

by Brewer and Haber,<sup>1</sup> who have studied the equilibria of linear and cyclic dimethylpolysilazanes at elevated temperatures and pressures and found that the tendency of ring formation is larger in the silazanes than in siloxanes.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE KANSAS STATE COLLEGE AND THE UNIVERSITY OF CONNECTICUT]

## The Vibrational Spectra and Thermodynamic Functions of Lead Tetramethyl, Tin Tetramethyl and Germanium Tetramethyl

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The Raman and infrared spectra of  $\text{Pb}(\text{CH}_3)_4$ ,  $\text{Sn}(\text{CH}_3)_4$ , and  $\text{Ge}(\text{CH}_3)_4$  are given and compared with earlier investigations. The spectra have been used to make a detailed assignment of frequencies to the normal modes of vibration and to calculate values of  $C_p$ ,  $(H^\circ - E_0^\circ)/T$ ,  $-(F^\circ - E_0^\circ)/T$ , and  $S^\circ$  from 300 to 1500°K. Heat of combustion measurements were made on  $\text{Pb}(\text{CH}_3)_4$  and  $\text{Sn}(\text{CH}_3)_4$  and the results used to calculate the free energy of formation, the enthalpy of formation and entropy of formation at several temperatures for both compounds.

### Introduction

While the tetramethyl compounds of the elements of the fourth group have come in for considerable spectroscopic study, there are still uncertainties in the assignments of their modes of vibration. These uncertainties stem in main from the facts that, one, the data in the literature are incomplete, and that, two, no one worker has carried through a complete study of a number of these compounds. The authors, having had at their disposal Raman spectrographs of high speed and resolving power, and infrared equipment covering a wide spectral range, felt that a re-examination of the infrared and Raman spectra of germanium, tin and lead tetramethyls would help to clear up some of the difficulties.<sup>2-7</sup>

The assignment of frequencies made from the spectra of these compounds was used to calculate their thermodynamic functions.

**Preparations.**—The sample of  $\text{Pb}(\text{CH}_3)_4$  was supplied by Dr. Charles E. Waring of the Chemistry Department, University of Connecticut. After fractional distillation under vacuum, this sample had a b.p. 109° at 720 mm.

Tin tetramethyl was prepared by slowly adding  $\text{SnCl}_4$  to  $\text{CH}_3\text{MgI}$  in ethyl ether solution. The product was fractionated with a simple Vigreux column, washed with NaF solution, then with cold water and then with concentrated  $\text{H}_2\text{SO}_4$ . After careful fractionation, the product boiled at 78.3° at 740 mm.;  $n_D^{20}$  1.4393, yield 45%.

Germanium tetramethyl was prepared by very slowly adding  $\text{GeCl}_4$  to  $\text{CH}_3\text{MgI}$  in *n*-butyl ether solvent. The  $\text{Ge}(\text{CH}_3)_4$  was distilled off, washed with cold, concentrated  $\text{H}_2\text{SO}_4$ , and fractionated in a good micro-column, b.p. 44.3° at 740 mm.;  $n_D^{20}$  1.3882. An alternate preparation with ethyl ether solvent was found to give a 10% yield as compared with a 40% yield in *n*-butyl ether solvent.

**Raman Spectra.**—The Raman spectra of  $\text{Pb}(\text{CH}_3)_4$  and  $\text{Sn}(\text{CH}_3)_4$ , in the liquid state, were obtained using a Zeiss 3-prism instrument in the spectroscopy laboratory at the

Massachusetts Institute of Technology. The instrument had a camera lens aperture of  $F/4.5$ , and a plate factor at 4500 Å. of 30 Å./mm. Excitation was accomplished using six General Electric AH-2 arcs filtered with 10 mm. of saturated  $\text{NaNO}_2$  and Rhodamine DGN-extra (0.01 g./l.). The excitation unit has been described elsewhere.<sup>8</sup>

All Raman spectra were taken at 25°. Exposure times varied from 30 to 90 minutes. Semi-quantitative depolarization factors were determined by a single exposure method making use of a split polaroid and a half-wave plate. The split polaroid had the plane of polarization of one half perpendicular to that of the other half, and was used to split the Raman beam, which was excited by radiation from a given direction, into parallel and perpendicular components. The half-wave plate was placed behind that half of the polaroid which transmitted the parallel component. Its function was to rotate the plane of polarization of the parallel component into that of the perpendicular component. In this way, unequal polarization of one component over the other by the spectrograph was avoided.

Other Raman spectra of  $\text{Sn}(\text{CH}_3)_4$ , and Raman spectra of  $\text{Ge}(\text{CH}_3)_4$ , were obtained using a Hilger E 612 glass spectrograph at the University of Connecticut. This instrument had a camera aperture of  $F/5.7$ . Exposure times varied from 3 to 15 minutes. These short exposure times are to be attributed to the efficiency of the Hilger excitation unit, which has MgO reflectors.<sup>9</sup> The filters used were as described above. All spectra were taken on Kodak 103 aJ plates. The plates were read with a travelling microscope, and the lines converted to wave numbers with a calibration curve made from iron arc readings. The dimmer lines were read from an enlarged print made on Kodak Fast Projection Standard photographic paper. Finally, the positions of a few very dim lines were estimated, with the aid of a magnifier, by visually examining the plate against a diffusely lighted background.

The observed Raman spectra of  $\text{Pb}(\text{CH}_3)_4$ ,  $\text{Sn}(\text{CH}_3)_4$  and  $\text{Ge}(\text{CH}_3)_4$ , are given in Tables I, II and III, respectively, along with those reported by other workers.<sup>1,5,6</sup> Our spectra differ from those of previous workers in several respects. First, we observe lines not reported by other workers and, in some cases, do not observe lines reported by them as being strong. Second, we observe some lines in different positions than reported by previous workers. Third, we have resolved a number of lines reported as singlets, into doublets. The Raman spectra reported by us for  $\text{Pb}(\text{CH}_3)_4$  differ from the data of Duncan and Murray, and Siebert, mainly in that we find a number of lines which they fail to observe, namely, the weak lines at 634, 700, 1019, 1300, 1400, 1544, and 1622  $\text{cm}^{-1}$ . The line observed at

(1) (a) Kansas State College; (b) University of Connecticut.

