

*Some Thermodynamic Properties of Compounds of the Formula MX<sub>4</sub>.  
Part II.\* Tetra-alkyl Compounds.*

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The melting points, heats of fusion and transition, and heat capacities from  $\sim 95^\circ \text{K}$  to about  $20^\circ$  above the melting point have been measured for the following substances: tetramethyl-tin and -lead, tetraethylmethane (3:3-diethylpentane), tetraethyl-silicon, -germanium, -tin, and -lead. The observations made with the last two compounds supplement the work described in Part I\* on their unusual polymorphism. Which of the numerous forms of these two substances are produced on crystallization appears to depend on factors such as the degree of purity, the nature of the surfaces of the confining vessel, and the thermal history of the sample before crystallization. Tetraethylgermanium can crystallize in two forms, but only one melting point has been recorded for each of the other four substances.

The properties of the tetramethyl and tetraethyl compounds of the Group IV elements are compared, with special reference to incidence of polymorphism, the trend of the melting points, the entropies of fusion, and the changes of heat capacity on melting.

Some experiments have been carried out with tetrapropyltin and tetrabutyltin. A value for the melting point of each has been recorded, but the liquids crystallize with such difficulty that no calorimetric work was attempted. Their crystallization (especially that of tetrabutyltin) provides an example of the so-called "memory effect," in that, although it is normally very reluctant to take place, yet it occurs much more readily if, after fusion, the temperature of the liquid is not allowed to rise more than  $2\text{--}3^\circ$  above the melting point before it is cooled again.

IN Part I (*loc. cit.*), the remarkable polymorphism of tetraethyl-tin and -lead was described. This polymorphism was discovered during calorimetric work on tetraethyltin, which formed part of a systematic study of the thermodynamic properties of the tetramethyl and tetraethyl compounds of Group IV elements. We report here the complete results of this study. Measurements have been made of  $c_p$  from  $\sim 95^\circ \text{K}$  to about  $20\text{--}30^\circ$  above

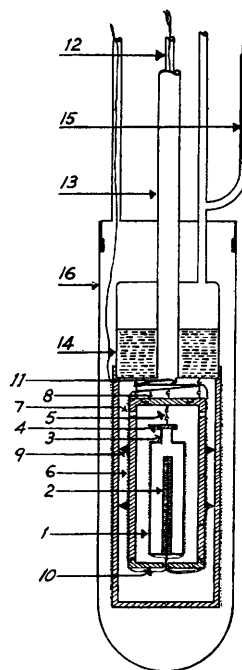
\* The paper by Staveley, Paget, Goalby, and Warren (*J.*, 1950, 2290) is to be regarded as Part I.

the melting point, and of heats of phase changes, for each of the seven substances enumerated in the Summary (above). Since Aston and his co-workers have already measured these quantities for tetramethylmethane (*neopentane*) (Aston and Messerly, *J. Amer. Chem. Soc.*, 1936, **58**, 2354) and tetramethylsilicon (Aston, Kennedy, and Messerly, *ibid.*, 1941, **63**, 2343), the work described here makes possible a comparison of some of the properties of the tetramethyl and tetraethyl compounds, and supplements the earlier observations on the unusual polymorphism displayed by some of these substances. In addition, some preliminary experiments have been carried out on tetrapropyltin and tetrabutyltin. Unfortunately, these liquids crystallized so reluctantly even when stirred that it is doubtful if they would do so at all in a calorimeter of conventional design.

#### EXPERIMENTAL

The experiments on tetramethyl-tin and -lead, and some of those on tetraethyltin and tetraethylmethane were carried out in the calorimeter described by Staveley and Gupta (*Trans.*

FIG. 1. *Calorimeter designated as calorimeter II.* 1, Copper inner container, wound with copper resistance thermometer-heater. 2, Three-junction thermocouple in re-entrant tube. 3, German silver filling-tube. 4, Removable cap. 5, Silk suspension. 6, Copper radiation shield. 7, Hole in shield. 8, Removable top. 9, Conical plastic plugs to centralize shield. 10, Threaded bottom of shield, with hole for electrical leads. 11, Cable of leads, which passes up the tube 12. 12, Tube for leads, situated behind the central tube. 13, Central tube for evacuation of inner compartments of calorimeter. 14, Copper vessel half-filled with lead. 15, Valve for introduction of refrigerant. 16, Chromium-plated outer brass can.



*Faraday Soc.*, 1949, **45**, 50), here referred to as calorimeter I. For the other measurements, the calorimeter was rebuilt to a new design. Fig. 1 shows the construction of this new calorimeter (calorimeter II). A disadvantage of calorimeter I was the liability of the platinum thermometer wound on the surface of the inner container to change its characteristics, necessitating frequent re-calibration. In calorimeter II, the temperatures at which measurements were made were determined with a previously calibrated three-junction copper-constantan thermocouple inserted in a re-entrant tube of the inner container. A copper wire (S.W.G. 48, resistance  $\sim 115$  ohms at  $0^\circ$ ) served both as a heater and as a resistance thermometer. It was calibrated *in situ* as a resistance thermometer against the thermocouple, and used to determine temperature changes in measurements of  $c_p$ . Its re-calibration could therefore be easily carried out at any time. The other main difference between calorimeters I and II was in the arrangements made for introducing the substance under investigation. In calorimeter I, this was done by condensation *via* a fixed inlet tube, an operation which was very slow with the less volatile alkyl compounds. In calorimeter II, the substance was inserted through a short filling tube, which was then closed with a cap sealed with low-melting solder. The apparatus had therefore to be dismantled and re-assembled with each change of substance. Other details of the construction of calorimeter II will be clear from Fig. 1 and the accompanying legend.

