

#### 470. *Polymorphism in Tetraethyl-tin and -lead.*

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Experiments on tetraethyltin, carried out on different samples in three types of apparatus, have shown that this substance can crystallise in at least ten forms. The melting points of all of these lie within the range  $137^{\circ}$  to  $148^{\circ}$  K. A less complete investigation of tetraethyl-lead has revealed at least six crystalline modifications, the melting points of which likewise fall in a range of only a few degrees. Tetramethyl-tin and -lead, however, and also 3 : 3-diethyl-*n*-pentane and tetraethylgermanium, do not show polymorphism of this kind.

Even if there is free rotation of the methyl groups in a particular tetramethyl molecule, the corresponding motion in the tetraethyl molecule is impeded by steric interference of the peripheral methyl groups, and moreover the freedom of movement of these groups must be further restricted in the condensed states by intermolecular interlocking. The magnitude of these steric effects will have a sensitive dependence on the size of the central atom. It is tentatively suggested that the unusual polymorphism of tetraethyl-tin and -lead results from the molecular dimensions enabling the molecules to pack into different lattices in which they have different configurations, so that interaction between the methyl groups of a molecule, and between those of adjacent molecules, differs from one crystalline form to another. In other words, in the solid state, at least, the molecules of these two polyalkyl compounds exhibit a form of rotational isomerism.

THIS paper describes the discovery and the investigation of an uncommon type of polymorphism, a preliminary note about which has already been published (*Nature*, 1949, **164**, 787) : tetraethyl-tin and -lead can exist in an unusually large number of crystalline forms. For each of these, however, the melting points of all the modifications fall within a few degrees. The phenomenon was discovered with tetraethyltin, and has been more fully investigated for it than for tetraethyl-lead. On the other hand, experiments with tetramethyl-tin and -lead and "tetraethylcarbon" (3 : 3-diethyl-*n*-pentane) gave no indication of more than one melting point, and preliminary observations on tetraethylgermanium suggest that this is true of this substance also. The comparison suggests that the ability of tetraethyl-tin and -lead to crystallise in a large number of different forms is a property which has a very sensitive dependence on molecular structure. This will be discussed further after the experimental facts have been presented.

#### EXPERIMENTAL.

Three series of experiments on tetraethyltin were carried out. The observations in series I were made with the low-temperature calorimeter described by Staveley and Gupta (*Trans. Faraday Soc.*, 1949, **45**, 50), those of series II in an apparatus constructed of glass so that the crystallisation and melting could be observed, and those of series III in an apparatus similar to that designed at the U.S. Bureau of Standards for the accurate measurement of m. p.s below room temperature (Mair, Glasgow, and Rossini, *J. Res. Nat. Bur. Stand.*, 1941, **26**, 591).

Temperature measurements in series I were made with a platinum resistance thermometer wound on the calorimeter and calibrated *in situ* against methyl bromide, methyl chloride, phosphine, ethylene, and methane vapour-pressure thermometers, the calorimeter itself serving as the bulb for the liquid.

The glass apparatus in which series II was carried out is shown in Fig. 1. M. p.s were measured with a built-in ethylene vapour-pressure thermometer. The vessel 1 which contained the alkyl had a capacity of about 10 c.c. and surrounding this in 2 was the liquid ethylene. The copper wire spiral 3 provided for uniformity of temperature in the ethylene jacket and also prevented bumping of the liquid during evaporation. The dimensions of 2 were such that some of the ethylene could be evaporated in order to cool vessel 1 and its contents, whilst sufficient remained for the temperature of the alkyl compound to be read accurately. The space 4 was evacuated, or, alternatively, hydrogen was admitted into it when thermal contact between 1 and 2 and the surroundings was necessary. The apparatus was immersed in a low-temperature thermostat, consisting of a 2-l. Dewar vessel with an unsilvered stripe down the side so that the tetraethyltin could be kept under observation. The thermostat was filled with isopentane

which was stirred by a rotating glass helix and kept at a constant temperature by the transference, at a controlled rate, of liquid oxygen into a copper tube in the bath-fluid. The temperature of this was determined with a separate ethylene vapour-pressure thermometer. The ethylene vapour pressures were read to 0.2 mm., which in the range in which the numerous m. p.s of tetraethyltin fall represents an accuracy of 0.02°.

The ethylene was prepared from absolute ethyl alcohol and syrupy phosphoric acid (Klemenc, "Die Behandlung und Reindarstellung von Gasen," Leipzig, 1938). Acid vapours were removed by concentrated aqueous potassium hydroxide, and alcohol vapour by a trap filled with glass-wool and cooled by solid carbon dioxide-acetone. The ethylene was condensed as solid in a trap cooled by liquid oxygen. It was purified by fractional distillation in a column of the type described by Clusius and Riccoboni (*Z. physikal. Chem.*, 1939, **38**, B, 81), the column being kept at an average temperature of -127° in a bath of ether and alcohol cooled by the passage of liquid oxygen through a copper spiral. In the calorimeter used for series I, the m. p. of a sample of ethylene prepared in this way changed by only 0.011° between 20 and 80% melted.

The apparatus employed in series III was designed to operate with a charge of about 20 c.c. of liquid. Temperatures were determined with a relative accuracy of 0.02° with 3-junction copper-constantan thermocouples. These had been calibrated and were frequently checked in the same apparatus at the f. p.s of mercury, chloroform, *n*-heptane, and carbon disulphide, and also in liquid air the temperature of which was measured with a carbon monoxide vapour-pressure thermometer. The values of the E.M.F. at the five known temperatures were then used to construct a deviation curve from the data given by Southard and Andrews (*J. Franklin Inst.*, 1929, **207**, 323).

**Tetraethyltin.**—Several samples were used. All were prepared from stannic chloride and ethyl-magnesium bromide (Krause and von Grosse, "Die Chemie der metall-organischen Verbindungen," Berlin, 1937, p. 315). According to these authors, this is the method best suited to the small-scale preparation of tin alkyls. Made in this way, the crude product usually contains triethyltin chloride. In the preparation of the sample used in series I (sample *A*), this chloride was removed by agitating the ethereal solution with aqueous-alcoholic potassium fluoride and filtering off the insoluble triethyltin fluoride. After removal of the ether, the tetraethyltin was dried over phosphoric anhydride and distilled at atmospheric pressure. It was then fractionated in an all-glass apparatus under reduced pressure, and the middle fraction refractionated under the same conditions (b. p. 39.5°/2 mm.). The middle cut from this process was stored over phosphoric anhydride until required, when it was degassed and condensed into the calorimeter. The following figures, indicating the purity of sample *A*, represent the temperatures recorded at different stages of the melting of the crystalline form later designated as *d*:

% melted .....	37.9	44.2	57.5	65.5	72.1
<i>T</i> (° K.) .....	140.44°	140.51°	140.52°	140.53°	140.54°

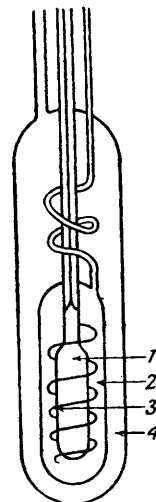
If the impurities are regarded as liquid-soluble but solid-insoluble, these figures lead, by conventional methods, to m. p. 140.56° for the actual sample and to m. p. 140.61° for the pure substance. This corresponds to an impurity concentration of 0.25 mole-%. It may be added that anomalously high heat-capacity values, caused by premelting, were not observed until the temperature was within 4° of a m. p.