(2) (a) A. B. F. Duncan and J. W. Murray, *J. Chem. Phys.*, **2**, 146, 642 (1934); (b) R. K. Shelton and K. S. Pitzer, *ibid.*, **18**, 595 (1950).

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(4) C. W. Young, J. S. Koehler and D. S. McKinney, *THIS JOURNAL*, **69**, 1410 (1947).

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(8) G. R. Harrison, J. R. Loofbourov and R. C. Lord, "Practical Spectroscopy," Prentice-Hall, Inc., New York, N. Y., 1948, p. 513.

(9) A. C. Menzies and J. Skinner, *J. Sci. Instruments*, **26**, 299 (1949).

1439  $\text{cm.}^{-1}$  by Siebert was found by us to lie at 1450  $\text{cm.}^{-1}$ . That these lines are due to more effective excitation, rather than to impurities, is indicated by the coincidence of these weak lines with infrared bands given by us and others.

TABLE I

RAMAN FREQUENCIES FOR  $\text{Pb}(\text{CH}_3)_4$  IN  $\text{CM.}^{-1}$ 

Duncan and Murray	Siebert	This work
130 s. (depol.)	136 (20 v.b.)	130 s., v. br. (depol.) (117-160)
460 v.s. (pol.)	460 (10)	459 v.s. (pol.)
473 m. (depol.)	472 (10)	478 v.s. (depol.)
577 v.w.		590 v.w. 634 v.w. 700 v.w.
767 w.	771 (2 v.b.)	767 m., br.
930 v.w.		930 w., br. 1019 w.
1155 m. (depol.)	1151 (10)	1154 v.s. (depol.)
1170 m. (pol.)	1167 (10)	1170 v.s. (pol.) 1300 v.w. 1400 w., br. 1450 w., br. 1544 v.w. 1622 w. 2292 v.w.
	1439 (0b.)	
2292 w.		2292 v.w.
2918 s. (pol.)	2920 (4)	2924 v.s. (pol.)
2999 s.	3001 (1b.)	2996 v.s. (depol.)
3679 v.w.		Extremely dim unre-
3755 v.w.		solved lines 3600-4000

TABLE II

RAMAN FREQUENCIES FOR  $\text{Sn}(\text{CH}_3)_4$  IN  $\text{CM.}^{-1}$ 

Pai	Siebert	This work
152 s.	151 (12v.b.)	150 (10v.b.) (136-172)
262 m.		
506 v.s. (pol.)	506 (10)	507 (10) pol.
526 m.	525 (8)	532 (10), 662 (0) br.
952 v.w.	769 (1b.)	772 (2)
1046 v.w.		1053 (1)
1200 s.	1197 (10b.)	1194 (10)
1262 v.w.		1205 (10) pol., 1346 (1), 1400 (2) 1451 (2)
	1434 (2b.)	
2915 m.	2909 (8b.)	2912 (6) pol.
2979 m.	2982 (6b.)	2988 (5)
		Dim line at about 3900

TABLE III

RAMAN FREQUENCIES FOR  $\text{Ge}(\text{CH}_3)_4$  IN  $\text{CM.}^{-1}$ 

Siebert	This work	Siebert	This work
189 (12 v.b.)	175 } 195 } 10	1445 (4b.)	1437 (1) 1878 (0)
560 (10)	558 (10)		2030 (0)
599 (6b.)	595 (9)		2223 (0)
806 (3)	825 (0)		2460 (1)
	1145 (2)		2495 (1)
	1234 (4)	2907 (8)	2907 (10)
1243 (3b.)	1247 (4)	2971 (8b.)	2978 (10)
	1331 (1)		
	1400 (1)		

Our Raman spectrum of  $\text{Sn}(\text{CH}_3)_4$  differs from that of Pai in two ways, in that we report lines not given by him, and he reports lines not observed in our work. The line given by Pai at 262  $\text{cm.}^{-1}$  has not been observed by us, even though our methods of preparation were the same, with the exception of the washing with NaF solution. Siebert did not observe 262  $\text{cm.}^{-1}$  in a sample prepared using Sn-Na

TABLE IV  
INFRARED SPECTRA OF LEAD TETRAMETHYL IN  $\text{CM.}^{-1}$ 

Liquid or gas (Sheline and Pitzer)	Gas (Kettering and Seator)	Liquid or gas (This work)
476 s. (gas)		470 (P) 478 (Q) 485 (R) } v.s. (gas)
	658 w.	
769 v.s. (gas)	774 w.	765 v.s. (gas)
931 w.	937 w.	930 w.
1022 w.	1032 w.	1017 w.
1051 v.w.		
1067 m.		
1122 s.		
1140		
1147 s. (gas)		1148 s.
1162		
	1169 s.	1166 sh.
1296 m.	1305 m.	1295 w.
1392 m. (gas)	1381 w.	1400 s.
1453 m. (gas)	1462 s.	1448 v.s.
1618 m.		1624 m.
1922 m.	1925 w.	1920 w.
2108 v.w.	2170 w.	
2290 m.		2295 m.
2910 s. (gas)		2920 v.s.
2982 s. (gas)	2980 s.	3000 v.s.
2992		
3380 v.w.		
3770 w.	3700 w.	
4050 w.		
4100 w.		
4360 w.	4400 w.	

alloy, but did observe it when his sample was prepared using the Grignard reaction. We feel, along with Siebert, that the lines at 262, 952 and 1262  $\text{cm.}^{-1}$  reported by Pai are due to an impurity.<sup>10</sup> Our table of Raman lines lists several lines not reported by Pai or Siebert. Since all of these lines can be assigned to fundamental, combination or overtones, we feel that these resulted from our highly efficient excitation unit.

We were able to resolve the intense line, given at 1200  $\text{cm.}^{-1}$  by Pai and at 1197  $\text{cm.}^{-1}$  by Siebert, into two lines at 1194 and 1205  $\text{cm.}^{-1}$ . The latter line was polarized. The broad band observed by us at 136-172  $\text{cm.}^{-1}$  showed signs of being partly resolved.