The three-junction thermocouple was calibrated (1) at the normal b. p. of oxygen, (2) at

four other temperatures against a strain-free platinum resistance thermometer of the Meyers type (*J. Res. Nat. Bur. Stand.*, 1932, **9**, 807). These temperatures were the f. p.s of carbon tetrachloride, chloroform, *n*-heptane, and carbon disulphide. To carry out the calibration at any one of these, a purified sample of the liquid, in which the platinum thermometer and thermocouple were immersed, was frozen slowly in an apparatus of the type described by Mair, Glasgow, and Rossini (*ibid.*, 1941, **26**, 591). This apparatus seems to be very suitable for calibration work of this kind. From the five pairs of temperature-E.M.F. values, a deviation curve was constructed, Scott's data for a standard thermocouple (*ibid.*, 1940, **25**, 459) being used. A smooth curve was drawn from which none of the experimental points was further removed than 0.5  $\mu$ v, which at 0° corresponded to  $\sim 0.004^\circ$  and at  $-180^\circ$  to  $\sim 0.01^\circ$ .

All E.M.F. measurements were carried out with a Tinsley Vernier Potentiometer, and could be made to 0.5  $\mu$ v over the range 0—180,000  $\mu$ v. The resistance of the copper thermometer-heater was determined at intervals of about 5° by current and voltage measurements. For convenience in converting resistance changes into temperature changes (which were estimated to 0.001°), the deviation curve method was again employed. A plot was made (to which tangents were then drawn) of the deviations of the observed resistances from those which would have been measured at the same temperatures had the resistance varied linearly between 0° and the lowest calibration temperature.

The energy input during a heating period was determined by measuring the current *C* through the thermometer-heater, and the voltage across it, *V*, and then plotting *CV* against time. For normal  $c_p$  measurements, this plot was linear, so that the estimation of the energy input was a simple matter. The time of heating was measured to 0.05 sec. with a stop-watch automatically switched on and off with the heating current, and calibrated against the Greenwich time signals.

The inner container of calorimeter II was the same as that of I, except that the copper vanes included in the latter were omitted from the second calorimeter. There was no marked increase in the time needed to reach thermal equilibrium. The quantity of substance under examination was usually 4—5 c.c.

With a calorimeter as small as this, the highest precision cannot be expected, since the total thermal capacity of the inner container and its contents is small, while the contribution of the inner container is relatively large. On the other hand, it is possible to make measurements on substances only available in small amounts. We do not claim a higher accuracy for our values of  $c_p$  and heats of phase changes than approximately 1%, or perhaps 0.5% in favourable cases. We consider, however, that this degree of accuracy is adequate for our main purpose in making these measurements, which is to obtain reasonably reliable thermodynamic information for groups of closely related compounds, with the object of studying the relation between physical properties and chemical constitution.

Tetramethyl-tin and -lead were prepared from stannic chloride and methylmagnesium iodide, and lead chloride and methylmagnesium chloride, respectively, as described by Krause and von Grosse ("Die Chemie der metall-organischen Verbindungen," Borntraeger, Berlin, 1937, pp. 315, 389). After removal of ether the crude tetramethyltin appeared to be contaminated with methyl iodide, from which it was freed by heating with pyridine in a sealed tube at 80° for 1½ hr. It was then twice fractionated at 0° in a column of the type described by Clusius and Riccoboni (*Z. physikal. Chem.*, 1937, *B*, **38**, 81). The impure tetramethyl-lead was likewise fractionated twice in the same column at a temperature of 10.5°.

A sample of tetraethylmethane was kindly supplied by the Anglo-Iranian Oil Co. Ltd. It had been prepared in the Dyson Perrins Laboratory, Oxford, by J. C. Smith and S. H. Morell. The quantity available was too small to permit further purification. Tetraethylsilicon was prepared from silicon tetrachloride by two methods, by reaction with ethylmagnesium bromide (Krause and von Grosse, *op. cit.*, p. 260), and also by reaction with ethyl-lithium (Gilman and Clark, *J. Amer. Chem. Soc.*, 1946, **68**, 1675). The product was purified by treatment with concentrated sulphuric acid to remove any triethylsilicon chloride, and fractionated twice. The sample of tetraethylgermanium was that referred to in Part I, but before the measurements described here were undertaken it was treated with potassium hydroxide pellets to remove hydrogen bromide, and then twice fractionated. The experiments with tetraethyltin were carried out with sample D (Part I). The tetraethyl-lead used was supplied by the Associated Ethyl Company, and further purified by a double fractionation. Some experiments were deliberately performed with a less pure sample of this substance.

Tetrapropyltin and tetrabutyltin were prepared from stannic chloride by the Grignard reaction. The *n*-propyl chloride and *n*-butyl chloride used to make the Grignard reagents had

been purified by fractionation. The ethereal solutions of the crude products were treated with ammonia to remove the trialkyltin chlorides, but only small amounts of these seemed to be present. After removal of the ether, the liquids were fractionated at  $\sim 4$  mm.

