MRI REPORT

SPACE THERMAL CONTROL BY USE OF SOLID/SOLID-PHASE CHANGE MATERIALS

ANNUAL SUMMARY REPORT NO. 1
25 June 1968 - 24 July 1969

Contract NAS8-21452
Control DCN 1-8-28-00053

MRI Project No. 3224-C

For

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama 35812

Attn: PR-SC

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by

E. Murrill
L. W. Breed

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PREFACE

This report was prepared by Midwest Research Institute, 425 Volker Boulevard, Kansas City, Missouri 64110, under Contract NAS8-21452, "Space Thermal Control by Use of Solid/Solid-Phase Change Materials." The work was administered under the direction of the Space Sciences Laboratory, George C. Marshall Space Flight Center, with Miss B. E. Richard acting as the Contracting Officer's technical representative.

This report covers work conducted from 25 June 1968 to 24 July 1969.

The work at Midwest Research Institute was designated 3224-C and was carried out by Dr. E. Murrill and Mr. L. W. Breed, who acted as Principal Investigator, under the supervision of Dr. C. C. Chappelow, Jr., Head, Organic and Polymeric Materials Section.

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8 September 1969

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ABSTRACT

Mechanisms of solid/solid-phase transitions and available data in the literature suggest that transitions in substances that exhibit a plastic crystalline phase may have sufficiently large enthalpies for use in passive thermal control. In a broad qualitative screening of readily available candidate materials by differential thermal analysis, 33 substances with plastic crystalline phases that had not been previously identified were found. Quantitative differential thermal calorimetry showed that five of these substances had enthalpies of transition greater than 45 cal/g: 2-Hydroxymethyl-2-methyl-1,3-propanediol (46 cal/g at 354°K), 2-amino-2-methyl-1,3-propanediol (63 cal/g at 349-354°K), 2-amino-2-hydroxymethyl-1,3-propanediol (68 cal/g at 404-407°K), 2-methyl-2-nitro-1,3-propanediol (48 cal/g at 353-356°K), and 2,2-bis(hydroxymethyl)propionic acid (69 cal/g at 425-428°K). Correlations of the qualitative and quantitative data suggest structural criteria which may provide additional substances within the target range of greater than 56 cal/g at 270°-370°K. Crystallization studies indicate that the solid/solid-phase transition can occur without excessive supercooling.

I. INTRODUCTION

In order to satisfy the requirements for potential applications of phase change materials in spacecraft,[1] it is necessary that new materials exhibit equilibrium temperatures within the range that would afford protection for spacecraft components; have high latent heats of transition; show low coefficients of thermal expansion; undergo transitions with small temperature ranges; not be prohibitive in cost; and be nonhazardous for manned space flight. Specific limitations have been outlined by George C. Marshall Space Flight Center. Transition equilibrium temperature should occur between 270° and 370°K, and the latent heat of transition should be greater than 56 cal/g. Ninety-five percent of the heat effect should occur within ± 5°K of the equilibrium temperature, and a maximum of 3°K supercooling below the equilibrium temperature should be required for initiation of the new phase. Thermal expansion should not exceed 15% between ± 50°K of the equilibrium temperature. The material must be stable within this range. The goal of this work is to find and characterize four materials that meet these requirements. The equilibrium temperatures of the four materials will preferably be nearly equally spaced between 270°K and 370°K.

The specific approach that is being followed in this work is to consider the potential usefulness of substances that exhibit mesocrystalline phases, and to select and characterize materials that exhibit high latent heats of transition between the crystalline and plastic crystalline states. The initial effort included a search of the literature to find new potential candidate materials or families of candidate materials in which changes in the transition temperatures can be effected by minor chemical modification. After the existence of a mesocrystalline phase in candidate materials was verified by qualitative differential thermal analysis, latent heats of transition of selected materials were determined by differential thermal calorimetry. The first objective of the research was to identify four candidate materials. Not only were pure substances considered, but also the possibility of the existence of eutectic mixtures.

General discussions of the theoretical aspects of plastic crystals and many examples of these substances can be found in the general references cited in this report. On the basis of the information summarized in these reviews, a number of the general properties characteristic of plastic crystals were used as criteria for the selection of new materials.

1. Plastic crystals are soft, waxy solids that can be extruded under considerably less pressure than ordinary crystals.

2. The ΔS_m of a plastic crystal is frequently small in comparison with the ΔS_t. Plastic crystals are sometimes defined as those substances in which the upper limit of ΔS_m is 5 e.u.

3. Plastic crystals have unusually high vapor pressures for solids.

4. Plastic crystals are usually higher melting than their non-plastic isomers. For example, neopentane becomes a plastic crystal at -142°C and melts at -16°C, while the isomer n-pentane does not form a plastic crystal, but melts at -141°C. Disorder may become so great in this solid state that substances may have very narrow liquid ranges. For example, 2,2,3,3-tetramethylbutane melts at 102°C and boils at 107°C.

5. Structurally, the molecules of a plastic crystal are characterized as "globular" in shape. Examples of substances that form plastic crystals include neopentane, adamantane, camphor and its derivatives, pentaerythritol, and cyclohexane and many of its derivatives. It should be emphasized that molecules in plastic crystals are not completely spherical, nor does free rotation occur in this phase. The diameter that will just circumscribe the freely rotating molecules, as in the liquid state, is always 15-20% greater than the distance between the centers of neighboring molecules in plastic crystals. For this reason, the volume change during the transition may be small.

II. MECHANISMS OF SOLID-SOLID TRANSITIONS

The initial step in the research included a search of the literature on substances known to exhibit solid-solid transitions and a review of the mechanisms and other phenomena related to these changes. Data were accumulated on substances known to exhibit a solid mesophase, including the transition temperatures and enthalpies, and summarized in Table A-1 to A-6 in Appendix I. The search was not limited to substances with transitions in the target temperature range since it was the purpose to use these data, together with the data to be accumulated on the experimental program, to establish correlations that would be useful in selecting target materials. Some generalizations based on the literature search that are relevant to the use of substances with solid-solid transitions as phase change materials can be made.

A. Solid-Solid Transitions as Order-Disorder Phenomena

Ubbelohde[1] considers the disorder in the melting process to be a result of two principal mechanisms. Positional disorder involves movement of the center of gravity of the particles; orientation disorder probably involves randomization of the axes of the molecules. Melting of crystals ordinarily includes both types of disorder, and the entropy of fusion is frequently a sum of the entropies for each type of disorder ($S_m = S_{pos} + S_{or}$).

Inert gases have no barrier to orientational disorder since they are perfectly spherical. Therefore, numerical values of the entropy increment for positional disordering can be given a norm from data for crystals of rare gases. Where contributions from zero point energy can be neglected, the entropy of positional disordering on fusion of these crystals is about 3.3 e.u.[1]

Some nearly spherical plastic crystals also have fusion entropies very close to three entropy units. At the fusion point they probably also only gain positional freedom. However, they undergo a solid-solid transition below the melting point, with an increase in entropy. This increased freedom can be attributed at least partly to orientational disorder.

The entropy of fusion for a structure that does not exhibit the mesocrystalline phase may approximate the sum of entropy of transition and the entropy of fusion for related materials with mesocrystalline phases. For example, ΔS_m for malonitrile, glutaronitrile, and acetonitrile are 7.9, 9.4, and 9.3 cal/mole-deg., respectively. Succinonitrile, which has a plastic crystalline phase, has a ΔS_t of 6.35 and a ΔS_m of 2.68, the sum being 9.03 cal/mole-deg.[2] Thus, in similarly structured molecules the entropy of transition in the material that exhibits a plastic crystalline phase may not be expected to be greater than the entropy of fusion of a material that undergoes simple melting.

Not only are order-disorder effects in transitions attributable to the onset of positional disorder and new orientations allowable by the alignment of molecular and crystal symmetry elements, but also to conformational disorder. Conformational disorder can lead to a very large number of new states of disorder and consequently to very high entropy changes.

Since positional disorder is not achieved as a condition of solid-solid transition, only a portion of the entropy change that would have occurred had the compound melted will be observed in the transition. However, the largest part of the entropy will occur in the transition because there is a relatively small difference in the number of statistically possible states in a liquid and a solid lacking only positional disorder. Some positional disorder may be achieved as the substance is heated through the plastic crystalline phase so that the entropy of melting may be exceedingly small.

The change of entropy in a phase transition is expressed by the relationship $\Delta S = R \ln (N_2/N_1)$, where N_2/N_1 is the ratio of the number of states of disorder statistically occupied in the two phases. Because some observed entropies of transition from one solid state to another are small, for example, of the order of 3 e.u., a large change in the ratio N_2/N_1 is not inherent in the transition from a crystalline to a rotor solid. In theoretical calculations of the energy contributions of various changes in compounds with large transitional heat effects, a large part of the entropy change must be attributed to new possible orientations of groups of atoms within the molecule. The change in the energy and geometry of the system during the solid-solid transition allows these new states that are not possible in the phase which is stable at lower temperatures. But in order to obtain a transition with a large heat effect, molecular reorientation must occur simultaneously with the freedom of groups to reorient within the molecule. Although the two types of effects may occur discretely so that several solid-solid transitions of relatively low heat effect may occur, the changes more often occur simultaneously and create the possibility for a large heat effect in the solid-solid transition.

Methods for deducing energy changes cannot usually be applied in solid/solid-phase transitions having entropy increments greater than 10 cal/mole-deg. such as pentaerythritol because orientations of very low or no symmetry occur as well as positional disorder and it becomes very difficult to identify the allowed orientations in the crystal lattice. Pentaerythritol with an entropy of transition of 22.8 e.u.[3] has approximately 6×10^4 times as many possible disordered states after it has gone into its second solid phase than it had in the first phase. Neopentane on the other hand with a transition entropy of 4.4 e.u.[4] has only approximately nine times as many states in its second solid phase as it does in the first phase.

Nitta[5] attributes 1,458 of those disordered states of pentaerythritol or 14.47 e.u. to the two possible positions of the CH_2 tetrahedron, nine total orientations for the oxygen atom, and 81 positions of the hydrogen atom. Pentaerythritol still has approximately eight positions which neopentane does not possess in addition to the 1,458 states Nitta analyzed.

In another attempt to correlate entropy increment of a more complex molecule with distinguishable orientations, Guthrie and McCullough[2] identified 120 possible orientations for 2-methyl-2-propanethiol and found good agreement for the experimental and calculated entropy increments.

For the fusion process, entropy changes of 8-15 e.u. are most frequently observed. Because of the molecular weight relationship, for a compound with an entropy change of 11 e.u., the molecular weight must not exceed 54 for the target heat of transition of 56 cal/g to be achieved at 273°K.

$$\Delta H \text{ (cal/g)} = \frac{\Delta S}{T \times \text{formula weight}}$$

The formula weight limitation makes it necessary that substances with much higher entropy changes, and therefore compounds in which there are a large number of new possible states, be selected to obtain a heat of transition of 56 cal/g. In small molecules, the large number of new states of conformational disorder can be best achieved through the presence of functional groups such as CH_2OH, NH_2, NO_2, and CN. Large increases in heat effects are observed when these groups are substituted for CH_3.

For compounds with similar symmetries (Table 1), a linear correlation can be obtained between enthalpy of transition and transition temperature.[2] Stated differently, materials with the same symmetries can be expected to exhibit similar numbers of random orientations in the same state, and therefore have the similar entropies of transition between the states. The analogy of this observation to Trouton's rule is apparent.

It is generally agreed that the principal factors that determine the existence of a mesocrystalline phase and its transition temperature are dipole-dipole and dispersion forces and molecular size and shape. The effect of shape and size is evident in the example of pentaerythrityl tetrafluoride which has a transition, while the tetrachloride, -bromide, and -iodide do not. On the other hand, groups with similar sizes and shapes can be interchanged in a structure without disrupting the formation of a mesophase. However, many of these groups have large differences in their dipole effects as well as their polarizability, which can account for the different temperature at which the transitions occur.

TABLE 1

TRANSITION AND FUSION DATA FOR COMPOUNDS WITH SIMILAR SYMMETRIES

	T_m (°K)	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_T (°K)	ΔH_T (cal/mole)	ΔH_T (cal/g)	ΔS_T (e.u.)
CH_4	90.68	225	14.03	18.7	20.5	1.17	0.91
CD_4	89.78	216	10.77	27.10 22.25			
CF_4	89.47	167	1.898	76.23	350	3.977	4.6
CMe_4	256.6	777.498	10.78	140	616	8.54	4.4
CCl_4	250.3	600	3.90	225.5	1,090	7.09	4.8
CBr_4	363.3	980	2.95	320.1	1,500	4.52	4.7
$C(SMe)_4$	338.7	990	4.9	296.4 318.7	1460 1820	7.29 9.08	5.71 4.93
$C(NO_2)_4$	286.15	987.22	5.04				5.7

B. Classes of Substances With Solid-Solid Transitions

Structural classes of compounds that exhibit a mesocrystalline phase include the following: Tetrahedral compounds, including neopentane and its derivatives, and the tertiary-butyl halides; octahedral molecules including ethane and disilane derivatives; cyclic compounds, including cyclohexane and its derivatives; and cage compounds, including adamantane, triethylenediamine, and camphor and its derivatives. The ability of each of these classes to form a rotor phase is associated with its near spherical or globular shape. The high degree of symmetry allows molecular reorientation to occur within the cubic face- or body-centered crystal structure. In other words, stable crystal structures exist in which centers of gravity of the molecules are spaced in such a way that reorientation can occur provided the reorientational changes do not sweep out too large a volume. The plastic crystalline state practically always occurs in substances with face- or body-centered crystal habits.[6]

More compounds with high entropy changes are known in the tetrahedral class; for example, pentaerythritol has an entropy change of 22.8 e.u. The chief reason for this observation is the ease of preparation and availability of functional derivatives of the tetrahedral nucleus with many potential states of disorder. Cyclic derivatives are often limited by having several solid-solid transitions with no single transition having a large heat effect. Known cage compounds usually have low heat effects, chiefly because very few multi-functional derivatives have been examined.

Entropy changes for transition for the parent hydrocarbon structures of tetrahedral, octahedral, cyclic, and cage structures represent minimum values for the series (Table 2). The transition entropy change for the tetrahedral neopentane and the octahedral 2,2,3,3-tetramethylbutane are approximately equivalent, indicating little difference in the ratio of the number of states of disorder in the two phases of each series. Hence, a difference in the inherent value of these structures is not apparent in these data except insofar as the possibility of a greater multiplicity of substitution that is possible in the octahedral structure.

A property of the octahedral structure not immediately evident in these data can be observed by the comparison of the data in Table 3. A rationalization of the marked difference in the entropy changes in the series can be demonstrated with molecular models with the assumption that the onset of rotation about the bond between the central carbon or silicon atoms occurs concurrently with the initiation of the mesocrystalline phase.

TABLE 2

TRANSITION DATA FOR VARIOUS HYDROCARBONS

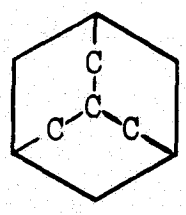
	T_T (°K)	ΔH_T (cal/g)	ΔS_T (e.u.)
Tetrahedral			
CH_4	20.5	1.17	0.91
$C(CH_3)_4$	140	8.54	4.4
Octahedral			
$(CH_3)_3CC(CH_3)_3$	152.49	4.18	3.14
Cyclic			
C_4H_8	145.7	24.31	9.36
C_5H_{10}	122.4	16.61	9.52
	138.1	1.18	0.60
C_6H_{12}	186.09	19.14	8.66
C_7H_{14}	134.8	12.09	8.81
	198.2	0.70	0.35
	212.4	1.09	0.51
C_8H_{16}	166.5	13.43	9.05
	183.8	1.02	0.62
Cage			
	131	10.26	7.53
	3.0	0.19	0.06
	164	9.91	6.66
	208.6	5.92	3.87

TABLE 3

TRANSITION DATA FOR SOME OCTAHEDRAL COMPOUNDS

	T_T (°K)	ΔH_T (cal/g)	ΔS_T (e.u.)
$(CH_3)_3CC(CH_3)_3$	152.49	4.18	3.14
$(CH_3)_3CCH(CH_3)_2$	121.4	5.85	4.83
$(CH_3)_2CHCH(CH_3)_2$	136.1	10.02	11.41
$(CH_3)_3CCH_2(CH_3)$	126.8	15.0	10.20
$(CH_3)_2C=C(CH_3)_2$	196.8	10.03	4.29
$(CH_3)_3SiSi(CH_3)_3$	221.9	15.92	10.5

Rotation about the central bond will be sterically restricted in the hexamethylethane and pentamethylethane derivatives; however, the restriction will be much less in the two tetramethylethane derivatives. Steric restrictions can be diminished not only by the removal of methyl groups, but also by the increase of the atomic radii of the central atoms. Thus, the entropy change for hexamethyldisilazane is similar to the entropy change for the two tetramethylethanes. When the rotation of the central bond is restricted by the multiple bonding, in tetramethylethylene, the lower entropy change is again observed. It is apparent that higher entropy changes are inherently possible in the octahedral structure through conformational disorder than in the tetrahedral structure.

The minimum entropy change for the cyclic hydrocarbons in Table 2 is about 9 e.u., a value that appears with remarkable consistency for cyclobutane, cyclopentane, cyclohexane, cycloheptane, and cyclooctane. It is usually assumed that the transition to the mesocrystalline state in the cycloalkanes is associated with rotational reorientations. However, it is not uncommon for the cycloalkanes and their derivatives to show a series of transitions, each of which can be associated with a new type of molecular freedom. Interconversion of the various isomers possible in the cycloalkane series can be one of the ways in which new randomness can be introduced into the molecule.

C. Volume Changes

Volume changes observed in the formation of a rotor phase are usually of the order of 5-10%. For example, Nitta[7] found that the volume change of pentaerythritol at the transition point was 9.08% of the volume at 20°C.

A portion of the entropy effect is the contribution of the volume change at the transition. Little data are available for estimating this change. The entropy contribution of volume to the solid-solid transition in succinonitrile is reported as 0.15 cal/mole-deg. Wulff and Westrum[8] calculated this entropy increment from a volume change of 7.8% on the basis of the relationship $\Delta S = R \ln V_2/V_1$.

D. Functional Group Effects

From the survey of known plastic crystalline materials, it is apparent that a parent structure can be subject to considerable chemical modification without changing its ability to form the mesocrystalline phase. For example, not only does cyclohexane form plastic crystals, but in addition, the following derivatives behave similarly: Cyclohexanol, cyclohexanone, chlorocyclohexane, trifluoromethylcyclohexane, cyclohexene, and cyclohexyl nitrile.

Although the effects of functional groups on heat changes are likely to be of considerable importance in the selection of materials with high enthalpy changes, the data and correlations are meager. In Table 4, the marked effect of functional group substitution can be observed for a series of symmetrically substituted compounds. Compounds in which a series is formed by substituting a single group are reported in Table 5. On the basis of data available before this investigation, few meaningful correlations could be drawn.

E. Initiation and Propagation of the New Phase

Lack of specific knowledge concerning the process of phase changes in the solid state is exemplified by the different opinions that can be found in the literature relative to the mechanism. Some claim that the process is a simple one of reorientation requiring just a single shift in atomic centers to form a new lattice. An example that can be cited is the martensitic transformation from a face-centered cubic to a body-centered tetragonal structure during the hardening of steel. The atomic displacements are very small (about a lattice distance) and essentially no diffusion is required. Because of the rapidity of the change (about 10^{-4} sec.),

TABLE 4

TRANSITION AND FUSION DATA FOR SOME SYMMETRICALLY SUBSTITUTED COMPOUNDS

	T_T (°K)	ΔH_T (cal/g)	ΔS_T (e.u.)
$C(CH_3)_4$	140	8.54	4.4
$C(CH_2F)_4$	249.7	21.91	12.7
$C(CH_2OH)_4$	457	76.53	22.8

TABLE 5

TRANSITION AND FUSION DATA FOR SOME UNSYMMETRICALLY SUBSTITUTED COMPOUNDS

	T_T (°K)	ΔH_T (cal/g)	ΔS_T (e.u.)
$C(CH_3)_4$	140	8.54	4.4
$C(CH_3)_3Cl$	183	3.43	6.32
	220	15.01	2.24
$C(CH_3)_3OH$	286.14	2.67	0.69
$C(CH_3)_3SH$	151.6	10.78	1.16
	157.0	1.72	0.99
	199.4	2.56	6.41

it is usually not possible to suppress the transformation by very rapid cooling to low temperatures where atomic diffusion is slow, a procedure that is effective for the suppression of most processes that do depend on diffusion.[9] The claim has been made elsewhere that there is no predictable connection between the parent and the daughter phase and therefore a solid-solid transition does not differ in nature from the transformation of a liquid to a solid.[9] If the first opinion is true, supercooling should not be a problem between phases; if the second opinion is true, the usual consideration of nucleation should be applicable.

III. QUALITATIVE STUDIES

It was the purpose of the qualitative studies to develop additional criteria for the existence of a solid mesocrystalline state in substances and for predicting the temperature at which the transition between the two solid states occurs. In the course of the screening work at least 33 substances were found with previously unidentified solid-solid transitions.

A large number of substances were examined in the screening step by qualitative differential thermal analysis. Most of the substances were chosen for examination for one of the following reasons: Narrow liquid range, ease of sublimation, low fusion entropy, or structural similarity to other substances with solid mesocrystalline phases. The results of these screening experiments are recorded in appropriate tables in the experimental section and classified on the basis of the substances' correspondence to the various structural types of plastic crystals: Tetrahedral, octahedral, cyclic, or cage. It should be pointed out that only the specified temperature ranges were examined and that some of the substances may exhibit solid-solid transitions outside those temperature ranges.

A. Tetrahedral Substances

Although the existence of a mesocrystalline phase could be predicted with some degree of reliability, many substances that appeared to meet the necessary criteria did not have transitions. Some of the results are summarized in Figure 1. In the alcohol series transitions are observed for compounds substituted with one, two, three, or four hydroxy groups; however, substitution of an ethyl group for hydroxymethyl group, both of which should occupy about the same space, inhibits the transition. Transitions are also observed in all the examples of hydroxy-substituted nitro compounds. It is then surprising that the first two

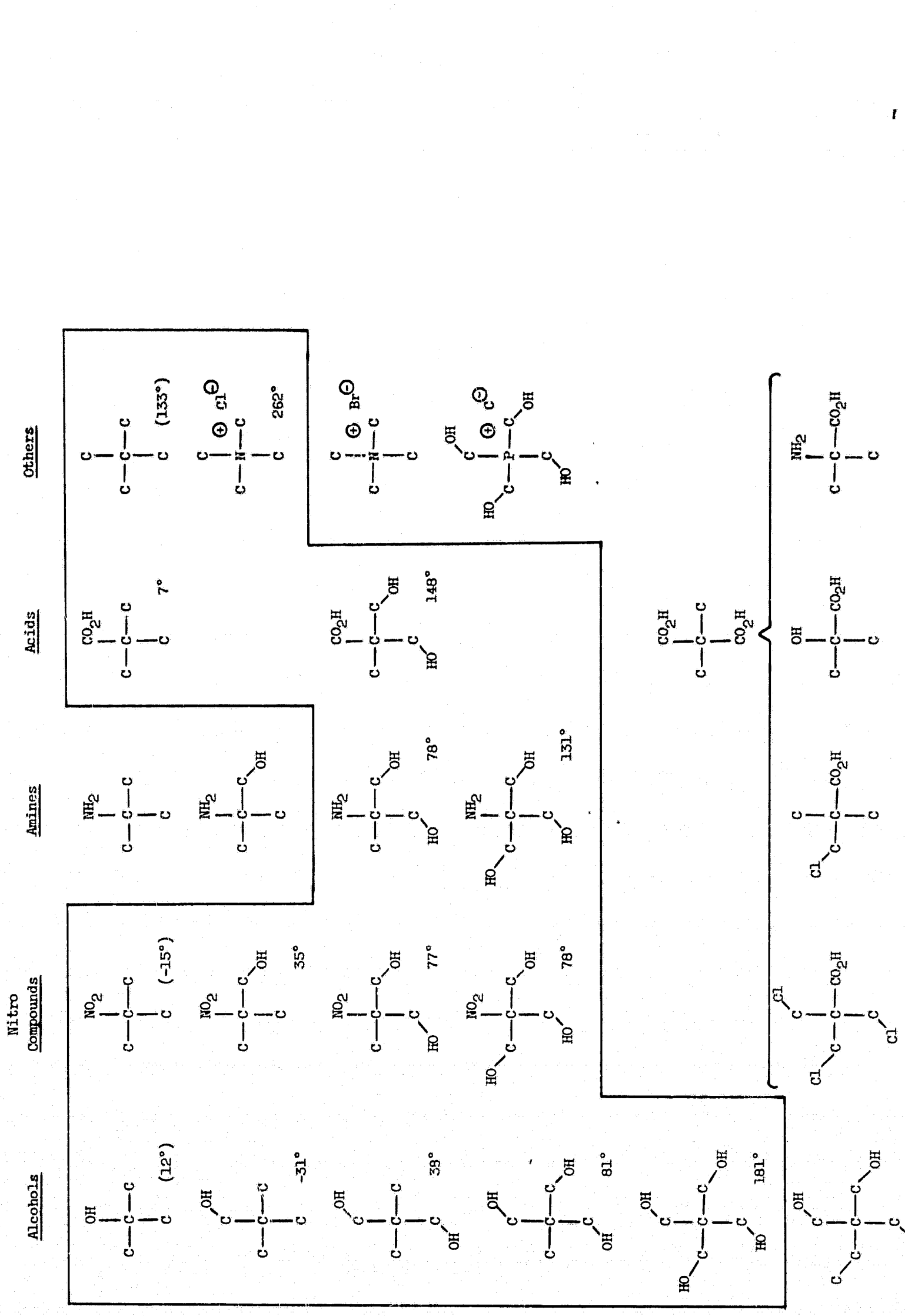
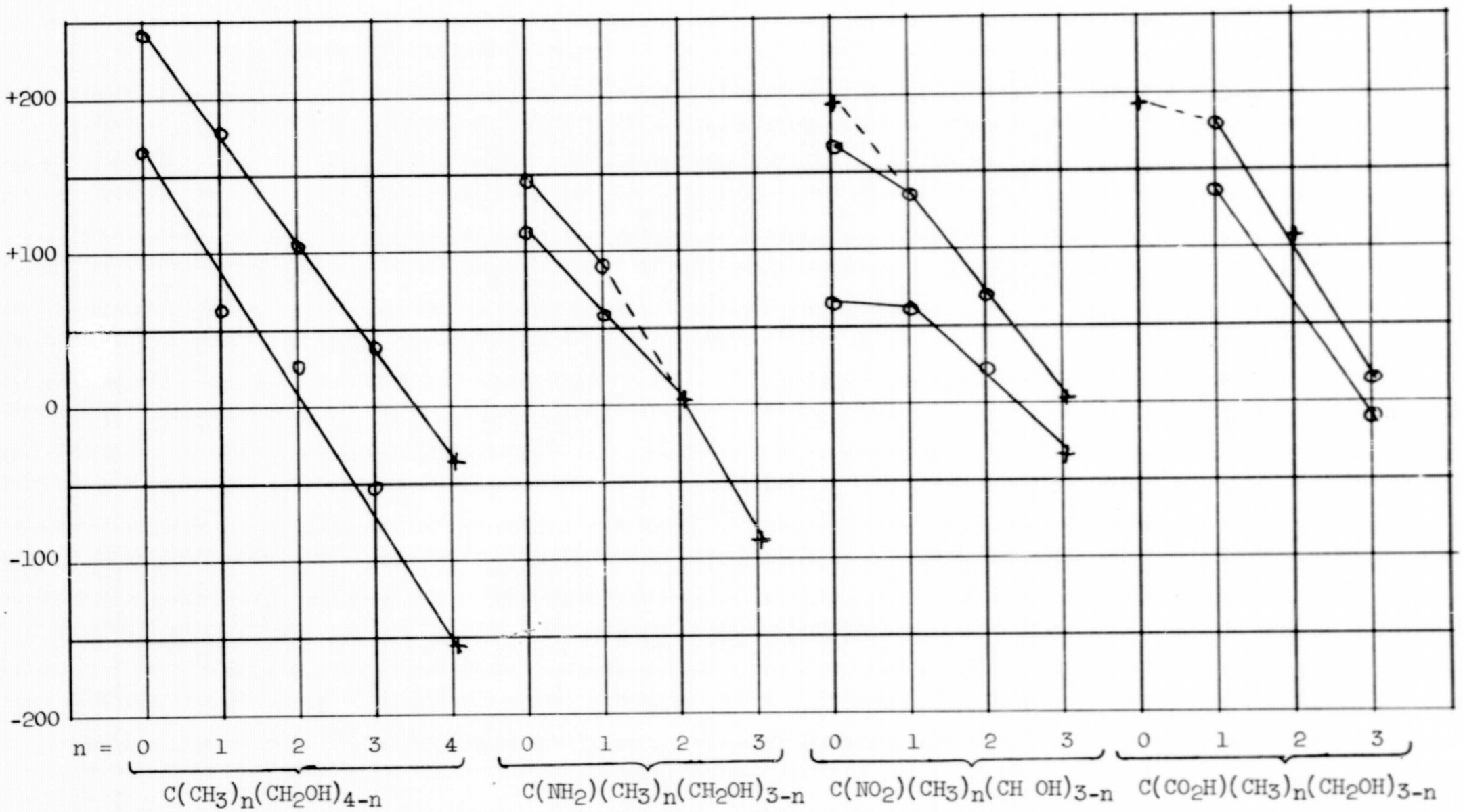


Figure 1 - Mesocrystalline Phase in Tetrahedral Substances
(Substances in enclosed area have solid-solid transitions. Their transition temperatures in °C are shown.)

substances in the amine series do not exhibit transitions. The available hydroxy-substituted acids seem to indicate that a mesocrystalline phase can be expected throughout the series, but other acid derivatives that meet the structural criteria do not exhibit a phase change. These acids include dimethylmalonic acid, tris(chloromethyl)acetic acid, β-chloropivalic acid, 2-methyllactic acid, and α-aminoisobutyric acid. Although one substance with a heteroatom at the center of the tetrahedron had a plastic crystalline phase, similar substances did not. The presence of a mesophase in tetramethylammonium chloride and the absence of one in tetramethylammonium bromide is particularly surprising since the tetramethyl ammonium cation should be the species that contributes new disorder at the transition.