Two new samples *B* and *C* were made for the experiments of series II. Sample *B* was purified by aqueous-alcoholic potassium fluoride as for *A*, and the crude specimen was fractionated under atmospheric pressure in an all-glass apparatus, the fraction of b. p. 175–177° being collected. This was then refractionated at 26.5 mm. (b. p. 93.5°). In a test for halides, a sample of the distillate was refluxed with aqueous sodium hydroxide and, after acidification, gave no precipitate with silver nitrate solution. The resulting sample *B* was dried over phosphoric anhydride, degassed, and distilled into the apparatus *in vacuo*.

Sample *C* was freed from halides by an alternative procedure described by Krause and von Grosse (*op. cit.*), namely, by passing dry ammonia through the dry ethereal solution of the alkyl until no more precipitate (a double compound of the triethyltin halide with two moles of ammonia) appeared. The precipitate was filtered off and the ethereal solution dried (CaCl<sub>2</sub>). After removal of the ether, the crude tetraethyltin was distilled twice at atmospheric pressure, the fraction of b. p. 175–177° being nearly the entire sample. This was then fractionated under reduced pressure and the middle fraction collected. A halide test at this point proved entirely negative. However, when it was cooled to -125°, an unidentified white substance was precipitated. This was filtered off at this temperature, and the liquid refractionated under reduced pressure. The product was Sample *C*, which was kept over phosphoric anhydride and then vacuum-distilled into the apparatus.

The glass apparatus in which the experiments of series II on samples *B* and *C* were conducted was primarily designed to permit observation of the crystallisation and melting, and was not ideally suited to the precise determination of m. p.s. Moreover, as will be described more fully later, in this apparatus the substance tended to crystallise in several forms simultaneously rather than largely in one. This made it difficult to assess the purity of the samples used in series II from the melting curves, but at least

FIG. 1.  
All-glass apparatus used for experiments of series II on tetraethyltin.



there appeared to be satisfactory agreement between the corresponding figures obtained with the two samples *B* and *C*. Thus *m. p.s* were found at :  $145.75^\circ \text{K}$ . for *B*, and at  $145.8^\circ \pm 0.1^\circ$  for *C*; at  $143.1^\circ$  for *B* and at  $143.15^\circ$  for *C*; at  $142.1^\circ \pm 0.1^\circ$  for *B* and *C*.

Sample *D* used in series III consisted of samples *B* and *C*, together with a new portion from which the halide impurities had been removed by treatment with ammonia, as for sample *C*. The mixture was dissolved in dry ether and again treated with ammonia. The product was then twice fractionated in a 12-plate column, the middle fractions being collected. Sample *D* had  $d_4^{20}$  1.1913, and  $n_D^{20}$  1.4719 at  $20^\circ$ , 1.4702 at  $23^\circ$ , and 1.4696 at  $25^\circ$ . The results are in excellent agreement with those obtained by K6rsching (*Z. Naturforsch.*, 1946, 1, 219) on a carefully purified sample ( $d_4^{20}$  1.1916,  $n_D^{20}$  1.4717,  $n_D^{25}$  1.4693).

**Tetraethyl-lead.**—A sample of this substance was obtained from the Associated Ethyl Company. It was stated to be of high purity and was used without any further treatment. While the experiments carried out on this substance have sufficed to show that it also exists in several crystalline forms it appeared that the purity of the material used deteriorated gradually under the experimental conditions, perhaps owing to oxidation, and it is intended to re-investigate the melting phenomena with more highly purified specimens.

#### Results for Tetraethyltin.

**Series I.**—In these experiments crystallisation never occurred until the substance had been considerably supercooled. The usual procedure was to supercool the substance by about  $30^\circ$  and then to heat it electrically. A sudden increase in the rate of temperature rise indicated that crystallisation had started, but sometimes the cooling and heating had to be repeated several times before this happened. Crystallisation generally began about  $25^\circ$  below the temperature at which most of the solid later melted. Once crystallisation had commenced the electrical heating was stopped and the temperature allowed to rise of its own accord. Then the sample was re-cooled, and a run carried out by heating it electrically and taking time-temperature readings while maintaining adiabatic conditions throughout. Sometimes the sample was heated continuously, until it was all liquid, with the object of carrying out the run as quickly as possible and thereby reducing the chance of any recrystallisation or interconversion of the various forms. In such experiments thermal equilibrium between the walls of the calorimeter and its contents was not properly established, and the arrests in the corresponding temperature-time curves are inclined and not horizontal. In other experiments, heating was periodically interrupted during melting and the calorimeter allowed to attain a steady temperature.

On three occasions the liquid crystallised spontaneously on cooling, when the temperature had fallen to approx.  $120^\circ \text{K}$ . In two of these experiments this resulted in the production of the form with the lowest melting point observed in this series (form *a*).

Some 20 experiments in all were carried out. Temperature-time curves for 8 of these are plotted in Fig. 2, which between them indicate at least five different *m. p.s*. The temperatures of arrests in the remaining experiments, not represented in Fig. 2, were all consistent with one or other of these 5 *m. p.s*.

As we do not consider that we have necessarily measured *all* the *m. p.s* which this substance possesses, we shall not follow the usual practice of designating the polymorphic forms I, II, III, etc., in order of decreasing *m. p*. Instead the different forms will be provisionally labelled *a, b, c, etc.*, in the order in which they are described.

The modification (*a*) of lowest *m. p*. was obtained in two experiments only, both of which were carried out early in the investigation, before the complexities of the system had been fully realised. While neither was conducted in the manner best suited to a precise *m. p*. determination the *m. p*. of *a* can be given with reasonable precision as  $138.1^\circ \pm 0.1^\circ \text{K}$ . Form *b* appeared on 5 occasions, but never alone or in sufficient quantity for accurate observation. The data are, however, consistent with *m. p*.  $138.7^\circ \pm 0.2^\circ \text{K}$ . The presence of modification *c* was revealed in 6 experiments, in all of which it was accompanied by one or two of the other forms. From a run in which it formed the major part of the crystals and which was carried out with intermittent heating the *m. p*. of *c* was estimated to be  $139.80^\circ \pm 0.05 \text{K}$ . Form *d* appeared 4 times, and once was unaccompanied by any other modification; from this run, the value obtained for the *m. p*. of *d* was  $140.61^\circ \text{K}$ .