## RESULTS

*Melting Points.*—We shall first present the additional information obtained in this work about the polymorphism in these compounds. Previously, this had been most fully investigated for tetraethyltin. In the experiments with this substance in calorimeter II three forms were obtained, namely, those which had been designated *b*, *e*, and *g* in Part I, and in contrast to the experiments of Series I, Part I, the substance now crystallized exclusively in one of these forms. In 15 crystallizations, *e* was produced ten times, *b* four times, and *g* only once. Rapid cooling seemed to favour crystallization into form *b*, whereas crystallization on warming the glass formed by slow cooling normally gave form *e*. Attempts to measure accurately the m. p. and heat of fusion of form *b* were defeated by its spontaneous passage on melting into form *e*. The m. p. of *b* was confirmed, however, as being  $138.7^\circ \pm 0.1^\circ$  K. The form *g* had never before been obtained in calorimetric work. A stepwise determination of its m. p. was not carried out, but from a continuous-fusion run the m. p. was estimated as  $143.05^\circ$  K, which agrees quite well with the value given in Part I.

These further experiments with tetraethyltin, and more particularly with tetraethyl-lead, have shown that which of the numerous forms of these substances appears on crystallization seems to be markedly affected by the purity of the sample. Thus, our most highly purified specimen of tetraethyl-lead (with 0.08 mole % of impurity), in each of 20 experiments in which the thermal treatment was varied as much as possible, crystallized in one form only, melting at  $142.94^\circ$  K, whereas the highest-melting form which we had hitherto obtained melted at  $141.5^\circ$  K. This difference prompted us to make measurements on a sample which, owing to decomposition or oxidation (or both), was much less pure ( $\sim 1.2$  moles % of impurity). With this, the form melting at  $142.94^\circ$  K was never obtained in 8 experiments. Crystallization gave four forms with the following m. p.s (after correction for the depression due to the impurity present):  $136.6^\circ \pm 0.1^\circ$  (once; on this occasion most of the substance crystallized in the form melting at  $138.56^\circ$ );  $138.56^\circ$  (five times);  $139.3^\circ \pm 0.1^\circ$  (twice);  $141.5^\circ \pm 0.1^\circ$  (once). (The second was accurately estimated by a stepwise determination. The other values are less accurate, as they depended on runs in which the sample was continuously heated.) The form melting at  $138.56^\circ$  was that most frequently observed in the work described in Part I. Combining the results of this earlier work (Part I) with those just given (II), we have the following list of m. p.s for tetraethyl-lead: *a*,  $135.6^\circ$  (I); *b*,  $136.6^\circ$  (I, II); *c*,  $137.4^\circ$  (I); *d*,  $138.2^\circ$  (I); *e*,  $138.55^\circ$  (I, II); *f*,  $139.3^\circ$  (II); *g*,  $141.5^\circ$  (I, II); *h*,  $142.94^\circ$  K (II).

The thermodynamic properties of tetramethyl-lead, tetraethyl-lead, and tetraethylmethane have been investigated independently by Dr. G. B. Guthrie, jun., at the Petroleum Experiment Station of the U.S. Bureau of Mines. We are very grateful to him for giving us details of his results before their publication. He reports finding five m. p.s for tetraethyl-lead, four of which agree within  $0.1^\circ$  with our values *e*, *f*, *g*, and *h*; and in addition he obtained evidence that there are forms with lower m. p.s.

In Part I, the possibility of correlating the m. p.s of the numerous forms of tetraethyltin with those of the lead compound was briefly considered. No finality can be reached even now in this matter, but the discovery of a form of the lead compound with a higher m. p. ( $142.94^\circ$  K) suggests the following as the most likely pairing:

M. p. (Sn)	$147.1^\circ$	$145.8^\circ$	$144.1^\circ$	$143.15^\circ$	$142.12^\circ$	$141.87^\circ$	$140.6^\circ$	$139.8^\circ$	$138.7^\circ$	$138.1^\circ$
M. p. (Pb)	$142.9$	$141.5$	$139.3$	$138.55^\circ$ or $138.2^\circ$	$137.4$	—	$136.6$	$135.6$	—	—
$\Delta(\text{Sn} - \text{Pb})$	4.2	4.3	4.8	4.6 or 4.95	4.7	—	4.0	4.2	—	—

The preliminary experiments with tetraethylgermanium described in Part I did not show any evidence of crystallization in more than one form. The behaviour of the purer sample used in the present investigation was carefully examined. On cooling, crystallization usually occurred rapidly about  $10^\circ$  below the m. p., and in 22 out of 23 experiments (in which the thermal treatment was varied as much as possible), the solid produced melted at  $\sim 180.1^\circ$ , the corrected m. p. being  $180.47^\circ$  K. In the remaining experiment, however, the liquid supercooled to  $90^\circ$  without crystallizing, and when the glass was warmed it crystallized into a form which melted at  $183.3^\circ$ . Although this experiment could not be reproduced there is no reason to doubt its validity, and it is interesting that this higher m. p. is near the only one previously recorded for this substance ( $183.1^\circ$ ; Dennis and Hance, *J. Amer. Chem. Soc.*, 1925, **47**, 370).

