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CRYOGENIC THERMODYNAMIC STUDIES ON SOME GLOBULAR MOLECULES AND ON THE SYSTEM TETRAMETHYLAMMONIUM CHLORIDE–TETRAMETHYLAMMONIUM HYDROGEN DICHLORIDE

by

Shu-Sing Chang

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy in the
University of Michigan
1961

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PART I

CRYOGENIC THERMODYNAMIC STUDIES ON SOME GLOBULAR MOLECULES

Introduction

Plastic Crystals and Rotation in the Solid State

Phase transitions in the solid state are frequently exhibited by molecular crystals, especially in those composed of relatively simple molecules with a high degree of symmetry and low intermolecular forces. Many of these transitions have been described as resulting from the onset of rotational motion of molecules in the crystal lattice as well as from order-disorder phenomena.

While compiling data on physical constants of crystalline organic compounds, Timmermans[1] encountered a number of compounds having exceptionally low values of entropy of fusion at the melting point. The values of the entropy of fusion for these substances are generally less than 5 e.u. in contrast to the range of 9 to 11 e.u. for most organic compounds[2]. Invariably, solid-solid transition occurs in these compounds involving substantial transitional entropy increment comparable to or exceeding the magnitude of the entropy of fusion, such that the sum of the fusional and transitional entropies usually comes within the range for the entropy of fusion of a normal compound. It is apparent that such a transition may play an important role in the process of solid-liquid transformation. The molecules in

the solid phase stable above the transition point may have acquired rotational freedom similar to that in the liquid state. As the temperature increases, the ever present torsional-vibration motion of the molecules in the crystal lattice increases its magnitude and eventually a complete rotation of the molecules sets in. However the crystal still persists until the translational vibration of the molecules at their lattice sites are vigorous enough to cause the breakdown of the crystal lattice and hence the substance changes into the liquid state.

The idea of the probable occurrence of molecular rotational motion in the crystalline state has been suggested by Simon and Simson[3] to account for the existence of the face-centered cubic modification of solid hydrogen chloride immediately below the melting point. Some theoretical treatment was given by Pauling[4] for the rotation of certain simple molecules and ions in the solid state. Various experimental techniques, such as X-ray diffraction analysis, measurement of dielectric constants and nuclear magnetic resonance spectroscopy, seem to encourage the establishment of such an idea for a great number of compounds including many large and complex molecules.

X-ray structural analysis shows that the crystal modification stable above the transition point has in general a space group of higher apparent symmetry than that corresponding to the constitution and the number of molecules in each

unit cell, and that only a few diffractions of very low order are observed due to the very rapid fall-off in intensity with increasing reflection angle and the considerable background caused by the rotating or disordered scatterers[5]. The solid phase stable in between the transition point and the melting point crystallizes almost invariably in the face-centered cubic or close-packed hexagonal space groups, although the crystal stable below the transition point may be in some structure of lower symmetry. The close-packed structures are preferred by spheres of low interacting forces. The molecules in the high temperature phase fulfill these requirements by having weak intermolecular forces, such as the van der Waals forces, and by approximating a sphere through rotation or at least statistically.

For polar molecules or ions the dielectric constants may change abruptly at the transition point from a low value for the low temperature phase to a value similar in size and temperature dependence to that of the liquid state due to the increased rotational freedom of the molecules in the high temperature "rotator" phase, and hence to the orientational polarizability[6].

The nuclear magnetic spectrum of a solid is generally broader than that of a liquid due to the effect of magnetic dipolar interaction between the nuclei. Such interaction is reduced and the center portion of the spectral line

narrowed when the frequency of reorientation of the molecules is in the order of the spectral width, in practice in the order of 10^3 cycles per second or about one gauss in terms of the field strength[7]. Thus the measurement of temperature dependence of the line width or of the second moment (mean square width) provides a sensitive method in detecting such molecular motion occurring at a rate above a few kilocycles per second. Measurements of the correlation time provide additional information about frequency distribution and activation energy for the reorientation process.

The term "free rotation" of molecules has been widely used by many investigators in describing these solid-solid transitions. However from the present stage of knowledge, the rotational motion in the solid state is hardly a free one, but must be rather restricted due to the force environment exerted upon the molecules in the crystal lattice. The free rotation of molecules in the crystalline state has been reported only for some very particular cases, such as the oxygen[8] and methane[9] molecules trapped in the β-hydroquinone clathrates as estimated by magnetic susceptibility measurements and analysis of heat capacity data. Methane molecules were reported to have almost free rotation near its melting point through analysis of the heat capacity measurement[10]. In most cases comparison of the space available in the crystal with the van der Waals envelope

of the molecules leads to the conclusion that there is not enough room in the crystal lattice for the molecules to rotate freely[11]. This is true even for some molecules in the liquid state[12]. Therefore these molecular motions would be better described as frequent and probably random reorientation of the molecules from one preferred position to another and may involve cooperative mechanisms of some complexity, and thus could be treated satisfactorily in many cases as orientational order-disorder phenomena[13]. Calorimetric measurements provide quantitative information about the transitional entropy increment and thus about the degree of disorder in the phases above and below the transition point. In general the results from various experimental investigations neither prove nor disprove the existence of reorientational rotation of molecules in the crystalline state and are equally consistent with the order-disorder phenomena. For example, nuclear magnetic resonance and x-ray diffraction measurements cannot be expected to distinguish such orientational disordering from relatively free rotation.

The compounds which show such transitions are usually composed of molecules having a globular envelope and exceptionally high melting points in comparison with their homologs which do not have a rotator phase before melting. The high melting point introduces a high vapor pressure for the solid and therefore a very narrow liquid range,

and in some cases the liquid phase may be absent under atmospheric pressure due to the fact that the solid-liquid-vapor triple point occurs at a higher pressure.

The rotator phases of these compounds in most cases have a waxy appearance[14]. Quantitative comparison of the plasticity of the rotator phase with that of the low temperature non-rotator phase shows that the pressure required to deform by a standard amount in the rotator phase is from 2 to 14 times smaller than that required in the rigid non-rotator phase[15]. Such plastic flow is similar to the high temperature creep of certain metals and may result from the diffusion of vacancies from one side of a crystal to the another. The term "plastic crystal"[16] is probably derived from the plastic nature of the rotator phase of these compounds.

The plastic crystalline state was suggested as a mesomorphic state[16] of matter, in parallel to the mesomorphic state of liquid crystals[17], between the normal solid and liquid states under favorable molecular conditions. Liquid crystals are usually formed by long and rigid or large and flat molecules with suitable polar end groups; they flow like a liquid but are optically anisotropic attributed to the formation of macroscopic clusters of ordered molecules. The plastic crystals in contrast are formed by globular molecules of low intermolecular forces and are isotropic in the phase immediately below the

melting point. The structure of liquid is still not clear because of the varied degree of short range ordering in different conditions. This is true also for liquid crystals. Studies on the long range ordered plastic crystals should enhance the understanding of the solid-liquid transformation process.

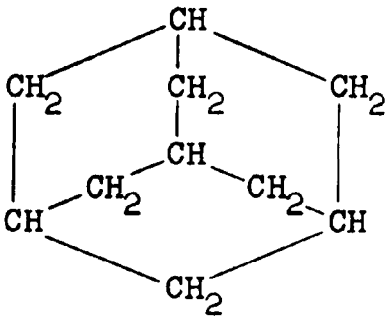
Cage-type Globular Molecules

This portion of the dissertation describes calorimetric measurements made on two types of globular molecules. The compounds of the first type are composed of highly symmetrical cage molecules with their cage-forming atoms arranged in such a fashion as to resemble that of a so-called "characteristic cell"[18] of the diamond crystal lattice. The second type of compounds is also composed of cage molecules, but are less symmetrical and have the shape of a symmetrical top. Four compounds of the first type and one of the second were studied (Table I). The particular compounds chosen for investigation were based largely upon the considerations given to the symmetry of the molecules and also the relative availability of the substance in adquate calorimetric quantities, i.e., about 100 ml. in volume.

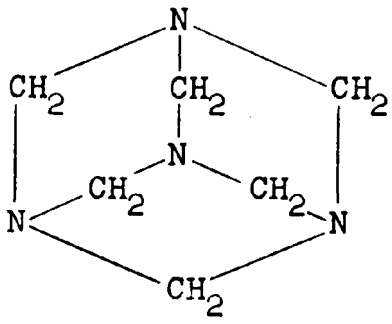
Adamantane, tricyclo[3.3.1.$1^{3,7}$]decane (Figure I), is a saturated polycyclic hydrocarbon, $C_{10}H_{16}$, with all its carbon atoms situated in a strainless cage formed by four chair-form cyclohexane rings fused together in such a manner that every adjacent pair of C-C bonds is shared

Table I

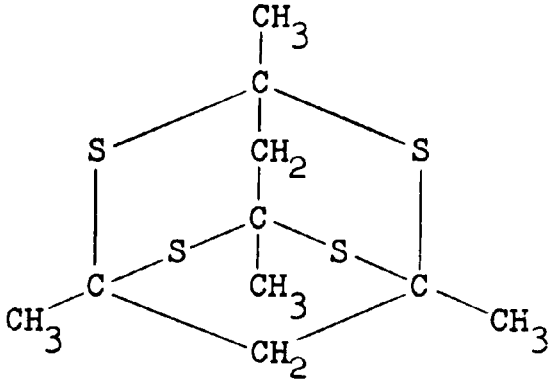
Five Globular Molecules



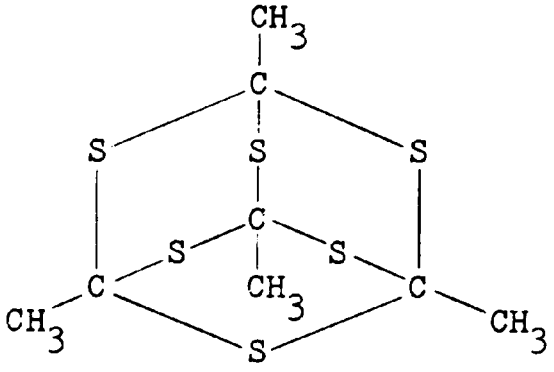
Adamantane, $C_{10}H_{16}$



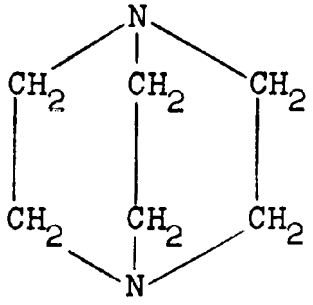
Hexamethylenetetramine, $C_6H_{12}N_4$



1,3,5,7-Tetramethyl-2,4,6,8-tetrathia-adamantane, $C_{10}H_{16}S_4$



1,3,5,7-Tetramethyl-2,4,6,8,9,10-hexathia-adamantane, $C_8H_{12}S_6$



Triethylenediamine, $C_6H_{12}N_2$

Figure I

Molecular Models of Adamantane and

Hexamethylenetetramine

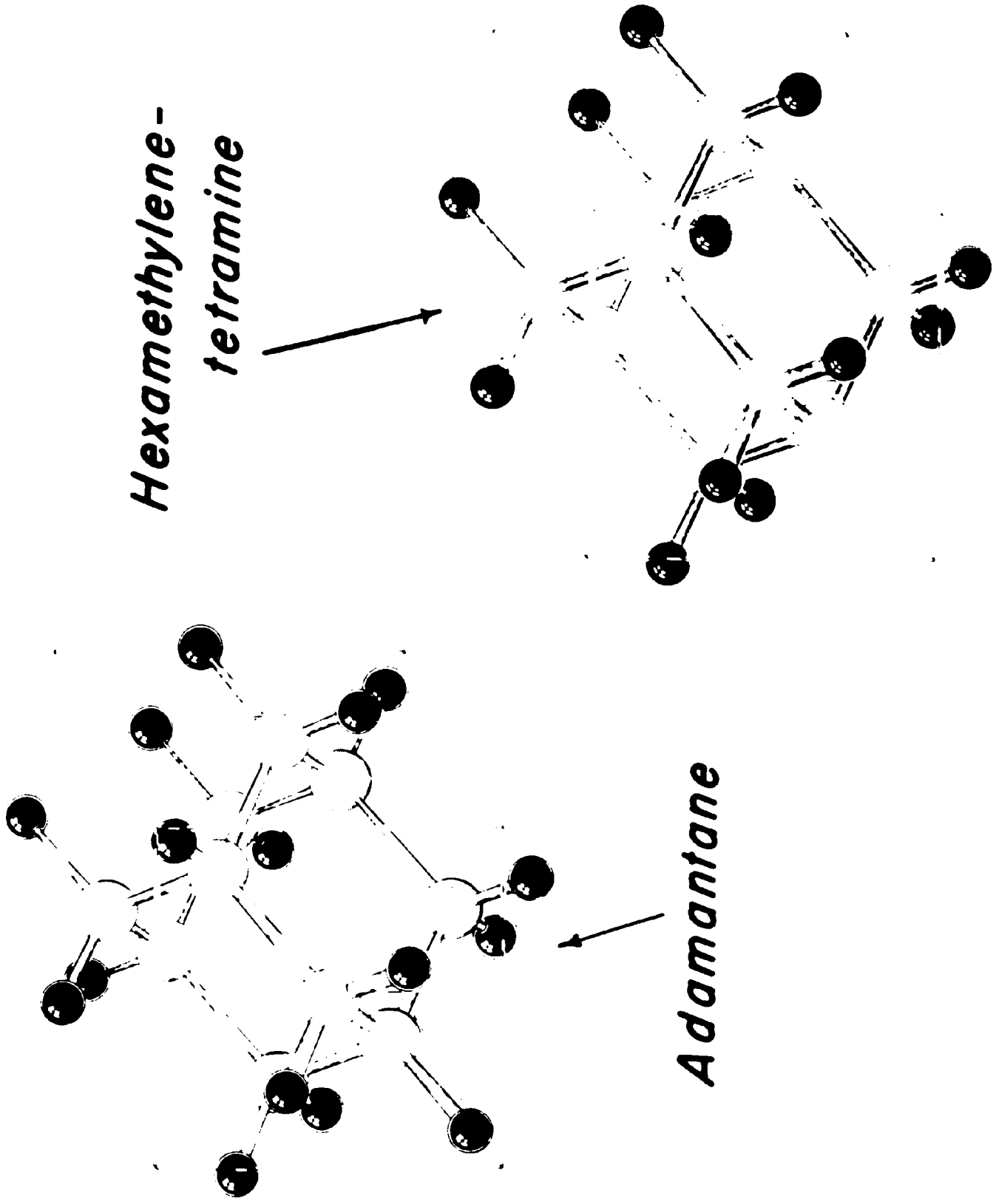


Figure I

by two rings. Adamantane was first isolated by Landa and his co-workers[19] as a minute constituent in the naphtha from Hodonin, Czechoslovakia in 1933. The content of adamantane was reported as 0.03%[20] by weight and 0.0004%[21] by volume for petroleum oils of different origins. The urotropine-like structure was suggested on the basis of its chemical inertness, high volatility, the isotropic nature of the crystals and its exceptionally high melting point of 270°C. (in a sealed capillary tube). For normal C_{10} aliphatic and alicyclic hydrocarbons the melting points are in general in the range of -20 to -100°C., with the exception of certain globular molecules such as camphane which melts at 199°C. and is known to exist in a rotator phase.

A number of synthetic methods[22,23] have been devised, but with long tedious procedures and with very poor overall yields. Recently Schleyer[24] pointed out that adamantane could be prepared in 15% yield as a by-product of a rearrangement reaction. By employing a similar reaction with a different kind of catalyst, a yield of 30% has been claimed[25]. The mechanism of the formation of adamantane from this kind of reaction has been proposed[24]. This two-step reaction thus provided an efficient way to prepare the calorimetric sample of this rather unusual and interesting compound.

The chemical aspects of adamantane and its deriva-

tives have been quite extensively explored by the research groups of Stetter and of Landa (cf. Appendix I).

Hexamethylenetetramine, $C_6H_{12}N_4$ (Figure I), probably the earliest known member of this family of compounds, is formed through the condensation of formaldehyde with ammonia, and is used medicinally under the name of urotropine. It is also the first organic compound for which a complete structural analysis by X-ray diffraction techniques[26] was performed. Although replacement of the four bridge-head or tertiary carbon atoms of an adamantane molecule by nitrogen atoms to form a hexamethylenetetramine molecule does not change the molecular symmetry, the latter molecule seems to have less sphericity than the former one.

Two sulfur-containing diamondoid compounds, $C_{10}H_{16}S_4$ and $C_8H_{12}S_6$, known long before the discovery of adamantane, are the dimers of dithioacetylacetone[27] and that of dithioacetic anhydride[28]. It has been proposed lately by Fredga[29,30] that these two compounds are also composed of cage molecules with structures similar to the skeleton of the adamantane molecule. Spectral investigations[31] are also in favor of the newly proposed structural formula. Therefore these two compounds could be named, according to Stetter's nomenclature for compounds with urotropine-like structure[32], as 1,3,5,7-tetramethyl-2,4,6,8-tetrathia-adamantane and 1,3,5,7-tetramethyl-2,4,6,8,9,10-

hexathia-adamantane, respectively. The former molecule has the four co-planar methylene groups and the latter all six methylene groups of an adamantane molecule replaced by corresponding numbers of sulfur atoms. In addition, there is one methyl group in place of the hydrogen atom for each of the four bridge-head or tertiary carbon atoms in both cases. It seems that the hexathia-compound would have the same molecular symmetry as that of the adamantane molecule, and that the tetrathia-compound would have less symmetry.

About twenty ring systems[33,34,35] (including inorganic ones) are known with an adamantane-like skeleton, but only half of them yield simple, highly symmetrical, spherical molecules. Only the organic ring systems are listed in Appendix I. Stetter and his co-workers have contributed a great deal to the development of a large variety of compounds of this series.

Triethylenediamine, $N(CH_2CH_2)_3N$, is the only compound of the second family studied calorimetrically. The commercial name Dabco stands for the abbreviation of its systematic nomenclature, 1,4-diazabicyclo[2.2.2]octane. Although the molecules of triethylenediamine are less symmetrical than that of the adamantane, it is still rather spherical in shape. Because of the reported transition occurring at 74°C. and associated with a change in crystal structure[36,37], and also that it is available commercially, it is chosen as the first compound to be in-

vestigated in the bicyclo[2.2.2]octane series.

More than 20 ring systems[35] are known to exist in the bicyclo[2.2.2]octane-like structure, and are listed in Appendix II.

Preparation and Purification of Samples

Preparation of Adamantane

Adamantane was prepared as a by-product of the rearrangement reaction transforming endo-tetrahydrodicylopentadiene into its exo-isomer[23]. The endo-isomer was obtained by saturating the readily available α-dicylopentadiene with hydrogen.

The raw material, dicyclopentadiene from Esso Standard Oil Company, was fractionally distilled under reduced pressure. The fraction between 99-101°C./80 mm. Hg was collected. Upon cooling under tap water, a large portion of the collected distillate solidified. The soft solid substance was then collected as purified α-dicyclopentadiene. This was converted into saturated endo-tetrahydrodicyclopentadiene in a low-pressure Paar hydrogenator using platinum black as catalyst, and cyclohexane as solvent. After the mixture had taken the calculated amount of hydrogen or the hydrogenation had virtually stopped, the catalyst was filtered off, and sulfuric acid was then introduced to remove any remaining unsaturated compounds. After being washed with dilute sodium bicarbonate solution and water and dried over anhydrous sodium sulfate, endo-tetrahydro-dicyclopentadiene was obtained in almost quantitative yield upon concentrating the hydrogenation products. It was recrystallized twice from anhydrous methanol. The crystal melts at 76°C.

Endo-tetahydro-dicyclopentadiene was mixed with 20-25% of its weight of pulverized aluminum chloride. The mixture was heated with an oil bath between 180-190°C. and under constant stirring for 48 hours. The reaction mixture was first decomposed by dilute hydrochloric acid and then followed by steam distillation. Most of the adamantane from the reaction was collected in a flask placed immediately beyond the distilling head and before the condenser. A small portion of adamantane could be recovered from the organic layer, mainly exo-tetrahydro-dicyclopentadiene, of the distillate by cooling to dry-ice temperatures.

Adamantane was purified by recrystallizing three times from anhydrous methanol. The final product consists of tetrahedral crystals of about 1-3 mm. in diameter. X-ray powder patterns of this sample showed a face-centered cubic lattice with a cell dimension of 9.52 A. Carbon and hydrogen determinations indicated the following composition: 88.35% C and 11.65% H; (theoretical: 88.16% C, and 11.84% H for $C_{10}H_{16}$). Gas chromatographic analysis by using a Super Tide column and operated at 150°C. gave only one peak in addition to the solvent (chloroform) peak.

Preparation of Hexamethylenetetramine Sample

Hexamethylenetetramine made by Eastman Kodak Company was purified by subliming twice in a vacuum sublimation apparatus capable of handling large quantities of materials.

The sublimation assembly is constructed by inverting

a No. 3480 heavy-walled Pyrex vacuum distillation apparatus made by Corning Glass Works. The distillation apparatus originally consisted of a distilling tube, a hemispherical lid and a cylindrical pot of about 6" in diameter and 4" in depth. The distilling tube is replaced by a tube attached with a stopcock and two tungsten rods serving as lead-in wires for supplying power to the heater. The rods are tipped with platinum to facilitate soldering to the heater leads. The sample to be sublimed is placed in a cup made of Pyrex glass, around which a Fiberglass insulated Constantan wire of approximately 100 ohm resistance is wound to serve as a heating element. Sublimed products are collected in the cylindrical top of the assembly, which is actually the inverted bottom pot of the distillation apparatus. The sample collector is cooled by an air stream if necessary. A rubber O-ring of appropriate size and fit with a aluminum inner guard ring is placed between the ground glass surfaces of the lid and the top part of the assembly. This increases greatly the ease in disassembling the sublimation apparatus.

The final product was composed largely of transparent crystals of rhombic-dodecahedral habit about 3 mm. in diameter from the slow sublimation process. Microchemical analyses showed a composition of: 51.52% C, 8.48% H and 40.00% N; (theoretical: 51.40% C, 8.63% H and 39.97% N for $C_6H_{12}N_4$).

Preparation of 1,3,5,7-Tetramethyl-2,4,6,8-tetrathia-adamantane

The calorimetric sample of this compound was prepared in accordance to the method described by Fredga and Brändstrom[30]. A 20% solution of acetylacetone in absolute ethanol saturated with anhydrous hydrogen chloride at 0°C. was prepared. After the solution was chilled in a bath of dry ice and ethanol, a strong stream of hydrogen sulfide was passed in until an excess amount had been introduced. The mixture was then allowed to warm up slowly to room temperature in order to expel the surplus hydrogen sulfide. The solid precipitate was collected and washed with concentrated hydrochloric acid. The yellowish tint which could not be removed after several crystallizations was removed by dissolving the crystals in alcohol and refluxing the alcoholic solution with a small amount of active carbon Norit. The crystals were further purified by recrystallizing twice from anhydrous methanol. The final sample consisted of crystals in the shape of long prismatic needles with a melting point of 168°C. Analysis showed the following composition: 45.56% C, 6.05% H and 48.21% S (calculated: 45.41% C, 6.10% H and 48.49% S for $C_{10}H_{16}S_4$).