Large molecules often do not show transitions. It is known that pentaerythrityl fluoride has a transition while pentaerythrityl chloride and bromide do not. In this work the highly symmetrical pentaerythrityl tetraacetate, and tetramethylsulfonate as well as tetra-t-butyl thiopentaerythritol did not. All phenyl-substituted tetrahedral substances that were examined did not have solid-solid transitions. However, mesocrystallinity should not be ruled out on the basis of size alone since tetrakistrimethylsilylsilane does exhibit a solid-solid transition. It is probable that with large molecules, it is more difficult to meet the symmetry requirements for a rotor solid.

Since the tetrahedral group contains series with progressive substitution of functional groups, it is possible to make some correlations that allow the prediction of fusion and transition temperatures. In Figure 2, the regularity of the increments in the fusion temperatures of pentaerythritol, 2-methyl-2-hydroxymethyl-1,3-propanediol, 2,2-dimethyl-propanediol, neopentyl alcohol, and neopentane are evident, and a similar, though not so regular, correlation can be made for the transition temperatures. Similar correlations are also made for the amine, nitro, and acid series. In all the series, good correlations are obtained between results from this work and literature values. The point for 2-amino-2-methyl-1-propanol was taken from the literature although the materials were also studied in this work. The material that was examined exhibited a broad fusion range even after two careful distillations on an efficient distillation column; therefore, the existence of a solid-solid transition cannot be entirely precluded, but if one does exist the mesocrystalline range must be so small that it cannot be determined by differential thermal analysis. The failure of the reported melting point to fall on a straight line with the melting points of the higher members of the series is reasonable evidence that there is no mesocrystalline phase.



0 = This work.
x = Literature Values.

Figure 2 - Correlation of Transition and Fusion Temperatures of Tetrahedral Substances

Values were obtained for the most highly substituted members of the nitro and acid series that were lower than expected. A value is reported in the literature for 2-hydroxymethyl-2-nitro-1,3-propanediol that falls on a straight line with other substances in the series. However, the lower value, also reported in the literature and obtained in this work, was also a decomposition temperature so may not accurately represent the fusion of the pure compound. The transition temperature, also lower than expected, would not be affected by this consideration.

A similarly low value was found in the literature for the most highly substituted compound in the acid series. A sample of this acid, bis(hydroxymethyl)hydracrylic acid, will become available in the near future, and it will be of considerable interest to determine the fusion and transition temperatures of a pure sample.

All of the initial screenings were carried out on samples in the purity they were received in order that a broad spectrum of structural types could be examined. Subsequently, however, some of the tetrahedral compounds were subjected to recrystallization or sublimation as a check of their purity. The best values obtained for the fusion temperatures are compared in Table 6 with melting points reported in the literature. The literature values are probably mostly capillary values and therefore interpreted as occurring in a narrower temperature range than would be obtained by differential thermal analysis. The fusion temperature for plastic crystals is a relatively good index of purity. Since molar freezing point depression is inversely proportional to the heat of fusion, the lower heats of fusion would cause the fusion temperatures to be more depressed than the transition temperatures. The best comparison of values is probably the upper temperature of the temperature range obtained by the two methods.

During the recrystallizations, no attempt was made to protect the substances from contact with atmospheric moisture. This failure probably led to the observation that the melting points of two of the tetrahedral substances, 2-amino-2-hydroxymethyl-1,3-propanediol and 2-methyl-2-nitro-1,3-propanediol, decreased on successive recrystallizations. The 2-amino-2-hydroxymethyl-1,3-propanediol could be restored to its original purity through two sublimations with adequate precautions against contact with moisture. When the melting point of the compounds was taken five months after it had been received and the container had been opened numerous times, the melting point had decreased about 10°. In any case, it appears that the absorption of moisture can be a significant contaminant in some of the materials.

TABLE 6

COMPARISON OF FUSION TEMPERATURES OBTAINED BY DIFFERENTIAL THERMAL ANALYSIS WITH LITERATURE VALUES

Substance	Best Value (This Work) (°C)	Reported Value (°C)	Reference
Pentaerythritol	258-260	263	a
		265.8	b
2-Hydroxymethyl-2-methyl 1,3-propanediol	197-198	202-203	c
2,2-Dimethyl-1,3-propane-diol	125-126	126-127	d
Neopentyl alcohol	51-55	54.4-55.5	e
2-Amino-2-hydroxymethyl-1,3-propanediol	166-169	169-170	f
2-Amino-2-methyl-1,3-prop-anediol	107-109	108-110	g
2-Amino-2-methyl-1-propanol	12-20	23-25	g
2-Hydroxymethyl-2-nitro-1,3-propanediol	dec. 184	168 dec.	h
		172	i
		180	j
		214	j
2-Methyl-2-nitro-1,3-prop-anediol	150-154	154-156	j
		146-147	g
2-Methyl-2-nitro-1-propanol	88-89	87-88	k
2,2-Bis(hydroxymethyl)prop-ionic acid	194-197	183	l
		192-194	j
Pivalic acid	32-36	35.5	m

a/ Reference 10
b/ Reference 11
c/ Reference 12
d/ Reference 13
e/ Reference 14
f/ Reference 15
g/ Reference 16
h/ Reference 17
i/ Reference 18
j/ Reference 19
k/ Reference 20
l/ Reference 21
m/ Reference 22

B. Octahedral Substances

Relatively few octahedral substances were examined because few were available. Several examples are shown in Figure 3. Tetramethylsuccinic acid and tetramethylsuccinonitrile were of some interest because of their functional group substitution. Some of the substances that did not show a solid-solid transition may well have one below the temperature range examined, which was frequently from about -60°C to the melting point.

C. Cyclic Substances

In spite of the many cyclic compounds that are known to have solid state transition, relatively few new ones were found in the screening. Some of these are shown in Figure 4. A number of the functional derivatives shown in Figure 4 did not have solid state transitions even though substances with the same functional groups in the other series did exhibit transitions. The frequently observed phenomenon of multiple transitions often observed in cyclic compounds was also found in this work.

The very specific requirement for substitution of groups on a cyclic nucleus can be illustrated by the report that methyl substitution of cyclohexane in position 1,1 and cis-1,2 reduces the entropy of melting while substitution in any other position seems to actually inhibit rotation in the solid state, increasing the entropy fusion over that of the parent cyclohexane, which also shows a transition.

Sugars were considered as possible candidates because of their many hydroxy groups, high melting points, and sometimes-observed sublimation properties. However, none of the sugars proved to have a mesocrystalline phase.

The cyclobutane derivatives, 2,2,4,4-tetramethyl-1,3-cyclobutanediol and its dione, have narrow liquid ranges; in fact, the range of the dione is only 47°C, but neither showed a solid-solid transition.

D. Cage Substances

From examples of cage materials that were examined (Figure 5), the variety of cage configurations that exhibit transitions is apparent. The greater tendency for derivatives of the parent structures to exhibit solid-solid transitions makes this series somewhat more flexible than the cyclic series. Unfortunately, the availability of functional derivatives of cage substances is very limited.

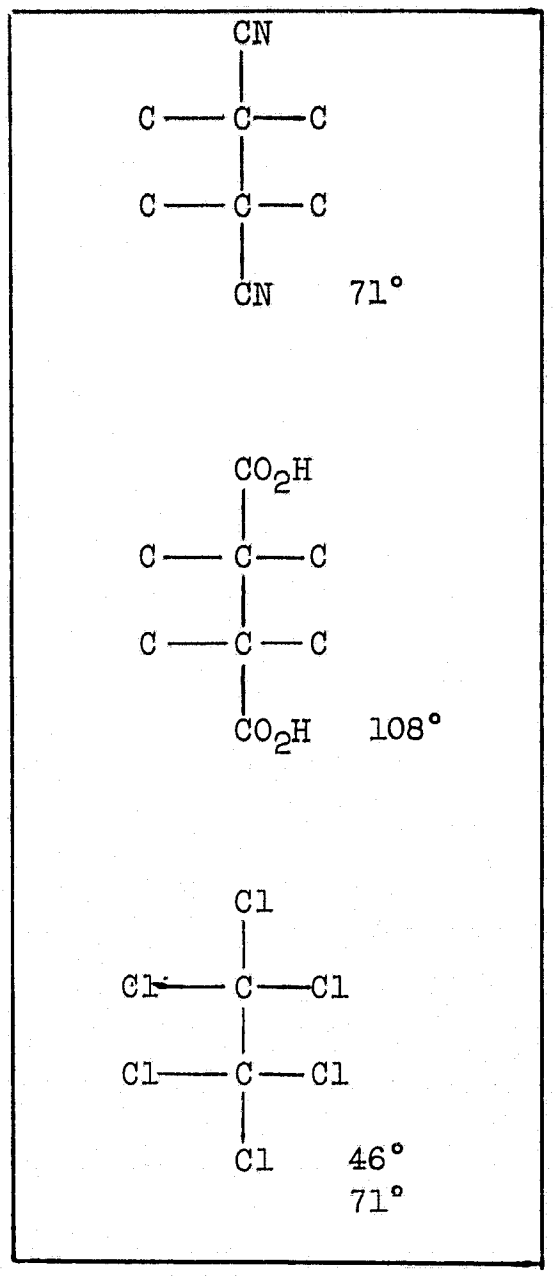
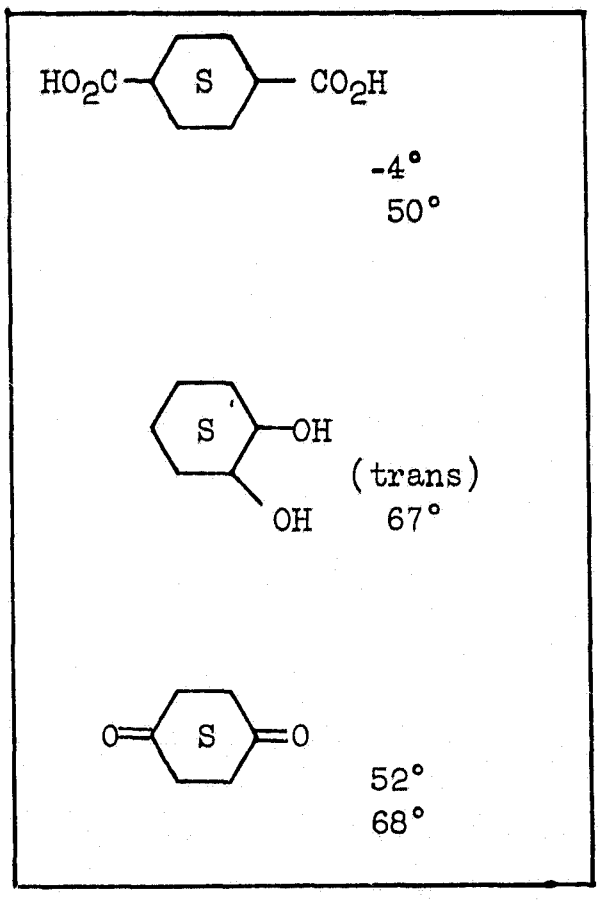
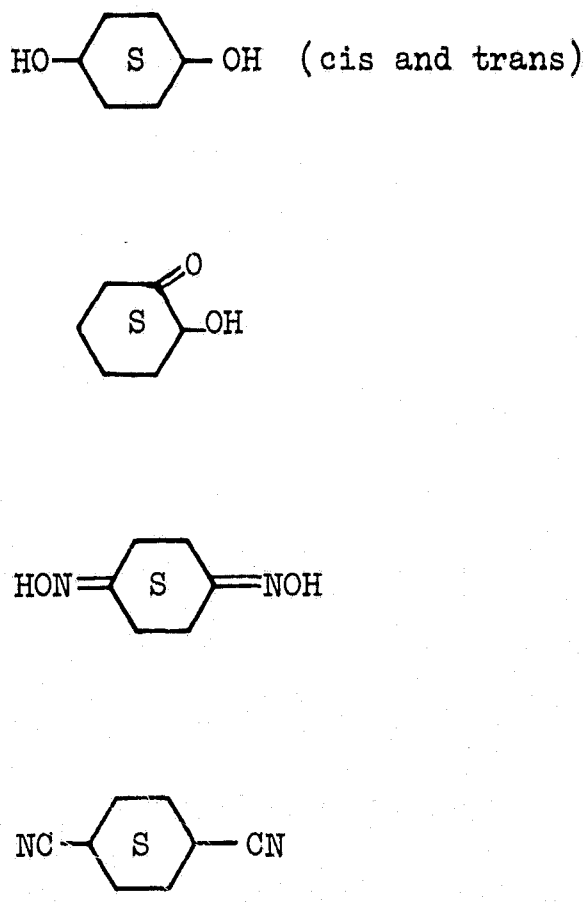
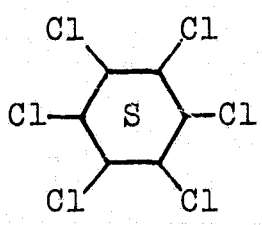


Figure 3 - Mesocrystalline Phase in Octahedral Substances. (Substances in enclosed area have solid-solid transitions. Their transition temperatures in °C are shown.)







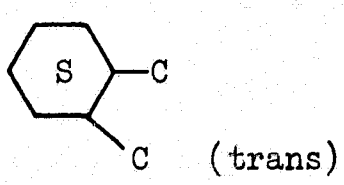


Figure 4 - Mesocrystalline Phase in Cyclic Substances (Substances in enclosed area have solid-solid transitions. Their transition temperature in °C are shown.)

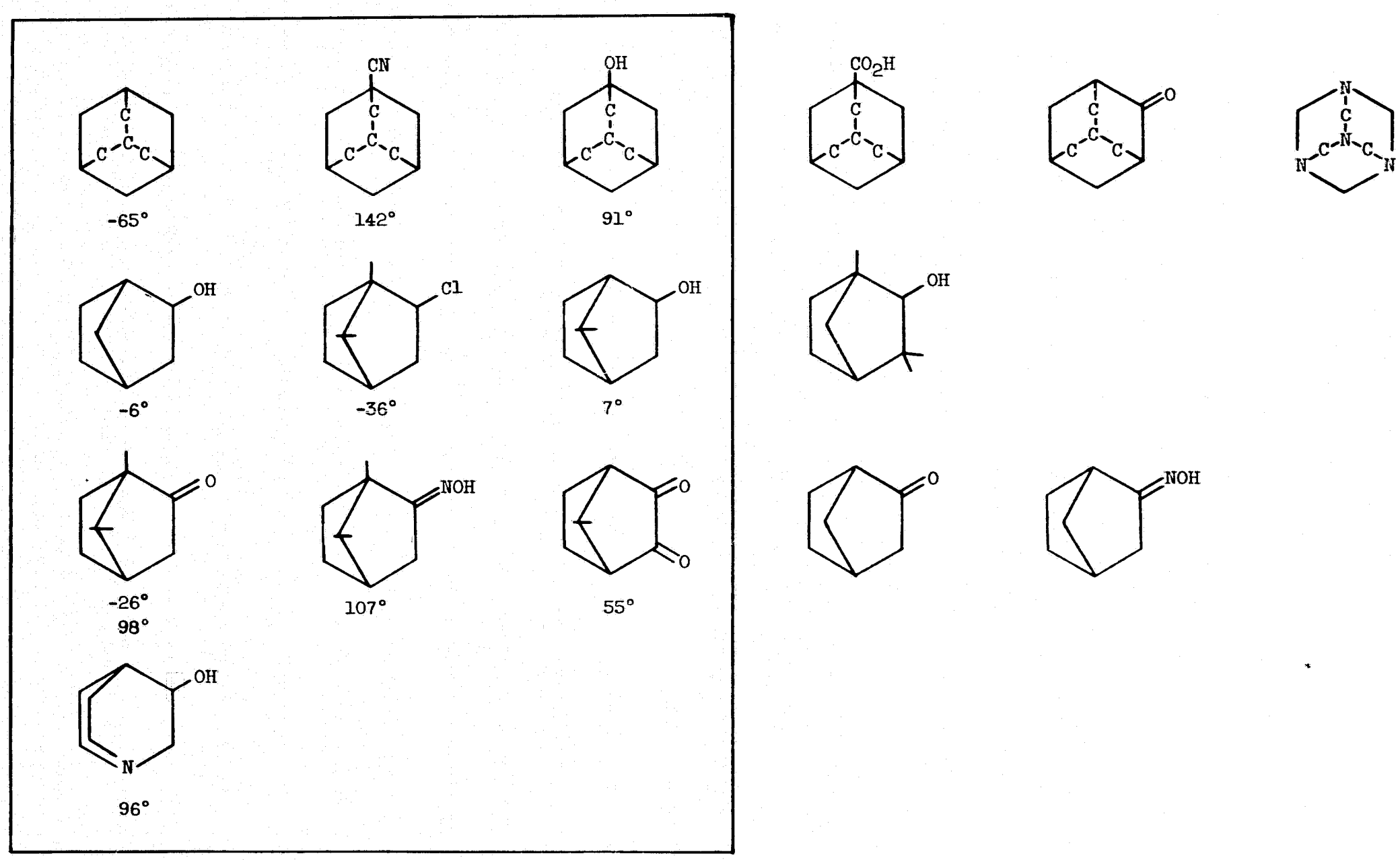


Figure 5 - Mesocrystalline Phase in Cage Substance
(Substances in enclosed area have solid-solid transitions. Their transition temperature in °C are shown.)

IV. QUANTITATIVE STUDIES

The actual selection of candidate structures for thermal control applications must depend upon the quantity of heat absorbed or liberated during transitions. A substantial portion of the effort has been concerned with determination of heats of transition by differential thermal calorimetry and the correlation of these values with chemical structure. Because of the need to establish structural criteria and correlations, the determinations were not limited to those substances with large enthalpies.

A. Procedures and Calibration

Two series of enthalpy data were obtained. Throughout the initial work in obtaining the enthalpy data reported as Series I, a great deal of difficulty was encountered in obtaining adequate repeatability with the calorimeter cell. Subsequently, the cell was examined by the manufacturer's representative and found to be defective in a manner that accounted for the erratic results. A replacement cell was obtained and used in determining the Series II data. Although the Series II data are much more reliable than the Series I data, differences in the results for many of the substances were not extremely large.

Establishing a calibration for the calorimetor provided some difficulty, particularly with respect to finding reliable standards within the 0° to 100°C temperature range. Ultimately, the most satisfactory calibration procedure was to plot a calibration curve based on the mercury, acetamide, indium, and tin points. Average values for calibration runs for the fusion of p-dichlorobenzene and for the transitions of ammonium nitrate and pentaerythritol varied 6% or less from the calibration curve in Series II. The variability of the values obtained in the individual experiments used to calculate the averages was reasonably small: less than $\pm$ 1% for 53% of the data; less than $\pm$ 2% for 84% of the data; and less than $\pm$ 3% for 92% of the data. Thus, the magnitude of the differences in values for the calibration coefficients of p-dichlorobenzene, ammonium nitrate, and pentaerythritol cannot be attributed to experimental variation in this work, but must be attributed to other factors such as sample purity, procedural differences in obtaining data, or errors in the literature values. A possible source of difference between literature data based on conventional calorimetry and differential scanning calorimetry is that heats of solidification are usually obtained in the former while heats of fusion are obtained in the latter. The two values may not be identical because all the new degrees of freedom contributing to the heat fusion process may not be frozen out in the solidification process and, consequently, the heat of fusion may exceed the heat of solidification.

A comparison of experimental heats of fusion and transition based on the Series II calibration curve with literature values is provided in Table 7.

The difference in the reliability of Series I and Series II data is reflected in the scatter of the values for individual determinations of standards. In Series I, the maximum scatter for 95% of the data was 14.3% while for Series II the maximum scatter for 95% of the data was 4.1%.

A summary of the data obtained in Series I and Series II experiments is given in Tables 8 to 10. Since the scatter was so large in the Series I data, no effort was made to sort out unacceptable data in establishing the averages reported in the tables. In computing averages for Series II, all values that introducted a variation greater than $\pm$ 5% for enthalpies greater than 10 cal/g and $\pm$ 10% for enthalpies less than 10 cal/g were not used. Enthalpy data for a number of substances fell within these limits, and when the procedures in the determinations are considered, such a variation is not unreasonable. Variability greater than that amount in the experimental work can probably be attributed to procedural error or lack of definition of the system.

Several other procedural variables were examined. Less erratic results were obtained with hermetically sealed calorimeter pans. Within the limits examined, sample weight did not have a significant effect on the results. A heating rate of 10°/min was used throughout the experimental work. Changes in heating rates caused significant differences in enthalpy values when calculations were based on the 10°/min calibration, but error introduced by small variations in the heating rate was less at 10°/min than at slower rates.

B. Interpretation of Quantitative Experiments

It is readily apparent from Tables 8 to 10 that the only substances that have been identified with heats of transition above 56 cal/g are in the tetrahedral series. Heat effects, in general, were greater in the tetrahedral series than in the octahedral, cyclic, or cage series. It is assumed that the reason for this observation is due at least in part to the greater availability of multiply substituted derivatives of the tetrahedral nucleus. Since highly substituted tetrahedral substances are more readily prepared than the corresponding octahedral or cage structures, it seems more probable that target materials will be found in the tetrahedral class.

TABLE 7

COMPARISONS OF SELECTED EXPERIMENTALLY DETERMINED HEATS OF FUSION AND TRANSITION WITH LITERATURE VALUES

	ΔH (cal/g)	
	Literature	Experimental
Neopentyl alcohol (fusion at 324°K)	12.02[a]	11.02
Hexachloroethane (transition at 344°K)	8.29[b]	6.37
Camphorquinone (fusion at 472°K)	9.66[c]	8.12
Acetamide (fusion at 352°K)	63.5[d]	63.57
Pivalic acid (fusion at 305°K)	7.84[c]	5.75
Pentaerythritol (transition at 454°K)	76.53[e]	72.48
Pentaerythritol (fusion at 528°K)	12.67[e]	8.80
Ammonium nitrate (transition at 298°K)	12.62[d]	13.15
Ammonium nitrate (transition at 357°K)	3.998[d]	4.21

a/ Reference 23 (The reference incorrectly states the fusion temperature as 264°K)
b/ Reference 24
c/ Reference 25
d/ Reference 26
e/ Reference 3

TABLE 8

SUMMARY OF ENTHALPY DATA FOR TRANSITIONS AND FUSIONS: TETRAHEDRAL SUBSTANCES

Compound	Heat of Transition (cal/g) Series I	Heat of Transition (cal/g) Series II	Heat of Fusion (cal/g) Series II
Pentaerythritol	--	72.48	8.80
2-Hydroxymethyl-2-methyl-1,3-propanediol	48.31	46.02	10.67
2,2-Dimethyl-1,3-propanediol	33.58	31.30	10.82
Neopentyl alcohol	10.30	12.74	11.02
2-Amino-2-hydroxymethyl-1,3-propanediol	62.29	67.61	6.00
2-Amino-2-methyl-1,3-propanediol	55.47	63.38	7.58
2-Hydroxymethyl-2-nitro-1,3-propanediol	32.95	39.33	(decomposes)
2-Methyl-2-nitro-1,3-propanediol	46.55	47.66	7.65
2-Methyl-2-nitro-1-propanol	--	34.46	7.45
2,2-Bis(hydroxymethyl)propionic acid	69.48	68.64	6.41
Pivalic acid	18.07	20.49	5.75
Trimethylacetonitrile	---	1.86	--
Tetramethylammonium chloride	26.50	22.86	--
Ammonium nitrate (I)	3.21	5.54	--
(II)	3.70	4.21	
(III)	11.73	13.15	
Tetrakis(trimethylsilyl)silane	8.24	8.42	8.29

TABLE 9

SUMMARY OF ENTHALPY DATA FOR TRANSITIONS AND FUSIONS:
CAGE SUBSTANCES

Compound	Heat of Transition (cal/g) Series I	Heat of Transition (cal/g) Series II	Heat of Fusion (cal/g) Series II
3-Quinuclidinol	34.41	28.49	14.26
Adamantane carbonitrile	2.08	2.41	--
1-Adamantanol	19.11	19.44	--
Adamantane	--	4.80	--
dl-Camphorquinone	22.56	16.86	8.12
d-Camphor	15.17	18.36	9.35
Camphene	5.47	5.53	5.46
dl-Camphorsulfonic acid	20.40	--	--
dl-Isoborneol	3.69	3.05	--
5-Norbornene-2,3-dicarboxylic acid	23.27	--	--
Norborneol	3.45	--	--
d-Camphor oxime	0.86	--	--
Dicyclopentadiene dioxide	4.27	--	--
Bornyl chloride	0.86	--	5.56
Tris(propan-2-ol)amine borate	2.60	--	--

TABLE 10

SUMMARY OF ENTHALPY DATA FOR TRANSITIONS AND FUSIONS: CYCLIC, OCTAHEDRAL, AND MISCELLANEOUS SUBSTANCES

Compound	Heat of Transition (cal/g) Series I	Heat of Transition (cal/g) Series II	Heat of Fusion (cal/g) Series I	Heat of Fusion (cal/g) Series II
Tris(trimethylsilyl)amine	7.80	8.53	--	1.81
Tetramethylsuccinonitrile	28.96	31.77	--	12.54
Tetramethylsuccinic acid	18.38	18.43	--	8.88
Hexachloroethane	--	(I) 2.63 (II) 6.37	--	--
Dihydroxymaleic acid	28.51	--	--	--
2,3-Dimethylsuccinic acid	6.89	--	--	--
Succinamide	11.24	--	--	--
1,4-Cyclohexanedione	12.28	13.15	22.88	--
2,2-Bis(hydroxymethyl)-1-butanol	--	--	38.86	33.95
2-Amino-2-methyl-1-propanol	--	--	31.11	18.26
Pentaerythritol tetramethanesulfonate	--	--	26.57	--
Tetra-t-butylthiopentaerythritol	--	--	14.05	--
Thioacetamide	--	--	75.16	62.26
Acetamide	--	--	76.15	63.57
Chloral hydrate	--	--	50.64	--
Hexadecane	--	--	58.64	48.80

Some relatively high heat values were observed in the cage series for 3-quinuclidinol and 1-adamantanol, considering that each of these substances is substituted by only a single hydroxy group. The increase in the entropy increment for the transition of adamantane from 3.1 e.u. to 8.1 e.u. for 1-adamantanol reflects the substitution of this hydroxy group. The low values of the entropy increment for the parent structure indicate the rigidity of the cage and the few possible states of disorder in the transition.

