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SOLID SOLUTION, TRANSITIONS, AND THERMODYNAMICS OF MIXING IN THE PLASTICALLY CRYSTALLINE SYSTEM TETRAMETHYLMETHANE-TETRACHLOROMETHANE

by

Elfreda Chang

A dissertation submitted in partial fulfillment
of the requirements for the degree of
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1962

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INTRODUCTION

One of the reasons for studying mixtures is that of providing an insight into the physical forces acting between molecules of different species. Another reason is that the possibility of varying the proportions of the components yields phenomenological information concerning various types of phase equilibria. Moreover, mixtures are examined (i.e., by heat capacity, dielectric constant, and nuclear magnetic resonance measurements on mixed crystals) to obtain information on the nature of the transitions occurring in pure components. For as Mandleberg and Staveley[1] have explained in their report on the binary system ammonium chloride-ammonium bromide in which both components exhibit λ-type transitions that "since mixed crystal formation involves an alteration in the molecular or ionic environment in the lattice, which must necessarily have repercussions on what are essentially cooperative phenomena, it would seem that studies of such binary systems should provide one useful experimental line of attack on the problem of the nature and causes of these gradual transitions."

The problems that one encounters while studying mixtures depend to a large extent on the nature of the system under consideration. Mixtures of molecules of about the same size, of isotopes, of high polymer solutions, of alloys, and of dipoles all present some different aspects of the problem of mixing. For example, the problem of orientational

effects (i.e., hydrogen bonding) in mixtures of dipoles, the quantum effects due mainly to the differences in mass in mixtures of isotopes (i.e., He^3 - He^4), and the structural effects in mixtures of polymers are all problems of scientific interest as well as practical importance.

In considering the properties of a binary system, for convenience one often refers to their deviations from ideality. In actual practice few solutions obey ideal solution laws (i.e., Raoult's law and Henry's law) rigorously, but deviate more or less primarily from differences in the nature and strength of the intermolecular forces between the different components in the system. These deviations from ideality or the increment on mixing are called the enthalpy of mixing, the free energy of mixing, and the volume of mixing, etc.* Usually, for theoretical calculations, they are more conveniently expressed in a somewhat different form known as the excess functions.* The theoretical relationship between the excess functions is very complex and depends critically upon the assumptions made about the differences in the interactions, the molecular shapes, and the molecular sizes, etc. Table A in the appendix shows the relation between the assumptions made about the intermolecular forces and the corresponding excess functions. Therefore, one would expect that experimental data on the excess functions would provide information on the differences in the intermolecular forces.

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* For definition of the mixing function and excess function see page 132 in the appendix.

During the last twenty years, a considerable amount of theoretical and experimental work has been performed on the properties of liquids and liquid mixtures. For example, the cell model, the lattice model, the theory of conformal solutions, the average potential model, etc., have been devised. However, many if not most of the quantitative predictions of these theories are in disagreement with the existing experimental data. The poor agreement between experiment and theory is due in part to the difficulty of obtaining good experimental mixing data and in part to the imperfection of the present state of development of the theory of fluids.

It is observed that several of these theories attempt to base the liquid state on a more or less regular structure. And, since the liquid state has many features in common with the solid state (i.e., large number of first neighbors and local order), measurement of the excess functions of mixtures in the solid state or solid solution should permit in many instances a better test between these existing theories of mixtures and experiment than is possible in the liquid state.

For an initial endeavor in this direction the calorimetric investigation of the system tetramethylmethane-tetrachloromethane (i.e., heat capacity measurements from 5 to 300°K of four different compositions with mole fraction of tetrachloromethane = 0.334, 0.501, 0.666, and 0.826 of this system) was undertaken so that the experimental results of this study together with existing mixing data and heat capacity data for the pure components would provide a means of correlating and experimentally testing some of the modern

theories of solutions in the solid state.

Before the start of the calorimetric investigation of this system a literature survey in search of an optimum system for this study was made. A system that formed a continuous series of solid solution and in which good heat of mixing data was available was sought. Also, in this study it was important that equilibrium be achieved at each stage of the process, and in particular that "frozen-in" equilibria be avoided in the solid state. For these reasons it was considered desirable to make the initial measurements on systems of plastic crystals which have approximately the same molecular diameters and which are spherically symmetrical so that the intermolecular forces may be considered as central. The result of the literature survey found that there are several binary systems of plastic crystals that satisfied some of the above requirements. Unfortunately, none of the previous studies on mixtures of a particular system provided adequate information on the system for it to be chosen for this investigation. For example, previous studies on the systems 2,2-dimethylbutane-cyclopentane[2,3,4] and 2,2-dimethylbutane-2,3-dimethylbutane[2,5] established that both systems form continuous series of solid solutions below the melting points; however, no enthalpy of mixing experiments have been made on these systems; both mixing properties[6] and phase equilibria studies[7,8] on the system tetrachloromethane-cyclohexane have been reported but unfortunately this system does not form solid solution; study by heat capacity measurements has recently been made on the

system ethylene dichloride-ethylene dibromide[9] but, in addition to the lack of enthalpy of mixing data, no data on the heat capacity, enthalpies of fusion and transitions were reported; and, studies on the systems tetramethylmethane-tetrachloromethane,[10,11] tetramethylmethane-cyclohexane,[11] and cyclopentane-cyclohexane,[11] etc. have provided reasonably good mixing data but no phase equilibria data were reported for these systems. In view of these difficulties, the system tetramethylmethane-tetrachloromethane was chosen because the similarity of shape and size of the tetramethylmethane and tetrachloromethane molecules and their isotropic lattices in the region just below the freezing point made it seem probable that these two substances would form a continuous series of solid solution. Moreover, both tetramethylmethane and tetrachloromethane form plastic crystals and have the ability to re-orient in the solid state to become apparently spherically symmetrical so that the intermolecular forces may be considered as central. Table B in the appendix is a summary of some systems of which both components are plastically crystalline just below the freezing point. References for their phase diagram determinations and some references for mixing properties are also given.

The following dissertation includes a description of the calorimetric equipment and method used together with a detailed account of the experimental procedure and results. A discussion of the enthalpy of mixing in the solid state, i.e., solid solution, and the temperature dependence of the

enthalpy of mixing for the system tetramethylmethane-tetrachloromethane is presented. The experimental values of the enthalpy of mixing for this system in the solid state are compared with the values predicted by solution theories.

The results of this investigation also provide study of phase equilibria. Therefore, a discussion of the phase diagram formed by tetramethylmethane and tetrachloromethane below room temperature is given. Further investigation will be required to elucidate the details.

EXPERIMENTAL

Purification and Storage of Sample

Tetramethlymethane

The tetramethylmethane (neopentane) used in this research work was obtained from Philips Petroleum Company, Special Products Division, Bartlesville, Oklahoma. It was research grade tetramethylmethane with a reported purity of 99.92 mole per cent, determined by melting point measurements on a representative sample of a lot (No. 674). The most probable impurity is reported to be n-butane. The tetramethylmethane was stored as a liquid under pressure in its original container (metal cylinder) until ready for use, and no further purification was applied except repeated freezing and evacuation of the desired amount of sample just before use.

Tetrachloromethane

The tetrachloromethane (carbon tetrachloride) used in this investigation was Merck reagent grade tetrachloromethane purified by drying over calcium chloride; i.e., it was shaken with calcium chloride and left in contact with it for over 24 hours. Then it was twice distilled, using a heated glass column packed to a height of about 21 inches with glass rings and topped with an 18-inch high reflux condenser. The entire distillation system was connected by ground glass joints and

openings to the atmosphere were provided with drying tubes. During distillation, a reflux ratio of 20 to 1 was used. This corresponded to a distillation rate of about 19 cm^3 per hour. Each time, the first and last quarters of the product were rejected. From an initial two liters of reagent grade tetrachloromethane, about 500 to 600 cm^3 of final purified tetrachloromethane were collected.

The tetrachloromethane was then stored in a sealed-off Pyrex glass bulb (the original receiver) of about one-liter capacity which was provided with a "break-off-ski" seal. A high vacuum Hoke (type A-431) valve was connected to the tetrachloromethane storage bulb by means of a glass to metal "Kovar" seal. The Hoke valve was provided with fittings to enable one to connect it to the stainless steel manifold described on page 9. After the tetrachloromethane storage bulb was connected to the manifold, the bulb was immersed in liquid nitrogen; when the tetrachloromethane was completely solidified, the valve was opened to the vacuum pump, the "break-off-ski" seal was broken, and the bulb and its contents were evacuated for about half an hour. The valve was then closed, the liquid nitrogen bath was removed, and the tetrachloromethane was allowed to melt and warm to room temperature. This process of freezing, evacuating, and melting was repeated two more times. Finally, the tetrachloromethane was stored in the liquid phase, sealed off within the bulb until ready for use.

Calorimetric Equipment

Loading System

An all-metal vacuum line was designed and fabricated to permit transferring and loading of sample without contamination with vacuum grease. This system consisted of a stainless steel manifold 0.5 inch in diameter and 18 inches long. The manifold was connected to a conventional vacuum system (i.e., regular glass line, Hg diffusion pump, mechanical pump, etc.) by a metal to glass "Kovar" seal. The connection between the metal and glass lines was controlled both by a "Veeco" brass valve and by a glass stopcock.

The manifold had six additional outlets for connections to sample storages, sample bulbs, thermocouple gauge, and calorimeter. Each of these outlets was provided with appropriate fittings to facilitate connecting or changing of sample bulbs or storage cylinders, or sealing off an outlet by means of a screwed-on plug or valve when not in use. The flow of tetramethylmethane from storage was controlled by the cylinder valve, while the flow of tetrachloromethane from its storage bulb was controlled by the Hoke valve mentioned.

The removable sample bulbs were designed to have a capacity of about 100 cm^3 (1 inch diameter and 4 inches long) and to be able to withstand pressure (i.e., at least 2.3 atm.) and repeated freezing in liquid nitrogen. Each sample bulb was fitted with a light-weight, high-vacuum, needle-type valve (fabricated by modifying the design of a high-vacuum, needle valve developed at the National Bureau of Standards).

The outlet used as filling line to the calorimeter contained first a high-vacuum needle valve to control the opening and closing of the filling line; then, a "screw-driver" valve to control the opening and closing of the demountable valve (described on page 16) on the calorimeter.

The sixth outlet on the manifold was provided with a sealed off 0.25 inch diameter "Kovar" seal onto which one may attach a vacuum gauge if desired. The entire system was leak tested with a helium leak detector.

The Mark II Cryostat

All the heat capacity measurements of this investigation (i.e., four different compositions of mixtures of the system tetramethylmethane-tetrachloromethane, pure tetrachloromethane, and the empty Calorimeter W-23 heater-thermometer assembly) were carried out in the Mark II cryostat. A simplified schematic cross-sectional diagram of this cryostat is shown in Figure I. It is similar in design to the cryostat described by Westrum, Hatcher, and Osborne,[12] and recently described by Carlson.[13]

The entire inner cryostat assembly (Figure I) is suspended from the top plate of the cryostat and may be raised and separated from the outer, chromium-plated, copper can by unscrewing and manually lifting the top plate. The lower portion of the outer can (M) is connected to the vacuum pump. Vacuum sealing between the top plate and the outer can is made by the O-ring gasket (G), and Allen screws are used to

Figure I

Cross-Sectional Schematic Diagram of the Mark II Cryostat

Legend:

A - Liquid nitrogen tank

B - Liquid helium tank

C, D, and E - Radiation shields

F - Adiabatic shield

G - O-ring gasket sealing brass vacuum jacket

H - Effluent helium vapor exchanger ("economizer")

I - Helium exit tube

J - Ring for adjusting temperature of leads

K - Calorimeter assembly

L - Platinum-resistance thermometer

M - Connection to vacuum diffusion pump

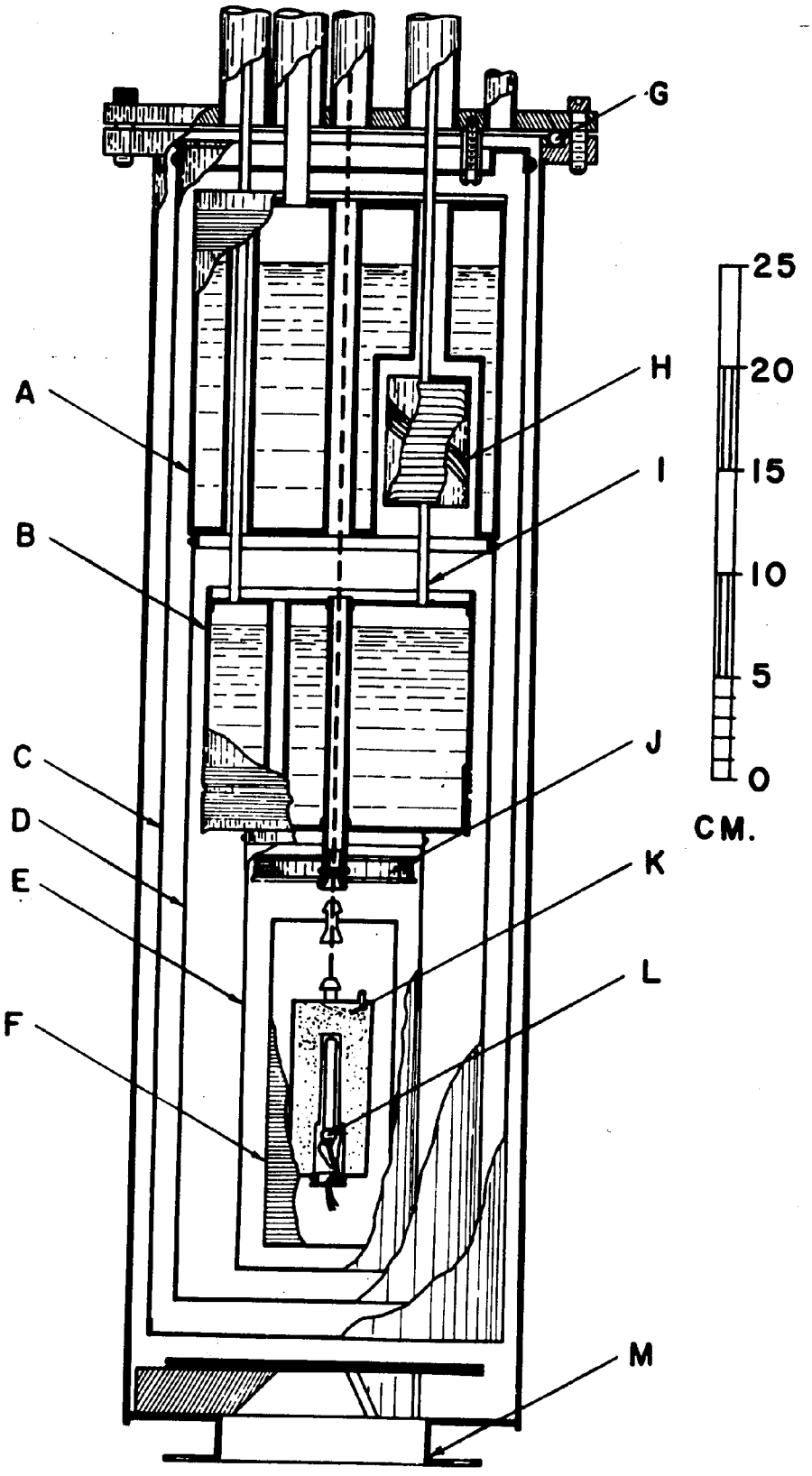


Figure 1

keep the plate in place.

The chromium-plated copper tanks (A) and (B) are provided for use as thermal sinks. Tank (A), the nitrogen refrigerant tank, has a capacity of 2.7 liters; the helium refrigerant tank, (B), has a capacity of 1.2 liters and is provided with a heater around its lower part. For heat capacity determinations above 90°K liquid nitrogen is used in both tanks. For the range between 60 and 90°K the helium tank is evacuated to produce solid nitrogen for refrigerant. For the range from 4 to 60°K liquid helium is used in the helium tank and the nitrogen tank is evacuated.

The calorimeter (K) is suspended by a braided silk line and can be raised and lowered by a windlass not shown in the figure. Surrounding the calorimeter is the floating adiabatic shield (F). The temperature of the adiabatic shield is maintained to within a few thousandths of a degree of that of the calorimeter at all times (except when cooling) by three separate heaters (bifilarly-wound Fiberglas-covered Constantan wires cemented on by baked Formvar enamel) on the top, central, and bottom surfaces of the adiabatic shield (chromium-plated, copper can).

Various cooling rates can be obtained in the cryostat by regulating the distance between the calorimeter and the helium refrigerant tank. The "operate" position (i.e., slowest rate) is depicted in Figure I. For the "contacted-to-shield" position, the calorimeter is raised until the cone on top of the calorimeter is brought into thermal contact

with the bottom cone on the adiabatic shield. The maximum cooling rate is obtained when the calorimeter and shield are brought into thermal contact with the helium refrigerant tank (through the cone at the bottom of the helium tank). The "can" position is intermediate between the "shield" and "maximum" positions.

Chromium-plated, copper radiation shields for the nitrogen tank, helium tank, and adiabatic shield are (C), (D), and (E), respectively. The floating ring (J) is provided with a separate heater. It is used to moderate the temperature difference of the lead wires from that of the helium tank to that of the adiabatic shield. (H) is a heat exchanger provided as an economizer of liquid helium. It makes use of the large heat capacity of the cold, effluent helium gas to cool the leads, thus reducing the loss of helium by conduction of heat down the lead wires. (I) is the exit tube for gases from the helium tank.

The platinum-resistance thermometer and heater assembly (L) is used to measure the temperature of the calorimeter and to serve as heater during energy input. The vacuum in the cryostat is monitored by a thermocouple vacuum gauge during the initial pump-down period, and by an ionization gauge during normal operation (i.e., about 10^{-5} mm Hg). The temperature of the helium and nitrogen tanks are measured by absolute copper-Constantan thermocouples. Temperature differences between the bottom (bash) and central portion (mash) of the adiabatic shield, the top (tash) and mash, ring and mash,

and mash and calorimeter are measured by two-junction, copper-Constantan thermopiles.

The Calorimeter W-23

The calorimeter of laboratory designation W-23 was constructed for use in the calorimetric investigation of the system tetramethylmethane and tetrachloromethane. Calorimeter W-23 is of the same design as Calorimeter W-14[13], which is in turn of the same basic design as Calorimeter W-9[14], both of which have been described elsewhere. The only differences between W-23 and W-14 are that W-14 is fabricated from silver while W-23 is fabricated from copper (both are gold-plated over all surfaces) and that the wall thickness of W-14 is 0.020 inch while that of W-23 is 0.015 inch.

The calorimeter is constructed essentially of three parts soft-soldered together: the top, the central cylinder, and the well. The central cylinder has a diameter of 1.50 inches and a length of 3.00 inches. The well portion of the calorimeter is machined from a solid copper rod and consists of the calorimeter bottom, the thermometer-heater well, and eight, thin (0.015 inch), horizontal, circular vanes equally spaced along the well. On each vane there are six 3/16-inch-diameter holes, 60° apart for aid in circulation of liquids. Soldered to the top portion of the calorimeter are a cone for hanging the calorimeter and for making thermal contact with the helium refrigerant tank and a demountable valve which is designed for loading and sealing off liquids in the calorimeter.

The valve on top of the calorimeter is made of stainless steel. It consists of three parts: the outer tube, the valve seat, and the threaded valve plug. The outer tube is threaded both on the outside (10-32) and inside (3-56) for connection to the "screw-driver" valve on the filling line and for holding the threaded valve plug, respectively. The valve seat is threaded (3-56) and silver-alloy brazed into the bottom of the outer part of the valve. Both the outer tube and the valve seat are topped with knife edges for making a vacuum-tight seal with gold gaskets. The threaded (3-56) valve plug has a slot at its top so that it may be turned by the screw-driver of the "screw-driver" valve. It is designed to carry a gold gasket at its lower surface for sealing against the knife edge of the valve seat. There are also two holes in the valve plug, one along the axis and a radial one to the axis hole. These are drilled to allow for the flow of fluids past the plug during loading and unloading processes.

Calorimeter W-23 has a mass of 82.293 grams <u>in vacuo</u> (when run empty) and a calculated internal volume of 79.31 cm^3. The plug of the valve on the calorimeter had an original mass of 0.075 grams. That of the gold gasket used with the valve was 0.014 grams.

Measuring Circuits

The temperature of the calorimeter and sample is calculated from the resistance of a capsule-type, platinum-

resistance thermometer (laboratory designation A-5, calibrated by the National Bureau of Standards), which is determined by measuring the current and the potential applied across the thermometer. A Rubicon thermofree, double, six-dial potentiometer and a Rubicon photo-electric galvanometer system are used to measure the potential across the thermometer on one set of its six dials and the potential across a standard resistor in series with the thermometer on the other set. In the higher range, the Rubicon potentiometer, together with the photo-electric galvanometer, permits direct reading of voltages from 0 to 111, 111 μv in steps of 0.1 μv. By switching to the lower range, voltages from 0 to 11, 111.1 μv in steps of 0.01 μv may be read directly.

During energy inputs the Rubicon potentiometer and photo-electric galvanometer are also used, for the electrical energy dissipated by the heater is likewise measured by observing the potential drop across the heater and that across a standard resistor in series with the heater.

The clock that records the duration of an energy input is controlled electrically (i.e., it is started and stopped automatically as the energy is turned on and off); it is run by a 60-cycle, alternating current from a calibrated tuning fork and amplifier circuit with a precision of 0.01 seconds.

The direct current used for energy inputs is provided by low discharge lead storage batteries. Measurements of the thermometer (temperature), heater (energy), and absolute

thermocouples (i.e., temperature of refrigerant tanks) are succesively selected by a master control switch.

Control of Adiabatic Shield

The temperature of the adiabatic shield in the Mark II cryostat may be controlled either manually by an experienced operator or automatically by a system composed of commercial electronic instruments. Automatic shield control may be used over the entire temperature range (i.e., 4 to 350°K). However, it was found that in the liquid helium temperature region (i.e., 4 to 60°K) where rapid operation is required, an experienced operator is preferred over the automatic controller. Although the speed of operation is slower, the accuracy and sensitivity of the automatic shield control is comparable to that of manual control in the liquid helium temperature range. In the transition region where long equilibration periods (i.e., 2 to over 12 hours) are required the automatic shield control is indispensable in making reliable heat capacity measurements. Therefore, unless manual shield control is specifically stated, it may be assumed that automatic shield control was used.