The only previously reported Raman spectrum of  $\text{Ge}(\text{CH}_3)_4$  is that of Siebert. We report all the lines given by him, and a number of new lines in addition. We again attribute this to our more efficient excitation unit. The medium line reported by him at 806  $\text{cm.}^{-1}$  we find to be a very weak line at 825  $\text{cm.}^{-1}$ . We have resolved the 1243  $\text{cm.}^{-1}$  band of Siebert into two lines at 1243 and 1247  $\text{cm.}^{-1}$ . By using a narrow slit setting on our spectrograph, we have definitely resolved the 189  $\text{cm.}^{-1}$  band of Siebert into two bands, lying at 175 and 195  $\text{cm.}^{-1}$ .

It is noteworthy that  $\text{Pb}(\text{CH}_3)_4$ ,  $\text{Sn}(\text{CH}_3)_4$  and  $\text{Ge}(\text{CH}_3)_4$  all show a weak line in the vicinity of 1400  $\text{cm.}^{-1}$  in our work, while no previous workers report this line. We have assigned this to the  $\nu_6$  degenerate mode of vibration.

**Infrared Spectra.**—The infrared spectra were taken on two instruments. At the Spectroscopy Laboratory of the Massachusetts Institute of Technology a modified Perkin-Elmer model 12B spectrometer with KBr and thallium bromide-iodide prisms was used to obtain spectra in the region 13-40  $\mu$ . A Beckman IR-2 recording spectrometer at the University of Connecticut was used to obtain spectra in the rock salt region, 2-15  $\mu$ . For the liquid spectra, 0.1- or 0.23-mm. liquid absorption cells of standard design were used, with windows of the appropriate materials. All

(10) As yet unpublished work done by Mr. Phillip Mercier and by us shows that this impurity is not  $(\text{CH}_3)_2\text{SnI}$  or  $(\text{CH}_3)_2\text{SnI}_2$ .

vapor spectra were taken in 10-cm. cells at pressures varying from 1 to 90 mm.

The vapor spectra were taken in two stages. First, the spectrum was run using normal speeds and slit widths, to locate the bands. Then, the regions where strong bands were found were run down at low speed, using the smallest practicable slit width, and the optimum gas pressure. In this manner, several bands which appeared to be single on the first run were resolved into doublet or P-Q-R structure on the second run.

Absorption peaks are accurate to within 2 cm.<sup>-1</sup> from 250 to 1700 cm.<sup>-1</sup>, to within 5 cm.<sup>-1</sup> from 1700 to 2500 cm.<sup>-1</sup>, and to within about 15 cm.<sup>-1</sup> in the region 2500-3500 cm.<sup>-1</sup>.

TABLE V  
THE INFRARED SPECTRA OF TIN TETRAMETHYL IN CM.<sup>-1</sup>

Kettering and Sleator (12-cm. cell; 17, 52 cm. Hg) Gas	This work		Liquid (0.23-mm. cell)	1249 R	1235 P 1240 Q s. 1300 w. sh. 1385 1408 s. 1428 1435 sh. s.	1225 } 1235 } s.
	(10-cm. cell; 0.75-2 cm. Hg on strong bands) Gas	(10-cm. cell; 8 cm. Hg; 0.75-2 cm. Hg on strong bands) Gas				
	520 sh. P } 528 Q } s. 536 R }	528 v.s.		928 v.w. sh.		998 w. 1005 w. 1015 w. 1025 w. 1090 w. sh .
660 v.w.	760 s. } 770 v.s. } 774 s. sh. }	772 } 777 } v.s. 788 } 795 }		1017 v.w.	1065 v.w. 1099 sh. } 1107 } w. 1116 } 1132 1143 w. 1158	1080 v.w. 1100 1110 m. 1120 s. 1130
940 w.	795 s. sh. }	992 v.w.		1236 P } 1244 Q } s. 1251 R }		
1020 v.w.		1025 w.		1298 w. sh.		
1060 v.w.		1045 w.		1413 m.		
1205 s.	1192 P } 1198 Q } s. 1206 R }	1187 s.		1434 sh. 1442 m. 1469 w. sh.		
1370 w.	1330 w. 1390 w. 1410 w. sh. 1438 } s. 1448 }	1340 m. sh. 1392 s. 1430		1508 sh. 1525 m. 1546 sh. 1648 v.w.		
1465 m.	1702 m. 1718 m. 1733 m.	1700 s. 1725 s.		1806 m. 1848 m. 1940 v.w. 2068 w. 2140 v.w. 2230 v.w. 2284 sh. v.w. 2368 v.w. 2468 w. 2675 w. 2820 sh. m.		
1735 m.	1733 m.			1818 w. 1851 w. 2075 v.w.		
2040 v.w.	1970 w.	1840 w. 1950 w. 2050 w. 2115 w. 2200 w.		2075 v.w. 2140 v.w. 2230 v.w. 2284 sh. v.w. 2368 v.w. 2468 w. 2675 w. 2820 sh. m.		
2270 v.w.	2920 s.	2585 w. 2920 s.		2824 2839 2908 P sh. 2916 Q s. 2923 R sh. 2974 2981 v.s. 2988 3091 w. 3175 w.		
2460 v.w.	3000 s. 3070 s.	3000 s.		2820 sh. m. 2839 2908 P sh. 2916 Q s. 2920 s. 2923 R sh. 2974 2981 v.s. 2988 3090 s. 3190		
3000 m.	3070 s.	3000 s.		2075 v.w. 2140 v.w. 2230 v.w. 2284 sh. v.w. 2368 v.w. 2468 w. 2675 w. 2820 sh. m.		
3770 v.w.	3700 m.	3690 m.		2820 sh. m. 2839 2908 P sh. 2916 Q s. 2920 s. 2923 R sh. 2974 2981 v.s. 2988 3090 s. 3190		
4340 v.w.				2980 s. 3060 m. 3160 w. 3620 w. 3730 w. 3910 v.w. 4060 (sh.)w. 4155 w. 4200 (sh.)w. 4360 w. 4460 (sh.)v.w. 4550 (sh.)v.w. 5700 v.w. 5850 v.w.		