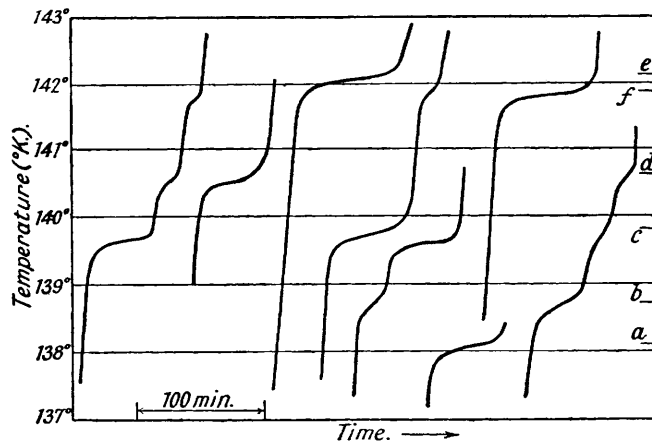
The form most frequently produced in series I was that with the highest *m. p*. This form *e* was obtained in 7 experiments and in 4 of these was the only form present. If a heating run indicated the presence of *e* after any other forms had melted, then if the temperature was reduced a little just after the fusion of *e* had started the whole sample crystallised out in this modification. Its *m. p*. was  $142.12^\circ \text{K}$ . In 5 runs it seemed that a form *f*, with a slightly lower *m. p*. than that of *e*, had appeared, for which a *m. p*. of  $141.87^\circ \text{K}$ . was obtained (cf. the 4 curves in Fig. 2 which indicate melting in the neighbourhood of  $142^\circ$ ). Unfortunately the position was complicated by a change, during the experiments, of the characteristics of the platinum thermometer. The resistance of this thermometer (which was wound on the calorimeter) increased, suggesting that the wire had been stretched owing to strain on the calorimeter walls. (In one experiment in series II the glass vessel containing the alkyl compound was shattered by the strain set up on crystallisation.) Fortunately, this change in the thermometer, which happened suddenly, did *not* occur until the existence of the four forms *a—d*, and of either *e* or *f*, had been established. We regard the existence of the two forms *e* and *f* (rather than that of one form *e* only) as probable, but not proven, and for this reason in our preliminary note (*loc. cit.*) only one form was stated to melt in the neighbourhood of  $142^\circ \text{K}$ ., and a mean value of  $142.05^\circ \text{K}$ . for the *m. p*. was adopted.

The conclusion that all the arrests in the temperature-time curves of series I did in fact represent melting and that none could be connected with transitions was reached by a quantitative consideration of these curves assisted by a direct determination of the heat of fusion of form *e*. As this conclusion was amply confirmed by the experiments of series II and III, the argument need not be given in detail here. In addition to the heat of fusion of *e*, the heat capacities of the liquid alkyl compound and of the solid

crystallised in different ways were also measured. Owing to a slight uncertainty in the mass of the alkyl compound in the calorimeter the publication of these results will be withheld until further experiments have been completed. Three facts may be provisionally stated, however. First, that the entropy of fusion of form *e* is approximately 15 cal./g.-mol./degree, *i.e.*, of a magnitude which makes it unlikely that for this form at least there are any transitions with at all large entropy changes. Secondly, there is reason to believe that the heat capacities of the different forms may differ considerably. Thus that of form *d* just below its m. p. appears to be about 4 kcal./g.-mol. less than that of *e*. Lastly, there is a very considerable difference between  $C_p(\text{solid})$  and  $C_p(\text{liquid})$  at the m. p.s. For form *e*,  $C_p$  increases on melting by about 16 kcal./g.-mol. (Experiments in this laboratory have shown that for tetramethyltin this increase is about 10 kcal./g.-mol., for tetramethyl-lead about 7 kcal./g.-mol., and for 3 : 3-diethyl-*n*-pentane almost nil.)

FIG. 2.

Temperature-time curves obtained on warming crystalline tetraethyltin (series I). The letters on the right-hand side refer to the various solid modifications, and the small lines give the corresponding melting points.



*Series II.*—The experiments of this series were planned so as to vary as far as possible the conditions under which the substance crystallised. To cool the substance rapidly the apparatus was surrounded by liquid oxygen, with hydrogen in the outer space 4 (Fig. 1). Slower cooling was achieved either by using liquid oxygen and evacuating the outer space 4, or, with the vessel in the thermostat and the outer jacket evacuated, by evaporating liquid ethylene from space 3 by condensation into a cooled trap. Once the substance had been crystallised the thermostat was brought to a constant temperature a few degrees above the highest m. p., and temperature-time readings were taken as the solid warmed. During this process the outer space 4 was evacuated if it was desired that the warming rate should be as small as possible. Under these conditions complete melting took about 4–5 hours. To produce greater rates of warming a trace of hydrogen was admitted into 4: a run could then usually be covered in an hour. Occasionally a run was started with the space 4 evacuated, and after melting had begun, hydrogen was admitted to 4 and then pumped away after substantially more of the solid had melted.

The substance was more reluctant to crystallise in this apparatus than in either of the other two, presumably owing to the absence of the stirring employed in the experiments of series III, and because the enclosing glass surfaces were much smoother than the walls of the calorimeter used in series I. On one occasion the alkyl compound remained as a glass for over 70 hours before attempts to crystallise it by varying the temperature succeeded. Once the formation of crystals had started, however, it proceeded throughout the whole mass rapidly, sometimes in a matter of seconds. Crystallisation usually started at the top or the bottom of the tetraethyl compound and transformed the glass into a mass of interlocking, apparently needle-like crystals. By varying the thermal treatment of the alkyl compound it was found that crystallisation was induced most easily by cooling it rapidly with liquid oxygen and then allowing it to stand. On only two occasions did crystallisation occur on warming of the vitreous solid. In one of these two experiments this caused the containing vessel to break. The warming run in the other experiment was the only one in series II in which the crystals melted completely in the temperature range converging the m. p. of series I. All other crystallisations of series II produced forms with higher m. p. than any we had hitherto recorded.

In two experiments melting was stopped before fusion was complete and the substance re-cooled. This, as was to be expected, induced rapid crystallisation, mainly into that form with which the melt had been seeded.