The set-up and operation of the automatic shield control has been described in detail elsewhere.[13] Briefly, the operation of the automatic shield control is as follows: when a temperature difference between the calorimeter and the central cylindrical part of the adiabatic shield (mash) is sensed by the differential thermopile, a signal is channeled

to a preamplifier (Leeds and Northrup Stabilized DC Indicating Amplifier) where it is amplified and fed to a recorder (Leeds and Northrup Speedomax Type G Recorder). At the "Speedomax", besides recording potential differences, the imbalance of the amplified signal against the preset control point of the recorder causes an output signal to be fed to a Current Adjustment Type (CAT) control unit. The CAT unit has three types of control action: proportional band, rate time, and reset controls. Part of the DC control signal from the CAT unit is transformed to AC (Brown converter), amplified (20 W Pilotone Amplifier), put through another transformer, and sent to the shield control selector to provide the necessary power to maintain the adiabatic shield at its control temperature (i.e., usually within 0.001°K of the temperature of the calorimeter). At the beginning and end of an energy input, temperature differences of the order of from 0.005 to 0.01°K may persist momentarily between the calorimeter and shield as a consequence of the sudden large change in shield power demand.

The top (tash) and bottom (bash) parts of the adiabatic shield are controlled by similar channels of instrumentation. However, in these cases, the differential thermopiles are set up between mash and tash and between mash and bash.

In manual shield control the entire action is controlled manually. Thus the timing, amount and rate pattern of energy input to the shield required to maintain the temperature of the adiabatic shield at its control point are selected by

the individual on the basis of previous experience, galvanometer deflection and anticipation of run behavior.

Calorimetric Procedure

Loading

The general procedure used for loading a sample into the calorimeter was as follows: the desired amounts in volume and mass of each component to make up a particular molar composition are calculated from the known densities, molecular weights, and the internal volume of the calorimeter. A few cm^3 of vapor space were left in the calorimeter at 0°C on each loading.

First the approximate desired volume of a component was transferred from storage by vacuum distillation into a sample bulb. After this amount was adjusted to within 0.1 gram of the desired mass it was transferred by vacuum distillation into the calorimeter (previously evacuated to constant weight). When the transfer into the calorimeter had been completed, the calorimeter was immersed in liquid nitrogen until its contents were completely solidified (or about one-half hour). Then the calorimeter and its contents were evacuated for a few minutes before it was sealed-off by turning the screw-driver of the "screw-driver" valve. The calorimeter was left on the loading line until it had warmed up to room temperature, and the valve on the calorimeter was tightened securely before removal from the line.

Finally, after washing and drying the exterior of the calorimeter with benzene and air, respectively, the calorimeter was weighed. The exact amount of sample transferred into the calorimeter was determined by difference (i.e., weight of calorimeter plus sample in vacuo minus weight of empty calorimeter in vacuo).

The same procedure was followed for loading the second component except that after freezing and evacuating, a predetermined amount (mm Hg) of helium gas was added to the sample before finally closing the valve.

It was found that when transferring sample from storage to sample bulb, a liquid nitrogen bath may be used around the sample bulb; while transferring sample from sample bulb to calorimeter, a dry ice cooling bath around the calorimeter is preferred, for the liquid nitrogen bath tends to cause freezing of sample in the valve on the calorimeter, thus blocking the transfer completely. And it was also found that when loading, it is better to load the calorimeter with the less volatile component first (i.e., tetrachloromethane).

After the loading operation was completed, it was found advisable to check the weight of the loaded calorimeter over a day or two, because during the process of repeated freezing and screwing on and off the calorimeter to and from the "screw-driver" valve, a slight strain and internal pressure tend to weaken the solder joints around the valve on the calorimeter. A leak, which is difficult to detect over a short period of time, may thus develop. The high vapor pressure of

tetramethylmethane at room temperature makes it possible for a small leak to be detected over a longer period of time by the persistent loss in weight beyond fluctuations caused by changes in temperature, barometric pressure, and humidity.

During the loading operation of the various compositions of mixtures, leaks in the calorimeter developed several times. These leaks were usually not detected until the loading operation was completed. When a leak was detected, its location had to be found before any repairs could be made. It was determined that the most efficient way to locate the leak is to submerge the loaded calorimeter in warm (about 35°C) distilled water and watch for the evolution of bubbles. In each case of a detected leak, the calorimeter was unloaded, repaired (i.e., by flaming the solder joint or completely resoldering), tested and reloaded. Silver-alloy brazing or redesign would be desirable on subsequent condensed gas calorimeters. The various repairs made on Calorimeter W-23 during this investigation occasioned the solder corrections applied for each of the compositions shown in Table I, page 33.

After completion of the loading operation, mixing was effected by freezing and melting the mixture several times (i.e., immersing the loaded calorimeter in a liquid nitrogen bath for about two hours and then removing the liquid nitrogen, and allowing the calorimeter to warm to room temperature slowly while remaining in the cooled dewar). Before each freezing operation, additional aid in mixing was furnished by

shaking the calorimeter with a rotating motion in all directions (i.e., around both the cylindrical and perpendicular axes).

Cooling

Mixtures of tetramethylmethane and tetrachloromethane are easily undercooled. The degree of undercooling has large effects on the reproducibility of the heat capacity measurements in the transition region (135 to 230°K) of this system. A high degree of undercooling can make it impossible to get the transition to occur from the "rotating" to the "non-rotating" form. (See Series VI, Run F of N_{CCl_4} = 0.334; and Series II of N_{CCl_4} = 0.501.) This effect has also been reported to occur in other systems, e.g., the system 2,2-dimethylbutane and 2,3-dimethylbutane.[5] Therefore, the cooling rate before the start of a series of heat capactity measurements is an important factor in the calorimetric investigation of the system tetramethylmethane-tetrachloromethane.

In order to ascertain the fastest cooling rate that is permissible and still insure equilibration and reproducibility of the measurements, a series of different cooling rates were tested involving runs of Series I through Series VIII of the first composition studied (N_{CCl_4} = 0.501). After this experimentation it was found that reproducible results are obtained with the slower cooling rates. The following cooling procedure gave reproducible

heat capacity measurements in the transition region and was adapted for the subsequent compositions studied.

After assembling the cryostat with the loaded calorimeter, pumping down the entire system, and adding the liquid nitrogen to the refrigerant tanks, etc., the calorimeter was left to cool at the "operate" position instead of cooling the calorimeter and sample as usual by bringing the calorimeter into thermal contact with the helium refrigerant tank. The calorimeter was cooled at this position from room temperature down to the region between 160 to 180°K where the temperature gradient between the calorimeter and its immediate surrounding became too low for any appreciable heat transfer (reaching this region usually required about four days after the beginning of the cooling process). Then the calorimeter was contacted to the "shield" position and cooled until below 130°K (i.e., below the first transition). This usually took another one to two days of cooling. Below this temperature the cooling rate had no effect on the reproducibility of the heat capacity measurements. Therefore, below 130°K, the calorimeter and sample were cooled at the maximum rate (calorimeter brought into thermal contact with the helium refrigerant tank) to the desired temperature.

It was found that due to the relatively large heat capacity this system had at low temperatures, it took almost twice as long to cool a sample of this system as other compounds. Cooling at the maximum rate from 130 to 66°K took at least a day; cooling from 66 to 5°K (with liquid helium

in the helium tank) required an addition day.

In view of the fact that the reproducibility of the heat capacity measurements over the transition region from 135 to 235°K can be affected by the manner in which a sample was cooled prior to the series of measurements, a detailed account of the thermal history together with certain experimental exigencies of all the runs (presented chronologically in Appendix III) is relevant to the understanding of the results obtained.

Heat Capacity Measurements

In general, heat capacity measurements were made by observing the temperature rise (ΔT) of the calorimeter and sample produced by a measured amount of energy input (Q). The rise in temperature is determined by the equilibrium temperatures of the calorimeter and sample before and after the energy input. These temperatures are corrected for the slight non-adiabaticity between the calorimeter and the adiabatic shield by extrapolation of the equilibrium drifts before and after the energy input to the mid-point of the energy input.

The thermometer (laboratory designation A-5) used for temperature measurements has been calibrated at the National Bureau of Standards by measuring its electrical resistances at four fixed points on the International Temperature Scale (i.e., the boiling point of oxygen, the ice-point, the steam-point, and the boiling point of sulfur). From these

measured resistances the constants of the Callender-Van Dusen equation were evaluated. The thermometer has also been compared at 19 temperatures between 10 and 90°K with the Bureau's platinum-resistance scale. A provisional temperature scale has been set up for the temperature range between 4 and 10°K. The values of dR/dT at 10°K, and of the resistances of the thermometer at 10°K and the boiling point of liquid helium were used to evaluate the constants in the equation $R = A + BT^2 + CT^5$ for the temperature scale of this region.

The absolute values of the temperature on this scale (thermometer A-5) are believed to agree with the thermodynamic temperature scale to within 0.1° below 10°K, 0.03° from 10 to 90°K, and 0.04° from 90 to 350°K. Determinations of the temperature increment (ΔT) are probably correct to 0.001°.

The temperature increment of a run depended on the temperature range. Usually it was 1° below 10°K, 10% of the mean temperature between 10 and 90°K, and 9° above 90°K.

The measured energy input was determined by the current through and the potential drop across the heater during energy input and the time duration of energy input. The time duration of energy input varied from four minutes to ten minutes and was selected to make the rate of heating no greater than 1° per minute. Finally, the apparent heat capacity of the calorimeter and sample was determined by the quantity ($Q/\Delta T$).

The heat capacity measurements in the transition region (135 to 245°K) of mixtures of the system tetramethylmethane-tetrachloromethane deviate somewhat from the usual procedure. In this study, measurements across a transition or fusion consisted of a continuous series of approximately constant energy inputs (i.e., using the same current for approximately the same time duration, usually 70 to 100 ma for 10 minutes to produce an energy input of between 90 to 180 calories) from the region below the transition to completion of the transition. In this manner, the progress across the transition is indicated by the size of the temperature increments of the runs; the completion of the transition is indicated by the near constancy of the final runs (i.e., measurements were continued without interruption until the entire region was covered.).

The time required for equilibration after an energy input was generally long. For example, in the region of Transition I* (135 to 150°K) equilibration required three to four hours; in the range from 150 to 180°K equilibration took on the average of four to five hours; in the region of Transition II* (180 to 195°K) equilibration obtained after three hours; in the region of Transition III* (195 to 220°K) equilibration required about two hours; in the plastically crystalline region (the region between Transition III and fusion) equilibration took less than one hour; and in the fusion region equilibration was relatively fast, requiring around two hours. Measurements in the peak region of all

* based on consecutive numbers with increasing temperature

the transitions and fusion routinely required over twelve hours for final thermal equilibration. Outside the transition region (both below 138°K and in the liquid range) the time required for equilibration was normal, i.e., about 20 to 30 minutes, and around 10 to 15 minutes in the liquid helium temperature region.

After studying the results of measurements in the transition region, it is believed that in most cases only apparent equilibrium was reached when the drift measurements were stopped and that true equilibrium within the sample would probably require a considerably longer period for equilibration.

In addition, a final test of the magnitude of each transition determined by integration of the apparent heat capacity was made with series of enthalpy-type and ΔH of transition runs (runs with a relatively long period of energy input, i.e., 30 to 60 minutes with a constant current of 70 to 100 ma, over a 20 to 30°K temperature interval or across a transition, respectively) spanning the entire transition region. Due to the long period of time required to attain thermal equilibrium within the sample after an energy input and the uncertainty between attainment of apparent equilibrium with true equilibrium (i.e., constant but comparatively large drifts) the accuracy of the heat capacity measurements in the transition region was considerably poorer than normal. In most regions the error is within 0.5%, except in the regions of Transition I and

between 150 to 180°K where it is around 1%. However, these factors do not affect the accuracy of the enthalpy increments over the transition region which were determined by the enthalpy-type and ΔH of transition runs as mentioned above. Outside the transition region the accuracy and precision of the measurements are normal.

Treatment of Data

Calculation of the apparent heat capacities of the calorimeter plus sample from currents, potentials and time durations of energy input measurements is facilitated by use of an IBM computer program written by Dr. Bruce H. Justice[15] for use with the Mark II cryostat, A-5 thermometer, and the Rubicon potentiometer. The calculated apparent heat capacities outside the transition region are adjusted for curvature by an analytical expression applied to the apparent heat capacity to correct for the difference between dH/dT (the true heat capacity) and $\Delta H/\Delta T$ or $Q/\Delta T$ (the apparent heat capacity) due to the finite temperature increment (ΔT) of the run. This correction is usually less than 0.1% of the total heat capacity.

The molal heat capacity is obtained by subtracting the value of the heat capacity of the empty Calorimeter W-23 heater-thermometer assembly (determined by a separate experiment) from the total curvature-corrected heat capacity and multiplying the result by a molal factor. After removal of the empty calorimeter-heater-thermometer assembly's heat

capacity, adjustments for the small differences in the amounts of helium contact gas in the calorimeter, Apiezon-T grease in the thermometer well, and 50-50 lead-tin and Cerroseal solders on the calorimeter (due to repairs made on the calorimeter) when the calorimeter was run as empty and when it was run loaded, are applied before the resulting heat capacity of the sample is multiplied by the molal factor.

The calculations involved in curvature correcting and molalling the adjusted heat capacity values are also accomplished by using an IBM (704 and 709) computer program written by Dr. Bruce H. Justice.[15] The heat capacity of the calorimeter-heater-thermometer assembly represented less than 32% of the total heat capacity at all temperatures for the mixtures studied. It varied from a minimum of about 3% at 10°K to about 30% at 90°K, a maximum between 30 and 32% in the range 90 to 130°K, and about 25% in the liquid range. At the peak of the transitions and fusion it is less than 10%, and between transitions it represented a relative maximum of about 28% of the total heat capacity. The combined correction for helium, grease, and solder is less than 0.1% over the entire range.

The heat capacity data in the transition region (135 to 245°K) were not corrected for curvature, but the other corrections (i.e., helium, grease, and solder) were applied. Data in the transition region were molalled by using a "MAD" program written by John C. Trowbridge[16] for the IBM 704 or 709 computer.

Corrections for vaporization of the sample of the highest vapor pressure mixture studied (i.e., the N_{CCl_4} = 0.334 mixture) were minimized by nearly complete filling of the calorimeter and amounted to less than 0.02% of the total heat capacity, which is well within the experimental error of the heat capacity measurements; therefore, corrections for vaporization were not applied.

Due to the difficulties (cf. Appendix III, Thermal History of Runs) encountered during heat capacity measurements (i.e., "oscillations", and long and large drifts) further corrections were applied to the heat capacity measurements in the transition region. For the runs marked with the superscript "b" in Tables III and IV the final temperature (T_2) of the run was corrected from apparent equilibrium conditions (i.e., apparently steady but long and comparatively large, negative drifts) by extrapolation to the estimated true equilibrium condition (i.e., final temperature at essentially zero drift). For the runs marked with the superscript "c", the energy of the run was corrected for "oscillations". "Oscillations" during energy input can also be detected by the calculated heater resistance value. Errors in the calculated energy input caused by "oscillations" are adjusted by using the correct heater resistance value at the same temperature from another series of measurements and the apparent heater resistance value of the run with "oscillations" to determine a correction factor.

A summary of the mass (<u>in vacuo</u>), molar composition,

and molal factor of each mixture used for the molal heat capacity determinations are tabulated in Table I. The calculated vapor space at 273°K and at liquid nitrogen temperature, the pressure of helium gas, and corrections for differences in the amounts of helium, grease, and solder between those used when the calorimeter-heater-thermometer assembly was run empty, and those used on the loaded calorimeter are also tabulated in Table I.

TABLE I. SUMMARY OF MOLAL FACTOR AND CORRECTIONS

Composition Code	2 - 1	1 - 1	1 - 2	1 - 5	CCl_4
Mass in Vacuo - grams of:					
CCl_4	35.364	56.521	77.888	99.474	128.146
CMe_4	33.111	26.404	18.592	9.850	0
Gram-Moles in Sample of:					
CCl_4	0.2299	0.3674	0.5128	0.6466	0.8330
CMe_4	0.4589	0.3660	0.2577	0.1365	0
Mole Fraction (in sample) of:					
CCl_4	0.334	0.501	0.666	0.826	1.000
CMe_4	0.666	0.499	0.334	0.174	0
Total Moles of Sample	0.6888	0.7334	0.7705	0.7831	0.8330
Molal Factor	1.4518	1.3636	1.2979	1.2769	1.2005
Vapor Space Left in Calorimeter - cm^3					
Calculated at 273.15°K	3.49	1.48	0.59	2.28	0.84
Estimated at 77°K	3.88	1.64	0.70	2.50	0.93
Corrections in grams					
Helium	+ 0.000112	- 0.000197	- 0.000228	- 0.000042	- 0.000206
Solder - 50-50 Pb-Sn	+ 0.0845	+ 0.0078	+ 0.0875	+ 0.1248	+ 0.0875
- Cerroseal	0	0	0	- 0.0115	- 0.0115
Grease - Apiezon - T	0	0	+ 0.0054	+ 0.0054	+ 0.0054

RESULTS

Results of Heat Capacity Measurements

The heat capacity of the empty Calorimeter W-23 heater-thermometer assembly was determined by using the Mark II cryostat with automatic shield control throughout the entire temperature range from 5 to 350°K. The Rubicon potentiometer and the A-5 thermometer were used for the measurements. The empty Calorimeter W-23 had a mass of 82.293 grams (*in vacuo*), a calculated internal volume of 79.31 cm^3, and contained 1.8 cm Hg at 26°C of helium gas. The curvature corrected heat capacity determinations for the Calorimeter W-23 heater-thermometer assembly are tabulated in Table II.

The molalled experimental heat capacity determinations of four different compositions (i.e., N_{CCl_4} = 0.334, 0.501, 0.666, and 0.826) of mixtures of the system tetramethylmethane-tetrachloromethane are tabulated in Tables III, IV, and V. In Table III, the molal heat capacity determinations of each mixture are listed in chronological order. The values given are based on the defined thermochemical calorie of 4.1840 absolute joules and the ice point as 273.15°K. The molecular weights of the components used for the calculations are tetramethylmethane = 72.151 grams per mole and tetrachloromethane = 153.839 grams per mole (based

TABLE II. HEAT CAPACITY OF CALORIMETER W-23 AND HEATER-THERMOMETER ASSEMBLY (Units: cal, °K)

T	C_p	T	C_p
Series I		56.10	2.658
		62.99	3.222
5.48	0.008	70.24	3.765
6.34	0.010	77.64	4.271
7.38	0.011	85.10	4.740
8.32	0.016	92.32	5.128
9.47	0.022	100.03	5.489
10.46	0.029	107.79	5.813
11.55	0.037	115.31	6.090
12.63	0.046	122.96	6.345
13.88	0.062	131.30	6.591
15.27	0.080	140.29	6.822
16.81	0.106	149.60	7.027
18.44	0.140	159.83	7.229
20.19	0.185	169.55	7.389
22.07	0.242	178.77	7.523
24.15	0.321	187.84	7.640
26.37	0.416	196.95	7.745
28.91	0.549	206.11	7.840
		215.15	7.929
Series II		224.09	8.006
		233.07	8.082
21.93	0.238	242.08	8.151
24.82	0.348	251.09	8.212
27.53	0.476	260.11	8.272
30.44	0.638	269.15	8.329
33.79	0.854	278.25	8.382
37.20	1.099	287.21	8.428
40.73	1.372	296.31	8.475
44.48	1.679	305.46	8.524
48.59	2.025	314.65	8.566
53.03	2.401	323.88	8.602
		332.14	8.637
Series III		339.45	8.667
		346.73	8.695
50.52	2.189		

TABLE III. HEAT CAPACITIES OF MIXTURES OF THE SYSTEM TETRAMETHYLMETHANE-TETRACHLOROMETHANE*
(Units: cal, gram-mole solution, °K)

N_{CCl_4} = 0.334

T	C_p	T	C_p	T	C_p
Series I		**Series II**		**Series V**[a,s]	
78.15	14.12	9.36	0.839	**Transition (I) Runs E**	
84.79	15.07	9.96	1.018		
91.52	16.00	10.93	1.281	**Series VI**[s]	
98.62	16.99	12.09	1.608		
105.84	18.07	13.25	2.008	**ΔHt(I) Run F**	
112.50	19.11	14.44	2.439		
119.74	20.38	15.79	2.921	**Series VII**	
127.24	21.81	17.37	3.485		
134.97	23.78	19.22	4.128	134.73	23.49
ΔHt(I) Runs A[a,b]		21.32	4.824	ΔHt(I) Run G[b]	
		23.56	5.523		
151.89	24.65[b]	25.83	6.172	Enthalpy Run H[b]	
156.31	26.01[b]	28.26	6.799		
164.10	30.05[b]	30.90	7.411	ΔHt(II) Run I	
171.51	32.92[b]	33.70	8.010		
178.75	37.99[b]	36.89	8.598	Enthalpy Run J	
183.52	43.07[b]	40.41	9.198		
Transition (II) Runs B[b]		44.08	9.731	Fusion Run K	
		47.87	10.25		
199.35	28.39	**Series III**		**Series VIII**	
203.53	28.50	46.34	10.05		
207.68	28.62	51.03	10.67	ΔHm Run L	
211.83	28.51	55.98	11.28		
215.98	28.60	61.04	11.93	248.59	34.19
220.10	28.86	66.34	12.60	255.53	34.55
224.21	29.07	72.02	13.31	263.61	34.97
228.28	29.31	78.53	14.17	271.91	35.45
				279.91	35.85
Fusion Runs C		**Series IV**[a]		287.83	36.25
				295.85	36.66
250.83	34.27	Transition (I) Runs D			

TABLE III (Cont.)