TABLE VI

THE INFRARED SPECTRA OF GERMANIUM TETRAMETHYL IN CM.<sup>-1</sup>

Young, Koehler and McKinney Prism	Gas	This work	
		(10-cm. cell; 9 cm. Hg; 1.5 cm. Hg on strong bands) Gas	(0.23-mm. cell) Liquid
		602 m. 610 w. sh.	598 m.
745 w. sh.			765 w.
793 m.			775 w.
830 v.s.		828 v.s.	810 v.s.
899 w. sh.			

<sup>a</sup> Obscured by water vapor bands.

The infrared spectra of Pb(CH<sub>3</sub>)<sub>4</sub>, Sn(CH<sub>3</sub>)<sub>4</sub> and Ge(CH<sub>3</sub>)<sub>4</sub> are presented in Tables IV, V and VI, along with those given by other workers. Our spectrum of liquid Pb(CH<sub>3</sub>)<sub>4</sub> agrees best with that of Sheline and Pitzer<sup>2</sup> although we fail to observe their absorption peaks listed at 1051 (vw), 1067 (w) and 1122 (s) cm.<sup>-1</sup>.

Our vapor infrared spectrum for Sn(CH<sub>3</sub>)<sub>4</sub> differs from that reported by Kettering and Sleator<sup>3</sup> in several ways. First, we have resolved a number of bands, so that a doublet of P-Q-R structure is visible. Second, they report a number of weak or very weak peaks which we have been unable

TABLE VII  
 ASSIGNMENT OF THE FUNDAMENTAL FREQUENCIES OF  $\text{Pb}(\text{CH}_3)_4$ ,  $\text{Sn}(\text{CH}_3)_4$  AND  $\text{Ge}(\text{CH}_3)_4$ 

	Species	$\text{Pb}(\text{CH}_3)_4$		In- active	$\text{Sn}(\text{CH}_3)_4$		In- active	$\text{Ge}(\text{CH}_3)_4$		In- active
		Infrared	Raman		Infrared	Raman		Infrared	Raman	
$\nu_1$ $\text{CH}_3$ stretching	$A_1$		2924(v.s.)pol.			2912(6)			2907(10)	
$\nu_2$ $\text{CH}_3$ deformation	$A_1$		1170(v.s.)pol.			1205(10)			1247(4)	
$\nu_3$ Skeletal stretching	$A_1$		459(v.s.)pol.			507(10)			558(10)	
$\nu_4$ $\text{CH}_3$ rotation	$A_2$									
$\nu_5$ $\text{CH}_3$ stretching	$E$		2996(v.s.)depol.			2988(5)			2978(10)	
$\nu_6$ $\text{CH}_3$ deformation	$E$		1400(w.)			1400(2)			1400(1)	
$\nu_7$ $\text{CH}_3$ rocking *	$E$		700(v.w.)			772(2)			825(0)	
$\nu_8$ Skeletal distortion	$E$		130(s.)depol.			145(10)			175(9)	
$\nu_9$ $\text{CH}_3$ stretching	$F_1$			(3000)			(2988)			(2978)
$\nu_{10}$ $\text{CH}_3$ deformation	$F_1$			(1450)			(1451)			(1437)
$\nu_{11}$ $\text{CH}_3$ rocking	$F_1$			(765)			(772)			(825)
$\nu_{12}$ $\text{CH}_3$ rotation	$F_1$									
$\nu_{13}$ $\text{CH}_3$ stretching	$F_2$	3000(v.s.)	2996(v.s.)depol.		3000 s.	2988(5)		2981(v.s.)	2978(10)	
$\nu_{14}$ $\text{CH}_3$ stretching	$F_2$	2920(v.s.)	2924		2920 s.	2912(6)		2920(s)	2907(10)	
$\nu_{15}$ $\text{CH}_3$ deformation	$F_2$	1448(v.s.)	1450(w.)		1443(s)	1451(2)		1428(s.)	1437(1)	
								1435(s.)		
$\nu_{16}$ $\text{CH}_3$ deformation	$F_2$	1148(s.)	1154(v.s.)depol.		1198 s.	1194(10)		1240(s.)	1234(4)	
$\nu_{17}$ $\text{CH}_3$ rocking	$F_2$	765(v.s.)	767(m.)		770(v.s.)	772(2)		828(v.s.)	825(0)	
$\nu_{18}$ Skeletal stretching	$F_2$	478(v.s.)	478(v.s.)depol.		528(s.)	532(10)		602(m.)	595(9)	
$\nu_{19}$ Skeletal distortion	$F_2$		145(v.s.)depol.			160(10)			195(9)	

to locate. This might be due to their use of greater pressures or longer path lengths. Third, we list a number of absorption peaks at somewhat different  $\text{cm}^{-1}$  values. For instance, we observe the peak reported by Kettering and Sleator at  $1465 \text{ cm}^{-1}$  as a doublet at  $1438$  and  $1448 \text{ cm}^{-1}$ . This latter peak is in good agreement with the Raman line which we observe at  $1451 \text{ cm}^{-1}$ .

Our vapor infrared spectrum of  $\text{Ge}(\text{CH}_3)_4$  is in essential agreement with that given by Young, Koehler and McKinney.<sup>4</sup> They report a number of weak or very weak bands which we do not observe. This presumably is due to their use of greater pressures and longer path lengths.

The liquid infrared spectra differ from the vapor infrared spectra in an understandable way. First, all rotational structure had disappeared. Second, some peaks have shifted their positions, probably because of the effect of liquid forces. Third, these liquid forces have caused a number of forbidden fundamentals, combination tones and overtones to appear.

**Assignment of Frequencies.**—From the infrared and Raman data given in Tables I–VI, we have made an assignment of frequencies (Table VII) to the normal modes of vibration of the  $\text{Pb}(\text{CH}_3)_4$ ,  $\text{Sn}(\text{CH}_3)_4$  and  $\text{Ge}(\text{CH}_3)_4$  molecules, on the basis of a tetrahedral symmetry ( $T_d$  point group). Our designation of frequencies is the same as that used by Young, Koehler and McKinney.<sup>4</sup> While our assignments are in general the same as theirs, there are several points of difference.