Preparation of 1,3,5,7-Tetramethyl-2,4,6,8,9,10-hexathia-adamantane

This compound was prepared by the method described as

that for "tetraethenyl hexa-sulfide"[38]. Thiolacetic acid was refluxed with one-third of its weight of crushed, fused zinc chloride overnight. The solid residue from the reaction mixture was washed with dilute hydrochloric acid and water to dissolve away the zinc compounds. It was then recrystallized twice from absolute ethanol. The crystals melt at 232°C. with slight decomposition. Analytical results indicated the following composition: 31.94% C, 4.14% H and 64.17% S (calculated: 31.97% C, 4.02% H and 64.01% S for $C_8H_{12}S_6$).

Preparation of Triethylenediamine

A quantity of research grade triethylenediamine sample was furnished by the Houdry Process Corporation under the trade name of Dabco. The sample provided was purified by subliming twice in vacuum utilizing the apparatus used for the purification of hexamethylenetetramine in order to remove extraneous and colored materials. Large hexagonal tabular crystals were thus obtained. These transparent crystals appeared to be very stable in dry air, but when in contact with ambient atmospheric air they lost their lustre at once and became translucent. The effect is probably caused by the strong tendency of these crystals to absorb water molecules with the probable formation of monohydrate[36].

In order to assure the purity of the calorimetric sample, the doubly sublimed crystals were twice more re-

sublimed in vacuum with the entire sublimation apparatus assembled inside a dry box with an anhydrous nitrogen atmosphere. The sample thus obtained was kept in the dry box, with all the handling processes including that of loading and unloading of calorimeter also performed within the dry box.

The final product is composed of crystals in the form of hexagonal platelets of approximately a centimeter in diameter and with a waxy appearance. They are rather soft and can be bent to a certain degree before rupturing. The capillary melting point of this sample was found to be 158.5°C. (uncorrected). Chemical analyses gave the following composition: 64.39% C, 10.81% H and 24.75% N* (calculated: 64.24% C, 10.78% H and 24.96% N for $C_6H_{12}N_2$).

*Microanalyses were performed by the following sources: Spang Microanalytical Laboratory, Ann Arbor, Michigan; Micro-Tech Laboratories, Skokie, Illinois; and Mikroanalytisches Laboratorium im Max-Planck-Institut für Kohlenforschung, Mülheim (Ruhr), Germany.

Calorimeter Equipment

The Cryostat

The Mark I cryostat was employed for the measurement of heat capacities of the five cage molecules in the range from 5 to 350°K. Its cross-sectional view is schematically shown in Figure II. It is similar to the one described by Westrum, Hatcher and Osborne[39].

The entire cryostat assembly shown in the figure, except the outer brass can (8) and the O-ring gasket, is attached and suspended from the head plate (21) and could be separated from the brass can by lifting the ring (18) with a block and tackle. The brass can is connected to a liquid nitrogen trap, an oil diffusion pump and then a mechanical pump. A thermocouple vacuum gauge is provided for monitoring the vacuum during the pump-down period, and an ionization gauge is used during the normal operation of the cryostat under a high vacuum of about 10^{-5} mm. Hg.

Two refrigerant tanks are used. The nitrogen tank (10) and the helium tank (14) are of 2.7 and 1.9 liters in volume respectively. Both tanks are equipped with its own radiation shields (13 and 17) in addition to the outer radiation shield (9). The refrigerants employed depend on the temperature range in which heat capacity measurements are performed. Above 90°K. liquid nitrogen is used in both nitrogen and helium tanks. In the range between 55 and 90°K. liquid nitrogen in the helium tank is pumped on in

Figure II

Cross Sectional Schematic Diagram of Mark I Cryostat

Legend:

1. Helium exit connector
2. Helium transfer tube
3. Nitrogen inlet and outlet connector
4. Sleeve fitting to helium transport Dewar
5. Nitrogen filling tube

6. Helium transfer tube extender and cap
7. Screw fitting at inlet of the helium transfer tube
8. Brass vacuum can
9. Outer "floating" radiation shield
10. Nitrogen tank

11. Helium exit tube
12. "Economizer" (effluent helium vapor exchanger)
13. Nitrogen radiation shield
14. Helium tank
15. Bundle of lead wires

16. Adiabatic shield
17. Helium radiation shield
18. Ring for block and tackle
19. Windlass
20. Vacuum seal and thermal plate for leads

21. Head plate
22. O-ring gasket
23. Coil spring
24. Supporting string
25. "Floating" ring

26. Calorimeter assembly

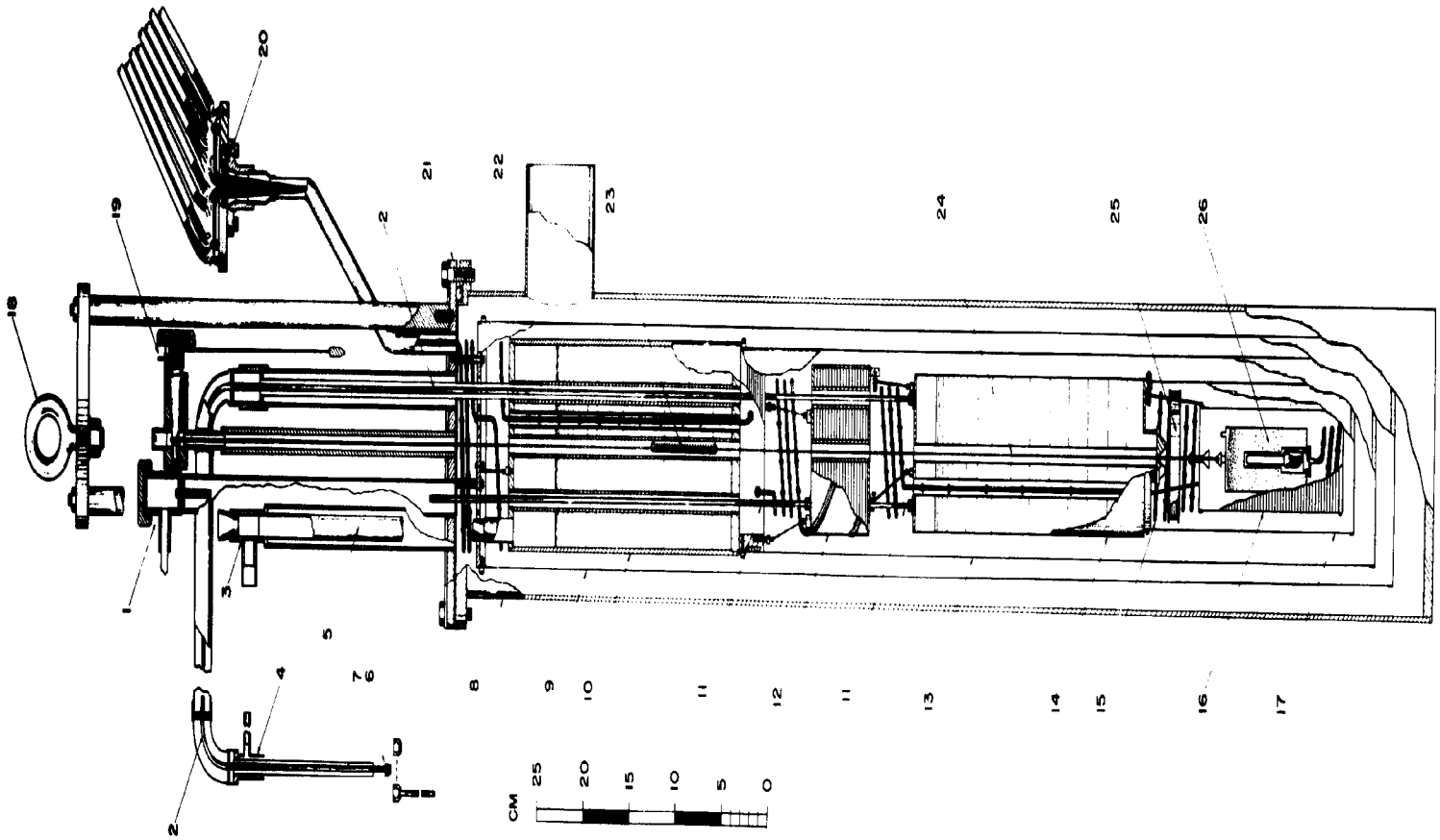

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Figure II

order to produce solid nitrogen in the tank. For operation in the range of 4.2 to 60°K., after the helium tank has been precooled by solid nitrogen and the nitrogen later driven off by means of a heating coil provided, the helium tank is filled with liquid helium. A heat exchanger called the economizer (12) is provided between the two tanks. The effluent helium gas is employed here to lower the temperature of the bundle of leads to some temperature lower than that of the nitrogen tank and thus reduces the loss of liquid helium through the heat conduction of the lead wires.

The adiabatic shield has three separately controlled heater windings, one each for the central cylindrical portion and the two flat top and bottom plates. The bottom plate is removable to facilitate the placement of the calorimeter. A floating ring (25) provided with an independent heater is used to bring the temperature of the bundle of leads between the helium tank and the adiabatic shield to several tenths of a degree below that of the shield and the calorimeter.

The calorimeter is suspended by a knot at the end of a piece of braided silk flycasting line (24) attached to the windlass shaft (19). The calorimeter can be drawn upwards from its normal operation position to make thermal contact with the refrigerants by turning the windlass. As the windlass is turned the cone on the top of the calorime-

ter engages the bottom cone of the adiabatic shield and draws the shield along until the upper cone engages the cone on the bottom of the helium tank.

The bundle of electric lead wires enters the cryostat by means of a perforated Lucite disk (20) which is made vacuum tight with Apiezon-W wax. The bundle is anchored thermally to the nitrogen tank, the economizer, the helium tank, the ring and finally the adiabatic shield before terminating at the resistance thermometer, various heaters and thermocouple junctions.

Calorimeter Assembly

Gold-plated copper calorimeters, Laboratory designations W-9 and W-10, were used for the heat capacity measurements. They are about 3.8 cm. in diameter and 7.7 cm. in length. The thickness of the shell is about 0.4 mm. Calorimeter W-9 has four vanes of 0.1 mm. copper foil to aid the establishing of thermal equilibrium. It also has a Monel neck for the removable top. Calorimeter W-10 differs from W-9 in that it has no internal vanes and that the entire top of the calorimeter is of copper and removable. An axial re-entrant well is provided in the calorimeter to accommodate the heater-thermometer assembly which consists of a capsule-type platinum-resistance thermometer within a cylindrical copper heater sleeve carrying 150 ohms of bifilarly wound, Fiberglas-insulated Advance wire.

After the sample is weighed into the calorimeter, and the cover soldered on with a low-melting (117°C.) Cerroseal solder (50-50 indium-tin), the calorimeter is evacuated and then sealed off with a few cm. pressure of helium to improve heat conduction between the calorimeter and the sample. Apiezon-T grease is used to provide thermal contact between the calorimeter and the heater-thermometer assembly.

Measuring and Controlling Circuits

The resistance and hence the temperature of the platinum thermometer is measured in terms of the potential applied across and the current passing through the thermometer. An autocalibrated White double potentiometer is used to observe the potential across the thermometer on one set of its dials. The other set of four dials is used to measure the potential drop across a standard resistor in series with the thermometer. A thermometer current of 4 ma. is used in the liquid helium range and 2 ma. is used above 60°K. The White potentiometer in combination with a high sensitivity galvanometer having a light path of 5 meters between the scale and the telescope provides a working sensitivity of 0.03 μv/mm.

Electrical energy dissipated by the heater is also measured on the White potentiometer in terms of the mean potential drop of the heater and that across a standard resistor connected in series to the heater. A ganged

master switch is provided to alternate the energy and the temperature measurements and also to permit the reading of absolute thermocouples. The time durations of the energy input are measured with electrical interval timers starting and stopping automatically as the energy is turned on and off by the master switch. The timers operated by an accurate 60-cycle alternating current from a calibrated tuning fork and amplifier provide a precision of 0.01 sec. for the time interval measurement. A bank of low-discharge lead storage batteries are used to provide direct current for the energy inputs to the calorimeter. Standard resistors used in the potential dividers of the measuring circuits and unsaturated Weston standard cells are calibrated by National Bureau of Standards.

Absolute thermocouples are provided for the checking of the temperature of the refrigerant tanks and the calorimeter. Differential thermocouple junctions are provided to facilitate the control of the adiabatic shield and the floating ring. Two galvanometers with working sensitivities of 0.01 μv/mm. are used to indicate the temperature differences between the calorimeter and the top, middle and bottom parts of the adiabatic shield, and between middle adiabatic shield and the ring. The three adiabatic shield heaters and the ring heater are supplied with alternating current manually controlled by autotransformers, decade resistor switches and 10-turn helipots between the

power source and the heaters. The temperature of the adiabatic shield is generally controlled to within 0.002°K except for a few seconds at the start and the finish of the energy input.

Experimental Results

Method of Calorimetric Measurements and Calculations

The apparent total heat capacity of the sample and the calorimeter at the mean temperature, $(T_1 + T_2)/2$, is obtained as $Q/\Delta T$, where T_1 and T_2 are the initial and final temperatures before and after the energy input Q, respectively, and ΔT is the increment in temperature of the run.

The temperature is measured as the corresponding resistance of the platinum thermometer which has been calibrated by the National Bureau of Standards against the standard fixed points on the International Temperature Scale at the boiling point of oxygen, the ice point, the steam point and the boiling point of sulfur in order to determine the constants for the Callendar-Van Dusen equation.[40] It has also been compared at 19 temperatures with the Bureau's platinum thermometer[41]. Below 10°K. a provisional temperature scale is obtained by fitting the constants in the equation[41] $R = A + BT^2 + CT^5$ to the observed resistances at the boiling point of helium and at 10°K., and to dR/dT at 10°K. The temperature scale thus defined is believed to agree with the thermodynamic scale to 0.1° below 10°K., 0.03° from 10 to 90°K. and 0.04° from 90 to 350°K. Precision is considerably better, and the temperature increments are probably correct to 0.001° after corrections for the quasi-adiabatic drifts.

The temperature drift of the calorimeter is observed before and after the energy input until a small or virtually zero equilibrium drift is obtained. The drifts are then used to extrapolate the initial and final temperatures to the middle point of the energy input in order to correct for the heating effects produced by the thermometer current and the quasi-adiabatic conditions between the calorimeter and the adiabatic shield. The drift correction for a typical 20-minute period is in general less than 0.005°.

The energy is calculated as the product of the duration of the energy input, the mean potential drop across and the mean current flowing through the heater. The potential drop across the heater is assumed to vary linearly with the time during the energy input and is read at the middle of the energy input. The time dependence of the heater current is assumed to be not higher than a quadratic function. Therefore the true average of the heater current is given by the mean value of two readings taken at 21% and 79% of the duration of the energy input[42]. The resistance of the lead wires between the heater terminals and the potential dividers for measuring the potential drop across the heater is monitored by a resistance bridge and appropriate adjustments made.

The true total heat capacity, expressed as the limit of $Q/\Delta T$ as ΔT approaches zero, is obtained by applying an analytically determined curvature correction[43] to the

observed apparent total heat capacity at the mean temperature of the interval ΔT in order to correct for the finite temperature increment used in determining this quantity. The curvature correction in general is less than 0.1%.

The molal heat capacity of the sample is calculated first by substracting the heat capacity of the empty calorimeter from the above values just derived, and the resulting net sample heat capacity is then divided by the number of moles of sample used to obtain the desired quantity.

The heat capacity of the empty calorimeter is determined in a separate series of measurements using the same heater-thermometer assembly. The weights of Cerroseal solder and of Apiezon-T grease are adjusted to nearly the same value in both cases. Adjustments are applied for the slight differences in the amounts of helium gas, grease and the solder used, if necessary. The heat capacity of the empty calorimeter represents in general about 15 to 30% of the total heat capacity in the range of 5 to 30°K., 30 to 50% in 30 to 100°K., and then decreasing slowly from 50 to 40% in the range from 100 to 350°K.

The temperature interval of energy input varies from 1° below 10°K., to 10% of T between 10 and 90°K., and to 9° above 90°K. The time duration of the energy input also varies from 4 to 10 minutes such that the heating rate is less than 1° per minute.

Data and Results

The weights (in vacuo) of the individual samples used for heat capacity determinations, along with the pressure of helium gas, and the calorimeter used, are tabulated in Table II. The adjustments made on the excess or deficient amounts of helium, solder and grease employed against that used on the empty calorimeter are also given in the Table II.

The actual heat capacity determinations are listed in chronological order in terms of the defined thermochemical calorie as 4.1840 absolute joules and the ice point as 273.15°K., in Table III for adamantane, hexamethylene-tetramine, tetramethyl-tetrathia-adamantane, tetramethyl-hexathia-adamantane and triethylenediamine. The approximate temperature increment of the run could be inferred from the mean temperatures of the adjacent runs in Table III. The molal heat capacity versus temperature curves for adamantane and hexamethylenetetramine are shown in Figure III, the two sulfur compounds in Figure IV, and that for triethylenediamine in Figure V.

The over-all accuracy of the calorimetric measurement was ascertained by determining the heat capacity of a standard sample of benzoic acid. The normal heat capacity values are considered to have a probable error of 0.1% above 25°K., 1% at 10°K. and about 5% at 5°K.

The enthalpy values are calculated by numerical

Table II

Calorimetric Loading and Adjustment Data for Five Globular Molecules

Sample	Weight g. (vacuo)	Helium mm. Hg (300°K.)	Adjustments (mg.)		
			Helium	Solder	Grease
$C_{10}H_{16}$	42.831	60	0.0	0.0	0.0
$C_6H_{12}N_4$	76.282	76	0.0	0.0	0.0
$C_{10}H_{16}S_4$	49.912	60	+0.5	-2.0	+15.2
$C_8H_{12}S_6$	45.383	105	+1.2	+3.9	+15.2
$C_6H_{12}N_2$	54.043	80	0.0	0.0	0.0

Table III

The Heat Capacities of Five Globular Molecules

[in cal./(deg. mole)]

T, °K	C_p	T, °K	C_p	T, °K	C_p
Adamantane; ($C_{10}H_{16}$, 1 mole = 136.238 g.)					
Series I		186.93	26.41	151.75	20.43
		194.32	28.29	154.28	20.78
5.09	0.040	202.35	31.12	156.76	21.13
5.69	0.055	207.64	285.27	158.88	21.47
6.76	0.088	212.37	52.33	160.97	21.75
8.06	0.170	221.29	32.52	163.76	22.21
9.11	0.278	231.48	34.04	167.25	22.72
10.06	0.405	240.92	35.55	171.89	23.43
11.07	0.562	249.94	36.97		
12.24	0.783	258.71	38.45	Series IV	
13.54	1.083	256.55	38.05		
15.05	1.482	265.30	39.48	201.89	31.03
16.81	1.996	274.05	41.00	204.90	32.46
18.80	2.617	282.76	42.57	207.05	34.50
20.97	3.311	291.46	44.13	208.09	65.20
23.28	4.039	300.15	45.85		
25.81	4.803	308.83	47.41	Series V	
28.66	5.584	317.54	48.72		
31.81	6.369	326.25	50.15	208.62	2688.94
35.32	7.138	335.20	51.76	208.75	535.22
39.38	7.887	344.25	53.39	209.55	48.41
43.80	8.577			211.77	31.74
48.40	9.185	Series II			
53.20	9.730			Series VI	
58.23	10.24	193.23	27.98		
59.60	10.39	198.49	29.69	269.14	40.21
64.78	10.91	201.61	30.87	277.61	41.72
70.44	11.39	204.08	32.07	278.44	41.75
76.62	11.95	206.48	34.04	287.47	43.48
83.29	12.60	208.10	125.48	296.45	45.05
90.64	13.32	208.57	2470.76	305.10	46.81
98.73	14.14	208.61	3513.07	313.33	48.18
106.56	14.96	208.64	3864.16	321.79	49.41
114.49	15.81	208.66	4389.12	331.19	51.10
122.91	16.75	208.74	1583.61	341.03	52.91
131.08	17.77	210.00	44.73		
139.61	18.83	212.10	31.41	Series VII	
148.44	20.08	213.92	31.47		
157.32	21.38			208.64	3150.43
166.07	22.54	Series III		208.70	2402.83

Table III (continued)

T, °K	C_p	T, °K	C_p	T, °K	C_p
174.72	23.83				
183.32	25.57	149.09	20.07		

Hexamethylenetetramine; ($C_6H_{12}N_4$, 1 mole = 140.178 g.)

Series I

51.54	9.894
55.54	10.19
61.85	10.62
68.74	11.01
75.72	11.39
82.61	11.81
89.74	12.25
97.37	12.72
105.56	13.29
113.61	13.91
121.25	14.54
114.72	14.00
123.58	14.74
131.97	15.50
140.09	16.28
148.29	17.08
156.88	17.96
165.80	18.92
174.79	19.92
183.92	20.96
193.03	22.04
201.84	23.10
210.50	24.18
208.24	23.89
218.07	25.16
227.43	26.37
236.29	27.56
245.15	28.79
254.10	30.03
263.21	31.31
272.39	32.57
281.55	33.96
290.59	35.28
299.71	36.63
308.93	38.00
317.90	39.32
327.18	40.69
336.90	42.14
346.36	43.54

Series II

31.87	7.301
34.20	7.764
37.40	8.309
41.26	8.845
45.65	9.349
50.28	9.790
55.46	10.19

Series III

5.04	0.027
6.25	0.069
6.98	0.110
7.50	0.167
8.04	0.220
8.67	0.326
9.63	0.490
10.85	0.780
12.16	1.155
13.55	1.610
15.05	2.134
16.64	2.728
18.32	3.338
20.11	3.982
22.16	4.691
24.60	5.461
27.49	6.269
30.68	7.041
34.00	7.728

1,3,5,7-Tetramethyl-2,4,6,8-Tetrathia-adamantane

($C_{10}H_{16}S_4$, 1 mole = 264.502 g.)

Series I

4.85	0.136
5.38	0.203
6.13	0.321
7.09	0.503
7.97	0.741
8.87	1.003
9.86	1.325
10.82	1.664
11.75	1.984
28.25	7.460
31.15	8.111
34.28	8.750
37.71	9.410
41.50	10.097
45.72	10.899

Series III

46.48	11.06
51.56	12.11
162.20	42.26

Series V

167.74	43.16
176.38	45.10
185.00	47.08
193.81	49.01
202.71	50.84
211.60	52.74
220.61	54.73

Table III (continued)

T, °K	C_p	T, °K	C_p	T, °K	C_p
		56.75	13.28	229.78	56.60
Series II		62.55	14.71		
				Series VI	
6.31	0.337	Series IV			
7.23	0.545			235.14	57.63
8.11	0.794	64.89	15.36	244.41	59.61
9.07	1.064	70.92	16.93	253.66	61.60
10.13	1.420	77.79	18.87	262.70	63.44
11.26	1.839	85.34	21.18	271.53	65.33
12.48	2.266	93.59	23.56	280.34	67.14
13.74	2.755	101.97	25.93	289.28	69.09
15.04	3.276	110.07	28.27	298.33	70.80
16.47	3.826	118.33	30.32	307.47	72.44
18.06	4.423	126.80	32.89	316.86	74.22
19.82	5.039	135.42	35.18	326.43	76.12
21.85	5.716	144.25	37.46	336.00	78.09
24.14	6.399	153.29	39.88	345.56	80.00
25.47	6.769				

1,3,5,7-Tetramethyl-2,4,6,8,9,10-Hexathia-adamantane

($C_8H_{12}S_6$, 1 mole = 300.580 g.)

