192. *The System Silicon Tetrafluoride–Trimethylamine.*

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Pressure–composition isotherms show that silicon tetrafluoride and trimethylamine form two crystalline compounds, SiF_4,NMe_3 and $SiF_4,2NMe_3$. Both compounds sublime congruently at atmospheric pressure, and melt congruently at higher pressures. Since no comparable system appears to have been examined previously, the equilibria involved in the interconversion of the compounds, and the conditions determining whether sublimation will be congruent or incongruent, are discussed theoretically.

The behaviour of halides of Group IV elements towards co-ordinating reagents has not been extensively studied, but several recent reports indicate a certain complexity in the interactions of silicon halides with tertiary amines, in so far as one or more compounds of the types AB, AB_2, and AB_4 (A = halide, B = amine) have been identified in various systems. Trost (*Nature*, 1952, **169**, 289) found that a number of tertiary amines form both AB_2 and AB_4 compounds with silicon tetrachloride, and that dimethylaniline forms an AB compound as well. Miller (*ibid.*, 1946, **158**, 950) reported the AB compound, SiF_4,NMe_3. Burg (" Fluorine Chemistry," Vol. I, J. H. Simons, editor; Academic Press, New York, p. 108) confirmed the existence of this compound and also mentioned (*ibid.*, p. 109) the compound $SiHF_3,NMe_3$.

The present paper deals with the system silicon tetrafluoride–trimethylamine as it shows certain unusual features. In preliminary experiments on compound formation between amines and various silicon fluorides it was noticed that a second compound, $SiF_4,2NMe_3$, is also formed in this system, and indeed, of the systems examined in a wider investigation, it alone yielded AB and AB_2 addition compounds. Moreover, the system is most unusual as regards the phase equilibria involved. So far as could be ascertained, no comparable system containing two volatile components and forming two compounds, both of them melting congruently and at least one of them subliming congruently, is known with certainty.

The existence of two addition complexes is shown by the form of the pressure–composition isotherm (Fig. 1), determined by making successive additions of trimethylamine to silicon tetrafluoride. The sharp breaks which occur close to the 1 : 1 and 1 : 2 molecular ratios indicate the formation of a 1 : 1 compound which is converted into a 1 : 2 compound by reaction with more amine. Beyond the 1 : 2 molecular ratio excess of gaseous amine accumulates until condensation of liquid occurs. Both compounds were appreciably volatile at 0°, and the detailed theoretical form of the isotherm is discussed below. Complementary experiments on the quantitative synthesis of the compounds indicated that, with excess of silicon tetrafluoride the 1 : 1 complex is formed, and with excess of trimethylamine the 1 : 2 complex.

Vacuum distillation of the latter complex leads to almost quantitative deposition of the former when the vapour is pumped through a trap at −55° (or lower). The crystalline mono-compound is not, however, the stable solid phase because it slowly reacts with trimethylamine under the experimental conditions. Conversion of the di- into the mono-complex upon distillation is evidently due to rapid formation from the dissociated vapour of crystals of the latter which undergo no appreciable conversion into the former before the remaining uncombined trimethylamine is pumped from the trap. An excess of trimethylamine was used by Miller (*ibid.*, and private communication) in the experiments leading to identification of the 1 : 1 complex. The procedure involved a vacuum distillation in which at least some (and perhaps the greater part) of the 1 : 2 complex which was doubtless formed was distilled through a trap at −55°, so causing its decomposition.

The freezing-point curve (Fig. 2) confirms the existence of both compounds. A maximum occurs at 89° and about 67% of trimethylamine, a eutectic at 72·5° and 55·5% of amine, and a plateau at 81·5° extends from about 50% to at least 44% of amine. It is assumed that the existence of the plateau is due to very low solubility of silicon tetrafluoride in the melt, and there is no reason to believe that the compound melts incongruently. Freezing-point measurements were not extended further into the tetrafluoride-rich region owing to the high pressures involved. From Table 1, which includes vapour-pressure data, it will be seen that the m. ps. of the two pure compounds lie considerably above their normal sublimation points. The values for the 1 : 1 complex are in close accord with those given by Burg (marked *). The dissociation pressures of the two compounds are remarkably close (see also Table 3). As shown on p. 930, a theoretical consequence is that both compounds should sublime congruently, and this was confirmed by other experimental evidence.

