ranging from 4 to 24 (*3*). On the basis of the inherent sensitivity of the two calorimeters used and the good agreement with Wu *et al.*, the present results are believed more accurate.

The values of RTh_0 for the CsCl with LiCl and the KCl with LiCl mixings are large, and change by 20 to 30% in the concentration range 1 to 3*m*. The concentration dependence could be due to either ion atmosphere effects on like-charged pairs, or triplet interactions (*1, 5, 9*). The 20 to 30% change in RTh_0 indicates that these effects are only 20 to 30% as large as the like-charged pair interactions. This behavior is similar to the behavior of most alkali chloride mixtures (*3, 4, 9*).

The results of the CsCl with KCl mixings are more unusual. The value of RTh_0 is comparatively small; this means that the heat of interaction of a Cs^+–K^+ pair is almost the average of the heat of interaction of a Cs^+–Cs^+ pair and a K^+–K^+ pair, since this is the change in pair interactions that takes place in the mixing process (*1*). The other interesting thing about the CsCl with KCl mixing is that RTh_0 changes sign as the concentration increases. This is the first example of this for a symmetrical mixture. Evidently, the like-charged pair interactions are small enough that, at high concentrations, triplet interactions are large enough to change the sign of RTh_0. Because of this change in sign, this mixture at $I = 3$ violates the sign-predicting rule of Young and coworkers (*6, 10, 11*). This is not too surprising, since the rule really predicts like-charged pair interactions (*7*), and it is the triplet interactions that produce a negative RTh_0 in this mixing at $I = 3$.

ACKNOWLEDGMENT

This study was aided by a grant from the Office of Saline Water, U. S. Department of Interior, Washington, D. C. The authors would also like to thank Gerald C. Kratz for help in constructing the calorimeter.

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RECEIVED for review February 27, 1969. Accepted November 6, 1969.

Ternary Systems: Water–Alkali Metal Hexafluorosilicates

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The existence of $Na_3Li(SiF_6)_2$, $NaLiSiF_6$, $KLiSiF_6$, $RbLiSif_6$, and $CsLiSiF_6$ was discovered from solubility measurements on the systems M_2SiF_6–Li_2SiF_6–H_2O at 25° C. ($M = Na$, K, Rb, Cs). X-ray data indicate that these salts are orthorhombic, $a = 8.680$, $b = 6.500$, $c = 7.026$; orthorhombic, $a = 9.600$, $b = 9.143$, $c = 9.300$; orthorhombic, $a = 9.823$, $b = 5.805$, $c = 7.560$; orthorhombic, $a = 11.230$, $b = 9.693$, $c = 8.783$; and hexagonal, $a = 11.334$, $c = 9.271$ A., respectively. The space groups of $KLiSiF_6$, $RbLiSiF_6$, and $CsLiSiF_6$ are *Pcam* or $Pca2_1$, *Pbcn*, and $P6_322$, respectively. Solid solutions occur in the systems M_2SiF_6–Rb_2SiF_6–H_2O ($M = K$, Cs). The remaining systems are simple. The isothermally invariant saturated solutions in the systems M_2SiF_6–Na_2SiF_6–H_2O ($M = K$, Rb, Cs) are: K_2SiF_6, 0.096 ± 0.002, Na_2SiF_6, 0.759 ± 0.019; Rb_2SiF_6, 0.138 ± 0.001, Na_2SiF_6, 0.789 ± 0.014; Cs_2SiF_6, 0.83 ± 0.01, Na_2SiF_6, 0.793 ± 0.011%, respectively.

AQUEOUS TERNARY SYSTEMS of alkali metal hexafluorosilicates were investigated by solubility and x-ray methods in a search for double salts with no hydrogen bonding. The suggestion has been made that such double salts are actually complex salts, structures of two ions only (*2*). This idea is supported by the discovery of $Na_3Li(SiF_6)_2$, $NaLiSiF_6$, $KLiSiF_6$, $RbLiSiF_6$, and $CsLiSiF_6$ reported here, particularly in view of the known tendency of the lithium ion to form complexes and the absence of double salts in the alkali metal hexafluorosilicate systems where the ion was not present.