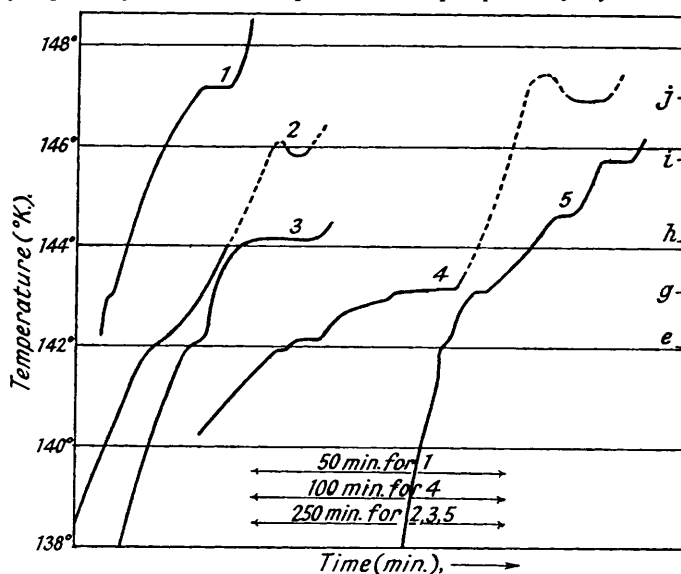
On 2 occasions, as soon as crystallisation started, the outer space 4 (Fig. 1) was rapidly evacuated and the solid and the liquid were left to come to a steady temperature. This proved to be much lower than the melting temperatures later recorded when the sample was subsequently re-cooled to complete crystallisation and then allowed slowly to warm. We shall later describe another experiment (in series III) in which the steady freezing and melting temperatures in the same experiment were definitely different.

In the later stages of the melting process in any one experiment, the remaining solid was, of course, at the bottom of the vessel, while heat was being communicated from the thermostat down the glass tubes at the top. This must have tended to cause the upper layers of liquid alkyl compound, and hence of the surrounding liquid ethylene, to have a higher temperature than the solid alkyl compound, and accordingly some ambiguity may attach to the interpretation of any steady temperatures recorded when most of the crystals had melted.

In all, 13 temperature-time curves for the fusion of the crystalline solid were determined in series II. Five of these are plotted in Fig. 3. Again it will be seen that there is a correspondence between the temperatures of arrest in these curves, which can scarcely be fortuitous. The lowest m. p. represented in Fig. 3 appeared in at least 5 experiments as an arrest in the temperature-time curve which always coincided with the first appearance of liquid. In 2 other experiments there was a small kink in the curve at this temperature, again coincident with the first visible signs of melting. The temperature corresponding to this arrest was  $142.1^\circ \pm 0.1^\circ \text{K.}$ , and the crystal form involved would therefore appear to be identical with *e* of series I. The next form *g* was present on at least 3, and possibly 4, occasions, and was assigned m. p.  $143.15^\circ \pm 0.05^\circ \text{K.}$  In one experiment there was an arrest for over an hour at  $144.1^\circ \pm 0.15^\circ \text{K.}$  and there was evidence that the form (*h*) responsible for this had constituted part of the crystal mass in 2 other runs. The modification (*i*) with the next highest m. p. appeared more frequently, in 6 of a total of 13 experiments, although in 2 of these it was produced by seeding from a

FIG. 3.

Temperature-time curves obtained on warming crystalline tetraethyltin (series II). In the experiments represented by curves 2 and 4, hydrogen was admitted to the outer jacket at the stages represented by the dotted lines after partial fusion had taken place and was pumped away before melting was complete.



previous run. All 6 m. p. values were consistently  $145.80^\circ \pm 0.05^\circ \text{K.}$  Finally, on 5 occasions a form *j* with a still higher m. p. ( $147.1^\circ \pm 0.15^\circ \text{K.}$ ) was present. There was slightly more variability in this m. p. than in the others, presumably because there was relatively little solid remaining in the vessel by the time this arrest was reached.

The temperature-time curves sometimes showed small arrests at other temperatures. In curve 5 of Fig. 3, for example, there appears to be an arrest at  $144.6^\circ$ . It may be that these are evidence of the existence of yet other forms, or alternatively that they represent false equilibria arising from recrystallisation or interconversion, the possibility of which we shall consider in due course. We therefore attach no significance to arrests only encountered once. It must be stressed that each of the arrests in series II which have been ascribed to the existence of forms *e-j* appeared on not less than three occasions, with the degree of reproducibility given above. It is worth recording that the highest m. p.s tended to be encountered when the solid was heated comparatively rapidly.

In the one run with crystals which had been produced by warming of the glass, the melting behaviour was quite different. The temperature-time curve for this experiment is plotted in Fig. 4. It has several horizontal or almost horizontal portions, which fall in the temperature range covering the m. p.s observed in series I. Whether or not all the arrests represent m. p.s, there is no doubt that in this experiment melting started at about  $138.8^\circ \text{K.}$ , and that fusion was complete at  $142^\circ \text{K.}$ , *i.e.*, at a temperature at which, in the other experiments of series II, the alkyl compound was still all solid or only just beginning to liquefy. Some, but not all, of the arrests can be correlated with the m. p.s of series I. We shall defer further discussion of this, however, until all the experimental evidence has been presented.

*Series III.*—In this apparatus crystallisation sometimes occurred with less supercooling than in the experiments already described. When this happened it was possible to carry out measurements of the freezing as opposed to the melting temperatures. Just before crystallisation started the air was pumped away from the space separating the alkyl compound from the cooling agent (liquid oxygen), and temperature-time readings were taken until stirring became impossible. When, however, the supercooling was greater, with the result that considerable quantities of the substance froze rapidly as soon as crystallisation commenced, the stirrer became embedded, and on subsequent warming of the solid by replacing the liquid-oxygen bath by one of solid carbon dioxide-acetone, the temperature as recorded by the thermocouple almost always passed the m. p. by several degrees before the stirrer became free. With the resumption of stirring the temperature fell to the m. p., but shortly afterwards started to rise

FIG. 4.

Temperature-time curve for tetraethyltin (*series II*), showing the existence of forms of lower melting point than those revealed in Fig. 2. The lower vertical arrow indicates the stage at which the first signs of melting were observed, the upper that at which fusion was seen to be complete.

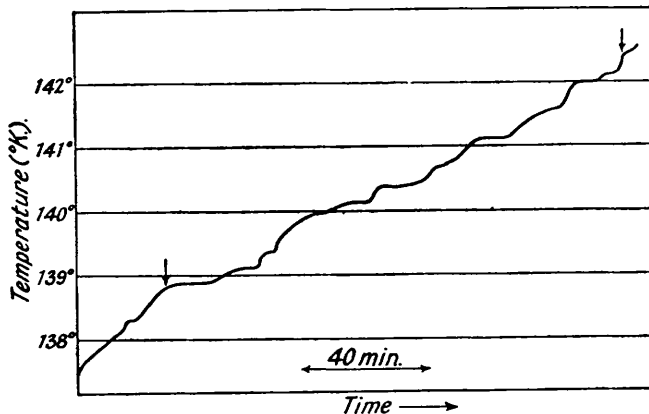
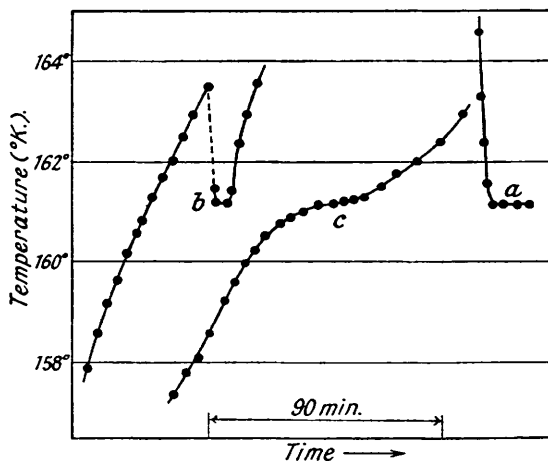


FIG. 5.