They assign the  $\nu_8$  doubly degenerate frequency to 100, 100 and  $110 \text{ cm}^{-1}$  for  $\text{Pb}(\text{CH}_3)_4$ ,  $\text{Sn}(\text{CH}_3)_4$  and  $\text{Ge}(\text{CH}_3)_4$ , respectively. We observe no bands in this region in any case, but assign the  $\nu_8$  frequency in the three molecules to 130, 145 and  $175 \text{ cm}^{-1}$ , respectively. The reason for this is the following: the lowest band in the Raman spectra of all these compounds is broad and asymmetric, with peak intensity lying toward the low wave number side. We interpret this to mean that this band is double, and, indeed, we have succeeded in resolving it for  $\text{Ge}(\text{CH}_3)_4$ . By analogy with  $\text{Si}(\text{CH}_3)_4$ , we assign  $\nu_8$  to the peak intensity, and estimate  $\nu_{19}$ , the triply degenerate frequency, to lie somewhat higher. In this way, we arrive at values of 145, 160 and  $195 \text{ cm}^{-1}$ , respectively, for the values of  $\nu_{19}$ . The values for  $\text{Ge}(\text{CH}_3)_4$  were read from the resolved band, and involve little error other than experimental uncertainty.

We assign the  $A_1$  metal–methyl stretching fre-

quency  $\nu_3$  to 459, 507 and  $558 \text{ cm}^{-1}$ , respectively, and the  $F_2$  metal–methyl stretching frequency  $\nu_{18}$  to 478, 532 and  $595 \text{ cm}^{-1}$ , respectively, for  $\text{Pb}(\text{CH}_3)_4$ ,  $\text{Sn}(\text{CH}_3)_4$  and  $\text{Ge}(\text{CH}_3)_4$ . We have in all cases assigned the doubly degenerate deformation frequency,  $\nu_6$ , at  $1400 \text{ cm}^{-1}$  on the basis of our observation of a weak frequency in the Raman spectra. Young, Koehler and McKinney estimated this line to lie at about  $1453 \text{ cm}^{-1}$ . We have assigned  $\nu_4$  and  $\nu_{12}$  to internal rotational degrees of freedom associated with the freely spinning methyl groups.

In  $\text{Pb}(\text{CH}_3)_4$ ,  $\nu_{16}$  and  $\nu_2$  have been assigned to 1154 and  $1170 \text{ cm}^{-1}$ . We have resolved the Raman lines reported by Siebert to lie at  $1197 \text{ cm}^{-1}$  in  $\text{Sn}(\text{CH}_3)_4$ , and  $1243 \text{ cm}^{-1}$  in  $\text{Ge}(\text{CH}_3)_4$  into doublets, at 1194, 1205 and 1234,  $1247 \text{ cm}^{-1}$ , respectively. Since the higher line was found to be polarized in  $\text{Sn}(\text{CH}_3)_4$ , we have assigned 1194 and  $1234 \text{ cm}^{-1}$  to  $\nu_{16}$ , and 1205 and  $1247 \text{ cm}^{-1}$  to  $\nu_2$ .

The triply degenerate  $\nu_{17}$ , the inactive triply degenerate  $\nu_{11}$  and the doubly degenerate  $\nu_7$  have all been assigned to  $772 \text{ cm}^{-1}$  in  $\text{Sn}(\text{CH}_3)_4$ , and to  $825 \text{ cm}^{-1}$  in  $\text{Ge}(\text{CH}_3)_4$ . The justification for this assignment is that both the liquid and vapor spectra of  $\text{Sn}(\text{CH}_3)_4$  show considerable fine structure, which suggests the piling up of several bands. The vapor spectrum of  $\text{Ge}(\text{CH}_3)_4$ , however, does not show such fine structure, although the liquid spectrum does. In  $\text{Pb}(\text{CH}_3)_4$ , we have assigned  $\nu_7$  to a very weak Raman line at  $700 \text{ cm}^{-1}$ ,  $\nu_{11}$  and  $\nu_{17}$  to  $767 \text{ cm}^{-1}$ .  $\nu_{15}$  and the inactive  $\nu_{10}$  have been assigned to 1450, 1451 and  $1437 \text{ cm}^{-1}$  in  $\text{Pb}(\text{CH}_3)_4$ ,  $\text{Sn}(\text{CH}_3)_4$  and  $\text{Ge}(\text{CH}_3)_4$ , respectively. These bands show evidence of being broad and double in the infrared spectra of all three compounds.

The remainder of the assignments of fundamentals is identical with the assignment of Young, Koehler and McKinney. Assignments for non-fundamental frequencies are given in Tables VIII, IX and X. It has been possible to make assignments for all observed frequencies.

**Thermodynamic Function of  $\text{Pb}(\text{CH}_3)_4$ ,  $\text{Sn}(\text{CH}_3)_4$  and  $\text{Ge}(\text{CH}_3)_4$ .**—In making the thermodynamic calculations of  $C_p^0$ ,  $(H^0 - E_0^0)/T$ ,  $-(F^0 -$

TABLE VIII

ASSIGNMENT OF NON-FUNDAMENTAL OBSERVED RAMAN AND INFRARED FREQUENCIES FOR  $\text{Pb}(\text{CH}_3)_4$ 

Infrared	Raman	Assignment	Species
	590 v.w.	3 + 8	E
	634 v.w.	17 - 8	$F_1 + F_2$
930 w.	930 w.	3 + 18	$F_2$
1017 w.	1019 w.	16 - 8	$F_1 + F_2$
1166		3 + 7	E
1295 w.	1300 w.	19 + 16	$A_1 + E + F_1 + F_2$
	1544 v.w.	2 (17)	$A_1 + E + F_2$
1624 m.	1622 w.	2 + 3	$A_1$
1920 w.		18 + 15	$A_1 + E + F_1 + F_2$
2295 m.	2292 v.w.	2 (16)	$A_1 + E + F_2$