EXPERIMENTAL

Solubility. The hexafluorosilicate salts were prepared as described earlier (*2*). Analyzed lithium hexafluorosilicate solutions were used instead of the solid in the preparation of half of the mixtures in each of the systems M_2SiF_6—Li_2SiF_6—H_2O ($M = Na$, K, Rb, Cs). Mixtures of known composition were equilibrated at 25° C. for 30 to 60 days. The saturated solutions were analyzed finally either for total solids and one metal, except cesium, or directly for two metals.

In the first procedure, which was applied to the sys-

Table I. Systems M_2SiF_6(A)–Li_2SiF_6(B)–H_2O(W) at 25° C.

Complex		Solution		Solid Phase Calcd., %A[a]	Solid Phase
%A	%B	%A	%B		
		M = Na			
11.82	7.86	0.63	8.48	96.9	ss[b]
9.85	8.46	0.60	8.98	96.4	ss
8.98	11.84	0.61	12.43	94.2	ss
9.15	13.25	0.56	12.64	81.6	ss + 3A·B[c]
8.88	13.52	0.56	12.64	79.1	ss + 3A·B
8.24	14.57	0.56	13.75	78.0	3A·B
8.92	15.83	0.54	15.17	78.7	3A·B
7.93	17.12	0.52	16.64	78.3	3A·B
7.84	18.25	0.48	17.87	78.1	3A·B
9.23	19.21	0.45	18.67	76.6	3A·B
9.05	20.07	0.44	19.87	78.3	3A·B
9.74	22.62	0.44	20.19	68.4	ss[c]
8.85	23.23	0.40	20.10	58.4	ss
9.20	24.26	0.34	20.63	56.4	A·B
7.96	24.16	0.34	21.02	56.0	A·B
10.16	25.96	0.28	21.96	55.6	A·B
7.75	27.30	0.24	24.68	55.9	A·B
7.02	29.03	0.17	26.71	53.6	A·B
8.98	31.27	0.15	28.55	54.5	A·B
7.47	32.34	0.13	29.76	52.0	A·B + B
10.71	46.86	0.14	29.82	27.0	A·B + B
2.61	37.82	0.13	29.55	16.35	A·B + B
1.29	39.30	0.13	29.64	7.65	A·B + B
		M = K			
9.81	4.49	0.11	5.01	100.4	A
8.86	11.86	0.17	13.04	100.6	A
8.03	14.95	0.19	15.65	92.6	A + A·B
7.50	17.13	0.19	15.68	70.4	A + A·B
7.68	19.54	0.17	16.44	59.2	A·B
7.79	20.35	0.17	17.29	59.1	A·B
9.09	26.91	0.11	24.44	59.3	A·B
9.83	29.66	0.09	27.24	58.3	A·B
6.76	32.59	0.08	29.76	49.4	A·B + B
1.47	36.52	0.07	29.65	11.96	A·B + B
		M = Rb			
9.51	5.14	0.17	5.68	100.1	A
7.93	8.28	0.26	9.02	100.7	A
9.42	10.32	0.29	11.30	99.3	A
8.67	11.89	0.24	11.33	83.2	A + A·B
8.73	13.20	0.29	11.29	72.4	A + A·B
7.75	17.06	0.22	15.01	66.9	A·B
8.56	20.18	0.15	18.38	67.3	A·B
7.99	25.42	0.10	24.40	67.0	A·B
8.39	27.12	0.09	26.41	67.9	A·B
7.66	31.21	0.08	29.76	59.0	A·B + B
1.85	36.44	0.09	29.58	14.44	A·B + B
		M = Cs			
10.06	4.69	1.18	5.09	99.3	A
8.91	11.84	1.80	12.83	101.0	A
9.96	12.14	1.90	13.11	98.5	A
9.34	17.99	2.52	19.33	99.8	A
10.14	19.84	2.67	20.96	92.5	A + A·B
13.11	20.01	2.63	20.94	86.5	A + A·B
9.63	21.44	2.72	20.84	73.1	A·B
8.24	24.09	2.16	23.91	74.0	A·B
9.64	26.75	1.82	26.79	73.6	A·B
10.41	27.76	1.75	27.75	72.2	A·B
7.47	32.07	1.54	29.57	50.0	A·B + B
3.45	31.58	1.64	29.45	33.3	A·B + B
1.47	37.79	1.47	29.66	1.47	B

[a] Tie lines extrapolated to %A at 0%W. [b] Solid solution. [c] Assignment based on x-ray data.

