[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

The Fluorination of Chlorodisiloxane. Silicon Oxyfluoride[1]

BY HAROLD SIMMONS BOOTH AND REUBEN ALEXANDER OSTEN[2]

It has been repeatedly observed in this Laboratory that after boiling off from glass ampules liquefied silicon fluoride small amounts of a white residue which volatilize at about room temperature remain, unless the glass ampules are thoroughly dried by flaming while being rinsed many times with dry air. Partial hydrolysis of silicon tetrafluoride to a volatile oxyfluoride seemed a likely source of the residues.

In a study by Glenn McIntyre in this Laboratory, of the fundamental reactions[3] involved in the smelting of enamel frits, it was found that fluoxysilicates exist in the final product of the reaction of certain metallic fluorides on silica. While it has always been assumed that silicon tetrafluoride and boron fluoride were the gaseous fluorides evolved in frit smelting, the possibility that here, too, an unknown silicon oxyfluoride was also formed, led us to attempt its synthesis.

Experimental

Preliminary Experiments.—The attempt was made to duplicate the conditions under which the residues believed to be silicon oxyfluoride were formed. Glass wool, and silica gel, were placed in ampules and treated with liquid silicon tetrafluoride sufficient to cover the samples. However, the yield of residue was disappointing, and the method was abandoned for an indirect method of attack.

Fluorination of Hexachlorodisiloxane.—Stepwise fluorination of hexachlorodisiloxane ($Cl_3SiOSiCl_3$) by antimony trifluoride might be expected to yield the following simple products: one monofluoro- derivative, Si_2OCl_5F: two difluoro- isomers, $Si_2OCl_4F_2$: two trifluoro- isomers, $Si_2OCl_3F_3$: two tetrafluoro- isomers, $Si_2OCl_2F_4$: one pentafluoro- derivative, Si_2OClF_5: and the completely fluorinated product, Si_2OF_6.

The fluorination flask[4] was charged with 200 cc. of crude hexachlorodisiloxane, prepared as described by Schumb and Holloway.[5] The temperature of the oil-bath in which the flask was partly immersed was then raised to about 60° and the manometer controls adjusted to the vapor pressure corresponding to that of hexachloro disiloxane at 60°. Sublimed antimony trifluoride was added slowly by means of the screw feed, and an immediate evolution of gases was noted. The gases were collected by condensation in ampules. The antimony trifluoride was added exceedingly slowly to allow it to react completely and to permit the evolved heat to be dissipated, but even with these precautions the reaction became so violent on occasion as to get out of control. At the end of the reaction, excess antimony trifluoride was added and the temperature was raised to 100°.

In subsequent fluorinations the pressure, temperature, and the amount of antimony pentachloride, $SbCl_5$, used as catalyst, were varied. The percentage by volume of the catalyst ranged between zero and 15%: apparently it made little difference how much was added. Since the yield of non-condensable silicon tetrafluoride was large and because partially fluorinated products were desired, the fluorination temperature was maintained near room temperature and the pressure was held correspondingly low.

Purification of the Products.—In order to remove from the products the silicon tetrafluoride the mixture was fractionally sublimed from one ampule to another several times. The liquid residue was transferred to a low-temperature distilling column[6] and refluxed until all the dissolved silicon tetrafluoride was removed. The remaining liquid was distilled at atmospheric pressure to separate it into fractions and to obtain a distillation curve, which was automatically graphed by a Micromax recording potentiometer. Each fraction was then distilled several times at pressures ranging from 100 mm. to one atmosphere.

The large quantity of silicon tetrafluoride obtained from the fluorination was redistilled under pressure to recover the small amounts of the other products in it.

Besides the large quantity of silicon tetrafluoride there was obtained a liquid which boiled at approximately −23° and which was later identified as hexafluorodisiloxane, Si_2OF_6. This product was easily purified and gave readily reproducible physical constants. A second plateau on the recording potentiometer time-temperature curve was observed at about −5 to −6°, but this was so brief that the fraction could not be collected separately.