Series I		233.80	60.06	14.77	3.592
		242.98	61.89	16.27	4.188
69.54	18.07	251.84	63.63	18.01	4.858
74.91	19.71	260.63	65.30	20.01	5.566
82.00	22.10	269.53	67.13	22.22	6.272
89.41	24.55	278.57	68.60	24.64	6.972
96.73	26.85	287.71	70.42	27.30	7.641
104.45	29.16	296.88	72.05	30.27	8.326
		306.29	73.10	33.53	9.010
Series II		315.81	74.91		
		324.55	76.06	Series VII	
114.68	32.21	332.03	77.38		
123.31	34.76	339.62	78.58	32.86	8.875
131.88	37.15	346.93	79.98	36.52	9.622
140.47	39.50			40.49	10.423
149.14	41.88	Series V		44.62	11.297
				49.14	12.345
Series III		4.94	0.164	54.23	13.618
		5.50	0.233	59.83	15.167
166.71	45.95			65.72	16.939
175.74	47.93	Series VI		72.00	18.798
184.82	50.05				
194.01	52.02	5.14	0.185	Series VIII	
203.45	54.07	6.29	0.392		

Table III (continued)

T, °K	C_p
212.94	56.05
Series IV	
215.55	56.51
224.50	58.27

T, °K	C_p
7.33	0.662
8.42	1.023
9.54	1.423
10.71	1.890
11.99	2.419
13.35	2.988

T, °K	C_p
151.87	42.77
161.37	44.78
Series IX	
291.48	71.05

Triethylenediamine; ($C_6H_{12}N_2$, 1 mole = 112.178 g.)

Series I	
103.00	14.39
111.02	15.04
119.16	15.71
127.95	16.44
137.06	17.23
145.92	18.01
154.21	18.75
162.56	19.53
171.47	20.38
180.58	21.28
189.58	22.21
198.72	23.18
Series II	
77.10	12.25
83.34	12.81
90.25	13.39
97.71	13.97
105.36	14.58
Series III	
35.72	6.307
39.50	7.184
43.59	8.015
48.17	8.836
53.39	9.638
59.07	10.38
65.38	11.12
72.38	11.80
79.81	12.48
Series IV	
4.91	0.014
5.91	0.027
7.15	0.055
8.28	0.099
9.34	0.161
10.36	0.238
11.46	0.340
12.65	0.481
13.86	0.657
15.11	0.871
16.48	1.144
18.05	1.500
19.84	1.947
21.86	2.495
24.12	3.136
26.76	3.895
29.25	4.604
31.87	5.330
34.90	6.119
Series V	
198.65	23.17
207.55	24.14
216.80	25.20
226.24	26.33
235.33	27.45
244.16	28.59
252.95	29.76
Series VI	
251.68	29.55
260.51	30.81
269.38	31.99
278.77	33.44
288.25	34.93
297.29	36.43
306.48	37.99
315.85	39.73
325.24	41.66
334.60	43.91
343.87	46.66

Figure III

Heat Capacities of Adamantane and Hexamethylenetetramine



○ Adamantane

● Hexamethylenetetramine

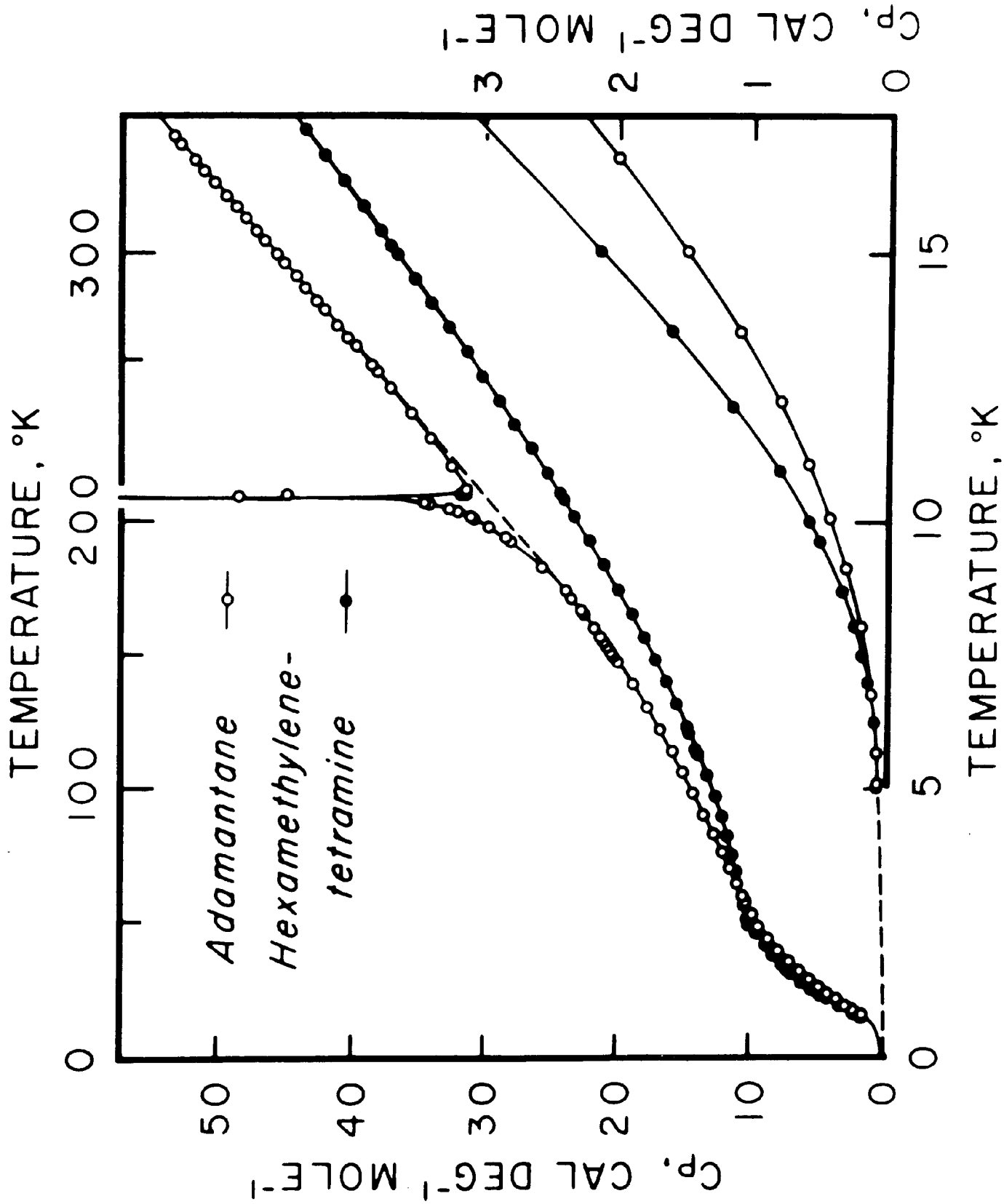

TEMPERATURE, °K
0
100
200
300
Cp, CAL DEG⁻¹ MOLE⁻¹
0
10
20
30
40
50
Adamantane
Hexamethylene-
tetramine
TEMPERATURE, °K
0
5
10
15
Cp, CAL DEG⁻¹ MOLE⁻¹
0
1
2
3

Figure III

Figure IV

Heat Capacities of Tetramethyl-tetrathia-adamantane and Tetramethyl-hexathia-adamantane

○ $C_{10}H_{16}S_4$

□ $C_8H_{12}S_6$

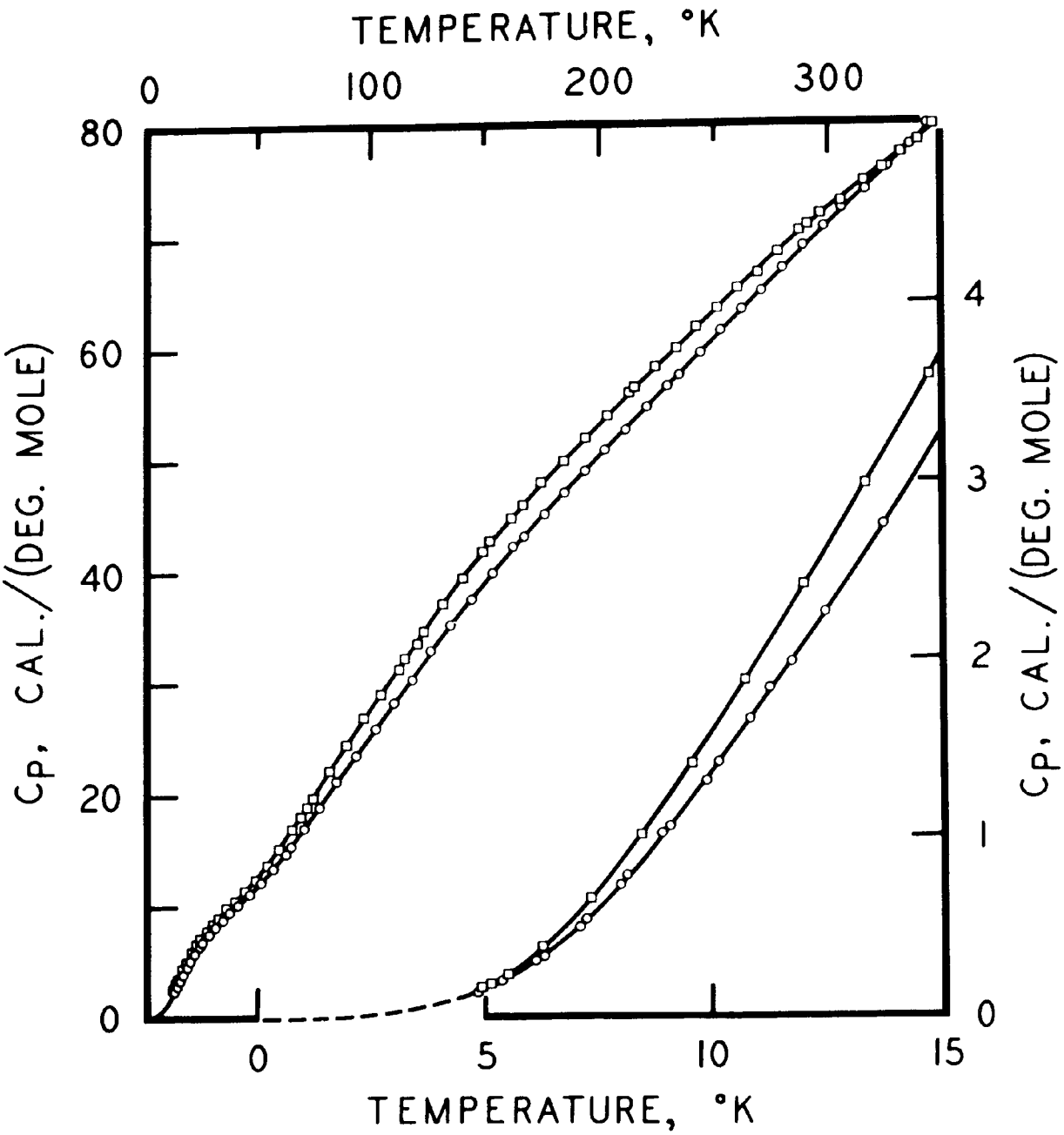

TEMPERATURE, °K
0
100
200
300
80
60
40
20
0
C_P, CAL./(DEG. MOLE)
4
3
2
1
0
C_P, CAL./(DEG. MOLE)
0
5
10
15
TEMPERATURE, °K

Figure IV

Figure V

Heat Capacity of Triethylenediamine

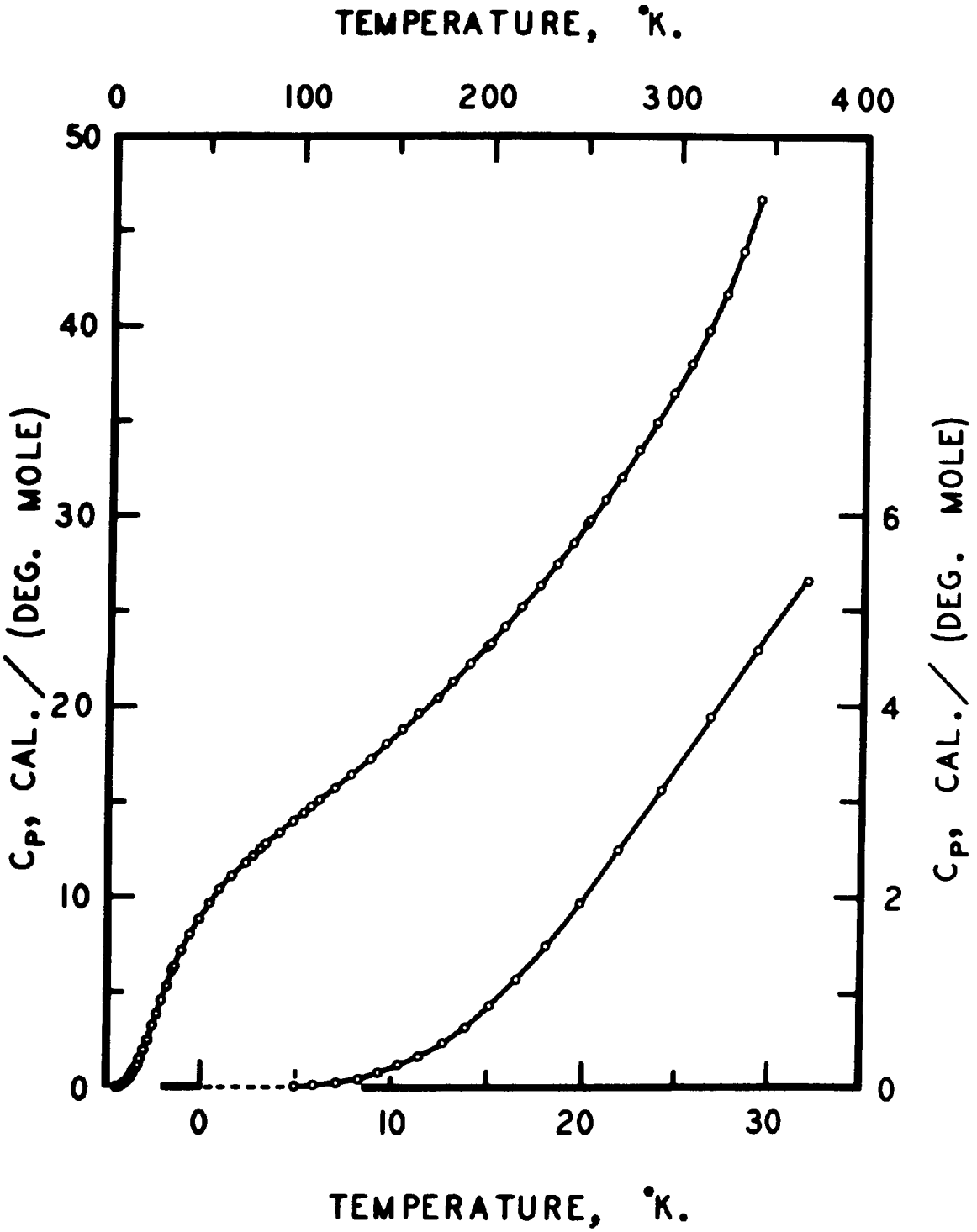

TEMPERATURE, °K.
0
100
200
300
400
50
40
30
20
10
0
C_p, CAL./(DEG. MOLE)
6
4
2
0
0
10
20
30
TEMPERATURE, °K.

Figure V

quadrature of the smoothed heat capacity versus temperature curve, the entropy values by that of the heat capacity versus logarithm of the temperature or of C_p/T versus the temperature curves, and the free energy functions from the relationship: $(F - H_0)/T = (H - H_0)/T - S$.

The molal values of heat capacity, enthalpy, entropy and free energy functions for these five compounds at selected rounded temperatures are tabulated in Table IV. The data are extrapolated below 5°K. with the Debye T^3 relationship. The estimated probable error in the thermodynamic functions is 0.1% above 100°K. The entropies and free energy functions do not include contributions from nuclear spin and isotopic mixing and are hence practical values for chemical thermodynamic purposes.

A sharp, apparently first order transition has been observed at 208.62°K. in adamantane. Thermal equilibrium was achieved quite rapidly (within an hour) in the transition region. Apparent heat capacity as high as 4,500 cal./(deg. mole) has been noticed. If an attempt is made to resolve the transitional contribution from the lattice (as shown by the dotted curve in Figure III), a transitional enthalpy increment of 807 cal./(deg. mole) and a corresponding entropy increment of 3.87 e.u. are obtained. As a further test of the precision of the calorimetry and of the heat capacity-type runs, several enthalpy-type runs, each covering the entire anomalous region, were made and compared

Table IV

Thermodynamic Properties of Five Globular Molecules

(In units of cal., molecular wt., and °K.)

T	C_p	S°	$H°-H_0°$	$-(F°-H_0°)/T$
	Adamantane ($C_{10}H_{16}$, 1 mole = 136.238 g.)			
5	0.040	0.013	0.0501	0.003
10	0.391	0.111	0.8550	0.026
15	1.468	0.450	5.217	0.102
20	3.000	1.076	16.29	0.262
25	4.559	1.915	35.25	0.505
30	5.937	2.872	61.59	0.819
35	7.070	3.875	94.21	1.183
40	7.988	4.881	131.93	1.583
45	8.740	5.867	173.81	2.004
50	9.375	6.821	219.14	2.439
60	10.43	8.627	318.35	3.322
70	11.36	10.306	427.35	4.201
80	12.28	11.882	545.50	5.063
90	13.25	13.384	673.07	5.905
100	14.27	14.832	810.63	6.726
110	15.33	16.242	958.63	7.527
120	16.43	17.623	1117.4	8.311
130	17.61	18.984	1287.5	9.080
140	18.88	20.334	1469.9	9.835
150	20.24	21.683	1665.4	10.580
160	21.64	23.033	1874.8	11.316
170	23.12	24.389	2098.4	12.045
180	24.87	25.758	2338.0	12.769
190	27.14	27.161	2597.6	13.489
200	30.08	28.625	2883.1	14.209
210	(41.55)			
220	32.33	35.168	4252.2	15.840
230	33.81	36.638	4583.0	16.712
240	35.36	38.110	4928.8	17.573
250	36.98	39.586	5290.4	18.424
260	38.65	41.068	5668.6	19.266
270	40.37	42.559	6063.7	20.101
280	42.13	44.059	6476.2	20.930
290	43.90	45.568	6906.3	21.754
300	45.68	47.087	7354.2	22.573

Table IV (continued)

T	C_p	S°	$H^\circ-H_0^\circ$	$-(F^\circ-H_0^\circ)/T$
350	54.31	54.787	9857.3	26.623
273.15	40.92	43.031	6191.7	20.363
298.15	45.35	46.805	1270.0	22.422
Hexamethylenetetramine ($C_6H_{12}N_4$, 1 mole = 140.188 g.)				
5	0.025	0.008	0.0313	0.002
10	0.572	0.134	1.081	0.026
15	2.118	0.635	7.525	0.133
20	3.941	1.496	22.72	0.360
25	5.581	2.558	46.66	0.691
30	6.885	3.695	77.96	1.097
35	7.902	4.836	115.03	1.550
40	8.688	5.945	156.59	2.030
45	9.294	7.005	201.61	2.525
50	9.772	8.010	249.32	3.023
60	10.49	9.859	350.84	4.011
70	11.08	11.521	458.77	4.967
80	11.65	13.038	572.41	5.883
90	12.25	14.444	691.89	6.757
100	12.91	15.769	817.66	7.592
110	13.64	17.033	950.35	8.394
120	14.44	18.253	1090.6	9.165
130	15.31	19.443	1239.3	9.910
140	16.25	20.611	1397.1	10.632
150	17.25	21.766	1564.5	11.336
160	18.30	22.913	1742.2	12.024
170	19.39	24.055	1930.6	12.698
180	20.52	25.195	2130.1	13.361
190	21.68	26.335	2341.1	14.014
200	22.87	27.477	2563.8	14.658
210	24.11	28.623	2798.7	15.296
220	25.39	29.774	3046.2	15.928
230	26.72	30.932	3306.7	16.555
240	28.08	32.098	3580.6	17.178
250	29.46	33.272	3868.3	17.798

Table IV (continued)

T	C_p	S°	$H°-H°_0$	$-(F°-H°_0)/T$
260	30.87	34.454	4169.9	18.416
270	32.29	35.646	4485.7	19.032
280	33.73	36.846	4815.8	19.647
290	35.19	38.056	5160.4	20.261
300	36.67	39.274	5519.7	20.874
350	44.08	45.483	7538.4	23.944
273.15	32.74	36.023	4588.1	19.226
298.15	36.40	39.048	5452.2	20.761

Table IV (continued)

T	C_p	S°	$H°-H_0°$	$-(F°-H_0°)/T$
	1,3,5,7-Tetramethyl-2,4,6,8-tetrathia-adamantane			
	($C_{10}H_{16}S_4$, 1 mole = 264.502 g.)			
5	0.154	0.052	0.194	0.013
10	1.374	0.464	3.515	0.112
15	3.252	1.368	14.98	0.369
20	5.107	2.563	35.98	0.764
25	6.639	3.874	65.49	1.254
30	7.864	5.199	101.9	1.802
35	8.865	6.488	143.8	2.380
40	9.803	7.733	190.5	2.971
45	10.76	8.943	241.9	3.568
50	11.79	10.129	298.2	4.165
60	14.10	12.478	427.4	5.355
70	16.72	14.845	581.3	6.541
80	19.53	17.259	762.4	7.729
90	22.43	19.927	972.2	8.925
100	25.34	22.241	1211.1	10.130
110	28.22	24.792	1478.9	11.347
120	31.02	27.368	1775.2	12.575
130	33.75	29.959	2099.1	13.812
140	36.40	32.558	2450.0	15.058
150	38.95	35.157	2826.8	16.312
160	41.41	37.750	3228.7	17.571
170	43.77	40.332	3654.7	18.834
180	46.04	42.898	4103.8	20.099
190	48.22	45.446	4575.2	21.366
200	50.35	47.974	5068.1	22.634
210	52.43	50.481	5582.0	23.900
220	54.50	52.968	6116.6	25.165
230	56.57	55.436	6671.9	26.427
240	58.67	57.888	7248.1	27.687
250	60.79	60.326	7845.4	28.944
260	62.93	62.752	8464.1	30.198
270	65.05	65.167	9104.0	31.448
280	67.13	67.570	9765.0	32.695
290	69.14	69.961	10446.4	33.939
300	71.06	72.338	11147.4	35.180

Table IV (continued)

T	C_p	S°	$H°-H°_0$	$-(F°-H°_0)/T$
350	80.74	84.018	14942.3	41.326
273.15	65.71	65.925	9310.0	31.841
298.15	70.71	71.899	11016.3	34.950

1,3,5,7-Tetramethyl-2,4,6,8,9,10-Hexathia-adamantane

($C_8H_{12}S_6$, 1 mole = 300.580 g.)