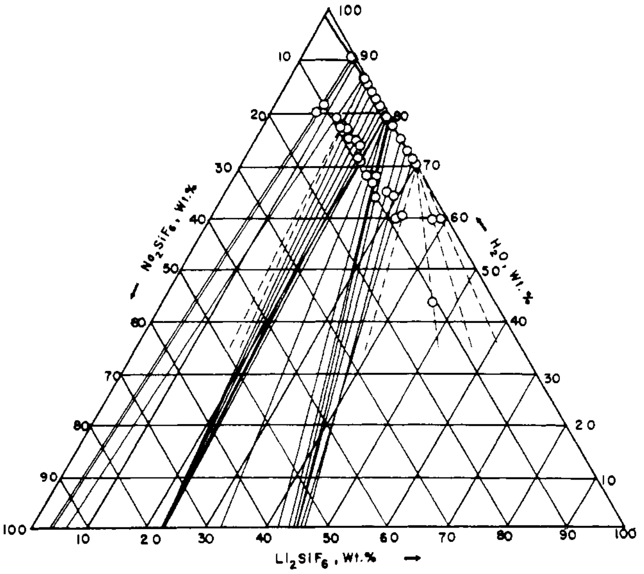

Figure 1. System Na_2SiF_6—Li_2SiF_6—H_2O at 25° C.

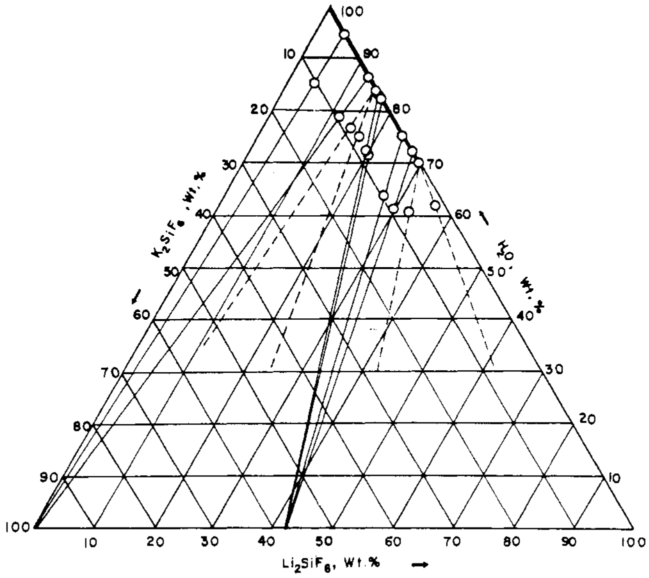

Figure 2. System K_2SiF_6—Li_2SiF_6—H_2O at 25° C.

tems M_2SiF_6—Li_2SiF_6—H_2O (M = Na, K, Rb, Cs) and Na_2SiF_6—Cs_2SiF_6—H_2O, the solutions were evaporated to dryness in platinum, and the residue was dried at 110° to 120° C. and weighed as mixed hexafluorosilicates. Sodium, potassium, or rubidium in these residues was determined by flame photometry with an EEL (Evans Electroselenium, Ltd., England) instrument; lithium was determined, only in the residues containing both lithium and cesium, by decomposition of lithium hexafluorosilicate to lithium fluoride at 400° C. In the second procedure, which was applied to the systems M_2SiF_6—Na_2SiF_6—H_2O (M = K, Rb), the evaporation step was omitted and both alkali metals were determined by flame photometry. However, potassium, rubidium, and cesium could not be determined in the presence of each other by these procedures. Attempts were made to use inorganic ion exchangers in conjunction with flame photometry in these instances. The results obtained were not sufficiently accurate to warrant presenting the solubility data pertaining to the three system involving pairs of hexafluorosilicates of these metals. All equilibrium solid phases were filtered with the aid of suction or centrifugation, rinsed with small portions of 95% ethanol, air-dried, and stored over calcium chloride prior to x-ray and density measurements or chemical analyses.