$N_{CCl_4} = 0.501$

Series I[a,b,n]	
162.48	26.10
167.61	28.27
174.16	31.21
180.74	35.02
186.99	41.60
Series II[n]	
183.21	27.32[b,s]
189.89	28.22[b,s]
199.09	29.48[a,b]
△Ht(III) Runs A[a,b]	
△Hm Runs B[a]	
249.86	33.39
264.25	33.94
273.88	34.35
283.41	34.77
292.85	35.16
Series III	
245.39	33.19
253.63	33.54
261.79	33.84
270.65	34.23
280.15	34.64
289.54	35.03
Series VI[a,b,n]	
134.67	22.49
△Ht(I) Runs C	
163.55	27.81
172.97	30.65
180.87	35.63
Series V[n]	
178.51	31.85[a,b]
Transition$_a$(I) Runs H[a]	
148.83	23.56[b]
152.41	24.97[b]
155.83	26.30[b]
160.98	27.12[b]
167.32	27.89[b]
173.82	31.60[b]
179.78	34.66[b]
Transition (II) Runs I[a,b]	
Series VIII	
180.29	33.02[b,s]
183.03	36.23[b,s]
Transition$_b$(II) Runs J[b]	
Transition$_b$(III) Runs K[b]	
230.69	29.69
△Hm Run L	
Series IX	
70.41	13.08
73.79	13.48
Series X	
63.51	12.29
69.23	12.95
75.05	13.64
81.48	14.48
88.51	15.42
96.17	16.38
104.30	17.45
112.45	18.60
120.89	19.89
129.29	21.33
Series XIV	
4.88	0.078
5.74	0.149
6.80	0.277
7.77	0.455
8.78	0.698
9.73	0.985
10.63	1.227
11.70	1.540
13.14	2.054
14.87	2.698
16.63	3.383
18.46	4.044
20.47	4.741
22.62	5.419
25.11	6.200
Series XV	
Enthalpy Run N	
25.77	6.407
28.62	7.120
32.06	7.872
35.91	8.624
39.72	9.264
43.84	9.847
48.98	10.53
54.81	11.22
61.00	11.97
Series XVI	
59.40	11.78
65.85	12.56
Enthalpy Run O	
135.79	22.74
△Ht(I) Run P	
Series XVII	
Enthalpy Run Q	

TABLE III (Cont.)

184.35	36.98[a,b]

△Ht(II) Runs D[a,b]

△Ht(III) Runs E[a,b]

Fusion Runs F

Series VI

130.96	21.54
134.91	22.41
138.71	23.64

△Ht(I) Runs G[a]

Series VII

124.77	20.52
128.89	21.27
132.88	22.07
136.72	23.01

Series XI

71.21	13.17
78.32	14.05
85.43	15.01
92.55	15.91
99.98	16.86

Series XII

Test Runs M

Series XIII

8.94	0.746
9.66	0.966
10.58	1.206
11.68	1.528
12.95	1.990
14.35	2.515
15.90	3.100
17.75	3.790

△Ht(II) Run R

Enthalpy Run S

Transition[b] (III) Runs T[b]

227.26	29.73[b]
229.81	29.74[b]

△Hm Runs U

Series XVIII

Fusion Runs V

247.12	33.26
255.28	33.62
263.77	33.91
272.60	34.33
281.63	34.74
290.86	35.03
300.15	35.57

$N_{CCl_4} = 0.666$

Series I

10.37	1.313
10.99	1.450
11.96	1.767
13.03	2.177
14.17	2.628
15.42	3.121
16.87	3.690
18.66	4.365
20.67	5.076
22.76	5.762
25.03	6.441
27.68	7.138
30.81	7.844
34.24	8.523
37.86	9.159
107.63	17.47
115.37	18.45
123.05	19.47
130.92	20.61

△Ht(I) Runs A[a,b,c]

155.33	23.28[b,c]
159.81	24.54[b,c]
164.15	26.15[b,c]
168.29	26.22[b,c]
172.44	28.07[b,c]
176.38	28.96[b,c]
180.22	31.20[b]
183.86	33.27[b]

Transitions[b] (II, III) Runs B[b]

Series V

134.70	21.16

△Ht(I) Run E[b,c]

Enthalpy Run F[b,c]

△Ht(II, III) Run G[b]

204.07	30.57

Series VI

△Ht(II) Run H[b,c]

△Ht(III) Run I[b,c]

TABLE III (Cont.)

Series II

39.08	9.341
43.16	9.902
47.48	10.45
52.17	11.00
57.40	11.59
63.37	12.29
69.88	13.00

Series III

73.61	13.57
79.52	14.21
85.60	14.94
92.19	15.68
99.66	16.53
208.01	28.74[c]
211.87	28.80[c]
215.74	29.14[c]
219.37	29.49[c]
222.78	29.86[c]

Fusion Runs C[c]

242.65	32.34[c]

Series IV

133.61	21.10

Transition[b] (I) Runs D[b,c]

243.99	32.36
250.86	32.58
259.12	32.82
267.44	33.07
275.68	33.31
283.87	33.51
291.99	33.80
300.12	33.40

Enthalpy Run J[c]

ΔHm Run K[c]

Series VII[c]

ΔHm Run L

$N_{CCl_4} = 0.826$

Series I

6.13	0.187
7.48	0.444
8.33	0.662
9.13	0.918
9.95	1.219
10.86	1.493
11.92	1.857
13.18	2.373
14.65	2.983
16.22	3.621
17.87	4.284
19.73	4.970
21.99	5.749
24.67	6.572
27.92	7.418
31.55	8.205

Series II

30.85	8.055
34.57	8.769
38.29	9.390
99.52	16.20
108.26	17.13
116.42	18.03
124.51	18.94
130.35	19.61
136.56	20.48

ΔHt(I) Runs A[b]

147.20	21.55[b]
151.57	21.43[b]
156.77	22.12[b]
162.64	23.40[b]
168.27	24.46[b]
173.15	25.41[b]
177.37	26.17[b]
181.45	27.62[b]
185.33	29.09[b]
189.03	30.92[b]

ΔHt(II) Run B[b]

Transition[b] (III) Runs C[b]

129.31	19.30
136.62	20.44

Transition[b] (I) Runs E[b]

Series V

ΔHt(I) Run F

Enthalpy Run G[b]

168.80	24.96[b]
171.19	26.83[b]
173.51	25.07[b]
175.86	26.28[b]
178.15	26.92[b]
180.40	27.29[b]

Enthalpy Run H

Transition[b] (II) Runs I[b]

TABLE III (Cont.)

42.49	9.930			ΔHt(III) Run J[b]	
47.23	10.53	227.05	29.22		
52.30	11.09	231.25	29.60	Enthalpy Run K	
57.98	11.71	234.87	30.14		
				ΔHm Run L	
Series III		Fusion Runs D			
				250.18	31.78
62.18	12.19	245.88	31.65	257.78	31.98
68.32	12.83	249.37	31.74	266.61	32.16
75.28	13.57			276.10	32.36
82.07	14.34	Series IV		285.38	32.54
90.51	15.28			294.63	32.74

* Interpretation of superscripts:

a = Run made under non-equilibrium drift condition

b = T_2 of run has been corrected from apparent equilibrium condition by extrapolation to estimated equilibrium state

c = Energy of run has been corrected for "oscillations" in external circuit

n = Run made after non-equilibrium cooling

s = Run made on undercooled phase

on the 1957 international atomic weights). Besides the corrections for curvature and for the differences in the amounts of helium, grease, and solder, additional corrections were applied to some of the runs in the transition region as indicated by the superscripts mentioned before. The approximate temperature increment of each run may usually be estimated from the adjacent mean temperatures (Table III).

The transition region of each mixture is shown in detail in Table IV. As previously indicated, the transitions are numbered in the order of increasing temperature, i.e., the lowest temperature (142.5°K) transition is designated as Transition I. The experimental enthalpy increments across a transition determined by a single run or a continuous series of runs are presented after adjustment to common temperature ranges, (e.g., 135 to 150°K) to facilitate comparison between runs. The weighted averages given are the values used when calculating the thermodynamic functions and enthalpies of transition, etc. For runs in the transition peak region, temperature increments of the runs are given in addition to the mean temperature and heat capacities of each run.

Table V provides a comparison of the directly-measured enthalpy increments with the integral under the smoothed heat capacity curve for various regions of each mixture.

The heat capacity versus temperature curves for the mixtures of mole fraction N_{CCl_4} = 0.334, 0.501, 0.666, and 0.826 of the system tetramethylmethane-tetrachloromethane are shown in Figures II, III, IV, and V respectively.

TABLE IV. THERMAL MEASUREMENTS IN THE TRANSITION REGIONS OF MIXTURES OF THE SYSTEM TETRAMETHYLMETHANE-TETRACHLOROMETHANE* (Units: cal, gram-mole solution, °K)

$N_{CCl_4} = 0.334$

TRANSITION (I)

T_i	T_f	ΔH or $\Sigma\Delta H$	$H_{150} - H_{135}$
Series I, Runs A (2 runs) [a,b]			
138.90	147.73	609.29	759.97
Series VI, Run F[s]			
139.12	152.17	409.03	456.53
Series VII, Run G[b]			
136.91	145.88	625.14	773.62
		Average	773.62

(For average used Run G only. Runs A had poor shield control and Run F was done on undercooled sample.)

T	ΔT	C_p
Series IV, Runs D (3 runs)[a]		
138.00	4.37	24.76
141.17	1.97	116
143.71	3.11	88.91
Series V, Runs E (4 runs)[a,s]		
140.46	3.27	35.68
142.39	0.60	287
143.82	2.26	54.97[b]
147.14	4.16	24.77[b]

TABLE IV (Cont.)

TRANSITION (II)

T_i	T_f	ΔH or $\Sigma\Delta H$	$H_{200} - H_{180}$
Series I, Runs B (5 runs)[b]			
184.71	197.25	581.26	856.53
Series VII, Run I			
180.84	202.30	890.23	858.18
		Average	857.36

T	ΔT	C_p
Series I, Runs B (5 runs)[b]		
185.83	2.24	46.52
188.01	2.11	50.08
190.04	2.01	53.28
192.34	2.56	53.95
195.44	3.62	34.79

FUSION

T_i	T_f	ΔH or $\Sigma\Delta H$	$H_{245} - H_{230}$
Series I, Runs C (7 runs)			
230.31	247.95	1055.74	964.10
Series VII, Runs K (8 runs)			
230.36	245.44	967.28	962.92
Series VIII, Run L			
230.97	245.54	954.81	964.97
		Average	964.00

TABLE IV (Cont.)

T	ΔT	C_p
Series I, Runs C (7 runs)		
232.31	4.01	29.78
236.20	3.77	32.43
239.30	2.42	56.90
241.06	1.14	134
241.96	0.74	214
242.60	0.61	262
245.41	5.08	40.70
Series VII, Runs K (8 runs)		
232.10	3.48	29.55
235.50	3.36	30.97
238.44	2.58	43.75
240.40	1.38	92.42
241.44	0.81	165
242.15	0.66	205
242.84	0.78	171
244.32	2.24	52.23

$N_{CCl_4} = 0.501$

TRANSITION (I)

T_i	T_f	ΔH or ΣΔH	$H_{150} - H_{135}$
Series IV, Runs C (3 runs)[a,b,n]			
136.66	157.81	750.73	589.44
Series VI, Runs G (2 runs)[a]			
140.56	146.63	421.41	629.91
Series VII, Runs H (4 runs)[a]			
138.61	147.18	492.71	642.10

TABLE IV (Cont.)

Series XVI, Run P

139.79	154.10	628.64	638.16
		Average	636.72

(For average used Runs G, H, and P. Runs C had poor shield control and some undercooling of sample.)

T	ΔT	C_p
Series VII, Runs H (4 runs)[a]		
140.15	3.08	31.10
142.07	1.08	146
143.26	1.71	72.66
145.54	3.27	27.07

TRANSITION (II)

T_i	T_f	ΔH or ΣΔH	$H_{200} - H_{180}$
Series V, Runs D (3 runs)[a,c]			
187.06	199.65	648.63	923.16
Series VIII, Runs J (7 runs)[b]			
184.50	200.55	810.73	958.78
Series XVII, Run R			
181.97	200.03	905.09	974.49
		Average	974.49

(For average used Run R only. Runs D and J had poor shield control and some undercooling of sample.)

T	ΔT	C_p
Series VII, Runs I (2 runs)[a,b]		
185.24	5.18	39.42
189.38	3.10	72.84

TABLE IV (Cont.)

Series VIII, Runs J (7 runs)[b]

185.76	2.51	38.65
188.16	2.28	43.50
190.41	2.21	45.00
191.55	0.59	405
193.13	2.56	37.16
195.96	3.08	29.38
199.02	3.05	29.56

TRANSITION (III)

T_i	T_f	ΔH or $\Sigma\Delta H$	$H_{230} - H_{200}$
Series II, Runs A (3 runs)[b]			
205.10	229.82	871.01	1036.43
Series V, Runs E (5 runs)[a,c]			
199.66	227.98	974.28	1024.25
Series VIII, Runs K (10 runs)[b]			
200.44	227.56	930.05	1015.72
Series XVII, Run S and Runs T (7 runs)[b]			
200.01	226.16	896.88	1011.03
		Average	1013.38

(For average used runs of Series VIII and XVII only. Runs of Series II and V were made after non-equilibrium cooling.)

T	ΔT	C_p
Series VIII, Runs K (10 runs)[b]		
201.95	3.02	29.91
204.80	2.66	35.26
207.45	2.59	36.53
209.99	2.61	36.12
212.53	2.66	35.22
215.15	2.55	37.06
217.75	2.60	36.16
220.40	2.65	35.31
222.53	2.84	32.15
225.09	2.96	30.33

TABLE IV (Cont.)

Series XVII, Runs T (7 runs)[b]

209.58	2.54	36.76
212.06	2.56	36.98
214.60	2.48	38.34
217.15	2.57	36.61
219.80	2.69	34.36
222.53	2.87	30.00
225.09	2.15	30.14

FUSION

T_i	T_f	ΔH or $\Sigma\Delta H$	$H_{245} - H_{230}$
Series II, Runs B (2 runs)			
229.83	240.31	759.05	909.14
Series V, Runs F (4 runs)			
227.98	241.93	867.85	909.46
Series VIII, Run L			
233.88	243.61	746.15	907.16
Series XVII, Runs U (3 runs)			
231.27	247.20	944.15	908.96
Series XVIII, Runs V (8 runs)			
230.59	243.09	825.64	909.43
		Average	908.83

T	ΔT	C_p
Series V, Runs F (4 runs)		
231.10	6.25	30.00
235.45	2.45	93.12
236.96	0.58	427
239.59	4.68	43.49

TABLE IV (Cont.)

Series XVIII, Runs V (8 runs)

232.07	2.94	29.92
234.63	2.21	43.42
236.06	0.73	154
236.64	0.44	267
237.09	0.46	250
237.71	0.77	145
239.20	2.29	41.30
241.71	2.75	33.04

$N_{CCl_4} = 0.666$

TRANSITION (I)

T_i	T_f	ΔH or $\Sigma\Delta H$	$H_{150} - H_{135}$
Series III, Runs A (3 runs)[a,b,c]			
134.92	153.05	597.24	526.62
Series V, Run E[b,c]			
137.01	148.31	448.30	529.47
		Average	528.04

T	ΔT	C_p
Series IV, Runs D (5 runs)[b,c]		
138.12	4.39	21.91
141.32	2.04	70.86
143.46	2.52	50.40
146.63	4.11	24.47
150.86	4.34	22.52

TRANSITIONS (II) and (III)

T_i	T_f	ΔH or $\Sigma\Delta H$	$H_{205} - H_{185}$

TABLE IV (Cont.)

Series V, Run G[b]			
188.12	202.36	966.21	1157.35
Series VI, Run H[b,c]			
185.68	196.66	649.39	
Series VI, Run I[b,c]			1154.48
196.66	205.30	490.57	
		Average	1155.92

T	ΔT	C_p
Series III, Runs B (9 runs)[b]		
187.30	3.36	35.64
190.04	2.12	62.06
191.60	0.97	147
193.28	2.36	54.55
195.56	2.21	58.91
197.67	2.00	65.91
199.54	1.82	73.59
201.38	1.76	76.27
204.17	3.79	30.03

FUSION

T_i	T_f	ΔH or ΣΔH	$H_{240} - H_{225}$
Series VI, Run K[c]			
223.42	239.03	1035.52	1019.43
Series VII, Run L[c]			
225.77	241.20	1040.26	1019.27
		Average	1019.35

T	ΔT	C_p

TABLE IV (Cont.)

Series III, Runs C (9 runs)[c]

226.18	3.39	30.40
229.30	2.86	38.06
231.76	2.29	49.77
233.88	1.98	59.37
235.11	0.48	280
235.39	0.09	1556
235.53	0.22	624
236.73	2.19	52.70
239.44	3.22	32.31

$N_{CCl_4} = 0.826$

TRANSITION (I)

T_i	T_f	ΔH or $\Sigma \Delta H$	$H_{150} - H_{135}$
Series III, Runs A (2 runs)[b]			
138.85	145.01	220.73	407.29
Series IV, Runs E (5 runs)[b]			
139.85	147.66	262.69	412.03
Series V, Run F			
135.64	145.37	314.90	
		Average	409.66

(Run F - obsolete, timer trouble)

T	ΔT	C_p
Series IV, Runs E (5 runs)[b]		
140.83	1.96	24.84
142.23	0.79	77.90
143.25	1.19	46.35
144.72	1.74	29.05
146.63	2.06	22.99

TABLE IV (Cont.)

TRANSITION (II)

T_i	T_f	ΔH or $\Sigma\Delta H$	$H_{193} - H_{190}$
Series III, Run B[b]			
190.82	192.32	132.86	184.86
Series V, Runs I (4 runs)[b]			
190.27	193.45	192.58	183.40
		Average	184.13

T	ΔT	C_p
Series V, Runs I (4 runs)[b]		
190.91	1.28	33.97
191.69	0.26	204
191.93	0.78	61.7
192.88	1.25	38.52

TRANSITION (III)

T_i	T_f	ΔH or $\Sigma\Delta H$	$H_{225} - H_{193}$
Series III, Runs C (13 runs)[b]			
192.32	224.65	1627.97	1605.52
Series V, Run J[b]			
193.46	223.48	1543.12	1604.70
		Average	1605.11

T	ΔT	C_p
Series III, Runs C (13 runs)[b]		
193.80	2.96	39.92

TABLE IV (Cont.)

196.64	2.73	44.08
199.25	2.51	48.59
201.64	2.26	54.85
203.80	2.05	61.58
205.75	1.84	69.82
207.48	1.61	81.00
209.05	1.52	86.99
210.49	1.35	98.41
212.08	1.82	70.46
214.65	3.26	34.93
218.05	3.54	31.37
222.24	4.82	29.08

FUSION

T_i	T_f	ΔH or $\Sigma\Delta H$	$H_{245} - H_{235}$
Series III, Runs D (6 runs)			
236.67	244.13	802.84	880.83
Series V, Run L			
234.17	246.56	957.28	882.68
		Average	881.75

T	ΔT	C_p
Series III, Runs D (6 runs)		
238.17	3.00	38.25
240.12	0.94	145
240.83	0.56	252
241.33	0.50	280
241.81	0.51	277
243.09	2.08	60.5

* Interpretation of superscripts: cf. Table III.

TABLE V. COMPARISON OF DIRECTLY-MEASURED ENTHALPY INCREMENTS WITH INTEGRAL UNDER THE SMOOTHED C_p CURVE (Units: cal, gram-mole solution, °K)*

T_i	T_f	ΔH	$\Delta H_{Calc.}$
		$N_{CCl_4} = 0.334$	
Series VI, Run H[b]			
145.89	180.83	1064.47	1048.42
Series VII, Run I			
180.84	202.30	890.23	889.19
Series VII, Run J			
202.31	230.37	808.37	807.70
		$N_{CCl_4} = 0.501$	
Series XV, Run N			
14.72	24.47	43.22	42.97
Series XVI, Run O			
69.19	131.77	1068.42	1068.12
Series XVII, Run Q			
149.68	181.97	929.34	931.13
Series XVII, Run S			
200.01	208.31	274.05	275.50

$N_{CCl_4} = 0.666$

Series V, Run F[b,c]			
148.31	188.11	1096.00	1093.39
Series VI, Run J[c]			
205.31	223.42	528.02	528.65

$N_{CCl_4} = 0.826$

Series V, Run G[b]			
145.38	167.60	501.86	500.35
Series V, Run H[b]			
181.51	190.22	257.38	256.52
Series V, Run K[b]			
223.48	234.17	315.42	314.34

---

* Interpretation of superscripts: cf. Table III.

The curve for the N_{CCl_4} = 0.334 mixture shows two distinct heat capacity anomalies in addition to fusion which occurs at 241 ± 1°K. The first anomaly, Transition I, takes place over the temperature range from about 138 to 148°K with a peak at 142.5°K. Transition I is similar in shape to the "rotational" transition of tetramethylmethane at 140.02°K. The second anomaly, Transition II, takes place over a rather wide temperature range. It starts soon after the completion of Transition I, rises with increasing slope to a peak at 191.6°K, and drops abruptly after the peak. The transition is definitely "λ-shaped." It spans a 50° temperature range at its base and has a peak height of about 30 calories above its base. There is some evidence for anomalous behavior in the form of a small shoulder in the heat capacity curve between 155 and 175°K. Moreover, immediately after the completion of Transition II (i.e., 200 to 210°K) a small anomaly in the heat capacity curve appears. Aside from these anomalies in the transition region the heat capacity versus temperature curve for the N_{CCl_4} = 0.334 mixture shows the characteristic temperature dependent behavior of an organic compound both in the low temperature and the liquid regions (cf. Figure II).

The heat capacity versus temperature curve for the N_{CCl_4} = 0.501 mixture (Figure III) shows an additional transition, Transition III, besides the two transitions shown by the N_{CCl_4} = 0.334 mixture. The first two transitions (i.e., with peak temperatures of 142.5 and 191.6°K,

Figure II. Heat Capacity of the Sample with Mole Fraction of CCl_4 = 0.334 in the System Tetramethylmethane-Tetrachloromethane.

