constant is important in discussions of the solvent properties,[5] we are reporting these results, which are in general agreement with one set of values, but which deviate significantly from both.

Experimental

Trifluoroacetic Acid.—Anhydrous material was prepared from the sodium salt by the method given by Norton.[6] A second distillation was carried out over sulfuric acid in a desiccated fractionating column. The middle cut was obtained at the normal boiling temperature within a 0.1° range. The observed melting point, −15.2 ± 0.05°, agrees with the literature value.[7]

Method.—For preliminary measurements, we employed coaxial cylindrical electrodes made of gold plated brass. These electrodes were visibly attacked, and large drifts in measured values of capacitance and conductance were observed. Subsequently, another coaxial cell was fabricated from platinum and used in all the measurements. The spacing between electrodes of this cell was approximately 1.5 mm., and its air capacity was 17.8 $\mu\mu f$. Electrical measurements were made with a wide range capacitance–conductance bridge which incorporates the best features of two recent bridges[8,9] and which will be described elsewhere.

The results reported here were obtained after pouring the freshly distilled acid into the cell, with precautions to minimize exposure to moisture from the air, since the dry material is highly hygroscopic. No greases were used on the ground-glass joints of the cell because they are attacked by the acid. The values for the dielectric constant were reproducible, indicating negligible uptake of water during the course of the measurements. Nevertheless, further checks of the possible effect of water were made. These included a separate measurement at 25° on a sample which was distilled in a dry atmosphere directly into the cell, which gave agreement within 0.05 dielectric constant unit, and separate measurements on a sample to which small portions of water were deliberately added. It was concluded that the probable error from moisture uptake is less than 0.1 unit. The precision of the measurements was within 0.05 unit.

The measurements were made at a frequency of 20 kc./sec., after it had been established that the capacitance and conductance were substantially independent of frequency between 100 c.p.s. and 100 kc. The results, together with those of the earlier investigators, are presented in Table I.

TABLE I

DIELECTRIC CONSTANT OF TRIFLUOROACETIC ACID

Temp., °C.	Dielectric constant: Simons and Lorentzen	Dannhauser and Cole	This research
−10	..	9.16	9.54 ± 0.1
0	29.5	8.90	9.21
10	34.5	8.65	8.90
20	39.0	8.42	8.55
30	44.5[a]	8.22	8.26
40	..	8.02	..
50	..	7.83	..

[a] Extrapolated value.

Discussion

Our values for the dielectric constant are very different from those of Simons and Lorentzen, and are in qualitative agreement with those of Dannhauser and Cole. The former authors did not evaluate electrode polarization effects which could cause anomalies since nickel electrodes were employed; the latter authors observed a large electrode polarization effect at low frequencies, probably because their stainless steel electrodes would be slowly attacked by the acid. With the platinum electrodes used in this research, no electrode polarization difficulties were encountered. Our conductivity values agreed, within experimental error, with those of Dannhauser and Cole.

The differences between our results and those of Dannhauser and Cole are larger than the estimated probable errors, particularly at the lower temperatures. We find $d\epsilon/dt$ equals −0.032 dielectric constant unit per degree throughout the temperature range; Dannhauser and Cole's results give a temperature coefficient which increases as the temperature is raised, and has the value −0.020 at 25°.

There is evidence for an unusually large atomic polarization in the symmetrical carboxylic acid dimers. The mechanism of this polarization, which is of general interest where hydrogen bonds are involved, will be discussed in a forthcoming publication.[10] An approximate treatment of the dielectric properties of the liquid already has been published.[11] This treatment assumes that the atomic polarization is negligible, and that all of the orientation polarization can be ascribed to a low concentration of a "self-ionized" highly polar rigid dimer species. Since, in addition to the atomic polarization, one cannot rule out the possibility of significant contributions from non-cyclic polar dimers, and higher polymers, a definitive evaluation of the relative importance of the various possible configurations in the liquid state remains to be made.

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(5) J. H. Simons and K. E. Lorentzen, THIS JOURNAL, **74**, 4746 (1952).

(6) T. R. Norton, *ibid.*, **72**, 3527 (1950).

(7) F. Swartz, *Bull. sci. roy. acad. Belg.*, **8**, 343 (1922).

(8) R. H. Cole and P. M. Gross, Jr., *Rev. Sci. Instr.*, **20**, 252 (1949).