Temperature-time curves for carbon disulphide, the apparatus being that of *Series III*.



again. Since the apparatus was suitable only for observations on the first stages of freezing and the final stages of melting, it was modified after a number of experiments of this kind had been carried out. The stirrer was removed and replaced by a pile of 30 perforated copper discs, 0.1 mm. thick, soldered at a distance of 2 mm. apart to a central metal tube which closely fitted the thermocouple tube. The height of the pile of discs was such that the top disc was just below the surface of the liquid alkyl compound. With this arrangement it was possible to measure the temperature at which fusion of the crystalline mass started, but not the temperatures at which any higher-melting forms present may have begun to liquefy. Experiments were carried out on a pure sample of carbon disulphide, as representing a substance with a single and accurately known m. p., to ensure that with such a substance the melting and the freezing temperature measured in these different ways were in fact identical. In Fig. 5 are shown temperature-time curves for carbon disulphide obtained (a) by slow freezing with continuous

stirring, (b) by warming the completely crystallised sample, the stirrer being started as soon as it became free, and (c) by warming the completely crystallised sample by the copper discs. It will be seen that the value to which the temperature falls in (b) as soon as the stirrer operates, and the temperature at which the warming curve (c) shows a horizontal point of inflexion are in fact the same as the steady temperature recorded during freezing in (a).

FIG. 6.

Temperature-time curves for fusion of tetraethyltin (series III).

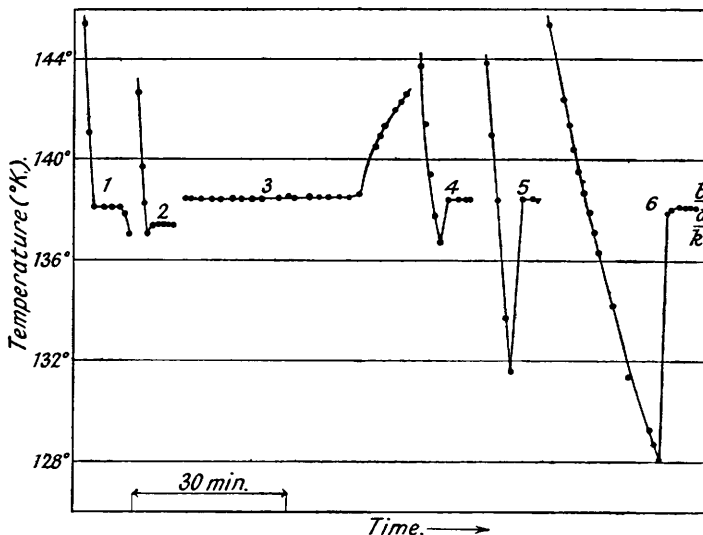
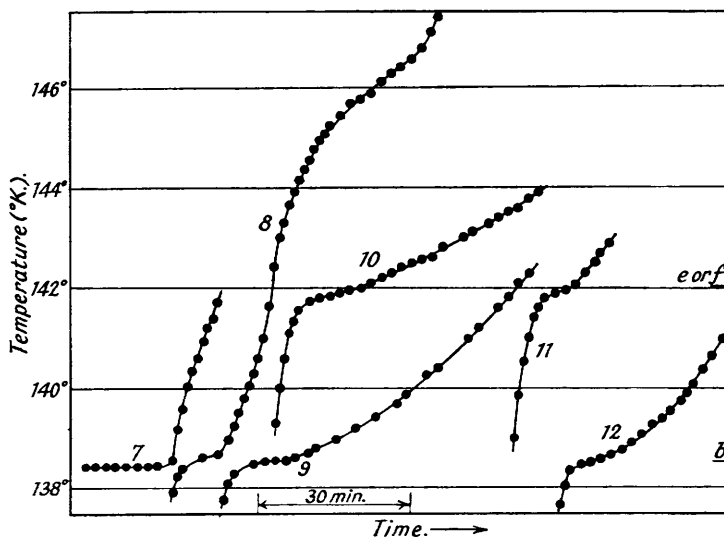


FIG. 7.

Temperature-time curves for fusion of tetraethyltin (series III).



When the alkyl compound was cooled sufficiently rapidly, crystallisation frequently occurred without extensive supercooling, and this always produced the forms with the lowest m. p.s. Slow cooling, however, usually gave the glass, which was then induced to crystallise by gradually raising its temperature.

A representative selection of the temperature-time curves obtained in series III is shown in Figs. 6 and 7. Curve 1 is an example of an experiment in which freezing occurred with scarcely any supercooling, and the corresponding freezing temperature of  $138.11^{\circ}\text{K}$ . suggests that the substance had crystallised in form *a*, twice obtained in series I. The same form was obtained in a later experiment (curve 6) in

which its appearance was preceded by extensive supercooling. Curves 2 and 3 are of particular interest: the arrest in the freezing curve 2 took place at  $137.43^\circ \text{K}$ . and must be ascribed to the production of a new form *k* which has the lowest m. p. we have measured for tetraethyltin. As soon as the movement of the stirrer became sluggish the alkyl compound was allowed to warm, and, with the stirrer operating continuously, the warming curve 3 was obtained. There is an arrest in the warming curve which corresponds to m. p.  $138.5^\circ \pm 0.05^\circ \text{K}$ ., *i.e.*, close to the value ascribed to form *b* of series I. The freezing and melting temperatures for curves 2 and 3 are definitely different, and it would seem that in the interval between the cessation of the measurements made during freezing and the start of those made during melting the very low-melting form *k* first produced had spontaneously changed into *b*. Furthermore, the form *b* was frequently produced directly on cooling (curves 4 and 5). In all, form *b* was produced 10 times in series III, its f. p. being obtained in 5 cooling curves, and concordant values for the m. p. in 5 other experiments which are represented in Figs. 6 and 7 (curves 3, 7, 8, 9, and 12).

In 7 of the experiments in which the crystalline alkyl compound was warmed by using the copper-disc technique, the temperature-time curve showed a horizontal or almost horizontal point of inflexion at  $141.9^\circ \pm 0.1^\circ \text{K}$ . This is illustrated by curves 10 and 11 of Fig. 7. This presumably represents the melting of form *e* or *f*, which were frequently produced in series I and II. Finally, in one experiment carried out on crystals obtained by warming the glass, the temperature when the stirrer ultimately became free fell to  $145.8^\circ \text{K}$ . and remained at this temperature for 4 minutes before rising again. This agrees with the m. p. of form *i* which was obtained 6 times in series II. Very possibly some of the alkyl compound was present in this form in the experiment represented by curve 8 of Fig. 7. The course of this curve in the neighbourhood of  $146^\circ \text{K}$ . suggests that further melting was taking place in this region. In this case the copper-disc technique was employed and an accurate value for the higher m. p. cannot be given, but at least it seems clear that the crystalline alkyl compound was partly in the form *b* and partly in a form with a m. p. higher than that of *e* or *f* ( $\sim 142^\circ \text{K}$ ).