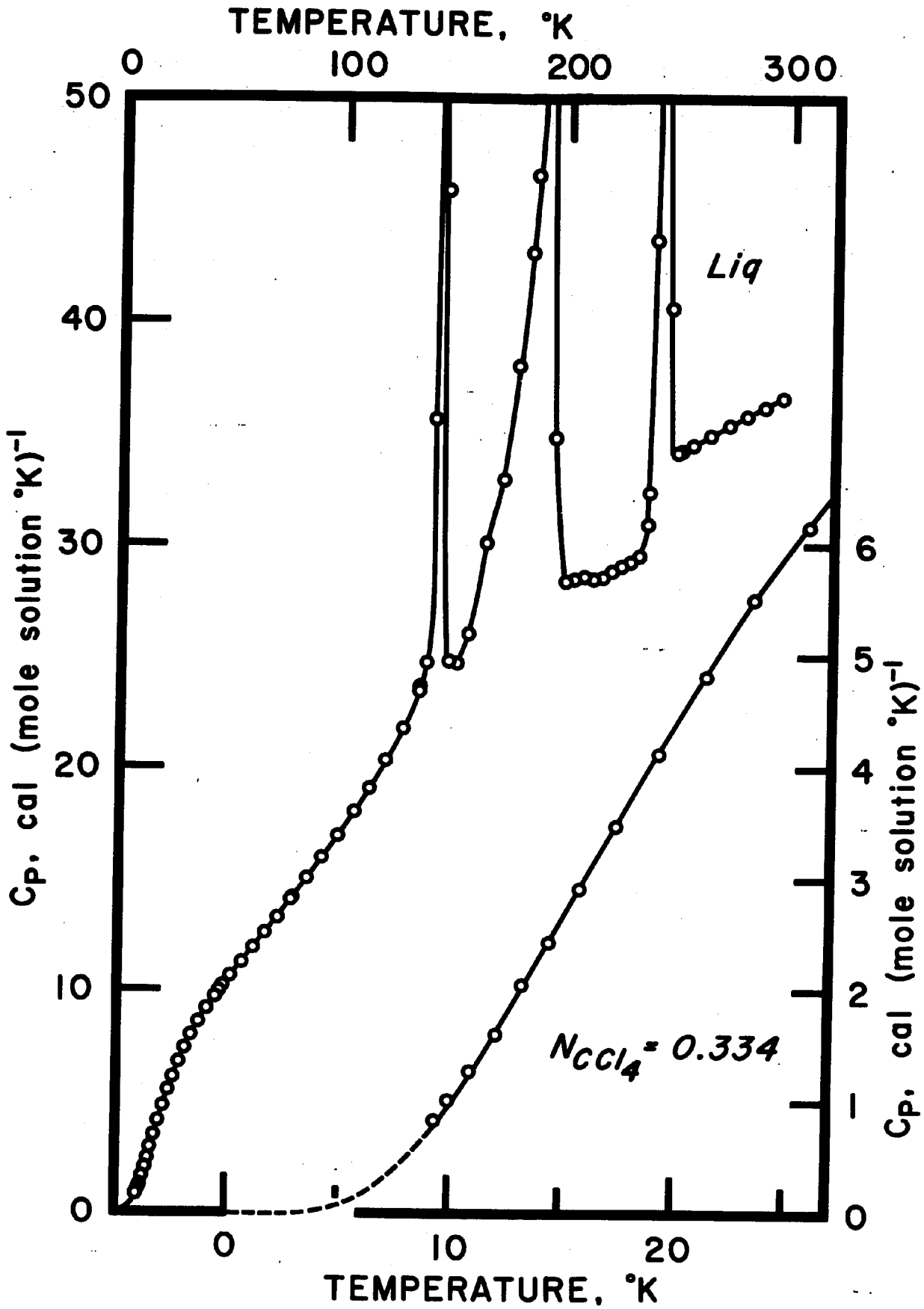

TEMPERATURE, °K
0
100
200
300
50
40
30
20
10
0
Liq
N_{CCl_4} = 0.334
C_p, cal (mole solution °K)$^{-1}$
C_p, cal (mole solution °K)$^{-1}$
6
5
4
3
2
1
0
0
10
20
TEMPERATURE, °K

Figure II

Figure III. Heat Capacity of the Sample with Mole Fraction of CCl_4 = 0.501 in the System Tetramethylmethane-Tetrachloromethane.

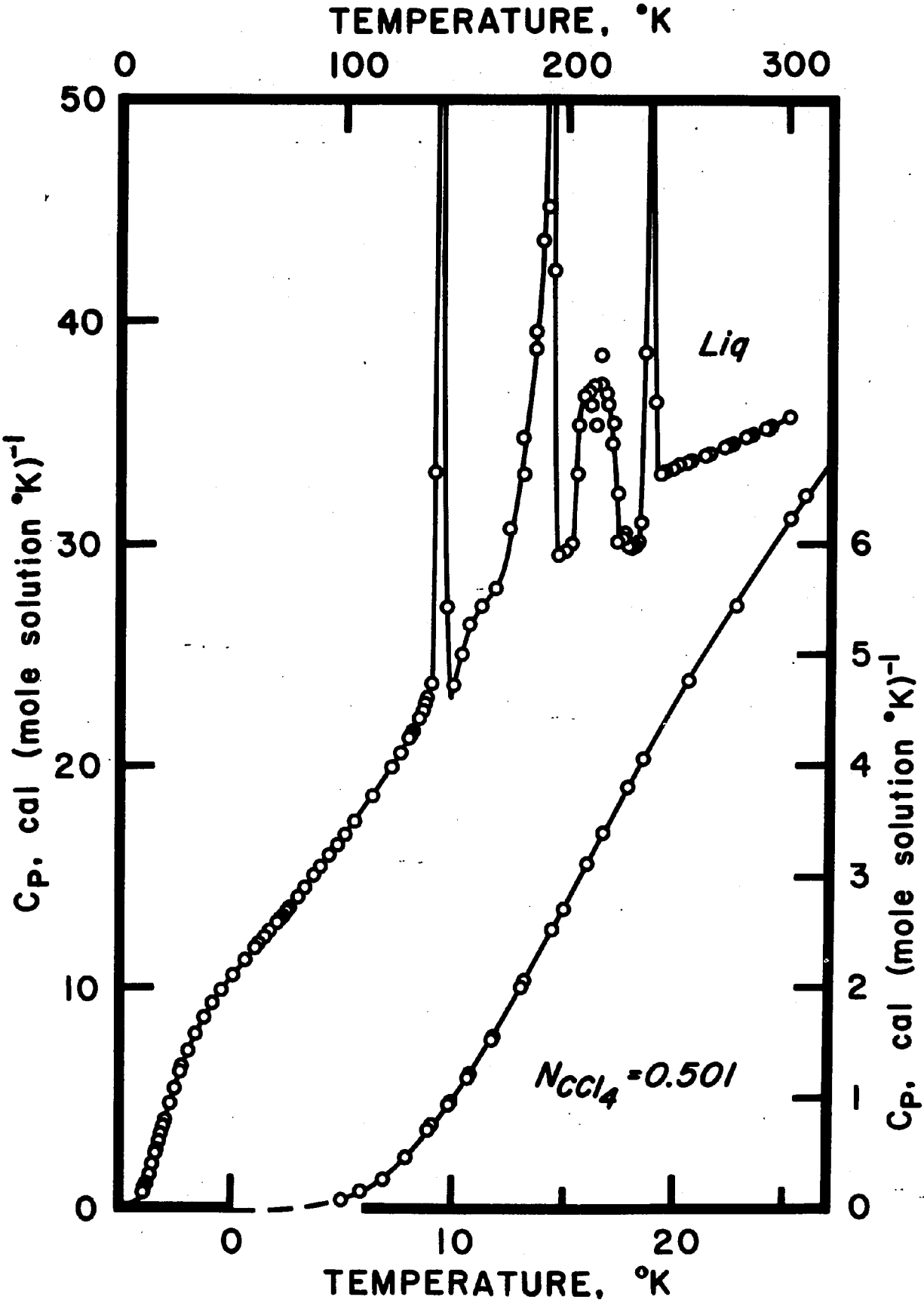

TEMPERATURE, °K
0
100
200
300
50
40
30
20
10
0
Liq
N_{CCl_4} =0.501
C_p, cal (mole solution °K)$^{-1}$
C_p, cal (mole solution °K)$^{-1}$
6
5
4
3
2
1
0
0
10
20
TEMPERATURE, °K

Figure III

respectively) of this composition of mixture are similar in behavior to Transitions I and II mentioned before. The shoulder in the heat capacity curve between the two transitions is more conspicuous in the N_{CCl_4} = 0.501 mixture than in the N_{CCl_4} = 0.334 mixture, and it spans from about 150 to 170°K. The heat capacity anomaly for Transition III of this composition is broad and "hump-like." It has a width at its base of about 20°K, and a height of only 17 calories above its base. Before and after Transition III the heat capacity is fairly constant (near 30 calories) over a short range about 8° on both sides. The phase between Transitions II and III of this composition is easily undercooled to below the peak temperature of Transition II (see dotted line in Figure VI). In Figure III only the data points of Series VI through Series XVIII and excluding Series XII are shown. Fusion for the N_{CCl_4} = 0.501 mixture takes place over a temperature range of about 2° with the peak temperature at about 237°K.

Figure IV depicts the heat capacity versus temperature curve for the N_{CCl_4} = 0.666 mixture. Examination of the transition region on the main scale of the plot reveals almost the same heat capacity behavior as that for the N_{CCl_4} = 0.334 mixture, i.e., two distinct transitions followed by fusion and a shoulder in the heat capacity curve between 155 and 175°K. However, on careful examination of the second transition, it is found that this transition actually consists of two overlapping transitions with

Figure IV. Heat Capacity of the Sample with Mole Fraction of CCl_4 = 0.666 in the System Tetramethylmethane-Tetrachloromethane.

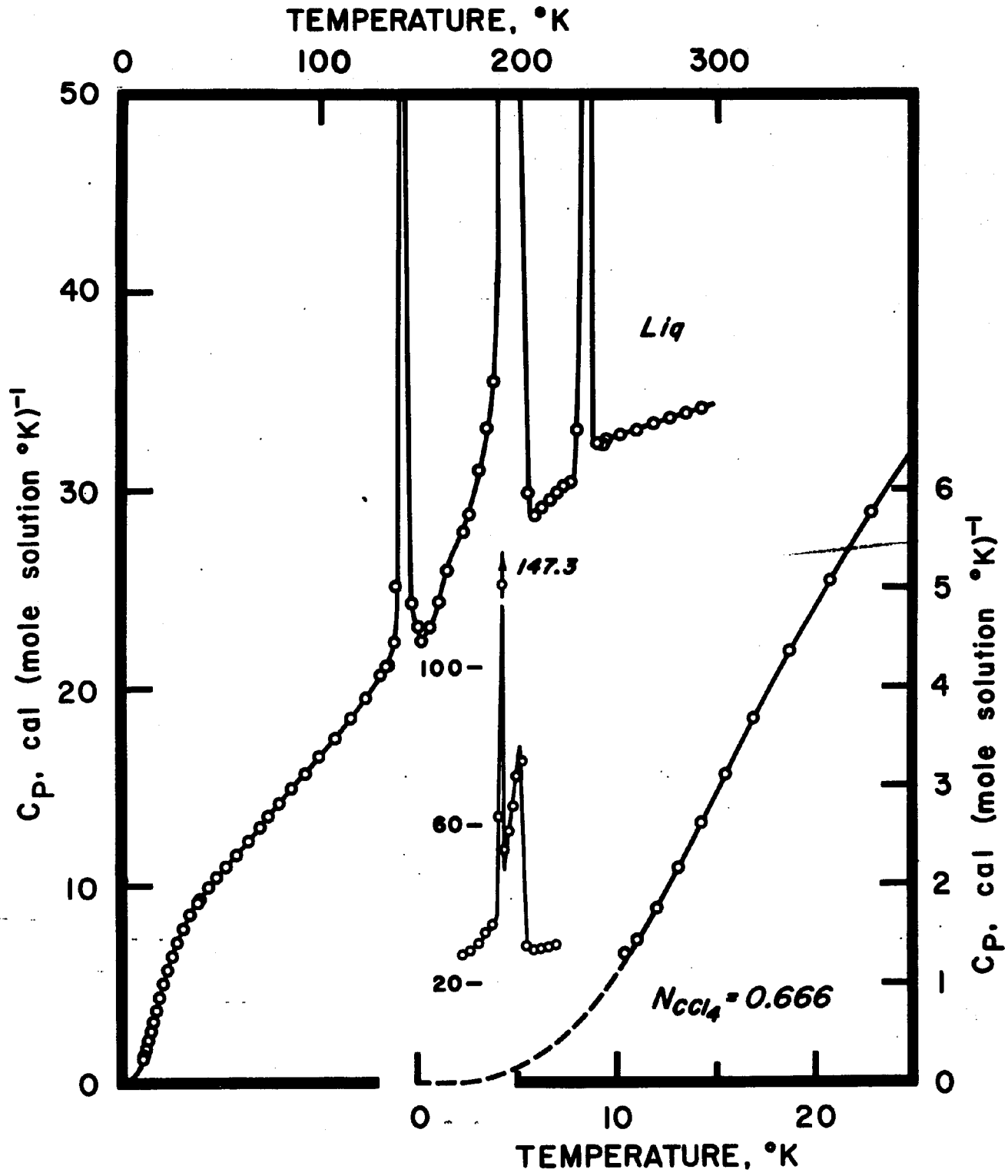

TEMPERATURE, °K
0
100
200
300
50
40
30
20
10
0
Liq
147.3
100
60
20
C_p, cal (mole solution °K)$^{-1}$
N_{CCl_4} = 0.666
6
5
4
3
2
1
0
0
10
20
TEMPERATURE, °K

Figure IV

distinct peaks. (See inset of Figure IV, plotted on the same temperature scale as the main curve but with compressed scale for the heat capacity.) The first part of the split transition, Transition II, has a peak temperature of 191.6°K (i.e., the same temperature as Transition II in the N_{CCl_4} = 0.334 and 0.501 mixtures). Transition II of this composition takes place over a considerably narrower temperature range (about 5°K) than in the other two compositions. The second part, Transition III, is different in behavior from Transition III of the N_{CCl_4} = 0.501 mixture. This Transition III is "λ-shaped." The combined width at the base of Transitions II and III is about 55°K, and the peak height of Transition III is about 53 calories above the base. Transition I of this composition is similar to the corresponding transition of the other compositions and has the same peak temperature of 142.5°K. The range between the last transition and fusion (i.e., the plastically crystalline region) is about 22°K. Except for some pre-melting, fusion for this composition takes place over a narrow (0.3°K) temperature range around 235.5°K.

The heat capacity versus temperature curve of the fourth composition, N_{CCl_4} = 0.826, is shown in Figure V. The transition region of this composition is similar to that of the N_{CCl_4} = 0.666 mixture in that it also contains two overlapping transitions (i.e., Transitions II and III). The region where the shoulder in the heat capacity curve appeared was studied with a series of small ΔT runs. It seems

Figure V. Heat Capacity of the Sample with Mole Fraction of CCl_4 = 0.826 in the System Tetramethylmethane-Tetrachloromethane.

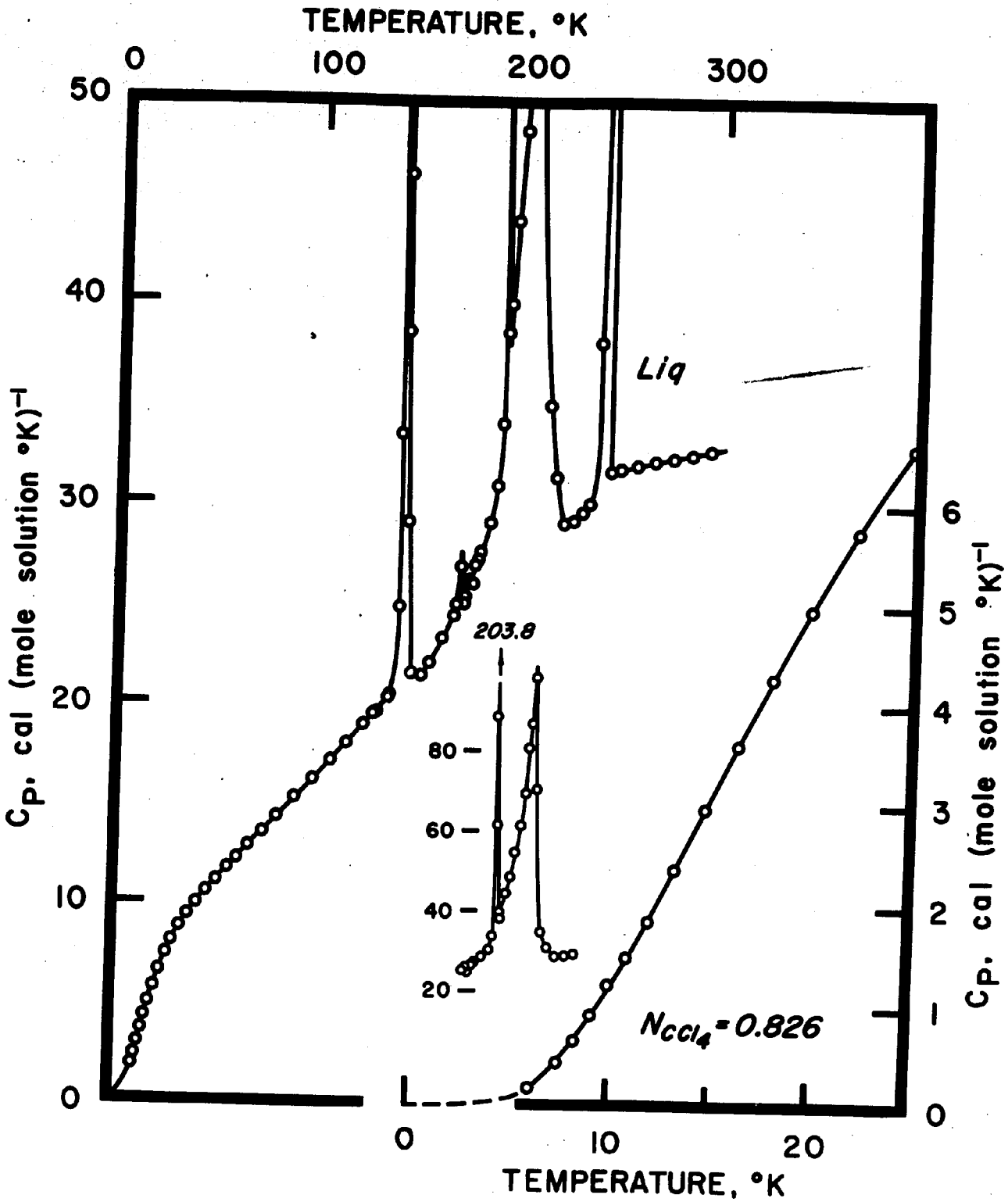

TEMPERATURE, °K
0
100
200
300
50
40
30
20
10
0
C_p, cal (mole solution °K)$^{-1}$
Liq
203.8
80
60
40
20
N_{CCl_4} = 0.826
6
5
4
3
2
1
0
0
10
20
TEMPERATURE, °K

Figure V

possible that there is a small anomaly involving around 19 calories with a peak height of a few calories at 172°K. Transitions I and II have the same peak temperatures of 142.5 and 191.6°K as the other transitions designated I and II. Transition III of this composition of mixture is similar to the one of the $N_{CCl_4} = 0.666$ mixture. It is "λ-shaped", has a combined width with Transition II at the base of about 50°K and a peak height of around 70 calories above the base. The plastically crystalline range is about 18°K and fusion takes place over a 2° range around the peak at 241.6°K.

Thermodynamic Functions

In Table VI the molal values of the heat capacities, the entropy and enthalpy increments, and the free energy functions are tabulated at selected temperatures for each of the four compositions of mixtures of the system tetramethylmethane-tetrachloromethane studied. The values reported beyond the transition region (i.e., from 5 to 135°K and from 245 to 300°K) were obtained by integration of the curve generated by an IBM 709 computer fitting a least-squares polynomial through all the data points of the region. For the evaluation of these functions, the heat capacity of each mixture was extrapolated to below 5°K by means of the Debye T^3 limiting law.

Contributions from nuclear spin, isotope mixing, and the zero point entropy and enthalpy of mixing were not included in the values reported for these functions.

TABLE VI. THERMODYNAMIC FUNCTIONS OF MIXTURES OF THE SYSTEM TETRAMETHYLMETHANE-TETRACHLOROMETHANE
(Units: cal, gram-mole solution, °K)

T	C_p	$S^\circ - S^\circ_0$	$H^\circ - H^\circ_0$	$-[(F^\circ - H^\circ_0)/T - S^\circ_0]$
		$N_{CCl_4} = 0.334$		
5	(0.072)	(0.025)	(0.10)	(0.006)
10	0.987	0.293	2.29	0.065
15	2.634	0.992	11.18	0.247
20	4.392	1.993	28.79	0.554
25	5.940	3.145	54.74	0.955
30	7.210	4.344	87.72	1.420
35	8.251	5.536	126.46	1.923
40	9.120	6.696	169.95	2.448
45	9.870	7.815	217.46	2.982
50	10.55	8.890	268.53	3.520
60	11.80	10.924	380.28	4.586
70	13.05	12.836	504.5	5.629
80	14.37	14.663	641.5	6.645
90	15.77	16.436	792.1	7.635
100	17.22	18.172	957.0	8.602
110	18.72	19.883	1136.6	9.550
120	20.39	21.582	1332.0	10.482
130	22.46	23.291	1545.7	11.401
135	23.80	24.163	1661.3	11.858
150	24.42	29.594	2434.9	13.361
180	39.13	35.108	3355.8	16.465
200	28.36	39.636	4213.5	18.568
230	29.43	43.653	5076.4	21.582
245	34.00	47.673	6041.3	23.015
250	34.26	48.363	6211.9	23.515
260	34.78	49.717	6557.2	24.497
270	35.31	51.039	6907.6	25.455
280	35.83	52.333	7263.3	26.392
290	36.35	53.599	7624.2	27.309
300	36.88	54.840	7990.4	28.206

TABLE VI (Cont.)