Another fraction distilled over between +14 and +20°. There was no sharp break in the curve but a gradual, continual rise in temperature. Difficulty of separation was increased because the fraction could only be obtained in relatively small quantities, but by repeatedly distilling it at various pressures it was finally divided into two separate components. The lower-boiling component (b. p. +16.3°) was later identified as a tetrafluorodichlorodisiloxane, $Si_2OF_4Cl_2$, and the small quantity of the higher-boiling fraction was thought to be octafluorotrisildioxane, $Si_3O_2F_8$.

The highest boiling product obtained distilled at about +42°. The distillation temperature remained constant at all times and it was at first thought to be a pure liquid; however, all attempts to obtain a freezing point proved unsuccessful. The cooling curve was gradual, without inflection, down to the temperature of liquid air where it had solidified to a vitreous solid. Moreover, it had been observed that, when the gases slowly diffused to the storage ampule upon distillation, crystals were formed in the upper, warmer part of the tube, whereas the distillate remained liquid in the lower colder part of the ampule which was immersed in Dry Ice. This was interpreted as indicating it to be a mixture rather than a pure substance and, in fact, suggested a method for purifying this fraction.

Repeated distillation at various pressures caused no change in the composition or physical constants of the distillate. The fraction was either an azeotropic mixture, the fractionating column was not efficient enough to separate the components, or rearrangement of the product occurred.

The diffusion-condensation method of von Elbe[7] appeared to be the most likely to achieve separation. The modified apparatus consisted of a vertical tube, 12 mm. in diameter and 1 meter in length, closed at the bottom end and connected to the gas manifold at the other end. A stopcock and conical joint were connected to the tube in the form of a T-seal about eight inches above its lower end. Just above this seal the tube was constricted so that it could be sealed off readily. This lower part formed the

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(3) Glenn H. McIntyre, Doctoral Dissertation, Western Reserve University, 1939.

(4) H. S. Booth and W. C. Morris, THIS JOURNAL, **58**, 90 (1936).

(5) W. C. Schumb and D. Holloway, *ibid.*, **63**, 2753 (1941).

(6) H. S. Booth and A. R. Bozarth, *Ind. Eng. Chem.*, **29**, 470 (1937).

(7) G. von Elbe and B. B. Scott, *Ind. Eng. Chem., Anal. Ed.*, **10**, 284 (1938).

receiver for the liquid and was connected to the manifold by means of the conical joint after sealing the constriction. Just above the constriction there was a larger tube which surrounded and extended to the top of the diffusion tube. The larger tube formed a jacket into whose annular space refrigerant was placed.

To operate this apparatus the tube was first thoroughly rinsed with dry air and evacuated. The liquid-receiver tube was immersed in a Dry Ice–acetone slush and the annular jacket was filled with the same refrigerant. A cold, empty Dewar was placed around the ampule containing the liquid, and the vapor was then permitted to diffuse into the tube. At the low vapor pressures the impurity, which had the higher freezing point, condensed and froze on the walls of that part of the tube which was surrounded by the jacket. The other component condensed in the lower part of the tube and drained into the liquid-receiver. No reflux action was possible because the liquid in the receiver was at the same temperature as the tube above it. The receiver was finally sealed off and the liquid transferred to a distilling column where it was redistilled. The component which froze on the walls of the tube, was added to the crude fraction boiling at 14 to 20°. Reproducible physical constants and analyses showed that the liquid fraction was sufficiently pure for study after two of these treatments and it proved to have the composition corresponding to $Si_2OF_3Cl_3$.

Analysis.—For the elementary analysis, samples of the three purified substances were taken in glass bulbs[8] of about one cubic centimeter capacity. These were attached to the manifold by means of conical joints. After drying the bulbs they were weighed empty, then attached to the manifold, rinsed repeatedly, and then filled half full of liquid. While the sample was frozen the bulb was sealed off from the conical joint at an S–shaped constriction. The bulb containing the sample and the conical joint were then weighed together after allowing both parts to come to room temperature. The weight of the sample was then obtained from the difference between the two weighings. The sample was frozen, the bulb was scratched with a file at the constriction and after breaking was quickly dropped into 200 cc. of freshly distilled water contained in a waxed Erlenmeyer flask. The flask was immediately stoppered and swirled. Reaction with water was vigorous and rapid.