The results of the three independent series of experiments are summarised in Table I.

TABLE I.

*Melting points of the various crystalline forms of tetraethyltin.*

(The number in parentheses after each m. p. is the number of times that form was obtained.)

Form.	Series I.	Series II.	Series III.
<i>k</i>	—	—	$137.43^\circ$ (2)
<i>a</i>	$138.1^\circ \pm 0.1^\circ$ (2)	—	$138.11$ (2)
<i>b</i>	$138.7 \pm 0.2$ (5)	—	$138.5$ (10)
<i>c</i>	$139.8 \pm 0.05$ (6)	—	—
<i>d</i>	$140.61$ (4)	—	—
<i>f</i> } <i>e</i> }	{ $141.87$ (7) $142.12$ (5)	—	$141.9 \pm 0.1$ (7)
<i>g</i>	—	$142.1^\circ \pm 0.1^\circ$ (5, ?7)	—
<i>h</i>	—	$143.15 \pm 0.05$ (3, ?4)	—
<i>i</i>	—	$144.1 \pm 0.15$ (1, ?3)	—
<i>j</i>	—	$145.8 \pm 0.1$ (6)	$145.8$ (1, ?2)
		$147.1 \pm 0.15$ (5)	—

*Results for Tetraethyl-lead.*

All the experiments on this substance were carried out in the apparatus used for series III of the tetraethyltin work. It was never possible to make temperature measurements during freezing. Crystallisation could only be induced by warming the supercooled substance, and started at least  $10^\circ$  below the lowest m. p. recorded. The formation of crystals, once begun, was usually so rapid that the stirrer became frozen in, although in 2 experiments (curves 2 and 4 of Fig. 8) it was possible to keep the stirrer just in motion throughout. Consequently all observations were made during melting, either with mechanical stirring (as soon as this became possible), or else by the copper-disc technique. A representative selection of the temperature-time curves obtained is shown in Fig. 8.

The lowest m. p. observed was at  $135.6^\circ \pm 0.1^\circ \text{K}$ . This form *a* was obtained in 3 of a total of 13 experiments. The results of one of these are shown in curve 5. A second form *b* with m. p.  $136.6^\circ \pm 0.1^\circ \text{K}$ . appeared on two occasions (curves 1 and 2). In the second of these, stirring never completely ceased, and the temperature, after remaining at  $136.6^\circ \text{K}$ . for 4 minutes, then rose very irregularly before again becoming constant at  $137.4^\circ \text{K}$ . Evidence of a form *c* with m. p.  $137.4^\circ \text{K}$ . was furnished by 2 other runs, and accordingly it is possible that, in the experiment which gave curve 2, some of the liquid produced from form *b* crystallised again as *c*, and that during the two arrests the system was not in equilibrium, the temperature oscillation being due to the opposing thermal effects associated with the crystallisation of *c* and the fusion of the remaining *b*.

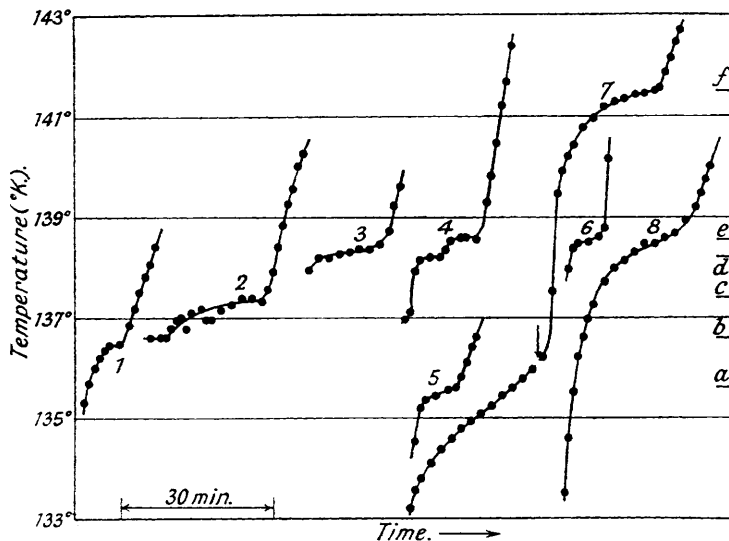
Curve 4 indicates the melting of two forms *d* and *e* with m. p.  $138.2^\circ$  and  $138.55^\circ \text{K}$ . respectively. The modification *d* also seemed to have been produced in the experiment represented in curve 3, perhaps again accompanied by a small amount of *e*, but crystallisation as *e* was altogether more common. In all it appeared to be present on 8 occasions. Lastly, curve 7 provides evidence for the existence of a form *f* with a much higher m. p. ( $141.5^\circ \text{K}$ ). The lower part of this curve, the measurements for which were made while the stirrer was still immovable, suggests the presence of a low-melting modification, probably *a*. As soon as the stirrer was started (at the point shown by the gap in the curve) the temperature rose extremely rapidly, suggesting that crystals were once more being formed, and then followed the course shown.



Since the experiments of series III on tetraethyltin revealed the existence of only about half of the modifications found altogether, the polymorphism of tetraethyl-lead may not be limited to the 6 forms just described, and in particular there may be other modifications of higher rather than lower m. p. The question arises whether any correlation exists between the m. p.s of the different forms of the two alkyl compounds, and it is interesting that it is possible to associate 5 of the alkyl-lead forms with 5 of the tetraethyltin modifications, so that the differences in m. p. between the members of each pair are almost constant. The pairs are as follows (the first letter of each pair refers to the alkyl tin, and the figures give the amount by which the m. p. of the tin exceeds that of the lead compound): *h-f*, 2.6°; *d-d*, 2.4°; *c-c*, 2.4°; *b-b*, 2.1°; *a-a*, 2.5°. This parallelism may, however, be fortuitous, as the m. p.s of the several forms of any one substance are so close together. Almost equally constant m. p. differences (of  $\sim 5.5^\circ$ ) in fact are found for the pairs *j-f*, *h-e*, *g-c*, *e-* or *f-b*, *d-a*.

FIG. 8.

Temperature-time curves for the fusion of crystalline tetraethyl-lead. In the experiment represented by curve 7, the stirrer came into operation at the gap in the curve indicated by the arrow.