TABLE 1.

	SiF_4,NMe_3		$SiF_4,2NMe_3$
Melting point	81·5°	80·0°*	89°
Normal sublimation point	63·5	63·5°*	63·0°
Dissocn. press. eqn. $\log p_{mm.}$ = ...	$11{\cdot}774 - 2995/T$	$11{\cdot}796 - 3001^*/T$	$11{\cdot}890 - 3029/T$
Lat. heat of subl., kcal./mole	13·7	13·7*	13·9

Vapour-density measurements indicate that the compounds are almost completely dissociated upon volatilisation. The vapour from SiF_4,NMe_3 being assumed to behave as a perfect gas, the results corresponded to 91% dissociation at 42·1°. However, since trimethylamine itself shows a negative deviation from ideal behaviour of almost 3% at this temperature (Lambert and Strong, *Proc. Roy. Soc.*, 1950, *A*, **200**, 566) the actual dissociation figure must be even greater.

Theoretical Form of the Pressure–Composition Isotherm.—We shall consider in turn the isotherms for : (i) a system of two gaseous components, A and B, which yield a single volatile crystalline compound AB; (ii) a similar system forming a volatile crystalline compound AB_2 only; and (iii) the system silicon tetrafluoride–trimethylamine which forms both types of compound. It will be assumed that the compounds are completely dissociated upon volatilisation, and that the components behave as perfect gases both separately and in admixture. The pressure which a component would exert separately in the reaction vessel will be used as a measure of its quantity.

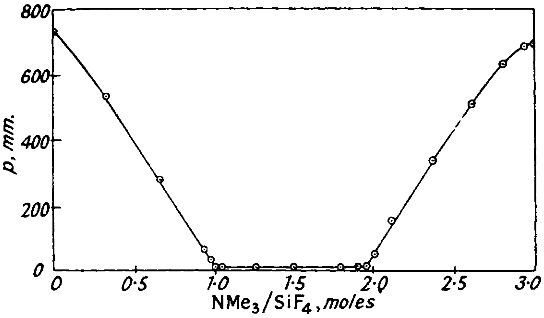


FIG. 1. *Pressure–composition isotherm at 0°.*

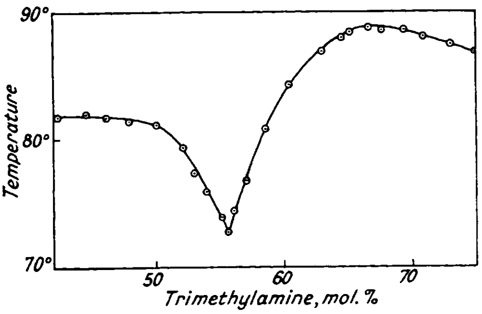


FIG. 2. *Freezing-point curve.*

(i) Suppose there are initially *a* mm. (= aV/RT g.-mols.) of component A and that *b* mm. of component B are added. Let *x* mm. of each combine so that the relation

$$(a - x)(b - x) = \tfrac{1}{4}P_1^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which P_1 is the dissociation pressure of the compound, is satisfied. The total pressure P_T exerted by the system is

$$P_T = a + b - 2x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and on elimination of *x* between (1) and (2), P_T is found to be given by (the positive branch of) the hyperbola

$$P_T = \sqrt{(a - b)^2 + P_1^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

(ii) When a compound AB_2 is formed the equations corresponding to (1) and (2) are

$$(a - x)(b - 2x)^2 = 4P_2^3/27 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and

$$P_T = a + b - 3x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Elimination of *x* between (4) and (5) gives

$$\{P_T + (2a - b)\}\{2P_T - (2a - b)\}^2 = 4P_2^3$$

or

$$4P_T^3 - 3(2a - b)^2P_T + (2a - b)^3 = 4P_2^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The curve for this cubic equation has two branches *TUV* and *XYZ* (Fig. 3), asymptotic to the lines $P_T = -(2a - b)$ and $2P_T = (2a - b)$. The branch *TUV* corresponds to negative values for the partial pressure of trimethylamine and must therefore be rejected.