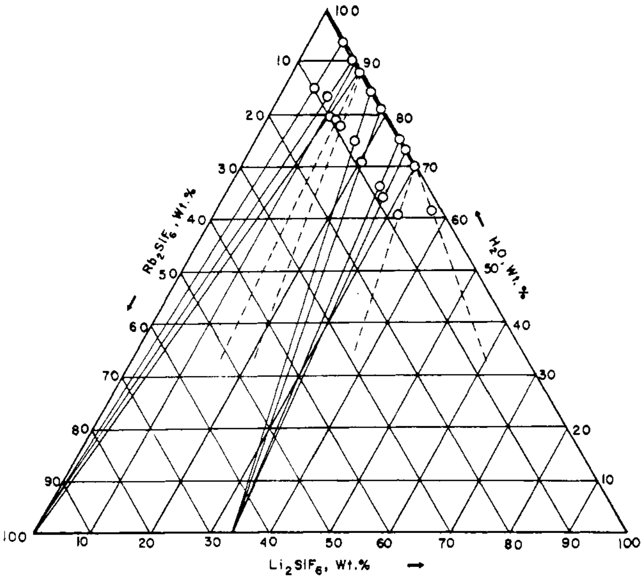

Figure 3. System Rb_2SiF_6—Li_2SiF_6—H_2O at 25°C.

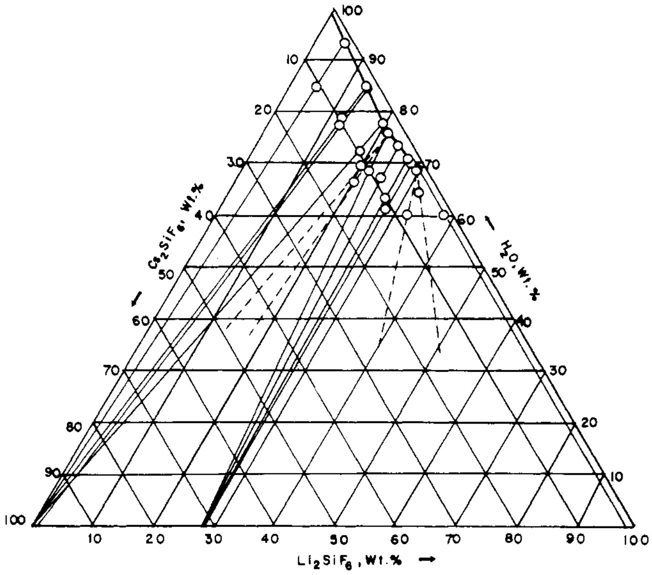

Figure 4. System Cs_2SiF_6—Li_2SiF_6—H_2O at 25° C.

Detailed solubility information pertaining to the double salts is summarized in Table I and plotted in Figures 1 to 4. The mathematical extrapolations of the tie lines (*1*) of the mixtures in which $Na_3Li(SiF_6)_2$, $NaLiSiF_6$, $KLiSiF_6$, $RbLiSiF_6$, and $CsLiSiF_6$ appear as pure solid

Table II. Invariant Solutions in Systems M_2SiF_6—Na_2SiF_6—H_2O at 25° C.

(M = K, Rb, Cs)

M	Wt. % M_2SiF_6	Wt. % Na_2SiF_6
K	0.096 ± 0.002	0.759 ± 0.019
Rb	0.138 ± 0.001	0.789 ± 0.014
Cs	0.83 ± 0.01	0.793 ± 0.011

Table III. X-Ray Data for $Na_3Li(SiF_6)_2$, $NaLiSiF_6$, $KLiSiF_6$, $RbLiSiF_6$, and $CsLiSiF_6$
(CuKα = 1.5405 A.)

$Na_3Li(SiF_6)_2$

d_{obsd},A.	I/I_0	*hkl*
4.82	8	011
4.34	100	200
3.538	45	002
3.276	31	020, 102
2.740	16	202
2.503	2	212
2.239	41	302
2.215	9	013
1.986	5	131
1.890	2	023
1.850	2	032
1.767	22	004
1.635	4	040
1.555	9	141

$NaLiSiF_6$

d_{obsd},A.	I/I_0	*hkl*
4.68	4	002
4.29	100	201
4.22	93	102, 210
3.463	83	202
3.212	37	022, 300
2.688	13	222
2.456	9	123
2.421	7	132
2.325	3	004
2.197	91	114
1.953	5	233
1.937	10	422
1.816	5	015
1.726	39	025
1.600	4	334
1.581	2	035
1.532	11	016, 106
1.424	9	145
1.346	4	163