In the octahedral series tetramethylsuccinonitrile gave a relatively high entropy of transition (12.6 e.u.). The relatively low value for tetramethylsuccinic acid (8.4 e.u.) in comparison with the entropy change for the parent structure, tetramethylbutane (3.1 e.u.), suggests that possible reorientations are inhibited by the crowding of groups.

The consequence of lowering heats effects through the crowding of groups seems to be of particular importance in the octahedral series and seems to inherently limit this series even though it would appear to be capable of many more reorientational possibilities than the tetrahedral series. However, this effect can also be observed in the heats of fusion of two highly substituted pentaerythritol derivatives, pentaerythritol tetramethanesulfonate and tetra-t-butylthiopentaerythritol.

Heats of fusion were also determined for several substances, thioacetamide, acetamide, hexadecane, and chloral hydrate, which would be expected to exhibit large enthalpies. Both acetamide and thioacetamide had heats of fusion of about 63 cal/g. In spite of its high molecular weight, chloral hydrate had a heat of transition of 50.6 cal/g (ΔS = 24.2 e.u.) making the consideration of the fluorine analogues attractive.

Another interesting observation concerning the tetrahedral compounds is that the entropy increment for tetramethylammonium chloride, 4.7 e.u., is practically the same as the reported value for neopentane, 4.4 e.u. Such a result should be expected since the cation of tetramethylammonium chloride is isoelectronic and isosteric to neopentane. The contribution of the anion of the salt to formula weight, however, will make such salts have inherently lower heats of transition.

Entropy data for certain substances in the tetrahedral series are summarized in Table 11. Although changes in the entropy increments with regular changes in structure are not always additive, it is apparent that a number of examples can be cited in which the substitution of a methylol group for a methyl group increases the entropy increment by about 5 e.u. Increasing the extent of functional substitution generally does increase the entropy increment. Several anomalies, however, merit comment.

TABLE 11

SUMMARY OF ENTHALPY AND ENTROPY CHANGE DATA TRANSITIONS IN VARIOUS SUBSTANCES

Compound	T (°K)	ΔH (cal/g)	ΔS (e.u.)
Neopentyl alcohol	242	12.7	4.6
2,2-Dimethyl-1,3-propanediol	313-316	31.3	10.3
2-Hydroxymethyl-2-methyl-1,3-propanediol	354	46.0	15.6
Pentaerythritol	454-456	72.5	21.7
2,2-Bis(hydroxymethyl)-1-butanol (fusion)	329-332	34.0	13.9
2-Amino-2-methyl-1-propanol (fusion)	285-293	18.3	5.7
2-Amino-2-methyl-1,3-propanediol	349-354	63.4	19.1
2-Amino-2-hydroxymethyl-1,3-propanediol	404-407	67.6	20.3
2-Methyl-2-nitro-1-propanol	308-312	34.5	13.3
2-Methyl-2-nitro-1,3-propanediol	353-356	47.7	18.2
2-Hydroxymethyl-2-nitro-1,3-propanediol	351-354	39.3	16.9
Pivalic Acid	280-282	20.5	7.5
2,2-Bis(hydroxymethyl)propionic acid	425-428	68.6	21.7

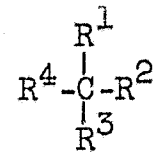
Although there is a regular increase of about 5 e.u. through the series, neopentyl alcohol, 2,2-dimethyl-1,3-propanediol, 2-hydroxymethyl-2-methyl-1,3-propanediol, pentaerythritol, the value for neopentyl alcohol is nearly the same as the literature value for neopentane, 4.4 e.u. The reason for the similar number of new states of disorder in the transitions for these two substances is obscure.

The lower-than-expected fusion and transition temperatures for 2-hydroxymethyl-2-nitro-1,3-propanediol were observed earlier in this report, and it is shown in Table 11 that the compound also has a smaller entropy increment for transition than 2-methyl-2-nitro-1,3-propanediol. Most similar pairs of substances in which a methyl group is substituted by a methylol group show an increase of about 5 e.u. One possible cause for this anomaly could be that the large size of the nitro group sterically inhibits certain modes of disorder in such a highly substituted substance. However, a related pair of compounds, 2-amino-2-methyl-1,3-propanediol and 2-amino-2-hydroxymethyl-1,3-propanediol, in which the same kind of substitution occurs show an increase of only 0.8 e.u. This observation in the amino derivative, which would not be subject to the steric restrictions of the nitro group, suggests that the limitation is not steric.

Originally, it had been assumed that there was nothing peculiar to the possibility of a mesocrystalline state in a given substance that would allow a higher entropy of transition than would be observed in the fusion of a similar structure, provided approximately the same number of new degrees of orientational freedom were possible in the two substances. If this reasoning is followed, the entropy of transition of 2-hydroxymethyl-2-methyl-1,3-propanediol should be less than the entropy of fusion of 2,2-bis(hydroxymethyl)-1-butanol, but the entropy change actually increases by 1.7 e.u. More striking is the comparison between the entropy change in 2-amino-2-methyl-1-propanol and 2-methyl-2-nitro-1-propanol. Both substances should have the same number of new orientational possibilities, but the amino derivative, which does not have a plastic crystalline phase, exhibits an entropy change of 5.7 e.u. while the nitro derivative, which does have a mesocrystalline phase, exhibits an entropy change of 13.1 e.u.

Since the number of reorientational and translational degrees of freedom for the two pairs of substances would be approximately the same in the liquid state, it must be assumed that fewer degrees of freedom may be possible in the low temperature phase for the highly symmetrical substances that can undergo mesocrystalline transformations. Under these circumstances, a greater entropy change would be observed. Although this observation has been made on relatively few substances, it opens the possibility that large heat changes may be inherently associated with the mesocrystalline transformation, particularly in the tetrahedral series.

It is apparent that high heats of transition will be most readily obtained in the tetrahedral series, which can be represented by the following general formula, where R^1, R^2, R^3, and R^4 are functional groups that are alike or different.



Owing to the different possibilities each group can contribute to new orientational states, the magnitude of the contribution of specific groups to the entropy change in the transition can be estimated on the basis of the group identity. Largely from these data, but also on the basis of some data from the literature, the various functional groups can be listed in the following order with respect to their contribution to the entropy change on transition.

$$CO_2H > NO_2 \cong NH_2 > CH_2OH > CH_2F > CH_3 \cong Cl \cong Br$$

Although such a series can be used to predict structures most likely to have high heats of transition, unique limitations in particular structures may lead to anomalies similar to those that have been described. Other groups that may also be effective, but which cannot be placed in the series because of the lack of data, include the following.

$$OH,\ SH,\ CN,\ CH_2CN,\ CH_2NH_2,\ CH_2SH,\ CHO$$

Some potentially effective candidate materials that have been prepared and reported in the literature are listed in Table 12. Solid state transitions have not been reported for any of these compounds. The extent of functional substitution in these compounds indicates a high probability for large heats of transition.

TABLE 12

TYPICAL CANDIDATE MATERIALS

Compound No.	Structure	mp (°C)
1	$C(CH_2NH_2)_4 \cdot H_2O$	41-42
2	$C(CH_2OH)(CH_2NH_2)_3$	121
3	$C(CH_2OH)_3(CH_2NH_2)$	207
4	$C(CH_2OH)_3(CH_2Cl)$	141
5	$C(CH_2OH)_2(CH_2Cl)_2$	79-80
6	$C(CH_2OH)_3(CH_2CO_2H)$	121
7	$C(CH_2SH)_4$	73-74
8	$C(CH_2SH)_2(CH_2OH)_2$	97
9	$C(CH_2SHN)_4$	215-216
10	$C(CH_2OH)_3CO_2H$	206-207
11	$C(CO_2H)(CH_2OH)(CH_3)_2$	123
12	$C(CHO)(CH_2OH)(CH_3)_2$	89-90
13	$C(NO_2)_2(CH_3)(CH_2OH)$	95
14	$C(NO_2)_2(CH_2OH)_2$	145
15	$C(NO_2)_3(CH_2OH)$	72-73

V. OTHER EXPERIMENTAL WORK

A. Effect of Purity on Enthalpy Changes

The results of determining heats of transition before and after various kinds of purification steps are summarized in Table 13. Both Series I and Series II data are included in the tabulation because some of the substances were used in the purity they were received for Series I, but were recrystallized for the Series II determinations. Subsequent to the Series II determinations, some of the substances were subjected to additional purification procedures, and the values obtained in these experiments are also reported. For most of the substances, changes in enthalpies were not significant (less than 10% variation).

The tendency of 2-amino-2-methyl-1,3-propanediol to absorb moisture was observed in the discussion of the qualitative work, and the absorption of moisture did seem to significantly reduce the transition enthalpy for this substances. No particular precaution was taken to exclude moisture during the recrystallizations, and the enthalpies of transition decreased with additional recrystallization. But when the compound was sublimed in a dry atmosphere, transition enthalpies increased with repeated sublimation. The other substance whose melting point decreased on exposure to moisture, 2-methyl-2-nitro-1,3-propanediol, did not show a significant change in its transition enthalpy.

The only substance that contained a substantial portion of impurity, 2-hydroxymethyl-2-nitro-1,3-propanediol, showed a considerable variation in transition enthalpy in average values from three sets of the data, but it is difficult to make any specific conclusion concerning the effect of impurity on the basis of the data that is available.

B. Two-Component Systems

Some data were obtained on two-component systems. A phase diagram was prepared for the 2-hydroxymethyl-2-methyl-1,3-propanediol-2,2-bis(hydroxymethyl)-1-butane system, a mixture of a mesocrystalline substance with a nonmesocrystalline material. The phase diagram is reproduced in Figure 6. The system has a congruent melting point at 66°C with about 12% trimethylolethane and a eutectic at 58°C with about 8% trimethylolethane. No mesocrystalline phase is observed at either point and the values are very close to the 59°C m.p. of trimethylolpropane. Since the eutectic composition is largely trimethylolpropane, the enthalpy of melting would not differ too greatly from the enthalpy of melting of trimethylolpropane and would not benefit greatly from the higher value of trimethylolethane.

TABLE 13

COMPARISON OF ENTHALPY CHANGES OF TRANSITION WITH CHANGES IN PURITY

Substance[a]	ΔH (cal/g)
Pentaerythritol	
Series II	72.48
Recrystallized once	70.47
Unpurified redetermined	68.25
2,2-Dimethyl-1,3-propanediol	
Series I	33.58
Series II (recrystallized)	31.30
2-Amino-2-hydroxymethyl-1,3-propanediol	
Series I	62.29
Series II (recrystallized)	67.61
2-Amino-2-methyl-1,3-propanediol	
Series I	55.47
Series II	63.38
Recrystallized once	53.22
Recrystallized five times	50.24
Sublimed once	55.59
Sublimed twice	57.31
Unpurified redetermined	54.12[b]
2-Hydroxymethyl-2-nitro-1,3-propanediol	
Series I	32.95
Series II	39.33
Recrystallized five times	35.50
2-Methyl-2-nitro-1,3-propanediol	
Series I	46.55
Series II	47.66
Recrystallized five times	45.50
2,2-Bis(hydroxymethyl)propionic acid	
Series I	69.48
Series II (recrystallized)	68.64

a/ See the text for an explanation for the values listed as Series I, Series II, Recrystallized, and sublimed.

b/ Total from overlapping transition and fusion endotherms-redetermined after 5 months.

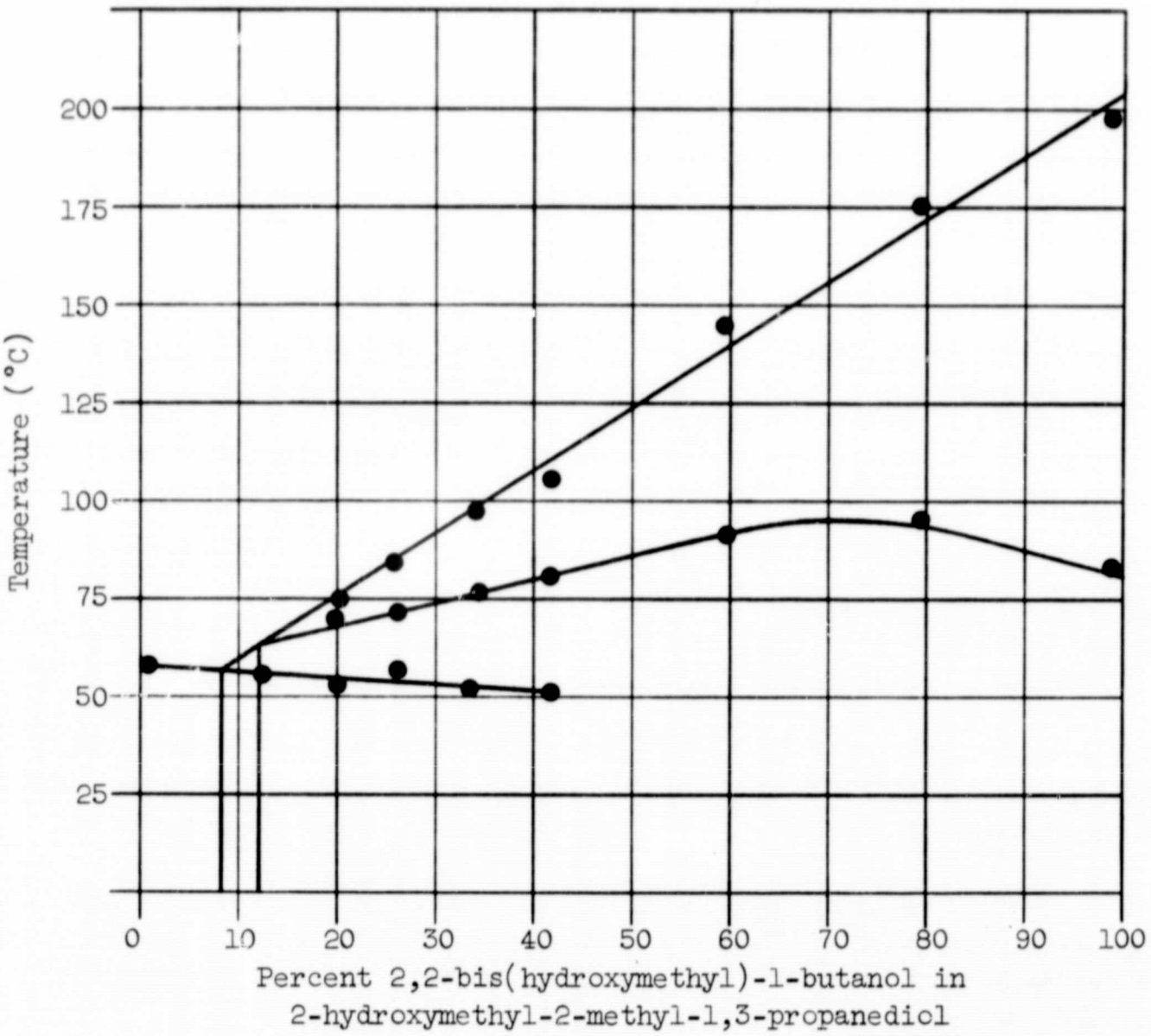


Figure 6 - Phase Diagram for the System 2,2-Bis(hydroxymethyl)-1-butanol and 2-Hydroxymethyl-2-methyl-1,3-propanediol

A second two-component system of a mesocrystalline and a non-mesocrystalline material, pentaerythritol and trimethylolpropane, was examined but the phase diagram, which was somewhat similar to the first, was less well defined. The mesocrystalline phase disappeared somewhat more rapidly with increasing concentration of 2,2-bis(hydroxymethyl)-1-butanol. A eutectic, if it were present, had a melting point that did not differ from the melting point of 2,2-bis(hydroxymethyl)-1-butanol.

Three two-component systems of mesocrystalline substances were also screened. The 2,2-dimethyl-1,3-propanediol-2-hydroxymethyl-2-methyl-1,3-propanediol system and the 2-hydroxymethyl-2-methyl-1,3-propanediol-pentaerythritol system appeared to form solid solutions at all concentrations. In the pentaerythritol-2,2-dimethyl-1,3-propanediol system, the transition temperatures were too far apart to give meaningful results.

Two other sets of mixtures were prepared, one from 2-amino-2-methyl-1,3-propanediol and trimethylolethane and the other from 2-amino-2-methyl-1,3-propanediol and 2-amino-2-hydroxymethyl-1,3-propanediol. Both of these systems formed glasses when the melts were cooled. These results suggest that an effective nucleating agent will be necessary in these two particular mixtures.

C. Crystallization Studies

Initial crystallization studies were undertaken on the basis of the originally proposed approach of using the differential thermal analyzer to determine the extent of supercooling at various cooling rates. It was felt that extrapolation of such data to a zero cooling rate would provide a fair assessment of the extent of supercooling of candidate substances.

Of the four compounds examined, all exhibited excessive supercooling, except 2-hydroxymethyl-2-methyl-1,3-propanediol. Also, there was no evidence that there was any correlation between extent of supercooling and cooling rate.

When a number of potentially useful nucleating agents were examined under the conditions of these experiments, no response was observed with any of the conventionally used materials. The only significant change effected in the extent of supercooling was by the incorporation of a small quantity of pentaerythritol in 2-hydroxymethyl-2-methyl-1,3-propanediol. With this composition and a cooling rate of 5°C/min or less, the extent of supercooling was reduced to 4-5°C, which approaches the target requirements for phase change materials. Presumably, this system was effective because of the similar crystal habit of the two substances and the high transition temperature of pentaerythritol.

Although there were insufficient experimental data to establish the fact, the large extent of supercooling observed in the other substances (up to 70°C) appeared to be characteristic of the functional groups present. The fact that the greatest supercooling was observed in the two substances containing the amino group seemed to confirm this observation.

The results with 2-hydroxymethyl-2-methyl-1,3-propanediol suggested that excessive supercooling was not an inherent characteristic of solid/solid-phase transitions; however, closer examination of some of the data indicated that the experimental procedure used to obtain these data did not fully and accurately describe the nature of the solid-solid transition. At the same cooling rate, many of the results were not repeatable. The failure of the substances to respond to commonly used nucleating agents is also suspect, but in the experiments optimum particle sizes and concentrations may not have been used. It was observed that when some of the samples were cooled considerably below the transition temperature with no exotherm, then reheated, phase transition occurred during the heating cycle. Also, several substances exhibited substantially different extents of supercooling, when they were used in quantitative determinations of heats of transition and cooled.

Because of the questions about the validity of the crystallization data obtained by differential thermal analysis, the cooling characteristics of 3-g. samples of several of the substances were determined by conventional procedures. Under these conditions, the maximum supercooling of all the substances examined was 3°C. 2-Hydroxymethyl-2-methyl-1,3-propanediol, 2-methyl-2-nitro-1,3-propanediol, and pentaerythritol underwent crystalline transformation without the addition of nucleating agents; 2-amino-2-hydroxymethyl-1,3-propanediol and 2-amino-2-methyl-1,3-propanediol could be nucleating by scratching the glass container with a metal spatula.

The data that have been obtained are only preliminary but indicate that excessive supercooling is not a characteristic of the transformations and that the techniques that had employed the differential thermal analyzer were not valid.

D. Compound Preparation

A small amount of effort was spent on compound preparation. Method followed those described in the literature for the substances prepared or for structurally related compounds. The following were prepared: Tetrakis(trimethylsilyl)silane; tetramethylsuccinonitrile, tetramethylsuccinic acid, tetra-t-butylthiopentaerythritol, pentaerythritol tetramethanesulfonate, and tetrakis(aminomethyl)methane monohydrate.

VI. EXPERIMENTAL PART

A. Qualitative Thermal Data

All data were obtained with a DuPont Differential Thermal Analyzer with a heating rate of 15°/min in an air atmosphere. Temperature ranges in the qualitative experiments were taken as the temperature between the extrapolated onset of the transition to the maximum height of the endotherm. These data are presented in detail in Tables 14 to 23.

B. Quantitative Standardization

The DuPont Differential Scanning Calorimeter module was standardized for the quantitative determinations through the determination of a calibration constant E for selected substances and plotting the E values against peak temperatures.

$$E = \frac{\text{specific heat (cal/g)} \times \text{heating rate (°C/min)} \times \text{wt. (mg.)}}{\text{plotted area (in}^2\text{)} \times \text{T scale (°C/in)} \times \Delta T \text{ (°C/in)}}$$

For the Series I calibration data, which are reported in Table 24, the average values were treated with a computer programmed to determine the best curve to fit the data. The index of determination for the hyperbolic curve was 0.973055; the 95% confidence limits were calculated as ± 5.8%. For the Series II calibration data in Table 24, the best smooth curve was drawn for the average values as shown in Figure 7. Both calibration curves were based on the use of sealed sample pans. The calibration data for open sample pans in Table 26 were not used. Subsequent checks and corrections of the calibration curves were necessary from time to time during the experimental work. These corrections were based on E values redetermined for acetamide, indium, and tin. Data for such a series redetermined several months after the calibration data in Table 25 are reported in Table 27.

C. Quantitative Thermal Data

Quantitative determinations were carried out with a suitably standardized DuPont Differential Scanning Calorimeter with a heating rate of 10°C/min in an atmosphere of air. Two series of determinations were made. The scatter of the data in the first series of determinations (Series I) was so large that a replacement cell was obtained and many of the values were redetermined (Series II). Series I data are reported in Tables 28 to 32 and Series II data in Tables 33 to 36.

(Text continued on p. 78.)