5	0.168	0.056	0.209	0.014
10	1.605	0.533	4.065	0.127
15	3.681	1.574	17.26	0.424
20	5.563	2.900	40.52	0.874
25	7.065	4.309	72.24	1.420
30	8.269	5.709	110.7	2.018
35	9.300	7.062	154.7	2.643
40	10.31	8.369	203.7	3.277
45	11.39	9.645	257.9	3.914
50	12.56	10.905	317.7	4.550
60	15.22	13.424	456.3	5.819
70	18.22	15.992	623.3	7.088
80	21.41	18.632	821.4	8.365
90	24.63	21.340	1051.6	9.656
100	27.82	24.101	1313.9	10.962
110	30.90	26.898	1607.6	12.283
120	33.87	29.715	1931.5	13.619
130	36.70	32.538	2284.5	14.965
140	39.41	35.358	2665.2	16.321
150	41.99	38.166	3072.3	17.684
160	44.45	40.955	3504.6	19.051
170	46.80	43.721	3960.9	20.421
180	49.05	46.460	4440.3	21.792
190	51.22	49.171	4941.7	23.162
200	53.31	51.851	5464.3	24.529
210	55.35	54.502	6007.7	25.894
220	57.36	57.123	6571.3	27.254
230	59.35	59.717	7154.8	28.609
240	61.32	62.284	7758.2	29.959
250	63.29	64.828	8381.3	31.303

Table IV (continued)

T	C_p	S°	$H°-H_0°$	$-(F°-H_0°)/T$
260	65.24	67.348	9023.9	32.641
270	67.15	69.846	9685.9	33.972
280	68.99	72.321	10366.6	35.298
290	70.74	74.773	11065.4	36.617
300	72.39	77.200	11781.1	37.929
350	80.58	88.945	15596.0	44.385
273.15	67.74	70.628	9898.3	34.391
298.15	72.09	76.753	11647.5	37.687

Triethylenediamine ($C_6H_{12}N_2$, 1 mole = 112.172 g.)

5	0.014	0.005	0.017	0.002
10	0.209	0.055	0.430	0.012
15	0.851	0.242	2.854	0.052
20	1.987	0.633	9.782	0.144
25	3.391	1.225	23.17	0.298
30	4.816	1.970	43.72	0.513
35	6.132	2.813	71.14	0.780
40	7.290	3.709	104.77	1.090
45	8.285	4.627	143.77	1.432
50	9.135	5.545	187.37	1.797
60	10.50	7.337	285.87	2.572
70	11.58	9.040	396.47	3.376
80	12.51	10.648	517.0	4.185
90	13.35	12.171	646.4	4.989
100	14.16	13.620	784.0	5.780
110	14.96	15.007	929.6	6.556
120	15.77	16.344	1083.3	7.316
130	16.61	17.640	1245.2	8.061
140	17.48	18.902	1415.7	8.790
150	18.38	20.139	1594.9	9.506
160	19.30	21.354	1783.3	10.208
170	20.25	22.552	1981.0	10.899
180	21.23	23.737	2188.4	11.580
190	22.25	24.912	2405.7	12.251
200	23.31	26.080	2633.5	12.913

Table IV (continued)

T	C_p	S°	$H°-H_0°$	$-(F°-H_0°)/T$
210	24.42	27.244	2872.1	13.568
220	25.58	28.407	3122.0	14.216
230	26.80	29.571	3383.9	14.858
240	28.06	30.738	3658.1	15.495
250	29.36	31.909	3945.2	16.128
260	30.72	33.087	4245.5	16.758
270	32.14	34.272	4559.7	17.385
280	33.63	35.468	4888.5	18.009
290	35.21	36.676	5232.6	18.632
300	36.88	37.897	5593.0	19.254
350	(48.70)	(44.350)	(7693.4)	(22.369)
273.15	32.60	34.65	4662.	17.58
298.15	36.56	37.67	5525.	19.14

with the heat capacity determinations in Table V. Excellent confirmation was obtained.

No thermal anomaly has been observed for the other four compounds in the temperature range of 5 to 350°K., investigated.

The heat capacity values given for the compounds adamantane and triethylenediamine have not been corrected for vaporization, and are actually the total heat capacity values under saturation vapor pressure. However the correction is less than 0.1% estimated from the vapor pressure data for triethylenediamine[44] and hence within the probable error. Hexamethylenetetramine has a very small vapor pressure[45] in the temperature range investigated calorimetrically, and the two sulfur compounds probably have negligible vapor pressures.

The heat of combustion of adamantane reported by Landa and Macháček[19] was converted into an enthalpy increment. The enthalpy of formation of hexamethylenetetramine reported by Delépine and Badoche[46] was corrected to graphite as the standard state for carbon and to modern enthalpies of formations[47] of CO_2 and H_2O. Combining these results with practical entropies and the data of present studies, the increments for the formation reactions at 298.15°K. listed in Table VI were obtained.

Differential thermal analyses were performed for adamantane, hexamethylenetetramine, and the two globular

Table V

Enthalpy and Entropy Increments over the Transition Region in Adamantane

Energy Increments	T_{final}, °K.	$T_{initial}$, °K.	$H_{225°K.}-H_{195°K.}$ cal./mole	$S_{225°K.}-S_{195°K.}$ cal./(deg.mole)
7	211.20	205.30	1679.6	8.029
7	213.29	206.43	1678.4	8.017
1	212.17	205.02	1679.0	8.019
1	211.94	205.27	1679.4	8.023
Average			1679.2 ± 0.3	8.022

Table VI

Enthalpy, Entropy and Free Energy Increments of Formations of Adamantane and Hexamethylenetetramine at 298.15°K.

Substance	ΔH_f° Kcal./mole	ΔS_f° e.u.	ΔF_f° Kcal./mole
Adamantane	-31.6	-216.484	32.9
Hexamethylene-tetramine	28.8	-247.911	102.7

sulfur compounds, $C_{10}H_{16}S_4$ and $C_8H_{12}S_6$, from room temperature up to their melting point, except in the case of hexamethylenetetramine only up to about 240°C at which temperature a severe decomposition occurs. A mixture composed of equal volumes of the sample and of Al_2O_3 is compared with pure Al_2O_3 in the DTA process. The heating rate is about 2 to 3° per minute. No thermal anomaly has been detected for these compounds below their melting or decomposition temperatures at which sharp peaks with heights of about 5° were observed.

Discussion

Adamantane

Adamantane was found by these calorimetric studies to have a transition at 208.6°K. The sharp, apparently first order transition is associated with an entropy of transition of 3.87 e.u. and with a change in its crystal structure. This is probably a plastic transition; the high temperature phase is likely in the plastic crystalline state in which the molecules have presumably some degree of rotational freedom. Evidence of molecular rotation or disordering in the high temperature phase has been provided by more recent X-ray diffraction and nuclear magnetic resonance studies.

The crystal structure of the high temperature phase stable at room temperature has been reported as a face-centered cubic lattice of the space group T_d^2–$F\bar{4}3m$[48] or T^2–$F23$[49] with four molecules in a unit cell. The unit cell dimension was reported as 9.43 A. by Nowacki and 9.54 A. by Giacomello and Illuminati[49]. Both structures were based upon results from powder patterns. Recent X-ray studies done on adamantane single crystals by Nordman[50] indicated a disordered structure in a face-centered cubic lattice of the space group O_h^5–$Fm3m$ with a cell dimension of 9.45 A., instead of the ordered structure in the space group $F\bar{4}3m$, although the difference between these two space groups is not very large. At temperatures below the transition point

adamantane crystallizes in an ordered structure in the tetragonal lattice of the space group $D_{2d}^{4}-P\bar{4}2_1c$, with the cell dimensions: a = 6.641 A. and c = 8.875 A. and having two molecules for each unit cell, as also found by Nordman from single crystal X-ray diffraction studies.

In the low temperature phase, two of the six octahedrally arranged methylene groups are different crystallographically from the other four. The two oppositely situated groups are parallel to the c-axis, and the other four form a plane perpendicular to the c-axis. However all six methylene groups are equivalent in the high temperature form.

Actually the two structures do not differ from each other greatly. It is apparent that by cooling the crystal through the transition, only one of the three cubic axes of the high temperature phase shrinks by about 6% and becomes the c-axis of the low temperature modification. The other two remain almost unchanged ($2^{1/2}$ x 6.641 A. = 9.39 A.), i.e., the spacings between the centers of gravity of the molecules in the plane perpendicular to the particular axis are preserved.

Presumably in the high temperature phase the molecules at the lattice sites may have sufficient thermal agitation to approximate spheres by either rotating or assuming different orientations. Since there are only van der Waals forces involved among these non-polar hydrocarbon molecules, the formation of a close-packed crystal structure is obvious.

At low temperatures these molecular motions may be sufficiently restricted to allow the adamantane molecule to form a more compact structure permitted by the actual molecular shape which deviates somewhat from sphericity. Cruickshank[51] interpreted this transition from another point of view. By examining the crystal structure of hexamethylenetetramine and P_4O_{10}, where the tetrahedral molecules have their spikes fit into the holes of tetrahedrally situated neighboring molecules, he reached the conclusion that the face-centered cubic arrangement does not allow these interlocking positions and is not the most stable crystal structure for the molecular geometry of adamantane. Therefore an adjustment of crystal structure at lower temperatures should be within expectation.

Nuclear magnetic resonance studies[52] on adamantane revealed that the line width or the second moment narrows at about -110 to -130°C. to a value corresponding to that of free rotation of molecules in the solid. The activation energy was estimated to be 5.8 kcal. from the temperature dependence of correlation time. However if one compares the maximum van der Waals diameter of the molecule, 7.55 A., with the distance between molecular centers in the crystal, 6.68 A., one sees that free rotation is not quite possible[31]. The transition temperature reported by the nuclear magnetic resonance studies is about 45 to 65° lower than that detected thermally, which is the case for many other com-

pounds with a rotational transition. This is due to the differences of the techniques used in detecting the onset of rotational motion of some molecules at a low rate and the cooperative phenomenon where almost all molecules are involved.

If one applies Guthrie and McCullough's hypothesis of orientational disordering to this problem, one may assume that the adamantane molecules are situated at the cubic lattice sites in such a way as to give an effective total point group of D_{2d}. Six distinguishable "rotational" orientations are possible in a disordered state, hence the calculated transitional entropy from an ordered state is R ln 6 = 3.56 e.u. The 0.21 e.u. discrepancy between the calculated and the observed values could be attributed to the increased over-all libration of the molecules.

Hexamethylenetetramine

Although hexamethylenetetramine and adamantane have similar molecular structure and symmetry, they are different in crystallographic aspects. Hexamethylenetetramine exists in a body-centered cubic lattice of the space group T_d^3-$I\bar{4}3m$ with a = 7.02 A[53]. This structure is presumed to remain unchanged even to very low temperatures and up to its decomposition. Both heat capacity measurements from 5 to 350°K. and thermal analysis studies from room temperature up to about 240°C have failed to detect any anomalous behavior in the thermal properties. Extensive investi-

gations on the thermal decomposition of hexamethylenetetramine have been reported[54-56].

The body-centered cubic lattice is probably the result of the molecular symmetry and intermolecular hydrogen bonding. The hexamethylenetetramine molecule can be viewed as composed basically of a regular tetrahedron formed by four nitrogen atoms at the corners. On each of the six edges of the tetrahedron there is a methylene group and there are three hydrogen atoms projecting out perpendicularly from each of the four tetrahedral faces. The molecules in the crystal are so arranged as to have the corner of one molecule pointed normally toward the center of the face of another molecule, and the two are related by a simple translation along the line linking the corner and the center of the face. By repeating this type of arrangement with respect to all four corners and four faces of a molecule, a body-centered cubic lattice is built with each molecule having eight such interactions between the nitrogen and hydrogen atoms of neighboring molecules.

Schaffer[57] concluded from his X-ray oscillation photographs taken at various temperatures that the hydrogen bonding does not interfere greatly with the torsional vibration of the hexamethylenetetramine molecules. However the hydrogen bonding among the molecules has apparently increased the potential barrier for the molecules to such an extent as to preclude them from undergoing a plastic transi-

tion similar to that occurring in the adamantane crystal and to confine them in the body-centered cubic lattice within the entire temperature range before its decomposition near 500°K.

The entropy and the heat capacity of hexamethylenetetramine crystals have been calculated by Cruickshank and his co-workers[51]. They are in fairly good agreement with our observed values. In the calculations Couture-Mathieu's frequency assignments[58] were used for contributions from internal vibrations. The lattice characteristic temperatures and their temperature dependences for the translational acoustic and vibrational optical branches were estimated from their three dimensional X-ray studies as $\Theta_D = 111 - 0.03\ T$ and $\Theta_E = 74 - 0.03\ T$, respectively. The calculated entropy values are in general higher by 0.01 to 0.05 e.u. in the temperature range from 5 to 50°K. and about 0.3 e.u. from 50 to 350°K. After applying an empirically determined constant $A = 4.75 \times 10^{-6}$ for the Nernst and Lindemann's relationship[59]: $C_p/C_v = (1 + ATC_p)$ from the calculated C_v and observed C_p values, C_p values could also be estimated from the lattice and molecular vibrations, the calculated values agree in general within $\pm$ 0.1 cal./(deg. mole).

Tetramethyl-tetrathia-adamantane and Tetramethyl-hexathia-adamantane

No thermal anomaly has been observed in the heat

capacity measurements of both compounds from 5 to 350°K. and by thermal analysis up to their melting points. Failure to find transitions similar to that occurring in adamantane is not unexpected for these two compounds. Intermolecular forces and the barrier height for the rotation of molecules may be increased somewhat due to the presence of sulfur atoms in the molecules. However it is most likely that the four methyl groups present in the molecules prevent the rotational reorientation of molecules in the crystal through steric hindrances. These two sulfur-containing molecules are in the form of large tetrahedrons having methyl groups extending out from each corner; therefore a much greater volume is needed to turn these tetrahedrons around.

Tetramethyl-hexathia-adamantane has been reported to exist in a crystal lattice of rather low symmetry, i.e., in the monoclinic lattice of the space group C_{2h}^{5}-$P2_1/c$ with molecules which do not posses any element of crystallographic symmetry[29].

The heat capacity versus temperature curves for these two compounds are very similar in shape to each other, but they are distinctively different from that of adamantane and hexamethylenetetramine which form another pair.

Other Adamantane-like Molecules

It would be of interest to note that hexathia-adamantane[60] also crystallizes in the space group $P\bar{4}2_1c$ or

in the same space group as that of the low temperature form of adamantane. Hexathia-adamantane is a hard, non-volatile solid with a density of 2.07 g./cm.^{3} and is insoluble in almost any solvent. It is believed that the molecules do not rotate in the crystal in this compound, or at least not until some elevated temperature is reached. It has the same molecular symmetry as that of adamantane, and the molecular dimensions should be quite identical in both cases, since the van der Waals radius for sulfur, 1.85 A., is very close to that of the methylene group, 2.0 A.[61]

The crystal structure of 1-aza-adamantane[62] has been reported as a face-centered lattice of either the space group $F\bar{4}3m$ or F23, which is identical to that that has been reported for the high temperature phase of adamantane. The compound is rather volatile. The molecular symmetry of aza-adamantane is C_{3v}. Since there is no four-fold axis of any sort present in the molecule and molecular association would rarely occur for this compound, the existence of the cubic crystal lattice could be attributed to either disordered or rotating molecules.

2-Thia-adamantane[63] gives crystals of regular octahedral habit, and therefore is in the cubic class. It is highly volatile. The molecular symmetry of this molecule is C_{2v}, and it has neither 4-fold nor 3-fold axis; therefore, the same argument as used on aza-adamantane could be applied as well to thia-adamantane.

Other simple adamantane-like molecules such as diaza-adamantane, triaza-adamantane, 2,4,10-trioxa-adamantane (cis-phloroglucitol orthoformate), trimorpholine and trithia-trimorpholine should also provide valuable information about the nature of plastic transitions as occurred in the adamantane crystal.

Triethylenediamine

It was reported[37] that there is a transition in triethylenediamine occurring at 74°C. associated with a change in the crystal structure. However this transition was not observed in the temperature range from 5 to 350°K. by this calorimetric measurement. The heat capacity versus temperature curve, nevertheless, indicated an abnormal increase in the slope near the upper limit of the temperature range investigated. A more recent unpublished study[64] on the heat capacity behavior of triethylenediamine from 300 to 450°K. revealed a sharp, apparently first order transition occurring at 351.1°K. with an transitional entropy of 7.19 e.u. The calorimetric sample melts at 432.98°K. with an entropy of fusion of 4.10 e.u. The heat capacity curve for the liquid region is almost the continuation of the curve for the plastic crystal region or the region between the transition point and the melting point. It was estimated from the fractional melting of this sample that the impurities, assumed to be soluble in the liquid phase but insoluble in the solid phase, was less than 0.005 mole per-

cent[64]. Studies by differential thermal analysis on this compound[44] yielded semi-quantitative information about the heats of transition and fusion in similar magnitudes as obtained calorimetrically.

The structural change during the transition has not yet been determined. At room temperatures triethylenediamine has been reported[44] to crystallize in a hexagonal lattice of the space group C_{6h}^2-$P6_3/m$ with the cell dimensions: a = 6.20 A. and c = 9.58 A. and with two molecules per each unit cell. The crystal structure of the high temperature phase would probably be in one of the close-packed lattices with still higher symmetry, if this is a transition to the plastic crystalline phase.

The large entropy of transition, corresponding to a value of about R ln 36, could not be successfully explained by Guthrie and McCullough's hypothesis of orientational disorder following their treatment of bicyclo[2.2.1]heptane[13] using the currently adopted molecular symmetry of D_{3h}, since this gives a calculated transitional entropy of only R ln 8. This leads to suspicion of the present molecular model which has six pairs of hydrogen atoms belonging to three ethylene groups situated at their most unfavorable positions or at the positions where the potential energy is at a maximum. The modified structure may have the molecules twisted to avoid such maxima and puts the molecular symmetry to the class of C_3. More investigations by X-ray diffraction,

spectroscopy and other techniques would obviously be desirable.

PART II

CRYOGENIC THERMODYNAMIC STUDIES ON THE SYSTEM TETRAMETHYLAMMONIUM CHLORIDE– TETRAMETHYLAMMONIUM HYDROGEN DICHLORIDE

Introduction

The fact that the proton in the hydrogen difluoride ion is situated in a single minimum potential energy well midway between the two fluoride ions has been well recognized. Evidence for the existence of such a symmetrical hydrogen difluoride ion has been provided by evaluation of the residual entropy[65], infrared spectroscopy[66] with polarized infrared radiation[66a], Raman spectroscopy[67], and neutron diffraction[68], and nuclear magnetic resonance studies[69] on potassium hydrogen difluoride. The hydrogen difluoride ion contains the strongest hydrogen bond known. With the hydrogen atom in the middle of two fluoride ions, the hydrogen atom may be considered to form a half bond with each of the fluoride ion and have a bond number corresponding to that of the bridge hydrogen atoms in boranes[61].

Waddington[70], after examining the infrared spectrum of tetramethylammonium hydrogen dichloride, suggested that the hydrogen dichloride ion $(Cl\text{-}H\text{-}Cl)^-$ might be another example of symmetrical hydrogen bonding. It is the purpose of this part of work to establish the evidence for the symmetry of the hydrogen dichloride ion through entropy evaluations.

A third law cycle is constructed for the reaction:

$$(CH_3)_4NHCl_2\ (s) = (CH_3)_4NCl\ (s) + HCl\ (g)$$

The entropy change of the reaction derived from direct measurement of the equilibrium constants for the reaction is compared with the values calculated by means of the third law of thermodynamics from low temperature heat capacity measurements on tetramethylammonium chloride and on tetramethylammonium hydrogen dichloride together with statistically calculated entropy values for gaseous hydrogen chloride from spectroscopic data.

If the substances involved in the reaction are perfectly ordered crystals at low temperatures and hence have no residual entropy, and there are no solid solutions in the system, the two values derived from direct equilibrium measurement and from third law evaluation should agree with each other. However if the hydrogen is not symmetrically situated in the $(Cl\text{-}H\text{-}Cl)^-$ ions, then a disordered structure is expected for tetramethylammonium hydrogen dichloride at low temperatures with a residual entropy of R ln 2. Therefore, the value obtained from third law entropies for the above mentioned reaction would be R ln 2 = 1.38 e.u. higher than that obtained from decomposition pressure measurement.

Preparation and Purification of Samples

Tetramethylammonium Chloride

Tetramethylammonium chloride made by Eastman Kodak Company was purified by recrystallizing three times in anhydrous methanol. The original (impure) sample was highly hygroscopic, but this property is much less pronounced for the recrystallized calorimetric sample. The latter sample, however, was kept in a vacuum dessicator for about a week and then transfered into a dry box with an anhydrous nitrogen atmosphere in order to avoid the possible contamination of the sample by the solvent and moisture. Calorimetric loading and unloading processes were also done in the dry box. Chemical analysis indicated the following composition: 43.85% C, 11.19% H and 12.89% N (calculated: 43.83% C, 11.04% H and 12.78% N for $(CH_3)_4NCl$).

Tetramethylammonium Hydrogen Dichloride

Tetramethylammonium hydrogen dichloride has usually been prepared by passing dry hydrogen chloride over tetramethylammonium chloride or by condensing the gas on the solid neutral salt[70,71].

With the aid of a vacuum system set-up, gaseous hydrogen chloride from the Matheson Company was first passed through a trap cooled in a bath of a mixture of dry ice and denatured alcohol, and then condensed into a

container at liquid nitrogen temperature. After a sufficient amount, about 90 ml., of hydrogen chloride has been collected, the liquid nitrogen bath was changed to a carbon disulfide slush bath. Hydrogen chloride was then distilled at this temperature, -111°C., into containers cooled at liquid nitrogen temperatures. The first and the last 10-15 ml. were discarded. The middle portion was kept for preparation purposes.

The distilled hydrogen chloride was again distilled into a bulb containing about 30 g. of purified tetramethylammonium chloride. The temperature of the reaction flask was changed frequently between that of the carbon disulfide slush bath and that of a dry ice and alcohol mixture, and occasionally liquid nitrogen was used. This stirred the mixture of tetramethylammonium chloride and liquid hydrogen chloride rather effectively, until a completely clear solution was obtained. Excess hydrogen chloride was then allowed to distill out slowly at the temperature of the carbon disulfide slush bath.

The sample thus obtained was in the form of a brittle polycrystalline powder. The weight of hydrogen chloride absorbed by tetramethylammonium chloride was checked by a solution balance. Acidimetric titration indicated the content of HCl in the sample to be 24.88%, i.e., the sample was composed of 99.20% of $(CH_3)_4NHCl_2$ and 0.80% of $(CH_3)_4NCl$, assuming that both starting materials were pure.

Keeping the sample under atmospheric pressure of gaseous hydrogen chloride for two weeks did not change the composition in any significant amount. Handling of this compound was done in a dry box with an anhydrous nitrogen atmosphere in order to prevent the absorption of moisture, and was kept to a minimum in order to avoid the change of composition due to its substantial dissociation pressure.

Cryogenic Equipment and Technique

The Mark I cryostat used for the determination of heat capacity of tetramethylammonium chloride, has been described in the first part of this dissertation. The heat capacity of tetramethylammonium hydrogen dichloride was measured in the Mark III cryostat, which is similar to Mark I in design, except that it has no heat exchanger to precool the bundle of leads before it comes into contact with the liquid helium tank.

Calorimeter W-9 was modified (thus became calorimeter W-9A) by soldering on a 3-hole thermocouple well to accomodate the multi-junction differential thermocouple to the middle portion of the adiabatic shield of the Mark III cryostat. The heat capacity of the empty calorimeter W-9A with the heater-thermometer assembly was therefore redetermined. In determining the heat capacities, calorimeter W-9 was loaded with 30.021 g. (in vacuo) of tetramethylammonium chloride and was sealed in with helium at 13.7 cm. Hg pressure at 300°K. Calorimeter W-9A was loaded with 33.712 g. (in vacuo) of tetramethylammonium hydrogen dichloride with 9.2 cm. pressure of helium at 300°K. The heat capacity of the empty calorimeter-heater-thermometer assembly represented from 30 to 20% of the total observed heat capacity from 5 to 20°K., from 20 to 50% from 20 to 100°K. and from 50 to 40% from 100 to 350°K. Thermometer A-3 was used for the measurement of temperature in both

cases.