The following compounds crystallized in one form only: tetramethyl-tin and -lead, tetraethylsilicon, and tetraethylmethane. The experiments with the first two substances were carried out before the discovery of the polymorphism of their tetraethyl analogues, and consequently a deliberate search for more than one crystalline form was not made. Tetraethylmethane and tetraethylsilicon, in spite of many variations in thermal treatment, each always gave one and the same form. The tetramethyl compounds always crystallized very readily. With the tetraethyl compounds, the degree of supercooling before crystallization (or alternatively, the difficulty experienced in effecting crystallization) increased progressively with increasing molecular weight, probably because with the passage from the carbon to the lead compounds the molecules become less compact and so interlock more in the liquid state, with the result that the reorientation or alignment necessary for the formation and growth of crystal nuclei becomes more and more difficult.

The experiments with tetrapropyltin and tetrabutyltin were carried out with the apparatus used for the experiments of Series III, Part I, so that crystallization could be assisted by stirring, since all attempts to crystallize tetrapropyltin in glass vessels without stirring had failed. Even with stirring, these two liquids were very reluctant to crystallize, tetrapropyltin particularly so. Attempts to freeze small samples (of different degrees of purity) with which to inoculate the main bulk were unsuccessful, and the addition of powdered glass had no effect. Below about 140° K for tetrapropyltin, and 158° K for tetrabutyltin, the supercooled liquids were too viscous for the stirrer to operate.

It was established without doubt that tetrapropyltin has an m. p. at  $163.9^\circ \pm 0.1^\circ$  K, and tetrabutyltin one at  $176.1^\circ \pm 0.05^\circ$  K. These values were derived from temperature-time curves during fusion, but it was not possible to follow these curves for sufficiently long to permit the estimation from them of the impurity content of the samples, and so to correct the observed m. p.s for the depression due to the impurities. It appeared, however, that the samples were of satisfactory purity, and that these corrections would be small.

There was some indication in two runs with tetrapropyltin that another form was present of m. p. a few tenths of a degree above that just quoted, but we were unable to obtain more definite information.

Although these liquids ordinarily crystallized with great difficulty, it was found (especially with tetrabutyltin) that crystallization took place much more readily if, after the fusion of the crystals, the temperature was not allowed to rise more than 2–3° above the m. p. before the liquid was cooled again. This effect, sometimes known as the "memory" effect, has been observed and studied for other liquids, *e.g.*, by Richards for salol and benzophenone (*J. Amer. Chem. Soc.*, 1932, **54**, 179) and by Turnbull for gallium (*J. Chem. Phys.*, 1950, **18**, 198). The effect is probably due to the persistence of crystal nuclei just above the m. p. in cavities in the walls of the containing vessel or in the surfaces of heterogeneous impurities. If a liquid can crystallize in more than one form, therefore, it might be expected that the crystal nuclei would induce crystallization back into the modification of which they are the residue, so to speak, so the effect is of doubtful value in a search for other crystalline forms.

*Transitions in Tetraethylmethane.*—Within the temperature range from  $\sim 95^\circ$  K to the m. p., the only substance found to have transitions was tetraethylmethane. In our first experiments on this compound it appeared to possess one transition at about 210° K, taking place over a range of about 1° and attended by considerable superheating and supercooling, and having a heat of transition of  $\sim 300$  cal./mole. We were then privately informed by Dr. G. B. Guthrie that he had discovered two transitions, at 208.4° and 210.4° K. On carefully re-examining the behaviour of the crystals in this region, we also observed two transitions, for which transition temperatures of  $208.8^\circ \pm 0.2^\circ$  and  $210.1^\circ \pm 0.2^\circ$  K were recorded. These were the temperatures at which the rates of increase of temperature with time were a minimum during runs in which the crystals were heated continuously, though very slowly, through the transition region. (As there was considerable supercooling, each such run was preceded by repeated variation of the temperature between  $\sim 170^\circ$  and that of the lower transition. Even so, in several such runs there was no evidence of any transition, so that the solid must have remained throughout in the high-temperature form.) Two such runs showed arrests at 210.1–210.2° only. In two further runs, however, there were arrests at  $\sim 208.8^\circ$  (preceded by slight superheating) followed by very small arrests at 210°, the amount of heat absorbed at this higher temperature being undoubtedly much less than in the first two runs. If we denote the form stable from 210° to the m. p. as I, that stable from 208.8° to 210° as II, and that stable below 208.8° as III, these observations would appear to mean that sometimes in the heating run it was supercooled II which was being heated, but that sometimes after III had changed into II this did *not* then

change completely into I at 210°. This seems curious, particularly in view of the fact that reproducible values were obtained for the heat of fusion and m. p., showing that it was always form I which was melted. We do not fully understand our observations on the transitions in this compound, which seem to merit more detailed investigation.

TABLE 1. *Combined heat of the transitions in tetraethylmethane,  $\Delta H_{tr}$ , in cal./mole* (Throughout this paper, the calorie is the thermochemical calorie, *i.e.*, 4.184 absolute joules.)