TABLE IX

ASSIGNMENT OF NON-FUNDAMENTAL FREQUENCIES OBSERVED IN SPECTRA OF TIN TETRAMETHYL

Infrared Gas	Liquid	Raman	Assignment	Species
		662	3 + 19	$F_2$
		992	2 + 3	$A_1$
		1025	3 + 18	$F_2$
	1045	1053	16 - 8	$F_1 + F_2$
	1070		2 - 8	E
	1118		3 + 7 - 19 (?)	$F_1 + F_2$
1330	1340	1346	2 + 8	E
1702	1700		2 + 3	$A_1$
1718	1725		2 + 18	$F_2$
1733			2 + 18	$F_2$
	1840		8 + 2 + 3	E
1970	1950		3 + 10	$F_1$
	2050 sh.		3 + 6 + 8	$A_1 + A_2 + E$
	2115		3 + 8 + 10	$F_1 + F_2$ or E
			or 1 - 7	
	2200		9 - 7	$F_1 + F_2$
	2585		6 + 16	$F_1 + F_2$
3070			14 + 17	$A_1 + E + F_1 + F_2$

TABLE X

ASSIGNMENT OF NON-FUNDAMENTAL FREQUENCIES OBSERVED IN SPECTRA OF GERMANIUM TETRAMETHYL

Infrared Gas	Liquid	Raman	Assignment	Species
			8 + 18	$F_1 + F_2$
		765 } 790	18 + 19	$A_1 + E + F_1 + F_2$
		775 }	7 + 8	$A_1 + A_2 + E$
		998	7 + 8	$A_1 + A_2 + E$
		1005	7 + 8	$A_1 + E + F_1 + F_2$ or $F_1 + F_2$
		1015	19 + 17 or 19 + 7	$A_1 + E + F_1 + F_2$ or $F_1 + F_2$
		1025	19 + 7 or 19 + 17	$A_1 + E + F_1 + F_2$ or $F_1 + F_2$
		1080	14 - 7	$F_1 + F_2$
		1100 } 1120	2(3)	$A_1$
		1110 }		
		1130 }		
		1145	18 + 3	$F_2$
		1331	19 + 3 + 18	$A_1 + E + F_1 + F_2$
(1510) } <sup>a</sup>				
1528 } 1520			2 18 + 19	$A_1 + E + F_1 + F_2$
(1540) }				
	1635	1650	2 (17)	$A_1 + E + F_2$
	1727		2 18 + 3	$A_1 + E + F_2$
	1818	1808	2 (7) + 8	$A_1 + A_2 + E$
	1851	1840	18 + 2	$F_2$
		1878	11 + 17 + 19	$A_1 + E + F_1 + F_2$
		1948	3 + 6	E
		2030	15 + 18	$A_1 + E + F_1 + F_2$
	2075	2065	2 + 7	E
		2225	6 + 17	$F_1 + F_2$
		2470	2 (16)	$A_1 + E + F_2$
	2490	2495	2 (2)	$A_1$
		2650	2 + 6	E
	2820		2 (6)	$A_1 + E$
	3090	3120	1 + 19	$F_2$
	3190		13 + 19	$A_1 + E + F_2$
		3650	2 (6) + 7	$A_1 + A_2 + E$
		3720	7 + 14 or 11 + 14	$F_1 + F_2$ or $A_1 + E + F_1 + F_2$

<sup>a</sup> Observed by water vapor bonds.

In all cases, the points fell on a smooth curve. The data are given in Table XI.

**Heats of Combustion.**—The heats of combustion of  $\text{Pb}(\text{CH}_3)_4$  and  $\text{Sn}(\text{CH}_3)_4$  were determined by standard methods in a Parr Series 1300 Plain Jacket Oxygen Bomb Calorimeter. The water equivalent of the calorimeter was determined by igniting standard benzoic acid pellets in the calorimeter. The "radiation" heat losses were corrected for by the method of H. C. Dickinson.<sup>18</sup> The measured value of the water equivalent was checked by determining the heats of combustion of pure naphthalene and benzene, and checking against the literature values.

The liquid samples were held in Parr Standard Gelatine Capsules. It was found that the conditions, such as oxygen pressure, length of fuse wire, and ignition voltage, had to be carefully adjusted in order to get complete combustion of the sample.  $\text{Pb}(\text{CH}_3)_4$  went over mainly to  $\text{Pb}_2\text{O}_4$ , although traces of  $\text{PbO}$  were present.  $\text{Sn}(\text{CH}_3)_4$  went over mainly to  $\text{SnO}_2$ , although in one run traces of  $\text{Sn}$  were present.

The reported heats of combustion represent the average result of five runs for  $\text{Pb}(\text{CH}_3)_4$  and three runs for  $\text{Sn}(\text{CH}_3)_4$ . The values were corrected to the standard state using a conventional formula, but it was found that the correction was smaller than the experimental error (mean deviation from the mean).

It is felt that the experimental error is due for the main part to irregular heat losses from the calorimeter, although there is undoubtedly some variation due to the variation in the combustion products. All possible precautions were taken to avoid errors not inherent in the calorimeter used for the measurements. The values of the liquid heats of combustion for lead tetramethyl and tin tetramethyl corrected to constant pressure were  $837.6 \pm 3$  and  $903.5 \pm 10$  kcal./mole, respectively.

(13) H. C. Dickinson, *Natl. Bur. Standards (U. S.) Bull.*, **11**, 189 (1915).

$E_0^0/T$ , and  $S^0$ , four different contributions to the partition functions are needed: translational, vibrational, rotational and internal rotational.

For the rotational contributions, the molecules were treated as a system of four freely rotating  $\text{CH}_3$  tops attached to a rigid tetrahedral frame. The moments of inertia were calculated by an elementary geometric analysis, using bond distances from electron diffraction data.<sup>10a</sup> In calculating the external rotational contribution, the tops were considered as fixed, so that the molecular symmetry number could be taken as twelve. The contribution of the four tops was taken as four times the contribution of a single top. The free internal rotational contribution of one spinning top to  $S^0$  and  $-F_0^0/T$  was determined using a symmetry number of three, and a moment of inertia of  $5.53 \times 10^{-40}$  g. cm.<sup>2</sup><sup>11</sup> The remainder of the calculations was made by standard methods.<sup>12</sup>

The final results were checked for accuracy by plotting the thermodynamic functions against  $T$ , °K.

(10a) L. O. Brockway and H. O. Jenkins, *THIS JOURNAL*, **58**, 2036 (1936).

(11) G. Herzberg, "I. R. and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 512.

(12) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945, Chapter V; Taylor and Glasstone, "Treatise on Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1942.