The scheme of analysis used can be understood from the following representative case. The sample was hydrolyzed with distilled water in a waxed Erlenmeyer flask and titrated immediately with sodium hydroxide for the total acidity, in the presence of phenolphthalein.[9]

$$Si_2OCl_3F_3 + 6HOH = 3HCl + 3HF + 2SiO_2{\cdot}xH_2O \quad (1)$$

$$3HCl + 3HF + 2SiO_2.xH_2O + 6NaOH = 3NaCl + 3NaF + 2SiO_2{\cdot}xH_2O + 6H_2O \quad (2)$$

To the resulting mixture excess $NaHF_2$ and hydrofluoric acid were added to convert the silica to fluosilicate.

$$4NaHF_2 + 4HF + 2SiO_2 = 2Na_2SiF_6 + 4H_2O \quad (3)$$

This mixture was transferred to a platinum dish and evaporated to dryness on a steam-bath. Sodium formate[10] was then added to buffer acidity and the mixture was again evaporated to dryness. Then the silicon was determined by titrating the sodium fluosilicate, Na_2SiF_6, while hot, with standard sodium hydroxide using phenolphthalein as indicator.[11,12]

$$Na_2SiF_6 + 4NaOH = 6NaF + SiO_2{\cdot}xH_2O \quad (4)$$

This mixture was filtered and washed and the filtrate analyzed for chloride by the Mohr method.

$$NaCl + AgNO_3 = AgCl + NaNO_3 \quad (K_2CrO_4 \text{ indicator}) \quad (5)$$

Since the total equivalents of acid (eq. 2) and the equivalents of chloride (eq. 5) were known, the acidity due to fluorine was equal to the difference. The fluorine content of Si_2OF_6 was also confirmed on a different sample by filtering off most of the silica (from reaction 1) and determining it directly by the method of Rowley and Churchill.[13,14] Analytical results are given in Table I.

TABLE I

ANALYSIS OF FLUORINATION PRODUCTS

	Silicon, %		Fluorine, %		Chlorine, %	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
Si_2OF_6	30.15	31.1	61.25	61.0		
		30.7		61.2		
				61.2[a]		
				61.3[a]		
$Si_2OF_4Cl_2$	23.81	23.6	34.71	34.5	32.34	31.7
		24.3		34.9		31.5
$Si_2OF_3Cl_3$	22.13	23.0	24.20	24.4	45.17	44.6
		22.8		23.6		45.1
Si_2OCl_6	18.30				74.42	74.3
						74.7

[a] Confirmed by the method of Rowley and Churchill.

Determination of Physical Constants.—The molecular weights of the gaseous products, determined by means of a gas density balance,[15] and that of the liquids by the Regnault globe method,[16] are shown in Table III. Freezing points were determined by the method described by Booth and Martin.[17]

The freezing point of trichlorotrifluorodisiloxane, $Si_2OF_3Cl_3$, was difficult to obtain. Upon cooling, it slowly solidified to a viscous, transparent, glassy solid which upon further cooling crystallized with lightning rapidity, accompanied by a crackling sound. Obviously no equilibrium point between solid and liquid state could be observed. However, if the substance was first

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(8) H. S. Booth and W. D. Stillwell, THIS JOURNAL, **56**, 1531 1934).

(9) A. Hileman, *Z. anorg. Chem.*, **51**, 158 (1906).

(10) V. Ya. Tartakovskii, *Chem. Abs.*, **26**, 3751 (1932); **27**, 2650 (1933).

(11) N. Sahlbom and F. Hinrichsen, *Ber.*, **39**, 2609 (1906).

(12) M. Travers, *Compt. rend.*, **173**, 714 (1921).

(13) R. J. Rowley and H. V. Churchill, *Ind. Eng. Chem., Anal. Ed.*, **9**, 551 (1937).

(14) *J. Am. Water Works Assoc.*, "Methods of Determining Fluorides," **33**, 1965 (1941).

(15) H. S. Booth and A. R. Bozarth, THIS JOURNAL, **61**, 2927 (1939).

(16) A. F. O. Germann, *J. Phys. Chem.*, **19**, 451 (1915).