273.15	35.47	51.45	7019	25.75
298.15	36.78	54.61	7922	28.04

$N_{CCl_4} = 0.501$

5	(0.084)	(0.029)	(0.11)	(0.007)
10	1.008	0.306	2.37	0.069
15	2.749	1.029	11.58	0.257
20	4.593	2.076	30.00	0.576
25	6.164	3.276	57.03	0.995
30	7.431	4.516	91.13	1.478
35	8.462	5.742	130.95	2.000
40	9.301	6.928	175.43	2.542
45	10.01	8.065	223.73	3.093
50	10.66	9.155	275.46	3.645
60	11.85	11.205	388.09	4.737
70	13.03	13.120	512.5	5.799
80	14.28	14.941	649.0	6.829
90	15.58	16.697	798.2	7.828
100	16.90	18.407	960.6	8.801
110	18.26	20.081	1136.4	9.750
120	19.72	21.731	1326.1	10.680
130	21.48	23.376	1531.7	11.593
135	22.58	24.207	1641.8	12.045
150	23.96	28.679	2280.0	13.479
180	34.99	33.840	3131.6	16.442
200	29.67	38.924	4106.1	18.393
230	29.75	43.641	5118.8	21.385
245	33.18	47.470	6027.3	22.868
250	33.39	48.142	6193.7	23.367
260	33.79	49.460	6529.6	24.346
270	34.19	50.742	6869.5	25.300
280	34.60	51.993	7213.4	26.231
290	35.05	53.215	7561.7	27.140
300	35.56	54.412	7914.7	28.029
273.15	34.32	51.14	6977	25.60
298.15	35.46	54.19	7849	27.87

TABLE VI (Cont.)

$N_{CCl_4} = 0.666$

5	(0.108)	(0.037)	(0.14)	(0.009)
10	1.103	0.348	2.66	0.082
15	2.951	1.131	12.62	0.289
20	4.850	2.245	32.22	0.634
25	6.427	3.504	60.57	1.081
30	7.673	4.790	95.94	1.592
35	8.664	6.050	136.88	2.139
40	9.484	7.262	182.31	2.704
45	10.14	8.418	231.41	3.276
50	10.74	9.518	283.62	3.845
60	11.90	11.578	396.80	4.965
70	13.08	13.501	521.7	6.048
80	14.26	15.325	658.4	7.095
90	15.42	17.072	806.9	8.107
100	16.58	18.756	966.8	9.088
110	17.77	20.392	1138.5	10.042
120	19.05	21.992	1322.5	10.971
130	20.49	23.572	1520.0	11.880
135	21.34	24.361	1624.6	12.327
150	22.43	28.068	2152.6	13.717
185	34.08	33.696	3099.9	16.940
193.5	51.92	36.290	3592.2	17.726
205	29.49	39.633	4255.9	18.873
225	30.06	42.354	4840.2	20.842
230	30.55	43.020	4991.7	21.317
240	32.29	46.709	5859.6	22.294
250	32.57	48.033	6183.9	23.297
260	32.86	49.316	6511.1	24.273
270	33.15	50.562	6841.1	25.224
280	33.43	51.772	7174.0	26.151
290	33.72	52.950	7509.7	27.055
300	34.01	54.098	7848.4	27.937
273.15	33.24	50.95	6946	25.52
298.15	33.95	53.89	7786	27.78

TABLE VI (Cont.)

$N_{CCl_4} = 0.826$

5	(0.066)	(0.023)	(0.08)	(0.006)
10	1.166	0.330	2.61	0.069
15	3.120	1.160	13.17	0.281
20	5.075	2.332	33.78	0.643
25	6.662	3.642	63.29	1.111
30	7.883	4.969	99.79	1.643
35	8.847	6.260	141.69	2.211
40	9.626	7.494	187.94	2.795
45	10.28	8.666	237.74	3.383
50	10.86	9.779	290.60	3.967
60	11.93	11.854	404.59	5.111
70	13.01	13.774	529.3	6.213
80	14.11	15.583	664.9	7.273
90	15.21	17.309	811.5	8.292
100	16.28	18.967	969.0	9.278
110	17.33	20.568	1137.0	10.232
120	18.40	22.122	1315.6	11.158
130	19.58	23.640	1505.4	12.060
135	20.25	24.392	1605.0	12.503
150	21.27	27.268	2014.7	13.837
167.5	24.35	29.762	2411.5	15.365
175	25.71	30.865	2600.8	16.003
190	31.45	33.181	3025.1	17.259
193	38.72	34.138	3209.2	17.510
225	28.94	41.875	4814.3	20.478
230	29.46	42.518	4960.6	20.950
245	31.64	46.818	5991.5	22.362
250	31.75	47.458	6150.0	22.858
260	31.97	48.708	6468.6	23.828
270	32.19	49.918	6789.4	24.772
280	32.41	51.093	7112.5	25.691
290	32.64	52.234	7437.7	26.587
300	32.86	53.344	7765.2	27.460
273.15	32.26	50.29	6891	25.06
298.15	32.82	53.14	7704	27.30

The values of the functions reported for the transition region were obtained as follows: the heat capacity values were read off a smooth curve from a large scale heat capacity versus temperature plot of the transition region; enthalpy increments were obtained by using the weighted average values of the enthalpy increments reported in Table IV; entropy increments were obtained by integration of the values of C_p/T, or when a continuous series of small ΔT runs was available by summation of Q/T of the runs, or the average of the two values was used. The particular selected temperatures were chosen to facilitate calculation of entropy and enthalpy increments across each transition. The values at 230°K were reported for use in the determination of the enthalpy of mixing in the plastically crystalline region discussed in another section.

Determination of Liquidus, Solidus, and Transition Temperatures

The solidus and liquidus temperatures can be obtained from thermal measurements in several ways.[2,17] When data for a continuous series of energy inputs (i.e., from some temperature in the solid phase to some temperature in the liquid range) are available, one of the methods for obtaining the liquidus and solidus temperatures is to plot the observed equilibrium temperature after each addition of energy versus total relative enthalpy over the entire range.[2] Then, on this plot the solidus temperature is the point of

intersection of the curve in the two-phase region extrapolated to that extended from the solid phase; and the liquidus temperature is the point of intersection of the curve in the two-phase region and that for the liquid. The amount of curvature in the part of the curve connecting the curves for the solid phase and the two-phase region is an indication of the amount of pre-melting in the sample.

Another method is to plot the heat capacity of the sample versus temperature.[2] In this case the break preceding the heat capacity curve for the liquid and the break following the heat capacity curve for the solid are taken to represent the liquidus and solidus temperatures, respectively.

For this study, the liquidus and solidus temperatures are determined by the first method described. A list of equilibrium temperatures and relative enthalpies and the liquidus and solidus temperatures for each of the four compositions of mixtures studied are tabulated in Table VII, and the plot of equilibrium temperature versus relative enthalpy is shown in Figure VI.

The transition temperature reported for each of the transitions is determined as follows: when the transformation is represented by high heat capacities over a narrow temperature range, i.e., as in the case of Transitions I and II, the transition temperature for that particular tranformation is determined by extrapolating the heat capacities in the peak region to obtain the peak temperature. In the

TABLE VII. EQUILIBRIUM TEMPERATURES AND RELATIVE ENTHALPIES FOR THE DETERMINATION OF SOLIDUS AND LIQUIDUS TEMPERATURES
(Units: cal, gram-mole solution, °K)

N_{CCl_4} =	0.334		0.501		0.666		0.826	
	Relative Enthalpy	Eq. Temp.	Relative Enthalpy	Eq. Temp.	Relative Enthalpy	Eq. Temp.	Relative Enthalpy	Eq. Temp.
	0	234.32	0	230.59	0	224.48	0	229.43
	122.17	238.08	88.01	233.54	103.12	227.87	108.12	233.08
	260.03	240.51	183.91	235.73	211.91	230.73	216.63	236.67
	413.00	241.63	296.11	236.42	326.12	232.90	331.25	239.66
	570.63	242.33	413.47	236.86	443.93	234.87	467.16	240.59
	729.72	242.91	528.50	237.32	577.48	235.35	609.23	241.12
	936.25	247.95	640.13	238.09	715.02	235.43	751.52	241.58
	1134.2	253.72	734.83	240.35	851.03	235.64	893.65	242.06
			825.63	243.09	966.29	237.82	1019.48	244.13
			1093.50	251.14	1070.42	241.05	1130.35	247.63
					1174.44	244.26	1241.21	251.12
Solidus Temp.	240.7		236.0		235.3		240.1	
Liquidus Temp.	243.2		237.7		235.6		242.3	

Figure VI. Equilibrium Temperature versus Relative Enthalpy Curves for the Determination of Liquidus and Solidus Temperatures of Mixtures of the System Tetramethylmethane-Tetrachloromethane.

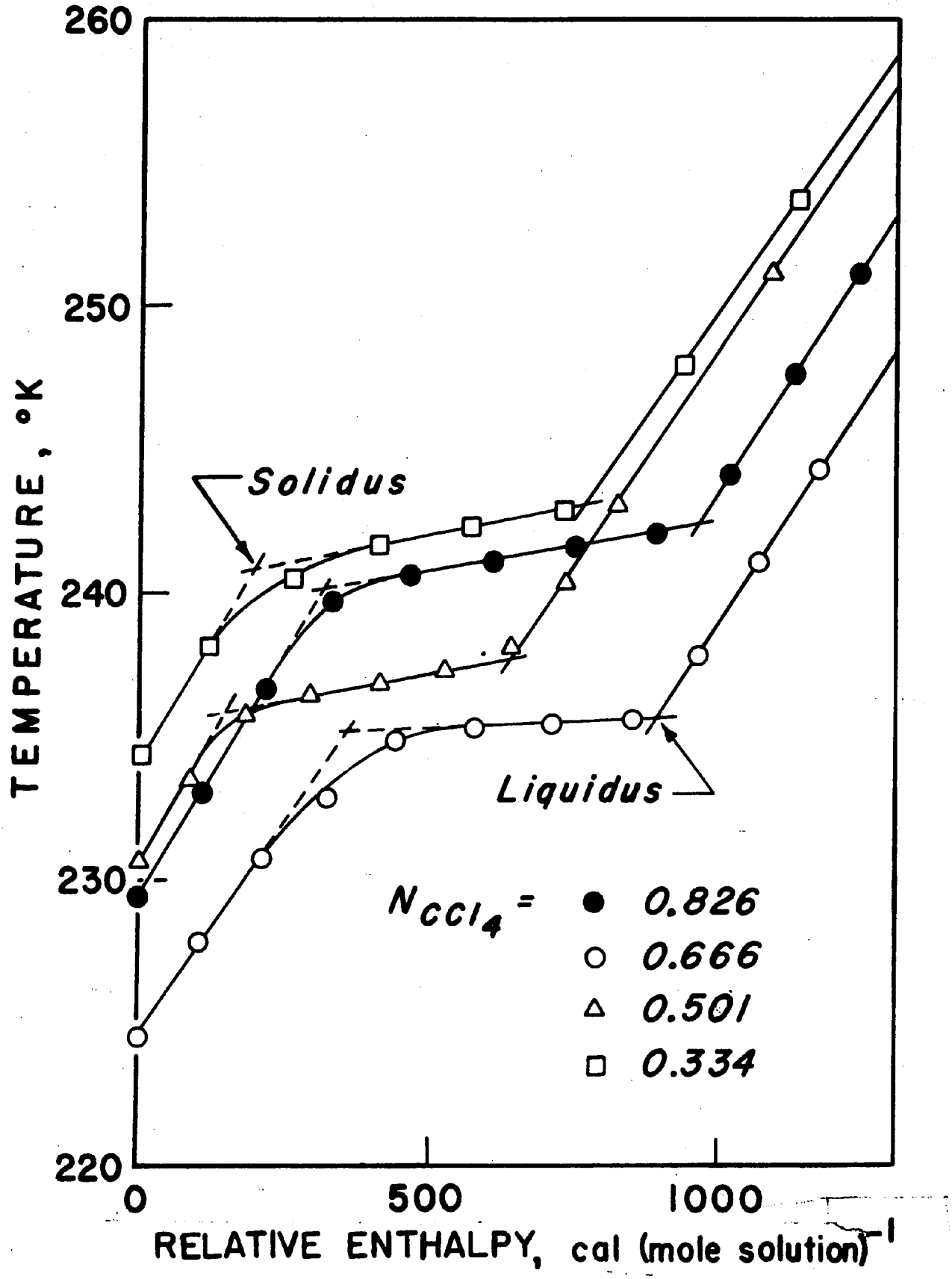

260
250
240
230
220
TEMPERATURE, °K
Solidus
Liquidus
N_{CCl_4} =
0.826
0.666
0.501
0.334
0
500
1000
RELATIVE ENTHALPY, cal (mole solution)$^{-1}$

Figure VI

case of a broad or "λ-shaped" transition (i.e., Transition III), the temperature of completion of the transition is reported together with the peak temperature. The temperature of completion is determined in the same manner as that used for the liquidus temperatures.

Determination of Enthalpy and Entropy of Transition and of Fusion

Figure VII is an enlarged plot of the transition region heat capacity versus temperature curves of the system tetramethlymethane-tetrachloromethane. Curves for all four compositions of mixtures studied are shown on the same plot in order to show the similarities and differences between the heat capacity anomalies of the different compositions. The dashed curves are drawn to represent the estimated heat capacity contribution due to the lattice heat capacity of each mixture. Dashed curves for the tetramethylmethane-rich mixtures are drawn so that they resemble the heat capacity curve for pure tetramethylmethane; and for the tetrachloromethane-rich mixtures they are drawn to resemble that of pure tetrachloromethane in the respective regions.

The enthalpy of transition is determined by subtracting the estimated lattice contribution to the enthalpy increment (i.e., calculated by integration of the dashed curve) over a given temperature interval from the experimentally determined enthalpy increment over the same temperature interval. The entropy of transition is determined

Figure VII. Heat Capacity of the Transition Regions of Mixtures of the System Tetramethylmethane-Tetrachloromethane.

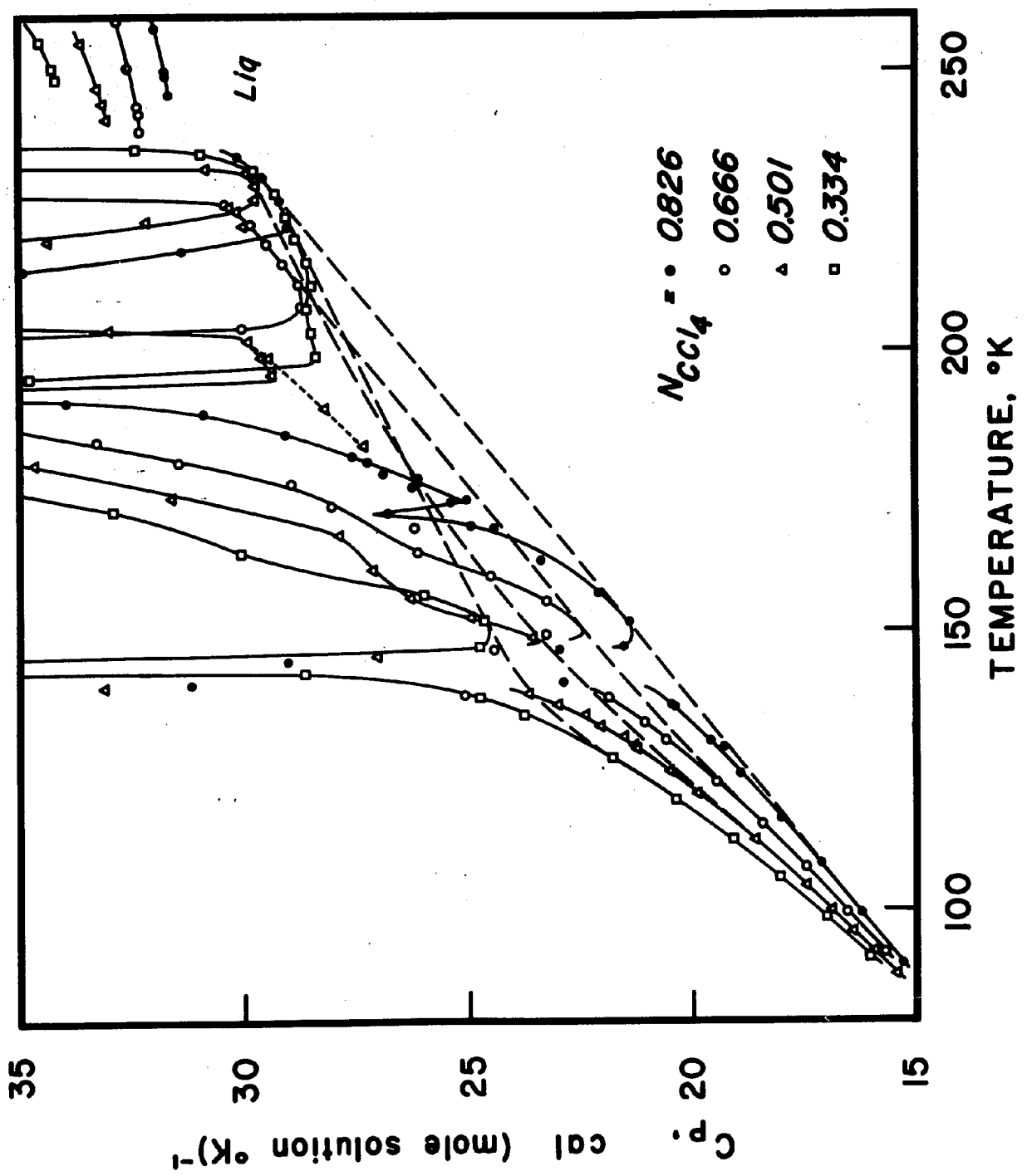

Liq
N_{CCl_4} = • 0.826
○ 0.666
△ 0.501
□ 0.334
TEMPERATURE, °K
100
150
200
250
C_p, cal (mole solution °K)$^{-1}$
15
20
25
30
35

Figure VII

in the same manner by the difference of the entropy increments.

The enthalpy increment of Transition I is considered to include the energy involved in the pre-transition region, in some cases, extending as far down as 95°K. In all the mixtures Transition I is complete at 150°K. All the excess enthalpy from above 150°K to the completion of Transition II is included in the enthalpy increment of Transition II. The remaining excess enthalpy before fusion is considered as belonging to the enthalpy increment of Transition III. In the case of overlapping transitions the transitions are divided at the point of intersection of the two curves extending down from the two peaks.

The enthalpy of fusion of the mixture is determined by subtracting from the enthalpy increment through fusion over a given temperature interval (1) the enthalpy increment of the solid phase extended to the peak temperature of fusion and (2) that of the liquid phase extended to the same temperature (i.e., by treating the mixture as a single component system). An alternative calculation of the enthalpy of fusion--by subtracting from the enthalpy increment through fusion (1) the enthalpy increment of the solid phase extended to the solidus temperature, (2) the enthalpy increment of the liquid phase extended to the liquidus temperature, and (3) the enthalpy increment of the two phase region (determined by assuming the enthalpy increment between the solidus and liquidus temperatures is equal to

the temperature increment multiplied by the average heat capacity value at the solidus and liquidus temperatures)--gave an enthalpy of fusion only a few calories lower than that calculated by the first method. The enthalpies of fusion reported in Table VIII were determined by the first method.

The transition region heat capacity versus temperature curves for the four compositions studied are shown in Figure VI together with their respective estimated lattice heat capacity curves.

Table VIII is a summary of the transition regions of the four mixtures and of the two pure components, tetramethylmethane[18] and tetrachloromethane.[19] It will be noted that the enthalpy increment of Transition I based on one mole of tetramethylmethane in the mixture, and the enthalpy of fusion based on the ideal additive enthalpies of fusion of the components are also reported in Table VIII. Also, it is interesting to note (Table VIII) that the sum of the enthalpy increments of transition including that of fusion is almost the same for the four mixtures and is close to the values for the pure components.

Calorimetric Determination of the Purity of Tetrachloromethane

The purity of the tetrachloromethane used in this study was determined calorimetrically. Details of the calorimetric method have been described by several authors.[20,21,22]

TABLE VIII. SUMMARY OF THE TRANSITION REGIONS OF MIXTURES OF THE SYSTEM TETRAMETHYLMETHANE-TETRACHLOROMETHANE

Composition Code	Pure CMe_4	2 - 1	1 - 1	1 - 2	1 - 5	Pure CCl_4
Mole Fraction CCl_4	0.000	0.334	0.501	0.666	0.826	1.000
Mole Fraction CMe_4	1.000	0.666	0.499	0.334	0.174	0.000
			Transition I			
Transition Temp. °K	140.0	142.5	142.5	142.5	142.5	-----
ΔH_t (mole soln)$^{-1}$	615.9	416.9	303.6	205.9	105.9	-----
ΔH_t (mole CMe_4)$^{-1}$	615.9	626.0	608.4	616.5	608.6	-----
ΔS_t (mole soln)$^{-1}$	4.39	2.92	2.13	1.45	0.74	-----
ΔS_t (mole CMe_4)$^{-1}$	4.39	4.38	4.27	4.34	4.25	-----
			Anomaly Between Transitions I and II			
Transition Temp. °K	-----	-----	-----	-----	171	-----
ΔH_t (mole soln)$^{-1}$	-----	-----	-----	-----	18.9	-----
ΔS_t (mole soln)$^{-1}$	-----	-----	-----	-----	0.10	-----
			Transition II			
Transition Temp. °K	-----	191.6	191.6	191.6	191.6	-----
ΔH_tcal (mole soln)$^{-1}$	-----	481.3	531.3	369.4	161.9	-----

TABLE VIII (Cont.)

ΔS_t cal (mole soln, °K)$^{-1}$	-----	2.59	2.82	1.98	0.85	-----
Transition III						
Transition Temp. °K						
Peak	-----	-----	215.0	200.5	210.0	225.35
Completion	-----	-----	219.0	202.0	214.0	-----
ΔH_t cal (mole soln)$^{-1}$	-----	-----	148.8	352.9	739.2	1095
ΔS_t cal (mole soln, °K)$^{-1}$	-----	-----	0.70	1.77	3.59	4.86
Fusion						
Liquidus Temp. °K	256.53	243.25	237.69	235.62	242.31	250.3
Solidus Temp. °K	256.53	240.69	235.95	235.34	240.09	250.3
ΔH_m cal (mole soln)$^{-1}$	778.2	505.1	433.7	553.4	571.6	601
cal (mole ideal soln)$^{-1}$	778.2	719*	689*	659*	631*	601
ΔS_m cal (mole soln, °K)$^{-1}$	3.03	2.08	1.83	2.36	2.37	2.40
Total Effect						
ΔS (trans. + Fusion)	7.42	7.59	7.48	7.57	7.66	7.26

*Note: Based on the ideal additive enthalpy of fusion of the components.