The adiabatic shield was controlled manually in the Mark I cryostat and below 100°K in the Mark III cryostat. Above 100°K., the temperature of the adiabatic shield in the latter cryostat was controlled automatically through electronic devices. The signal from the differential thermocouple was fed into a Leeds and Northrup D. C. Microvolt Amplifier. This amplifier served as the preamplifier for the L. and N. Speedomax type G recorder. The off-balance signal against the control point from the recorder was in turn fed into a three action Current Adjusting Type control chassis having proportional, rate time and reset controls. The control signal from the CAT unit, after being chopped, was amplified through a 20W Pilot high-fidelity power amplifier to furnish the necessary energy to maintain the temperature of the adiabatic shield at the control point. The impedance of the output from the power amplifier was matched to an autotransformer for finer controls. The bottom and top parts of the adiabatic shield were also controlled by similar set-ups, but the activating signals were derived from differential thermocouples between the particular part of the adiabatic shield and the middle or cylindrical portion. The temperatures were usually controlled within 0.002°K., with momentary upset of the order of 0.05°K. caused by the start or termination of the energy input.

Calorimetric Results

The experimental heat capacity determinations for the two compounds are listed in Table VII in chronological order in terms of the thermochemical calorie defined as 4.1840 absolute joules. The ice point is taken as 273.15 °K. An analytically determined curvature correction was applied to the observed values of $\Delta H/\Delta T$. The approximate temperature increments usually can be inferred from the adjacent mean temperatures in Table VII. Molal values of the heat capacity at constant pressure, the entropy, the enthalpy increment and the free energy function are listed at selected rounded temperatures in Table VIII. These values were obtained from a smooth curve fit by least squares to the experimental data by means of a digital computer or by appropriate integration based on the curve. The reported values of the heat capacity data are believed to have probable errors less than 0.1% at temperatures above 25°K., about 1% at 10°K. and 5% at 5°K. The probable errors of the thermodynamic functions are considered to be less than 0.1% above 100°K.

Two transitions have been observed in the heat capacity behavior of tetramethylammonium chloride (Figure VI). A sharp, apparently first order transition occurs at 75.76°K., while a lambda type anomaly is found at 184.85°K. Attempt has been made to resolve the transitional contributions from the lattice, transitional

Table VII

Heat Capacities of Tetramethylammonium Chloride and Tetramethylammonium Hydrogen Dichloride

[in cal./(deg. mole)]

Tetramethylammonium Chloride [$(CH_3)_4NCl$, 1 mole = 109.605 g.]

T, °K	C_p	T, °K	C_p	T, °K	C_p
Series I		ΔH run number 3		ΔH run number 5	
		ΔH run number 4			
5.09	0.021	198.47	28.41	**Series IX**	
6.00	0.041				
6.94	0.065	**Series IV**		72.96	14.56
7.92	0.102			75.45	32.44
8.97	0.164	200.15	28.49	75.75	78.21
10.04	0.246	209.45	29.33	75.84	64.59
11.01	0.334	218.72	30.17	76.00	39.15
12.11	0.460	228.08	30.89	76.26	22.53
13.29	0.601	237.19	31.83	76.58	17.08
14.52	0.792	246.30	32.68	76.90	15.70
15.83	1.025	255.35	33.54		
17.21	1.309	264.32	34.37	**Series X**	
		273.13	35.10		
Series II		281.78	36.00	175.44	27.49
		290.36	36.72	177.14	27.65
8.03	0.110	298.94	37.60	178.29	27.89
9.00	0.166			179.43	28.07
12.93	0.559	**Series V**		180.55	28.32
17.25	1.318			181.66	28.60
18.94	1.709	302.14	37.86	182.77	28.89
20.69	2.161	311.87	38.78	183.89	29.68
22.62	2.705	321.43	39.68	184.99	30.26
24.92	3.393	330.84	40.58	186.09	27.58
27.63	4.233	339.21	41.38	187.24	27.54
30.59	5.176	346.70	42.14	189.01	27.64
33.88	6.206			191.35	27.79
37.38	7.248	**Series VI**		193.64	27.97
41.18	8.302				
45.46	9.390	66.89	13.61	**Series XI**	
50.01	10.45	72.47	14.43		
55.00	11.48	76.71	25.09	163.64	26.08
60.54	12.57	79.62	14.56	172.96	27.23
65.86	13.45	83.43	16.02	179.98	28.26
71.88	14.42			182.70	28.86
ΔH run number 1		**Series VII**		183.20	29.13
ΔH run number 2				183.65	29.33
		71.75	14.37	184.00	29.73

Table VII (continued)

T, °K	C_p
Series III	
85.97	16.39
93.55	17.39
101.21	18.40
109.64	19.49
118.31	20.59
127.00	21.68
135.92	22.66
144.90	23.89
153.99	24.96
162.90	26.01
171.46	27.14
74.85	14.87
75.37	15.37
75.56	34.65
75.67	75.35
75.76	83.18
75.89	58.61
76.20	26.64
76.65	16.88
77.75	15.31
81.47	15.73
Series VIII	
184.25	30.18
184.45	30.85
184.64	31.39
184.84	32.91
185.03	30.84
185.23	28.07
185.43	27.71
185.64	27.60
185.90	27.54
186.31	27.53
187.22	27.55

Tetramethylammonium Hydrogen Dichloride

$[(CH_3)_4NHCl_2$, 1 mole = 146.070 g.]

Series I	
128.72	28.30
Series II	
154.31	31.77
162.91	32.87
171.73	33.94
180.52	34.98
189.18	36.02
197.83	37.04
206.71	38.08
215.75	39.12
224.84	40.20
Series III	
5.82	0.069
6.41	0.100
7.19	0.148
8.08	0.232
8.95	0.331
9.87	0.465
10.94	0.664
12.18	0.940
13.49	1.300
14.86	1.728
16.35	2.250
18.04	2.897
19.99	3.692
21.94	4.521
24.46	5.613
27.39	6.869
30.57	8.183
33.84	9.470
37.40	10.81
41.34	12.03
45.67	13.36
50.49	14.67
55.94	15.98
61.95	17.32
68.40	18.61
Series IV	
70.35	18.93
77.01	20.14
Series V	
73.59	19.50
80.38	20.78
87.52	22.11
95.09	23.27
103.13	24.53
111.45	25.83
Series VI	
116.25	26.49
124.69	27.75
132.84	28.89
140.91	29.99
149.24	31.11
Series VII	
228.99	40.65
237.57	41.64
245.99	42.69
254.64	43.64
263.66	44.78
272.80	45.90
282.00	47.01
291.10	48.18
299.96	49.27
308.81	50.45
317.62	51.65
326.67	52.97
335.81	54.64
344.86	56.29

Table VIII

Thermodynamic Properties of Tetramethylammonium Chloride and Tetramethylammonium Hydrogen Chloride

(In units of cal., molecular wt., and °K.)

T	C_p	S°	$H°-H°_0$	$-(F°-H°_0)/T$
		Tetramethylammonium Chloride		
		$[(CH_3)_4NCl$, 1 mole = 109.605 g.]		
5	0.030	0.010	0.036	0.002
10	0.242	0.072	0.546	0.018
15	0.877	0.275	3.152	0.065
20	1.976	0.667	10.103	0.162
25	3.417	1.259	23.49	0.319
30	4.988	2.020	44.48	0.537
35	6.546	2.907	73.35	0.811
40	7.986	3.876	109.74	1.133
45	9.276	4.893	152.95	1.494
50	10.44	5.931	202.28	1.886
60	12.45	8.018	317.05	2.734
70	14.11	10.066	450.11	3.636
80	15.55	12.422	627.0	4.585
90	16.94	14.333	789.3	5.563
100	18.24	16.186	965.3	6.533
110	19.51	17.984	1154.1	7.492
120	20.82	19.738	1355.7	8.440
130	22.08	21.454	1570.3	9.375
140	23.27	23.134	1797.1	10.298
150	24.46	24.780	2035.7	11.209
160	25.69	26.398	2286.5	12.108
170	26.84	27.991	2549.2	13.000
180	28.21	29.560	2823.7	13.872
190	27.72	31.098	3108.2	14.739
200	28.51	32.539	3389.3	15.593
210	29.36	33.951	3678.6	16.434
220	30.25	35.337	3976.6	17.262
230	31.17	36.702	4283.7	18.077
240	32.10	38.048	4600.0	18.881
250	33.03	39.377	4925.6	19.675

Table VIII (continued)

T	C_p	S°	$H°-H°_0$	$-(F°-H°_0)/T$
260	33.97	40.691	5260.7	20.458
270	34.91	41.991	5605.1	21.231
280	35.84	43.277	5958.8	22.000
290	36.76	44.551	6321.8	22.751
300	37.68	45.813	6694.1	23.499
350	42.48	51.974	8695.7	27.129
273.15	35.20	42.40	5716	21.47
298.15	37.51	45.58	6625	23.36

Tetramethylammonium Hydrogen Dichloride

$[(CH_3)_4NHCl_2$, 1 mole = 146.070]

5	0.039	0.014	0.051	0.003
10	0.488	0.139	1.075	0.031
15	1.774	0.552	6.382	0.126
20	3.697	1.315	19.89	0.321
25	5.848	2.370	43.73	0.621
30	7.957	3.625	78.28	1.015
35	9.907	5.000	123.02	1.485
40	11.65	6.439	176.99	2.014
45	13.18	7.901	239.14	2.587
50	14.54	9.361	308.50	3.191
60	16.87	12.225	465.9	4.460
70	18.89	14.980	644.9	5.767
80	20.72	17.623	843.0	7.085
90	22.44	20.163	1058.9	8.398
100	24.05	22.612	1291.4	9.680
110	25.59	24.977	1539.7	10.980
120	27.07	27.268	1803.1	12.242
130	28.49	29.491	2080.9	13.484
140	29.87	31.653	2372.7	14.705
150	31.20	33.759	2678.1	15.905
160	32.49	35.815	2996.6	17.085
170	33.74	37.822	3327.8	18.246
180	34.94	39.784	3671.2	19.389
190	36.12	41.705	4026.5	20.513
200	37.28	43.587	4393.6	21.620

Table VIII (continued)

T	C_p	S°	$H°-H_0°$	$-(F°-H_0°)/T$
210	38.45	45.435	4772.2	22.710
220	39.61	47.250	5162.5	23.784
230	40.78	49.037	5564.5	24.843
240	41.95	50.797	5978.2	25.888
250	43.13	52.534	6403.6	26.919
260	44.32	54.249	6840.8	27.938
270	45.53	55.944	7290.1	28.944
280	46.77	57.622	7751.6	29.938
290	48.04	59.285	8225.6	30.921
300	49.31	60.935	8712.3	31.894
350	57.35	69.090	11359.3	36.625
273.15	45.92	56.47	7434	29.26
298.15	49.07	60.63	8621	31.72

Figure VI

Heat Capacity of Tetramethylammonium Chloride

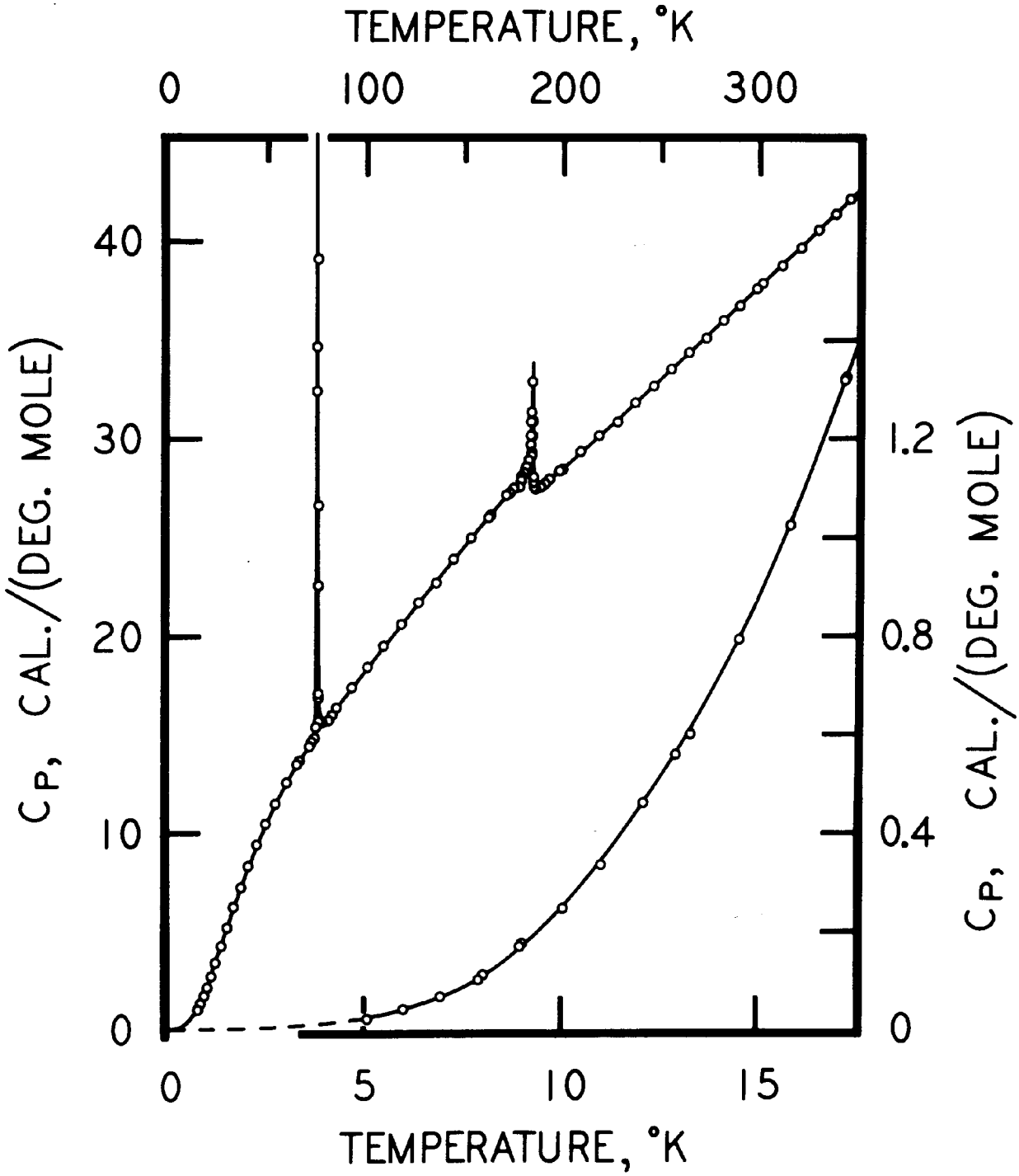

TEMPERATURE, °K
0
100
200
300
40
30
20
10
0
C_P, CAL./(DEG. MOLE)
1.2
0.8
0.4
0
C_P, CAL./(DEG. MOLE)
0
5
10
15
TEMPERATURE, °K

Figure VI

enthalpy increments of 27.8 cal./(deg. mole) and 25.9 cal./mole, corresponding to entropy increments of 0.37 e.u. and 0.14 e.u. obtained from the lower and higher temperature transitions, respectively. These probably represent minimal values.

Heat capacity-type runs and several enthalpy-type runs in the transitional regions were compared in Table IX. These comparisons test the over-all accuracy of the calorimetric measurements.

No thermal anomaly has been found in the acid salt from 5 to 350°K. by these calorimetric studies (Figure VII). Unlike that of the neutral salt, the slope of the heat capacity of the acid salt increases markedly in the region above 300°K. Differential thermal analysis extended to about 150°C. has failed to detect any thermal anomaly. Its heat capacity values listed in Table VII have been corrected for the decomposition at temperatures above 250°K. by means of the decomposition pressure data and heat of reaction obtained by direct equilibrium measurement. The correction term is less than 0.01% at 250°K., is 0.1% at about 300°K. and about 0.6% at about 350°K. Assuming that tetramethylammonium hydrogen dichloride was prepared from pure starting materials and that there is no solid solution formed, then the true molal heat capacity of the acid salt C_1 could be obtained from the apparent molal heat capacity of the acid salt C_1^* as given by the following equation:

Table IX

Enthalpy and Entropy Increments Over the Transition Regions in Tetramehylammonium Chloride

Transition I, T_t = 75.76°K.

Energy Increments	T_{final} °K.	$T_{initial}$ °K.	$H_{80°K.}-H_{70°K.}$ cal./mole	$S_{80°K.}-S_{70°K.}$ cal./(deg. mole)
2	81.55	68.31	176.70	2.351
1	78.53	74.55	176.83	2.352
8	78.63	75.25	176.81	2.353
4	76.09	75.20	177.11	2.356
Average			176.86 ± 0.12	2.354

Transition II, T_t = 184.85°K.

Energy Increments	T_{final} °K.	$T_{initial}$ °K.	$H_{190°K.}-H_{180°K.}$ cal./mole	$S_{190°K.}-S_{180°K.}$ cal./(deg.mole)
5	185.54	184.55	284.31	1.538
1	185.53	184.46	284.47	1.539
3	186.65	183.32	284.51	1.539
8	190.20	179.99	284.58	1.539
Average			284.47 ± 0.10	1.539

Figure VII

Heat Capacity of Tetramethylammonium

Hydrogen Dichloride

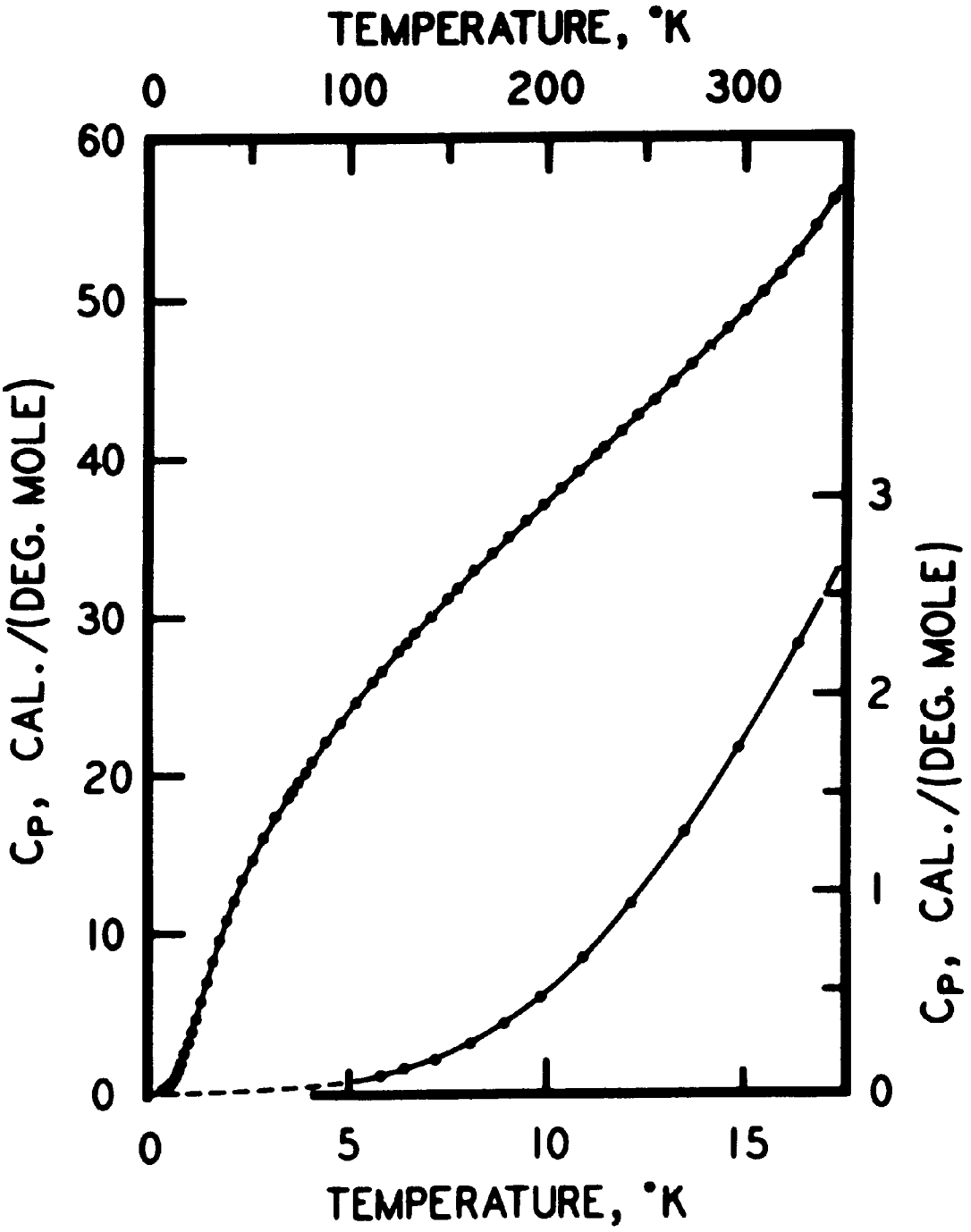

TEMPERATURE, °K
0
100
200
300
60
50
40
30
20
10
0
C_P, CAL./(DEG. MOLE)
3
2
1
0
C_P, CAL./(DEG. MOLE)
0
5
10
15
TEMPERATURE, °K

Figure VII

$$C_1 = C_1^* + \frac{1-a}{a} \left(C_1^* - \frac{MW_1}{MW_2} C_2 \right)$$

where a is the fraction in weight of the acid salt in the sample, C_2 the molal heat capacity of the neutral salt, and MW_1 and MW_2 the molecular weight of the acid and neutral salt respectively. The correction term is about +0.25% in the temperature range from 5 to 30°K., and then decreasing from +0.2 to 0.0% from 40 to 80°K., and less than -0.02% above 80°K. Therefore the correction has not been applied to the apparent molal heat capacity reported in Table VII.

Decomposition Pressure Measurement

The decomposition pressure of tetramethylammonium hydrogen dichloride was first measured in an isoteniscope-type apparatus with mercury as the confining liquid. A capillary tube is provided at the bottom of the U-tube of the isoteniscope and fitted with a stopcock leading to a mercury reservoir in order to facilitate the filling and removal of the confining liquid. The acid salt was prepared in the sample tube in situ by reacting the neutral salt with hydrogen chloride as described before. The usual boiling off procedure to carry out extraneous gas was not followed. After the system had been subjected to a high vacuum, while the sample was kept at 0°C., mercury was allowed to fill the U-tube and measurement proceeded as usual utilizing mercury in the U-tube as a null-indicator. The composition of the sample could be changed by first removing the confining liquid back to the mercury reservoir and then pumping-off a certain amount of the vapor evolved. However the results from these measurements were not very reproducible and showed a scattering of about $\pm 2\%$ to the smooth curve as obtained by a later experiment described below. Since the vapor phase was composed mainly of hydrogen chloride, it was considered that some reaction might have occurred between the vapor and the confining liquid mercury and thus caused the low reproducibility by contaminating the glass wall of the U-tube.