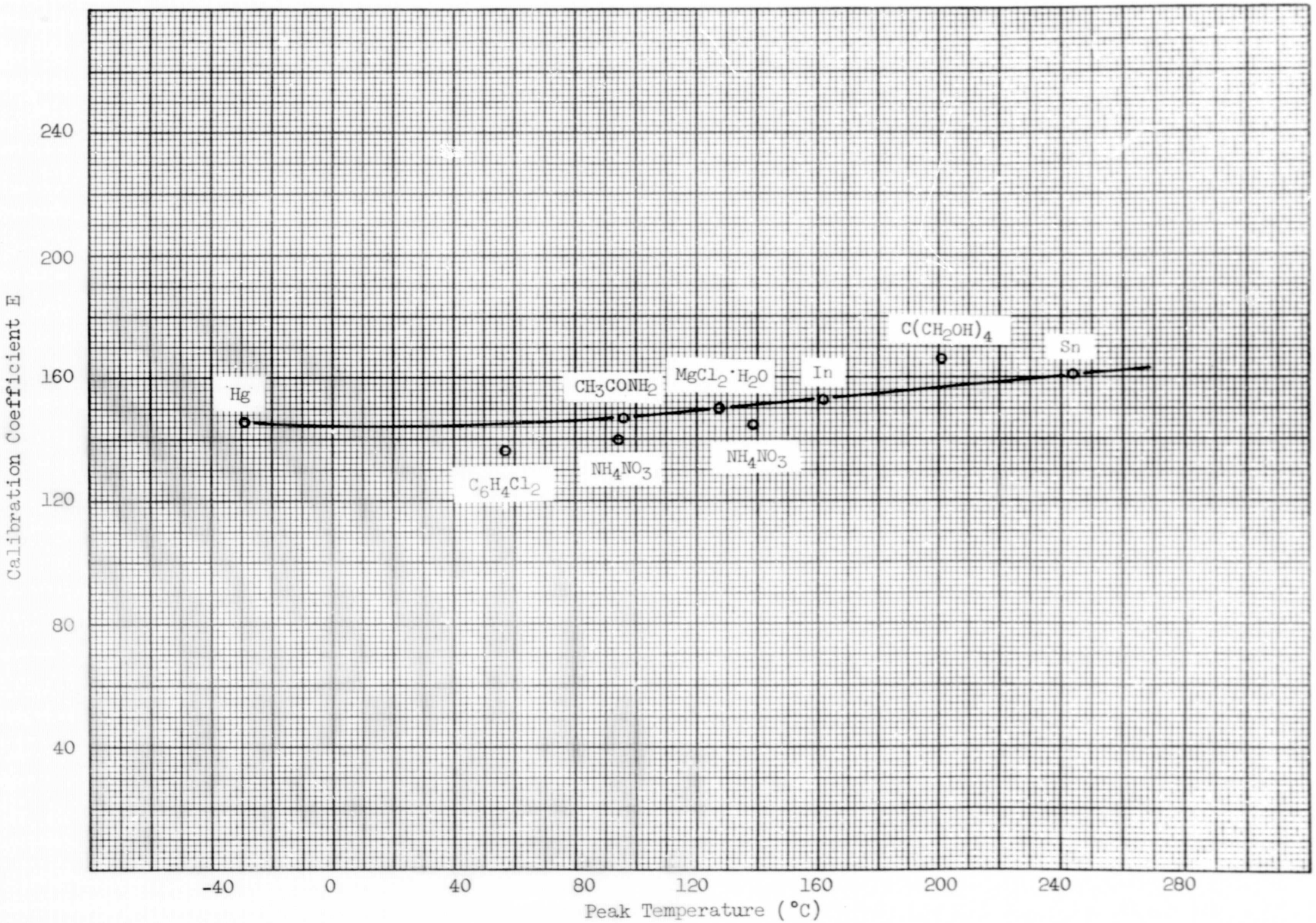
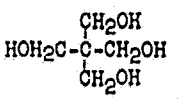
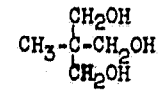
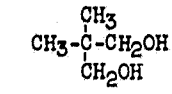
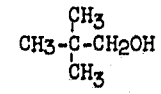
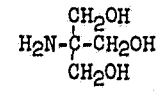
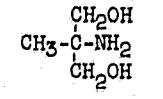
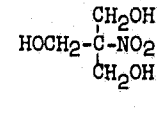
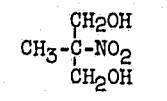
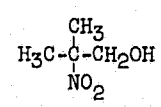
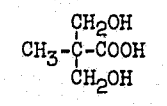
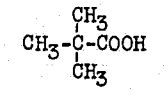
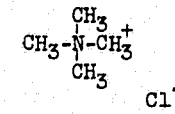
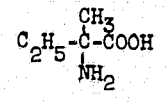
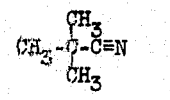


Figure 7 - Calibration Curve for the Differential Scanning Calorimeter Cell

TABLE 14

QUALITATIVE EXPERIMENTAL DATA FOR TETRAHEDRAL COMPOUNDS WITH SOLID-SOLID TRANSITIONS[a]

Name	Structure	Transition Range (°C)	Melting Range (°C)
Pentaerythritol		181-183	255-259
Recrystallized once		184-185	258-260
2-Hydroxymethyl-2-methyl-1,3-propanediol		81	197-198
2,2-Dimethyl-1,3-propanediol		38-41	120-126
Recrystallized once		40-43	125-126
Neopentyl alcohol		-31	51-55
2-Amino-2-hydroxymethyl-1,3-propanediol		131-132	164-169
Recrystallized once		131-137	166-169
2-Amino-2-methyl-1, 3-propanediol		78-80	107-108
Recrystallized once		76-80	107-108
Recrystallized twice		77-81	101-104[b]
Recrystallized four times		77-81	105-108
Recrystallized five times		77-81	105-108
Sublimed		78-80	105-108
Sublimed twice		78-80	107-109
Unpurified after five months		77-78	97-100
2-(Hydroxymethyl)-2-nitro-1,3-propanediol		78-81	167-177
Recrystallized once		79-81	159-168[b]
Recrystallized twice		79-80	Dec. 184
Recrystallized three times		80-82	Dec. 184
2-Methyl-2-nitro-1,3-propanediol		77-78	151-154
Recrystallized twice		79-80	149-153
Recrystallized four times		79-80	149-153
Recrystallized five times		76-79	136-149[b]
2-Methyl-2-nitro-1-propanol		35-39	88-89
2,2-Bis(hydroxymethyl)-propionic acid		148-153	188-192
Recrystallized once		152-155	194-197
Pivalic acid		7-9	32-36
Tetramethylammonium chloride		262-264	Sublimed above 320
dl-2-Amino-2-methyl-butyric acid		83-86 98-104 ~100-108	Sublimed above 310
Trimethylacetonitrile		-34	15-20

a/ Data collected in the laboratories of Midwest Research Institute.
b/ See text.

TABLE 15

QUALITATIVE EXPERIMENTAL DATA FOR TETRAHEDRAL COMPOUNDS NOT SHOWING SOLID-SOLID TRANSITIONS[a]

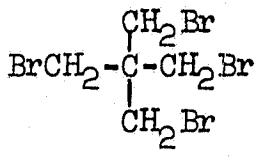
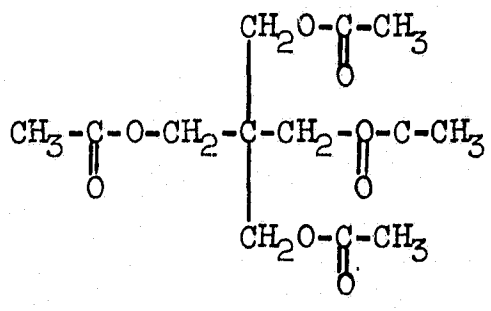
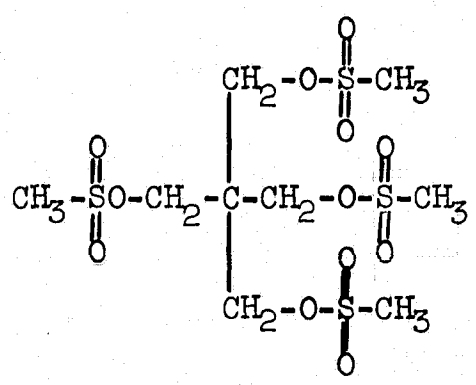
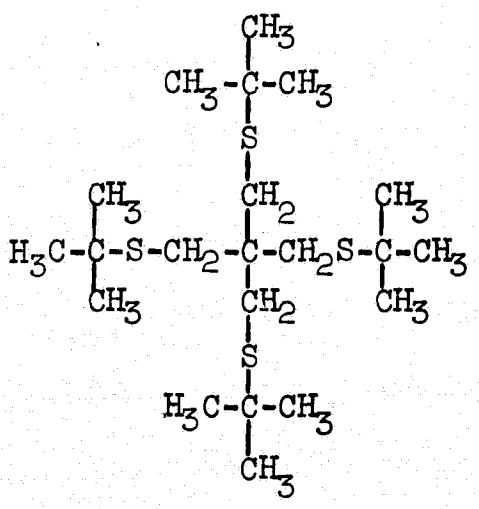
Name	Structure	Temperature Range Examined (°C)
Pentaerythrityl tetrabromide		-180 and 160 (m.p.)
Pentaerythrityl tetraacetate		-60 to 79 (m.p.)
Pentaerythritol tetramethane-sulfonate		-50 to 202 (m.p.)
Tetra-t-butyl thiopentaery-thritol		-60 to 116 (m.p.)

TABLE 15 (Continued)

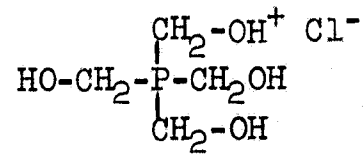
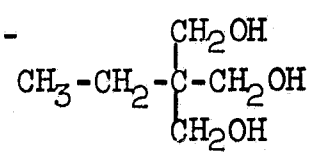
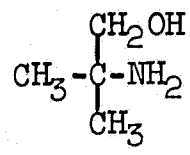
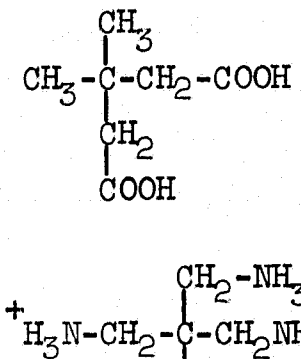
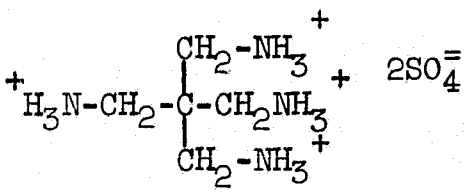
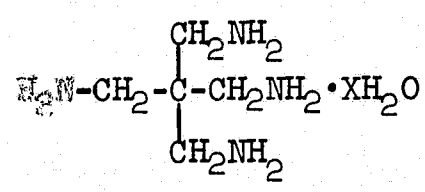
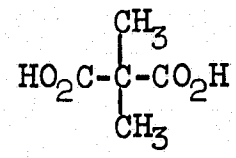
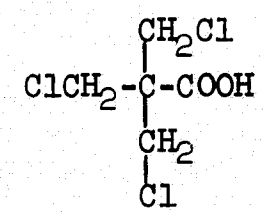
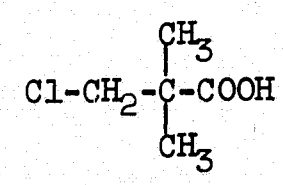
Name	Structure	Temperature Range Examined (°C)
Tetrakis(hydroxymethyl)phosphonium chloride		0 to 450
2,2-Bis(hydroxymethyl)-1-butanol		-50 to 56 (m.p.)
2-Amino-2-methyl-1-propanol		-70 to 17 (m.p.) (Melting range 7-17°)
3,3-Dimethylglutaric acid		-80 to 101 (m.p.)
Tetrakis(aminomethyl)methane sulfate		25 to 320 (m.p.)
Tetrakis(aminomethyl)methane hydrate		-70 to 43 (m.p.)
Dimethylmalonic acid		-50 to 198 (m.p.)
Tris(chloromethyl)-acetic acid		-60 and 108 (m.p.)
β-Chloropivalic acid		-30 and 38 (m.p.)

TABLE 15 (Continued)

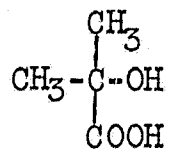
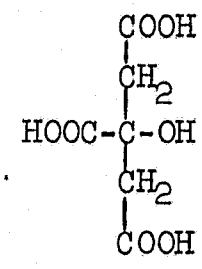
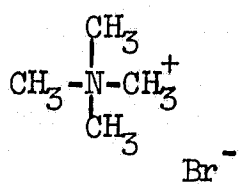
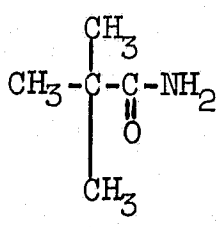
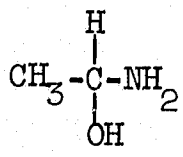
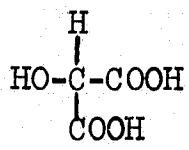
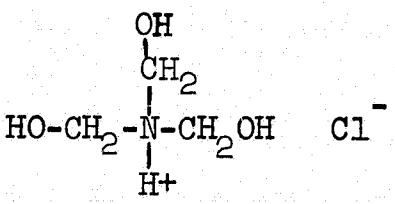
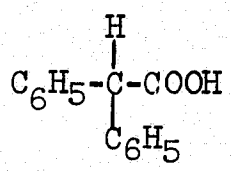
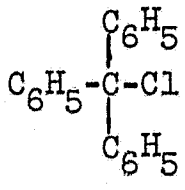
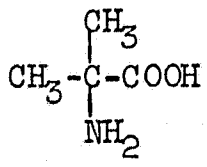
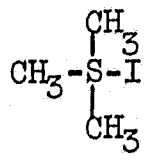
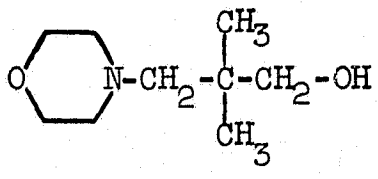
Name	Structure	Temperature Range Examined (°C)
2-Methyllactic acid		-80 to 80 (m.p.)
Citric acid		-60 to 153 (m.p.)
Tetramethyl-ammonium bromide		0 to 392 (sub.)
Trimethylacetamide		-40 to 152 (m.p.)
Acetaldehyde ammonia		-30 to 93 (m.p.)
Tartronic acid		-140 to 154 (dec.)
2,2',2"-Nitrilo-triethanol hydrochloride		-60 to 178 (m.p.)
Diphenylacetic acid		-80 to 146 (m.p.)

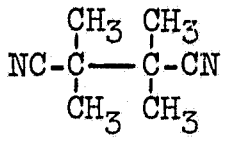
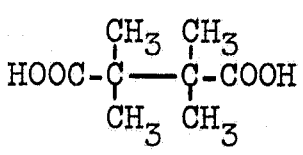
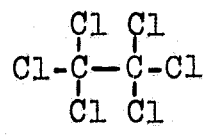
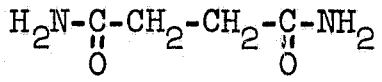
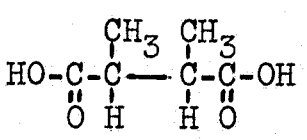
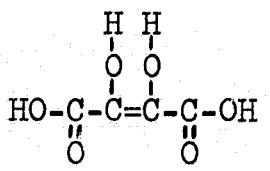
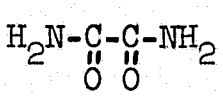
TABLE 15 (Concluded)

Name	Structure	Temperature Range Examined (°C)
Chlorotriphenyl-methane		-140 to 109 (m.p.)
α-Aminoisobutyric acid		-140 to 300 (sublimed above 300)
Trimethylsulfonium iodide		-40 to 207 (m.p.)
N-(2,2-dimethyl-3-hydroxypropyl)-morpholine		-80 to 247 (b.p.)

a/ Data collected in the laboratories of Midwest Research Institute.

TABLE 16

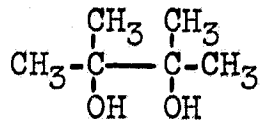
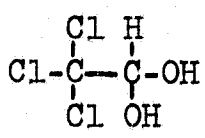
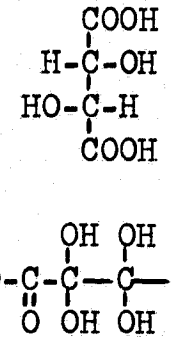
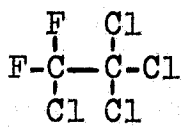
QUALITATIVE EXPERIMENTAL DATA FOR OCTAHEDRAL COMPOUNDS WITH SOLID-SOLID TRANSITIONS[a]

Name	Structure	Transition Range (°C)	Melting Range (°C)
Tetramethyl-succino-nitrile		71 to 73	168 to 170
Tetramethyl-succinic acid		108 to 111	190 to 193
Hexachloroethane		46 to 48 71 to 72	179 to 184
Succinamide		203 to 204	263 to 268
2,3-Dimethyl-succinic acid		119 to 123	188 to 190
Dihydroxymaleic acid		115 to 121	144 to 161
Oxamide		325 to 335	Not melted at 375

a/ Data collected in the laboratories of Midwest Research Institute.

TABLE 17

QUALITATIVE EXPERIMENTAL DATA FOR OCTAHEDRAL COMPOUNDS NOT SHOWING SOLID-SOLID TRANSITIONS[a]

Name	Structure	Temperature Range Examined (°C)
Pinacol		-80 and 38 (m.p.)
Chloral hydrate		-40 to 52 (m.p.)
Tartaric acid		-60 and 170 (m.p.)
Dihydroxytartaric acid		40 and 108 (dec.)
Difluorotetrachloro-ethane		-25 to 37 (m.p.)

a/ Data collected in the laboratories of Midwest Research Institute.

TABLE 18

QUALITATIVE EXPERIMENTAL DATA FOR CAGE COMPOUNDS WITH SOLID-SOLID TRANSITION[a]

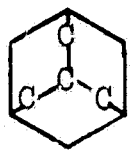
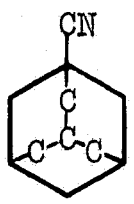
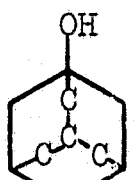
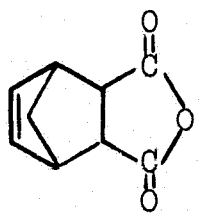
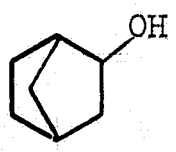
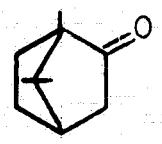
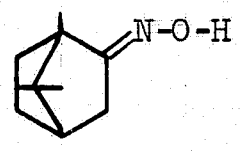
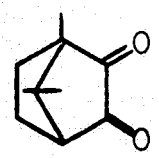
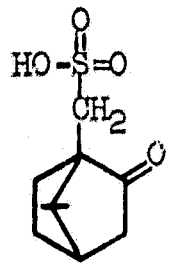
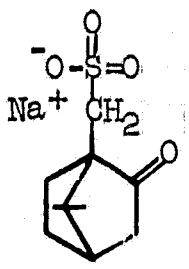
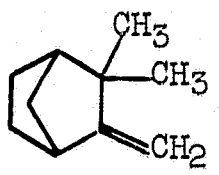
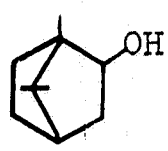
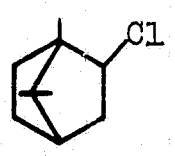
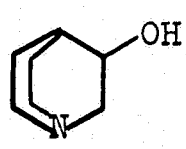
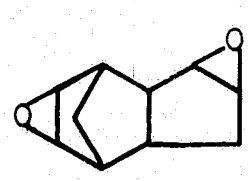
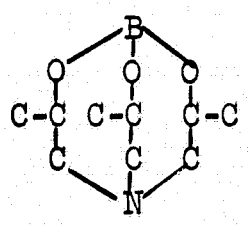
Name	Structure	Transition Range (°C)	Melting Range (°C)
Adamantane		-64.5	206 to 209
1-Adamantane-carbonitrile		142 to 148	180 to 189
1-Adamantanol		91 to 92	239 to 245
5-Norbornene-2,-3-dicarboxylic anhydride		98 to 101	Indefinite[b]
Norborneol (mixture of <u>end</u> and <u>exo</u>)		-6 to -2	128 to 131
<u>d</u>-Camphor		-26 to -23 and 98 to 100	178 to 179
<u>d</u>-Camphor oxime		107 to 112	111 to 115
<u>dl</u>-Camphorquinone		55 to 61	199 to 201

TABLE 18 (Concluded)

Name	Structure	Transition Range (°C)	Melting Range (°C)
dl-10-Camphor-sulfonic acid		95 to 102	195 to 200
dl-10-Camphor-sulfonic acid sodium salt		112 to 117	--
Camphene		-97 to -99	42 to 49
dl-Isoborneol		7 to 8	Sublimed above 210
Bornyl chloride		-36 to -34	122 to 125
3-Quinuclidinol		96 to 102	221 to 223
Dicyclopentadiene dioxide (mixture of endo and exo)		60 to 67	202 to 211
Tris(propan-2-ol)-amine borate		65 to 69	150 to 156

a/ Data collected in the laboratories of Midwest Research Institute.
b/ Reported, 164 to 166°, Eastman Organic Chemicals Catalogue, No. 44.

TABLE 19

QUALITATIVE EXPERIMENTAL DATA FOR CAGE COMPOUNDS NOT SHOWING SOLID-SOLID TRANSITIONS[a]

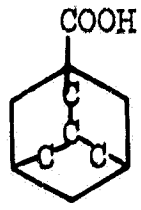
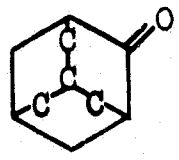
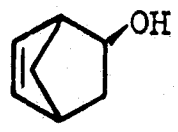
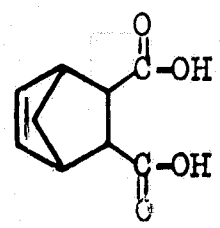
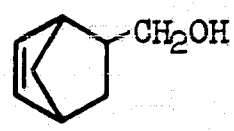
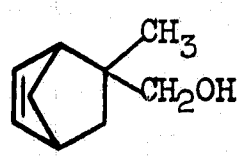
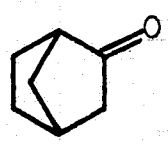
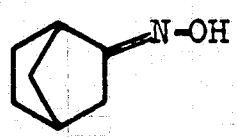
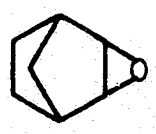
Name	Structure	Temperature Range Examined (°C)
1-Adamantanecarboxylic acid		0 to 175 (m.p.)
Adamantanone		-30 to 254 (sub.)
5-Norbornen-2-ol (mixture of endo and exo)		10 to 89 (m.p.)
5-Norbornene-2,3-dicarboxylic acid (mixture of endo and exo)		0 to 184 (dec.)
5-Norbornene-2-methanol		-70 to -10 (m.p.)
2-Methyl-2-methylol-5-norbornene		-35 to 50
Norcamphor		-40 and 88 (m.p.)
Norcamphor oxime		-80 to 180 (dec.)
exo-2,3-Epoxynorbornane		-30 to 127 (m.p.)

TABLE 19 (Continued)

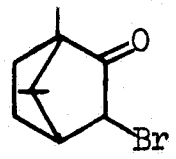
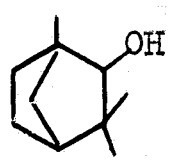
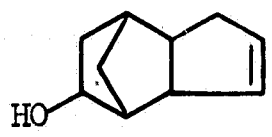
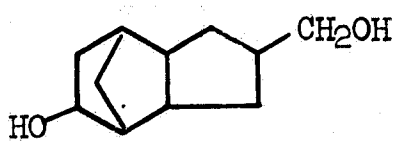
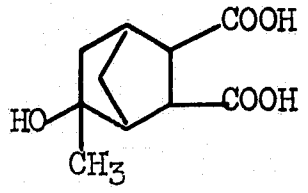
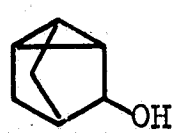
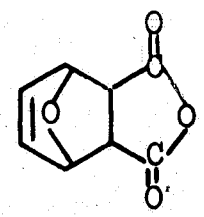
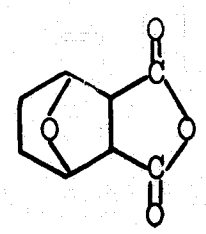
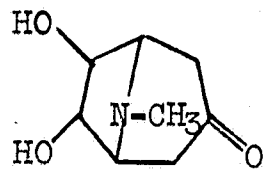
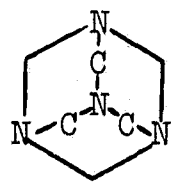
Name	Structure	Temperature Range Examined (°C)
d-3-Bromocamphor		-40 to 74 (m.p.)
Fenchyl alcohol		-65 to 25 (m.p.)
5-Hydroxy-4,7-methylene-4,7,8,9-tetrahydroindene		-60 to -40 (m.p.)
5-Hydroxy-2-methylol-4,7-methylenehexahydroindene		-30 to 100
5-Hydroxy-5-methylbicyclo-[2.2.1]-heptane-2-3-di-carboxylic acid		-70 to 171 (m.p.)
3-Hydroxytricyclo-[2.2.1.$0^{2,6}$]-heptane		-80 to 95 (m.p.)
7-Oxabicyclo[2.2.1]-hept-5-ene-2,3-dicarboxylic anhydride		-70 to 117 (dec.)
7-Oxabicyclo[2.2.1]-heptane-2,3-dicarboxylic anhydride		-40 to 87 (m.p.)

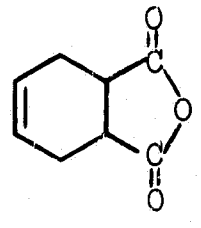
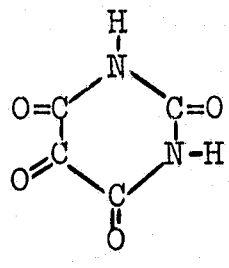
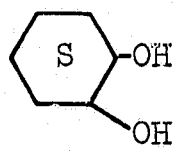
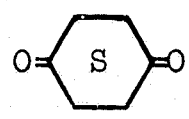
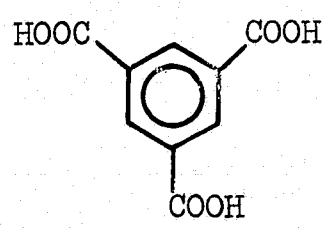
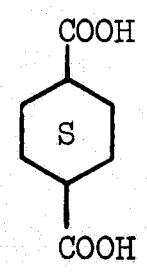
TABLE 19 (Concluded)

Name	Structure	Temperature Range Examined (°C)
Teloidione		10 to 190 (m.p.)
Hexamethylenetetramine		-65 to 285 (m.p.)

a/ Data collected in the laboratories of Midwest Research Institute.

TABLE 20

QUALITATIVE EXPERIMENTAL DATA FOR CYCLIC COMPOUNDS WITH SOLID-SOLID TRANSITIONS[a]

Name	Structure	Transition Range (°C)	Melting Range (°C)
cis-4-Cyclohexene-1,2-dicarboxylic anhydride		85 to 88	98 to 100
Alloxan		186 to 196	Decomp. > 260
trans-1,2-Cyclohexane-diol		67 to 77[a]	104 to 106
1,4-Cyclohexane-dione		52 to 55 and 68 to 70[b]	78 to 81
Trimesic acid		340 to 348[b]	413 to 416
trans-1,4-Cyclohexane-dicarboxylic acid		-4 to 0 and 150 to 156[b]	328 to 333

a/ Data collected in the laboratories of Midwest Research Institute.
b/ Very small heat effect.

TABLE 21

QUALITATIVE EXPERIMENTAL DATA FOR CYCLIC COMPOUNDS NOT SHOWING SOLID-SOLID TRANSITIONS[a]

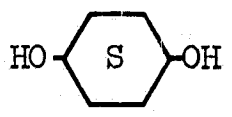
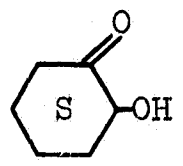
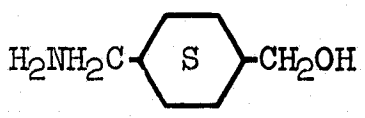
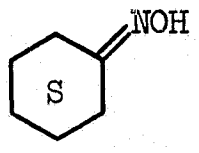
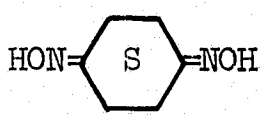
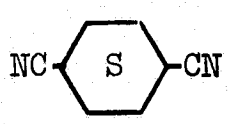
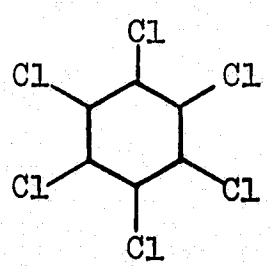
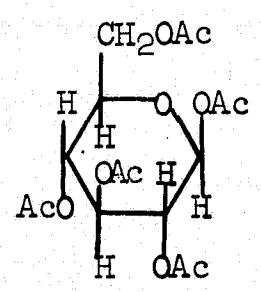
Name	Structure	Temperature Range Examined (°C)
1,4-Cyclohexanediol (cis-trans)		-10 to 95 (m.p.)
2-Hydroxycyclohexanone		-120 to 100 (m.p.)
4-Aminomethylcyclohexanemethanol		-140 to 36 (m.p.)
Cyclohexanone oxime		-70 to 89 (m.p.)
1,4-Cyclohexane dioxime		60 to 197 (m.p.)
1,4-Cyclohexanedicarbonitrile		-50 to 145 (m.p.)
α-Hexachlorocyclohexane β- γ- δ-		25 to 160 (m.p.) 40 to 304 (m.p.) -50 to 113 (m.p.) -20 to 144 (m.p.)
β-Glucose pentaacetate		-140 to 140 (m.p.)

