

373°K. is 6.38 ± 0.01^{23} cal. g.-atom⁻¹ deg.⁻¹; and with this the values of Meads, Forsythe and Giauque, which increase almost linearly from 6.183 at 200° to 6.418 at 300°K., obviously cannot be made to agree by any plausible extrapolation.

So far as the present measurements indicate, the heat capacity of solid lead increases uniformly with temperature above 273°K. It is noteworthy that the values of Meads, Forsythe and Giauque increase at almost exactly the same rate between 200 and 300°K. One is led to wonder whether the discrepancy between the two sets of values is due to a different state of the lead. Prior to their measurements they had crystallized theirs over a period of several days, whereas the sample of the present investigation had previously been melted and recrystallized rapidly. However, the heat content values on the solid for any one furnace temperature (of which the first was 300°) showed no trend with time, and it is difficult to believe that this metal could be held for a total of several hours at temperatures as near its melting point without the occurrence of thorough annealing.

In this connection, heat content measurements were made in this Laboratory a few years ago on samples of highly pure sodium following very slow and afterwards very rapid crystallization.³ The mean capacity after the latter treatment was found to be different by the following percentages: 0–59°, $0.4 \pm 0.15\%$ higher; 0–40°, $0.25 \pm 0.15\%$ and

$0.5 \pm 0.2\%$ lower.²³ This evidence, of course, is largely inconclusive.

The heat capacity of lead in the liquid state has been found to decrease with temperature over a considerable range just above the melting point. This has been found true of numerous other liquid metals, alloys, and salts. One such material may be the liquid eutectic alloy of lead and bismuth (45% Pb), for which the authors recently obtained an average heat capacity between 150 and 800° of 0.142 abs. joule g.⁻¹ deg.⁻¹, and an indication from the less precise results that the heat capacity may decrease with temperature by 0.01–0.02% per deg. The heat capacity of liquid lead, which according to equation 4 averages over the same temperature range 2–3% higher (per g. or per g. atom), decreases 0.01% per deg.

Acknowledgments.—The assistance of several members of the National Bureau of Standards is gratefully acknowledged: H. A. Bright furnished the sample of lead, B. F. Scribner and associates analyzed it, J. G. Thompson donated the pure bismuth used to prepare the eutectic alloy of lead and bismuth, and S. J. Rosenberg gave advice in the selection of a suitable container material. The Allegheny Ludlum Steel Corporation kindly donated the stainless steel type 446 used in constructing the container.

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[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

Lithium Fluoride: Heat Content from 0 to 900°, the Melting Point and Heat of Fusion¹

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RECEIVED APRIL 26, 1954

Using an ice calorimeter and a silver-core furnace, the relative heat content of lithium fluoride was measured from 0 to 900°. The melting point was found to be $848 \pm 1^\circ$. The derived heat capacity of the solid is believed accurate in general to $\pm 0.5\%$, and that of the liquid over the 42° range of measurement, to $\pm 1.5\%$. The heat capacity-temperature curve, which is in good agreement with recently reported values from –254 to –1°, possesses a point of inflection at approximately 450°. The values of entropy and free energy also were calculated.

The alkali halides, because of their structural simplicity and high stability, have been studied extensively for many years, with a relatively high degree of success in coordinating and explaining their properties. Yet much of this work has been handicapped by a lack of accurate data at high temperatures. The measurements reported here extend thermal values for lithium fluoride to 50° above its melting point.

Experimental

Sample.—The lithium fluoride was obtained from the Harshaw Chemical Co., Cleveland, Ohio, in the form of single crystals of approximately 1 cc. each. A spectrochemical analysis of the original sample showed the metallic impurities to be a few thousandths of 1% each of calcium, magnesium, sodium and nickel, plus traces of aluminum, chromium, iron and silicon. After the measurements in a nichrome container had been completed, similar analyses revealed in addition a few hundredths of 1% of chromium and a few thousandths of 1% of aluminum, manganese and silicon. The constancy of temperature during melting and freezing, described later, is in accord with these analyses.