(9) C. T. O'Konski, THIS JOURNAL, **73**, 5093 (1951).

(10) C. T. O'Konski, to be published.

(11) F. E. Harris and B. J. Alder, *J. Chem. Phys.*, **21**, 1306 (1953).

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Addition Compounds of Silicon Tetrahalides

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Silicon tetrahalides frequently have been reported to form addition compounds or coördinate covalent links with donor molecules. In such compounds one would expect (1) that their stability would be affected by the acid and base strengths but would depend to a greater extent on steric interference as Sisler has shown in his investigations of addition of oxygen bases to group IV halides[2]; (2) that addition would be reversible; and (3) that the coördination number of the central silicon atom would not exceed six.

We have found that although silicon tetrafluoride decomposes formamide at room temperature, with N,N-dimethylformamide (DMF) it forms a white solid of composition $SiF_4 \cdot 2DMF$. This solid sublimes readily at 100° in vacuum, is not hygroscopic, is insoluble in hydrocarbon solvents, and is decomposed by water liberating DMF. The infrared spectrum (Fig. 1A) is similar to that of DMF (Fig. 1B) in that the carbonyl absorption band is retained, but differs in that at 750 cm.$^{-1}$ a very intense band and shoulder appear. The supposed addition compound $SiF_4 \cdot 2NH_3$ (Fig. 1C) absorbs

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(1) Du Pont Fellow at Harvard University, 1953–1954.

(2) H. H. Sisler, E. E. Schilling and W. D. Graves, THIS JOURNAL, **73**, 426 (1951). See also A. B. Burg, *ibid.*, **76**, 2674 (1954), on the addition of trimethylamine to chlorosilanes.