TABLE XI  
THERMODYNAMIC FUNCTIONS FOR  $\text{Pb}(\text{CH}_3)_4(\text{g})$ ,  $\text{Sn}(\text{CH}_3)_4(\text{g})$   
AND  $\text{Ge}(\text{CH}_3)_4(\text{g})$

$T$ , °K.	$C_p$	$\frac{(H^0 - E_0^0)}{T}$	$-\frac{(F^0 - E_0^0)}{T}$	$S^0$
<b><math>\text{Pb}(\text{CH}_3)_4</math></b>				
298.2	34.42	22.97	76.89	99.86
300	34.53	23.03	77.03	100.06
400	41.57	26.78	84.14	110.92
500	47.73	30.42	90.55	120.97
600	52.80	33.72	96.42	130.15
700	57.30	36.81	101.83	138.64
800	60.17	39.61	106.94	146.55
900	64.62	41.20	111.75	153.85
1000	67.65	44.60	116.32	160.92
1100	70.30	46.80	120.58	167.38
1200	72.67	48.84	124.83	173.67
1300	74.81	50.81	128.86	179.67
1400	76.60	52.58	132.71	185.29
1500	78.23	54.24	136.39	190.63
<b><math>\text{Sn}(\text{CH}_3)_4</math></b>				
298.2	33.34	22.05	74.06	96.11
300	33.52	22.21	74.43	96.64
400	40.79	25.92	81.15	107.07
500	47.06	29.55	87.34	116.89
600	52.27	32.85	93.00	125.85
700	56.93	36.03	98.34	134.37
800	60.87	38.87	103.33	142.20
900	64.39	41.50	108.03	149.53
1000	67.52	43.99	112.56	156.55
1100	70.21	46.22	116.89	163.11
1200	72.61	48.36	120.98	169.34
1300	74.70	50.28	124.91	175.19
1400	76.56	52.12	128.81	180.93
1500	78.16	53.80	132.49	186.29
<b><math>\text{Ge}(\text{CH}_3)_4</math></b>				
298.2	31.98	20.89	71.10	91.99
300	32.10	20.92	71.17	92.09
400	39.55	24.67	77.70	102.37
500	46.03	28.33	83.62	111.95
600	51.53	31.78	89.15	120.93
700	56.24	34.92	94.22	129.14
800	60.33	37.82	99.14	136.96
900	63.94	40.49	103.62	144.11
1000	67.11	43.01	108.04	151.05
1100	69.97	45.43	112.37	157.80
1200	72.40	47.55	116.39	163.44
1300	74.50	49.52	120.24	164.76
1400	76.39	51.34	123.98	175.32
1500	78.02	53.10	127.59	180.69

**Thermodynamic Functions of Formation of Lead Tetramethyl.**—The thermodynamic functions of lead have been tabulated by Meads, Forsythe and Giauque<sup>14</sup> in the interval 0 to 300°K. The values at 300°K. were used as the starting point for calculations up to 600°K. The values for the heat capacity of crystalline lead, from room temperature to the m.p. given by Klinkhardt,<sup>15</sup> were converted to units of cal./degree mole and two plots made, one of  $C_p$  against  $T^\circ\text{K.}$ , and one of  $C_p/T$  against  $T^\circ\text{K.}$  A smooth curve was drawn

(14) P. F. Meads, W. R. Forsythe and W. F. Giauque, *THIS JOURNAL*, **63**, 1902 (1941).

(15) H. Klinkhardt, *Ann. Physik*, **84**, 167 (1927).

through the points, and the area under the curve determined at 100° intervals, starting from 300°K. by Simpson's rule or by counting squares. The values of  $(H^0 - E_0^0)/T$  and  $S^0$  were calculated from the areas thus determined.  $-(F^0 - E_0^0)/T$  was determined from the two former values. The error in reading the area is estimated to be smaller than the experimental error in the heat capacities (1.5%). These values are tabulated in Table XII.

TABLE XII  
THERMODYNAMIC FUNCTIONS FOR  $\text{Pb}(\text{s})$  AND  $\text{Sn}(\text{white})$

$T$ , °K.	$C_p^0$ cal./mole/deg.	$\frac{(H^0 - E_0^0)}{T}$ cal./mole	$-\frac{(F^0 - E_0^0)}{T}$ cal./mole	$S^0$ mole
<b>Pb</b>				
300	6.42	5.52	10.04	15.56
400	6.72	5.78	10.23	16.01
500	7.08	6.01	10.28	16.29
600 (s)	7.50	6.22	10.32	16.54
600 (l)	8.04			
700 (l)	7.58			
800 (l)	7.78			
<b>Sn (white)</b>				
10	0.23 <sup>a</sup>			
25	1.66			
50	3.69			
100	5.35			
150	5.85			
200	6.08			
300	6.30	5.0	7.3	12.3
400	6.61	5.4	8.7	14.1
500	7.27	5.7	9.9	15.6
530 (s)	7.60	5.8	10.3	16.1
530 (l)	7.36			
600 (l)	7.51			
700 (l)	7.65			
800 (l)	7.73			

<sup>a</sup> Interpolated from best curve drawn through combined data of K. K. Kelley and Klinkhardt.

The value for the heat of combustion for  $\text{Pb}(\text{CH}_3)_4$  was corrected to the standard state. The correction for the heat of vaporization of  $\text{Pb}(\text{CH}_3)_4$  was based on the value given in Landolt-Börnstein.<sup>16</sup> Using the values for the heat of formation of water, carbon dioxide and red lead given in the N.B.S. tables, and by Maier,<sup>17</sup> the heat of formation  $(\Delta H^0)_f$ , at 300°K. was calculated. Using this, the thermodynamic functions of Pb and  $\text{Pb}(\text{CH}_3)_4$  previously tabulated and the functions for C (graphite) and  $\text{H}_2(\text{g})$  given in the N.B.S. tables, a value of  $11.2 \pm 3$  kcal./mole was obtained for  $E_0^0$ . From this, the functions  $(\Delta H^0)_f$ ,  $(\Delta F^0)_f$ , and  $(\Delta S^0)_f$  were calculated at 100° intervals from 300 to 600°K., and are given in Table XIII.