TABLE 21 (Continued)

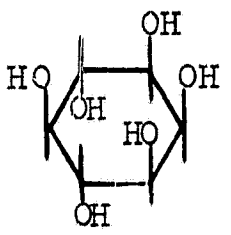
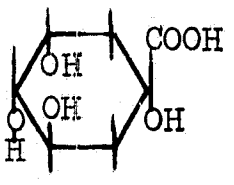
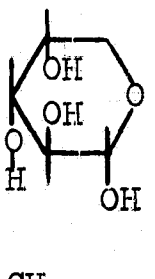
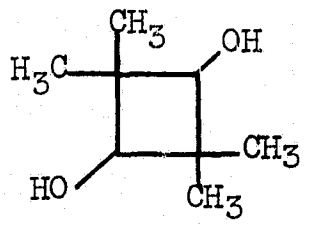
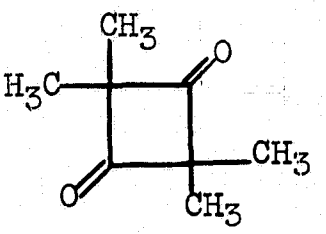
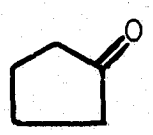
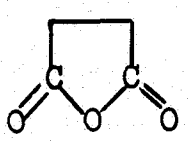
Name	Structure	Temperature Range Examined (°C)
Inositol		30 to 218 (m.p.)
D-Quinic Acid		-140 to 144 (m.p.)
Arabinose		-80 to 163 (m.p.)
2,2,4,4-Tetramethyl-1, 3-cyclobutanediol		-40 to 125 (m.p.)
2,2,4,4-Tetramethyl-1, 3-cyclobutanedione		-80 to 116 (m.p.)
Cyclopentanone		-80 to -56 (m.p.)
Succinic anhydride		-70 to 119 (m.p.)

TABLE 21 (Continued)

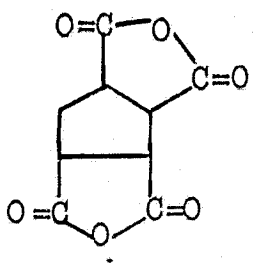
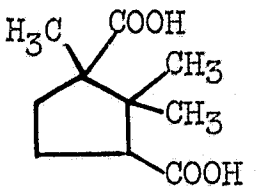
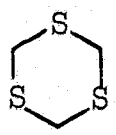
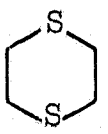
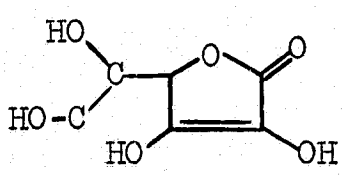
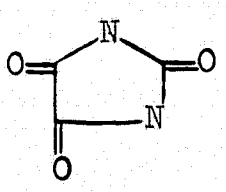
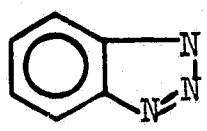
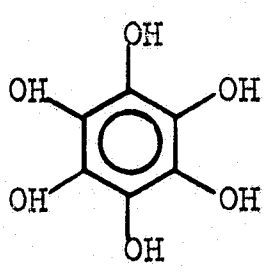
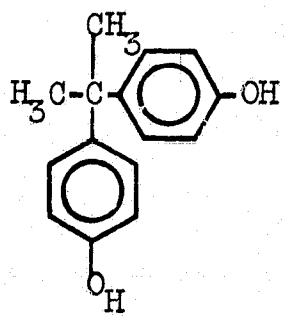
Name	Structure	Temperature Range Examined (°C)
1,2,3,4-Cyclopentane-tetracarboxylic-1,2,3,4-dianhydride		-60 to 215 (m.p.)
d-Camphoric acid		-70 to 182 (dec.)
s-Trithiane		-40 to 218 (m.p.)
p-Dithiane		0 to 111 (m.p.)
Hydantoin		-20 to 221 (m.p.)
Ascorbic acid		-140 to 168 (m.p.)
Parabanic acid		0 to 233 (dec.)

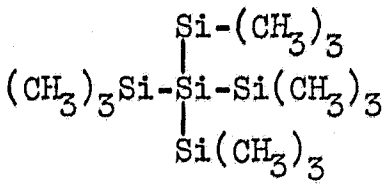
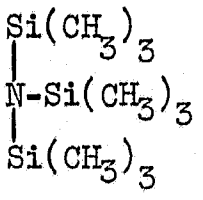
TABLE 21 (Concluded)

Name	Structure	Temperature Range Examined (°C)
1,2,3-Benzotriazol		-140 to 98 (m.p.)
p-Xylene		-80 to 14 (m.p.)
Benzenehexol		-60 to 200 (dec.)
4,4'-Isopropylidene diphenol		10 to 160 (m.p.)

a/ Data collected in the laboratories of Midwest Research Institute.

TABLE 22

QUALITATIVE EXPERIMENTAL DATA FOR ORGANOSILICON COMPOUNDS WITH SOLID-SOLID TRANSITIONS[a]

Name	Structure	Transition Range (°C)	Melting Range (°C)
Tetrakis(trimethylsilyl)silane		-32 to -29	282 to 285
Tris(trimethylsilyl)amine		-28	63 to 64

a/ Data collected in the laboratories of Midwest Research Institute.

TABLE 23

MISCELLANEOUS COMPOUNDS HAVING NO SOLID-SOLID TRANSITIONS[a]

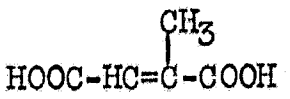
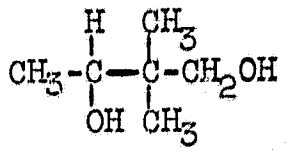
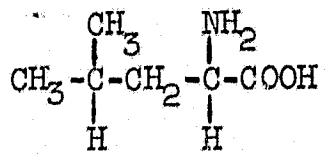
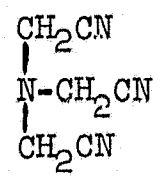
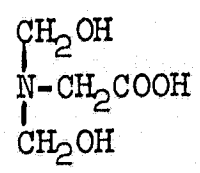
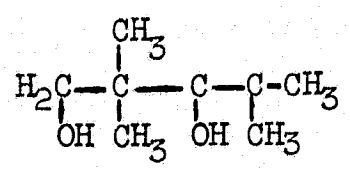
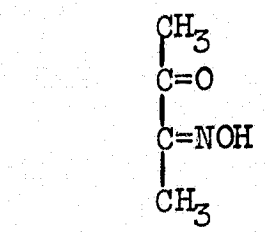
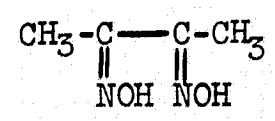
Name	Structure	Temperature Range Examined (°C)
Mesaconic acid		-40 to 203 (m.p.)
2,2-Dimethyl-3-hydroxy-1-butanol		-40 to -7 (m.p.)
d-Leucine		-80 to 202 (m.p.)
2-Butyne-1,4-diol		-60 to 50 (m.p.)
Nitrilotriaceto-nitrile		-50 to 127 (m.p.)
N,N-Bis(2-hydroxy-ethyl)glycine		-60 to 194 (dec.)
2,2,4-Trimethyl-1,3-pentanediol		-70 to 50 (m.p.)
Diacetyl monoxime		-140 to 74 (m.p.)
Dimethylglyoxime		-160 to 239 (dec.)

TABLE 23 (Continued)

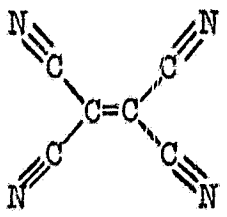
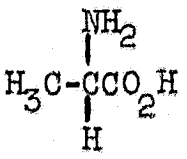
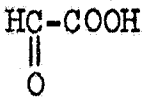
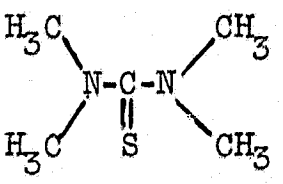
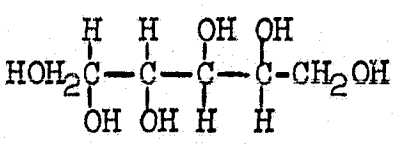
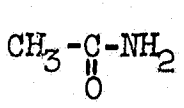
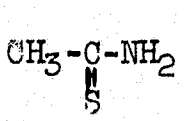
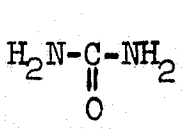
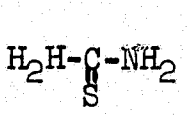
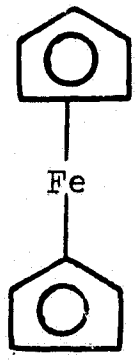
Name	Structure	Temperature Range Examined (°C)
Tetracyanoethylene		-30 to 200 (m.p.)
Hexadecane	$H(CH_2)_{16}H$	-8 to 20 (m.p.)
dl-Alanine		25 to 281 (m.p.)
Glycolic acid		-50 to + 80 (m.p.)
1,1,3,3,Tetramethyl-2-thiourea		-70 to 71 (m.p.)
Mannitol		-50 to 168 (m.p.)
Acetamide		10 to 82 (m.p.)
Thioacetamide		-95 to 114 (m.p.)
Urea		-80 to 132 (m.p.)
Thiourea		0 to 181 (m.p.)

TABLE 23 (Concluded)

Name	Structure	Temperature Range Examined (°C)
Ferrocene		20 to 173 (m.p.)

a/ Data collected in the laboratories of Midwest Research Institute.

TABLE 24

QUANTITATIVE THERMAL DATA ON STANDARD SUBSTANCES
DETERMINED IN SEALED CUPS: Series I[a]

Specific Heat (cal/g)	Peak Temperature (°C)	Substance	Number of Determinations	E Value	Average
2.74[b]	-31	Hg	1	111.7	
				126.9	121.7
				134.6	
				95.9	
				139.4	
22.3[c]	55	$C_6H_5COC_6H_5$	1	122.6	
			2	133.1	129.2
			3	131.8	
30.4[c]	63	$C_6H_4Cl_2$	1	125.3	
				146.5	137.1
				139.3	
40.3[a]	132	$MgCl_2 \cdot 6H_2O$	1	161.0	
			2	140.0	146.6
			3	138.8	
6.79[b]	165	In	1	150.7	
			2	142.0	
			3	133.8	
			4	150.7	
			5	142.0	
			6	155.9	147.0
			7	143.2	
			8	158.3	
			9	160.0	
			10	138.5	
			11	142.3	
76.53[e]	201	$C(CH_2OH)_4$	1	164.4	
			2	149.7	158.2
			3	160.6	
14.2[b]	244	Sn	1	171.2	
			2	156.7	
			3	190.5	
			4	229.7	169.1
			5	147.6	
			6	152.1	
			7	144.9	
			8	160.4	

a/ Data collected in the laboratories of Midwest Research Institute.
b/ Reference 27.
c/ Reference 28.
d/ Reference 26.
e/ Reference 3.

TABLE 25

QUANTITATIVE THERMAL DATA ON STANDARD SUBSTANCES DETERMINED IN SEALED CUPS: Series II[a]

Enthalpy (cal/g)	Peak Temperature (°C)	Substance	Number Of Determinations	Calibration Coefficient	Average
2.74[b]	-31	Hg	1	146.5	145.5
			2	144.2	
			3	147.1	
			4	148.8	
			5	147.9	
			6	145.5	
			7	138.3	
30.4[c]	57	$C_6H_4Cl_2$	1	136.3	136.2
			2	136.2	
3.996[d]	94	NH_4NO_3	1	137.1	139.5
			2	141.8	
63.5[d]	95	CH_3CNH_2	1	144.9	146.9
			2	149.9	
			3	146.0	
40.3[d]	128	$MgCl_2 \cdot 6H_2O$	1	156.5	149.6
			2	144.7	
				151.1	
				146.3	
12.62[d]	139	NH_4NO_3	1	146.7	145.0
			2	143.2	
6.79[b]	162	In	1	152.5	153.0
				149.6	
				156.5	
				155.4	
				150.2	
				153.9	
76.53[e]	201	$C(CH_2OH)_4$	1	162.6	165.8
			2	168.2	
			3	166.6	
14.2[b]	244	Sn	1	160.9	160.5
			2	165.3	
			3	160.9	
			4	164.5	
			5	157.9	
			6	159.2	
			7	160.4	
			8	153.9	
			9	161.7	

a/ Data collected in the laboratories of Midwest Research Institute.
b/ Reference 27.
c/ Reference 28.
d/ Reference 26.
e/ Reference 3.

TABLE 26

QUANTITATIVE THERMAL DATA ON STANDARD SUBSTANCES DETERMINED IN OPEN CUPS: Series II[a]

Specific Heat (cal/g)	Peak Temperature (°C)	Substance	Number of Determinations	E Value	Average
2.74[b]	-33	Hg	1	169.0	155.6
				154.2	
			2	154.3	
			3	145.0	
22.3[c]	55	$C_6H_5COC_6H_5$	1	133.7	133.2
			2	134.3	
			3	131.5	
30.4[c]	51	$C_6H_4Cl_2$	1	171.5	156.6
			2	140.6	
			3	157.7	
40.3[d]	128	$MgCl_2 \cdot 6H_2O$	1	248.2	188.6
			2	171.6	
			3	145.9	
6.79[b]	165	In	1	162.9	155.9
			2	148.6	
			3	157.2	
			4	155.0	
76.53[e]	201	$C(CH_2OH)_4$	1	177.7	182.42
			2	192.3	
			3	177.3	

a/ Data collected in the laboratories of Midwest Research Institute.
b/ Reference 27.
c/ Reference 28.
d/ Reference 26.
e/ Reference 3.

TABLE 27

QUANTITATIVE THERMAL DATA ON STANDARD SUBSTANCES
REDETERMINED IN SEALED CUPS:
(Series II: Second Calibrations)[a]

Enthalpy (cal/g)	Peak Temperature (°C)	Substances	Number of Determination	Calibration Coefficient	Average
63.5[b]	91	CH_3CNH_2	1	148.6	150.3
			2	145.1	
			3	149.3	
			4	(159.1)	
			5	154.4	
			6	154.1	
			7	(141.3)	
6.79[c]	167	In	1	161.0	158.0
			2	157.1	
			3	157.4	
			4	156.5	
76.53[d]	201	$C(CH_2OH)_4$	1	182.4	180.7
			2	176.0	
			3	(173.7)	
			4	181.6	
			5	177.1	
			6	(190.0)	
			7	183.3	
			8	181.3	
			9	181.3	
			10	182.8	
14.2[c]	240	Sn	1	170.1	170.0
			2	170.7	
			3	171.1	
			4	168.2	
			5	171.2	
			6	168.4	

[a] Data collected in the laboratories of Midwest Research Institute.
[c] Reference 27.
[c] Reference 28.
[b] Reference 26.
[d] Reference 3.

TABLE 28

TRANSITION ENTHALPY AND ENTROPY DATA FOR VARIOUS SUBSTANCES
(Series I: Tetrahedral Compounds)[a]

Compound	Formula Weight	Melting Temperature (°K)	ΔH (cal/g) Determination Number	ΔH (cal/g) Value	ΔH (cal/g) Average	ΔS (e.u.)- Average)
2-Hydroxymethyl-2-methyl-1,3-propanediol	120.15	356	1-open	49.20	46.35	15.04
			2-open	46.48		
			3-open	43.37		
			4-sealed	50.41	48.31	16.39
			5-sealed	51.40		
			6-sealed	46.80		
			7-sealed	43.60		
			8-sealed	53.60		
			9-sealed	45.64		
			10-sealed	48.85		
			11-sealed	46.15		
2,2-Dimethyl-1,3-propanediol	104.15	312-314	1-open	29.57	29.18	7.74
			2-open	28.28		
			3-open	29.68		
			1-sealed	34.04	33.58	11.21
			2-sealed	32.38		
			3-sealed	31.04		
			4-sealed	35.56		
			5-sealed	31.46		
			6-sealed	37.01		
Neopentyl alcohol	88.15	240-241	1-sealed	7.94	10.30	3.78
			2-sealed	9.18		
			3-sealed	11.09		
			4-sealed	9.42		
			5-sealed	10.50		
			6-sealed	11.12		
			7-sealed	11.07		
			8-sealed	12.00		
2-Amino-2-hydroxymethyl-1,3-propanediol	121.14	411-419	1-sealed	60.84	62.56	18.44
			2-sealed	64.09		
			3-sealed	62.75		
2-Amino-2-methyl-1,3-propanediol	105.14	352-357	1-open	76.05	62.29	18.61
			2-open	59.88		
			3-open	50.95		
			1-sealed	51.65	55.47	16.57
			2-sealed	59.29		
2-(Hydroxymethyl)-2-nitro-1,3-propanediol	151.12	351-353	1-open	33.71	34.34	14.78
			2-open	26.45		
			3-open	36.21		
			4-open	41.00		
			1-sealed	31.79	32.95	13.33
			2-sealed	34.11		
2-Methyl-2-nitro-1,3-propanediol	135.12	354-357	1-sealed	44.77	46.55	17.77
			2-sealed	47.08		
			3-sealed	47.80		

TABLE 28 (Concluded)

Compound	Formula Weight	Melting Temperature (°K)	ΔH (cal/g) Determination Number	Value	Average	ΔS (e.u., Average)
2,2-Bis(hydroxymethyl)-propionic acid	134.13	425-428	1- 1-sealed	68.74	69.48	21.93
			2-sealed	65.21		
			3-sealed	74.48		
Pivalic acid	102.13	280-282	1-sealed	17.36	18.07	6.59
			2-sealed	16.12		
			3-sealed	18.22		
			4-sealed	17.07		
			5-sealed	17.17		
			6-sealed	20.23		
			7-sealed	19.10		
			8-sealed	19.29		
Tetramethylammonium chloride	109.60	535-537	1-sealed	27.36	26.50	5.43
			2-sealed	26.07		
			3-sealed	27.54		
			4-sealed	25.03		
Ammonium nitrate	80.05	326	1-sealed	3.21	3.21	0.79
		365	1-sealed	3.70	3.70	0.81
		407	1-sealed	11.73	11.73	2.31
Tetrakis(trimethylsilyl)silane	200.59	241-244	1-sealed	9.18	8.24	6.86
			2-sealed	7.75		
			3-sealed	8.34		
			4-sealed	7.68		
Tris(trimethylsilyl)-amine	143.36	242	1-sealed	7.30	7.80	4.61
			2-sealed	7.94		
			3-sealed	7.71		
			4-sealed	7.64		
			5-sealed	8.43		

a/ Data collected in the laboratories of Midwest Research Institute.

TABLE 29

TRANSITION ENTHALPY AND ENTROPY DATA FOR VARIOUS SUBSTANCES
(Series I: Octahedral Compounds)[a]

Compound	Formula Weight	Transition Temperature (°K)	ΔH (cal/g) Determination Number	Value	Average	ΔS (e.u.) - Average
Tetramethylsuccinonitrile	136.19	344-346	1-sealed	30.08	28.96	11.47
			2-sealed	26.75		
			3-sealed	30.06		
Tetramethylsuccinic acid	174.19	381-384	1-sealed	15.74	18.38	8.40
			2-sealed	21.08		
			3-sealed	18.31		
Dihydroxymaleic acid	148.07	388-194	1-open	151.77	--	--
			2-open	134.64		
			3-open	153.13		
			1-sealed	30.42	28.51	10.88
			2-sealed	30.87		
			3-sealed	26.63		
			4-sealed	26.12		
2,3-Dimethylsuccinic acid	146.14	393-396	1-open	10.26	9.04	3.36
			2-open	7.81		
			1-sealed	5.09	6.89	2.86
			2-sealed	8.69		
Succinamide	116.12	476-477	1-sealed	11.51	11.24	2.74
			2-sealed	10.77		
			3-sealed	11.44		

a/ Data collected in the laboratories of Midwest Research Institute.

TABLE 30

TRANSITION ENTHALPY AND ENTROPY DATA FOR VARIOUS SUBSTANCES
(Series I: Cage and Cyclic Compounds)[a]

Compound	Formula Weight	Melting Temperature (°K)	ΔH (cal/g) Determination Number	Value	Average	ΔS (e.u.) - average
3-Quinuclidinol	127.19	369-375	1-sealed	33.03	34.41	11.80
			2-sealed	34.80		
			3-sealed	35.55		
Adamantane carbonitrile	161.25	415-421	1-sealed	2.28	2.08	0.81
			2-sealed	2.14		
			3-sealed	1.82		
1-Adamantanol	152.24	362-364	1-sealed	20.57	19.11	8.04
			2-sealed	18.84		
			3-sealed	17.92		
Camphene[b]	136.23	174-176	1-sealed	5.80	5.74	4.49
			2-sealed	5.29		
			3-sealed	5.29		
			4-sealed	4.83		
			5-sealed	5.81		
			6-sealed	5.88		
			7-sealed	5.90		
			8-sealed	7.10		
dl-Isoborneol	154.25	280-281	1-sealed	3.63	3.69	2.03
			2-sealed	3.59		
			3-sealed	3.86		
d-Camphor	152.24	247-250	1-sealed	13.80	15.17	9.35
			2-sealed	14.10		
			3-sealed	17.60		
d-Camphor oxime	167.09	385	1-sealed	0.79	0.86	0.37
			2-sealed	1.04		
			3-sealed	0.76		
1,4-Cyclohexandione	112.13	326-327	1-sealed	13.66	12.28	4.42
			2-sealed	13.33		
			3-sealed	12.98[c]		
			4-sealed	11.50[c]		
			5-sealed	11.34		
			6-sealed	10.84		
5-Norbornene-2,3-di-carboxylic acid anhydride	164.16	368-370	1-sealed	25.64	23.27	10.38
			2-sealed	19.08		
			3-sealed	29.65		
			4-sealed	21.38		
			5-sealed	20.93		
			6-sealed	22.97		
dl-Camphorsulfonic acid	232.30	373-379	1-sealed	18.63	20.40	12.70
			2-sealed	20.96		
			3-sealed	18.84		
			4-sealed	23.16		
dl-Camphorquinone	166.22	329-334	1-sealed	20.31	22.56	11.40
			2-sealed	22.88		
			3-sealed	24.48		
Dicyclopentadiene dioxide	164.2	390-394	1-sealed	3.95	4.27	1.80
			2-sealed	4.24		
			3-sealed	4.22		
			4-sealed	3.76		
			5-sealed	4.15		
			6-sealed	5.33		
			7-sealed	4.61		
			8-sealed	3.91		
		333-340	1-sealed	13.40	16.99	8.38
			2-sealed	20.41		
			3-sealed	17.96		
			4-sealed	16.18		
Norborneol (mixture of endo and exo)	112.17	267-271	1-sealed	3.32	3.45	1.45
			2-sealed	2.99		
			3-sealed	4.05		
Tris(propan-2-ol)amine borate	199.06	336-338	1-sealed	3.11	2.60	1.54
			2-sealed	1.76		
			3-sealed	2.56		
			4-sealed	2.96		

a/ Data collected in the laboratories of Midwest Research Institute.
b/ Based only on MeOH standard; E = 171.8 ± 7%.
c/ At 5°/min.

TABLE 31

FUSION ENTHALPY AND ENTROPY DATA FOR SOME MICROCRYSTALLINE SUBSTANCES[a] (Series I)[a]

Compound	Formula Weight	Melting Temperature (°K)	ΔH (cal/g) Determination Number	ΔH (cal/g) Value	ΔH (cal/g) Average	ΔS (e.u.) - average
2-Hydroxymethyl-2-methyl-1,3-propanediol	120.15	470-471	1-sealed	10.78	10.78	2.76
2,2-Dimethyl-1,3-propanediol	104.15	393-399	1-sealed 2-sealed	10.15 11.83	10.99	2.91
Neopentyl alcohol	88.15	324-329	1-sealed 2-sealed 3-sealed	8.83 5.68 5.13	6.55	1.78
Tris(hydroxymethyl)amino-methane	121.14	441-443	1-sealed 2-sealed 3-sealed	5.73 8.70 6.09	6.84	1.88
2-Methyl-2-nitro-1,3-propanediol	135.12	428-431	1-sealed	7.23	7.23	2.28
2,2,-Bis(hydroxymethyl)-propionic acid	134.13	461-465	1-sealed	6.87	6.87	2.00
Tris(trimethylsilyl)amine	233.58	336-337	1-sealed 2-sealed 3-sealed	1.86 2.09 1.81	1.92	1.33
Tetramethylsuccinic acid	174.19	463-466	1-sealed 2-sealed 3-sealed	8.39 11.21 11.84	10.48	3.94
2,3-Dimethylsuccinic acid	146.14	461-463	1-sealed 2-sealed 3-sealed	36.82 29.16 38.12	34.70	11.00
Tris(propanediol)amine borate	199.06	423-429	1-sealed 2-sealed 3-sealed 4-sealed	9.53 7.19 11.92 8.75	9.35	4.40
Norborneol (mixture of endo and exo)	112.17	401-404	1-sealed	12.62	12.62	3.53
Camphene	136.23	315-322	1-sealed	4.33	4.33	1.87
Bornyl chloride	172.69	395-398	1-sealed 2-sealed 3-sealed 4-sealed	6.82 6.13 6.23 6.38	6.39	2.79
Dicyclopentadiene dioxide	164.2	475-484	1-sealed 2-sealed 3-sealed 4-sealed	5.37 5.82 5.72	5.64	1.95
d-Camphor oxime	167.09	394	1-sealed 2-sealed 3-sealed	20.86 20.91 19.38	20.38	8.64
1,4-Cyclohexanedione	112.04	351	1-sealed	13.09	13.09	4.18

a/ Data collected in the laboratories of Midwest Research Institute.

TABLE 32

FUSION ENTHALPY AND ENTROPY DATA FOR SOME NONMESOCRYSTALLINE SUBSTANCES: a/
(Series I)

Compound	Formula Weight	Transition Temperature (°K)	ΔH (cal/g) Determination Number	ΔH (cal/g) Value	ΔH (cal/g) Average	ΔS (e.u. - average)
2,2-Bis(hydroxymethyl)-1-butanol	134.19	329-332	1-sealed	39.16	38.86	15.85
			2-sealed	38.56		
2-Amino-2-methyl-1-propanol	89.14	283-292	1-sealed	34.31	31.11	9.80
			2-sealed	27.00		
			3-sealed	22.97		
			4-sealed	30.65		
			5-sealed	34.87		
			6-sealed	35.74		
			7-sealed	32.21		
Pentaerythritol tetramethane-sulfonate	448.51	475-477	1-sealed	26.94	26.57	25.09
			2-sealed	26.20		
Tetra-t-butyl-thiopenta-erythritol	424.82	389-391	1-sealed	13.52	14.05	15.34
			2-sealed	14.57		
Thioacetamide	75.13	384-485	1-sealed	76.59	75.16	14.68
			2-sealed	73.74		
Acetamide	59.07	352	1-sealed	66.75	76.15	12.78
			2-sealed	78.92		
			3-sealed	82.88		
Chloral hydrate	165.40	346	1-sealed	49.76	50.64	24.21
			2-sealed	51.51		
Hexadecane	226.16	303	1-sealed	68.02	58.64	43.77
			2-sealed	49.25		

a/ Data collected in the laboratories of Midwest Research Institute.