Briefly, the method involves measurements of liquid-solid equilibrium temperatures at known liquid to solid ratios that are evaluated from the total heat input, enthalpy of fusion, and heat capacity. Treating the data as conforming to dilute solution laws, the freezing point lowering may be taken to be proportional to the mole fraction of impurity in the melt and thus proportional to the reciprocal of the fraction of the sample melted. The simplified equation for dilute, ideal solutions:

$$N_2 = \frac{\Delta Hm}{R\ T_o^2} \quad (T_o - T_1)$$

where N_2 = mole fraction of total impurity,

ΔHm = enthalpy of fusion at T_o,

T_o = melting point of pure substance, and

T_1 = melting point of sample

may be used to evaluate the total liquid soluble solid insoluble impurity.

In calorimetric determination of the purity, the energy required for fusion is generally supplied in five or six consecutive steps. The equilibrium temperatures are determined at the beginning and end of each energy input. From a plot of the equilibrium temperature versus the reciprocal of the fraction melted (F), the melting point of the sample (T_1) is determined as the temperature at which F = 1, and the melting point of the pure substance (T_o) is the temperature obtained by extrapolating to 1/F = 0.

The tetrachloromethane sample used in the purity

determination had a mass of 128.146 grams in vacuo. It was loaded in the same manner and run in the same calorimeter and cryostat (i.e., W-23 and Mark II) as described before for the mixtures. The adjustments for helium, grease, 50-50 lead-tin solder, and Ceroseal solder were 0.000206 grams, 0.0054 grams, 0.0875 grams, and 0.0115 grams, respectively (cf. Table I). Curvature corrections were not applied to the data. Additional corrections for "oscillations" were applied for some of the runs as indicated by the superscript "c".

The experimentally determined molal heat capacities in the fusion and liquid regions for tetrachloromethane are tabulated in chronological order in Table IX. Table X is a summary of the enthalpy of fusion determinations. The observed fusion region heat capacities, liquid-solid equilibrium temperatures, and the corresponding values of the reciprocal fraction melted are summarized in Table XI. The plot of reciprocal fraction melted versus temperature determined by Series I, Runs A is depicted in Figure VIII.

The melting points of the sample (T_1) and of the pure substance (T_o) are found by extrapolation to be 250.479 and 250.480°K respectively. Using the average value of ΔHm = 604.34 calories per mole, the difference in temperature ($T_o - T_1$) = 0.001°K, and assuming ideality of the solution, the calculated mole-fraction of impurity (i.e., liquid soluble solid insoluble) is 0.000005, or the purity of the tetrachloromethane used in this investigation is 99.999 mole

TABLE IX. HEAT CAPACITY OF TETRACHLOROMETHANE IN THE FUSION AND LIQUID REGIONS*
(Units: cal, gram-mole, °K)

T	C_p	T	C_p	T	C_p
Series I		256.80	31.04	Series IV	
		264.03	31.13		
234.00	28.58	271.93	31.20	242.82	29.49
240.35	28.97	280.17	31.26		
244.92	29.57	288.57	31.38	ΔHm Run D^c	
		296.75	31.44		
Fusion Runs A				Series V	
		Series III			
255.14	31.08			240.73	29.16^c
		242.98	29.27		
Series II		246.72	29.56	ΔHm Run E^c	
ΔHm Run B		Fusion Runs C		256.98	31.15^c

* Note: Superscript "c" indicates that the energy input of the run has been corrected for "oscillations".

TABLE X. ENTHALPY OF FUSION DETERMINATIONS OF TETRACHLOROMETHANE*
(Units: cal, gram-mole, °K)

T_i	T_f	ΔH or $\Sigma\Delta H$	ΔHm
Series I, Runs A (7 runs)			
246.53	253.59	817.80	604.04
Series II, Run B			
245.93	253.52	833.67	604.57
Series IV, Run D^c			
245.69	254.13	859.53	604.21
Series V, Run E^c			
246.57	254.21	836.33	604.52
		Average	604.34

* Interpretation of superscript: cf. Table IX.

TABLE XI. FUSION REGION OF TETRACHLOROMETHANE*
(Units: cal, gram-mole, °K)

T	ΔT	C_p	ΔH_{excess}	1/F	T_f
Series I, Runs A (7 runs)					
248.13	3.21	29.71	0.21	3022	249.737
250.11	0.74	162	97.82	6.176	250.473
250.475	0.003	48753	224.48	2.691	250.476
250.477	0.002	61188	351.16	1.720	250.4781
250.478	0.0002	639101	477.93	1.264	250.4783
250.488	0.019	6794			250.496
252.05	3.10	31.04			253.59
				(1.000)	250.479
				(0.000)	250.480
Series III, Runs C (6 runs)					
248.36	1.63	29.64	0		249.17
249.66	0.97	29.76	0		250.14
250.305	0.321	70.43	12.98	46.55	250.466
250.473	0.014	38093 [c]	576.38	1.049	250.480
250.85	0.75	75.06[c]			251.23
252.74	3.02	31.17[c]			254.25

* Interpretation of superscript: cf. Table IX.

Figure VIII. Liquid-Solid Equilibrium Temperatures of Tetrachloromethane.

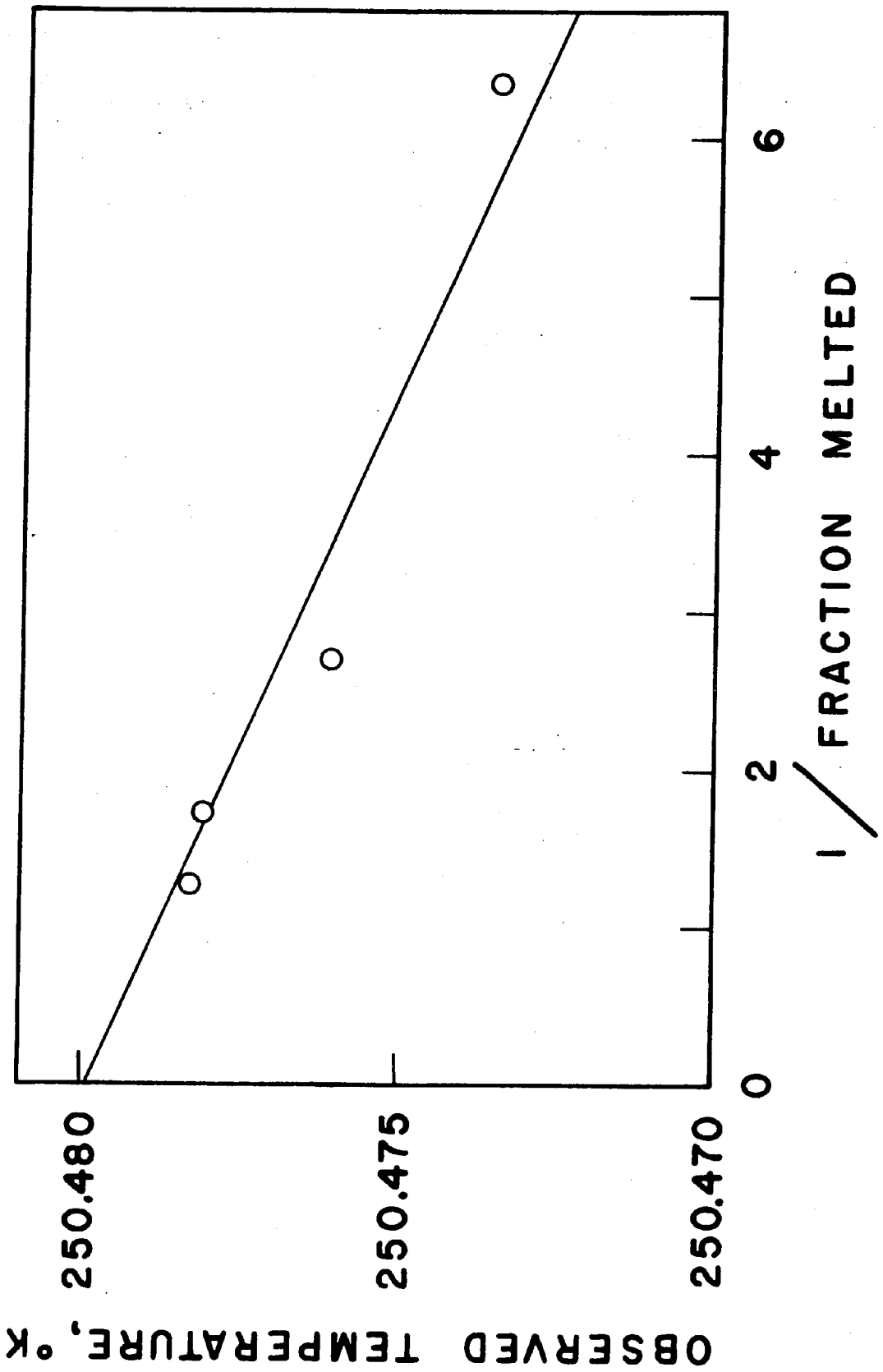

OBSERVED TEMPERATURE, °K
250.480
250.475
250.470
0
2
4
6
1/FRACTION MELTED

Figure VIII

percent. As a check on the method, the purity was also calculated by the heat content-temperature (HCT) method of J. H. Badley.[21] The same result was obtained. It is observed that the determined enthalpy of fusion and triple point temperature of this investigation differ somewhat from the values reported by Hicks, Hooley, and Stephenson (i.e., ΔH_m = 601 ± 2 calories per mole and T_o = 250.3 ± 0.1°K while their reported purity was 99.98 mole percent, ice point 273.19°K).[19] Their heat capacity values in the fusion region were about 0.5 to 0.1% lower in the solid phase and agreed within ± 0.2% in the liquid phase.

DISCUSSION

Enthalpy of Mixing and the System Tetramethylmethane-Tetrachloromethane

The thermodynamics of mixtures has been described in detail by several authors, e.g., Guggenheim,[23] Hildebrand and Scott,[24] and more recently by Prigogine[25] and Rowlinson.[26] The study of the excess functions has been shown to be a practicable means of obtaining information on the differences in the intermolecular forces between unlike species. Table A in the appendix, for example, is an illustration of how strongly the excess functions depend on the nature and strength of the intermolecular forces between the different components. Although many theories have been proposed and developed to describe the properties of liquids and liquid mixtures, the quantitative predictions of these theories often show poor agreement with the existing experimental data. In many instances this was due in part to the lack of adequate experimental results, or the lack of a suitable system for the purpose, or both. The excess thermodynamic properties of non-polar liquids have often been used to test the validity of statistical theories of solutions. Excess functions calculated by the cell model are compared with the experimental values for various non-polar systems in Table C in the appendix.

Methods of Determination

Although the methods of determining the various excess functions have been described by Rowlinson[27], the present endeavor is concerned primarily with the enthalpy of mixing or excess enthalpy; therefore, the methods of determining the enthalpy of mixing will be discussed briefly. The Gibbs-Helmholtz equation

$$H^E(x) = - T^2[\partial G^E(x)/\partial(1/T)]_P$$

gives the relationship between the enthalpy of mixing H^M (or H^E) and the excess free energy of mixing G^E at all compositions; but, in practice, this equation does not provide a satisfactory method of determining it,[28,29] for measurements of G^E are usually made over only a limited temperature range (i.e., about 15% of the absolute temperature). Moreover, the inherent error of the derived H^E is always an order of magnitude larger than the error in G^E (i.e., if G^E is known to 2% over a temperature range of 1.0 T to 1.1 T and if TS^E is about as large as G^E, then the probable errors in the derived values of H^E and TS^E, at 1.05 T, are 15% and 30%, respectively[30]).

The direct method using adiabatic or isothermal calorimetry is the method commonly used to obtain satisfactory H^E data. In this method the usual considerations of adiabatic calorimetry of exchange of heat with the surroundings, satisfactory stirring, rapid and sensitive measurement of temperature, plus the further difficulty of ensuring the absence

of any appreciable volume of vapor are encountered. In practice, H^E by the direct method can be measured to about 2% at room temperature and with less accuracy at higher temperatures.

Temperature Dependence of the Enthalpy of Mixing and the Excess Heat Capacity

Although measurements of the excess heat capacity C_p^E show how H^E varies with temperature, very few experimental investigations of C_p^E have been made. This neglect has been, in part, as Rowlinson stated, "probably due to the fact that even the best theories of solutions are not accurate enough to predict reliably the size of the second derivative of the excess free energy with respect to temperature to permit a test of theory."[31] However, in considering a mixture from the standpoint of its excess functions, it is necessary to know the excess free energy and excess enthalpy at the same temperature. Usually G^E is determined at a higher temperature than H^E, and knowledge of the excess heat capacity C_p^E of the system is required to correct H^E to the temperature of measurement of G^E. Calculating H^E at one temperature from the experimental value at another demands precise experimental investigation of the heat capacity, for the values of the excess properties are all relatively small and an error in the heat capacity of the order of 1% would lead to a comparatively large uncertainty in the derived H^E values.

From the only C_p measurements found by this investigator on binary non-polar systems carried out with this end in view (benzene-ethylene dichloride, benzene-tetrachloromethane, acetone-chloroform, and acetone-carbon disulfide reported by Staveley, Tupman, and Hart[32]) one may take for example the extensively investigated benzene and tetrachloromethane system for which the enthalpy of mixing has been determined at several temperatures and by several investigators.[33,34,35] Recent enthalpy of mixing measurements of Goates, Sullivan, and Ott[35] showed that the excess enthalpy curve for the system benzene-tetrachloromethane at 25°C had a maximum of 26 cal at the equimolar composition. At 40°C, the maximum has shifted slightly to the benzene-rich side with a value of about 31 cal. Using the excess enthalpy values of Goates et al. at 25°C and the heat capacity measurements of Staveley et al., the excess enthalpy values at 40°C were calculated for this system. The derived excess enthalpy curve at 40°C showed a maximum at the 40 mole percent tetrachloromethane composition with a value of about 37 cal (cf. Figure IX). Unfortunately, the C_p measurements of Staveley et al. extended over only a short range (20 to 60°C) in the liquid phase and their C_p values were accurate only to ± 1%; therefore, comparison at the lower temperature (10°C) could not be made. Taking into account the ± 1% accuracy of the C_p measurements over the temperature range from 25 to 40°C, thus giving the derived excess enthalpy at 40°C a value of 37 ± 5 cal (at 40 mole percent CCl_4), this

Figure IX. Temperature Dependence of the Excess Enthalpy in the System Benzene-Tetrachloromethane.

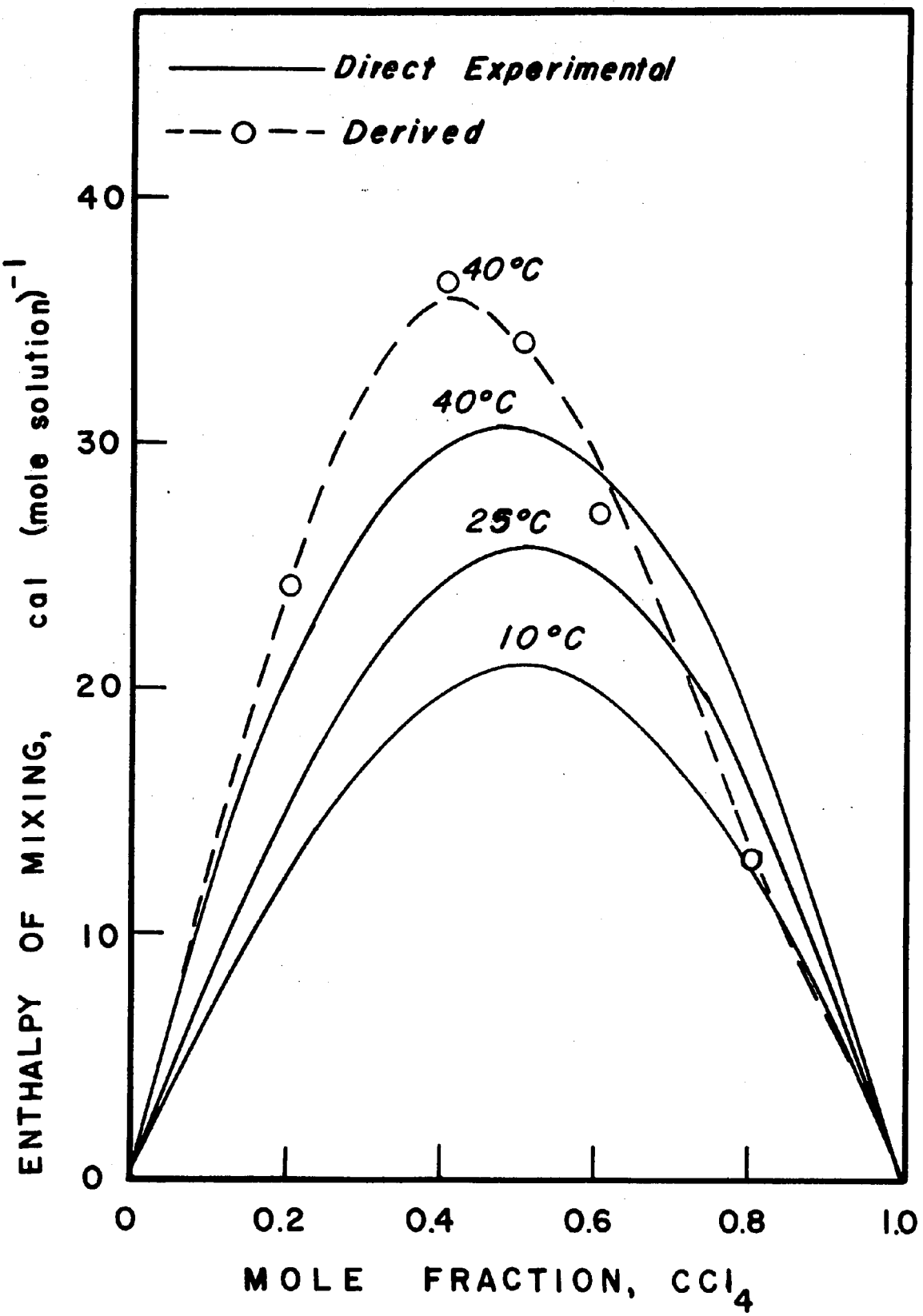

Direct Experimental
Derived
40°C
40°C
25°C
10°C
ENTHALPY OF MIXING, cal (mole solution)$^{-1}$
0
10
20
30
40
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION, CCl_4

Figure IX

showed that the derived value of the excess enthalpy is correct to within the experimental error of the C_p measurements. Although the C_p measurements of Staveley et al. probably gave an exaggerated account of the irregularity in the excess enthalpy at 40°C, this example moreover illustrates how important precise C_p measurements are in studying the temperature dependence of the enthalpy of mixing.

Excess Functions of the System Tetramethylmethane-Tetrachloromethane

Due to the similarity of the molecular shapes and sizes of the tetramethylmethane and tetrachloromethane molecules, the system tetramethylmethane-tetrachloromethane has been a favored testing ground of statistical theories of solutions. Moreover, the tetrahedral symmetry of the molecules closely approaches spherical symmetry which makes it possible to assume that the intermolecular forces are central.

The excess functions of this system at 0°C have been well investigated. In 1953, Mathot and Desmyter[11] studied the excess free energy and volume of mixing by measuring the total vapor pressures and densities, respectively, of several compositions of this system at 0°C. In 1955, Englert-Chwoles[10] studied the enthalpy and entropy of mixing at 0°C by adiabatic and isothermal calorimetry. The excess compressibility $(\partial V^E/\partial P)_T$ was studied by Jeener (1956)[36] by measuring the velocity of sound in liquid mixtures of

tetramethylmethane and tetrachloromethane. The experimental results of these investigations on the system tetramethylmethane-tetrachloromethane are summarized in Table XII, and the excess function curves, i.e., H^E, G^E, TS^E, and V^E are indicated in Figure X. It was found that this mixture is regular at 0°C and the equimolar values of the excess free energy, enthalpy, entropy (expressed as TS^E), and volume at 0°C are + 76 cal $mole^{-1}$, + 74 cal $mole^{-1}$, - 2 cal $mole^{-1}$, and - 0.5 cm^3 respectively. The magnitude of the excess volume decreases with increasing pressure.

This well-investigated system has been the subject of several attempts at theoretical interpretation. A comparison of some of the theoretically calculated excess functions with the experimental values of this system are shown in Table XIII. The cell model[37,38,39] is based on the assumption that each molecule is confined to its own cell, thus assuming a more or less regular structure with a mean intermolecular distance of the order of the molecular diameter. The smooth potential cell model[40] and the Lennard-Jones and Devonshire cell model[41] are two of the many attempts at interpretation of the thermodynamic properties with the cell model using different assumptions for the intermolecular forces. (Cf. references 40, 41.) The average potential model for mixtures developed by Prigogine, Bellemans, and Englert-Chwoles[42] combines the basic ideas underlying the theory of conformal solutions (i.e., theorem of corresponding states) with those of the cell model of

TABLE XII. EXPERIMENTAL EXCESS FUNCTIONS OF THE SYSTEM TETRAMETHYLMETHANE-TETRACHLOROMETHANE AT 0°C

Excess Free Energy G^E (Units: cal, mole solution, mm Hg)[11]

N_{CMe_4}	P	G^E
0.000	33.7	0
0.059	84.8	24
0.141	141.7	45
0.249	201.4	60
0.438	296.5	77
0.649	383.6	69
0.768	436.0	68
0.815	451.8	51
1.000	535.4	0

Excess Volume V^E (Units: cm^3, gram, mole solution)[11]

N_{CMe_4}	d	V^E
0.0000	1.6327	0.00
0.1094	1.5002	- 0.23
0.5356	1.0346	- 0.51
0.6765	0.8984	- 0.54
0.8610	0.7301	- 0.25
1.0000	0.6113	0.00

Excess Enthalpy H^E (Units: cal, mole solution)[10]

N_{CMe_4}	H^E
0.000	0.0
0.248	56.2
0.417	68.0
0.455	72.8
0.463	75.6
0.481	67.0
0.491	78.5
0.550	77.5
0.680	65.6
0.681	65.8
0.757	50.0
1.000	0.0

TABLE XII. (Cont.)