(17) H. S. Booth and D. R. Martin, THIS JOURNAL, **64**, 2198 (1942).

crystallized in the tube and then allowed to warm slowly a melting point could be obtained. Vapor pressures of gases[6] and liquids[18] were determined by the static method as previously described in papers from this Laboratory with several improvements such as the increase in constancy of the constant temperature bath by the use of photoelectric controls. The results are shown in Table II.

The liquid densities of the halosiloxanes were determined at 0° by means of a special pycnometer described by Booth and Herrman.[19]

Chemical Properties.—All three of the halosiloxanes obtained hydrolyze in water or alkaline solutions with the formation of halides and hydrated silica. Their odor is similar to that of silicon tetrafluoride. None of these substances attacks mercury, copper, or nichrome at ordinary temperatures.

Attempts were made to carry out reactions with $F_3SiOSiF_3$ analogous to those undergone by SiF_4. For example, when SiF_4 is passed into a solution of HF the complex acid, H_2SiF_6, is formed; with a solution of KF the insoluble salt, K_2SiF_6, results. It was expected that KF might coordinate with Si_2OF_6 to form an insoluble salt, $2K^+ \left[\begin{matrix}\mathrm{FF\ \ FF}\\ \mathrm{FSiOSiF}\\ \mathrm{FF\ \ FF}\end{matrix}\right]^{=} 2K^+$ which could be used in the analysis of the new compound. When Si_2OF_6 was bubbled into a solution of KF a white precipitate of no definite composition was obtained.

The halosiloxanes form clear liquids which freeze to white solids. The liquidus ranges of the chlorofluorides are greater than those of the fluorides.

Discussion

The fluorination of hexachlorodisiloxane by the Swarts reaction yielded large quantities of silicon tetrafluoride, hexafluorodisiloxane, Si_2OF_6, (b. p. −23.3°), trichlorotrifluorodisiloxane, $Si_2OCl_3F_3$ (b. p. +42.9°), smaller quantities of tetrafluorodichlorodisiloxane, $Si_2OCl_2F_4$ (b. p. +16.8°) and traces of two other gases whose composition could not be established definitely. One of the two was thought to be pentafluoromonochlorodisiloxane, Si_2OClF_5 (b. p. about −5°) and the other octafluorotrisilidioxane, $Si_3O_2F_8$ (b. p. about +20°).

The only evidence that the monochloro derivative, Si_2OClF_5, was formed was the short plateau in the time–temperature curve at about −5° upon distillation of the mixture. If this temperature approximates the boiling point, it falls about half-way between the hexafluoro- and the tetrafluoro- derivatives; the small fraction therefore might have been pentafluoromonochlorodisiloxane. Although the amount of crystalline material separated by diffusion from the $Si_2OF_3Cl_3$ was too small to establish its composition conclusively yet the evidence indicates it could be $Si_3O_2F_8$. This could have come from the complete fluorination of small amounts of $Si_3O_2Cl_8$ in the crude Si_2OCl_6. With a freezing point of −39° and boiling point of about +20° it has a shorter liquidus range than the chlorofluorides and resembles the fluorides. The molecular weight of the impure sample was 252, theory 268. The high molecular weight could not be attributed to a highly chlorinated compound as the analysis of the impure sample gave less chlorine than would have corresponded to Si_2OF_5Cl and was probably due to impurity.

The completely fluorinated derivative, Si_2OF_6, was obtained in good yields, was readily purified and gave readily reproducible physical constants and analyses. It forms a clear liquid which freezes to a white solid at −47.8°. When exposed to moist air it hydrolyzes immediately to form hydrogen fluoride and silica. Whether this gas is the same as the residue noted after boiling SiF_4 out of an undried ampule is not certain, though it might be one of the components of the residue.