TABLE 33

ENTHALPY AND ENTROPY DATA FOR VARIOUS SUBSTANCES
(Series II: Tetrahedral Compounds)[1]

Compound	Formula Weight	Transition				Fusion			
		Temperature (°K)	ΔH (cal/g) Value	Average	ΔS (e.u. - average)	Temperature (°K)	ΔH (cal/g) Value	Average	ΔS (e.u. - average)
Pentaerythritol	136.15	454-456	71.43 73.88 72.12	72.48	21.74	528-534	8.52[1] 9.20 8.69	8.80	2.2
2-Hydroxymethyl-2-methyl-1,3-propanediol	120.15	354	(42.52) 46.07 45.75 47.84 44.43 44.55 44.45 44.28 (41.40)	46.02	15.62	470-471	10.55 11.00 (11.78) 10.84 (9.46) 10.20 (9.15) (8.96)	10.67	2.76
2,2-Dimethyl-1,3-propanediol	104.15	313-316	32.25 30.30 30.78	31.30	10.34	398-399	10.76 10.52 11.20	10.82	2.43
Neopentyl Alcohol	88.15	242	(8.68) 12.58 12.96 (3.69) (5.81) (11.60) 12.69 (9.56) (10.68)	12.74	4.64	324-328	(5.06) 11.91 (33.46) 10.34 10.81	11.02	3.00
2-Amino-2-hydroxymethyl-1,3-propanediol	121.14	404-407	70.09 61.69 (74.69) 67.37 68.37	67.61	20.27	439-442	5.99 5.78 (7.07) 6.11 6.11	6.00	1.66

TABLE 33 (Continued)

Compound	Formula Weight	Transition Temperature (°K)	Transition ΔH (cal/g) Value	Transition ΔH (cal/g) Average	Transition ΔS (e.u. - average)	Fusion Temperature (°K)	Fusion ΔH (cal/g) Value	Fusion ΔH (cal/g) Average	Fusion ΔS (e.u. - average)
2-Amino-2-methyl-1,3-propanediol	105.14	349-354	62.97 66.35 63.30 60.90	63.38	19.09	380-381	7.18 8.33 7.54 7.28	7.58	2.10
2-Hydroxymethyl-2-nitro-1,3-propanediol	151.12	351-354	39.93 38.29 39.77	39.33	16.93	compound decomposes			
2-Methyl-2-nitro-1,3 propanediol	135.12	353-356	48.30 49.95 47.67 44.71 43.76 45.65	47.66	18.24	428-431	6.95 8.04 7.95	7.65	2.42
2-Methyl-2-nitro-1-propanol	119.12	308-312	34.12 34.66 34.61	34.46	13.33	361-362	7.72 7.49 7.15	7.45	2.46
2,2-Bis(hydroxymethyl)propionic acid	134.13	425-428	70.80 (118.79) 67.06 68.07	68.64	21.66	467-470	5.82 (10.74) 6.56 6.84	6.41	1.84
Pivalic Acid	102.13	280-282	(17.93) 21.45 20.45 19.56	20.49	7.47	305-309	(9.16) 6.03 5.58 5.63	5.75	1.93
Trimethylacetonitrile	83.13	239	1.75 (0.62) (0.44) (2.42) 1.88 (2.29) (2.22) (2.35) 1.96	1.86	0.65	288-291	(7.35) (2.57) (2.39) (16.91) (9.37) (11.48)		

TABLE 33 (Concluded)

Compound	Formula Weight	Transition Temperature (°K)	Transition ΔH (cal/g) Value	Transition ΔH (cal/g) Average	Transition ΔS (e.u. - average)	Fusion Temperature (°K)	Fusion ΔH (cal/g) Value	Fusion ΔH (cal/g) Average	Fusion ΔS (e.u. - average)
Tetramethylammonium chloride	109.60	535-537	22.70 (20.44) (19.00) 21.96 23.91	22.86	4.68	Compound Sublimes			
Tetrakis(trimethylsilyl)silane	320.85	241-244	(9.86) 8.36 (10.27) (10.71) 8.30 8.60 8.21 8.10 8.64 8.13 9.14	8.42	11.21	555-558	(9.30) 8.48 8.10 (7.18)	8.29	4.79
Tris(trimethylsilyl)amine	233.58	245	8.27 8.88 8.43	8.53	8.13	336-337	1.62 1.85 1.95	1.81	1.26
			Transition I						
Ammonium nitrate	80.05	324-236 (I) 361-363 (II) 400-403 (III)	(4.09) 5.65 5.41	5.54	1.37				
			Transition II						
			4.14 4.29	4.21	0.94				
			Transition III						
			13.31	13.15	2.64				

a/ Data collected in the laboratories of Midwest Research Institute.
b/ Calculations based on extrapolated E value.
c/ Values in parentheses were rejected.

TABLE 34

ENTHALPY AND ENTROPY DATA FOR VARIOUS SUBSTANCES

(Series II: Octahedral Compounds)[a/]

Compound	Formula Weight	Transition Temperature (°K)	Transition ΔH (cal/g) Value	Transition ΔH (cal/g) Average	Transition ΔS (e.u. - average)	Fusion Temperature (°K)	Fusion ΔH (cal/g) Value	Fusion ΔH (cal/g) Average	Fusion ΔS e.u. - average)
Tetramethylsuccinonitrile	136.19	344-346	32.71 31.01 31.60	31.77	12.58	441-443	(10.04) 12.63 12.45	12.54	3.87
Tetramethylsuccinic acid	174.19	381-384	18.19 17.82 18.81 18.88	18.43	8.43	463-466	8.58 9.05 8.85 9.04	8.88	3.34
Hexachloroethane	236.74	319-321 (I)	Transition I			compound reacts with aluminum pan			
		344-345 (II)	2.71 2.54 (2.20)	2.63	1.95				
			Transition II						
			6.62 6.44 6.04	6.37	4.38				

a/ Data collected in the laboratories of Midwest Research Institute.

TABLE 35

ENTHALPY AND ENTROPY DATA FOR VARIOUS SUBSTANCES

(Series II: Cage and Cyclic Compounds)[a/]

Compound	Formula Weight	Transition Temperature (°K)	Transition ΔH (cal/g) Value	Transition ΔH (cal/g) Average	Transition ΔS (e.u. - average)	Fusion Temperature (°K)	Fusion ΔH (cal/g) Value	Fusion ΔH (cal/g) Average	Fusion ΔS (e.u. - average)
dl-Camphorquinone	166.22	328-334	16.65 15.98 (18.42) 16.31 17.96 (14.66)	16.86	8.54	472-474	8.57 7.75 8.18 7.99 7.92 8.05	8.12	2.85
Bornyl chloride	172.69	237-239	0.91 0.81 0.86	0.86	0.63	395-398	5.50 5.66	5.58	2.44
3-Quinuclidinol	127.19	368-375	28.39 (24.37) 28.60 (25.76)	28.49	9.85	494-496	14.83 14.51 14.15 13.54	14.26	3.67
Adamantane carbonitrile	161.25	415-421	2.29 2.53 (1.55)	2.41	0.94	453-462	(12.76) (15.60)		
1-Adamantanol	152.24	364-365	(21.64) (17.53) 19.08 19.81	19.44	8.13	512-518	(16.76) (6.65)		
Adamantane	136.24	209	4.61 4.74 5.06	4.80	3.13				

TABLE 35 (Concluded)

Compound	Formula Weight	Transition Temperature (°K)	Transition ΔH (cal/g) Value	Transition ΔH (cal/g) Average	Transition ΔS (e.u. - average)	Fusion Temperature (°K)	Fusion ΔH (cal/g) Value	Fusion ΔH (cal/g) Average	Fusion ΔS (e.u. - average)
Camphene[b]	136.23	174-176	5.45[a] 5.83 5.31	5.53	4.33	315-322	5.40 5.51	5.46	2.36
dl-Isoborneol	154.25	280-281	3.15 2.99 3.02 2.85 3.18	3.05	1.68				
d-Camphor	152.24	247-250 I→II	18.75 18.11 18.22	18.36	11.32	451-452	9.55 9.15	9.35	3.16
1,4-Cyclohexanedione	112.13	325-328	13.27 13.03 13.15	13.15	4.54	351-354	23.47[c] 21.77 23.41	22.88	7.31

a/ Data collected in the laboratories of Midwest Research Institute.
b/ Calculations based on extrapolated E value.
c/ The fusion curve overlapped the 341° transition.

TABLE 36

ENTHALPY AND ENTROPY DATA FOR VARIOUS SUBSTANCES

(Series II: Miscellaneous Compounds)[a]

Compound	Formula Weight	Transition Temperature (°K)	Transition ΔH (cal/g) Value	Transition ΔH (cal/g) Average	Transition ΔS (e.u. - average)	Fusion Temperature (°K)	Fusion ΔH (cal/g) Value	Fusion ΔH (cal/g) Average	Fusion ΔS (e.u. - average)
Thioacetamide	75.02	No Transition				384	(55.54) 61.27 63.25	62.26	12.17
Acetamide	59.07	No Transition				352	64.48 63.95 62.27	63.57	10.67
Trimethylolpropane	134.19	No Transition				329-332	(29.99) 35.10 32.80	33.95	13.65
Hexadecane	266.45	No Transition				293	48.88 48.66 49.31 48.00 48.85 50.43 47.28	48.80	44.38
Tetrakis(aminomethyl)methane monohydrate	150.22	No Transition				318-320	(48.47) (39.36 + 10.06) (47.51) (12.59) (20.93) (24.25) (31.43) (30.32) (32.53)		
2-Amino-2-methyl-1-propanol	89.14	No Transition				285-293	18.75 (22.27) (22.32) (21.63) (17.03) 17.76 (16.30)	18.26	5.71

a/ Data collected in the laboratories of Midwest Research Institute.

Series I determinations were made in open or sealed pans as indicated; sealed pans were used in all Series II determinations. When possible 5-10 mg. of well-ground materials were used. Data illustrating the effects of sample weight and heating rate are summarized in Table 37.

D. Effect of Compound Purity on Thermal Properties

A number of the compounds were purified by recrystallization from the following solvents: Pentaerythritol from water; 2,2-dimethyl-1,3-propanediol from benzene; 2-amino-2-hydroxymethyl-1,3-propanediol from dry ethanol; 2-amino-2-methyl-1,3-propanediol from dry ethanol; 2-hydroxymethyl-2-nitro-1,3-propanediol from an ethyl acetate-benzene mixture; 2-methyl-2-nitro-1,3-propanediol from dry ethanol; and 2,2-bis(hydroxymethyl)propionic acid from water. 2-Amino-2-methyl-1,3-propanediol was also sublimed. It is probable in the recrystallizations of the amino derivatives that insufficient care was taken to exclude moisture. Qualitative experimental data for the materials after various purifications are included in Table 14. The quantitative results are reported in Table 38. The substance, 2-amino-2-methyl-1-propanol, which was expected to have a mesocrystalline phase, showed only a broad fusion endotherm. The data for this compound in Table 38 were obtained after two distillations of the substance through a 30-in. spinning band column.

E. Synthesis of Candidate Substances

1. Tetramethylsuccinonitrile: When 82 g. (0.50 mole) of azobisisobutyronitrile was decomposed in toluene solution according to the method of Bickel and Waters[29], 43.2 g. (71%) of tetramethylsuccinonitrile, m.p. 168-170°, was obtained (reported m.p., 167-167.5°).[29]

2. Tetramethylsuccinimide: Treatment of 37.0 g. (0.33 mole) of tetramethylsuccinonitrile with sodium hydroxide, water, and ethanol[29] gave 26 g. (52%) of tetramethylsuccinimide, m.p. 190-191° (reported m.p. 187-188°).[29]

3. Tetramethylsuccinic acid: Hydrolysis of 16.0 g. (0.10 mole) of tetramethylsuccinimide in an acidic solution by Bickel and Waters's method[29] gave 5.0 g. (29%) of tetramethylsuccinic acid, m.p. 188-189 (reported m.p. 190-192°).[29]

(Text continued on p. 81.)

TABLE 37

RELATION OF ENTHALPY DATA AND DIFFERENTIAL THERMAL ANALYSIS VARIABLES[a]

Pentaerythritol (Transition)

Wt. Sample (mg.)	ΔH (cal/g)
5.78	68.81
9.78	66.07
10.07	69.22
10.30	68.47
10.94	68.66

Tetrakis(trimethylsilyl)silane (Transition)

Wt. Sample (mg.)		ΔH (cal/g)
5.85		9.86
8.16	b/	8.60
8.16	b/	8.21
8.16	b/	8.10
8.64	b/	10.27
8.64	b/	10.71
9.45	b/	8.13
9.45	b/	9.14
10.13		8.36

2-Methyl-2-nitro-1,3-propanediol (Transition)

Wt. Sample (mg.)	ΔH (cal/g)
5.83	48.41
7.76	43.76
8.97	38.41
9.24	43.61
9.43	47.86
12.83	49.95
13.21	48.30
15.11	47.67

Heating Rate (°C/min)	ΔH (cal/g)
2.5	38.41
5	43.61
10	47.86
15	48.41

a/ Data collected in the laboratories of Midwest Research Institute.
b/ Replicate determinations on the same sample.

TABLE 38

ENTHALPIES OF TRANSITION AND FUSION FOR SUBSTANCES SUBJECT TO PURIFICATION STEPS[a/]

Compound	Formula Weight	Transition Temperature (°K)	Transition ΔH (cal/g) Value	Transition ΔH (cal/g) Average	Transition ΔS (e.u.- Average)	Fusion Temperature (°K)	Fusion ΔH (cal/g) Value	Fusion ΔH (cal/g) Average	Fusion ΔS (e.u.- Average)
Pentaerythritol									
Recrystallized once.	136.15	457-458	68.81	70.47	20.99	531-535	9.06	9.54	2.45
			71.30				9.49		
			72.27				9.72		
			69.10				9.88		
			70.88				9.57		
Unpurified		454-456	66.07	68.25	20.47	528-532	9.23	9.21	2.37
			68.47				9.28		
			69.22				9.45		
			68.81				9.08		
			68.66				8.89		
2-Hydroxymethyl-2-nitro-1,3-propanediol									
Recrystallized 3 times	151.12	353-355	33.78	35.50	15.20	Compound Decomposes			
			(28.57)						
			33.90						
			(25.98)						
			35.71						
			36.46						
			36.68						
2-Methyl-2-nitro-1,3-propanediol									
Recrystallized 4 times	135.12	352-353	44.45	45.50	17.47	422-426	6.91	6.84	2.19
			45.11				6.94		
			46.95				6.67		
2-Amino-2-methyl-1,3-propanediol									
Recrystallized once	105.14	349-353	53.87	53.22	16.03	380-381	5.89	5.87	1.62
			52.57				5.85		
Recrystallized 5 times		350-354	51.02	50.24	15.09	378-381	5.36	5.41	1.50
			53.17				5.90		
			49.86				5.20		
			47.93				5.40		
			49.24				5.20		
Sublimed		351-353	54.43	55.59	16.65	378-381	6.41	6.66	1.85
			56.48				6.84		
			55.86				6.72		
Sublimed twice		351-353	56.61	57.31	17.17	383-385	6.73	6.80	1.87
			56.51				6.63		
			58.80				7.05		
Redetermination of unpurified material			55.09	54.12					
			54.04						
			53.22						

a/ Data collected in the laboratories of Midwest Research Institute.

4. Tetra-t-butylthiopentaerythritol: The sealed tube method of Backer and Dykstra[30] gave 9.7 g. (46%) of tetra-t-butylthiopentaerythritol, m.p. 115-116° (reported m.p., 123.6°)[30], from 39.3 g. (0.35 mole) of sodium t-butylmercaptate and 19.5 g. (0.05 mole) of pentaerythrityl tetrabromide.

5. Pentaerythritol tetramethanesulfonate: When 9.5 g. (0.07 mole) of pentaerythritol was treated with 34.3 g. (0.30 mole) of methanesulfonyl chloride and pyridine by Buchman's procedure,[31] 17.6 g. (59%) of pentaerythritol tetramethanesulfonate, m.p. 212-213° (reported m.p. 209-209.5°)[31] was obtained.

6. 2,2,3,3-Tetramethylbutane-1,4-diol (attempted):

a. By reduction of the acid: Lithium aluminum hydride reductions[32] of 2,2,3,3-tetramethylsuccinic acid were attempted in both ether and tetrahydrofuran, but only the acid could be recovered.

b. Via the reduction of the ester or acid chloride: Conventional procedures for the synthesis of the acid chloride or the ethyl ester of 2,2,3,3-tetramethylsuccinic acid, which would be more readily reduced by lithium aluminum chloride than the free acid, gave only unchanged acid.

7. Tetrakis(aminomethyl)methane monohydrate:

a. Tetrakis-(p-toluenesulfonamidomethyl)methane: When 50 g. (0.30 mole) of sodio-p-toluenesulfonamide and 25 g. (0.07 mole) of pentaerythrityl tetrabromide were heated according to the procedures of Litherland and Mann,[33] 12.0 g. (25%) of impure tetrakis-(p-toluenesulfonamidomethyl)methane was obtained.

b. Tetrakis(aminomethyl)methane disulfate: Precipitation of the hydrolysate of 12.0 g. (0.016 mole) tetrakis(p-toluenesulfonamidomethyl)methane according to the procedure of Litherland and Mann[33] with sulfuric acid gave 2.7 g. (50%) of tetrakis(aminomethyl)methane disulfate.

c. Tetrakis(aminomethyl)methane monohydrate: Neutralization of and recrystallization of 2.5 g. (0.0070 mole) of tetrakis(aminomethyl)methane disulfate gave 0.5 g. (50%) of the monohydrate, m.p. 43-46° (report 40-41°).[34] On exposure to air the crystals changed to a gum.

8. Pentaerythrityl tetranitrile and tetrathiocyanate (attempted):

a. Pentaerythrityl tetrabenzenesulfonate and tetra-p-toluenesulfonate: When 65 g. (0.48 mole) of pentaerythritol was treated with 375 g. (2.12 moles) of benzenesulfonyl chloride in the presence of 325 g. of pyridine and the product was recrystallized from dry ethanol, 50 g. of pentaerythrityl tetrabenzenesulfate, m.p. 102-103° (reported, 103°),[31] was obtained. Pentaerythrityl tetra-p-toluenesulfonate was similarly prepared.

b. When pentaerythrityl tetrabenzenesulfonate or tetra-p-toluenesulfonate was heated with potassium cyanide or potassium thiocyanate in diethylene glycol at 140° according to Buchman's procedure,[31] only ill-defined decomposition products could be isolated. At lower temperature, unchanged reactants were recovered.

F. Two-Component Systems

Samples for the qualitative determinations of two-component mixtures were prepared by heating weighed materials in a sealed ampoule at a temperature slightly above the melting point of the system. The results for the system 2-hydroxymethyl-2-methyl-1,3-propanediol and 2-hydroxymethyl-2-ethyl-1,3-propanediol are summarized in Figure 6. A number of two-component mixtures of two mesocrystalline substances selected from Table 14 were also examined in a preliminary way, but no definitive results were obtained. One of the substances, 2-hydroxymethyl-2-nitro-1,3-propanediol, which is known to decompose above its melting point, created sufficient pressure in the sealed tube to rupture it.

G. Macro Studies of Crystallization

Into about 2.5 g. of each substance in a 150 x 15 mm. test tube was inserted an uncalibrated 360° glass-mercury thermometer in such a way that the substance covered the bulb of the thermometer. The test sample was heated to 10-15°C above its fusion temperature in an oil bath equipped with a magnetic stirrer, then allowed to cool at a rate determined by the difference in room temperature and the bath temperature. For the substances with transition temperatures of about 80°C, the difference between the bath temperature and the sample temperature was about 4°C at the transition For pentaerythritol it was about 12°C. Bath temperatures and sample temperatures were recorded every 0.5 min. to determine the equilibrium temperature for phase transition (plateau temperature) on cooling. The results of experiments with various modes of nucleation are reported in Table 39.

(Text continued on p. 84.)

TABLE 39

MACRO STUDIES OF CRYSTALLIZATION[a/]

Substance	Mode of Nucleation	Minimum Temp. Before Plateau (°C)	Plateau Temp. (°C)	Cooling Rate of Bath at Plateau (°C/min.)	Transition Temp. (°C)
2-Hydroxymethyl-2-methyl-1,3-propanediol	None	78.5	81	1	81
2-Methyl-2-nitro-1,3-propanediol	None	72	75	1	77-78
Pentaerythritol	None	178	179	4	181-183
2-Amino-2-hydroxymethyl-1,3-propanediol	None	129.5	130.5	2.5	
	Tube Scratched at 132.5	129.5	130	2.5	131-132
2-Amino-2-methyl-1,3-propanediol (recrystallized one)	None	51 No Plateau	--	--	78-80
	1% Zinc Acetate	51 No Plateau	--	--	
	1% Zinc Oxide	48.5 [b/] No Plateau			
	Tube Scratched at 84 and 79	72	74	1	
	1% Zinc Oxide; tube Scratched at 84 79 , and 74.5	72	74	1	

a/ Data obtained in the laboratories of Midwest Research Institute.
b/ When the tube was scratched at 48.5°, the new phase formed immediately and the temperature rose to 72°.

H. Micro Studies of Crystallization

Samples of 5-10 mg. of four substances were examined in a series of supercooling studies using the differential scanning calorimeter attachment of the differential thermal analyzer. The samples, with and without nucleating agents, were heated at a specified rate to 20° above the transition temperature, held at ± 5° of that temperature for 10 min., then cooled at a specified rate until an exotherm indicated that transition had occurred to form the phase stable at the lower temperature. Except where otherwise specified, sealed coated aluminum pans were used in the experiments. The results are summarized in Tables 40-43.

VII. GENERAL REFERENCES ON PLASTIC CRYSTALS

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(Text continued on p. 89.)

TABLE 40

MICRO STUDIES OF THE NUCLEATION OF THE SOLID/SOLID-PHASE CHANGE OF 2-HYDROXYMETHYL-2-NITRO-1,3-PROPANEDIOL

Conditions	Sample	Heating Rate (°C/min)	Cooling Rate (°C/min)	Temperature Difference Between Onset of Transition and Crystallization (°C)
Unnucleated	Not Recrystallized	9.2	9.7	9
		9.2	9.7	15
		4.3	4.7	7
		1.9	2.5	11
		1.9	2.5	11
		1.9	2.5	15
		cycled 4° below transition		6
Nucleated with copper metal (trace, fine powder)		9.2	9.7	9
		9.2	9.7	9.3
		9.2	9.7	9
		cycled 2° below transition		7
		cycled 2° below transition		5
Silica gel (trace, 200 mesh)		9.2	9.7	9
		9.2	9.7	13
		4.3	4.7	15
Pentaerythritol (trace, ground in mortar)		9.2	9.7	5.5
		4.3	4.7	4
		1.9	2.5	5
		1.9	2.5	4
		1.9	2.5	4

a/ Data collected in the laboratories of Midwest Research Institute.

TABLE 41

MICRO STUDIES OF THE NUCLEATION OF THE SOLID/SOLID-PHASE CHANGE OF 2-METHYL-2-NITRO-1,3-PROPANEDIOL[a]

Conditions	Sample[b]	Heating Rate (°C/min)	Cooling Rate (°C/min)	Temperature Difference Between Onset of Transition and Crystallization (°C)
Unnucleated	A	14.4	13.2	31
	A	9.0	9.0	26
	A	9.0	9.0	28
	A	4.3	4.4	18
	A	4.3	4.4	28
	A	4.6	4.4	26
	A	1.8	2.2	29
	A	2.0	1.7	29
	A	Cycled for 30 min. at 10° below transition		No crystallization
In an etched metal pan	B	9.0	9.0	31
	B	9.0	9.0	29
	B	9.0	9.0	27
	B	4.3	4.4	30

a/ Data collected in the laboratories of Midwest Research Institute.
b/ Sample A - Unrecrystallized material; Sample B - After five recrystallizations.

TABLE 42

MICRO STUDIES OF THE NUCLEATION OF THE SOLID/SOLID-PHASE CHANGE OF 2-AMINO-2-HYDROXYMETHYL-1,3-PROPANEDIOL[a]

Conditions	Sample	Heating Rate (°C/min)	Cooling Rate (°C/min)	Temperature Difference Between Onset of Transition and Crystallization (°C)
Unnucleated	Unrecrystallized	9.0	9.0	70
		9.0[b]	9.0	68
Nucleated with ground glass (~ 10% ground in mortar)		9.0	9.0	61
		9.0[b]	9.0	68
Nucleated with pentaerythritol (trace, ground in mortar)		9.0	9.0	63
		9.0[b]	9.0	66
Nucleated with silica gel (trace, ground in mortar)		9.0	9.0	64

a/ Data collected in the laboratories of Midwest Research Institute.
b/ Recycled.

TABLE 43

MICRO STUDIES OF THE NUCLEATION OF THE SOLID/SOLID-PHASE CHANGE OF 2-AMINO-2-METHYL-1,3-PROPANEDIOL[a]

Conditions	Sample[b]	Heating Rate (°C/min)	Cooling Rate (°C/min)	Temperature Difference Between Onset of Transition and Crystallization (°C)
Unnucleated	A	9.0	9.0	> 50
	B	9.0	9.0	> 50
	B	9.0	9.0	> 50[b]
	B	9.0	9.0	> 50[b]
	C	9.0	9.0	> 50
Nucleated with 2-amino-2-hydroxymethyl-1,3-propanediol	A	9.0	9.0	> 50
(trace, ground in mortar)	B	9.0	9.0	> 50
Nucleated with ZnO_2 (trace, pigment grade)	C	9.0	9.0	> 50
Nucleated with Lexan polycarbonate (trace, ground in mortar)	C	9.0	9.0	> 50
In uncoated aluminum pan	C	9.0	9.0	> 50
Nucleated with TiO_2 (trace, pigment grade)	C	9.0	9.0	> 50
Nucleated with copper metal (trace, very fine powder)	C	9.0	9.0	> 50
In an etched metal pan	A	9.0	9.0	> 50
Nucleated with pentaerythritol	A	9.0	9.0	> 50
(trace, ground in mortar)	C	9.0	9.0	> 50
	C	9.0	9.0	> 50
Nucleated with silica gel	A	9.0	9.0	> 50
(~ 10%, ground in mortar)	A	9.0	9.0	> 50
Nucleated with alumina	C	14.4	13.2	> 50
(~ 10%, ground in mortar)	C	14.4	13.2	> 50[c]
Nucleated with asbestine (~ 10%, pigment grade)	C	14.4	13.2	> 50
Nucleated with baryties (~ 10%, pigment grade)	C	9.0	9.0	> 50
Nucleated with titanium oxide chelate (~ 10%, ground in mortar)	C	9.0	9.0	> 50

a/ Data collected in the laboratories of Midwest Research Institute.

b/ Sample A - Unrecrystallized material; Sample B - After one recrystallization; Sample C - After five recrystallizations.

c/ Upon recycling the sample, an exotherm was observed during the heating cycle.