#### Experiments on Tetraethylgermanium.

Dennis and Hance (*J. Amer. Chem. Soc.*, 1925, **47**, 370) gave  $183.0^\circ \text{K}$ . as the m. p. of this substance. We have carried out preliminary experiments on a sample (specially prepared for us by the method described by Krause and Flood, *ibid.*, 1932, **54**, 1635), which unfortunately proved to be much less pure than was hoped. Eight experiments were carried out in the apparatus used for the tetraethyltin investigations. Crystallisation could be brought about by rapid cooling, with little if any supercooling. With slower cooling, the alkyl compound could be supercooled by about  $15^\circ$ . The 6 cooling and 3 warming curves obtained gave no indication that the substance had ever crystallised in any but one form, and, though an accurate value for the m. p. of this cannot at present be given, it is certainly within  $1-2^\circ$  of the value found by Dennis and Hance.

#### DISCUSSION.

As far as we are aware, no other known organic substance is capable of existing at ordinary pressures in as many crystalline forms as tetraethyltin. In the comprehensive investigation of the physical properties of hydrocarbons carried out at the National Bureau of Standards, Washington, a few of these substances have been found to crystallise in three different forms, e.g., 3 : 3-dimethylpentane and mesitylene (Streiff, Murphy, Sedlak, Willingham, and Rossini, *J. Res. Nat. Bur. Stand.*, 1946, **37**, 331), and menthol can exist in at least four solid modifications with melting points only a few degrees apart (Wright, *J. Amer. Chem. Soc.*, 1917, **39**, 1515). For tetraethyltin, however, there appear to be at least ten forms, and for tetraethyl-lead at least six. The only value in the literature for the melting point of tetraethyltin is  $161^\circ \text{K}$ ., quoted by Grüttner and Krause (*Ber.*, 1917, **50**, 1802), who do not, however, give any details about its determination. This value is considerably higher than any we have obtained.

One striking feature of our experiments has been the frequency with which crystallisation has produced more than one modification simultaneously, as shown from the resulting step-wise melting curves. In these circumstances the system during melting cannot really be in

equilibrium, and the fact that the melting curves so often resemble those which would be obtained by heating a mixture of substances which melt to quite immiscible liquids implies that, with the higher-melting forms at least, the velocity of crystallisation of any given form from the liquid at temperatures a little below the melting point is small in relation to the time of a melting experiment. In fact, in only one experiment did it definitely appear that the melting of a low-melting form was followed by rapid recrystallisation to a modification of higher melting point (see curve 7 in Fig. 8). The spontaneous change of one solid modification into another also appeared to be comparatively rare, although this definitely happened once with tetraethyltin in series III (curves 2 and 3 of Fig. 6) and probably also in series II, since when steady temperatures were recorded during freezing they were lower than those at which the crystal melted. It is also possible that either recrystallisation from the liquid or spontaneous change of one form into another, or both of the effects simultaneously, may have been responsible for the unusual temperature-time curve shown in Fig. 4. The combination of the thermal changes caused by these effects with those caused by melting of the crystals could produce chance arrests and changes of slope in the melting curve and may explain why not all the arrests in Fig. 4 can be correlated with the melting points observed in this region in series I or III. It is worth pointing out that the velocity with which a liquid freezes is sometimes very sensitive to the presence of traces of impurities (Timmermans, "Chemical Species," Macmillan, 1941, p. 103), and that the same may be true of the velocity of spontaneous change of one solid form of a substance into another. Consequently, effects due to recrystallisation and to interconversion of the crystal forms might be obtained with one sample of the alkyl compound but not with another which differs slightly in the amount and nature of the impurities present.

In seeking an explanation of the unusual polymorphism of tetraethyl-tin and -lead, we attach considerable importance to differences between these substances and certain analogues: calorimetric studies in this laboratory on tetramethyl-tin and -lead, tetraethylgermanium, and 3:3-diethyl-*n*-pentane have given no indication of multiple melting points. Aston and Messerly (*J. Amer. Chem. Soc.*, 1936, **58**, 2354) reported only one melting point for *neopentane*, although tetramethylsilicon crystallised in a stable and an unstable modification (Aston, Kennedy, and Messerly, *ibid.*, 1941, **73**, 2343). Among the Group-IV tetramethyl and tetraethyl compounds, therefore, tetraethyl-tin and -lead appear to be in a class by themselves with respect to their polymorphism. But there is a further important difference between the tetraethyl and tetramethyl compounds, concerned with the trend of the melting points on progression from carbon to lead. Table II records the melting points of these substances and of the tetrachlorides. Both for the tetramethyl compounds and for the tetrachlorides the melting point of the carbon

TABLE II.

Melting points ( $\kappa$ .) of compounds  $\text{MX}_4$ .

	M.	Cl.	$\text{CH}_3$ .	$\text{C}_2\text{H}_5$ .	M.	Cl.	$\text{CH}_3$ .	$\text{C}_2\text{H}_5$ .
C .....		250.3°	256.5°	240.1°	Sn .....	240°	218.3°	147.1° *
Si .....		203.3	174.1	—	Pb .....	258	242.9	141.5 *
Ge .....		224	185	183.0				

\* Highest melting point recorded.

compound is higher than that of the silicon compound. Thereafter the melting point rises with increasing molecular weight. The same is true for the bromides and iodides. The relatively high melting points of the carbon compounds are to be related to the fact that they all [*i.e.*,  $\text{C}(\text{CH}_3)_4$ ,  $\text{CCl}_4$ ,  $\text{CBr}_4$ , and  $\text{CI}_4$ ] exist in a low-temperature and a high-temperature form. For  $\text{CBr}_4$  and probably for the other tetra-halides the high-temperature form has a highly symmetrical lattice. The short C-X bond length leads to a compact and nearly spherical  $\text{CX}_4$  molecule and a lattice of considerable symmetry such that the molecules, even if they do not freely rotate, probably have considerable orientational freedom and behave as if they were effectively spherical. The greater Si-X bond length and the stronger intermolecular forces lead to a greater degree of intermolecular interlocking, and a lattice which, while perhaps isomorphous with the low-temperature form of  $\text{CX}_4$ , is certainly not isomorphous with the high-temperature form. Consequently, the melting-points of the  $\text{CX}_4$  compounds do not fall into line with those of the corresponding compounds of the later elements of the group. It may be remarked here that "tetraethylcarbon" (3:3-diethyl-*n*-pentane) has been found in this laboratory to undergo a transition some 30° below its melting point, which, as will be seen from Table II, is higher than that of the other known Group-IV tetraethyl derivatives.

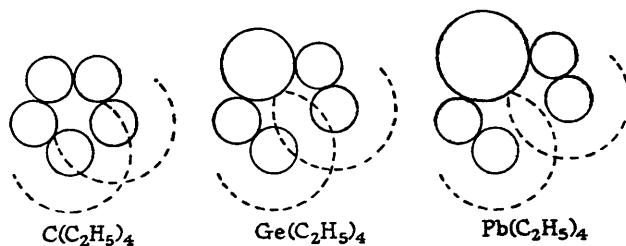
The tetraethyl have lower melting points than the corresponding tetramethyl compounds,

and there is no longer an upward trend from germanium to lead. The highest melting point of tetraethyltin is considerably lower than that of tetraethylgermanium. This suggests that, while for the tetramethyl compounds or a set of halides, the solids from silicon to lead are isomorphous, this is no longer true for the tetraethyl compounds, and that the change from germanium to tin means a departure from the crystalline form of solid  $\text{Ge}(\text{C}_2\text{H}_5)_4$  and the introduction of remarkable possibilities of polymorphism.