Calorimetric Procedure.—The method and apparatus have been described in detail previously.² Briefly, the sample in a container is heated in a furnace to a known temperature and is then dropped into an ice calorimeter that measures the heat evolved in cooling sample and container to 0°. Adequate time, as determined by special tests, was allowed for equilibration, with particular attention to those runs in which the furnace temperature was only a few degrees above the melting point. The heat contributed by the container and that lost during the drop into the calorimeter were accounted for by similar measurements on the empty container, which was constructed of Nichrome V and, after filling with helium, was sealed by a gold gasket. The temperature of the furnace core, maintained highly uniform by a housing of silver $\frac{1}{2}$ in. thick, was measured up to 600° by a platinum resistance thermometer and above 600° by a platinum-platinum-rhodium thermocouple. All measuring instruments were calibrated at the National Bureau of Standards, and very small corrections were applied for unavoidable inconsistencies in temperature and masses of container materials entering the calorimeter.

Melting Point.—A separate sample of lithium fluoride in a helium-filled Inconel container was suspended in the furnace. By maintaining the temperature of the latter constant to $\pm 0.1^\circ$ for successive periods of several min. each at approxi-

(1) This work was sponsored by the U. S. Air Force, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

(2) D. C. Ginnings, T. B. Douglas and A. F. Ball, *J. Research Natl. Bur. Standards*, **45**, 23 (1950); *THIS JOURNAL*, **73**, 1236 (1951).

mately 4, 7 and 12° above the m.p., the sample was completely melted. The differences in temperature between the furnace and the melting sample were measured by a chromel-alumel differential thermocouple, whose effective sensitivity was thereby determined in place. These differences were plotted against furnace temperature and extrapolation to zero difference gave a value for the melting point of the sample. Similar readings during solidification, with the furnace 3 and 11° below the sample temperature, extrapolated to a melting point 1/4° lower than that during fusion. The mean m.p. thus found was 848.1° (International Temperature Scale of 1948³), and is thought to be uncertain by $\pm 1^\circ$. The variation of sample temperature during fusion and solidification indicated the impurity to be 0.05 mole % or less, which is consistent with the spectrochemical analyses.

Heat Content Data.—The mean measured heat at each furnace temperature (International Temperature Scale of 1948³) is given for the empty container in Table I and for the container with sample in Table II, together with the average deviation from the mean.⁴ These values have been fully corrected except for the inaccurately known heat lost

TABLE I

EMPTY CONTAINER

Furnace temp., t , °C.	Measured heat (mean), ⁴ abs. joules		No. of runs	Smoothed heat, abs. joules
	Series A	Series B		
100.00	543.3 \pm 1.7		4	543.3
200.00	1123.4 \pm 1.8		7	1121.6
300.00	1723.7 \pm 2.2		6	1723.2
400.00	2343.7 \pm 1.5	2345.4 \pm 2.2	6	2344.8
500.00	2984.8 \pm 1.2	2982.8	1	2984.0
600.00	3649.3 \pm 3.3	3648.9 \pm 0.9	5	3648.7
699.3	4353.3 \pm 2.3		4	4353.2
796.4	5065.9 \pm 0.2	5067.2 \pm 0.9	4	5066.6
830.2				5315.9
853.9				5491.7
860.2		5538.5 \pm 2.5	4	5538.5
875.0				5648.5
896.0	5804.5 \pm 0.6	5805.4 \pm 3.0	6	5805.4

TABLE II

LITHIUM FLUORIDE

Furnace temp., t , °C.	Measured heat ^a (mean), container + LiF, abs. joules	No. of runs	Relative heat content of LiF ^a ($H_t - H_0$)	
			Mean obsd. abs. joules g. ⁻¹	Calcd. abs. joules g. ⁻¹
100.00	1252.2 \pm 0.5	3	166.55	-0.05
200.00	2607.3 \pm 0.6	4	349.05	- .07
300.00	4028.6 \pm 1.2	4	541.63	+ .15
400.00	5503.8 \pm 0.7	3	742.18	+ .22
	5496.0 \pm 1.4 ^b	2		
500.00	7028.8 \pm 1.8	4	950.29	- .33
600.00	8606.4 \pm 1.6	3	1164.76	- .16
	10249.6 \pm 0.6	4	1385.30	+ .34
699.3	10240.3 \pm 2.5 ^b	6		
	10240.5 \pm 0.4 ^c	2		
796.4	11922.7 \pm 2.3	3	1610.77	+ .03
830.2	12516.5 \pm 1.1 ^d	3	1691.71	- .11
853.9	17379.9 \pm 2.2 ^d	5	2793.02	+ .07
875.0	17762.1 \pm 1.3 ^d	3	2845.97	- .11
896.0	18141.8 \pm 2.8 ^d	6	2898.32	+ .06

^a Liquid above 848°. ^b After rapid freezing of the LiF.