It is notable that the trichlorotrifluoro- derivative, $Si_2OCl_3F_3$, is formed in preponderantly larger quantities than the other chlorofluorides, notwithstanding the great variation in reaction temperature and pressure. Booth and Bozarth[15] found that there exists a definite threshold temperature for each chlorofluoride at which fluorination proceeds, and that the rate of fluorination increases as the fluorine content of the halide is increased, and the threshold fluorination temperature drops. This phenomenon has been repeatedly observed in this laboratory in the partial fluorination of various non-polar halides. These observations are therefore of general validity and it appears highly probable that, when replacement of chlorine by fluorine has been initiated on one of the silicon atoms the tendency will be to complete the fluorination on that silicon atom because at the given temperature it should be fluorinated more readily and more rapidly since its threshold fluorination temperature will be lower than that of the unfluorinated $SiCl_3$ group. In other words, each $SiCl_3$ in $Cl_3SiOSiCl_3$ behaves as an independent molecule. On these assumptions the trichlorotrifluoro- derivative would have the structure $F_3SiOSiCl_3$. This also explains the absence of the expected isomers.

The fact that large quantities of silicon tetrafluoride were evolved in the reaction gives rise to the question as to source of the gas. That it was not due to reaction with the glass walls of the reaction vessel is shown by the fact that there was little evidence of etching. If water had been present in the reaction it could lead to a successive hydrolysis, *i. e.*, the liberated hydrogen fluoride would react with the oxyhalide to regenerate the water: $Si_2OF_6 + 6H_2O =$

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[18] H. S. Booth, H. M. Elsey and P. Burchfield, THIS JOURNAL, **57**, 2064 (1935).

[19] H. S. Booth and C. Herrman, *ibid.*, **58**, 63 (1936).

$2SiO_2 \cdot 3H_2O + 6HF$ and $SiO_2 + 4HF = SiF_4 + 2H_2O$. That no appreciable quantities of HF were liberated would at first thought appear to obviate this explanation, but it is apparent from the above equations that only a small quantity of HF would be necessary.

The analogous hydrolysis reported by Stock[20] is of interest in this connection. When disiloxane, $H_3SiOSiH_3$, is given a moderate treatment with water—for example, the use of partially hydrated phosphorus pentoxide—the peculiar reaction occurs

$$(SiH_3)_2O = SiH_4 + (SiH_2O)_x$$

which is explained by the intermediate reactions

$$(SiH_3)_2O + HOH = 2SiH_2O + 2H_2$$
$$(SiH_3)_2O + 2H_2 = 2SiH_4 + HOH$$

The small amounts of constantly reformed water act as catalyst.

It is interesting to compare boiling points of the siloxanes with the corresponding silanes. In general, the insertion of an oxygen atom between two silicon atoms modifies the volatility to only a very slight extent, which is not true of the corresponding carbon compounds.

Siloxanes	B. p., °C.	Silanes	B. p., °C.
$H_3SiOSiH_3$	−15.2	H_3SiSiH_3	−14.5
$F_3SiOSiF_3$	−25.3	F_3SiSiF_3	−19.0
$Cl_3SiOSiCl_3$	137.0	$Cl_3SiSiCl_3$	147.0
$Et_3SiOSiEt_3$	231.0	$Et_3SiSiEt_3$	251.0
H_3COCH_3	−24.0	H_3CCH_3	−88.0

While silicon compounds resemble carbon compounds in some respects, the analogy is usually only formal. Since $F_3SiOSiF_3$ is a structural analog of CH_3OCH_3, the former might be expected to have the properties of an ether. Coördination of BF_3 with CH_3OCH_3 produces a stable liquid, hence BF_3 may be expected to coördinate with $F_3SiOSiF_3$ to yield a compound. The tendency to polymerize, shown by the oxidation products of SiH_4, increases with the oxygen content and attains its maximum in silicic acid. There is no evidence of a tendency to polymerize in the siloxanes.