$KLiSiF_6$

d_{obsd},A.	I/I_0	*hkl*
4.91	4	200
4.17	100	111
4.12	22	201
3.782	32	002
3.751	4	210
3.168	12	012
3.015	89	112
2.996	27	202
2.901	37	020
2.855	32	310
2.661	4	212
2.612	3	121
2.499	2	220
2.456	3	400
2.305	11	022
2.277	66	312
2.263	28	410
2.241	21	122
2.167	6	411
2.061	2	402
1.941	4	412
1.892	6	004
1.842	3	131
1.801	3	014
1.722	2	032

$RbLiSiF_6$

d_{obsd},A.	I/I_0	*hkl*
5.68	2	200
4.90	5	210
4.87	11	020
4.40	< 1	002
4.28	80	211
4.25	76	021
3.974	16	121
3.690	3	220
3.470	22	202
3.258	100	022
2.833	20	103
2.812	28	222
2.808	16	400
2.720	< 1	113
2.424	< 1	040
2.366	23	402
2.310	8	303
2.228	45	240
2.123	20	042
1.998	< 1	024
1.884	4	224
1.881	6	333
1.833	< 1	440
1.799	2	611
1.734	9	404
1.694	5	442
1.629	6	044
1.614	64	060

$CsLiSiF_6$

d_{obsd},A.	I/I_0	*hkl*
5.78	12	110
4.95	47	020
4.90	44	111
4.64	10	002
4.36	47	021
4.05	17	012
3.712	35	120
3.601	18	112
3.373	88	121
3.324	100	022
2.976	10	103
2.901	25	122
2.833	36	220
2.447	17	040
2.419	24	222
2.396	36	123
2.366	19	401
2.333	29	132
2.316	19	004
2.249	19	230
2.225	31	033
2.169	23	042
2.152	14	114
2.096	26	024
2.026	36	232
1.947	3	142
1.720	24	242

Table IV. Summary of Crystallographic Data

	Unit Cell	Z	Dimensions, A.	Density, $D_x{}^a$	G./Cc., $D_m{}^b$
$Na_3Li(SiF_6)_2$	Orthorhombic	2	a = 8.680, b = 6.500, c = 7.026	2.99	2.78
$NaLiSiF_6$	Orthorhombic	8	a = 9.600, b = 9.143, c = 9.300	2.80	2.83
$KLiSiF_6$	Orthorhombic	4	a = 9.823, b = 5.805, c = 7.560	2.90	2.88
$RbLiSiF_6$	Orthorhombic	8	a = 11.230, b = 9.693, c = 8.783	3.26	3.21
$CsLiSiF_6$	Hexagonal	8	a = 11.334, c = 9.271	3.63	3.54

^aD_x = x-ray$_x$ ^bD_m = measured.

phases agree well with the calculated compositions of the double salts—78.3, 54.7, 58.6, 66.8, and 72.3% M_2SiF_6, respectively. Selected samples of these phases were analyzed for lithium hexafluorosilicate by ignition to lithium fluoride at 400° C. In most cases, the lithium values agreed with the theoretical ones within 0.5%. A discrepancy of the order of 3% in the case of $Na_3Li(SiF_6)_2$ and $NaLiSiF_6$ finally was traced, with the aid of heating tests, to the slight decomposition of Na_2SiF_6 during the ignition. Similar results were obtained with twinned crystals of these salts prepared as described below. The five salts are incongruently soluble. There is evidence from the solubility data that solid solutions are formed between Na_2SiF_6 and $Na_3Li(SiF_6)_2$. That these solid solutions exhibit a gap in miscibility is based on x-ray evidence not presented here. The conclusion that $Na_3Li(SiF_6)_2$ and $NaLiSiF_6$ also form solid solutions is based solely on x-ray data. The solubilities in the remaining systems were too low to be useful in the determination of the nature of saturating solid phases. The only significant data obtained, pertaining to the invariant solutions in the systems M_2SiF_6—Na_2SiF_6—H_2O (M = K, Rb, Cs), are given in Table II.