(iii) In the system silicon tetrafluoride–trimethylamine the crystalline 1 : 1 compound separates at *P* (Fig. 4) after addition of sufficient trimethylamine to pure silicon tetrafluoride. The isotherm follows the hyperbola *PQR* so long as this single solid phase is present. At *S*, or *S'*, a second crystalline phase $SiF_4,2NMe_3$ appears, and transformation of the 1 : 1 into the 1 : 2 compound continues along the horizontal tie-line to the point *W* or *W'* on the (cubic) curve *XYZ*.

The co-ordinates of the points S (or S') and W (or W') may be expressed in terms of the initial pressure of silicon tetrafluoride, a, and the dissociation constants, K_1 and K_2, of the 1 : 1 and the 1 : 2 compounds, respectively. At S (or S') the relations

$$p_{\mathrm{SiF_4}} \times p_{\mathrm{NMe_3}} = K_1\text{*} \qquad (1')$$

and

$$p_{\mathrm{SiF_4}} \times p^2_{\mathrm{NMe_3}} = K_2 \qquad (4')$$

are both satisfied. Hence

$$p_{\mathrm{NMe_3}} = K_2/K_1, \text{ and } p_{\mathrm{SiF_4}} = K_1^2/K_2$$

Now there were initially a mm. of silicon tetrafluoride, and at S (or S') K_1^2/K_2 mm. remain in the gas phase, so that $\{a - K_1^2/K_2\}$ mm. of tetrafluoride have combined with this same quantity of amine to give the 1 : 1 complex. There are also K_2/K_1 mm. of amine in the gas phase, so that the total amine which has been added at this point is

$$a - K_1^2/K_2 + K_2/K_1 \qquad (7)$$

Moreover, the total pressure at S (or S') is given by

$$P_T = p_{\mathrm{SiF_4}} + p_{\mathrm{NMe_3}} = K_1^2/K_2 + K_2/K_1 \qquad (8)$$

FIG. 3. *Theoretical pressure–composition isotherm when a single compound* AB_2 *is formed. The function* $(2a—b)$ *represents the composition (as in equation* 6).

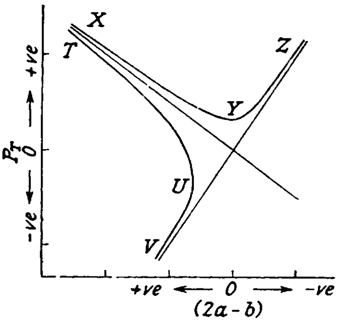
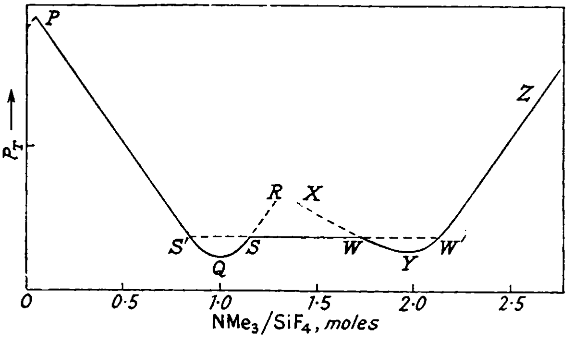


FIG. 4. *Theoretical isotherm when two compounds,* AB *and* AB_2*, are formed. (The minima are exaggerated.)*