^c After much slower freezing of the LiF. (Values marked ^b and ^c have not been adjusted to correct for prior fusion of the sample, and were not used in arriving at the net heats due to LiF.) ^d Approximately 10 joules has been added to correct to the conditions preceding the initial fusion of the LiF.

(3) H. F. Stimson, *J. Research Natl. Bur. Standards*, **42**, 209 (1949).

(4) After adjusting to the basis of an infinite number of observations by multiplying the observed variation by the factor $\sqrt{n/(n-1)}$, where n is the number of observations actually made at that temperature.

during the drop into the calorimeter, which very nearly canceled in subtracting the values of Table I from those of the second column of Table II to obtain the net heat due to the sample. The values of series A in Table I were measured a year earlier, and a correction of several tenths of 1% was necessitated by a different mass of the container at that time. The smoothed values of Table I were obtained from a smooth empirical deviation plot.

In the heat content measurements only one sample of lithium fluoride was used, the mass being 4.2564 g. In Table II the heats not bearing superscripts were determined before the sample had been melted and thereby came into intimate contact with the container. The remaining values, determined after the initial fusion, were in comparison several joules lower, but there was no subsequent trend with time except that the first two runs after initial fusion, made at 896.0°, were respectively, 18 and 11 joules higher than the subsequent six runs at this temperature, and were discarded. Furthermore, the second and third sets of values at 699.3° do not reveal any dependence of the heat capacity of the solid on the rate at which it had been crystallized. The drop in relative heat content after fusion was therefore attributed to two other causes: to the small contamination from the slightly oxidized container wall, as revealed by the subsequent spectrochemical analyses; and to a small change in the thermocouple calibration that probably occurred at the highest temperatures and was not detected till later. Each of the affected final heat values was therefore increased by an amount varying linearly with temperature (about 10 joules) to correct for this apparent systematic error. The calculated values referred to in the last column of Table II were obtained from the empirical equations given later.

Derived Properties.—By least squares the following equations were derived to represent the observed heat content of solid and liquid lithium fluoride in excess of that of the solid at 0°, in absolute joules per g. at t , °C.

$$H_t(\text{solid}) - H_0(\text{solid}) = 2.26938t + 8.6291(10^{-5})t^2 - 1.01322(10^{-7})t^3 + 1.6845(10^{-10})t^4 - 451.849 \log_{10}[(t + 273.16)/273.16] \quad (0 \text{ to } 848^\circ) \quad (1)^5$$

$$H_t(\text{liquid}) - H_0(\text{solid}) = 657.48 + 2.50101t \quad (848 \text{ to } 896^\circ) \quad (2)$$

Though the liquid was measured at three temperatures, the temperature range is too small to justify other than a linear equation. Equations 1 and 2 give at the melting point (848.1°) a value for the heat of fusion of 1043.6 absolute joules per g. Differentiation of the two equations gives for the heat capacity, in absolute joules per g. °C.

$$C_p(\text{solid}) = 2.2694 + 1.726(10^{-4})t - 3.040(10^{-7})t^2 + 6.738(10^{-10})t^3 - 196.23/(t + 273.16) \quad (0 \text{ to } 848^\circ) \quad (3)$$

$$C_p(\text{liquid}) = 2.501 \quad (848 \text{ to } 896^\circ) \quad (4)$$

The heat capacity values found in the present work are plotted in Fig. 1, together with representative values of Clusius, Goldmann and Perlick⁶ be-

(5) The use of a logarithmic term of this form was found to lead to a superior fit to the observed heat content of several ionic solids at elevated temperatures (L. F. Epstein, private communication).

(6) K. Clusius, J. Goldmann and A. Perlick, *Z. Naturforsch.*, **4A**, 424 (1949).

low 0° .⁷ Each experimental point above 0° was computed by dividing by the temperature difference the difference between two successive unsmoothed heat content values in Table II, and applying the small correction for curvature. The solid curve above 298°K. represents equation 3.