Mass of sample (g.)	Calorimeter	Temp. interval (°K)	$\Delta H_{tr}$	Mass of sample (g.)	Calorimeter	Temp. interval (°K)	$\Delta H_{tr}$
3.694	I	207.43—214.33°	319	3.289	II	206.20—215.71	322.2
"	I	206.98—216.00	302.5	"	II	203.70—213.49	290.7
"	I	206.95—216.52	296.5			Mean value	304
"	I	206.72—216.55	292				

No attempt was made to determine the separate heats of each transition, but a number of measurements were made of the extra heat absorbed in heating through the transition region, after the sample had been subjected to the thermal treatment mentioned above. The results are presented in Table 1, and show that the combined heats of transition amount to 304 cal./mole.

*Melting Points and Degrees of Purity of Samples Used.*—To assess the purity of the samples used, m. p.s were determined by the usual procedure of melting the solid in stages and measuring the steady temperature reached at the end of each stage. If these temperatures are plotted against  $1/F$  ( $F$  = fraction melted), a straight line should be obtained if the impurities are liquid-soluble and solid-insoluble and if the solution of them in the major component obeys Raoult's law. Extrapolation of the line to  $1/F = 0$  gives the m. p. ( $T_m$ ) of the pure compound. By using measured values of the latent heat of fusion, the impurity content of the actual sample can be determined. The results are given in Table 2. Some plots of  $T$  against  $1/F$  do not

TABLE 2. *Melting points and degrees of purity of samples used.* ( $T_m$  is the extrapolated m. p. for a 100% pure sample. The calculated impurity content,  $x$ , is given as moles %.)

SnMe <sub>4</sub> .....	% melted	16.5	32.7	50.0	67.7	} $T_m = 218.18^\circ$ ; $x = 0.26$
	$T$	217.47°	217.81°	217.97°	218.08°	
PbMe <sub>4</sub> .....	% melted	21.6	42.3	63.0	83.8	} $T_m = 242.92^\circ$ ; $x = 0.24$
	$T$	242.253°	242.558°	242.646°	242.716°	
CEt <sub>4</sub> .....	% melted	20	40	60	80	} $T_m = 240.13^\circ$ ; $x = 0.50$
	$T$	239.21°	239.61°	239.75°	239.84°	
SiEt <sub>4</sub> .....	% melted	21.7	43.4	65.1	86.8	} $T_m = 189.36^\circ$ ; $x = 0.10$
	$T$	189.30°	189.31°	189.32°	189.34°	
GeEt <sub>4</sub> .....	% melted	20	33	48	59	} $T_m = 180.47^\circ$ ; $x = 0.11$
	$T$	180.28°	180.35°	180.415°	180.428°	
					74.5	90
SnEt <sub>4</sub> .....	% melted	22.2	38.7	54.8	71.0	} $T_m = 142.15^\circ$ ; $x = 0.08$
	$T$	142.00°	142.12°	142.13°	142.135°	
PbEt <sub>4</sub> <sup>a</sup> .....	% melted	20	40	60	80	} $T_m = 142.94^\circ$ ; $x = 0.08$
	$T$	142.85°	142.87°	142.88°	142.90°	
PbEt <sub>4</sub> <sup>b</sup> ...	% melted	20	40	60	80	} $T_m = 138.56^\circ$ ; $x = 1.2$
	$T$	136.56°	137.51°	137.89°	138.02°	

<sup>a</sup> Purest sample used. <sup>b</sup> Impure sample which had crystallized in a form of lower m. p.

give good straight lines if all the points are given equal weight: for these, more importance has been attached to the points for the later stages of melting.

The values in Table 2 for tetraethyl-germanium, -tin, and -lead refer to that form of each substance which was most frequently formed. In addition, for the lead compound results are given for the less pure sample referred to above in connection with the polymorphism of this substance.

For tetramethyl-lead, Grüttner and Krause (*Annalen*, 1918, **415**, 338) gave  $-27.5^\circ$  c as the m. p., which is  $2.7^\circ$  higher than our figure. For tetraethylmethane, the most recent value in the literature is  $-33.110^\circ \pm 0.005^\circ$  (Streiff *et al.*, *J. Res. Nat. Bur. Stand.*, 1947, **38**, 53), which is  $0.08^\circ$  lower than our value.

FIG. 2.

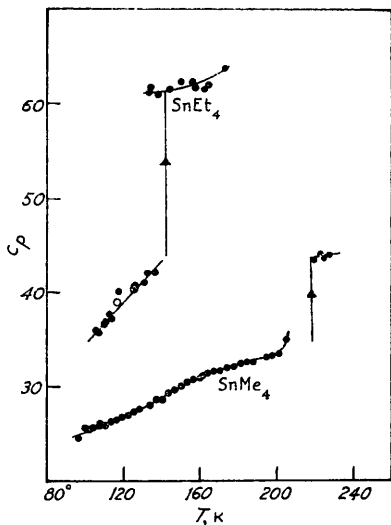


FIG. 2. Plot of experimental values of  $c_p$ , in cal./mole $^\circ$ , against temperature in  $^\circ\text{K}$  for tetraethyltin and tetramethyltin. The vertical lines in this figure and in Figs. 3 and 4 indicate the m. p. of that form of the compound to which  $c_p$  refers, and the length of these lines represents the increment in  $c_p$  on melting. The full circles for tetraethyltin refer for the solid to the form of m. p. 142-15 $^\circ\text{K}$ , and the two open circles refer to the solid form of m. p. 138.5 $^\circ\text{K}$ .

