which the above measurements were made it was found to react only with mesitylene and then very slowly (the viscosity curve where this was noticeable is broken). No effect on the cooling curve was noticed when measuring heats of mixing. Ether and ethyl acetate reacted more rapidly with sulphuryl chloride, and reproducible results could not be obtained with them. None of the other liquids interacted chemically provided they were pure and dry. Any oxidation of sulphur dioxide in mesitylene mixtures (compare de Carli, *loc. cit.*) was avoided by removing the air with nitrogen.

Tin or carbon tetrachloride when mixed with thionyl or sulphuryl chloride both gave negative heats of mixing, which were too small to be measured accurately. Ether and sulphuryl chloride evolve a considerable amount of heat on mixing, but results are complicated by a reaction which soon sets in. When sulphuryl chloride is first added to ethyl acetate there is a temperature rise, but after about $\frac{1}{4}$ minute the effect is reversed and the temperature falls, rapidly giving finally a negative heat of mixing. As further quantities of the chloride are added, the cooling effect lessens and the net heat of mixing is positive. The same thing happens if one starts with sulphuryl chloride, and as it is not to be ascribed to insufficient mixing, there is no obvious explanation of it.

Mesitylene gave yellow solutions with thionyl and sulphuryl chlorides and with sulphur dioxide, and xylene gave yellow solutions with sulphuryl chloride, otherwise the mixtures were colourless.

### Discussion of Results.

The viscosity isotherms of binary mixtures may be used to detect association in the same manner as vapour-pressure curves (Faust, *Z. physikal. Chem.*, 1912, **79**, 97; Yajnik and others, *ibid.*, 1925, **118**, 305; Tammann and Pilsbury, *Z. anorg. Chem.*, 1928, **172**, 243; Lorentz, *Z. Elektrochem.*, 1930, **36**, 336), for a positive curve (concave to the composition axis) indicates that association must be sufficient to overcome the normal effect which causes the " ideal " curve to be sagged (an effect which is increased as the components differ more widely in density and viscosity; Kendall and Monroe, *J. Amer. Chem. Soc.*, 1917, **39**, 1789).

The liquids used in this work are all normal and not appreciably associated. The following data are taken from Abegg's " Handbuch der Anorganischen Chemie " and from Arii (*Bull. Soc. Inst. Phys. Chem. Res. Japan*, 1929, **8**, 719, marked \*).

| | $SOCl_2$. | $SO_2Cl_2$. |
|---|---|---|
| Association factor (Ramsay and Shields) ......... | 1·08 | 0·97 |
| ,, ,, (Walden) ........................ | 1·10 | 1·02 |
| Trouton constant ..................................... | *21·4 } b. p. <br> *21·7 } 25° | 20·7 |
| Nernst–Trouton constant ........................... | *21·7 | 21·7 |

Sulphur dioxide also appears to be normal (Stowe, *J. Amer. Chem. Soc.*, 1929, **51**, 410). The viscosities of the aromatic hydrocarbons range only from 0·00583 (toluene) to 0·00652 (mesitylene), hence their viscosity curves with another component will be comparable and will indicate relative association. The viscosity curves, the heats of mixing, and the colour effects as far as they go show that association with the sulphur compounds increases in the order, benzene < toluene < xylene < mesitylene, the difference between the behaviour of these aromtic hydrocarbons and that of *cyclo*hexane being very striking.

It is noteworthy that with mixtures containing thionyl and sulphuryl chlorides and sulphur dioxide, an increase of viscosity, sometimes giving a maximum on the curve, is accompanied by an expansion, especially as viscosity increases are sometimes ascribed to increases in density (compare McLeod, *Trans. Faraday Soc.*, 1923, **19**, 17). Dilution of, say, thionyl chloride, with a less dense liquid like *cyclo*hexane causes a large expansion (there is a contraction with the denser stannic chloride), and with the aromatic hydrocarbons this effect is apparently not completely overcome by association. It is doubtful whether much importance should be attached to volume changes on mixing unless they are very large (compare Skraup and Eisemann, *Annalen*, 1926, **449**, 1); Schmidt (*Z. physikal. Chem.*, 1926, **121**, 228) shows that for a number of liquid mixtures these changes have no apparent connexion with the total vapour pressure or heats of mixing, but that the last two quantities run parallel, a positive heat of mixing being accompanied by a sagged vapour pressure curve.

Since the aromatic hydrocarbons behave like donor liquids, it is possible that they can form co-ordinate linkages with the sulphur compounds, increasing the covalency of the sulphur atom thus :

$$\begin{array}{c} C_6H_6 \\ Cl \searrow \downarrow \nearrow O \\ \phantom{Cl} S \\ Cl \nearrow \uparrow \searrow O \\ C_6H_6 \end{array}$$
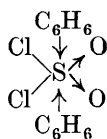
The precise mechanism by which the nucleus contributes two electrons to the sulphur atom is not clear, though a definite scheme was put forward to explain similar compound formation between aromatic hydrocarbons and nitro-compounds by Bennett and Willis
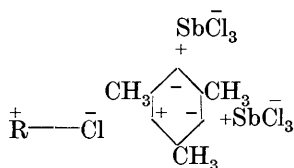
(J., 1929, 256).   Replacement of the hydrogen atoms of benzene by methyl groups will cause a drift of electrons to the nucleus (Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 668), which will now be more ready to part with electrons and so will have enhanced donor properties and increase the association.   This explanation depends on the sulphur compounds being acceptors; if they have any donor properties, these are very weak, for the results obtained with mixtures of thionyl and sulphuryl chlorides with stannic chloride (a " pure acceptor ") show no evidence of association, and Bond and Beach (*J. Amer. Chem. Soc.*, 1926, **48**, 348) conclude that there is no association between sulphur dioxide and stannic chloride or bromide.   Moreover, although ether and ethyl acetate associate with the sulphur compounds, they show no sign of doing so with the hydrocarbons.