X-Ray Data. The data in Table III were obtained with a General Electric XRD-5 diffractometer using Ni-filtered Cu*Kα* radiation. The spacings listed for $Na_3Li(SiF_6)_2$ are based on reflections common to all of the phases marked 3A · B in Table I, with certain weak reflections attributed to the presence of component salts omitted. The same is true of the spacings for $NaLiSiF_6$. These phases were extremely fine and difficult to free from adhering mother liquor. The intensities given are for the phases in equilibrium with the solution containing 17.87 and 21.96% Li_2SiF_6, respectively. Lattice parameters are only tentatively assigned in the case of $Na_3Li(SiF_6)_2$ and $NaLiSiF_6$ at this time. However, the data for $KLiSiF_6$, $RbLiSiF_6$, and $CsLiSiF_6$ were indexed with the aid of precession and Weissenberg photographs of single crystals, and films obtained with a Norelco 114.6-mm. powder camera on powdered single crystals. Also, the space groups were determined in these cases.

The diffraction symmetry of the zero- and first-level photographs of $KLiSiF_6$ and $RbLiSiF_6$ was 2mm. Systematic absences in $0kl$ reflections, when $l \neq 2n$, and in $h0l$, when $h \neq 2n$, indicated space group *Pcam* or $Pca2_1$ for $KLiSiF_6$. Absences in $0kl$, when $k \neq 2n$, $h0l$, when $l \neq 2n$, and $hk0$, when $h + k \neq 2n$, fixed the space group of $RbLiSiF_6$ as *Pbcn*. Precession about the c axis of $CsLiSiF_6$ yielded zero- and first-level photographs which exhibited 6mm. symmetry. The only absences noted were in $000l$ reflections, when $l \neq 2n$, in precession about the a axis. This indicated space group $P6_322$. In the case of the cesium salt, the precession photographs were obtained using Zr-filtered Mo*Kα* radiation. The crystals of $MLiSiF_6$ (M = Na, K, Rb, Cs) were obtained by dissolving 60 to 70 mg. of M_2SiF_6 in approximately 15 grams of hot 25% Li_2SiF_6 solution, which had been just saturated with M_2SiF_6 at 25°, and then cooling to 25° at a rate of 1° to 2° per hour. To obtain $Na_3Li(SiF_6)_2$, 17% $LiSiF_6$ solution was used. All the crystals were optically anisotropic. Those of the sodium salts were twinned and unsuitable for single-crystal work. The intensities given for $KLiSiF_6$, $RbLiSiF_6$, and $CsLiSiF_6$ in Table III were obtained with composite samples of equilibrium solid phases. Table IV summarizes the crystallographic data of the double salts. The densities of equilibrium phases appearing in the table were measured pycnometrically, benzene being the displaced liquid, with an estimated accuracy of 1 to 2%.

Within the limitations of diffractometer measurements, the solid phases in the systems M_2SiF_6—Na_2SiF_6—H_2O (M = K, Rb, Cs) and K_2SiF_6—Cs_2SiF_6—H_2O were mixtures of the pure components. These conclusions, as well as those which follow, were supported by powder camera films of crystals of similar habit and of composites of crystals which were obtained by the slow isothermal evaporation of various solutions in the systems. The diffractometer records of solid phases in the system K_2SiF_6—$RbSiF_6$—H_2O indexed completely on the basis of a single cubic phase. Several reflections are given in Table V to show the change in lattice dimensions. They indicate a slight negative deviation from Vegard's law (*3*).

Finally, all of the equilibrium solid phases in the system Rb_2SiF_6—Cs_2SiF_6—H_2O were cubic: One phase, which contained 91 mole % Rb_2SiF_6 could not be distinguished from pure Rb_2SiF_6; a second, which was 18 mole % $RbSiF_6$, gave a diffraction pattern similar to 100% Cs_2SiF_6, a = 8.919 A., but with a measurably different lattice dimension, a = 8.811 A.; a third phase, which was 56 mole % Rb_2SiF_6, yielded a diffraction pattern that appeared to be a composite of the first two. The measured dimension of the Cs_2SiF_6-rich phase in

Table V. X-Ray Data of Continuous Solid Solutions (Cubic) in System K_2SiF_6–Rb_2SiF_6–H_2O at 25° C.

Mole Fraction Rb_2SiF_6	d_{220}	d_{222}	d_{400}
0.000	2.877	2.351	2.034
0.250	2.877	2.360	2.045
0.333	2.901	2.366	2.047
0.397	2.910	2.381	2.061
0.500	2.933	2.399	2.079
0.585	2.940	2.401	2.076
0.750	2.964	2.418	2.095
1.000	2.996	2.440	2.113

this third case was $a = 8.798$ A. It was concluded from these data that a miscibility gap exists in the system.