FIG. 3.

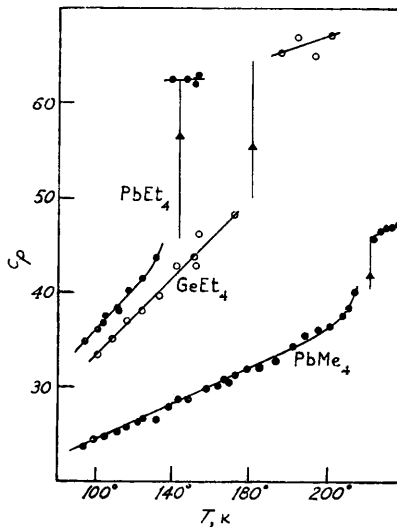


FIG. 3.  $c_p$  plotted against  $T$  (in  $^\circ\text{K}$ ) for tetramethyl-lead (full circles), tetraethylgermanium (open circles), and tetraethyl-lead (full circles).

FIG. 4.

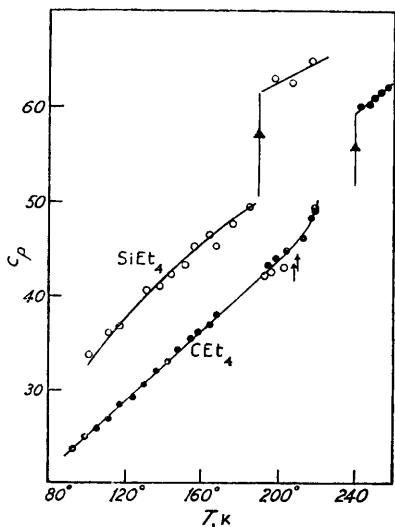


FIG. 4.  $c_p$  plotted against  $T$  (in  $^\circ\text{K}$ ) for tetraethylsilicon (open circles) and tetraethylmethane (full circles, calorimeter I; open circles, calorimeter II). The small arrows near the lower curve show the temperature of the transitions in tetraethylmethane.

FIG. 5.

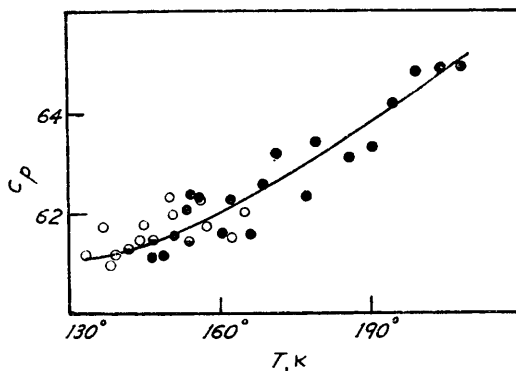


FIG. 5.  $c_p$  for liquid tetraethyltin plotted against temperature in  $^\circ\text{K}$ . Open circles, uncrystallized liquid (*i.e.*, the sample was cooled from room temperature to a few degrees below the m. p. without crystallization occurring and the  $c_p$  measurements were then made). Full circles, liquid obtained on melting form of m. p. 142-15 $^\circ$ . Half-shaded circles, liquid produced on melting form of m. p. 138.5 $^\circ$ .

TABLE 3. *Values of  $c_p$  (in cal./mole/degree) at regular temperature intervals, taken from smoothed curves through the experimental points after these had been corrected, where necessary, for premelting. (The horizontal line in each column separates the results for crystal and liquid. Tetramethyl-tin and -lead were studied in calorimeter I, tetraethylmethane in calorimeters I and II, and the remaining substances in calorimeter II. The figures for crystalline tetraethyl-germanium, -tin, and -lead refer to the forms of m. p. 180.47°, 142.15°, and 142.94° K, respectively.)*

$T$ (°K)	SnMe <sub>4</sub>	PbMe <sub>4</sub>	CET <sub>4</sub>	SiEt <sub>4</sub>	GeEt <sub>4</sub>	SnEt <sub>4</sub>	PbEt <sub>4</sub>
90	—	—	23.2	—	—	—	33.65
100	25.3	24.2	24.95	32.4	33.2	—	36.0
110	26.05	25.15	26.75	35.1	35.3	36.75	38.4
120	26.85	26.05	28.65	37.55	37.4	39.05	40.75
130	27.75	27.0	30.55	39.7	39.5	41.3	43.1
140	28.8	27.95	32.6	41.65	41.6	42.6 <sup>b</sup>	62.5 <sup>a</sup>
150	30.05	28.9	34.6	43.5	43.7	61.55	62.5
160	31.0	29.85	36.4	45.2	45.8	62.0	—
170	31.7	30.8	38.2	46.8	47.9	62.45	—
180	32.1	31.75	40.0	48.15	—	63.0	—
190	32.45	32.75	41.75	61.5	64.8	63.7	—
200	32.65	33.8	43.3	62.5	65.5	64.45	—
210	32.7	34.7	45.5 <sup>c</sup>	63.6	66.3	65.3	—
220	43.7	35.45	47.5 <sup>c</sup>	64.6	67.0	—	—
230	44.2	36.4	49.5 <sup>c</sup>	—	—	—	—
240	—	—	59.5 <sup>a</sup>	—	—	—	—
250	—	46.65	60.95	—	—	—	—
260	—	47.7	62.35	—	—	—	—

<sup>a</sup> Supercooled liquid. <sup>b</sup> Extrapolated. <sup>c</sup> Form stable above transition temperatures.