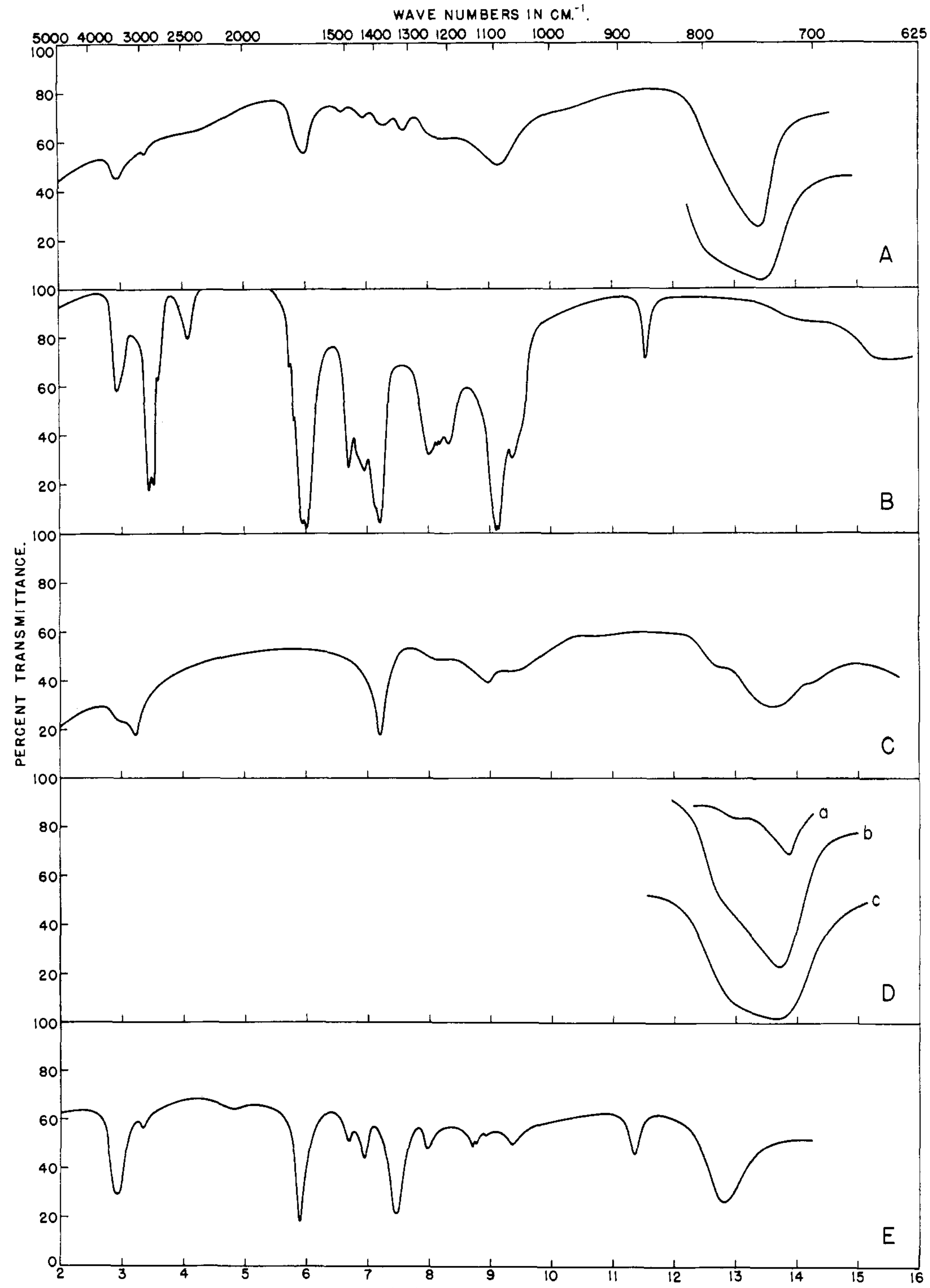

Fig. 1.—Infrared spectra of: (A) $SiF_4 \cdot 2DMF$; (B) DMF in $CHCl_3$; (C) $SiF_4 \cdot 2NH_3$; (D) Na_2SiF_6 (b is plotted from data in F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952)); (E) $SiBr_4 \cdot 6.8$ DMF. Spectra of solids were taken in pressed potassium iodide disks.

similarly. Comparison of the shape of this band with that of the silicon hexafluoride ion (Fig. 1D) and its energy with that of the stretching frequencies in silicon tetrafluoride (ν_1 = 800 cm.$^{-1}$ and ν_3 = 1031 cm.$^{-1}$)[3] strongly suggests that this band is due to the stretching of the silicon–fluorine bond in the octahedral position. Bonding in $SiF_4 \cdot 2DMF$ probably involves coördination to silicon to form an sp^3d^2 complex analogous to the silicon hexafluoride ion; and since the spectrum indicates a free carbonyl group, the donor atom must be nitrogen.

When silicon tetrachloride or tetrabromide is

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[3] E. A. Jones, J. S. Kirby-Smith, P. J. H. Woltz and A. H. Nielson, *J. Chem. Phys.*, **19**, 242 (1951).

mixed with DMF, it forms a deliquescent solid which slowly crystallizes on standing in DMF. DMF is readily recovered from these crystals upon hydrolysis. They are slightly soluble in DMF, exhibit fourfold symmetric extinction, but were not isolated since they are decomposed in part by vacuum drying at 56° or by washing with petroleum ether. Approximate analysis places their molar ratios between 1:7 and 1:9. The infrared spectrum of $SiBr_4 \cdot 6.8$ DMF (Fig. 1E) shows bands at 1340 and 780 cm.$^{-1}$ in addition to those of DMF; ν_3 of silicon tetrabromide (487 cm.$^{-1}$) was not active in this compound. The high molar ratio precludes addition. A plausible hypothesis which can explain the lability of some of the DMF is that some or all of the bromine atoms ionize,[4] each forming a silicon substituted quaternary ammonium salt, and that this ionic compound separates from DMF solution with several moles of DMF of crystallization.

Our experiments have confirmed A. Hardin's report of $SiCl_4 \cdot 2NC_5H_5$,[5] but we could find no evidence for addition of tri-*n*-butylamine or dimethylaniline to silicon tetrachloride. Mixing either of the latter two bases with silicon tetrachloride produces no precipitate nor any appreciable heating effect. Thermal analysis of the system silicon tetrachloride–dimethylaniline (Fig. 2) shows that if 1:1 and 1:2 addition compounds do form, they are liquid at room temperature and highly dissociated in the liquid phase. Of the three amines, pyridine has an intermediate basicity and is the least hindered donor, so steric interference seems to offer the only explanation of these results.