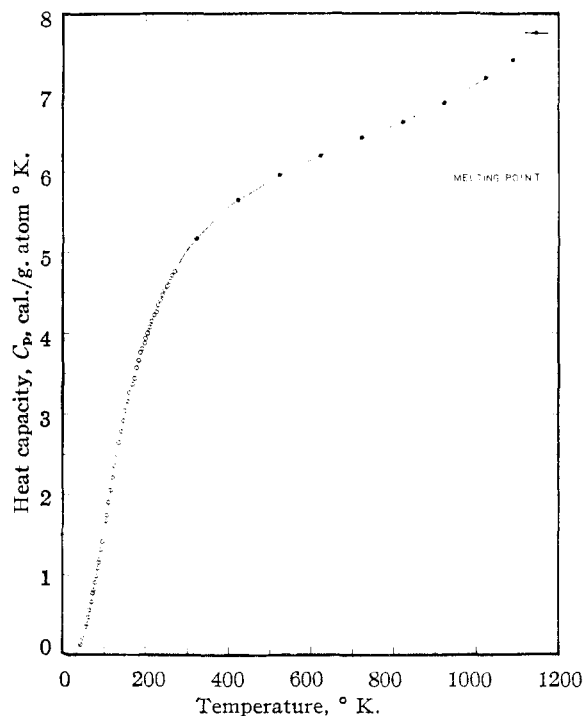


Fig. 1.—Heat capacity of lithium fluoride: ●, Douglas and Dever (1952); ○, Clusius, Goldmann and Perlick (1949).

A careful evaluation of the Third Law entropy of solid lithium fluoride at 298.16°K. , using the foregoing low temperature results, gave $8.52 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$. Kelley⁸ gave 8.32 ± 0.08 . The latter value, however, is based on an earlier paper⁹ giving values of C_v only, and the inadvertent use of C_v instead of C_p would actually lead to an entropy value at 298.16°K. that is $0.20 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$ too low.

From equations 3 and 4, the heat of fusion, and the value calculated by the authors for the absolute entropy at 298.16°K. , the common thermodynamic properties of solid and liquid lithium fluoride were computed and are given in Table III.

Discussion

The probable error of the mean heat content of lithium fluoride at each furnace temperature, relative to that at 0° , was in the present measurements close to ± 0.2 absolute joule g.^{-1} . This corresponds to an average of approximately $\pm 0.03\%$ of the heat content. The corresponding probable error of the mean heat capacity of the solid over the 100° intervals of measurement averages $\pm 0.15\%$, and that of the liquid over the whole 42° interval is approximately $\pm 0.5\%$. On consideration of major systematic errors also, the derived heat capacity

(7) The mean atomic weight of LiF is 12.97.

(8) K. K. Kelley, *U. S. Bur. Mines Bulletin*, **477**, 60 (1950).

(9) K. Clusius, *Z. Naturforsch.*, **1**, 79 (1946).

TABLE III
THERMODYNAMIC FUNCTIONS OF LITHIUM FLUORIDE^a
(cal. $\text{deg.}^{-1} \text{ mole}^{-1}$)

$T, ^\circ\text{K.}$	C_p^s	S^s	$\frac{H^s - H_{298.16}^s}{T}$	$-\left(\frac{F^s - H_{298.16}^s}{T}\right)$
298.16	10.015	8.52	0	8.52
300	10.042	8.582	0.062	8.520
325	10.377	9.399	0.842	8.556
350	10.667	10.179	1.534	8.645
375	10.919	10.924	2.152	8.772
400	11.142	11.636	2.707	8.929
425	11.341	12.317	3.209	9.108
450	11.520	12.971	3.666	9.305
475	11.682	13.598	4.083	9.515
500	11.831	14.201	4.467	9.734
525	11.969	14.781	4.821	9.960
550	12.098	15.341	5.149	10.192
575	12.220	15.882	5.454	10.428
600	12.336	16.404	5.738	10.666
650	12.557	17.401	6.254	11.147
700	12.770	18.339	6.712	11.627
750	12.982	19.227	7.123	12.104
800	13.200	20.072	7.496	12.576
850	13.430	20.879	7.838	13.041
900	13.677	21.654	8.156	13.498
950	13.945	22.400	8.453	13.947
1000	14.239	23.123	8.735	14.388
1050	14.563	23.825	9.005	14.820
1100	14.921	24.511	9.265	15.246
1121.3(s)	15.085	24.798	9.374	15.424
1121.3(l)	15.51	30.569	15.145	15.424
1125	15.51	30.620	15.146	15.474
1150	15.51	30.961	15.154	15.807
1175	15.51	31.294	15.161	16.133
1200	15.51	31.621	15.168	16.453