Further additions of trimethylamine will cause transformation of the 1 : 1 into the 1 : 2 compound, and the pressure will remain constant until the transformation is complete at the point W (or W'). The amount of trimethylamine required for this conversion will be $\{a - K_1^2/K_2\}$, and so the total amine added at W (or W') will be

$$2a - 2K_1^2/K_2 + K_2/K_1 \qquad (9)$$

From (7) it will be seen that the point " S " will lie at S to the right of the minimum Q (Fig. 4), at the minimum, or at S' to the left of the minimum according as K_2/K_1 is greater than, equal to, or less than K_1^2/K_2, *i.e.*, according as $K_2 >, =,$ or $< K_1^{3/2}$. Similarly, from (9) it follows that " W " will be to the right of, at, or to the left of the minimum Y according as $K_2/K_1 >, =,$ or $< 2K_1^2/K_2$, *i.e.*, according as $K_2 >, =,$ or $< \sqrt{2}K_1^{3/2}$. It is evident that the positions of " S " and " W " determine whether the isotherm will show minima at the respective ends of the tie-line. This, in turn, will determine whether the pure compounds can exist in contact with vapour of the same composition. The conclusions are summarised in Table 2.

The condition for congruent sublimation of both compounds, *viz.*, $\sqrt{2}K_1^{3/2} \nless K_2 \nless K_1^{3/2}$,

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* In this section the equilibrium constants, K_p, are not expressed in terms of dissociation pressures, since there is the possibility that one or other of the compounds may not sublime congruently.

may also be expressed as $3P_1/2\sqrt{2} \not< P_2 \not< 3P_1/2\sqrt[3]{4}$; *i.e.*, P_2 must not exceed $1{\cdot}061P_1$ or be less than $0{\cdot}945P_1$.

This criterion for congruent sublimation of both compounds is satisfied, since the measured dissociation pressures of the two (supposedly pure) compounds (Table 3) do lie within these limits. In confirmation, it was found that the pressure exerted by a mixture of the two compounds is greater than that of either of the pure compounds, thus indicating the presence of two minima in the isotherm. Moreover, the dissociation pressures of both compounds were found to be unchanged after portions were distilled off.

TABLE 2.

Condition	Position of "S"	Position of "W"	Type of isotherm	Behaviour on sublimation	
				SiF_4,NMe_3	$SiF_4,2NMe_3$
$K_2 > \sqrt{2}K_1^{3/2}$	Right of *Q*	Right of *Y*	Min. in hyperbola	Congruent	Incongruent
$K_2 = \sqrt{2}K_1^{3/2}$	Right of *Q*	At *Y*	Min. in hyperbola; Tie-line intersects cubic curve at min.	Congruent	Congruent
$K_2 < \sqrt{2}K_1^{3/2}$ $> K^{3/2}$	Right of *Q*	Left of *Y*	Min. in hyperbola and cubic	Congruent	Congruent
$K_2 = K_1^{3/2}$	At *Q*	Left of *Y*	Min. in cubic; Tie-line intersects hyperbola at min.	Congruent	Congruent
$K_2 < K_1^{3/2}$	Left of *Q*	Left of *Y*	Min. in cubic	Incongruent	Congruent

EXPERIMENTAL

The work was based on the use of a high-vacuum system. In addition to the usual fittings for purification, storage, and measurement of gases, special equipment was attached at ground joints as required.

Preparation of Components.—Silicon tetrafluoride was obtained by heating barium fluorosilicate in a steel tube in an electric furnace so as to maintain a steady evolution of gas. The gas was passed through concentrated sulphuric acid containing suspended silica, and collected in a liquid-air trap. It was purified by fractional condensation in the vacuum system, the material remaining uncondensed at −130° being retained.

Trimethylamine was boiled from aqueous solution, dried by passage through a tube containing potassium hydroxide pellets, and condensed. Any mono- or di-methylamine was removed by use of phosphoric oxide (Coates, *J.*, 1951, 2003) or acetic anhydride (Swift, *J. Amer. Chem. Soc.*, 1942, **64**, 115). The liquid was then distilled through a low-temperature fractionating column, and the distillate collected at 2·8—3·0°.

Determination of Pressure–Composition Isotherms.—A measured volume of silicon tetrafluoride was distilled into a reaction bulb having a manometer attached. Successive measured quantities of trimethylamine were introduced, and the steady pressure noted after each addition. Up to the 1 : 1 molecular ratio reaction occurred very rapidly, but as the ratio $SiF_4 : NMe_3$ approached 1 : 2 attainment of equilibrium became progressively slower since transformation of solid phases was involved.