**Thermodynamic Functions of Formation for Tin Tetramethyl.**—The heat of combustion for tin tetramethyl was corrected to the standard state using the heat of vaporization given by the N. B. S. Using this, the values for the heat of formation of water, carbon dioxide and values for the free

(16) Landolt-Börnstein, "Physikalische-Chemische Tabellen," Edwards Brothers, Ann Arbor, Michigan, II Ergbd., p. 1485.

(17) Maier, "Report of Investigations," Dept. of Interior, Bureau of Mines R. I. 3262 (1934); N.B.S. American Petroleum Institute Research Project 44, "Selected Values of Properties of Hydrocarbons."

TABLE XIII  
THERMODYNAMIC FUNCTIONS OF FORMATION FOR  $Pb(CH_3)_4$ -  
(g) AND  $Sn(CH_3)_4$ (g)

T, °K.	$(\Delta H^0)_f$ , kcal./mole	$(\Delta F^0)_f$ , kcal./mole	$(\Delta S^0)_f$ /mole
$Pb(CH_3)_4$ (g)			
300	$3.2 \pm 3$	$35.6 \pm 3.6$	$-108 \pm 2$
400	1.2	46.0	-112
500	-0.5	57.0	-115
600	-1.9	68.1	-117
$Sn(CH_3)_4$ (g) <sup>a</sup>			
300	$-13.6 \pm 10$	$19.0 \pm 10$	-109
400	-15.7	30.2	-115
500	-17.5	41.9	-119

<sup>a</sup> Based on  $(\Delta H^0)_f$  for  $SnO_2 = -138.8$  kcal./mole.

energy and entropy of formation of  $SnO_2$  given by N.B.S.,<sup>18</sup> the heat of formation,  $(\Delta H^0)$ , at 300°K.

(18) N.B.S. Circular 500 "Selected Values of Chemical Thermodynamic Properties."

was calculated. Using this, the calculated thermodynamic functions for  $Sn(s)$  and  $Sn(CH_3)_4(g)$ , and the functions for C(graphite) and  $H_2(g)$  given in N.B.S. tables, a value of  $E_0^0$  of  $-5.5 \pm 10$  kcal./mole, was obtained. The thermodynamic functions for  $Sn(s)$  were obtained from data given by Kelley<sup>19</sup> and Klinkhardt<sup>13</sup> and are tabulated in Table XII. From  $E_0^0$  the functions  $(\Delta H^0)_f$ ,  $(\Delta F^0)_f$  and  $(\Delta S^0)_f$  were calculated by standard methods and are tabulated in Table XIII from 300 to 500°K.

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(19) K. K. Kelley, Bureau of Mines Bulletin 350, (1932).

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### Absolute Entropies in Liquid Ammonia

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It is shown that a simple relationship exists between the partial molal entropies of ions in water and liquid ammonia if the absolute entropy of  $H^+$  is taken as  $-2$  e.u. in water and  $-25$  e.u. in ammonia. A new tabulation of thermodynamic data for ions in liquid ammonia is given.

From studies of relative ionic entropies in methanol,<sup>1</sup> and ammonia<sup>2,3</sup> and from the entropies of ionization of methanol, ethanol, acetic acid and ammonia,<sup>4</sup> it has been concluded that the absolute ionic entropies in these solvents are considerably more negative than the corresponding absolute entropies in water. The arguments for this conclusion are: (1) The entropies of solution of electrolytes in water are generally more positive than in the non-aqueous solvents, and (2) the entropy of ionization of water is more positive than the corresponding entropies of ionization of the non-aqueous solvents.

In the case of water, the absolute entropy of the hydrogen ion has been determined as  $-2.1$  e.u.<sup>5</sup> (very close to the usual arbitrary value of 0 e.u.)

- (1) W. M. Latimer and C. M. Slansky, THIS JOURNAL, **62**, 2019 (1940).
- (2) W. L. Jolly, Chem. Revs., **50**, 351 (1952).
- (3) S. P. Wolsky, E. J. Zdanuk and L. V. Coulter, THIS JOURNAL, **74**, 6196 (1952).
- (4) W. L. Jolly, *ibid.*, **74**, 6199 (1952).
- (5) J. C. Goodrich, F. M. Goyan, E. E. Morse, R. G. Preston and M. B. Young, *ibid.*, **72**, 4411 (1950).

and monatomic ion entropies may be well represented by the equation of Powell and Latimer<sup>6</sup>

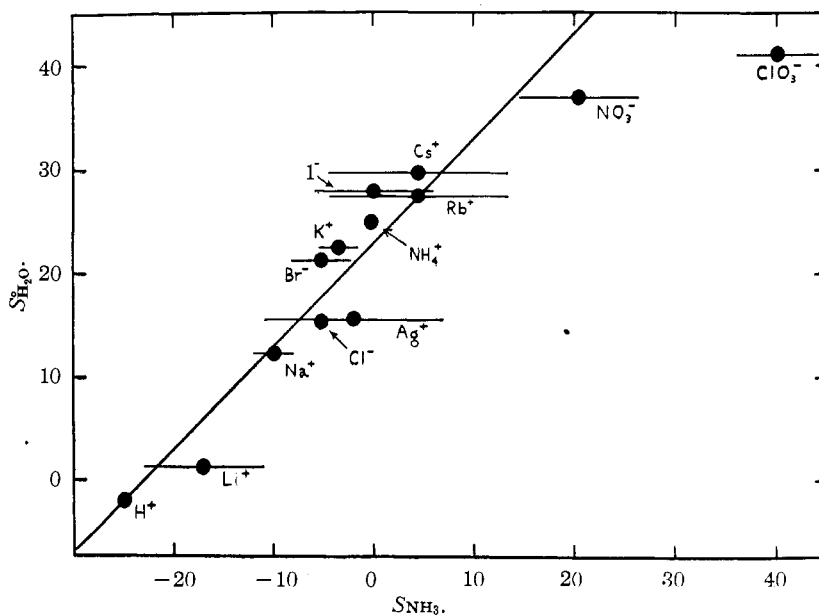


Fig. 1.

$$S^0 = 3/2R \ln M + 37 - 270Z/r_e2$$

If one plots absolute partial molal entropies in water against partial molal entropies in ammonia,

- (6) R. E. Powell and W. M. Latimer, J. Chem. Phys., **19**, 1139 (1951).