^a Mol. wt. = 25.94, 1 cal. = 4.1840 abs. joules, and $0^\circ\text{C.} = 273.16^\circ\text{K.}$

of the solid and the heat of fusion are believed accurate in general to $\pm 0.5\%$, and the mean heat capacity of the liquid between the melting point and 900° , to $\pm 1.5\%$.

As seen from Fig. 1, the previously reported low temperature measurements⁸ of the heat capacity of lithium fluoride give a curve that joins with approximate continuity the high temperature curve based on the present measurements. At 0° , where the latter are inherently less reliable than at higher temperatures, the difference amounts to 0.5% . The only other measurements previously reported seem to be those of Brönsted.¹⁰ This work, over the interval 0 to 19.6° , gave five measurements with a maximum variation of 0.8% , the mean being 1% lower than given by equation 3.

Various values for the melting point have been reported. In contrast to the authors' value of 848° , Jaeger¹¹ cited 840° , von Wartenburg and Schulz¹² gave 842° , and Kelley¹³ listed 847° . The commonly quoted value of 870° seems to have originated in measurements of the phase diagram of the fluorides of lithium and aluminum.¹⁴

Other than the authors' value of 1043.6 absolute joules g.^{-1} , no value of the heat of fusion appears to have been measured directly. Von Wartenburg and Schulz¹² measured the vapor pressure, and presumably from a closed cycle estimated 970 joules g.^{-1} . A value equivalent to 381 joules g.^{-1} was

(10) J. N. Brönsted, *Z. Elektrochem.*, **20**, 554 (1914).

(11) F. M. Jaeger, *Z. anorg. allgem. Chem.*, **101**, 201 (1917).

(12) H. von Wartenburg and H. Schulz, *Z. Elektrochem.*, **27**, 568 (1921).

(13) K. K. Kelley, *U. S. Bur. Mines Bulletin*, **393**, 66, 135 (1936).

(14) N. A. Puschin and A. B. Baskow, *Z. anorg. Chem.*, **81**, 347 (1913).

listed by Kelley,¹³ but this was estimated entirely from the phase studies referred to above.¹⁴

The point of inflection in the C_p -temperature curve of solid lithium fluoride at approximately 700°K. (Fig. 1) is outside the experimental error, and leads to an interesting marked rise below the melting point. On the other hand it is probable that the corresponding curve for the liquid has a small negative slope. (The measurements on lithium fluoride cover too small a temperature range to establish this, but such has been found to be true in the case of almost every other liquid salt measured in this Laboratory.) Thus there is some evidence from the present case for regarding the process of fusion as partly a second-order transition.

Nevertheless, any such quantitative treatment

of the available data on lithium fluoride would be difficult. C_p is generally regarded as the resultant of several rather delicately balanced factors. In the absence of compressibility measurements above 75°, it seems impossible to calculate reliable values of C_v at the high temperatures from the available C_p data. Using thermal expansion measurements made up to 800°, the linear extrapolation of compressibilities measured at 30° and 75°¹⁶ would lead to incredibly low values of C_v at high temperatures.

(15) A. Eucken and W. Dannöhl, *Z. Elektrochem.*, **40**, 814 (1934); the results of S. S. Sharma, *Proc. Indian Acad. Sci.*, **32A**, 268 (1950), obtained up to 400°, are in agreement within 1.5%.

(16) J. C. Slater, *Phys. Rev.*, **23**, 488 (1924).