Excess Compressibility $(\partial V^E/\partial P)_T$ (Units: cm^3, barye)[36]

N_{CMe_4}	$(\partial V/\partial P)_T \times 10^8$	$(\partial V^E/\partial P)_T \times 10^8$
1.0000	2.758	0.000
0.5808	1.765	0.186
0.4079	1.396	0.223
0.1611	1.030	0.115
0.0000	0.836	0.000

Figure X. Excess Functions of the System Tetramethylmethane-Tetrachloromethane at 0°C.

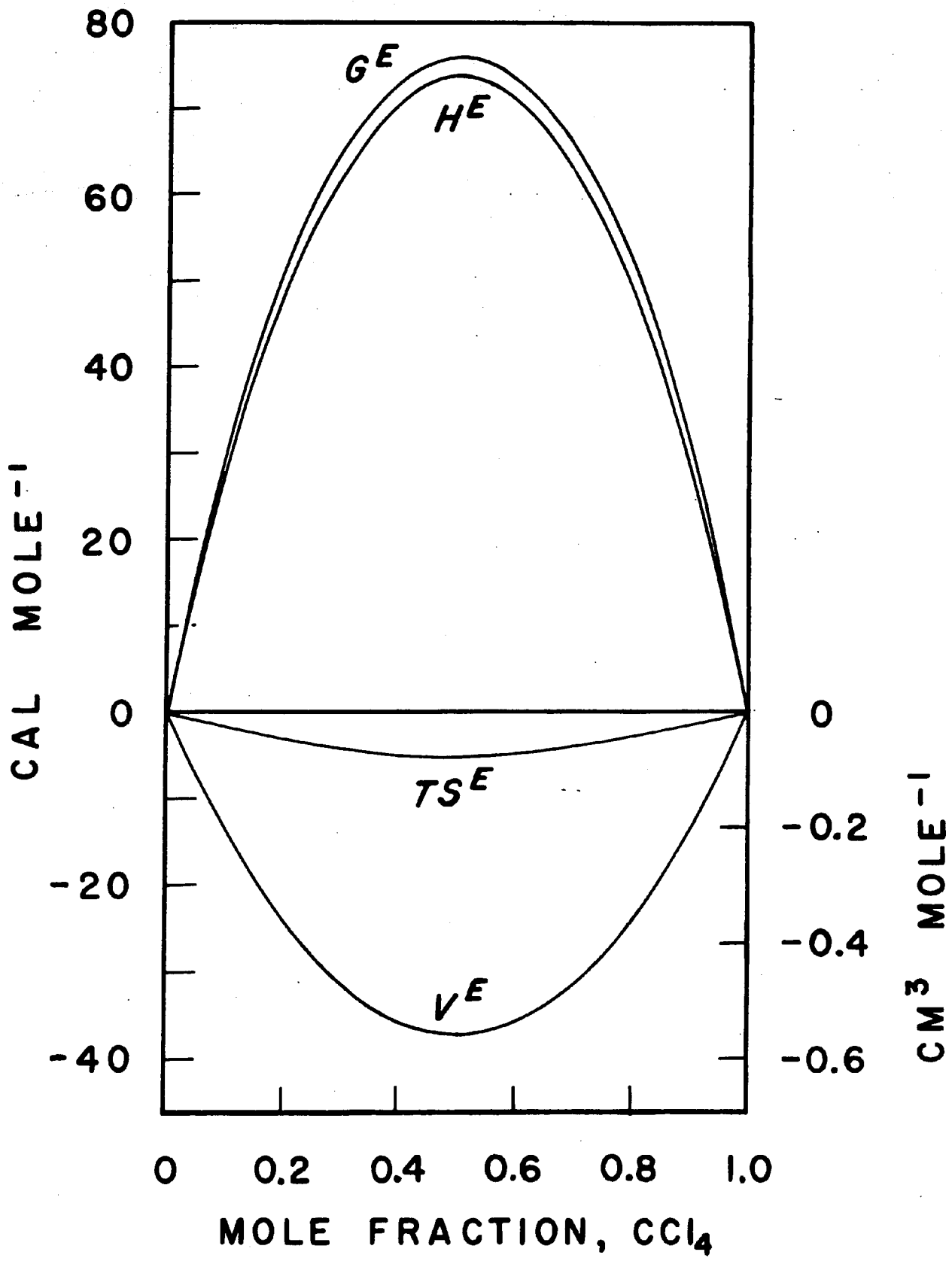

80
60
40
20
0
-20
-40
CAL MOLE⁻¹
G^E
H^E
TS^E
V^E
0
-0.2
-0.4
-0.6
CM³ MOLE⁻¹
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION, CCl_4

Figure X

TABLE XIII. COMPARISON OF THEORETICAL CALCULATIONS OF EXCESS FUNCTIONS WITH EXPERIMENT FOR THE EQUIMOLAR COMPOSITION OF THE SYSTEM TETRAMETHYLMETHANE-TETRACHLOROMETHANE (Units: cal, mole solution, °K, cm^3)

THEORY	T	H^E	TS^E	G^E	V^E	Ref.
Cell Model						
Smooth Potential	273	55	- 5	60	- 0.2	40
Lennard-Jones Devonshire	293	16	- 98	--	- 3	41
Average Potential Model	273	71	- 9	80	- 1.3	42
Scatchard-Hildebrand Formula	273	--	---	150	---	43
Lorentz-Berthelot Mixture						
Random	273	100	12	88	- 0.005	44
Fixed Volume	273	93	9	84	- 0.003	44
Fixed Pressure	273	67	5	62	- 0.008	44
Experiment	273	74	- 2	76	- 0.5	10,11

solutions. In this model the excess functions are expressed in terms directly related to the behavior of the pure components. The Hildebrand-Scatchard theory[43] expresses the excess energy in the form of a semi-empirical formula involving the latent heats of evaporation and volume fractions. The Lorentz-Berthelot mixture[44] is a mixture of Lennard-Jones molecules (6-12 potential) in which the unlike parameters, i.e., the mean diameter and the mean energy of interaction, are expressed by the arithmetic mean (Lorentz, 1881[45]) and the geometric mean (Berthelot, 1898[46]), respectively. The "random," "fixed volume," and "fixed pressure" theories are three variations of the Lorentz-Berthelot mixture based on the assumptions of a random assignment of spherical Lennard-Jones molecules to the N positions of each configuration; a lattice of fixed volume in which any molecule has neighbors chosen at random; and a deformable lattice, i.e., ordered at fixed pressure, respectively.[44]

It is observed that for most cases the quantitative agreement between theory and experiment is poor. However, in a few cases (i.e., the smooth potential cell model and the average potential model) the agreement is fair. The best agreement at 0°C (in the liquid phase) is obtained with the average potential model.

Temperature Dependence of the Enthalpy of Mixing and the Enthalpy of Mixing in the Plastically Crystalline Region of the System Tetramethylmethane-Tetrachloromethane

In view of the fact that several of the solution

theories mentioned before are based on a more or less regular structure with many features in common with the solid state, the calorimetric experimental investigation of the system tetramethylmethane-tetrachloromethane was made with the object of discovering whether some of the solution theories were applicable and whether better agreement between theory and experiment was obtainable in solid solutions.

The heat capacities (5 to 300°K) of four compositions of the system tetramethylmethane-tetrachloromethane were measured to obtain data on the temperature dependence of the enthalpy of mixing. The enthalpies of mixing of this system at several temperatures were determined from the available enthalpy of mixing data at 0°C,[10] the heat capacity data of the pure components[18,19], and the heat capacity data of this investigation in the following manner: The enthalpy of mixing H^M (or excess enthalpy, H^E) at a temperature T_o may be expressed as

$$H^E_{T_o} \quad \text{or} \quad H^M_{T_o} = H_{Mix,T_o} - X_1 H_{1,T_o} - X_2 H_{2,T_o}$$

where H refers to the relative enthalpy at the temperature T_o, and X refers to the mole fraction. The subscripts Mix, 1, and 2 refer to the mixture and components 1 and 2 respectively. The enthalpy of mixing at another temperature is therefore

$$H^E_T = H_{Mix,T} - X_1 H_{1,T} - X_2 H_{2,T} \ .$$

Since

$$H_T = H_{T_o} + \int_{T_o}^{T} C_p dT + (\Delta H_{Trans} \text{ or } \Delta H_{Fus} \ldots) ,$$

therefore,

$$H_T^M = H_{T_o}^M + \int_{T_o}^{T} C_p^E \, dT + \ldots$$

$$C_p^E = C_{p\ Mix} - X_1 C_{p\ 1} - X_2 C_{p\ 2}$$

or

$$H_T^M = H_{T_o}^M + (H_{Mix,T} - H_{Mix,T_o}) - X_1(H_{1,T} - H_{1,T_o})$$

$$-X_2(H_{2,T} - H_{2,T_o}).$$

The derived enthalpy of mixing and the excess heat capacity for this system at 280, 260, 255, 245, 230, and 0°K are tabulated together with the experimental value at 273.15°K (0°C) in Table XIV. And the enthalpy of mixing versus temperature plot is depicted in Figure XI. The values reported for 0°K may not be meaningful for this system; however, they are given to indicate that they can be obtained by this method for systems that exhibit a continuous series of solid solution at 0°K. Also note that the values for 255°K are the enthalpies of mixing for the undercooled liquid tetramethylmethane with liquid tetrachloromethane to form a liquid mixture; the values for 245°K are the enthalpies of mixing for two undercooled liquids (i.e., tetramethylmethane and tetrachloromethane) to form a liquid mixture; and the values for 230°K are the enthalpies of mixing of two solid components to form a solid solution. Values at other

TABLE XIV. TEMPERATURE DEPENDENCE OF THE EXCESS ENTHALPY AND EXCESS HEAT CAPACITY OF THE SYSTEM TETRAMETHYLMETHANE-TETRACHLOROMETHANE
(Units: cal, gram-mole solution, °K)

Temperature		280	273.15	260	255*	245**	230***	0
N_{CCl_4}	Property							
0.334	C_p^E	- 0.24	- 0.08	+ 0.23	+ 0.37	+ 0.64	- 0.15	0
	H^E	64.6	65.7	64.8	63.2	58.0	241.2	(34.5)
0.501	C_p^E	- 0.29	- 0.16	+ 0.10	+ 0.20	+ 0.39	+ 0.58	0
	H^E	72.5	74.0	74.2	73.7	70.6	278.7	(33.1)
0.666	C_p^E	- 0.28	- 0.18	+ 0.01	+ 0.08	+ 0.22	+ 1.77	0
	H^E	64.6	66.2	67.3	67.0	65.4	121.3	(6.2)
0.826	C_p^E	- 0.16	- 0.13	- 0.08	- 0.06	- 0.02	+ 1.07	0
	H^E	43.9	44.8	46.1	46.4	46.5	71.0	(- 9.8)

* Mixing of undercooled liquid CMe_4 with liquid CCl_4. ** Mixing of undercooled liquids CMe_4 and CCl_4. *** Mixing of solid CMe_4 with solid CCl_4.

Figure XI. Temperature Dependence of the Enthalpy of Mixing in the System Tetramethylmethane-Tetrachloromethane.

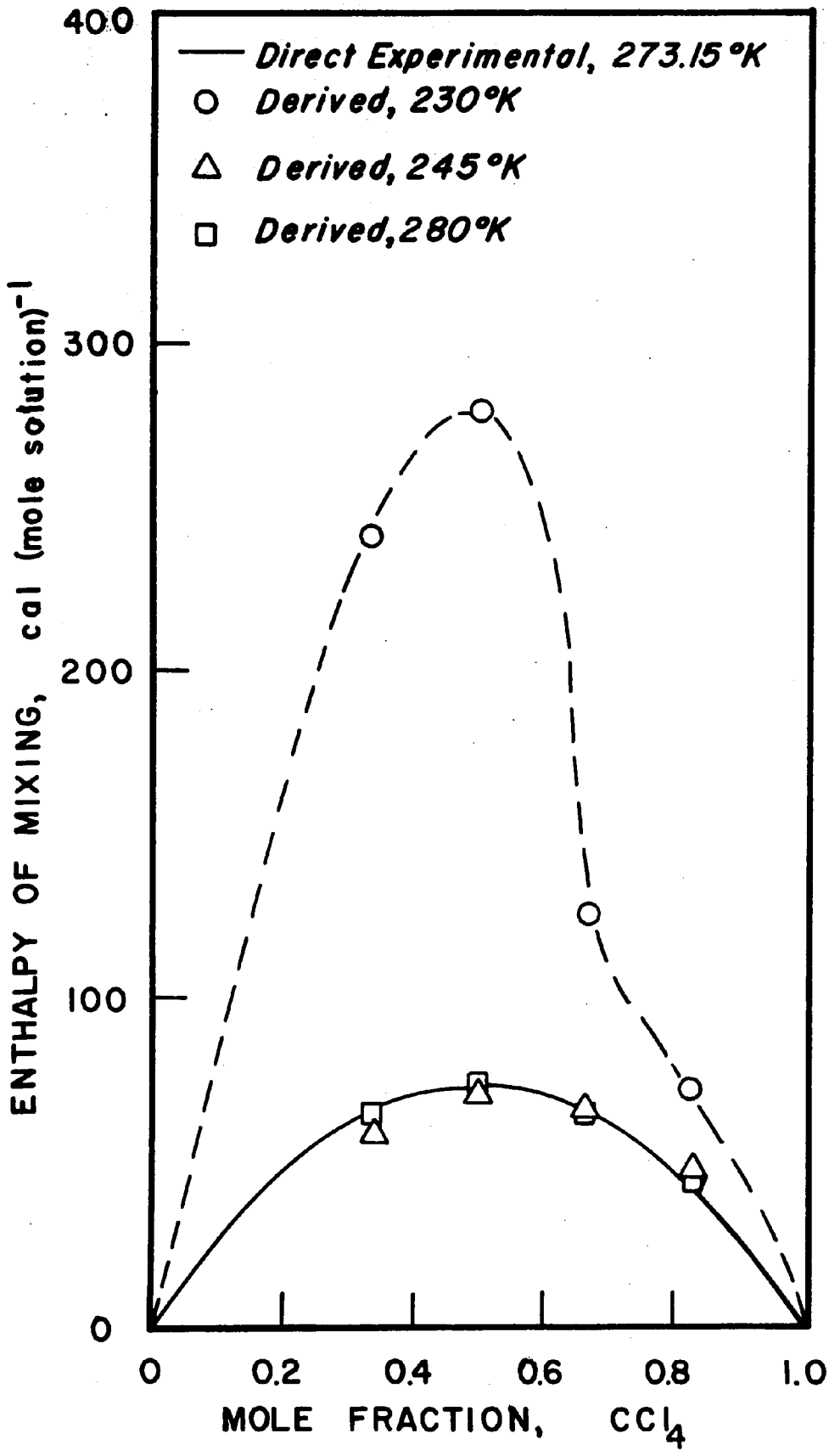

Direct Experimental, 273.15°K
Derived, 230°K
Derived, 245°K
Derived, 280°K
ENTHALPY OF MIXING, cal (mole solution)⁻¹
400
300
200
100
0
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION, CCl4

Figure XI

temperatures may be derived conveniently by using the relative enthalpy values tabulated in Table VI for the mixture and in Table D in the appendix for the pure components.

It is observed that in the liquid range the temperature dependence of the enthalpy of mixing for the system tetramethylmethane-tetrachloromethane is comparatively small (i.e., in comparison with that of the system benzene-tetrachloromethane). It is slightly negative in the liquid range where both components are liquids and slightly positive when one or both components are undercooled liquids. The excess enthalpy curve in the liquid solution range is more symmetrical at higher temperatures than at lower temperatures where the maximum in the curve is shifted slightly to the tetrachloromethane-rich side of the excess enthalpy versus composition diagram. (Cf. Table XIV and Figure XI.)

The derived enthalpy of mixing at 230°K in the plastically crystalline region shows comparatively large and irregular excess enthalpy behavior and possibly a discontinuity in the enthalpy of mixing curve between the compositions $N_{CCl_4} = 0.5$ and 0.6. Unfortunately, there are no data in this region to clarify this. An attempt to explain this irregular behavior in the plastically crystalline region will be given in the next section. Also, due to the phase separations that occur in this system, the plastically crystalline region extends over only a short temperature interval (cf. Figures II to V and XII). Only in the vicinity of 230°K does even the possibility of a continuous series of solid solution exist.

Some Comparisons With Theories

One of the theories chosen to study the excess enthalpy of solid solutions in this investigation was the cell model, for in this model the assumptions made about the structure of solution most closely resemble that of the solid state. As Prigogine has suggested, for high densities as in the solid state a harmonic potential approximation for the mean potential may be used.[47] The equation used to calculate the enthalpy of mixing was[40]

$$\frac{H^E}{NkT} = \frac{1}{2} \times 1.435\, X_A X_B \left[(\Lambda_{AA}/kT)^{1/2} - (\Lambda_{BB}/kT)^{1/2} \right]^2 + 4.83 \frac{V^E}{V^*}$$

$$\frac{V^E}{V^*} = 1.4125 \left[(kT/\Lambda_{AB}) - X_A(kT/\Lambda_{AA}) - X_B(kT/\Lambda_{BB}) \right]$$

where Λ is the interaction parameter, k is the Boltzman constant, N = Avogadro's number, and X is the mole fraction. (Detailed discussion of the theory and definition of the parameters may be found in reference 40.) The excess enthalpies at 230°K reported in Table XV by the harmonic oscillator cell model are calculated by using the above equations.

Since the average potential model gave good agreement with experiment at 273°K in liquid solutions of this system, a comparison is made at 230°K to determine whether the theory was applicable in solid solutions. The equation for

calculating H^E is[48]

$$\frac{H^E}{X_A X_B} = [-H_A + TC_{pA}]\left[\frac{1}{4}d^2 + 9\rho^2\right] - \frac{1}{2}T^2\left[dC_{pA}/dT - \frac{1}{4}dC_{vA}/dT\right]d^2$$

where the thermodynamic properties refer only to the configurational part of the properties, and d and ρ are interaction parameters. Detailed discussion of the theory and definitions of the parameters may be found in Prigogine's book.[49] The calculated excess enthalpy values by this model at 230°K are listed in Table XV.

A final attempt to compare the derived experimental excess enthalpy at 230°K with theory was made by means of Hildebrand's approach to solid solutions.[50] According to Hildebrand, the difference in the cohesive energy of liquid and solid is small; therefore, the enthalpy of mixing in solid solutions may be expected to be of the same order of magnitude as in the corresponding liquid phase. However, a distortion energy due to differences of size and shape must be added to the enthalpy of mixing based upon internal pressure considerations alone (i.e., the enthalpy of mixing given by the Hildebrand-Scatchard semi-empirical formula[43]). The distortion energy is peculiar to the solid phase and is lost on melting; therefore the part of the enthalpy of mixing arising from internal pressure differences should be much the same as in the liquid phase. The semi-empirical enthalpy of mixing formula based on internal pressure considerations[43]

TABLE XV. COMPARISON OF DERIVED EXPERIMENTAL EXCESS ENTHALPIES WITH THEORETICAL CALCULATIONS AT 230°K* (Units: cal, gram-mole solution)

N_{CCl_4}	0.334	0.501	0.666	0.826
H^E:				
Harmonic Oscillator Cell Model	78.0	101.6	100.5	78.3
Hildebrand's Empirical Approach				
Internal pressure considerations	88.4	101.4	92.1	60.8
Distortion energy	48.9	+ 57.5	+ 53.1	+ 35.8
Total	137.3	158.7	145.2	96.6
Average Potential Model				
CMe_4 as reference	204.9	230.3	204.9	132.4
CCl_4 as reference	156.1	175.3	156.1	105.0
Average	180.5	202.8	180.5	118.7
Derived Experimental	241.2	278.7	121.3	71.0

* Cf. Table XVI, next page

TABLE XVI. SUMMARY OF PROPERTIES OF TETRAMETHYLMETHANE AND TETRACHLOROMETHANE AT 273.15 and 230°K FOR CALCULATING THEORETICAL EXCESS ENTHALPY (Units: cal, gram-mole, $°K^{-2}$, cm^3)

Property	273.15°K*		230°K**		References for 230°K calculation
	CMe_4	CCl_4	CMe_4	CCl_4	
Interaction Parameters					
Λ/kT	15.68	21.60	17.54	28.30	11,51,52
d	0.30	- 0.23	0.61	- 0.38	11,25
ρ	- 0.04	0.04	- 0.05	0.05	11,25
Configurational					
- H	5070	7530	5609	8156	53,54,55
C_p	13	13.5	11.4	15.1	53,54,55
dC_p/dT	0.01	---	0.03	---	53,54,55
dC_v/dT	---	---	---	0.01	53,54,55
Molar Volume	117.54	94.19	101.91	89.94	56,57
Enthalpy of					
Vaporization	5210+	7830+	5974	8669	58
Fusion	778++	601++	705	557	18,19
Sublimation	---	---	6679	9226	58,18,19
Solubility Parameter					
δ of liquid	6.25+	8.6+	7.13	9.58	58,18,19
δ of solid	---	---	7.81	9.87	58,18,19

* From Prigogine or Hildebrand; ** calculated or estimated from data and by method indicated in references; + at 298°K; and ++ at melting point.

$$H^M = (N_1V_1 + N_2V_2)\,(\delta_1 - \delta_2)^2\,\phi_1\phi_2$$

where V refers to the molar volume, δ to the solubility parameter, N to the number of moles, and ϕ to the volume fraction; and the empirical distortion energy formula[59]

$$E^D = \frac{2\delta_1\delta_2\,(V_1V_2)^{1/2}(V_1 - V_2)^2}{(X_1V_1^2 + X_2V_2^2)}\,X_1X_2$$

for a binary solid solution of atoms of different sizes have been found to be valid for a large number of atomic lattices, i.e., metallic solutions.[60] Since the tetrahedral symmetry of some of the non-polar organic molecules closely approaches spherical symmetry (i.e., globular molecules), the dissolved molecules in solid solutions can be considered essentially monatomic; therefore, a treatment for atomic lattices would be expected to hold almost equally well for approximately spherical molecules, i.e., tetramethylmethane and tetrachloromethane. The calculated enthalpies of mixing by this approach in solid solutions at 230°K are listed in Table XV.