Probably the most important change in the  $\text{MX}_4$  molecules ( $\text{X} = \text{alkyl}$ ) in the progression from  $\text{M} = \text{C}$  to  $\text{M} = \text{Pb}$  is the  $\text{M-X}$  bond length, *viz.*,  $\text{C-C}$  1.54,  $\text{Si-C}$  1.93,  $\text{Ge-C}$  1.98,  $\text{Sn-C}$  2.18, and  $\text{Pb-C}$  2.29 Å. (Brockway and Jenkins, *ibid.*, 1936, 58, 2036). The most marked changes in bond length are associated with the stages  $\text{C} \rightarrow \text{Si}$  and  $\text{Ge} \rightarrow \text{Sn}$ . We have already considered the effect of the first of these. The second is believed to be intimately connected with the polymorphism of tetraethyl-tin and -lead.

There is reason to believe that the potential barrier restricting the rotation of a methyl group about the bond joining it to an atom decreases rapidly as this bond length increases, and that whereas in  $\text{C}(\text{CH}_3)_4$  this barrier height is 5000 kcal., in  $\text{Si}(\text{CH}_3)_4$  it is only 1300 kcal. (Aston, Kennedy, and Messerly, *loc. cit.*), and in  $\text{Sn}(\text{CH}_3)_4$  and  $\text{Pb}(\text{CH}_3)_4$  it is probably almost nil (French and Rasmussen, *J. Chem. Physics*, 1946, 14, 389). However, even if the methyl groups in compounds  $\text{M}(\text{CH}_3)_4$  rotate freely, the ethyl groups in  $\text{M}(\text{C}_2\text{H}_5)_4$  cannot do so owing to the overlap of the paths followed by the peripheral atoms. Fig. 9 shows, for  $\text{C}(\text{C}_2\text{H}_5)_4$ ,  $\text{Ge}(\text{C}_2\text{H}_5)_4$ ,

FIG. 9.  
Showing the relationship of two co-planar ethyl groups in tetraethyl-germanium and -lead and 3 : 3-diethyl-n-pentane.



and  $\text{Pb}(\text{C}_2\text{H}_5)_4$ , the position in which this overlap is greatest. The radii of the full circles are in proportion to the covalent radii of the atoms concerned. The dotted circles represent the effective van der Waals field of action of the peripheral methyl groups, the radius corresponding to 2 Å. (Stuart, "Molekülstruktur," Berlin, 1934, p. 47). It will be seen that even with the largest molecule (tetraethyl-lead) there is a considerable overlap of the regions swept out by the van der Waals' spheres of action of the methyl groups as the ethyl groups rotate. In an isolated molecule it will, of course, be possible for any one methyl group to proceed to any other position which free rotation about the  $\text{M-C}$  bond makes available to it, though this may require simultaneous and suitable movement on the part of the other methyl groups. (The potential energy of a pair of methyl groups could be approximately represented by an expression such as  $[(a/r^{12}) - (b/r^6)]$ , where  $r$  is the separation of their centres. It would be interesting to know if the total potential energy of all four such groups in a molecule, expressed in terms of co-ordinates defining their relative positions, has more than one minimum. Unfortunately, the mathematical difficulties involved in the solution of this problem appear considerable.)

The freedom of movement of the methyl groups of any one tetraethyl molecule will, however, be further restricted in the condensed states if under these conditions adjacent molecules tend to interlock. Nothing is known of the crystal structure of the solids. However, calculations from the van der Waals spheres of action of the methyl groups and the molar volumes show that there must be considerable intermolecular interlocking *in the liquid*, and presumably even more in the solid. This will be more pronounced the larger is the central atom. By means of models, it can be shown that for a tetraethyl molecule with a sufficiently large central atom, various forms can be constructed, differing in the relative positions of the methyl groups, such that the molecules of any one form can be packed together so as to prevent the methyl groups altering their positions to those of another form.

The polymorphism of tetraethyl-tin and -lead may not therefore be simply caused by packing of identical molecules into a suprisingly large number of different lattices, but rather by the molecular geometry and dimensions being such that different crystal forms exist in which the

relationship between the methyl groups in one molecule, and hence between those in adjacent molecules, is different from one form to another. (There may, of course, be polymorphism of the ordinary kind as well, in that some of the crystalline forms may contain molecules with identical configurations.) In other words it is suggested that, in the crystalline solids at least, these molecules exhibit a form of rotational isomerism. In the smaller molecules of the carbon and germanium series there is a larger potential barrier restricting free rotation of the ethyl groups about the bonds to the central atom, as well as greater overlap of the regions available to the peripheral groups and less pronounced intermolecular interpenetration (*i.e.*, the molecules are more compact and more nearly spherical). These factors may combine to make one configuration of the molecule in the lattice much the most stable.

If rotational isomers of tetraethyl-tin and -lead exist in the solid, the question of their possible persistence in the liquid state arises. For example, is the liquid produced as a high-melting form melts identical with that obtained by heating to the same temperature the liquid produced from a low-melting modification. If intermolecular equilibrium in the liquid is very rapidly established at all temperatures, so that the free energy of the liquid (at constant pressure) has a definite value at a given temperature (whatever the history of the liquid), then we should expect constant and reproducible melting points for the different solid forms of the pure substance (in the absence of complications such as spontaneous recrystallisation or inter-conversion). Comparatively slow attainment of the equilibrium in the liquid would lead to a time-variable free-energy curve and variable freezing and melting points (*i.e.*, the melting point of a given form should change as melting proceeds; the properties of systems such as this would have been fully discussed by Smits, in "The Theory of Allotropy," Longmans, 1922.) Our results appear to conform to the first type of behaviour, and suggest that, in the neighbourhood of the melting points at least, any equilibrium in the liquid is established relatively rapidly. This does not, however, rule out the possibility that the liquid shows time-variability in its properties, particularly at lower temperatures in the supercooled state, and it is hoped to investigate this further. Claims to have observed hysteresis in the thermodynamic properties of organic liquids are of doubtful reliability (see Aston and Schumann, *J. Amer. Chem. Soc.*, 1942, **64**, 1034; Guthrie and Huffman, *ibid.*, 1943, **65**, 1143; Aston, Rank, Sheppard, and Szasz, *ibid.*, 1948, **70**, 3525; Railing, *ibid.*, 1939, **61**, 3349; and Pitzer, *ibid.*, 1940, **62**, 331).

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