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[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DIVISION, ARGONNE NATIONAL LABORATORY]

Phase Equilibria in the Condensed Systems Uranium Hexafluoride-Bromine Trifluoride and Uranium Hexafluoride-Bromine Pentafluoride

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RECEIVED MAY 17, 1954

Investigation of the systems uranium hexafluoride-bromine trifluoride and uranium hexafluoride-bromine pentafluoride has shown that the systems are simple eutectic types. The solid phases in equilibrium with saturated solutions are the pure components. The uranium hexafluoride-bromine trifluoride system exhibits positive deviation from ideality and the activity coefficients for uranium hexafluoride have been calculated. The uranium hexafluoride-bromine pentafluoride system shows only a slight deviation from ideality.

The systems uranium hexafluoride-bromine trifluoride and uranium hexafluoride-bromine pentafluoride were investigated to obtain the solubility of uranium hexafluoride as a function of temperature, and to determine the solid phases which exist in equilibrium with saturated solutions. A study of the systems was made by obtaining time-temperature cooling curves of synthetic complexes. In the system involving bromine trifluoride the visual isoplethal method also was used.

Experimental

Materials.—Bromine trifluoride and bromine pentafluoride obtained from the Harshaw Chemical Company were purified by distillation in a forty inch nickel fractionation column, one-half inch in diameter and packed with one-eighth inch nickel helices. The melting points of the bromine trifluoride shown in Table I and bromine pentafluoride shown in Table IV, agreed with the literature values^{1,2} within 0.1°. The uranium hexafluoride has a melting point which also agreed with the literature value³ as indicated in Tables I and IV.

Apparatus.—The apparatus used for the determination of the time-temperature freezing and thaw curves was similar to one previously described.⁴ In order to prevent water from condensing and freezing on the apparatus at temperatures below the dew point, and to facilitate the attainment of cooling curves at low temperatures, the apparatus was placed in a box constructed of aluminum covered plywood. Dry air was passed into the box and when necessary Dry Ice and/or liquid nitrogen were added directly to the inside of the box. The components were introduced, under an atmosphere of helium, through a one fourth inch flared nickel fitting, into nickel or Monel tubes three-fourths inch in diameter and six inches long. Uranium

hexafluoride, at 75 to 80°, was dispensed from a nickel buret containing a fluoroethene (Kel-F) sight glass.

Isoplethal analysis was also tried in the uranium hexafluoride-bromine trifluoride system. The apparatus used in determining the temperature at which the solid phase disappeared consisted of a three-fourths inch Kel-F tube, six inches in length, which was flared at the top so that it could be closed with a nickel fitting. The fitting was provided with a one-fourth inch nickel thermocouple well which extended into the sample, and a one-fourth inch flared tube through which a sample could be introduced. The temperature of the tube was controlled by placing it in a twelve cubic foot air-bath in which it was shaken with a Burrell wrist action shaker, keeping the temperature of the sample constant within 0.1°.

Temperatures were measured with iron-constantan or copper-constantan thermocouples in conjunction with a multi-point Brown Recording Potentiometer. The thermocouples and recorder were calibrated against a standardized platinum resistance thermometer employing a Leeds-Northrup G-2 Mueller bridge.

Synthetic complexes were prepared by weighing the components, under an atmosphere of helium, in the metal or Kel-F tubes. Total weights of complexes were approximately 50 g. The maximum cooling rate employed was 0.5 deg./min. Thaw curves were obtained by heating the solidified mixtures at somewhat lower rates.

Results and Discussion

The data for the system uranium hexafluoride-bromine trifluoride in terms of mole per cent. uranium hexafluoride are listed in Table I and are plotted in the usual fashion in Fig. 1. The values in Table I are the average of several determinations for any one complex. Where the datum is representative of four or more cooling curves for a complex, the average deviation from the mean is given after the value. All points plotted in Fig. 1 are assumed to be accurate within $\pm 0.5^\circ$. Good agreements were obtained among the data taken from

(1) G. D. Oliver and J. Grisard, *This Journal*, **74**, 2705 (1952).

(2) O. Ruff and W. Menzel, *Z. anorg. allgem. Chem.*, **202**, 49 (1939).

(3) G. D. Oliver and J. Grisard, *This Journal*, **75**, 2827 (1953).

(4) J. Fischer and R. C. Vogel, *ibid.*, **76**, 1497 (1954).