TABLE II

VAPOR PRESSURE OF Si_2OF_6

$\log p$ (in mm.) $= -1125/T + 7.384$

Temp., °C.	P obs., mm.	P calcd., mm.	Deviation, mm.
−38.6+	385.6	386.4	−0.8
−37.4	405.8	408.3	−2.5
−35.9	438.3	437.5	0.8
−34.3	472.2	471.0	1.2
−33.2+	497.1	495.5	1.6
−32.2	520.4	518.8	1.6
−31.2+	545.1	542.0	3.1
−30.3	570.0	563.7	6.3
−29.2	596.7	591.6	5.1
−27.6	634.9	633.9	1.0
−26.4+	666.2	666.8	−0.6
−24.9	711.3	709.6	1.7
−23.4	756.9	756.8	0.1
−22.6	777.5	781.6	−4.1
VAPOR PRESSURE OF $Si_2OF_4Cl_2$ $\log p$ (in mm.) $= -1478.9/T + 7.9828$			
−38.3	61.0	48.3	12.7
−35.6	64.9	57.0	7.9
−30.5+	78.0	77.1	0.9
−25.0	102.6	105.1	−2.5
−20.3	135.8	135.8	0.0
−14.6	178.8	182.6	−3.8
− 9.8	229.5	232.3	−2.8
− 4.9+	292.4	294.2	−1.8
0.2	371.4	372.9	−1.5
4.9+	459.7	460.4	−0.7
9.6	561.9	564.3	−2.4
12.1+	625.2	627.2	−2.0
15.1	705.9	710.1	−4.2
16.8	756.6	761.0	−4.4
17.3	776.7	776.7	0.0
VAPOR PRESSURE OF $Si_2OF_3Cl_3$ $\log p$ (in mm.) $= -1598/T + 7.937$			
−38.0+	16.6	13.8	2.8
−34.0	19.9	18.0	1.9
−23.2+	35.3	34.9	0.4
−20.4	43.3	41.1	2.2
−14.4	57.9	57.6	0.3
0.3+	124.3	124.3	0.0
6.6	168.3	167.5	0.8
10.8+	204.1	203.8	0.3
14.7	244.2	242.7	1.5
22.8	346.5	344.5	2.0
27.3+	414.8	414.9	−0.1
28.5	437.4	435.5	1.9
30.3	469.6	468.8	0.8
34.8	560.6	559.8	0.8
35.1+	568.1	566.3	1.8
39.2	660.2	663.9	−3.7
42.4	745.8	744.0	1.8
43.2	770.2	770.9	−0.7

\+ Second sample.

TABLE III

SUMMARY OF THE PROPERTIES OF THREE FLUORINATION PRODUCTS OF HEXACHLORODISILOXANE

Substance	$Si_2OF_3Cl_3$	$Si_2OF_4Cl_2$	Si_2OF_6
Boiling point, °C.	42.9	16.8	−23.3
Freezing point, °C.	−100.0 ± 0.5	−60.0 ± 0.5	−47.8 ± 0.5
Liquidus range, °C.	143	76.8	25.3
Liquid density	1.467	1.432	1.358
Mol. wt., obs.	236	232	184.5
Mol. wt., calcd.	235	219	186.0
Heat of vapn., calcd., Cal.	7300	6770	5150
Trouton constant	23.1	23.3	20.6

Summary

The fluorination of hexachlorodisiloxane by the Swarts reaction has been described. The

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[20] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., p. 29 (1933).

identity of three of the fluorination products, hexafluoro-, tetrafluorodichloro- and trichlorotrifluoro-disiloxane was established. The formation of small amounts of what appears to be octafluorotrisiloxane, and pentafluoromonochloro-disiloxane, was indicated. None of these compounds has been reported previously. The boiling points freezing points, vapor pressures, gaseous and liquid densities of these compounds have been determined and are recorded along with a few of their chemical properties.

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[CONTRIBUTION FROM THE WESTERN REGION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Specific Heats at Low Temperatures of $(NH_4)_2SO_4$, $NH_4Al(SO_4)_2$ and $NH_4Al(SO_4)_2 \cdot 12H_2O$[1]

BY C. HOWARD SHOMATE[2]

The Pacific Experiment Station of the Bureau of Mines has undertaken a study of the thermochemical properties of compounds encountered in certain methods of extracting alumina from clays and alunite. One phase of this program concerns the measurement of low-temperature specific heats and entropies. This paper presents such data for ammonium sulfate, ammonium aluminum sulfate, and ammonium aluminum sulfate dodecahydrate. Similar data for anhydrous aluminum sulfate, aluminum sulfate hexahydrate, anhydrous potassium aluminum sulfate, and potassium aluminum sulfate dodecahydrate were reported in a recent paper.[3]

Materials

Reagent grade ammonium sulfate was heated at 75° for several days. Analysis gave 72.67% SO_4 (theoretical 72.70%). No corrections were made in the specific heat measurements for impurities. The sample used in the measurements weighed 122.87 g.