*Heat Capacities.*—These are plotted against temperature in Figs. 2, 3, and 4. Values at regular temperature intervals, obtained from smoothed curves after correction for premelting, are given in Table 3. For tetraethyl-tin and -lead, some measurements were made on the supercooled liquids. The results for crystalline tetraethyltin refer to the form melting at 142.15° K. Two  $c_p$  measurements on the form melting at 138.5° K were made, and within experimental error the values obtained were the same as for the form of m. p. 142.15° K.

In view of certain claims that, owing to some kind of rotational isomerism, certain liquids show a variable  $c_p$  depending on their thermal history, a careful examination of the heat capacity of liquid tetraethyltin in the neighbourhood of the m. p. was made;  $c_p$  was measured on liquid cooled from room temperature to about 130° K (without freezing), and on liquid produced by melting the crystals of m. p.s 138.5° and 142.15° K. The results are plotted in Fig. 5. As is usual, the  $c_p$  points for a liquid show a rather larger scatter than for a solid, but within experimental error there is no indication that  $c_p$  for the liquid varies according to its thermal history. This is to be expected, since (as pointed out in Part I) the constancy of the m. p.s of the different forms implies that any equilibrium in the liquid is established relatively quickly at these temperatures.

*Heat of Fusion.*—The results are given in Table 4.

TABLE 4. *Heats of fusion,  $\Delta H_f$ , in cal./mole. (For the polymorphic substances, the figures refer to the same forms as the results in Table 3.)*

Sub-stance	Mass of sample (g.)	Temp. interval	$\Delta H_f$	Mean	Sub-stance	Mass of sample (g.)	Temp. interval	$\Delta H_f$	Mean
SnMe <sub>4</sub>	5.323 *	191.77—222.16°	2251	2256	SiEt <sub>4</sub>	3.856 †	182.50—193.11°	3116	3110
		196.81—223.32	2268				186.04—197.61	3115	
		195.04—222.23	2238				184.52—194.29	3098	
PbMe <sub>4</sub>	8.158 *	220.16—249.41	2585	2581	GeEt <sub>4</sub>	5.051 †	176.72—191.64	2960	2965
		222.97—251.68	2577				172.62—190.53	2971	
		220.58—249.90	2580				175.09—191.22	2963	
CET <sub>4</sub>	3.694 *	226.09—244.55	2409	2398	SnEt <sub>4</sub>	5.8695 †	135.05—147.06	2191	2186
		226.08—244.57	2397				138.09—145.00	2203	
		225.04—244.99	2394				136.91—145.84	2179	
	3.289 †	231.50—245.19	2397				138.77—146.20	2170	
		225.96—243.58	2399		PbEt <sub>4</sub>	8.758 †	133.90—151.05	2108	2101
		227.41—245.56	2392				135.30—150.91	2095	

\* Calorimeter I.

† Calorimeter II.



## DISCUSSION

In Part I, the opinion was expressed that the ability to crystallize in numerous solid forms, so far as the tetramethyl and tetraethyl compounds are concerned, is probably confined to tetraethyl-tin and -lead, and it was suggested that the phenomenon arises because the molecules of these two substances exhibit in the solid state a form of rotational isomerism. The reasons given in Part I for this opinion still hold, and the views expressed there are not changed by the new facts presented in this paper, but at the same time it will now be clear that it is unwise to conclude that a substance of this kind cannot exist in more than one form simply because the same sample in the same apparatus always crystallizes in the same form, even in as many as twenty experiments. Thus, the polymorphism of tetraethyl-lead would never have been suspected from our own calorimetric experiments with the purer sample, while the fact that tetraethylgermanium in just one experiment out of 23 crystallized in a different form may mean that there are other undiscovered solid forms of this compound. Another illustration of the capricious nature of the crystallization process is the observation that in the earlier calorimetric work with tetraethyltin (Series I of Part I), two or three forms were sometimes produced simultaneously when the supercooled liquid crystallized, and in a continuous-fusion experiment these melted in turn without those of lower melting point changing into those of higher melting point. In the work reported here, only one form was produced on crystallization, and when this was that of m. p. 138.5° it tended to recrystallize into the form of m. p. 142.15° K. Presumably the crystallization process is strongly influenced by impurities, both heterogeneous and (in view of the results with tetraethyl-lead) homogeneous as well, and also perhaps by the nature of the walls of the containing vessel. In addition, the thermal treatment has an effect, as already pointed out.