Because of the corrosive properties of hydrogen chloride, a sickle-shaped Bourdon gauge made of Pyrex glass with its pointer connected to a lever amplification system[72] was used as the null indicator. Sensitivity of this gauge was about 5 mm. Hg for a 1 mm. deflection of the sharp pointer of the mechanical lever. With a 10X telescope, a pressure difference of 0.1 mm. Hg. could be easily detected. The reproducibility of the gauge was believed to be within a pressure of 0.3 mm. Hg. The envelope of this gauge was wrapped with aluminum foil, wound around with heating tape and then insulated with asbestos sheets. It was kept continuously at a temperature of about 150°C. The sealed sample tube assembly was immersed in an oil bath. The temperature of the Finol oil bath was controlled by a mercury thermoregulator in connection with a sensitive d.c. operated relay. An additional uncontrolled heater was used to reduce the fluctuation of the temperature of the bath. Variacs were also used for finer controls. It was believed that the temperature of the bath was uniform through strong stirring and that the fluctuation in temperature was less than 0.05°.

The sample used was taken from the bulk of the calorimetric sample in the dry box with an anhydrous nitrogen atmosphere. A break-off seal was used to insure the water-free condition. The sample tube was provided

with a side tube, a break-off seal and a parallel connecting tube between the side tube and the vacuum manifold. After the gauge was pumped down and then filled with dry helium, the break-off seal in the sample tube was cracked by actuating a glass-sealed iron plunger with a magnet. The sample was then cooled in an mixture of dry ice and denatured alcohol, and subjected to a high vacuum. The parallel connecting tube between the manifold and the side tube was then sealed off. The seal was placed below the surface of the oil bath in order to assure that there was no cold spot in the whole system. The measurements were then begun for the original composition of the sample. The composition of the sample could be varied by opening the break-off seal beside the sealed parallel tube and between the manifold and the side tube of the sample tube. After a certain amount of vapor had been pumped off, the side tube was sealed and measurements on the second composition could be made. The composition could be varied as many times as these break-off seals and parallel connecting tube assemblies permitted.

Temperature of the bath was measured by means of a Cenco 1/10 degree thermometer which has been calibrated by the National Bureau of Standards. Corrections were also made for the partially immersed mercury thread. The pressure was measured by means of a mercury manometer of 1 cm. in diameter. No meniscus corrections were applied.

The heights of the mercury column were corrected to the density of mercury at 0°C. and standard gravity.

Decomposition pressure of tetramethylammonium hydrogen dichloride were determined from 65 to 105°C. for the original composition and a composition of approximately 60% $(CH_3)_4NHCl_2$. Since the results from these two compositions lie on the same pressure versus temperature curve, probability of formation of solid solution is very remote. Results of the decomposition pressure measurement are listed in Table X in chronological order and are shown in Figure VI. The probable error in the temperature measurement is believed to be less than 0.1°C., hence the uncertainty in pressure caused by the error in temperature is in the order of 1 mm. Hg at about 100°C., and about 0.1 mm. Hg at about 70°C. However at temperatures near 70°C. reproducibility is lower than that expected from the uncertainty in the temperature measurement, this is caused by the lower reproducibility of the Bourdon gauge used, in the order of 0.5 mm. Hg, and presumably by the slower equilibrium process, with probably a higher absorption and lower diffusibility of hydrogen chloride at lower temperatures. The rate of establishment of pressure equilibrium in this system is rather slow, 10 to 20 hours are typical before further appreciable increase or drop of pressure can be detected. Points were obtained by approaching equilibrium both from higher and from lower temperatures and pressures. Table XI shows the time dependence of two

Table X

Decomposition Pressure Measurements on Tetramethylammonium Hydrogen Dichloride in Chronological Sequence

T, °K.	P, mm. Hg	t_T[a], hr.	t_e[b], hr.	Method[c]
Series I, 99.2% $(CH_3)_4NHCl_2$ [Calorimetric Ssample]				
372.87	187.0	21	10	h
357.12	95.1	25	10	h
347.71	60.1	26	8	h,l
352.63	76.8	24	10	h,l
361.04	112.7	12	8	h
365.43	136.8	13	9	h
372.72	185.1	7	5	l
365.41	135.6	16	10	h,l
348.20	61.7	95	80	h,l
358.15	99.5	22	18	h
367.13	140.6	100	95	l
372.06	176.4	56	50	h,l
378.32	229.8	24	18	l
363.16	123.7	22	14	h,l
Series II, About 60% $(CH_3)_4NHCl_2$ and 40% $(CH_3)_4NCl$				
364.54	128.3	22	8	h
360.23	106.9	25	15	h
343.96	49.9	48	30	h
338.77	39.0	50	30	h

a) t_T signifies total time of observation after reaching temperature T.

b) t_e signifies time during which pressure was observed to be substantially at equilibrium value.

c) Method: h signifies equilibrium approached from higher pressures and temperatures and l from lower pressures and temperatures.

Figure VIII

Decomposition Pressure of

Tetramethylammonium Hydrogen Dichloride

○ —— Series I observations

□ —— Series II observations

● —— Calculated

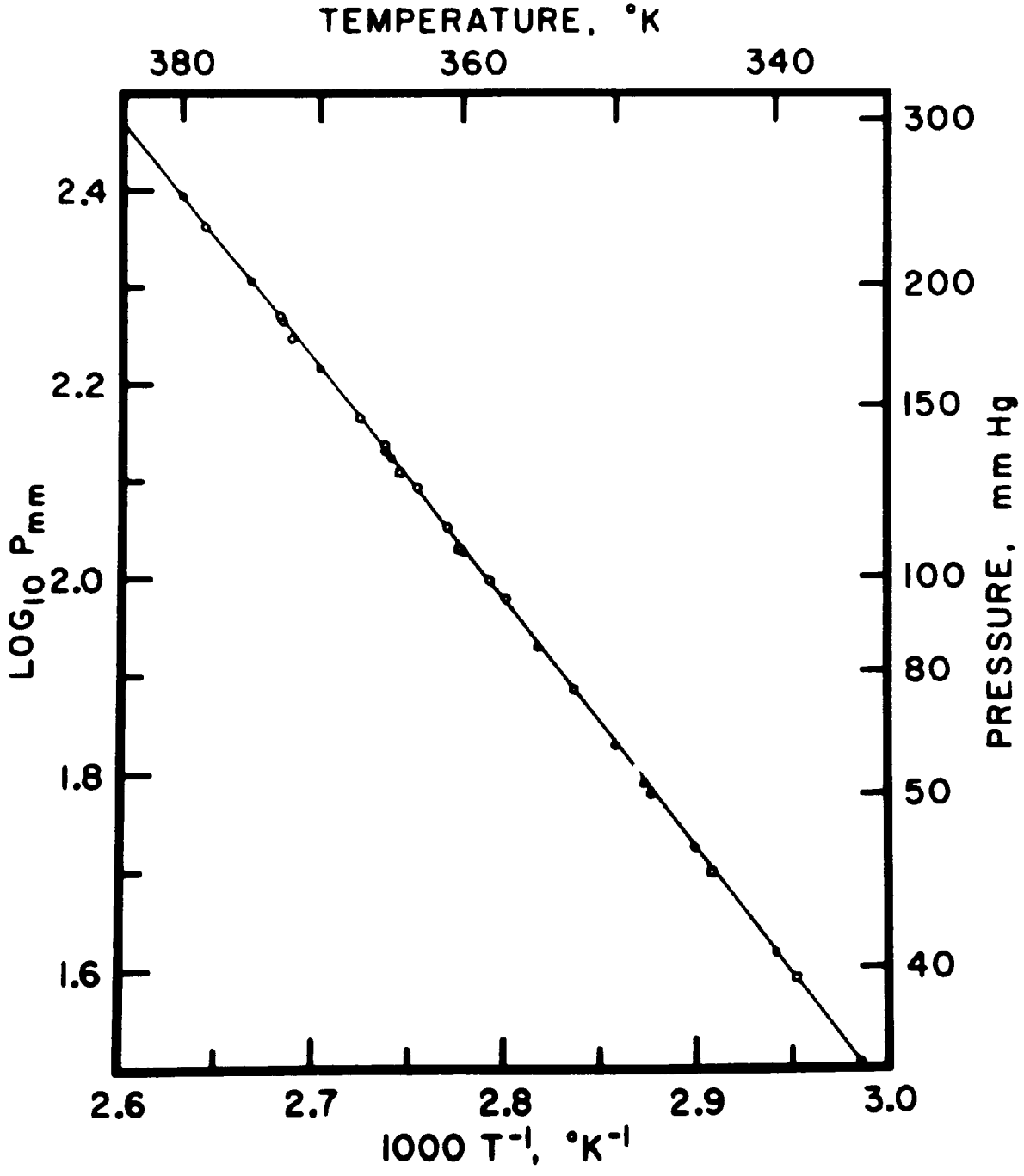

TEMPERATURE, °K
380
360
340
300
200
150
100
80
50
40
2.4
2.2
2.0
1.8
1.6
LOG10 Pmm
PRESSURE, mm Hg
2.6
2.7
2.8
2.9
3.0
1000 T-1, °K-1

Figure VII

Table XI

Sample Observations of the Decomposition Pressure of Tetramethylammonium Hydrogen Dichloride

Time, hr.	T, °K.	P, mm. Hg	Time, hr.	T, °K.	P, mm. Hg
0.00	347	60	0.00	377	230
0.10	347	60	0.35	376	230
0.20	355	60	0.40	371	225
0.28	362	70	0.45	367	213
0.30	365	79	0.46	363	200
0.33	368	106	0.47	363.2	175
0.35	366	112	0.50	363.2	160
0.37	363	114	0.55	363.2	150
0.39	360	106	0.60	363.2	146
0.40	358	106	0.70	363.2	138
0.42	345	100	0.90	363.2	135
0.44	351	94	1.1	363.2	132
0.45	350	91	2.0	363.2	128
0.47	348	88	3.0	363.2	126.5
0.50	350	85	6.0	363.2	125.5
0.57	352.6	83	8.0	363.2	125.0
0.90	352.6	81	10	363.2	124.8
1.25	352.6	79.5	15	363.2	124.0
1.8	352.6	78.7	20	363.2	123.7*
5.5	352.6	77.7	22	363.2	123.7*
7.0	352.6	77.6			
19.0	352.6	77.0*			
24.0	352.6	76.8*			
24.3	348	76			
24.4	333	69			
24.5	336	66			
24.7	342	65			
25.1	350	67			
25.3	352.6	71			
25.5	352.6	72			
27.2	352.6	75			
28	352.6	75			
33	352.6	76.6			
37	352.6	76.8*			
48	352.6	76.8*			

*Values considered to represent equilibrium. Calculated pressures at 352.6°K. = 76.3 mm. Hg and at 363.2°K. = 125.0 mm. Hg.

typical decomposition pressure measurements.

The equation for the equilibrium decomposition pressure was obtained with the aid of the differential heat capacity of the reaction, $\Delta C_p = 30.803 - 0.11215\ T$ cal./(deg. mole), obtained by extrapolating the heat capacity determinations for the acid and the neutral salts and by computed heat capacities for hydrogen chloride from molecular data[47]. This equation,

$$\log_{10} P_{mm} = -28.4677 - 1698.5\ T^{-1} + 15.302\ \log_{10} T - 0.012256\ T,$$

accords with the experimental data within 0.003 in units of $\log_{10} P_{mm}$, or about 1.5 mm. Hg at about 100°C. and less at lower temperatures. Decomposition pressures are calculated at 5° intervals from 335 to 380°K. and are shown together with the experimental values in Figure VI. Extrapolation of the equation indicates the pressures to be 1.8 mm. Hg at 298.15°K. and 760 mm. Hg at 410.8°K.

Discussion

Equilibrium Constant

Dissociation of tetramethylammonium hydrogen dichloride into the neutral salt and hydrogen chloride:

$$(CH_3)_4NHCl_2 = (CH_3)_4NCl + HCl \quad (1)$$

may involve complicating reactions at high temperatures, starting with the further dissociation of tetramethylammonium chloride into trimethylamine and chloromethane:

$$(CH_3)_4NCl = (CH_3)_3N + CH_3Cl. \quad (2)$$

Recombination of hydrogen chloride and trimethylamine to form trimethylamine hydrochloride is thus possible:

$$(CH_3)_3N + HCl = (CH_3)_3NHCl. \quad (3)$$

Further reaction of trimethylamine hydrochloride with hydrogen chloride to give dihydrochloride:

$$(CH_3)_3NHCl + HCl = (CH_3)_3N \cdot 2HCl \quad (4)$$

is less likely due to the low stability of the dihydrochloride at room temperature[73]. However, at elevated temperatures, trimethylamine hydrochloride may react with hydrogen chloride to give lower amine hydrochlorides and chloromethane:

$$(CH_3)_3NHCl + HCl = (CH_3)_2NH_2Cl + CH_3Cl \quad (5)$$

and eventually to give ammonium chloride and chloromethane:

$$(CH_3)_3NHCl + 3HCl = NH_4Cl + 3CH_3Cl. \quad (6)$$

Nevertheless, within the temperature range of the decomposition pressure measurement of tetramethylammonium hydrogen chloride in this research, the reaction (1) pre-

dominates, and the vapor phase can be viewed as composed almost entirely of hydrogen chloride, due to the very low decomposition pressure of the neutral salt and its slowness in reaching equilibrium at these temperatures. Therefore the total pressure of the vapor phase is taken as the equilibrium constant of the decomposition of tetramethylammonium hydrogen dichloride, since hydrogen chloride behaves almost ideally at these temperatures and pressures.

If we consider the equilibrium among the first three reactions starting from tetramethylammonium hydrogen dichloride, such that:

$$\underset{1-x}{(CH_3)_4NHCl_2\ (s)} = \underset{x-y}{(CH_3)_4NCl\ (s)} + \underset{x-z}{HCl\ (g)} \qquad (1)$$

$$\underset{x-y}{(CH_3)_4NCl\ (s)} = \underset{y-z}{(CH_3)_3N\ (g)} + \underset{y}{CH_3Cl\ (g)} \qquad (2)$$

$$\underset{y-z}{(CH_3)_3N\ (g)} + \underset{x-z}{HCl\ (g)} = \underset{z}{(CH_3)_3NHCl\ (s)} \qquad (3)$$

then x, y and z are measures of the respective conversion of the three reactions. Assuming that all gases behave ideally, the equilibrium constants for the decomposition reactions of $(CH_3)_4NHCl_2$, $(CH_3)_4NCl$ and $(CH_3)_3NHCl$, respectively, can be expressed as:

$$K_1 = (x - z)P/(x + 2y - 2z)$$

$$K_2 = (y - z)yP^2/(x + 2y - 2z)^2$$

$$K_3 = (y - z)(x - z)P^2/(x + 2y - 2z)^2$$

where P is the total pressure of the vapor phase. Since

the relationship, $1 \geqslant x \geqslant y \geqslant z \geqslant 0$, must hold, it can be shown that $z \geqslant 0$ only if $K_3 \leqslant K_1 K_2^{1/2}$, i.e., K_3 must be less than a certain value in order for reaction (3) to occur.

The decomposition pressure of tetramethylammonium chloride has been determined from 185 to 230°C. by Smith and Calvert[74]. Since the given pressure vs. temperature equation has a minimum in pressure at about 140°C., it is not suitable for extrapolation to lower temperatures. By fitting their data to an equation of the form $\log_{10} P_{mm} = A + BT^{-1}$, the coefficients A = 11.066 and B = -4165.4 are obtained. Extrapolation of this equation leads to a pressure of 0.8 mm. Hg at 100°C.

Considering that x is much greater than y and z, then K_1 is approximately equal to the observed decomposition pressure of tetramethylammonium hydrogen dichloride, the value at 100°C. is 191 mm. Hg. The value of K_2 at the same temperature can be calculated from the above extrapolated equilibrium decomposition data as 0.16 in terms of mm. Hg. Hence the decomposition pressure of trimethylamine hydrochloride, $2 K_3^{1/2}$, must be less than 17.5 mm. Hg in order that this compound would be formed during the equilibrium process.

No appreciable decomposition pressure, i.e., not in excess of 1 mm. Hg, was detected for trimethylamine hydrochloride by heating up to 130°C. for 24 hours in an isoteniscope-type apparatus with mercury as the confining

liquid, as found in this research. However it has been reported[75] that trimethylamine hydrochloride sublimes above 200°C. and decomposes above 275°C. Although the statements do not explicitly indicate whether the sublimation took place in air at atmospheric pressure or in vacuum, presumably the former is to be understood. Hence its decomposition equilibrium constant is comparable to that of tetramethylammonium chloride, and it would be formed eventually if the system is allowed to reach equilibrium. If this is the case, then adjustments have to be applied to the observed total decomposition pressure of the acid salt in order to compute the values of K_1, and precise low pressure measurements must be performed on the equilibrium constants for the neutral salt and for trimethylamine hydrochloride in the temperature range investigated for the acid salt in order to minimize the error in making such large adjustments.

However the foregoing treatments seem to be unnecessary, since it is likely that tetramethylammonium chloride is only very slightly decomposed and the effect could be neglected during the time required to measure the equilibrium pressure of the acid salt at a temperature of about 100°C.

The rate of decomposition of the neutral salt was reported[74] to be very slow even at 245°C. The pressure was said to reach only 182 mm. Hg during the first hour,

although the equilibrium pressure for this temperature is about 1060 mm. Hg. Since the rate of reaction is often changed by 2 to 3-fold for every 10° change in temperature, therefore, it is reasonable to assume that the rate of decomposition at 100°C. is extremely slow. In order to verify this fact more quantitatively, measurements on the rate of decomposition of the neutral salt at 203 and 235°C. were made by means of a Bourdon gauge similar in design and volume to that used for the acid salt. The result is presented in Table XII. The equilibrium decomposition pressures are in accord with the magnitude reported[74]. The rate of decomposition under the experimental conditions is found to be almost constant until about half or 2/3 of the equilibrium value is reached; the rate is about 25 mm. Hg/hr. at 235°C. and 1.5 mm. Hg/hr. at 203°C. In the closed system the pressure is directly proportional to amount of the solid decomposed and the rate far from equilibrium is substantially constant. If an Arrhenius relationship may be assumed, then the extrapolated rate of decomposition at 100°C. on the basis of the data in Table XII is in the order of 10^{-5} mm. Hg/hr. for conditions similar to those in the measurement of the decomposition of the acid salt. Hence decomposition of the neutral salt would be negligibly small even after a month at 100°C. Since all the other reactions depend on the products of the decomposition of the neutral

Table XII

Observations on the Rate of Decomposition of Tetramethylammonium Chloride

T = 476°K.		T = 508°C.	
Time, hr.	P, mm. Hg.	Time, hr.	P, mm. Hg.
0.0	5	0.0	158
1.5	9	0.3	170
2.0	11	0.7	178
3.8	15	0.5	196
5.3	17	1.8	205
0.5	20	2.0	208
17.0	39	2.8	231
20.0	44	3.4	270
21.0	46	3.8	277
22.5	48	5.0	283
27.0	58	6.3	319
28.5	60	6.7	328
30.5	61	7.4	344
43.5	78	8.3	363
45.5	80	8.5	367
46.5	82	9.5	391
52.0	100	10.9	424
53.0	102	11.8	442
54.5	104	12.5	457
66.5	119		

salt, reaction (2), these can also be neglected. Thus the observed total equilibrium pressure of the acid salt is considered to be due to the decomposition of the acid salt alone, reaction (1).

Evaluation of Residual Entropy

The third law of thermodynamics implies that the entropy of a perfectly ordered crystalline substance is zero at absolute zero. Hence the entropy of such a substance at temperature T can be evaluated by appropriate integration of the area under the curve of C_p versus ln T or of C_p/T versus T from 0 to T°K. The standard entropy change of a reaction can then be calculated by subtracting the sum of the entropies of the reactants from these of the products at the same temperature. It can also be derived from the temperature dependence of the standard free energy change of the reaction. If all the substances involved are perfectly crystalline substances at very low temperatures, then the two entropy values derived from heat capacity measurements and from equilibrium constant determinations should agree with each other.

Values of standard entropy changes for the decomposition of tetramethylammonium hydrogen dichloride into tetramethylammonium chloride and hydrogen chloride from the two sources are listed and compared in Table XIII.

Table XIII

Comparison of the Entropy Changes for the Reaction

$$(CH_3)_4NCHl_2 = (CH_3)_4NCl + HCl$$

T, °K.	S°_{HCl}	S°_{Cl}	$S^\circ_{HCl_2}$	ΔS°_{III}	ΔS°_{eq}	Δ
340	45.52	50.76	67.45	28.83	28.79 ± 10	.04
350	45.72	51.97	69.09	28.60	28.56 ± 10	.04
360	45.92	53.18	70.74	28.36	28.31 ± 10	.05
370	46.11	54.38	72.41	28.08	28.03 ± 10	.05
380	46.30	55.58	74.08	27.80	27.74 ± 10	.06

S°_{eq} represents the value derived from direct equilibrium constant measurements as $-[\partial(\Delta F^\circ)/\partial T]_p$ where $\Delta F^\circ = -RT \ln K_p = -RT \ln P$. The equilibrium decomposition pressure is considered to be identical with the equilibrium constant in this experiment on the basis that there are no solid solutions formed in changing the activity of the solid and that the fugacity of hydrogen chloride is identical, within experimental error, to the pressure. If a Berthelot equation of state is assumed, the activity coefficient, γ, can be calculated by the following relationship:

$$\ln \gamma = \ln \frac{f}{p} = \frac{9}{128} \frac{\pi}{\theta} \left(1 - \frac{6}{\theta^2}\right)$$

where π and θ are the reduced pressure and temperature, respectively. By taking the critical pressure and temperature of hydrogen chloride as 81.6 atm. and 324.7°K., γ is found at 200 mm. Hg. and 100°C. to be 0.9993, which is almost unity. The probable errors noted are based upon the uncertainties in temperature as 0.1° and in pressure as 0.5 mm. Hg. ΔS°_{III} denotes the entropy change of the reaction as calculated from the third law entropies of the reactant and products involved. S°_{HCl}, the entropy of hydrogen chloride gas, is obtained based upon the statistically calculated values[47] and interpolated to the particular temperatures by taking the mean heat capacity of hydrogen chloride gas from 300 to 400°K. as 6.964 ± .005 cal./mole. The entropy values of the neutral and of the

acid salts, S°_{Cl} and $S^{\circ}_{HCl_2^-}$, respectively are obtained by extrapolating the heat capacity values determined in this research.

Deviation of ΔS°_{III} from ΔS°_{eq} is in general within 0.1 e.u. as can be seen in the column Δ of Table XIII. The agreement is considered good because of the extrapolated entropy values for the neutral and the acid salts and because of the rather complicated nature of the decomposition reaction.

With the assumption that tetramethylammonium chloride and hydrogen chloride are perfectly crystalline substances at very low temperatures and that there are no solid solutions formed in the system, this agreement of a virtually zero residual entropy in the acid salt supports the existence of a symmetrical $(Cl\text{-}H\text{-}Cl)^-$ ion with a single minimum potential energy function. If the hydrogen atom is not centrally situated in between the two chlorine atoms, then a disordered structure for the acid salt may be expected. If the randomly oriented unsymmetrical HCl_2^- ion persists to very low temperatures, then a residual entropy of R ln 2 = 1.38 e.u. would arise for a symmetrically situated ion and the value of ΔS°_{III} would be expected to be 1.38 e.u. larger than that of ΔS°_{eq}.

APPENDIX I

Summary of Adamantane-like Ring Systems

Explanation of notations:

b-----Boiling point
d-----Density
e-----Electron deflection
h-----Hygroscopic
IR----Infrared spectrum
mass--Mass spectrum
m.p.--Melting point in °C. (underlined — with decomposition)
n-----Refractive index
NMR---Nuclear magnetic resonance
op----Optical isomers
R-----Raman spectrum
s-----Sublimable
TD----Thermodynamic or thermochemical properties
UV----Ultraviolet spectrum
X-----Crystal structure or habit

The name of the ring system is in general omitted when it appears at the end of the name of the compound. Salts, esters and derivatives for qualitative analysis are not listed.