Alternatively, the effects may be due to associations of dipole molecules (compare Errera, *Z. physikal. Chem.*, 1928, **138**, 332 ; 1929, **140**, 273 ; *Compt. rend.*, 1928, **187**, 727, 1278), but in that case the hydrocarbons used, which are normal liquids having dipole moments of not more than $0.6 \times 10^{-18}$ e.s.u., would give negative results with other polar liquids.   The author considers that this difficulty can be overcome, and other associations with aromatic hydrocarbons explained, by supposing that their nuclei can receive an induced moment on approaching a permanent dipole, thus extending the influence of the latter and causing association or increasing the rigidity of the solution.   The effect will only be apparent with molecules which are highly unsymmetrical or in which a large electronic shift is localised, as in such structures as $-N\langle^O_O$ and $-S\langle^O_O$ Release of electrons to the nucleus of the hydrocarbon by methylation should increase the induction effect and hence also the association.

This view explains complex formation with other un-ionised inorganic molecules besides those already described.   The many cases of solid compounds are of less interest than associations in the liquid, *e.g.*, those of benzene, naphthalene, and diphenylmethane

for polarisation, also give orange or red solutions with these substances; thus colour may well be produced by polarisation from without. Moreover, polarisation of the hydrocarbons is a very probable explanation of their activity in the Friedel–Crafts reaction and affords exactly the mechanism demanded by Schaarschmidt's explanation of it (*Z. angew. Chem.*, 1924, **37**, 386), but whether the free halides or more complex molecules produce polarisation, it is impossible to say in view of the complexity of the reaction (compare Olivier, *Rec. trav. chim.*, 1918, **37**, 205). However, the simpler reaction using antimony trichloride as catalyst in the ketone synthesis (Menschutkin, *J. Chim. physique*, 1914, **12**, 193) provides interesting confirmation of the present view. The values for the velocity constants with benzoyl chloride were as $1:12:21:32:80:478$ for benzene, toluene, *p*-, *o*-, *m*-xylene, and mesitylene respectively. Since two molecules of antimony trichloride form relatively stable complexes with one of hydrocarbon, and the velocity constants vary as the square of the catalyst concentrations, Menschutkin concluded that the reaction took place between one molecule of benzoyl chloride and one complex molecule $2SbCl_3,ArH$. Methylation increases the speed of reaction, presumably by increasing the polarisability of the nucleus, but methyl groups produce much bigger effects when oriented in the *m*-position with regard to each other, indicating that their effect is localised in the *o*-,*p*-positions; hence the situation at the beginning of the reaction is probably

$$\overset{-}{S}b\overset{}{C}l_3$$

$$\overset{+}{R}\text{———}\overset{-}{C}l \quad CH_3\diagdown\overset{-}{\diagup}CH_3 \quad +\overset{-}{S}b\overset{}{C}l_3$$

$$CH_3$$

(The $+$ and $-$ signs here indicate the drift of electrons that would give rise to the moment of the molecule caused by induction.) The first trichloride molecule causes nuclear electrons to concentrate in its neighbourhood, while the methyl groups release electrons *o*- and *p*- to themselves, thus reinforcing this effect. A second trichloride molecule can do likewise. The 5-position will become the positive end of the dipole (the relatively small methyl-group effect being swamped), and its incipiently ionised hydrogen atom will combine with the negative chlorine of the acid chloride, which will be attracted thither. According to Hückel (*Z. Physik*, 1931, **72**, 310; see also *Ann. Reports*, 1931, **28**, 18) substitution becomes easier where there is a defect of negative charge which can repel a hydrogen nucleus. Methyl groups in positions other than 2, 4, or 6, although increasing the polarisability, will (*a*) interfere by blocking

the approach of trichloride molecules, (b) block position 5 and so stop the reaction, and (c) fail to produce their full effects, which are in the o-,p-positions.

## Summary.

(1) The viscosities and densities of mixtures of thionyl and sulphuryl chlorides and sulphur dioxide with aromatic hydrocarbons were determined at 25°, as well as the heats of mixing. Comparative determinations were made with cyclohexane, stannic chloride, ether, and ethyl acetate.

(2) The aromatic hydrocarbons associate with these three sulphur compounds, in sharp contrast to cyclohexane, and behave like polar (donor) liquids. Methylation of the nucleus increases the association.

(3) The hydrocarbons may be electron donors, but it is thought probable that they can acquire an induced dipole moment from the inorganic molecule, thus giving rise to what amounts to a dipole association. The bearing of this view on the facts presented here and on other associations, and also on the mechanism of the Friedel–Crafts reaction, is discussed.