TABLE 5. *Melting points ( $T_m$ ) and entropies of fusion ( $\Delta S_f$ , in cal./mole/°) of compounds of formula  $MX_4$ .*

X = M	Cl		Me		Et	
	$T_m$	$\Delta S_f$	$T_m$	$\Delta S_f$	$T_m$	$\Delta S_f$
C .....	250.23°	7.10 <sup>a</sup>	256.53°	7.42 <sup>a</sup>	240.13°	11.43 <sup>a</sup>
Si .....	205.5	9.08	174.12	9.465	189.36	16.42
Ge .....	233.6	—	185	—	180.47 <sup>b</sup>	16.43
Sn .....	239.9	9.11	218.18	10.34	142.15 <sup>b</sup>	15.38
Pb .....	~258	—	242.92	10.62	142.94 <sup>b</sup>	14.70

<sup>a</sup> Combined entropies of fusion and transition. <sup>b</sup> Melting points of forms for which  $\Delta H_f$  was measured. Figures for  $CMe_4$  from Aston and Messerly, *loc. cit.*; for  $SiMe_4$  from Aston, Kennedy, and Messerly, *loc. cit.*; for the tetrachlorides, from Hildebrand and Scott, "The Solubility of Non-electrolytes," Reinhold Publishing Corp., New York, 1950, p. 59.

In Table 5, the entropies of fusion  $\Delta S_f$  and melting points  $T_m$  of the tetraethyl and tetramethyl compounds are presented, together with data for the tetrachlorides.  $T_m$  is abnormally high for the carbon compounds, as pointed out and commented on in Part I. In the tetrachlorides and tetramethyl compounds,  $T_m$  rises from silicon to lead, and  $\Delta S_f$  is almost constant or slowly increases. This is not so for the tetraethyl derivatives, where there is considerable drop in  $T_m$  on going from germanium to tin and a decrease in  $\Delta S_f$ . The tetraethyl series may not be the only one in which some rather sudden change of this kind occurs. The continuous fall in melting point found in this series is also encountered in the tetrabenzyl compounds (at least as far as the tin compound—the melting point of tetrabenzyl-lead has not been measured), and it is noteworthy that the tetrabenzyl molecules have the same sort of shape as those of the tetraethyl compounds. (There is no such steady or pronounced downward trend in melting point in the tetraphenyl and tetra-*p*-tolyl series.) Also, the value of 163.9° K recorded above for the melting point of tetrapropyltin is considerably lower than the value 200° K for tetrapropylgermanium given by Tabern, Orndorff, and Dennis (*J. Amer. Chem. Soc.*, 1925, **47**, 309), the difference being about the same as that between the melting points of tetraethyl-germanium and -tin.

For the tetramethyl compounds the values of  $\Delta S_f$  are somewhat greater than for the chlorides, and they rise with increasing size of the central atom. A possible reason for this may be the following. The potential barrier restricting rotation of the methyl groups decreases rapidly as the radius of the central atom increases, and for the tin and lead compounds the rotation is probably relatively free for molecules in the gaseous state (French and Rasmussen, *J. Chem. Phys.*, 1946, **14**, 389). In the condensed states, molecular interlocking may to some extent interfere with this internal rotation, especially in the solid state. When the crystal melts, the increase in volume should permit a greater degree of rotational freedom of the methyl groups, but the more compact molecules will have less to gain in this way, and the corresponding contribution to the entropy change will therefore increase on going from carbon to lead.

Larger values of  $\Delta S_f$  for the tetraethyl compounds are, of course, to be expected. It will be noticed that the trend in  $\Delta S_f$  has now disappeared. It would be interesting to have values for the different forms of the tin and lead compounds: if the "pairing" for these forms suggested on p. 1995 is correct, then the values given in Table 5 for tetraethyl-tin and -lead are not strictly comparable.

It is significant that the increments in  $c_p$  on melting are quite large for the tetraethyl compounds (C, 8; Si, 11.5; Ge, 14; Sn, 18; Pb, 16.5 cal./mole). The corresponding increments for the tetramethyl compounds are much smaller (C, 5; Si, 5; Sn, 9.5; Pb, 8 cal./mole). Admittedly, if  $c_v$  values were available the increments in  $c_p$  would no doubt be less, since  $(c_p - c_v)$  is generally greater for liquids than solids. However,  $(c_p - c_v)$  for liquids does not usually much exceed 10 cal./mole and may be less than this, while for the solid near the melting point it probably amounts to several cal./mole. Hence there is probably a considerable increase in  $c_p$  on melting, particularly for tetraethyl-germanium, -tin, and -lead. Part of this increase may well arise from the fact that for substances such as these which are liquid over a large range of temperature, there can be a considerable so-called configurational contribution to the heat capacity near the melting point (cf. Staveley, Hart, and Tupman, *Discuss. Faraday Soc.*, 1953, **15**, 130). Since the tin and lead compounds, while having the highest boiling points, have the lowest melting points, this configurational contribution at the melting point would be larger for them than for the other tetraethyl compounds. But it is also possible that some of the increase in heat capacity on melting may arise from the intramolecular degrees of freedom. Usually it is supposed (and for small molecules it is undoubtedly a good approximation) that the intramolecular contribution to the heat capacity of a substance depends only on the temperature and not on the physical state of the substance. But it is possible for molecules like those of the tetraethyl compounds, which are not only fairly complex but are also, as it were, potentially flexible molecules which must interlock somewhat in the condensed states, that on passing from the solid to the more expanded liquid there is a sufficient alteration in the frequencies of some of the internal vibrations to change appreciably the corresponding contribution to the heat capacity. It would be very interesting to make a comparative study of the vibrational frequencies of these tetraethyl molecules in the gaseous, liquid, and solid states, and also of the molecules of tetraethyl-tin and -lead in the different crystalline forms.

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