Ammonium aluminum sulfate was prepared from reagent-grade ammonium aluminum sulfate dodecahydrate by gradually heating the latter to 210° over a period of several days. The final heating was done in vacuum. Analysis showed 21.20% Al_2O_3 (theoretical 21.50%); 79.63% SO_4 (theoretical 81.02%); 7.31% NH_4 (theoretical 7.61%), and 0.39% alkali salts. For the purpose of correcting the specific heat results, it was assumed that the sample used in the measurements was 98.1% $NH_4Al(SO_4)_2$ and 1.9% H_2O. The data of Giauque and Stout[4] were used in correcting for the water impurity. The measurements were made on a 134.87-g. sample.

Analysis of the reagent grade ammonium aluminum sulfate dodecahydrate used in the measurements gave 11.22% Al_2O_3 (theoretical 11.24%). No corrections for impurities were made in the results. A 123.54-g. sample was used in the measurements.

Specific Heats

The method and apparatus used in the low-temperature specific heat measurements have been described previously.[5,6] The experimental results, expressed in defined calories (1 calorie =

TABLE I

SPECIFIC HEATS

$(NH_4)_2SO_4$		$NH_4Al(SO_4)_2$		$NH_4Al(SO_4)_2 \cdot 12H_2O$	
Mol. wt. = 132.14		Mol. wt. = 237.13		Mol. wt. = 453.32	
T, °K.	C_p, cal./mole	T, °K.	C_p, cal./mole	T, °K.	C_p, cal./mole
52.8	8.900	54.5	7.984	54.0	31.38
56.6	9.719	58.2	9.002	54.9	32.02
60.4	10.57	62.6	10.23	57.8	34.18
64.3	11.45	67.1	11.48	59.1	35.09
68.3	12.36	71.5	12.72	63.1	38.00
72.5	13.28	75.8	13.93	65.8	39.94
80.6	15.01	81.5	15.47	68.1	41.61
84.8	15.88	86.3	16.70	75.5	47.61
94.8	17.92	95.0	18.95	75.8	48.07
104.4	19.88	104.5	21.36	81.0	51.03
115.4	22.12	115.1	23.91	85.9	54.01
125.1	24.06	124.4	26.07	90.1	56.56
134.8	26.09	134.9	28.42	94.6	59.33
145.4	28.23	145.8	30.76	104.3	65.15
155.5	30.42	155.6	32.81	115.2	71.49
165.3	32.69	165.6	34.72	124.2	76.72
175.5	35.38	175.8	36.75	134.9	82.89
185.3	38.19	185.6	38.48	145.3	88.53
196.0	42.19	196.0	40.32	155.6	94.22
205.4	46.78	206.0	41.97	165.5	99.62
208.6	48.87	215.6	43.54	175.7	105.2
211.5	50.55	226.4	45.10	185.5	110.2
214.3	53.17	236.0	46.40	196.4	115.8
216.8	55.90	246.2	47.75	205.8	120.5
219.3	59.29	256.0	49.22	210.1	122.9
221.5	64.34	266.3	50.53	214.4	125.0
223.0	201.3	276.3	51.64	218.4	127.0
223.4	1324	286.0	52.74	222.4	128.8
224.5	78.75	296.2	53.90	226.3	131.0
227.1	39.66	(298.16)	54.12	235.7	135.0
230.2	39.77			246.0	139.8
233.3	39.90			256.1	144.7
237.0	40.19			266.0	149.2
246.7	41.00			276.5	153.8
256.7	41.98			285.9	157.8
266.0	42.48			296.1	162.0
276.4	43.25			(298.16)	163.3
286.0	43.96				
296.1	44.80				
305.7	45.35				
310.6	45.58				
(298.16)	44.81				

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(2) Chemist, Pacific Experiment Station.

(3) Shomate, THIS JOURNAL, **67**, 765 (1945).

(4) Giauque and Stout, *ibid.*, **58**, 1144 (1936).

(5) Kelley, *ibid.*, **63**, 1137 (1941).

(6) Shomate and Kelley, *ibid.*, **66**, 1490 (1944).