ACKNOWLEDGMENT

The principal author thanks Ben Post for the opportunity of doing the single-crystal work at Polytechnic Institute of Brooklyn while on sabbatical leave.

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RECEIVED for review March 5, 1969. Accepted August 15, 1969.

Enthalpy of Formation of Germanium Tetrafluoride

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The energy of formation of germanium tetrafluoride was measured by direct combination of the elements in a bomb calorimeter. From these measurements the standard enthalpy of formation $\Delta H_f°(GeF_4, g) = -284.42 \pm 0.38$ kcal. mole^{-1} was obtained.

THERMODYNAMIC STABILITIES of Group IV tetrafluorides can be measured by many techniques, but direct fluorinations should be the most reliable and lead to the fewest ambiguities. In an extended series of measurements, the authors studied the reaction of elemental germanium with fluorine, and repeated some earlier unpublished measurements which were cited by O'Hare *et al.* (*14*) as being approximately 10 kcal. mole^{-1} less negative than their value. This discrepancy has now been resolved, and the value obtained supports the other recently published results (*4*, *14*).

EXPERIMENTAL

Materials. Germanium, in ingot form, was purchased from Alfa Inorganics, Inc.; it had a specified purity of 99.995%. Spectrographic analysis failed to reveal any impurity. However, a sample which had been ground for combustion had an oxygen impurity of 225 ± 18 p.p.m. (fast neutron activation analysis). Fluorine, 99.8% pure, was supplied by the Allied Chemical Corp. Impurities of hydrogen fluoride were removed by passing the fluorine through a trap packed with sodium fluoride. Tungsten foil and wire, both 99.99% pure, were obtained from A. D. Mackay and Co. A listing of the nature and level of impurities in the tungsten was provided by the supplier. Calculations showed that the impurity level had no effect on the energy of fluorination of tungsten. The Teflon powder used in these experiments was manufactured by Du Pont (TE 3086, Lot 20022), and its energy of fluorination had been determined by Wood *et al.* (*16*).

Calorimeter and Combustion Technique. The calorimeter used was identical to the Argonne National Laboratory Design CT-3986. Combustions were carried out in a Parr 1004 nickel bomb adapted so the two-chamber principle (*9*) could be employed in effecting combustion. An inner nickel chamber, filled with helium, contained the sample, which was isolated from the fluorine in the main chamber by a diaphragm of tungsten 0.001 inch thick. The ignition system utilized a condenser discharge unit, similar to that described by Lacina *et al.* (*10*), delivering a pulse of 1.8 cal. of electrical energy. This ignition pulse reached the tungsten diaphragm via a short length of tungsten wire, ignited the diaphragm, and consequently initiated the reaction. Temperatures were recorded using a Dymec Model 2801-A quartz thermometer. The corrected temperature rise associated with the bomb reaction was calculated using standard methods (*1*) and a suitable computer program.

The energy equivalent of the calorimeter, ε(calor.) was measured by combustion of standard benzoic acid (NBS sample 39i with certified energy of combustion 26434 ± 3 abs. joules gram^{-1}). A series of six calibration experiments gave $\varepsilon\text{(calor.)} = 3706.02$ cal. deg.$^{-1}$ with a standard deviation of the mean of 0.5 cal. deg.$^{-1}$ (1 cal. $\equiv$ 4.184 abs. joules).

In a series of preliminary experiments, powdered germanium from Alfa Inorganics was burned, but answers consistently lower than previously published data were obtained. However, x-ray powder patterns of this material showed not only germanium lines, but also strong germanium oxide lines. The energy of fluorination per gram of this material would thus be expected to be less than that of pure germanium. The ground germanium ingot used in the final combustion experiments gave x-ray powder patterns which showed no indication of germanium oxide impurity.

After several exploratory experiments, essentially complete combustion was achieved when an intimate mixture of ground germanium ingot and Teflon was ignited in a prefluorinated nickel cup using 5.4 atm. of fluorine. Infrared spectra of the gaseous products, after removal of excess fluorine, showed the presence of GeF_4, CF_4, and WF_6 (*11*). No other gaseous products were identified. The small amount of solid residue remaining after combustion was weighed accurately. Analysis of the residue, from a typical experiment, by Schwarzkopf