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VIII. CONCLUSIONS

During the research period covered by this report, considerable data have been accumulated that support the original proposal that the target requirements for passive thermal control may be achieved through the use of solid/solid-phase change materials. In the screening procedure for commercially available materials, 33 substances were found that had previously unreported solid/solid transitions, and five of these substances had transition enthalpies greater than 45 cal/g although not all five of these substances exhibited transition within the target temperature range. Relevent data for these five substances is summarized in Table 44.

Through a consideration of the mechanism of solid/solid phase changes and a consideration of qualitative and quantitative data for substances with mesocrystalline phases, predictions can be made for candidate structures that may meet the specified criteria. These compounds, in particular, include various functional derivatives with the tetrahedral structure.

None of the presently available theoretical or experimental data precludes the achieving of target properties in solid/solid transitions. A number of substances have transition enthalpies greater than 56 cal/g; a number of substances exhibit transitions in the 270-370°K range. The problem remains to find substances that exhibit the required combination of these two properties. Available data indicate that density requirements and supercooling limitations should be readily met.

TABLE 44

PROPERTIES OF SUBSTANCES WITH TRANSITION ENTHALPIES GREATER THAN 45 CAL/G

Substance	T[a] (°K)	ΔH_F (cal/g)	T_T (°K)	ΔH_T[a] (cal/g)	Observed Supercooling in Transition (No Nucleating Agent Added) (°K)
2-Hydroxymethyl-2-methyl-1,3-propanediol	470-471	11	354	46	2.5
2-Amino-2-methyl-1,3-propanediol	380-381	8	349-354	63	2.0[b]
2-Amino-2-hydroxymethyl-1,3-propanediol	439-442	6	404-407	68	0.5[b]
2-Methyl-2-nitro-1,3-propanediol	428-431	8	353-356	48	3.0
2,2-Bis(hydroxymethyl)-propionic acid	467-470	6	425-428	69	--

a/ Procedural values obtained by differential thermal analysis.
b/ This value was obtained when the tube was scratched: Otherwise, the new phase was not initiated.

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APPENDIX I

TABLES A-1 TO A-7 AND REFERENCES

TABLE A-1

TRANSITION AND FUSION DATA FOR CERTAIN INORGANIC COMPOUNDS

Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u.)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u.)	Ref. a/
Argon	A	39.948	281	7.03	83.85 b/	-189.30	3.35						1 (A)
Hydrogen bromide	HBr	80.924	576	7.11	186.28	- 86.8	3.09	85.8	1.06	116.9	-156.3	0.734	1 (A)
Xenon	Xe	131.3	548	4.17	161.3	-111.9	3.40						1 (A)
Ammonium nitrate	NH_4NO_3	80.048	130.	16.24	442.8	169.6	2.936	1010	12.6	398.6	125.4	2.533	2 (D)
								320	4.00	357.6	84.4	0.895	2 (D)
								409.9	5.121	305.4	32.2	1.342	3 (A)
								110.8	1.384	256.2	-15.0	0.433	3 (A)
Carbon monoxide	CO	28.01	199.7	7.130	68.09	-205.06	2.933	151	5.39	61.55	-211.60	2.46	1 (A)
Hydrogen chloride	HCl	36.465	475	13.0	158.94	-214.21	2.99	284	7.79	98.38	-174.77	2.89	1 (A)
Phosphine	H_3P	34.00	270	7.9	139.35	-133.80	1.94	116	3.41	88.12	-185.03	1.32	4 (A)
								186	5.47	49.44	-223.71	3.76	
								19.7	0.579	30.31	-242.84	0.65	
Hydrogen sulfide	H_2S	34.08	569	16.7	187.63 1/	-85.52	3.03 1/	110	3.2	126.2 2/	-147.0	0.86 2/	1/1 (A)
								366	10.7	103.6 2/	-169.6	3.53 2/	2/5 (A)
Nitrogen	N_2	28.016	172.3	6.150	63.14	-210.01	2.729	54.70	1.952	35.61	-237.54	1.536	1 (A)
Potassium borohydride	KBH_4	50.95			decomp.			58.4	1.15	75.7	-197.5	0.77	6 (F)
Sodium borofluoride	$NaBF_4$	109.81						1300	12	511.4	238.2	2.5	7 (D)
Ammonium borofluoride	NH_4BF_4	114.86						1950	17	472.7	199.5	4.1	7 (D)
Ammonium thiocyanate	NH_4SCN	76.12			442	169 1/		789 2/	10.4	360.9	87.7 2/	2.19 2/	1/8 (F)
													2/9 (F)
Potassium borofluoride	KBF_4	125.92						1260	10	551.9	278.7	2.3	7 (D)
Potassium phospho-hexafluoride	KPF_4	184.08						280	1.4	257.6	-15.6	1.0	7 (D)
Thallium borotetra-fluoride	$TlBF_4$	291.21						1370	4.7	475.0	201.8	2.9	7 (D)

TABLE A-1 (Concluded)

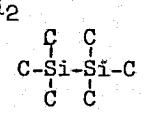
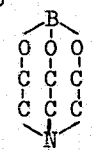
Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u.)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u.)	Ref.
Iridium hexafluoride	IrF_6	306.2	1200	3.92	317.1	43.9	3.77	1930	6.30	272.0	-1.2	7.08	10 (A)
Molybdenum hexafluoride	MoF_6	199.95			290.60	17.45				263.60	-9.55		11 (A)
Osmium hexafluoride	OsF_6	304.2	1110	3.65	306.4	33.2	3.63	2000.	6.57	274.5	1.3	7.29	10 (A)
Platinum hexafluoride	PtF_6	309.09	1270	4.1	334.8	61.60	3.8	1870	6.03	276.5	3.3	6.77	10 (A)
Rhenium hexafluoride	ReF_6	300.22	1040	3.46	291.7	18.5	3.56	2020	6.73	269.8	-3.4	7.49	10 (A)
Rhodium hexafluoride	RhF_6	206.91			343	70				280	7		12 (F)
Ruthenium hexafluoride	RuF_6	205.7			327	54				275.7	2.5		13 (F)
Sulfur hexafluoride	SF_6	146.07	1200	8.22	222.5	50.7	5.40	384	2.63	94.26	-178.89	4.07	1 (A)
Technetium hexafluoride	TcF_6	203			310	37				267.9	-5.3		14 (F)
Tungsten hexafluoride	WF_6	297.86	980.	3.29	275.2	2.0	3.56	2070	6.95	264.7	-8.5	7.81	10 (A)
Rhenium oxypentafluoride	$ReOF_5$	297.31	1220	4.10	314 (237.1 mm.)	40.8 (237.1 mm.)	3.886	1339	4.50	303 (144.6 mm.)	30.9 (144.6 mm.)	3.868	15 (E)
Potassium cyanide	KCN	65.118								213[1]	-60		1/16 (F)
								300-	4.61	168.3[3]	-104.9	1.78	2/17 (A)
										82.9[2]	-190.3		3/18 (A)
Ammonia triborane	$NH_3B_3H_7$	56.458						1233	21.84	297.10	23.95	4.150	19 (A)
Trimethylamine-triborane	$(CH_3)_3N:B_3H_7$	98.63						845.4	8.551	209.6	63.6	4.0	20 (A)

a/ In Tables A-1 to A-6 the letter in parenthesis following the literature citation indicates the experimental procedure followed. (A) Calorimeter, (B) Dielectric, (C) N.m.r. (nuclear magnetic resonance), (D) D.t.a. (differential thermal analysis), (E) Vapor pressure, (F) Technique not listed.

b/ Underlined numbers are literature values; those not underlined are calculated values.

TABLE A-2

TRANSITION AND FUSION DATA FOR CERTAIN ORGANOMETALLIC COMPOUNDS

Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u.)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u.)	Ref. a/
Dimethylcadmium	C_2H_6Cd C-Cd-C[b/]	142.47	1870	13.1	270.48	-2.67	6.93	364	2.55	254.35	-18.8	1.43	21 (A)
Tris(trimethylsilyl)-amine	$C_9H_{27}Si_3N$ $N(SiC_3)_3$	215.46			335-339	62-66[1/]				232 244	-41[2/] -29[1/]		1/22 (F) 2/23 (C)
Bis(trimethylsilyl)-(chlorodimethyl-silyl)amine	$C_8H_{24}Si_3NCl$ $(C_3Si)_2NSiC_2Cl$	237.89			331-333	58-60[1/]				248	-25[2/]		1/24 (F) 2/23 (C)
Bis(trimethylsilyl)-(dichloromethyl-silyl)amine	$C_7H_{21}Si_3NCl_2$ $(C_3Si)_2NSiCCl_2$	260.32			353-358	80-85[1/]				242	-31[2/]		1/25 (F) 2/23 (C)
Bis(trimethylsilyl)-(trichlorosilyl)amine	$C_6H_{18}Si_3NCl_3$ $(C_3Si)_2NSiCl_3$	282.75			353-358	80-85[1/]				237[2/]	-36[2/]		1/25 (F) 2/23 (C)
Bis(chlorodimethyl-silyl)-(trimethyl-silyl)amine	$C_7H_{21}Si_3NCl_2$ $C_3SiN(SiC_2Cl)_2$	260.32			341-349	68-76				276	3		22 (F)
Tris(chlorodimethyl-silyl)amine	$C_6H_{18}Si_3NCl_3$ $N(SiC_2Cl)_3$	282.75			353-364 346-348	80-91[1/] 73-75[2/]				287	14[1/]		1/26 (F) 2/27 (F)
Bis[(dimethylamino)-dimethylsilyl]-(tri-methylsilyl)amine	$C_{11}H_{33}Si_3N_3$ $C_3SiN(SiC_2NC_2)_2$	269.52			350-358	77-85				263-265	-10 to -8		22 (F)
Hexamethyldisilane	$C_6H_{18}Si_2$ 	146.38	721	4.94	287.7	14.5	2.51	2330	15.9	221.8	-51.4	10.5	28 (D)
Triethanolamine-borate	$C_6H_{12}O_3NB$ 	144.89	5760	39.8	511.86	238.71	11.3	1141	7.875	466.54	193.39	2.446	29 (A)

a/ In Tables A-1 to A-6 the letter in parenthesis following the literature citation indicates the experimental procedure followed.
(A) Calorimeter, (B) Dielectric, (C) N.m.r. (nuclear magnetic resonance), (D) D.t.a. (differential thermal analysis),
(E) Vapor pressure, (F) Technique not listed.

b/ C indicates CH_3, CH_2, or CH.

TABLE A-3

TRANSITION AND FUSION DATA FOR CERTAIN TETRAHEDRAL COMPOUNDS

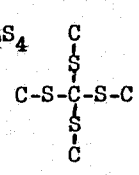
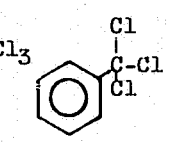
Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u.)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u)	Ref. a/
Germanium hydride	GeH_4	76.63	199.7	2.606	107.26	-165.89	1.86	129.6 130.7	1.691 1.706	76.5 73.2	-196.7 -200.0	1.69 1.79	30 (A)
Silicon hydride	SiH_4	32.12	159	4.95	88.5	-184.7	1.80	165.60	5.156	63.5	-209.7	2.32	1 (A)
Methane	CH_4	16.042	224	14.0	90.6	-182.6	2.48	15.7	0.979	20.4	-252.8	0.770	31 (A)
Deuteromethane	CD_4	20.0624	215.7	10.75	89.3	-183.9	2.42	58.7 19.7	2.93 0.982	26.3 21.4	-246.9 -252.8	2.23 0.921	31 (A)
Bromomethane	CH_3Br	94.95	1429	15.05	179.44	-93.71	7.964	113.4	1.194	173.8	-99.4	0.653	32 (A)
Carbon tetrabromide	CBr_4	331.67	945	2.85	363.2	90.0	2.61	1420	4.28	320.0	46.8	4.4	33 (A)
Carbon tetrachloride	CCl_4	153.838	601	3.91	250.3	-22.9	2.4	1095	7.118	225.35	-47.80	4.859	34 (A)
Carbon tetrafluoride	CF_4	88.01	165	1.87	89.5[1]	-183.7	1.84[1]	354	4.02	76.2[2]	-197.0	4.64[2]	1/35 (C) 2/36 (A)
Tetramethylortho-thiocarbonate	$C_5H_{12}S_4$ 	200.41	990	4.9	338.7	65.5	2.9	1820 1460	9.08 7.29	318.7 296.4	45.5 23.2	5.71 4.93	37 (F)
$\alpha\alpha\alpha$-Trichloro-toluene(Benzotri-chloride)	$C_7H_5Cl_3$ 	195.48	1130	5.8	268	-5	4.22						38 (F)
Monodeuteromethane	CH_3D	17.0390	217.5	12.76	90.5	-182.7	2.4	38.2 13.7	2.24 0.804	22.6 15.5	-250.6 -257.7	1.68 0.88	31 (A)
Methanol	CH_3OH	32.04	770	24	175.6	-97.6	4.4	150	4.7	155	-118	0.97	10 (A)
Methanethiol	CH_3SH	48.10	1411.4	29.34	150.16	-122.99	9.399	52.5	1.09	137.6	-135.6	0.350	39 (A)
Methylamine	CH_3NH_2	31.06	1465.8	47.19	179.70	-93.45	8.157	23.3	0.750	101.5	-171.7	0.23	40 (A)
Methanol-d	CH_3OD	33.05	726	22.0	173	-100	4.20						41 (A)

TABLE A-3 (Continued)

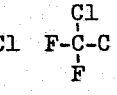
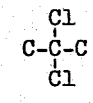
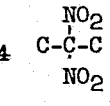
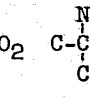
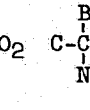
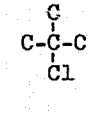
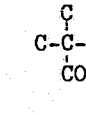
Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u.)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u.)	Ref.
Acetaldehyde	CH_3CHO 	44.05	775	17.6	150	-123	5.1						42 (A)
Acetaldehyde monohydrate	$C_2H_6O_2$ 	62.07	1200.	16.11	319	46	3.10						38 (F)
1,1,1-Trichloroethane	$C_2H_3Cl_3$ 	133.41	800[1]	6	240.4[1]	-32.8	3.3[1]	1786[1] -50[2]	13.39 0.4	224.2[1] 205[2]	-49.0 -68	7.97[1] 0.2	1/43 (A) 2/44 (A)
1,1,1-Trifluoroethane	$C_2H_3F_3$ 	84.04	1480	17.6	161.82	-111.33	9.146	70.92	0.844	156.35	-116.80	0.454	45 (A)
1-Chloro-1,1-difluoroethane	$C_2H_3F_2Cl$ 	100.50	640	6.4	142.4	-130.8	4.5						46 (F)
2,2-Dichloropropane	$C_3H_6Cl_2$ 	112.99	790[1]	7.0	238.5[1]	-34.7	3.3[1]			188.2	-85.0[2]		1/47 (A) 2/48 (B)
2,2-Dinitropropane	$C_3H_6N_2O_4$ 	134.09			326	53				268.1 266.1	-5.1 -7.1		44 (A)
2-Chloro-2-nitropropane	$C_3H_6ClNO_2$ 	123.54	320	2.6	251.6	-21.6	1.27	2280	18.5	215.7 213.8	-57.5 -59.4	10.69	44 (A)
2-Bromo-2-nitropropane	$C_3H_6BrNO_2$ 	168.00			256	-17				239 234	-34 -39		44 (A)
2-Chloro-2-methylpropane	C_4H_9Cl 	92.57	480[2]	5.2	248.2	-25.0[2]	2.0[1]	1400 420	15 4.5	219.7 183.2	-53.5[2] -90.0[2]	6.4[2] 2.3[2]	1/ 1 (A) 2/49 (A)
Pivalic acid (2,2-Dimethylpropanoic acid)	$C_5H_{10}O_2$ 	102.13	800.	7.8	308	35	2.6						38 (F)

TABLE A-3 (Continued)

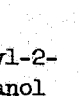
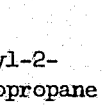
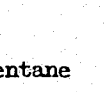
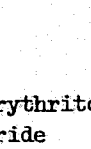
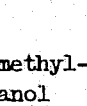
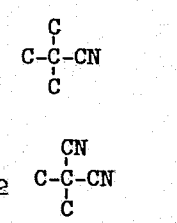
Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u.)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u.)	Ref.
2-Bromo-2-methyl-propane	C_4H_9Br 	137.03	470	3.4	256	-17	1.8	250 1350	1.8 9.85	231.6 208.7	-41.6 -64.5	1.1 6.5	49 (A)
2-Methyl-2-propanol	$C_4H_{10}O$ 	74.12	1602	21.61	298.97	25.82	5.359	198	2.67	286.14	12.99	0.691	50 (A)
2-Methyl-2-nitropropane	$C_4H_9NO_2$ 	119.12			296.5	23.3				258	-15		44 (A)
2-Methyl-2-propanethiol	$C_4H_{10}S$ 	90.186	593.2	6.578	274.42	1.27	2.162	232.0 154.9 972.0	2.572 1.717 10.78	199.4 157.0 151.6	-73.8 -116.2 -121.6	1.163 0.987 6.412	51 (A)
Neopentane	C_5H_{12} 	72.146	778.3	10.79	256.61	-16.54	3.033	620	8.6	140	-133	4.4	1 (A)
Pentaerythritol fluoride	$C_5H_8F_4$ 	144.11	1230	8.54	367[1]	94	3.35[1]	3170	22.0	249.40[2]	-13.75	12.7[2]	1/10 (A) 2/52 (F)
Pentaerythritol	$C_5H_{12}O_4$ 	136.15	1700	12.0	538.7	265.5	3.2	10500	77.1	460.9	187.7	22.8	53 (A)
2,2-Dimethyl-1,3-dinitropropane	$C_5H_{10}N_2O_4$ 	162.17			345	72				276	3		44 (A)
2,2-Dimethyl-1-propanol	$C_5H_{12}O$ 	88.15	1060[1]	12.0	264[1] 327.7-328.7	-9 54.5-55.5[2]	4.0[1]						1/48 (B) 2/54 (F)

TABLE A-3 (Concluded)

Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u.)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u.)	Ref.
Trichloroacetic acid	$C_2HCl_3O_2$ 	163.40	1410	8.63	332	59	4.2						38 (F)
Trimethylacetonitrile	C_5H_9N	83.130	2220	26.7	292.13	18.98	7.60	433 55	5.21 0.66	232.74 213	-40.41 -60	1.86 0.26	55 (A)
Dimethylmalonitrile	$C_5H_6N_2$	94.114	969	10.3	307.47	34.32	3.15	2358	25.05	302.6	29.4	7.792	56 (A)
Tetramethylammonium chloride	$C_4H_{12}NCl$ 	109.60						26 28	0.24 0.26	184.9 75.8	-88.3 -197.4	0.14 0.37	57 (F)

a/ In Tables A-1 to A-6 the letter in parenthesis following the literature citation indicates the experimental procedure followed. (A) Calorimeter, (B) Dielectric, (C) N.m.r. (nuclear magnetic resonance), (D) D.t.a. (differential thermal analysis), (E) Vapor pressure, (F) Technique not listed.

b/ Underlined numbers are literature values; those not underlined are calculated values.

TABLE A-4

TRANSITION AND FUSION DATA FOR CERTAIN OCTAHEDRAL COMPOUNDS

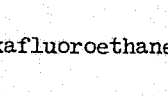
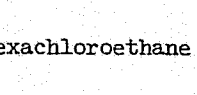
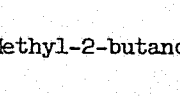
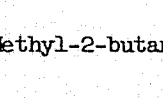
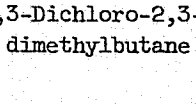
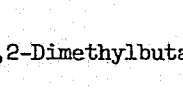
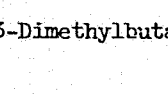
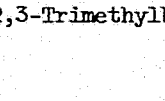
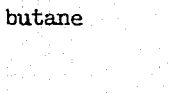
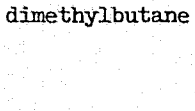
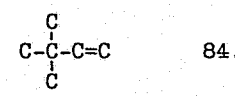
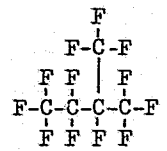
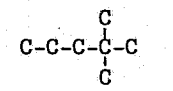
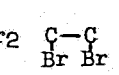
Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u.)	Ref. a/
Hexafluoroethane	C_2F_6 	138.01	642	4.65	173.10	-100.05	3.71	893	6.47	103.98	-169.17	8.59	59 (A)
Hexachloroethane	C_2Cl_6 	236.76	2330	9.84	458	185	5.09	1985 613	8.300 2.59	345 318	72 45	5.70 1.93	60 (F)
2-Methyl-2-butanol	$C_5H_{12}O$ 	88.15	1065	12.08	264.1	-9.1	4.03						61 (A)
2-Methyl-2-butanethiol	$C_5H_{12}S$ 	104.21	145.4	1.395	169.37	-3.78	0.858	1907.1	18.301	159.1	-114.1	11.99	62 (A)
2,3-Dichloro-2,3-dimethylbutane	$C_6H_{12}Cl_2$ 	155.08			432-433	159-160				263-277	-10 to +4		63 (B)
2,2-Dimethylbutane	C_6H_{14} 	86.172	138.5	1.607	174.16	-98.99	0.795	67.7 1289.2	0.786 14.96	140.88 126.81	-132.27 -146.34	0.480 10.166	64 (A)
2,3-Dimethylbutane	C_6H_{14} 	86.172	192	2.23	145.2	-128.0	1.32	1550	18.0	136	-137	11.4	64 (A)
2,2,3-Trimethylbutane	C_7H_{16} 	100.21	540.4	5.393	248.57	-24.58	2.174	585.8	5.846	121.4	-151.8	4.825	65 (A)
2,2,3,3-Tetramethylbutane	C_8H_{18} 	114.23	1602	15.78	373.97	100.82	4.82	478	4.18	152.5	-120.7	3.134	66 (A)
2,3-Dibromo-2,3-dimethylbutane	$C_6H_{12}Br_2$ 	244.0			decomp.	decomp.				348-383	75-110		63 (B)

TABLE A-4 (Concluded)

Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u.)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u.)	Ref.
2,3-Dimethyl-2-butene	C_6H_{12} 	84.16	1542	18.32	198.92	-74.23	7.75	884.0	10.50	196.82	4.29	4.491	67 (A)
3,3-Dimethyl-1-butene	C_6H_{12} 	84.16	262	3.11	138.4	-14.8	1.65	1039	12.35	124.9	-148.3	8.32	68 (A)
Perfluoroisopentane	C_5F_{12} 	288.05	350	1.22	176	-97	2						69 (A)
2,2-Dimethylpentane	C_7H_{16} 	100.198	1392.2	13.894	149.43	-123.72	9.317	2522	25.17	83.2	-190.0	30.3	65 (A)
Succinonitrile (Ethylene dicyanide)	$C_4H_4N_2$ NC-C-C-CN	80.09	888	11.1	331.3	58.1	2.68	1420	17.7	223.3	-49.9	6.35	10 (A)
Ethylene bromide	$C_2H_4Br_2$ 	187.88	2615.8	13.923	283.0	9.8	9.243	463.8	2.469	249.54	-23.61	1.859	58 (A)

a/ In Tables A-1 to A-6 the letter in parenthesis following the literature citation indicates the experimental procedure followed. (A) Calorimeter, (B) Dielectric, (C) N.m.r. (nuclear magnetic resonance), (D) D.t.a. (differential thermal analysis), (E) Vapor pressure, (F) Technique not listed.

b/ Underlined numbers are literature values; those not underlined are calculated values.

TABLE A-5

TRANSITION AND FUSION DATA FOR CERTAIN CYCLIC COMPOUNDS

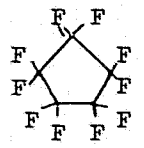
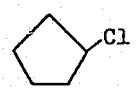
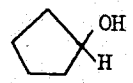
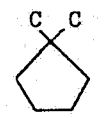
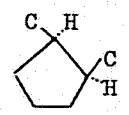
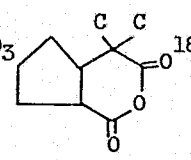
Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u.)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u.)	Ref. [a]
Cyclobutane	C_4H_8 	56.10	260.1	4.636	182.43	-90.72	1.426	1363.5	24.30	145.7	-127.5	9.358	70 (A)
Cyclopentane	C_5H_{10} 	70.13	144.1	2.055	179.7	-93.5	0.80	83 1165	1.2 16.61	138.1 122.4	-135.1 -150.8	0.60 9.52	71 (A)
Perfluorocyclopentane	C_5F_{10} 	250.05	849	3.40	283	10	3						69 (A)
1-Chlorocyclopentane	C_5H_9Cl 	104.58	290	2.8	178.9	-94.3	1.6	770.	7.36	168.1	-105.1	4.6	72 (A)
Cyclopentanol	$C_5H_{10}O$ 	86.13	367	4.26[1]	256.9[1]	-16.3	1.43[1]			201-203	-72 to -70[2]		1/73 (A) 2/63 (B)
1,1-Dimethylcyclopentane	C_7H_{14} 	98.18	257.8	2.626	203.68	-69.47	1.266	1551.1	15.80	146.8	-126.4	10.57	74 (A)
1-cis-2-dimethylcyclopentane	C_7H_{14} 	98.18	361.1	3.678	219.45	-53.70	1.645	1593.9	16.23	141.5	-131.7	11.26	74 (A)
Camphenic anhydride 2-(3-Carboxycyclopentyl)isobutyric anhydride	$C_{10}H_{14}O_3$ 	182.21	1990	10.9	496.7	223.5[1]	4.0[1]	8500[2]	47	408[2]	135	21	1/75 (A) 2/76 (F)

TABLE A-5 (Continued)

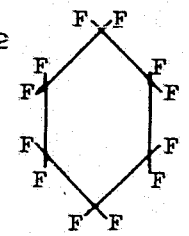
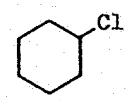
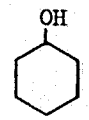
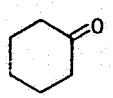
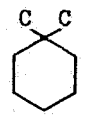
Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u.)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u.)	Ref.
Cyclopentene	C_5H_8 	68.114	803.9	11.80	138.13	-135.02	5.82	114.6	1.682	87.07	-186.08	1.316	77 (A)
Furan	C_4H_4O 	68.072	908.8	13.35	187.55	-85.60	4.846	489.2	7.186	150.0	-123.2	3.262	78 (A)
Thiophene	C_4H_4S 	84.13	1215.5	14.45	234.94	-38.21	5.174	152.4	1.811	171.6	-101.6	0.888	79 (A)
Dodecafluorocyclohexane (Perfluorocyclohexane)	C_6F_{12} 	350.06	1540[1]	4.40	336-336.2	62.8-63.0[b], [1]	4.6[c], [1]			168	-105[2]		1/80 (E) 2/31 (D)
Cyclohexane	C_6H_{12} 	84.156	639.8	7.602	279.82	6.67	2.286	1610.9	19.142	186.09	-87.06	8.655	82 (A)
1-Chlorocyclohexane	$C_6H_{11}Cl$ 	118.61	663[1]	5.59	230[1]	-43	2.9[1]	2370[1]	20.0	221.7[1]	-68 to -60[2]	10.7[1]	1/48 (B) 2/63 (B)
Cyclohexanol	$C_6H_{11}OH$ 	100.16	420	4.2	297	24	1.4	1960	19.6	263	-10	7.45	1 (A)
Cyclohexanone-α	$C_6H_{10}O$ 	98.14	360	3.7	241.8	-31.4	1.5	2130	21.7	223.5	-49.7	9.5	48 (B)
1,1-Dimethylcyclohexane	C_8H_{16} 	112.22	483.4	4.308	239.81	-33.34	2.016	1430.	12.74	153.15	-120.00	9.339	83 (A)

TABLE A-5 (Continued)

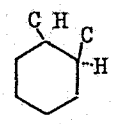
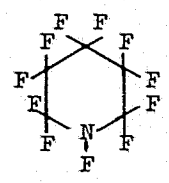
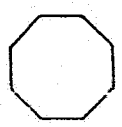
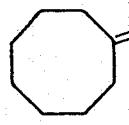
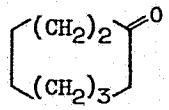
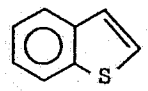
Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u.)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u.)	Ref.
cis-1,2-Dimethyl-cyclohexane	C_8H_{16} 	112.22	393.2	3.504	223.278	-49.87	1.761	1973	17.58	172.50	-100.7	11.440	83 (A)
Cyclohexene (1,2,3,4-Tetra-hydrobenzene)	C_6H_{10} 	82.14	787.1	9.582	169.67	-103.48	4.639	1015.9	12.37	138.7	-134.5	7.324	84 (A)
1,3-Cyclohexadiene (1,2-Dihydrobenzene)	C_6H_8 	80.13			184	-89				159-164	-114 to -109		63 (B)
Perfluoropiperidine	$C_5F_{11}N$ 	283.13	673	2.38	274.12	0.97	2.455	439.5 1584.0	1.552 5.595	171.9 161.0	-101.3 -112.2	2.557 9.839	85 (A)
Thiacyclohexane	$C_5H_{10}S$ 	102.196	585.2	5.726	292.25	19.1	2.002	1858.3 262.4	18.183 2.568	240.02 201.4	-33.13 -71.8	7.742 1.303	86 (A)
Cycloheptane	C_7H_{14} 	98.18	449.8	4.581	265.12	-8.03	1.697	107.5 69.2 1187.0	1.094 0.705 12.09	212.4 198.2 134.8	-60.8 -75.0 -138.4	0.506 0.349 8.806	87 (A)
Cycloheptatriene	C_7H_8 	92.13	277.4	3.011	197.92	-75.23	1.402	560.9	6.088	153.98	-119.17	3.643	87 (A)
Cyclooctane	C_8H_{16} 	112.21	575.9	5.132	287.98	14.83	2.00	1507.1	13.431	166.5	-106.7	9.052	87 (A)
Cyclooctanone (Azelaone)	$C_8H_{14}O$ 	126.20	630	5.0	315	42	2.0						88 (F)

TABLE A-5 (Concluded)

Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u.)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u.)	Ref.
Cyclononanone	$C_9H_{16}O$ 	140.22	450	3.2	301	28	1.5						88 (F)
2,3-Benzothiophene	C_8H_6S 	134.19	2826.8	21.066	304.50	31.35	9.283	719	5.36	261.6	-11.6	2.75	89 (A)

a/ In Tables A-1 to A-6 the letter in parenthesis following the literature citation indicates the experimental procedure followed. (A) Calorimeter, (B) Dielectric, (C) N.m.r. (nuclear magnetic resonance), (D) D.t.a. (differential thermal analysis), (E) Vapor pressure, (F) Technique not listed.

b/ Sealed in vacuo in capillary tube (sublimes at 326.0°K).

c/ Triple point.