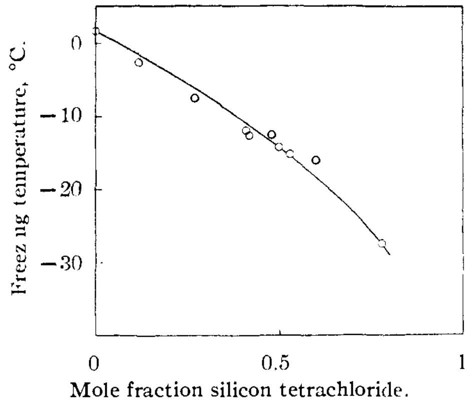

Fig. 2.—The system $SiCl_4$–$(CH_3)_2NC_6H_5$.

Experimental

Forty-five millimoles of DMF absorbed 23 millimoles of gaseous silicon tetrafluoride which was prepared by thermal decomposition of barium fluosilicate; the product was freed of excess silicon tetrafluoride by evaporation under vacuum. *Anal.* Calcd. for $SiF_4 \cdot 2DMF$: C, 28.80; H, 5.64; F, 30.4. Found: C, 28.81; H, 5.81; F, 30.6. Fluorine was determined by titration with thorium nitrate. When 31.0 millimoles of pyridine was added to 8.81 millimoles of silicon tetrachloride in carbon tetrachloride there was an immediate exothermic reaction to produce a white precipitate. The supernant liquid was analyzed for pyridine by separation as the hydrochloride and Volhard titration. The supernatant liquid contained 12.7 millimoles of pyridine; calcd. for a precipitate of $SiCl_4 \cdot 2NC_5H_5$, 13.4 millimoles. The infrared spectra were taken in pressed iodide disks with a Baird double beam recording spectrophotometer.

We take pleasure in expressing our gratitude to Professor M. K. Wilson for his helpful suggestions and his aid in interpreting the infrared spectra.

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[4] K. Gingold, F. G. Rochow, D. Seyferth, A. C. Smith, Jr., and R. West, THIS JOURNAL, **74**, 6306 (1952).

[5] A. Hardin, *J. Chem. Soc.*, **51**, 40 (1887).

Low Temperature Heat Capacity, Entropy at 298.16°K., and High Temperature Heat Content of Sphene ($CaTiSiO_5$)

BY E. G. KING, R. L. ORR AND K. R. BONNICKSON

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This paper covering fundamental research in mineral thermodynamics represents one phase of the Bureau of Mines research and development program directed toward the more effective utilization of our mineral resources.

Sphene ($CaTiSiO_5$) is a common accessory constituent of both igneous and metamorphic rocks, probably the most widely occurring titanium mineral other than ilmenite and rutile. No thermodynamic data have been available previously for this substance. This paper reports heat capacity measurements in the temperature range 51 to 298°K., the entropy at 298.16°K., and high temperature heat content measurements in the temperature range 298 to 1811°K.

Material.—Sphene was prepared from a stoichiometric mixture of reagent grade calcium carbonate, pure (99.95%) silica and pure (99.8%) titania. The mixture was heated in platinum to about 50° above the fusion temperature, held for a time to assure uniform composition and to permit complete evolution of carbon dioxide, and then poured onto a polished nickel plate. The resulting crystalline mass was broken up to a suitable size for filling the calorimeter containers. The X-ray diffraction pattern of the product agreed with that in the A. S. T. M. catalog. Chemical analysis gave 28.59% calcium oxide, 30.66% silica and 40.68% titania, as compared with the theoretical values—28.60, 30.65 and 40.75%. Further evidence regarding purity may be derived from the heat content data below the melting point, as will be mentioned later.

Measurements and Results.—The low temperature heat capacity measurements were made with previously described apparatus,[1] using 252.17 g. mass of sphene. The results, expressed in defined calories (1 cal. = 4.1840 abs. joules) per deg. mole, appear in Table I. The molecular

TABLE I

LOW TEMPERATURE HEAT CAPACITY OF $CaTiSiO_5$ (MOL. WT., 196.07)

T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole
52.30	3.888	114.30	14.04	216.12	26.89
56.37	4.448	124.31	15.62	226.14	27.82
60.99	5.161	135.90	17.37	235.99	28.67
65,43	5.899	146.05	18.84	245.69	29.49
70.04	6.653	156.20	20.18	255.73	30.28
74.51	7.377	165.86	21.41	265.82	31.04
79.65	8.320	176.14	22.67	278.23	31.94
82.94	8.814	185.86	23.79	287.65	32.60
93.10	10.54	196.01	24.87	296.95	33.09
103.65	12.27	206.19	25.88	298.16	(33.21)

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[1] K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686 (1946).