Synthesis of the Addition Complexes.—When the 1 : 1 compound was required, silicon tetrafluoride was used in slight excess, and the uncombined gas pumped off at −50° after reaction was complete. The 1 : 2 compound was obtained by using excess of amine, but some 1 : 1 compound was formed initially and complete conversion was uncertain at room temperature. The lower part of the reaction vessel was therefore warmed in a water-bath, and the solid distilled in the presence of the excess of amine on to the upper, cooler parts of the vessel. The reaction mixture was then kept at room temperature until the pressure had become constant, and the excess of amine removed at −50°. In a typical quantitative experiment designed to yield the 1 : 2 complex, 33·7 ml. of silicon tetrafluoride and 89·5 ml. of trimethylamine were allowed to react at room temperature; the excess of amine was distilled off and found to measure 21·7 ml. Hence the ratio $SiF_4 : NMe_3$ in which combination had occurred was 1 : 2·01.

Effect of Temperature on the Formation of $SiF_4,2NMe_3$.—The sample of 1 : 2 compound mentioned in the previous section was allowed to volatilise slowly (at 0°), and the vapour pumped through a trap at −55°. 34·2 Ml. of trimethylamine passed into the liquid-air trap beyond, so that the condensate was of composition $SiF_4 : NMe_3 = 1 : 1{\cdot}00$.

The slow reaction of the crystalline 1 : 1 compound with trimethylamine under these same conditions was demonstrated by distilling the trimethylamine back and forth through a trap containing the solid. Equivalent quantities of the complex and of trimethylamine being used, it was found that about 20% of the latter was absorbed after 15 distillations. A more rapid reaction occurred when the amine was available at higher pressure.

Determination of the Freezing-point Curve.—Measured volumes of the two components were sealed into tubes 70 × 4 mm., and of wall thickness about 1 mm. The rather heavy wall reduced the accuracy of the determination but was necessary to withstand the high pressures involved. The tubes were shaken in a thermostat bath whose temperature was raised at intervals. Temperatures were noted (about 0·25° apart) at which the crystals just melted, and just failed to melt, and the average was taken as the freezing point (Collett and Johnston, *J. Phys. Chem.*, 1926, **30**, 70). The temperatures were reproducible to 0·5°, or less, for different tubes containing the same composition.

Vapour-density Determination.—The compounds were synthesised in a detachable weighing tube and distilled into a " high-temperature bulb " of known volume (Sanderson, " Vacuum Manipulation of Volatile Compounds," Chapman and Hall, London, 1948, p. 79). The bulb was heated in a thermostat bath so that the solid volatilised completely, and the pressure was observed. In one experiment, 0·1593 g. of SiF_4,NMe_3 exerted a pressure of 113·3 mm. in 323·0 ml. at 42·1°, giving 0·908 for the " degree of dissociation."

Measurement of Dissociation Pressures.—The isoteniscope used was of standard design (Sanderson, *op. cit.*, p. 84), modified by substitution of a rotary control in place of the plunger for adjusting the amount of mercury in the limbs of the U-tube. The pure compounds were synthesised in the bulb of the isoteniscope before the thermostat bath was placed round the apparatus. Mercury levels were measured with a cathetometer and corrected to 0°.

Table 3 sets out observed dissociation pressures for each compound, and for mixtures of the two compounds ($P_{\text{mixt.}}$) at the same temperatures. For comparison, we also include the theoretical dissociation pressure of the mixture calculated according to equation 8, *viz.*,

$$P_{(\text{mixt.})} = K_1{}^2/K_2 + K_2/K_1 = 27P_1{}^4/64P_2{}^3 + 16P_2{}^3/27P_1{}^2$$

TABLE 3.

Temp.	0°	20·75°	35·0°	49·7°	62·85°
P_1, mm.	6·5	38·2	113·2	314	727
P_2, mm.	6·3	37·5	113·2	317	750
$P_{\text{mixt.}}$, obs., mm.	6·5	38·4	114·1	321	752
$P_{\text{mixt.}}$, calc., mm.	6·5	38·5	114·9	320	752

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