TABLE A-6

TRANSITION AND FUSION DATA FOR CERTAIN CAGE COMPOUNDS

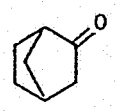
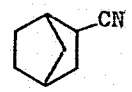
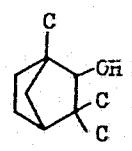
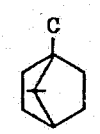
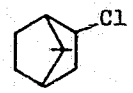
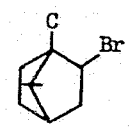
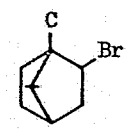
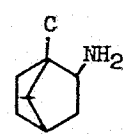
Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u.)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u.)	Ref. a/
Bicyclo[2,2,1]heptane (Norbornane) (Norcamphane)	C_7H_{12} 	96.17						18 986	0.19 10.3	306 131	33 -142	0.06 7.53	10 (A)
Norcamphor (2-Oxonorbornane) (2-Norbornanone) Santenone	$C_7H_{10}O$ 	110.15	1230	11.2	366	93	3.36						38 (F)
Exo-2-cyanobicyclo-[2,2,1]heptane	$C_8H_{11}N$ 	121.18	702	5.80	300.	27	2.34	1850	15.3	238	-35	7.79	10 (A)
Fenchyl alcohol	$C_{10}H_{18}O$ 	154.25	1790	11.60	315.3	42.1	5.7						75 (A)
Camphane	$C_{10}H_{18}$ 	138.25	1670	12.1	427	154	3.9						90 (A)
dl-Bornyl chloride (2-Chlorobornane)	$C_{10}H_{17}Cl$ 	172.69	1200	6.9	404	131	3.0						38 (F)
2-Bromo-1,7,7-trimethylbicyclo[2,2,1]-heptane, Isobornyl bromide	$C_{10}H_{17}Br$ 	217.15	1270	5.9	409	136	3.1						38 (F)
dl-2-Bromobornane	$C_{10}H_{17}Br$ 	217.15	878	4.04	363	90	2.42						38 (F)
2-Aminobornane	$C_{10}H_{19}N$ 	153.26	1440	9.4	437	164	3.3						38 (F)

TABLE A-6 (Continued)

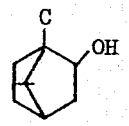
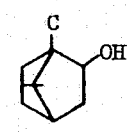
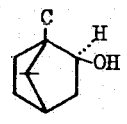
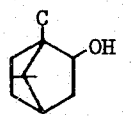
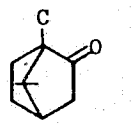
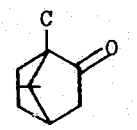
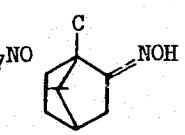
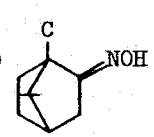
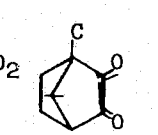
Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u.)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u.)	Ref.
d-Borneol 2-Hydroxybornane	$C_{10}H_{18}O$ 	154.25	1960[1]	12.7	208.6[1]	-64.6	4.1[1]	850	5.5[2]	340.9 - 344.8	67.7 - 71.6[2]	2.5	1/91 (A) 2/ 7 (D)
2-Hydroxybornane (2-Borneol)	$C_{10}H_{18}O$ 	154.25			207.8[1]	-65.4		740	4.8[2]	345.7	72.5[2]	2.1	1/92 (F) 2/ 7 (D)
Isoborneol	$C_{10}H_{18}O$ 	154.25	1545	10.02	485	212	3.1			285-319 173-223	12-46 -100 to -50		38 (F)
dl-2-Hydroxybornane (dl-Borneol)	$C_{10}H_{18}O$ 	154.25	1960	12.7	477	204[1]	4.1[1]	660	4.3[2]	343.4- 344.9	70.2- 71.7[2]	1.9	1/38 (F) 2/ 7 (D)
d-Camphor	$C_{10}H_{16}O$ 	152.23	1270[1]	8.34	451.60	178.45[1]	2.8[1]	150	1-1.5[2]	370.7	97.5[2]	0.41	1/91 (A) 2/ 7 (D)
dl-Camphor	$C_{10}H_{16}O$ 	152.23			450.7	177.5				375-376	102-103		93 (F)
d-Camphoroxime	$C_{10}H_{17}NO$ 	167.25					3.3[1]	1670	10[2]	380- 385.8	107- 112.6[2]	4.39	1/94 (F) 2/ 7 (D)
dl-Camphoroxime	$C_{10}H_{17}NO$ 	167.25	510	3.0	392.8	119.6[1]	1.3[1]	170	10[2]	377- 382.4	104- 109.4[2]	4.5	1/94 (F) 2/ 7 (D)
dl-2,3-Camphane-dione	$C_{10}H_{14}O_2$ 	166.21	1620	9.7	476	203[1]	3.4[2]			318-328	45-55[1]		1/63 (B) 2/38 (F)

TABLE A-6 (Continued)

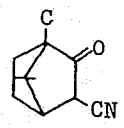
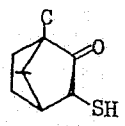
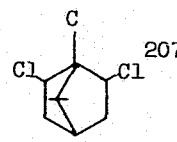
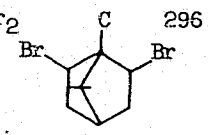
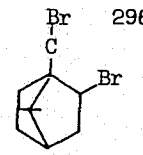
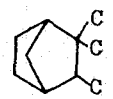
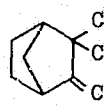
Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u.)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u.)	Ref.
3-Cyanocamphor	$C_{11}H_{15}NO$ 	177.25			402.5-402.7	129.3-129.5				363-389	110-116		63 (B)
dl-Thiocamphor	$C_{10}H_{16}SO$ 	184.79			411.8-412.2	138.6-139.0				243-263	-30 to -10		63 (B)
2,6-Dichlorocamphane	$C_{10}H_{16}Cl_2$ 	207.15	1430	6.9	447	174	3.2						38 (F)
2,6-Dibromocamphane	$C_{10}H_{16}Br_2$ 	296.07	1420	4.8	443	170	3.2						38 (F)
2,10-Dibromocamphane	$C_{10}H_{16}Br_2$ 	296.07	681	2.30	364	91	1.87						38 (F)
2-Bornene	$C_{11}H_{20}$ 	136.23	1200	9	386	113	3						95 (F)
2,2,3-Trimethyl-bicyclo[2,2,1]-heptane	$C_{10}H_{18}$ 	138.25	710	5.1	338	65	2.1						95 (F)
d-Camphene (2,2-Dimethyl-3-methylene bicyclo [2,2,1]-heptane)	$C_{10}H_{16}$ 	136.23			312.7-314.7	39.5-41.5				149-155	-124 to -118		63 (B)

TABLE A-6 (Continued)

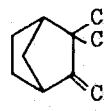
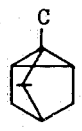
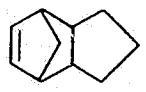
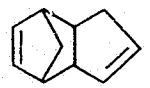
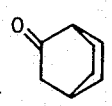
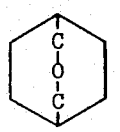
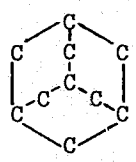
Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u.)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u.)	Ref.
dl-Camphene	$C_{10}H_{16}$ 	136.23	739	5.42	324	51	2.28						96 (F)
1,7,7-Trimethyltricyclo 2,2,1,$0^{2,6}$-heptane	$C_{10}H_{16}$ 	136.23	850	6.2	339.2	66.0	2.5						95 (F)
Dihydro-α-dicyclopentadiene	$C_{10}H_{14}$ 	134.21	610	4.5	323	50	1.9						97 (F)
Dicyclopentadiene (4,7-Methylene-4,7,8,9-tetrahydroindene)	$C_{10}H_{12}$ 	132.20	550	4.2	305	32	1.8						97 (F)
2,5-Endoethylene cyclohexanone	$C_8H_{12}O$ 	124.18	1520	12.2	451	178	3.38						38 (F)
Bicyclo[2,2,2]octane	C_8H_{14} 	110.19	1990	18.1	447	174	4.45	1090	9.89	164	-109	6.66	10 (A)
Bicyclo[2,2,2]octa-2-ene	C_8H_{12} 	109.18	945	8.66	389	116	2.43	1350 87	12.4 0.80	176 111	-97 -162	7.66 0.78	10 (A)
1-Azabicyclo[2,2,2]-octane (Quinuclidine)	$C_7H_{13}N$ 	111.18						1260	11.3	198	-75	6.34	10 (A)
1,4-Diazabicyclo-[2,2,2] octane	$C_6H_{12}N_2$ 	112.18	1780	15.9	433	160	4.10	2520	22.5	351	78	7.19	10 (A)

TABLE A-6 (Concluded)

Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u.)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u.)	Ref.
3-Oxabicyclo[3,2,2]-nonane	$C_8H_{14}O$ 	126.19	1620	12.8	448	175	3.61	1710	13.6	208	-65	8.22	10 (A)
3-Azabicyclo[3,2,2]-nonane	$C_8H_{14}N$ 	125.21	1660	13.3	467	194	3.55	3470	27.7	298	25	11.63	10 (A)
Adamantane	$C_{10}H_{16}$ 	136.23						807	5.92	208.6	-64.6	3.87	10 (A)

a/ In Tables A-1 to A-6 the letter in parenthesis following the literature citation indicates the experimental procedure followed. (A) Calorimeter, (B) Dielectric, (C) N.m.r. (nuclear magnetic resonance), (D) D.t.a. (differential thermal analysis), (E) Vapor pressure, (F) Technique not listed.

TABLE A-7

TRANSITIONS AND FUSION DATA COMPENDED FROM THIS REPORT[a]

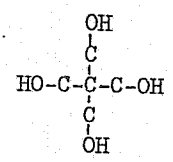
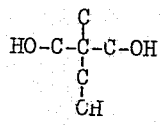
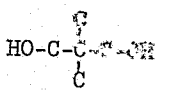
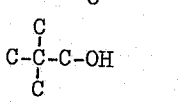
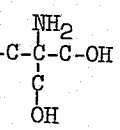
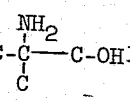
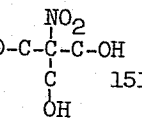
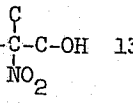
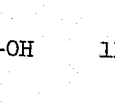
Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u.)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u.)
Tetrahedral Compounds												
Pentaerythritol	$C_5H_{12}O_4$ 	136.15	1198	8.80	531-533	258-260	2.26	9868	72.48	457-458	184-185	21.5?
2-Hydroxymethyl-2-methyl-1,3-propanediol	$C_5H_{12}O_3$ 	120.15	1282	10.67	470-471	197-198	2.76	5529	46.02	354	81	15.62
2,2-Dimethyl-1,3-propanediol	$C_5H_{12}O_2$ 	104.15	1127	10.82	398-399	125-126	2.83	3260	31.30	313-316	40-43	10.34
Neopentyl alcohol	$C_5H_{12}O$ 	88.15	971	11.02	324-328	51-55	3.00	1123	12.74	242	-31	4.64
2-Amino-2-hydroxymethyl-1,3-propanediol	$C_5H_{11}O_3N$ 	121.14	726.8	6.00	439-442	166-169	1.66	8190	67.61	404-410	131-137	20.27
2-Amino-2-methyl-1,3-propanediol	$C_5H_{11}O_2N$ 	105.14	797.0	7.58	380-381	107-108	2.10	6664	63.38	351-353	78-80	18.98
2-Hydroxymethyl-2-nitro-1,3-propanediol	$C_5H_9O_5N$ 	151.12				dec. 184		5944	39.33	353-355	80-82	16.89
2-Methyl-2-nitro-1,3-propanediol	$C_5H_9O_4N$ 	135.12	1034	7.65	422-426	149-153	2.42	6440	47.66	352-353	79-80	18.29
2-Methyl-2-nitro-1-propanol	$C_5H_9O_3N$ 	119.12	887.4	7.45	361-362	88-89	2.46	4105	34.46	308-312	35-39	13.33

TABLE A-7 (Continued)

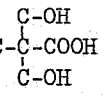
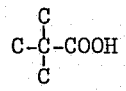
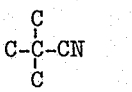
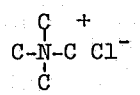
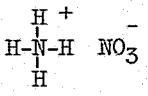
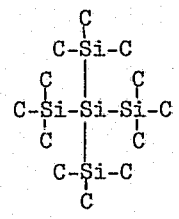
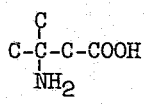
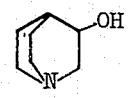
Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u.)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u.)
2,2-Bis(hydroxymethyl)-propionic acid	$C_5H_{10}O_4$ 	134.13	859.7	6.41	467-470	194-197	1.84	9207	68.64	425-428	152-155	21.66
Pivalic acid	$C_5H_{10}O_2$ 	102.13	587.2	5.75	305-309	32-36	1.93	2093	20.49	280-282	7-9	7.47
Trimethylacetonitrile	C_5H_9N 	83.13			288-293	15-20		154.6	1.86	239	-34	0.65
Tetramethylammonium chloride	$C_4H_{12}NCl$ 	320.85				sublimed above 320		7335	22.86	535-537	262-264	4.68
Ammonium nitrate	NH_4NO_3 	80.05						I 443.5 II 337.0 III 1053	5.54 4.21 13.15	324-326 361-363 400-403	51-53 88-90 127-130	1.37 0.94 2.64
Tetrakis(trimethylsilyl)silane	$C_9H_{36}Si_5$ 	320.85	2660	8.29	555-558	282-285	4.79	2702	8.42	241-244	-32 to -29	11.21
dl-2-Amino-2-methyl-butyric acid	$C_5H_{11}O_2N$ 					sublimed above 310		I II III		356-359 371-377 373-381	83-86 98-104 100-108	
Cage Compounds												
3-Quinuclidinol	$C_7H_{13}NO$ 	127.19	1814	14.26	494-496	221-223	3.67	3624	28.49	369-375	96-102	9.82

TABLE A-7 (Continued)

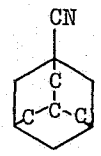
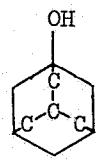
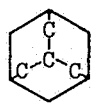
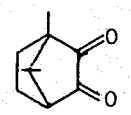
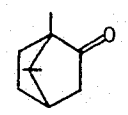
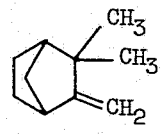
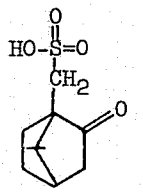
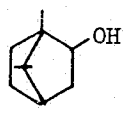
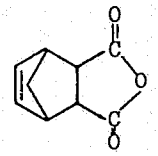
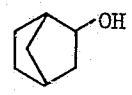
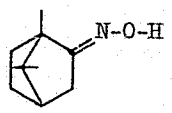
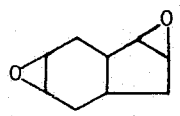
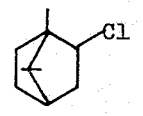
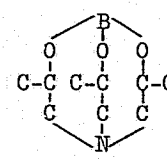
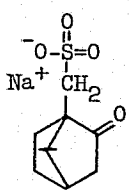
Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u.)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u.)
Adamantane carbonitrile	$C_{11}H_{15}N$ 	161.25			453-462	180-189		388.6	2.41	415-421	142-148	0.94
1-Adamantanol	$C_{10}H_{16}O$ 	152.24			512-518	239-245		2960	19.44	364-365	91-92	8.13
Adamantane	$C_{10}H_{16}$ 	136.24			479-482	206-209		654.0	4.80	208	-65	3.13
dl-Camphorquinone	$C_{10}H_{14}O_2$ 	166.22	1350	8.12	472-474	199-201	2.86	2802	16.86	328-334	55-61	8.54
d-Camphor	$C_{10}H_{16}O$ 	152.24	1422	9.35	451-452	178-179	3.16	I II 27.95	18.36	247-250 371-373	-26 to -23 98-100	11.32
Camphene	$C_{10}H_{16}$ 	136.23	743.8	5.46	315-322	42-49	2.36	753.4	5.53	174-176	-97 to -99	4.33
dl-Camphorsulfonic acid	$C_{10}H_{16}O_3S$ 	232.30			468-473	195-200		4739	20.40	368-375	95-102	12.70
dl-Isoborneol	$C_{10}H_{17}O$ 	154.25				sublimed above 210		470.5	3.05	280-281	7-8	1.68

TABLE A-7 (Continued)

Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u.)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u.)
5-Norbornene-2,3-dicarboxylic anhydride	$C_9H_8O_3$ 	164.16				indefinite		3820	23.27	371-373	98-100	10.38
Norborneol	$C_7H_{11}O$ 	112.17	1416	12.62	401-404	128-131	3.53	387.0	3.45	267-271	-2 to -6	1.45
d-Camphor oxime	$C_{10}H_{17}NO$ 	167.09	3405	20.38	384-388	111-115	8.87	143.7	0.86	380-385	107-112	0.38
Dicyclopentadiene dioxide	$C_{10}H_{12}O_2$ 	164.2	926.1	5.64	475-484	202-211	1.95	701.1 2790	4.27 16.99	333-340 390-394	60-67 117-121	8.38 1.80
Bornyl chloride	$C_{10}H_{17}Cl$ 	172.69	963.6	5.58	395-398	122-125	2.44	148.5	0.86	237-239	-34 to -36	0.63
Tris(propan-2-ol)-amine borate	$C_9H_{18}BNO_3$ 	199.06	1861	9.35	423-429	150-156	4.40	517.6	2.60	338-342	65-69	1.53
dl-Camphor-sulfonic acid sodium salt	$C_{10}H_{15}NaO_4S$ 					--				385-390	112-117	

Octahedral Compounds

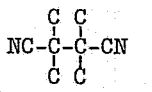
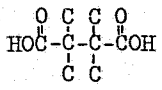
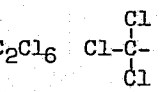
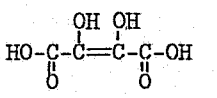
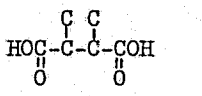
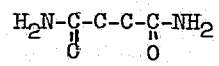
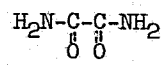
Tetramethylsuccino-nitrile	$C_8H_{12}N_2$ 	136.19	1708	12.54	441-443	168-170	3.87	4327	31.77	344-346	71-73	12.58
Tetramethylsuccinic acid	$C_8H_{14}O_4$ 	174.19	1547	8.88	463-466	190-193	3.34	3210	18.43	381-384	108-111	8.43

TABLE A-7 (Continued)

Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u.)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u.)
Hexachloroethane	C_2Cl_6 	236.74			452-457	179-184		I 622.6 II 1508	2.63 6.37	319-321 344-345	46-48 71-72	1.95 4.38
Dihydroxymaleic acid	$C_4H_4O_6$ 	148.07			417-484	144-161		4221	28.51	388-394	115-121	10.88
2,3-Dimethyl-succinic acid	$C_6H_{10}O_4$ 	146.14	5071	34.70	461-463	188-190	11.00	1007	6.89	392-396	119-123	2.57
Succinamide	$C_4H_8N_2O_2$ 	116.12						1305	11.24	476-477	203-204	2.74
Oxamide	$C_2H_4N_2O_2$ 					not melted at 375°				598-608	325-335	

Cyclic Compounds

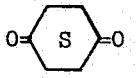
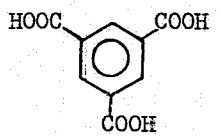
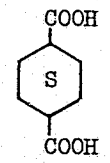
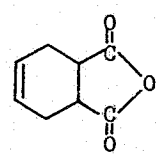
1,4-Cyclohexane-dione	$C_6H_8O_2$ 	112.13	2566	22.88	351-354	78-81	7.31	I 1475 II	13.15	325-328	52-55 68-70	4.54
Trimesic acid	$C_9H_6O_6$ 				371-373	98-100				358-361	85-88	
trans-1,4-Cyclo-hexanedicarboxylic acid	$C_8H_{10}O_4$ 					decomposes above 260				459-469	186-196	
cis-4-Cyclohexene-1,2-dicarboxylic anhydride	$C_8H_6O_3$ 				377-379	104-106				340-350	67-77	

TABLE A-7 (Continued)

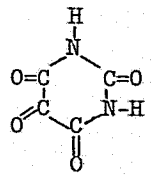
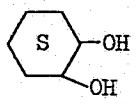
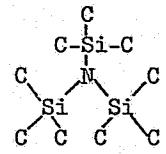
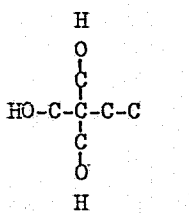
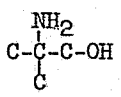
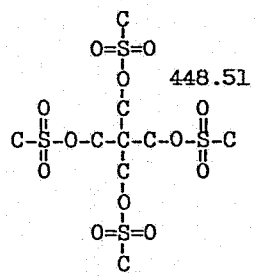
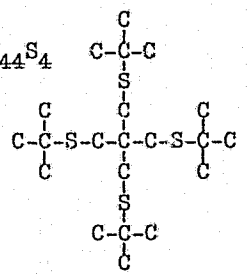
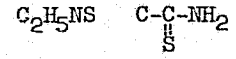
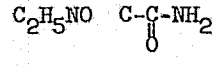
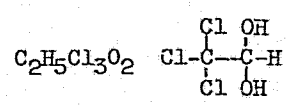
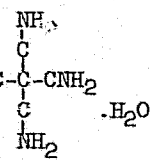
Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u.)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u.)
Alloxan	$C_4H_2N_2O_4$ 				613-621	340-348				686-689	413-416	
trans-1,2-Cyclohexanediol	$C_6H_{10}O_2$ 				601-606	328-333		I II		269-273 423-429	-4 to 0 150-156	
Miscellaneous Compounds Including Those Not Exhibiting Transitions												
Tris(trimethylsilyl)amine	$C_9H_{27}N_3Si$ 	233.58	422.8	1.81	336-338	63-65	1.26	1992	8.53	245	-28	8.13
2,2-Bis(hydroxymethyl)-1-butanol	$C_6H_{14}O_3$ 	134.19	4556	33.95	329-332	56-59	13.85					
2-Amino-2-methyl-1-propanol	$C_4H_{11}NO$ 	89.14	1628	18.26	285-293	12-20	5.71					
Pentaerythritol tetramethanesulfonate	$C_9H_{20}O_{12}S_4$ 	448.51	11920	26.57	475-477	202-204	25.09					

TABLE A-7 (Concluded)

Name	Structure	M.W.	ΔH_m (cal/mole)	ΔH_m (cal/g)	T_m (°K)	t_m (°C)	ΔS_m (e.u.)	ΔH_t (cal/mole)	ΔH_t (cal/g)	T_t (°K)	t_t (°C)	ΔS_t (e.u.)
Tetra-t-butyl-thiopentaerythritol	$C_{21}H_{44}S_4$ 	424.82	5969	14.05	389-391	116-118	15.34					
Thioacetamide	C_2H_5NS 	75.02	4671	62.26	384	111	12.16					
Acetamide	C_2H_5NO 	59.07	3755	63.57	352	79	10.67					
Chloral hydrate	$C_2H_5Cl_3O_2$ 	165.40	83.76	50.64	346	73	24.21					
Hexadecane	$C_{16}H_{34}$ $C(C)_{14}C$	266.45	13.000	48.80	293	20	44.38					
Tetrakis(amino-methyl)methane monohydrate	$C_5H_{18}N_4O$ 	150.22			318-320	45-47						

a/ These data were collected from various parts of this report and are not all equally reliable. Specific limitations are cited in the report.

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