Compound	M.P.	Other Properties
1. Adamantane (Tricyclo[3.3.1.1^{3,7}]decane)		
Adamantane	267-70[19,22-24,76]	d[19]; e[77]; IR[34]; Mass[78]; n[19]; NMR[52]; s[19]; TD[19,76]; X[48-50,79].
1-Chloro-	165[80]	s[80]
1-Bromo-	118-20[80-1]	IR[81]; s[80-1]
1-Iodo-	152.5[81]	s[81]
1-Nitro-	173[82]	
1-Amino-	160-90[82]	

Compound	M.P.	Other Properties
1-Hydroxy-	282-90[80-1]	IR[81]
1-Methyl-	103[80]	
1-Ethyl-	-58[20]	b[20]; n[20]
1-Propyl-	-1[20]	b[20]; n[20]
1-Cyclohexyl-	104.5[20]	IR[20]
1-Phenyl-	82-9[20,80]	IR[20], s[80]
Diadamantyl	296[20]	IR[20]
1-Hydroxymethyl-	115[80-1]	
Adamantane-1-al	225[83]	
Adamantane-1-carboxylic acid	181[80-1]	
1,3-Dibromo-	108-13[22,80,84]	
1,3-Dihydroxy-	315[84]	
Adamantane-1,3-dicarboxylic acid	276-81[22,84,85]	
1,3-Dimethyl-		b[85]; IR[85]; n[85]
1,3-Diisopropyl-	<-70[86]	b[85-6]; IR[86]
1,3-Diisopropenyl-		b[85-6]; n[85-6]
1,3-Bis(chloromethyl)-	64-5[85]	IR[85]
1,3-Bis(Bromomethyl)-	86-7[85]	
1,3-Bis(iodomethyl)-	86-7[85]	
1,3-Bis(hydroxymethyl)-	181-2[85]	
1,3-Bis(α-methyl-α-hydroxyethyl)-	161-7[85-6]	
1,3-Bis(α-methyl-α-chloroethyl)-	71-3[85-6]	

Compound	M.P.	Other Properties
1,3,5-Tribromo-	126-7[84]	
1,3,5-Trihydroxy-	>360[84]	
1,3,5,7-Tetrabromo-	315[84]	
Adamantane-1,3,5-7-tetra-carboxylic acid	229[87]	
Adamantane-2,6-dione-1,5-dicarboxylic acid	286[86]	
Adamantane-2,6-dione-1,3,-5,7-tetracarboxylic acid	345-6[88]	
2,6-Dichloro-adamantane-1,3,5,7-tetracarboxylic acid		op[89]
2,6-Dihydroxy-adamantane-1,3,5,7-tetracarboxylic acid	310[88]	
2-Hydroxy-adamantane-6-one-1,3,5,7-tetra-carboxylic acid	118-9[88]	
α-Adamantyl-1-ethanol	75-6[90]	
Adamantyl-1-acetic acid	136[80]	
Adamantanylacetic ester: $RCOCH_2CO_2Et$ (R=adamantyl-1)		b[90]
Diphenyl-(adamantyl-1)-chloromethane	150-2[83]	
Diphenyl-(adamantyl-1)-carbinol	127-8[83]	
Methyl-(adamantyl-1)-ketone	53-4[90]	
Bromomethyl-(adamantyl-1)-ketone	78-9[90]	
Phenyl-(adamantyl-1)-ketone	55-6[83]	

Compound	M.P.	Other Properties
1,2,-Di-(adamantyl-1)-ethylene glycol: $(RCHOH)_2$	257-65[83]	
Acyloin: RCHOHRCO	223-4[83]	
Diketone: $(RCO)_2$	219[83]	
Ketone: RCH_2RCO	227-8[83]	
1,4-Di-(adamantyl-1)-butadione-1,4	132-3[90]	
2,5-Di-(adamantyl-1)-furan	217[90]	
2,5-Di-(adamantyl-1)-pyrrol	227-8[90]	
1-Phenyl-3-Adamantyl-1-pyrazolone-5	138-9[90]	
2. 1-Aza-adamantane		
1-Aza-adamantane	257-8[91-2]	d[62]; n[62]; s[91]; X[62]
3. 2-Oxa-adamantane		
6,6-Dimethyl-2-oxa-adamantane	179-80[93]	
6-Methyl-6-dichloro-methyl-2-oxa-adamantane	125-7[93]	
4. 2-Thia-adamantane		
2-Thia-adamantane	320[63]	s[63]

Compound	M.P.	Other Properties
5. 1,3-Diaza-adamantane		
1,3-Diaza-adamantane	260-5[94-5]	h[95]; s[95]
5,7-Diphenyl-	217-9[96]	
1,3-Diaza-adamantanol-6	<u>270</u>[97]	h[97]; s[97]
5,7-Diphenyl-1,3-diaza-adamantanol-6	274[96]	
5,7-Diphenyl-1,3-diaza-adamantanone-6	257[96]	
5,7-Bisphenylmercapto-1,3-diaza-adamantanol-6	190-1[97]	
5,7-Bisphenylmercapto-1,3-diaza-adamantanone-6	245[97]	
5,7-Bisbenzenesulfonyl-1,3-adamantanone-6	337[97]	
6. 1,3,5-Triaza-adamantane		
1,3,5-Triaza-adamantane	<u>260</u>[98]	s[98]; X[98]
7-Methyl-	175[99]	
7. 1,3-Diaza-2-thia-adamantane		
1,3-Diaza-2-thia-adamantane	<u>160</u>[100]	s[100]
8. 2,4,9-Trioxa-adamantane		
7-Hydroxy-2,4,9-trioxa-adamantane	212[101]	s[101]
7-Hydroxy-1,3,5-trimethyl	164[101]	

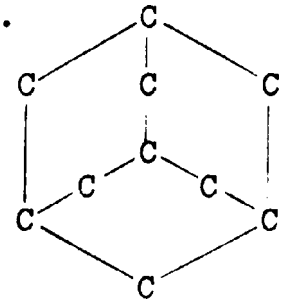
Compound	M.P.	Other Properties
7-Chloro-1,3,5,-trimethyl-	69[101]	
9. 2,4,10-Trioxa-adamantane		
2,4,10-Trioxa-adamantane	219-20[102]	
3-Methyl-	126[102]	
3-Ethyl-	38[102]	h[102]
3-Phenyl-	176-7[102]	h[102]; s[102]
3-Chloro-methyl-	107[102]	s[102]
3-Bromomethyl-	95[102]	s[102]
10. Hexamethylenetetramine(1,3,5,7-Tetraaza-adamantane)		
Hexamethylenetetramine	263[54] >280[45]	cf. Discussion in Part I. Many more references.
11. Trimorpholine (1-Aza-4,6-10-trioxa-adamantane)		
Trimorpholine	210-20[104]	
12. Trithio-trimorpholine (1-Aza-4,6,10-trithia-adamantane)		
Trithio-trimorpholine	147-8[105]	

Compound	M.P.	Other Properties
13. 1-Phospha-2,8,9-trioxa-adamantane		
1-Phospha-2,8,9-trioxa-adamantane	207[106]	
1-Phospha-2,8,9-trioxa-adamantane-1-oxide	267-8[106]	
1-Phospha-2,8,9-trioxa-adamantane-1-sulfide	250-1[106]	
14. 2,4-Dioxa-6,8-Dithia-adamantane		
1,3,5,7-Tetramethyl-2,4-dioxa-6,8-dithia-adamantane	138[107]	UV[107]
15. 2,6-Dioxa-4,8-dithia-adamantane		
1,3,5,7-Tetramethyl-2,6-dioxa-4,8-dithia-adamantane	131[107]	s[107]; UV[107]
1,3,5,7-Tetramethyl-2,6-dioxa-4,8-dithia-adamantane-4,8-bisdioxide	250[107]	
16. 2,4,6,8-Tetrathia-adamantane		
1,3-Di-t-butyl-2,4,6,8-tetrathia-adamantane	176[108]	
1,3,5,7-Tetramethyl-	163[30]	UV[107]; s[76]
1,3,5,7-Tetraethyl-	164[30]	

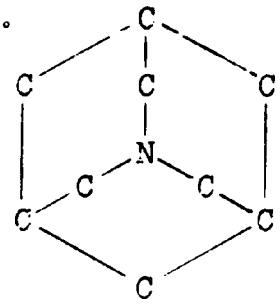
Compound	M.P.	Other Properties
1,3,5,7-Tetrapropyl-	137[108]	
1,3,5,7-Tetrahexyl-	92-3[108]	
1,3-Dimethyl-5,7-diethyl-	136-7[30]	
1,3-Dimethyl-5,7-dipropyl-	113[108]	
1,3-Dimethyl-5,7-dihexyl-	71[108]	
1,3-Dimethyl-5,7-di-t-butyl-	164[108]	
1,3-Dimethyl-5,7-di-(β-phenylethyl)-	110-1[108]	
1,3,5,7,9,10-Hexamethyl-	128[30]	
1,3,5,7,9,10-Hexamethyl-2,4,6,8-tetrathia-adamantane-2,4,6-trisdi-oxide	260[107]	
1,3,5,7,9,9,10,10-Octa-methyl-	227[109]	
1,3,5,7,9,9,10,10-Octa-methyl-2,4,6,8-tetrathia-adamantane-2,6-bisdisulfide	350[109]	
17. 1,3,5,7-Tetraaza-2-thia-adamantane		
1,3,5,7-Tetraaza-2-thia-adamantane-2-dioxide	224-5[110]	
18. 1,3,5,7-Tetraaza-2,6-dithia-adamantane		
1,3,5,7-Tetraaza-2,6-dithia-adamantane-2,6-bisdioxide	255-60[111]	

Compound	M.P.	Other Properties
19. 2,4,6,8,9,10-Hexathia-adamantane		
2,4,6,8,9,10-Hexathia-adamantane	330[112]	d[60,112]; IR[112-3]; X[60]
1,3,5,7-Tetramethyl-	224-5[28,38,29]	IR[31]; R[31]; UV[107]; X[114-5]; S[76]
1,3,5,7-Tetramethyl-2,4,6,8,9,10-hexathia-adamantane-2,6-bis-dioxide	250[38]	
1,3,5,7-Tetraethyl-	123-4[103]	
1,3,5,7-Tetrapropyl-	134[103]	
1,3,5,7-Tetrabutyl-	66-7[103]	
1,3,5,7-Tetrapentyl-	46-7[103]	
1,3,5,7-Tetrahexyl-	89-1[103]	
1,3,5,7-Tetraheptyl-	65-6[103]	
1,3,5,7-Tetradecyl-	64[34]	

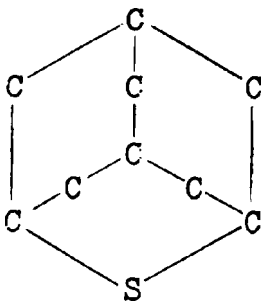
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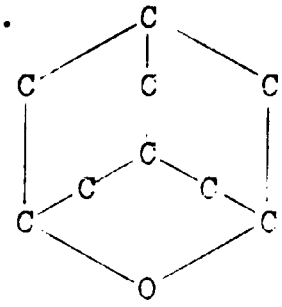
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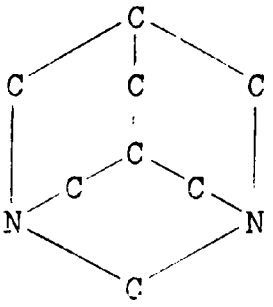
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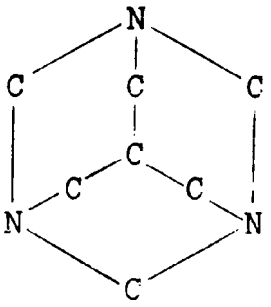
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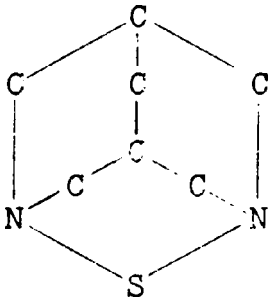
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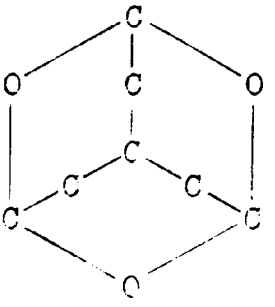
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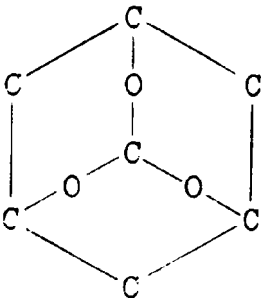
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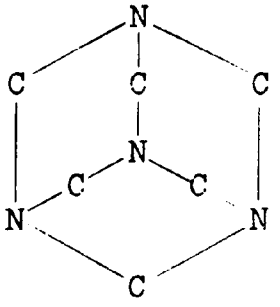
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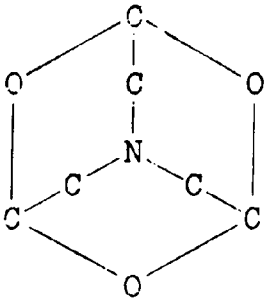
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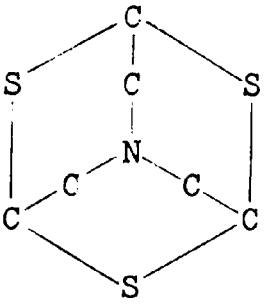
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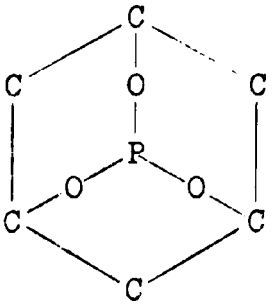
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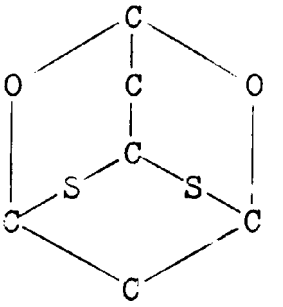
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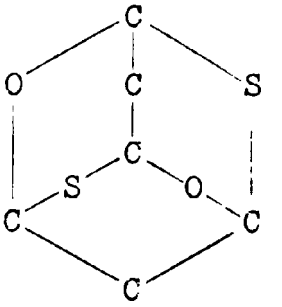
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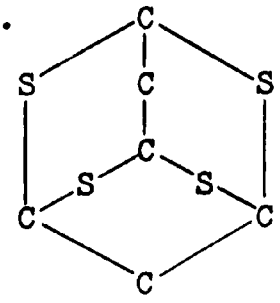
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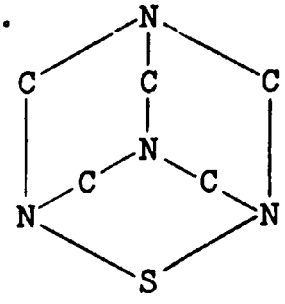
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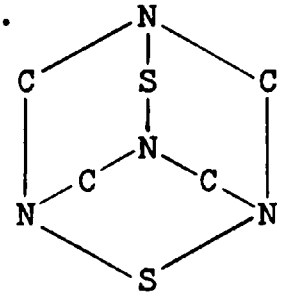
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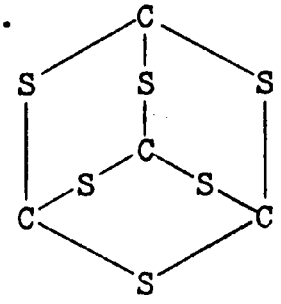
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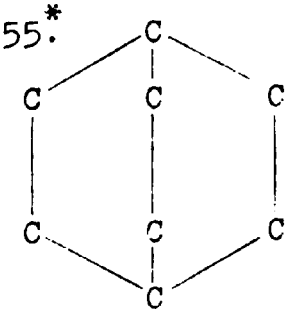


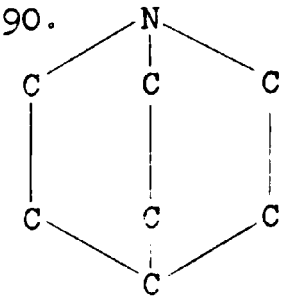
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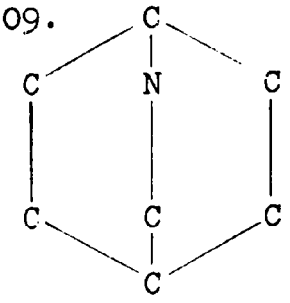


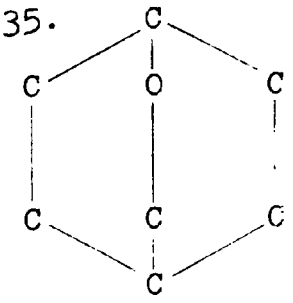
APPENDIX II

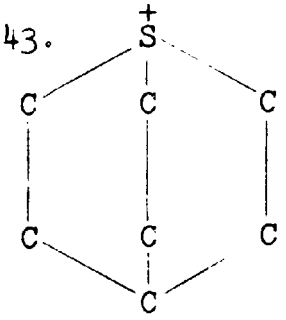
Summary of Bicyclo[2.2.2]octane-like Ring Systems

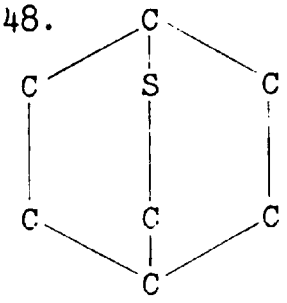
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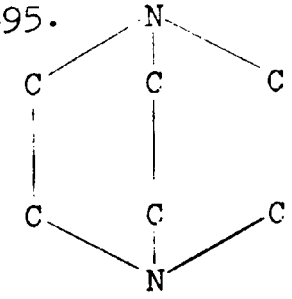
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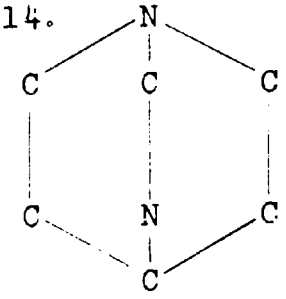
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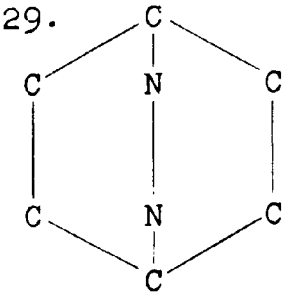
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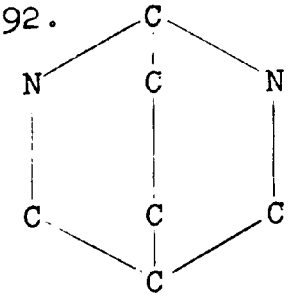
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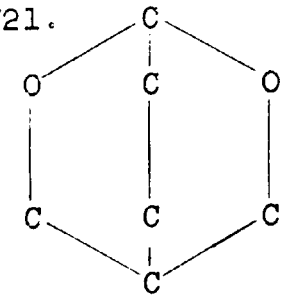
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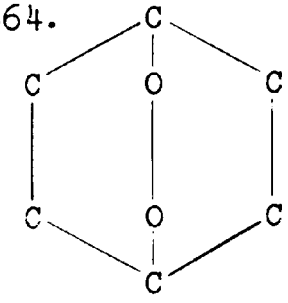
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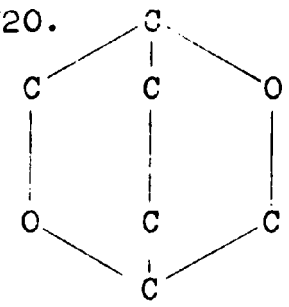
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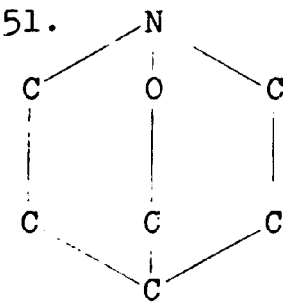
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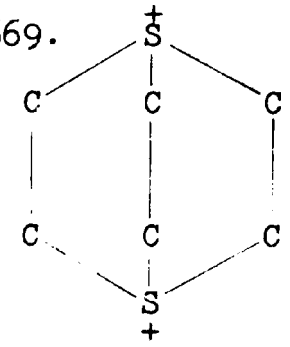
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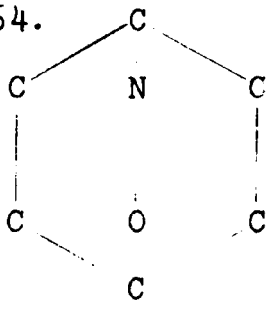
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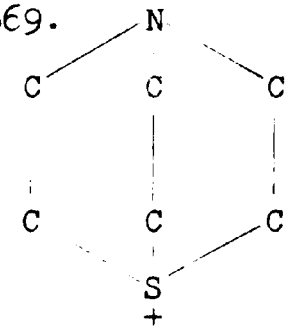
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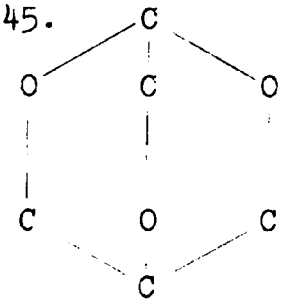
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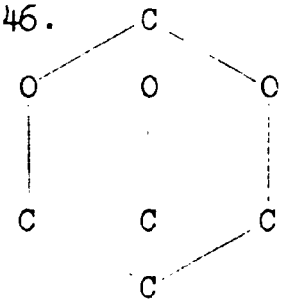
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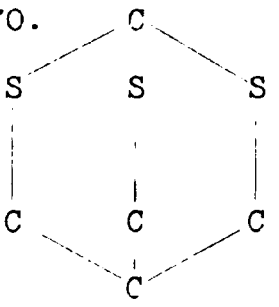
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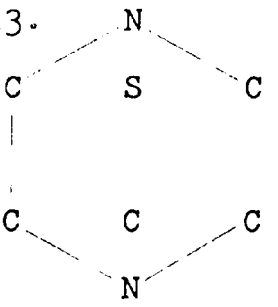
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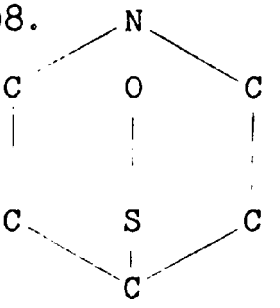
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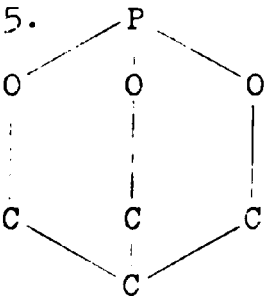
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1525.



*Numbers are that of the "Ring Index"[35].

APPENDIX III

Heat Capacity and Thermodynamic Properties of Tetramethylammonium Bromide

The two transitions observed in the tetramethylammonium chloride crystal at 75.8 and 184.9°K. have small transitional entropy increments. The lower transition appears as a sharp peak in the heat capacity versus temperature curve in a very narrow temperature range and is apparently a first order transition. However, the lambda shaped anomaly at higher temperature is apparently a higher order transition. It was noticed at the time when these results were obtained that tetramethylammonium uranium hexachloride and tetramethylammonium thorium hexachloride are reported[116] to show transitions of similar shapes and order of occurrence as that in the tetramethylammonium chloride, although both transition temperatures are higher. It is therefore possible that the transitions are due to the cation. Since the fluoride of this cation is less readily available while the iodide has already been studied calorimetrically[117] but showed no transitions, the bromide was chosen for further studies.

Tetramethylammonium bromide made by Eastman Kodak was purified by three recrystallizations from absolute methanol. Unlike the chloride, the bromide crystals appear as large, hard rectangular blocks. It is slightly hygroscopic in moisten air. It is therefore kept in a vacuum

dessicator and handling in ambient air is minimized in order to preserve its purity. Analytical data show the following composition: 31.26% C, 7.74% H, 8.81% N and 51.78% Br (calculated: 31.18% C, 7.85% H, 9.09% N and 51.84% Br for $C_4H_{12}NBr$).

The Mark I cryostat, calorimeter W-9 and thermometer A-3 were used for measuring the heat capacity of tetramethylammonium bromide. A sample weighing 47.643 g. (in vacuo) was loaded in the calorimeter. After evacuation, helium gas at a pressure of 8.2 mm. Hg at 300°K. was sealed in to facilitate heat conduction between the sample and the calorimeter.

The results of this investigation are presented in Table XIV for the actually measured heat capacity in chronological order, and in Table XV for derived thermodynamic properties at selected temperatures. The heat capacity versus temperature curve of tetramethylammonium bromide very closely follows that of the iodide and does not show any indication of anomaly in the temperature range studied. Deviation of the molal heat capacity of the iodide from the bromide is obtained by subtracting from the actual heat capacity data points of the iodide the corresponding heat capacity value of the bromide as read from a smoothed curve, and is shown in Figure IX. This figure also shows a similarly obtained plot for the deviation of molal heat capacity of the chloride against

Table XIV

Heat Capacity of Tetramethylammonium Bromide

$[(CH_3)_4NBr$, 1 mole = 154.060 g.]

T, °K	C_p	T, °K	C_p	T, °K	C_p
Series I		19.61	3.257	233.37	32.31
		21.66	3.969	242.63	33.25
78.21	15.74	23.85	4.730		
84.56	16.59	26.27	5.562	Series V	
91.67	17.44	28.96	6.448		
99.41	18.32	32.01	7.409	248.63	33.38
107.32	19.27	35.41	8.403	257.46	34.83
115.39	20.23	39.11	9.371	266.26	35.38
123.78	21.24	43.17	10.312	275.30	36.30
132.27	22.20	47.63	11.243	284.39	37.25
140.75	23.14			293.43	38.19
149.39	24.10	Series III		302.49	39.13
158.40	25.12			311.61	40.06
		49.88	11.67		
Series II		55.49	12.63	Series VI	
		61.62	13.58		
4.99	0.038	68.24	14.48	318.12	40.72
5.61	0.066	75.40	15.37	327.36	41.63
6.63	0.113			336.57	42.63
7.64	0.201	Series IV		345.60	43.51
8.52	0.306				
9.45	0.441	161.70	23.44	Series VII	
10.51	0.628	179.59	27.19		
11.67	0.872	188.32	28.01	157.32	24.96
12.92	1.172	197.02	28.82	166.60	25.92
14.28	1.546	205.94	29.66	175.28	26.75
15.86	2.030	215.07	30.51	183.44	27.53
17.66	2.605	224.17	31.36		

Table XV

Thermodynamic Properties of Tetramethylammonium Bromide

(In units of cal., molecular wt., and °K.)

$[(CH_3)_4NBr$ 1 mole = 154.064 g.]

T	C_p	S°	$H^\circ-H_0^\circ$	$-(F^\circ-H_0^\circ)/T$
5	0.042	0.013	0.047	0.003
10	0.534	0.147	1.154	0.032
15	1.757	0.575	6.630	0.133
20	3.397	1.299	19.42	0.328
25	5.128	2.244	40.74	0.614
30	6.788	3.328	70.61	0.975
35	8.272	4.488	108.3	1.393
40	9.576	5.680	153.0	1.854
45	10.71	6.875	203.8	2.346
50	11.70	8.056	259.9	2.858
60	13.34	10.339	385.4	3.916
70	14.72	12.502	525.9	4.990
80	15.97	14.550	679.4	6.058
90	17.19	16.501	845.2	7.111
100	18.40	18.375	1023.1	8.144
110	19.60	20.185	1213.1	9.157
120	20.80	21.942	1415.1	10.149
130	21.96	23.653	1629.0	11.122
140	23.09	25.322	1854.3	12.077
150	24.18	26.953	2090.7	13.015
160	25.23	28.547	2337.8	13.936
170	26.24	30.107	2595.2	14.842
180	27.22	31.635	2862.5	15.732
190	28.17	33.132	3139.4	16.609
200	29.11	34.601	3425.8	17.472
210	30.06	36.044	3721.7	18.322
220	31.01	37.464	4027.0	19.160
230	31.97	38.864	4341.9	19.986
240	32.95	40.245	4666.5	20.802
250	33.93	41.610	5000.9	21.607

Table XV (continued)

T	C_p	S°	$H^\circ-H_0^\circ$	$-(F^\circ-H_0^\circ)/T$
260	34.91	42.960	5345.1	22.402
270	35.88	44.296	5699.0	23.188
280	36.85	45.618	6062.6	23.966
290	37.83	46.928	6436.0	24.735
300	38.83	48.227	6819.2	25.496
350	44.02	54.601	8890.1	29.201
273.15	36.18	44.713	5812.5	23.434
298.15	38.64	47.988	6747.6	25.356

Figure IX

Differential Heat Capacities of

$(CH_3)_4NCl$ minus $(CH_3)_4NBr$ (○)

and

$(CH_3)_4NI$ minus $(CH_3)_4NBr$ (□)

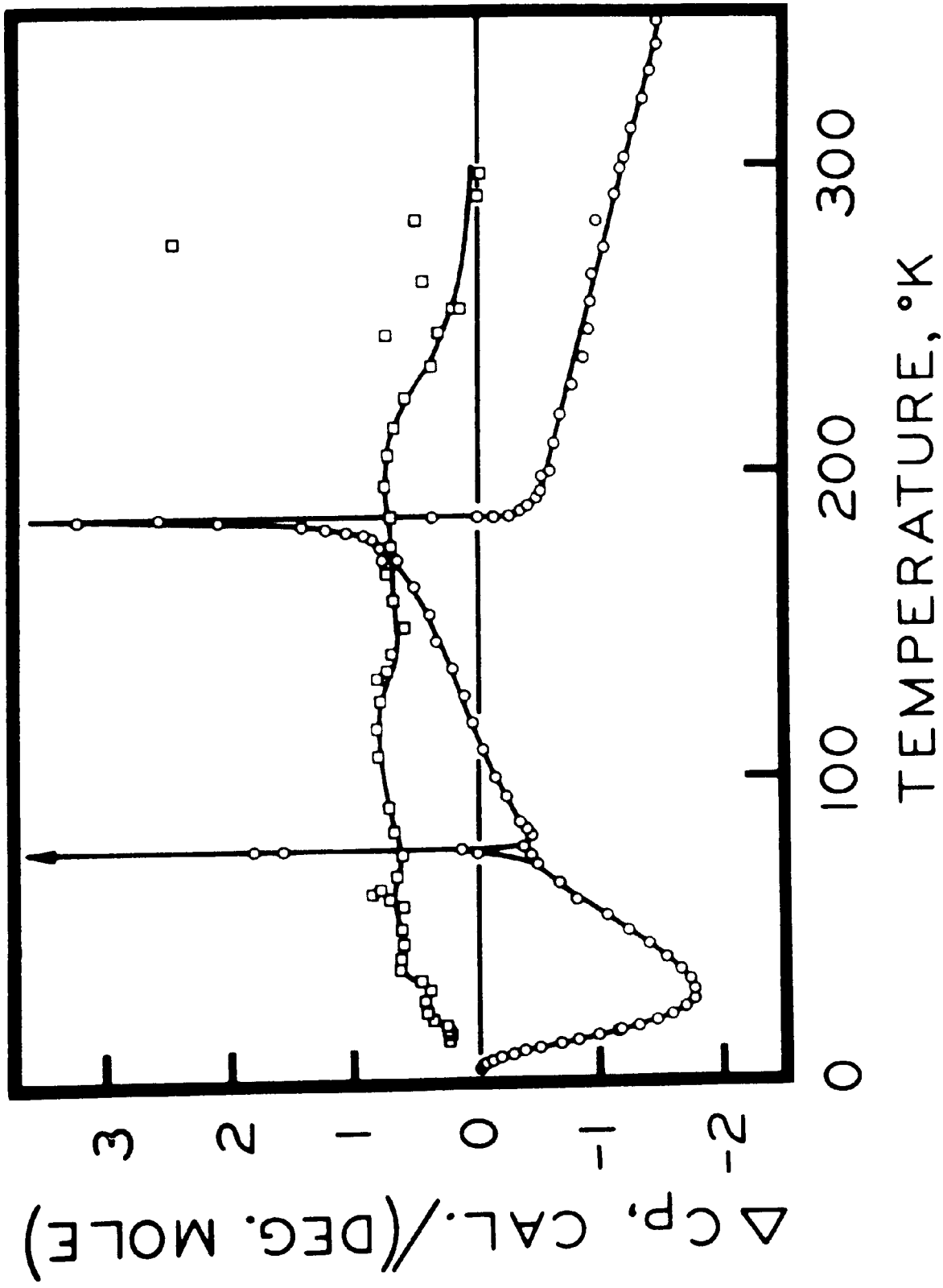


Figure IX

that of the bromide.

It is of interest to note that the crystals of the three halides at room temperatures are isostructural[118]. They belong to the same tetragonal lattice of the space group D_{4h}^{7}-P4/nmm and have two molecules for each unit cell. The cell dimensions a and b are: 7.78 and 5.53 A. for the chloride, 7.76 and 5.53 A. for the bromide and 7.96 and 5.75 A. for the iodide. Since the ionic radius for the chloride ion (1.81 A.) is less than that of the bromide ion (1.95 A.), it is apparent that the tetramethylammonium ion occupies a larger volume in the crystal of the chloride than that in the bromide or the iodide. This may result from the motions of the cation in the chloride lattice in the phase stable at room temperatures. However the reason for the occurrence of two transitions in the chloride crystal is still not clear. Further studies on dilatometry, precise X-ray patterns and even nuclear magnetic resonance, piezoelectricity and ferroelectricity are desirable to aid the interpretation of the transitions occurred in the tetramethylammonium salts.

BIBLIOGRAPHY

1. J. Timmermans, J. chim. phys. 35, 331 (1938).

2. R. R. Wenner, "Thermochemical Calculations", p. 24, McGraw Hill, N. Y., 1941.

3. F. Simon and C. von Simson, Z. Phys. 21, 168 (1924).

4. L. Pauling, Phys. Rev. 36, 430 (1930).

5. R. W. James, The Crystalline State, Vol. II, "The Optical Principle of the Diffraction of X-rays," p. 229, Bell, London (1954).

6. C. P. Smyth, Chem. Rev. 19, 329 (1936).

7. N. Bloemberger, E. M. Purcell and R. V. Pound, Phys. Rev. 73, 679 (1948).

8. H. Meyer, M. C. M. O'Brien and J. H. van Vleck, Proc. Roy. Soc. (London) 243A, 414 (1958).

9. N. G. Parsonage and L. A. Staveley, Mol. Phys. 3, 59 (1960).

10. L. A. Staveley, J. Phys. Chem. Solids 18, 46 (1961).

11. W. L. Dunning, J. Phys. Chem. Solids 18, 21 (1961).

12. A. A. K. Al-Mahdi and A. R. Ubbelohde, Proc. Roy. Soc. (London) 220A, 143 (1953).

13. G. B. Guthrie and J. P. McCullough, J. Phys. Chem. Solids 18, 53 (1961).

14. A. H. White and W. S. Bishop, J. Am. Chem. Soc. 62, 8 (1940); A. H. White, B. S. Biggs and S. O. Morgan, ibid. 62, 16 (1940).

15. A. Michils, Bull. soc. chim. Belges 57, 575 (1948).

16. J. Timmermans, Ind. chim. belge 16, 178 (1951).

17. G. Friedel, Z. Krist. 79, 1 (1931); G. H. Brown and W. G. Shaw, Chem. Rev. 57, 1049 (1957).

18. H. Decker, Angew. Chem. 37, 795 (1924).

19. S. Landa and V. Macháček, Collection Czech Chem. Commun. 5, 1 (1933); S. Landa, V. Machácěk and J. Mžourek, Chem. listy 27, 415 (1933); 27, 443 (1933); Petroleum Z. 30, 1 (1934).

20. S. Landa and S. Hála, Chem. listy 51, 2325 (1957); Collection Czech Chem. Commun. 24, 93 (1959); Erdöl u. Kohle 11, 698 (1958).

21. B. J. Mair, M. Schamaiengar, N. C. Krouskop and F. D. Rossini, Anal. Chem. 31, 2082 (1959).

22. V. Prelog and R. Seiwerth, Ber. 74B, 1644 (1941); ibid. 74B, 1769 (1941).

23. H. Stetter, O. E. Bänder and N. Neumann, Chem. Ber. 89, 1922 (1956).

24. P. v. R. Schleyer, J. Am. Chem. Soc. 79, 3292 (1957); P. v. R. Schleyer and M. M. Donaldson, J. Am. Chem. Soc. 82, 4645 (1960).

25. Belgian Patent 583,579, Oct. 12, 1959.

26. R. G. Dickinson and A. L. Raymond, J. Am. Chem. Soc. 45, 22 (1923).

27. F. Leuter, Compt. rend. 133, 48 (1901).

28. J. Bongartz, Ber. 19, 2182 (1886).

29. A. Fredga, Arkiv Kemi, Mineral. Geol. 25B, N:08, 1 (1948).

30. A. Fredga and A. Brändstrom, Arkiv Kemi, Mineral. Geol. 26B, N:04, 1 (1948).

31. R. Mecke and H. Spiesecke, Chem. Ber. 88, 1997 (1955).

32. H. Stetter and K. H. Steinacker, Chem. Ber. 85, 451 (1952).

33. H. Stetter, Angew. Chem. 66, 217 (1954).

34. A. Fredga, Svensk Kem. Tidskr. 72, 151 (1960).

35. A. M. Paterson, L. T. Campell and D. F. Walker, "The Ring Index", second edition, American Chemical Society, Washington, D. C. (1960).

36. A. Farkas, G. A. Mills, W. E. Erner and J. B. Maeker, Ind. Eng. Chem. 51, 1299 (1959).

37. A. Farkas, G. A. Mills, W. E. Erner and J. B. Maeker, J. Chem. Eng. Data 4, 334 (1959).

38. E. Fromm and G. Mangler, Ber. 34, 204 (1901).

39. E. F. Westrum, Jr., J. B. Hatcher and D. W. Osborne, J. Chem. Phys. 21, 419 (1953).

40. M. S. Van Dusen, J. Am. Chem. Soc. 47, 326 (1925).

41. H. J. Hoge and F. G. Brickwedde, J. Research Natl. Bur. Standards 22, 351 (1939).

42. W. F. Giauque, J. Am. Chem. Soc. 45, 93 (1923).

43. N. S. Osborne, H. F. Stimson, T. S. Sligh, Jr. and C. S. Cragoe, Bureau of Standards, Sci. Paper No. 501, 65 (1925).

44. T. Wada, E. Kishida, Y. Tomiie, H. Suga, S. Seki and I. Nitta, Bull. Chem. Soc. Japan 33, 1317 (1960).

45. G. Klipping and I. N. Stranski, Advances in Catalysis 9, 406 (1957).

46. M. Delépine and M. Badoche, Compt. rend. 214, 777 (1942).

47. "Selected Values of Chemical Thermodynamic Properties", Circular 500 National Bureau of Standards, Washington, D. C., 1952.

48. W. Nowacki, Helv. Chim. Acta 28, 1233 (1945).

49. G. Giacomello and G. Illuminati, Ricerca sci. 15, 559 (1945); Gazz. chim. ital. 75, 246 (1945).

50. C. L. Nordman, unpublished results.

51. D. W. J. Cruickshank, unpublished results.

52. D. W. McCall and D. C. Douglas, J. Chem. Phys. 33, 777 (1960).

53. H. W. Gonell and H. Mark, Z. phys. Chem. 107, 181 (1923); H. Mark, Ber., 57B, 1820 (1923); R. W. G. Wyckoff and R. B. Corey, Z. Krist. 89, 462 (1934); R. Brill, H. G. Grimm, C. Hermann and C. Peters, Ann. Physik 34, 383 (1939).

54. M. C. P. Varma, J. Appl. Chem. 8, 117 (1958).

55. G. Klipping and I. N. Stranski, Z. anorg. allg. Chem. 297, 23 (1958); A. T. Bogenschütz, G. Klipping and I. N. Stranski, ibid. 299, 69 (1959); I. N. Stranski, G. Klipping and H.-G. Maenning, Z. Electrochem. 63, 135 (1959); D. Hoene, G. Klipping and I. N. Stranski, Chem. Ber. 93, 2782 (1960).

56. H. Plischke, Z. Chem. 1, 25 (1960).

57. P. A. Schaffer, Jr., J. Am. Chem. Soc. 69, 1557 (1947).

58. L. Couture-Mathieu, J. P. Mathieu, J. Cremer and H. Poulet, J. chim. phys. 48, 1 (1951).

59. W. Nerst and F. A. Lindemann, Z. Electrochem. 17, 817 (1911).

60. E. K. Anderson and I. Lindqvist, Arkiv Kemi 9, 169 (1956).

61. L. Pauling, "The Nature of the Chemical Bond", third edition, Cornell, Ithaca, N. Y., 1960.

62. J. Bauer, Collection Czech Chem. Commun. 19, 715 (1954).

63. S. F. Birch, T. V. Cullum, R. A. Dean and R. L. Denyer, Nature 170, 629 (1952).

64. J. C. Trowbridge, unpublished results.

65. E. F. Westrum, Jr., and K. S. Pitzer, J. Am. Chem. Soc. 71, 1940 (1949).

66. J. A. A. Ketelaar, J. Chem. Phys. 9, 775 (1941); Rec. Trav. Chim. 60, 523 (1941); J. A. A. Ketelaar and W. Vedder, J. Chem. Phys. 19, 654 (1951). (a) R. Newman and R. M. Badger, J. Chem. Phys. 19, 1207 (1951).

67. L. A. Woodward and H. J. Tyrell, Trans. Faraday Soc. 38, 513 (1942).

68. S. W. Peterson and H. A. Levy, J. Chem. Phys. 20, 704 (1952).

69. J. S. Waugh, F. B. Humphrey and D. M. Yost, J. Phys. Chem. 57, 486 (1953).

70. T. C. Waddington, J. Chem. Soc., 1958, 1708 (1958).

71. F. Kaufler and E. Kunz, Ber. 42, 385 (1909).

72. S. G. Foord, J. Sci. Instr. 11, 126 (1934).

73. F. Ephraim, Ber. 47, 1842 (1914).

74. A. Smith and R. P. Calvert, J. Am. Chem. Soc. 36, 1363 (1914).

75. M. C. Vincent, Compt. rend. 84, 1139 (1877); ibid. 85, 667 (1878); M. Delépine, Ann. chim. phys. [7] 8, 451 (1896).

76. This research.

77. W. Nowacki and K. W. Hedberg, J. Am. Chem. Soc. 70, 1497 (1948).

78. Catalog of Mass Spectral Data, API Research Project 44, Carnegie Institute of Technology, No. 939.

79. R. Kaichev and D. Nenov, Compt. rend. acad. bulgare sci. 12, 199 (1959); cf. Chem. Abs. 54, 19073d (1960).

80. H. Stetter, M. Schwarz and A. Hirschhorn, Chem. Ber. 92, 1629 (1959).

81. S. Landa, S. Kriebel and E. Knobloch, Chem. listy 48, 61 (1954).

82. H. Stetter, J. Mayer, M. Schwarz and K. Wulff, Chem. Ber. 93, 226 (1960).

83. H. Stetter and E. Rauscher, Chem. Ber. 93, 1161 (1960).

84. H. Stetter and K. Wulff, Chem. Ber. 93, 1366 (1960).

85. S. Landa and Z. Kamýček, Chem. listy 52, 1150 (1958); Collection Czech Chem. Commun. 24, 1320 (1959).

86. S. Landa and Z. Kamýček, Chem. listy 50, 388 (1956); Collection Czech Chem. Commun. 21, 772 (1956).

87. L. Gross, Dissertation, Bonn (1953); cf. H. Stetter, Angew. Chem. 66, 217 (1954).

88. O. Böttger, Ber. 70, 314 (1937).

89. H. Stetter and O. E. Bänder, Chem. Ber. 88, 1535 (1955).

90. H. Stetter and E. Rauscher, Chem. Ber. 93, 2054 (1960).

91. R. Lukeš and V. Galík, Collection Czech Chem. Commun. 19, 712 (1954); Chem. listy 48, 858 (1954).

92. R. Fusco and G. Bianchetti, Atti accad. nazl. Lincei, Rend., Classe sci. fis., mat. e. nat. 15, 420 (1953); cf. Chem. Abs. 49, 6274a (1953).

93. H. Stetter and J. Mayer, Chem. Ber. 92, 2664 (1959).

94. F. Galinovsky and H. Langer, Monatsch. 86, 449 (1955).

95. H. Stetter and H. Henning, Chem. Ber. 88, 789 (1955).

96. H. Stetter, J. Schäffer and K. Kieminger, Chem. Ber. 91, 590 (1958).

97. H. Stetter, K. Dieminger and E. Rauscher, Chem. Ber. 92, 2057 (1959).

98. R. Lukeš and Syhora, Chem. listy 45, 731 (1952); Collection Czech Chem. Commun. 18, 654 (1953).

99. H. Stetter and W. Böckmann, Chem. Ber. 84, 834 (1951).

100. H. Stetter and R. Merten, Chem. Ber. 90, 868 (1957).

101. H. Stetter and M. Dohr, Chem. Ber. 86, 589 (1953).

102. H. Stetter and K. H. Steinacker, Chem. Ber. 86, 790 (1953).

103. A. Fredga and H. Bauer, Arkiv. Kemi 2, 113 (1950).

104. L. Wolff and R. Marburg, Ann. 363, 184 (1908).

105. D. Craig, J. J. Shipman, A. Hawthorne and R. Fowler, J. Am. Chem. Soc. 77, 1283 (1955).

106. H. Stetter and K. H. Steinacker, Chem. Ber. 85, 451 (1952).

107. A. Brändstrom, Arkiv. Kemi 3, No. 5, 41 (1951).

108 A. Fredga and A. Brändstrom, Arkiv. Kemi, 1, 197 (1949).

109 E. Fromm and P. Ziersch, Ber. 39, 3599 (1906).

110. A. M. Paquin, Angew. Chem. 60, 317 (1948).

111. G. Hecht and H. Henecka, Angew. Chem. 61, 365 (1949).

112. A. Fredga and K. Olsson, Arkiv. Kemi 9, 163 (1956).

113. H. Spiesecke and R. Mecke, J. Chem. Phys. 25, 577 (1956).

114. L. Déverin, Schweiz mineral. petr. Mitt. 18, 673 (1938).

115. G. Hägg and B. Nygardh, Arkiv. Kemi, Mineral. Geol. 25B, N:08, 4 (1948).

116. D. W. Osborne, unpublished results.

117. L. V. Coulter, K. S. Pitzer and W. M. Latimer, J. Am. Chem. Soc. 62, 2845 (1940).

118. R. W. G. Wyckoff, Z. Krist. 67, 91 (1928).