On examining the calculated theoretical values and the derived experimental values of the excess enthalpy at 230°K (cf. Table XV) it is apparent that at this temperature the solution is more complex than in the liquid phase. The excess enthalpy values are irregular as well as large, i.e., comparable with RT at the equimolar composition. On the tetrachloromethane-rich side of this system the derived experimental excess enthalpies agree fairly well with the values calculated by the harmonic oscillator cell model,

while on the tetramethylmethane-rich side the derived excess enthalpies are more than twice as large as those predicted by this model but are closer to the values predicted by the average potential model. The empirical approach of Hildebrand predicts excess enthalpies intermediate between those predicted by the harmonic oscillator cell model and the average potential model. Both the harmonic oscillator cell model and Hildebrand's approach predict unsymmetrical excess enthalpy versus mole fraction curves (the average potential model predicts a symmetrical excess enthalpy curve at all temperatures) with maxima on the tetrachloromethane-rich side of the system in contrast to what the derived experimental excess enthalpy curve shows.

That the situation in the solid is definitely more complex than in the liquid is further supported by the fact that this system exhibits a minimum in the melting point curve (cf. Figure XII). As Hildebrand has explained, when the deviations from ideality in the solid exceed those in the liquid, a minimum in the melting point curve can be expected. No definitive explanation for the irregular behavior of the derived experimental excess enthalpy at 230°K is offered; however, a possible explanation is that the large excess enthalpy on the tetramethylmethane-rich side of this system is due to phase separation at this temperature. A rough criterion for immiscibility is that when H^E is large and positive and the value of G^E exceeds $RT/2$, phase separation is likely;[61] also, when the difference in molar volume is

greater than 20%, the strain energy is so great that phase separation often occurs.[62] However, in this system G^E at 230°K is estimated (by $G^E = H^E - TS^E$) to be only about 124 cal $(mole)^{-1}$ (i.e., less than RT/2 which is about 230 cal $(mole)^{-1}$ at this temperature) for the equimolar composition, and the difference in molar volume is about 12%. Another possible indication of phase separation is that the enthalpy of fusion of the mixture shows a minimum around the equimolar composition, which may be analogous to the system oxygen-nitrogen whose enthalpy of fusion curve exhibited similar behavior and whose melting point curve exhibited a Type V eutectic diagram.[63] A discussion of the phase diagram of the system tetramethylmethane-tetrachloromethane will be given in the next section. It is unfortunate that the possibility of phase separation at 230°K has complicated this study. The calculated theoretical values of the excess enthalpy in solid solution may be used for qualitative comparison only for a great deal of approximation was used in deriving the values of the properties of the pure components and parameters at 230°K. (Cf. Table XVI.) It is apparent that further study of the present system and of other systems of globular molecules that form continuous series of solid solutions is necessary before the validity of this approach to solution theory can be assessed more fully. It is hoped that more measurements on properties of pure components as well as solutions both in the solid and liquid states will be made in order that more extensive comparisons can be made with similar systems.

Phase Diagram of the System Tetramethylmethane-Tetrachloromethane

The results of this investigation on the system tetramethylmethane-tetrachloromethane also provide phase equilibria data, which indicate that the phase diagram for a binary system of relatively simple globular molecules can be very complex! Under favorable conditions, two substances will crystallize together in the same crystal lattice to form a partial or complete series of solid solutions. In order to obtain a complete series of solid solutions the conditions that must be satisfied are:[60] the intermolecular potentials of the two components must not differ greatly; the molar volumes of the two components must be fairly similar; the two pure substances must exist in identical or similar crystal structures; and special forces tending to produce intermediate phases of different crystal structures must be absent. In practice, the most important solid solutions are those between metals, i.e., alloys. Among binary organic systems, due to the large effect of differences in size and shape, even when the intermolecular potentials are equal, the formation of a complete series of solid solutions is rare. In order to form a solid solution, certain molecules in the crystalline lattice of a pure substance must be replaced by molecules of the second component. If the molecules of the second component are markedly different in size or shape, a considerable amount of strain energy or distortion is introduced into the crystal, thus producing phase

separation. However, when the two substances are very similar in size and shape, solid solution formation is possible; i.e., possibly in the system tetramethylmethane-tetrachloromethane.

Both tetramethylmethane and tetrachloromethane are reported to crystallize in the face-centered, cubic crystal structure below their respective melting points.[56,57,64] At $-50 \pm 5°C$, the tetramethylmethane crystal is reported to be isotropic and has a unit cell with $a_o = 8.78$ Å and four molecules per cell. The density of the solid at this temperature is 0.708 g cm^3. At $-35°C$, the tetrachloromethane crystal is isotropic and has a unit cell with $a_o = 8.34$ Å and four molecules per cell. The calculated density of tetrachloromethane is 1.594 g cm^3 at $-35°C$. The calculated molar volumes and solubility parameters of tetramethylmethane and tetrachloromethane in the temperature range between 225 and 240°K are 101.9 and 89.9 cm^3 and 7.81 and 9.87 respectively. (Cf. Table XVI.) Moreover, both molecules have the tetrahedral symmetry and exhibit "reorientational rotation" in the plastically crystalline region. Therefore, in view of these observations, it was expected that this system would form a continuous series of solid solution.

A preliminary investigation by running a series of cooling curves across the entire composition range indicated that possibly a continuous series of solid solution would form in this system just below the melting point. At lower temperatures the cooling curve investigation gave

unsatisfactory ambiguous results. All the pertinent information for phase equilibria studies obtained by the calorimetric investigation of this system has been summarized in Table VIII on page 81. Information on the pure components tetramethylmethane and tetrachloromethane was obtained from investigations by Aston and Messerly[18] and by Hicks et al.,[19] respectively.

The tentative partial phase diagram for the system tetramethylmethane-tetrachloromethane depicted in Figure XII is obtained by plotting the various transition temperatures versus composition (N_{CCl_4}). (Cf. Table VIII.) This temperature composition relationship usually can be obtained by thermal analysis studies. However, in this system, due to the large undercooling effects and the long periods of time required for the sample to attain thermal equilibrium in the transition region, many of the transitions were obscured during the cooling curve determinations. Therefore, the equilibrium method of heat capacity measurements was required for the thermal study of this system. By this method not only the transition temperatures, but also the enthalpy effect of each of the solid-solid transitions and fusion, were accurately determined in the same process.

It is observed that in each of the compositions studied, transitions appeared at the apparently constant temperatures of 142.5 (Transition I) and 191.6°K (Transition II). These transitions were consistently similar in behavior, i.e., the heat capacity versus temperature curves of the

Figure XII. A Tentative Phase Diagram of the System Tetramethylmethane-Tetrachloromethane with the Type III Melting Diagram.

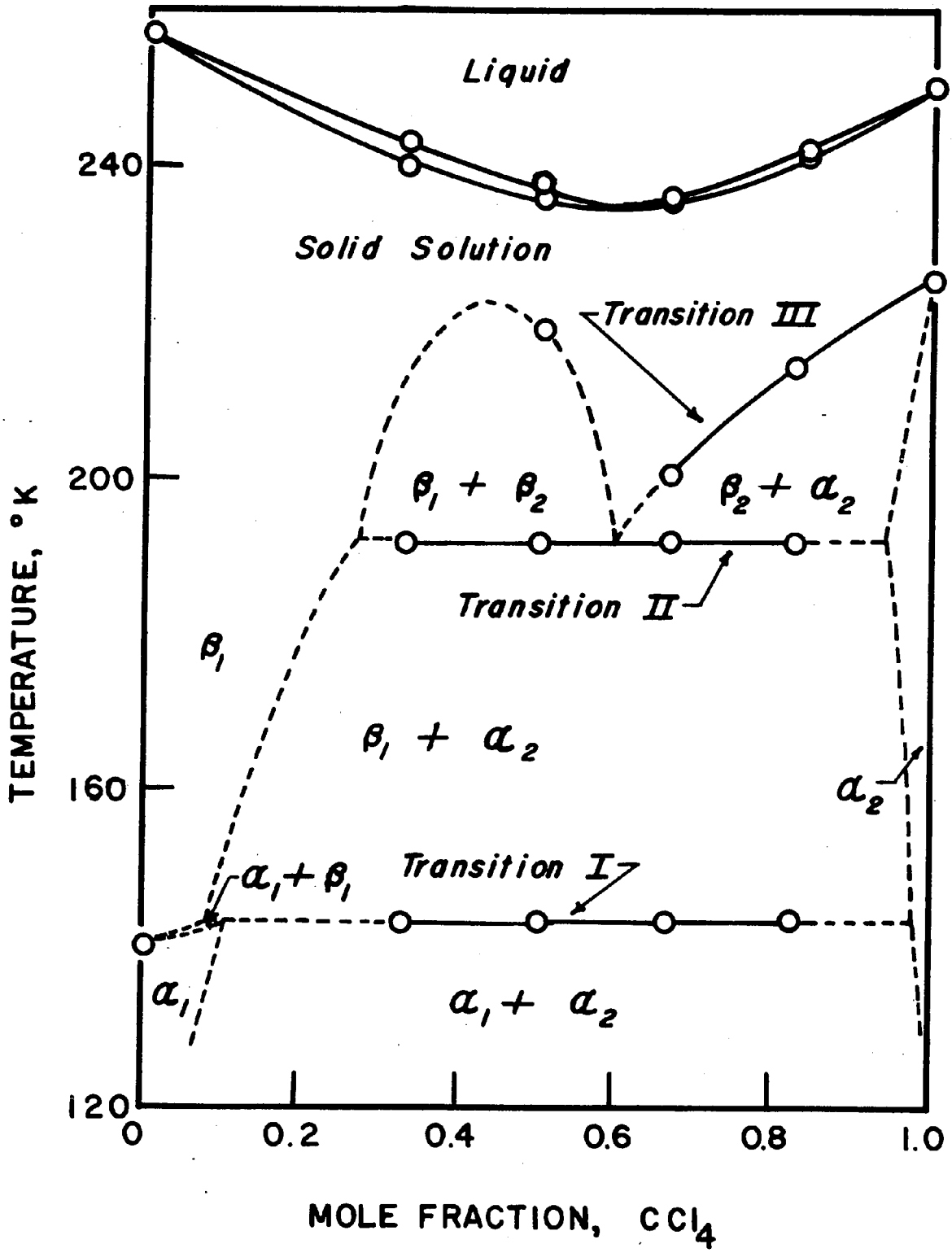

Liquid
240
Solid Solution
Transition III
200
$\beta_1 + \beta_2$
$\beta_2 + \alpha_2$
Transition II
β_1
$\beta_1 + \alpha_2$
160
α_2
$\alpha_1 + \beta_1$
Transition I
α_1
$\alpha_1 + \alpha_2$
120
0
0.2
0.4
0.6
0.8
1.0
TEMPERATURE, °K
MOLE FRACTION, CCl_4

Figure XII

142.5°K transitions had the same shape and the sample took about the same length of time to attain thermal equilibrium for each composition. The constancy of the temperature of Transition I, 142.5°K, and the fact that the magnitude of Transition I was directly proportional to the amount of tetramethylmethane in the sample (cf. Table VIII and Figure XIII) probably indicate that phase separation has taken place above this temperature. The increase in the transition temperature from that of 140.02°K in pure tetramethylmethane to 142.5°K in the mixtures may be due in part to the presence of small amounts of tetrachloromethane in the nearly pure tetramethylmethane phase and in part to the differences in the temperature scale in this region. Below 142.5°K (cf. Figure XII) there exist the two solid-solution phases α_1, rich in tetramethylmethane, and α_2, rich in tetrachloromethane. At 142.5°K, "reorientational rotation" takes place in the α_1 phase. Thus, above Transition I, the α_1 phase is designated the β_1 phase in which there is "reorientational rotation." Therefore, between Transitions I and II the phase diagram of this system is divided into three regions: on the tetramethylmethane side there is phase β_1, on the tetrachloromethane side there is α_2 and between there is a two-phase region of $\beta_1+\alpha_2$. The compositions of the β_1 and α_2 phases depend on the mutual solubility in this temperature range of tetrachloromethane in tetramethylmethane and tetramethylmethane in tetrachloromethane, respectively. The "shoulder-like" heat capacity anomaly that appears in the temperature range of 170 ± 5°K (cf. Figures II to V) may be due to an increase

Figure XIII. Enthalpy Increments of Transitions I, II, and III and of Fusion versus Composition in the System Tetramethylmethane-Tetrachloromethane.

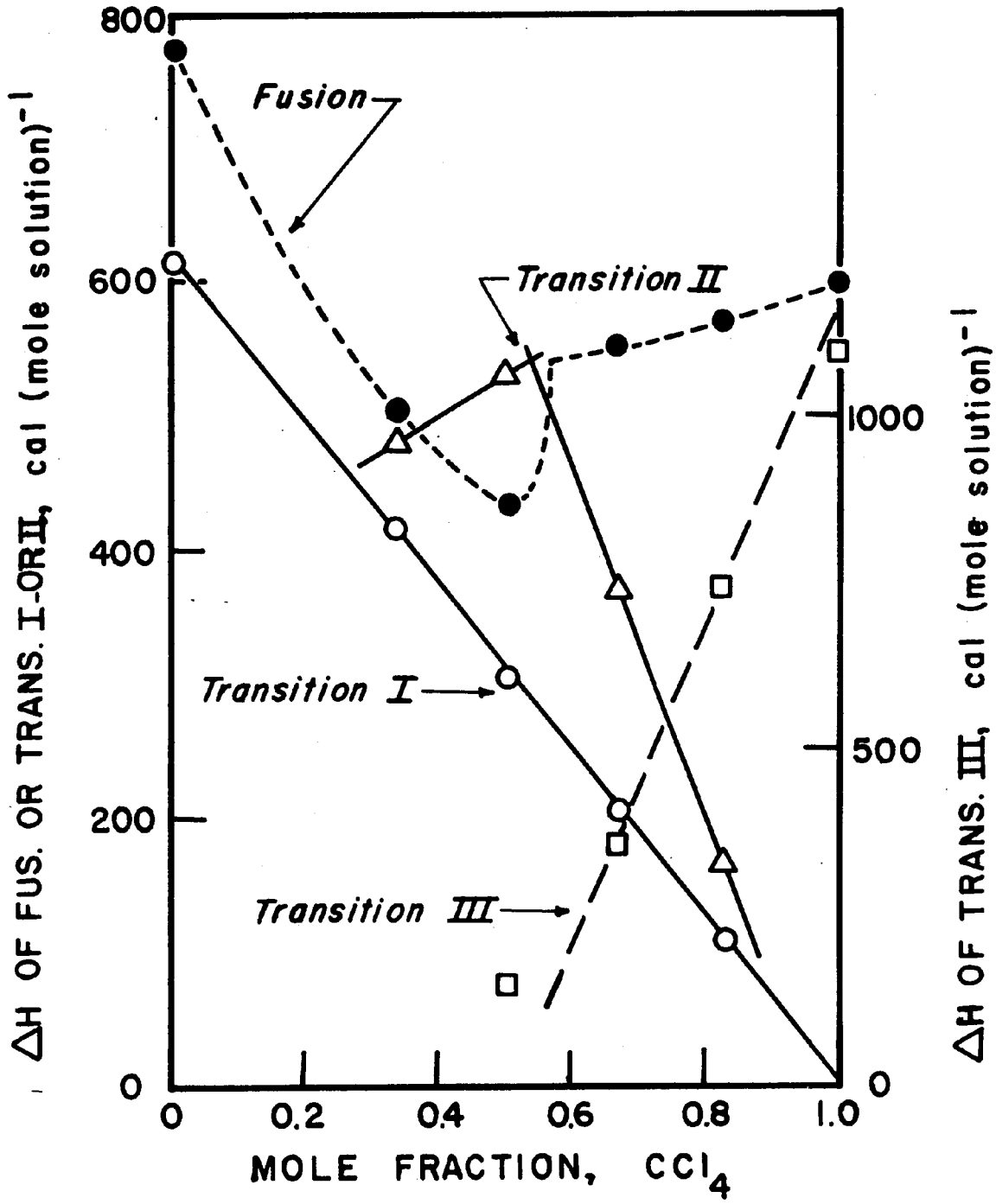

800
600
400
200
0
Fusion
Transition II
Transition I
Transition III
ΔH OF FUS. OR TRANS. I-OR II, cal (mole solution)⁻¹
ΔH OF TRANS. III, cal (mole solution)⁻¹
1000
500
0
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION, CCl4

Figure XIII

in "reorientational rotation" in the β_1 phase.

Transition II, at 191.6°K was a totally unexpected transition. It is considerably lower in temperature than the 225.3°K transition in pure tetrachloromethane. In three of the four mixtures (tetrachloromethane-rich) studied, it was one of two consecutive transitions (i.e., Transitions II and III); therefore, there was some difficulty in apportioning the enthalpy effects due to these successive transitions. In any event, it is observed that the enthalpy increment of this transition reached a maximum between the compositions N_{CCl_4} = 0.5 and 0.6 (cf. Figure XIII). This observation, together with the fact that Transition II appeared at essentially constant temperatures in all the compositions studied, indicates the probable presence of an eutectoid (a certain favored combination of β_1 and α_2) formed between the compositions of N_{CCl_4} = 0.5 and 0.6, and that 191.6°K is the eutectoid transformation temperature (probably involving only the α_2 phase in the eutectoid composition). A possible interpretation of this region is that on the tetrachloromethane side of the eutectoid composition the region between Transitions II and III is a two-phase region of the phases β_2 and α_2, (cf. Figure XII) where α_2 is as indicated above a solid solution of essentially pure tetrachloromethane, and β_2 is a solid solution of the eutectoid composition with "reorientational rotation". On the tetramethylmethane side of the eutectoid composition, the region between Transitions II and III is another two-phase region, β_1 and β_2, probably similar to the miscibility gap found in liquid solutions.

In the N_{CCl_4} = 0.666 and 0.826 compositions Transition III showed the expected lowering of the "reorientational" transition temperature of tetrachloromethane by the presence of tetramethylmethane. This transition may be interpreted as involving the onset of "reorientational rotation" in the α_2 phase in excess of that in the eutectoid composition. However, extrapolation of the enthalpy increments of this transition to that of pure tetrachloromethane gives a slightly larger enthalpy of transition for pure tetrachloromethane than the known one. (Cf. Figure XIII.) Therefore, the enthalpy effects of this transition probably are due to a large enthalpy of transition involving the α_2 phase plus a small enthalpy of mixing of the β_2 phase and the newly-transformed α_2 phase to form a homogeneous solid solution. It is observed that the heat capacity versus temperature curve of this transition is very similar in shape to the one obtained by Jura et al.[65] in going from a two-phase region to a homogeneous solution of the system perfluoronormal heptane and 2,2,4-trimethylpentane. In the N_{CCl_4} = 0.501 composition, Transition III may be interpreted as a critical solution temperature at which the two solid solutions β_1 and β_2 become one homogeneous solid solution; and the enthalpy involved is the enthalpy of mixing the two phases. Transition III was not detected for the N_{CCl_4} = 0.334 composition possibly because it was a small effect and it was so close to Transition II that it was obscured by it. Both the comparatively large enthalpy effect and the broadness of this Transition II tend

to support this view. (Cf. Figures II and XIII.) If Transition III were present in this composition, it probably would serve the same purpose as that of Transition III in the N_{CCl_4} = 0.501 mixture.

The dashed curve enclosing the two-phase region of $\beta_1+\beta_2$ was arbitrarily drawn through the completion temperature of Transition III of the N_{CCl_4} = 0.501 mixture and meets the horizontal line of Transition II close to the N_{CCl_4} = 0.334 composition. (Cf. Figure XII.) Above the curve designating Transition III and below the melting point curve there may be a region of a continuous series of solid solution of the system tetramethylmethane-tetrachloromethane.

The available data on the system tetramethylmethane-tetrachloromethane indicate that the melting point curve of this system is a Type III melting diagram, i.e., a melting point curve exhibiting a minimum.[66] There is considerable melting point depression (i.e., maximum about 20°K) in this system indicating that the deviation from ideality is much greater in the solid than in the liquid and that the distortion energy in the solid is comparatively large. The enthalpy of fusion versus composition curve (cf. Figure XIII) also shows some anomalous behavior. There is definitely a minimum or a discontinuity in the curve between the compositions of N_{CCl_4} = 0.5 and 0.6. This behavior is analogous to that of the oxygen-nitrogen system where it is known that the system had a eutectic Type V melting diagram.[63] If this situation also exists in the tetramethylmethane-tetrachloromethane

system, then the phase diagram depicted in Figure XII will have to be modified somewhat. The modified phase diagram will either be one of the transition diagram from the Type III to Type V where the miscibility gap in the solid just touches the minimum in the melting point curve, or a diagram of Type V but with a narrow two-phase region, i.e., as depicted in Figure XIV. In any event, the interpretation of the transitions and the phases present in the different regions will be essentially the same as previously discussed.

At the moment there is not enough evidence to distinguish between the Type III (cf. Figure XII) melting diagram or the Type V (cf. Figure XIV) melting diagram which represents a reasonable alternative interpretation of the extant data. It has been shown that although the enthalpy of mixing is large on the tetramethylmethane-rich side of this system, it is not large enough for phase separation to occur at 230°K at the equimolar composition. Also, the difference in molar volumes is not large enough to be critical. The temperature versus composition curves of Transition III and the melting point (cf. Figure XII), the enthalpy of fusion curve, and the enthalpy of transition curves of Transition II and III (cf. Figure XIII) all seem to indicate some kind of anomalous behavior in the composition range between $N_{CCl_4} = 0.5$ and 0.6. It is apparent that further investigation will be required on this system to elucidate the details. Investigations by other means such as dielectric constant measurements (e.g., as was done on the system

Figure XIV. An Alternative Phase Diagram of the System Tetramethylmethane-Tetrachloromethane with the Type V Melting Diagram.

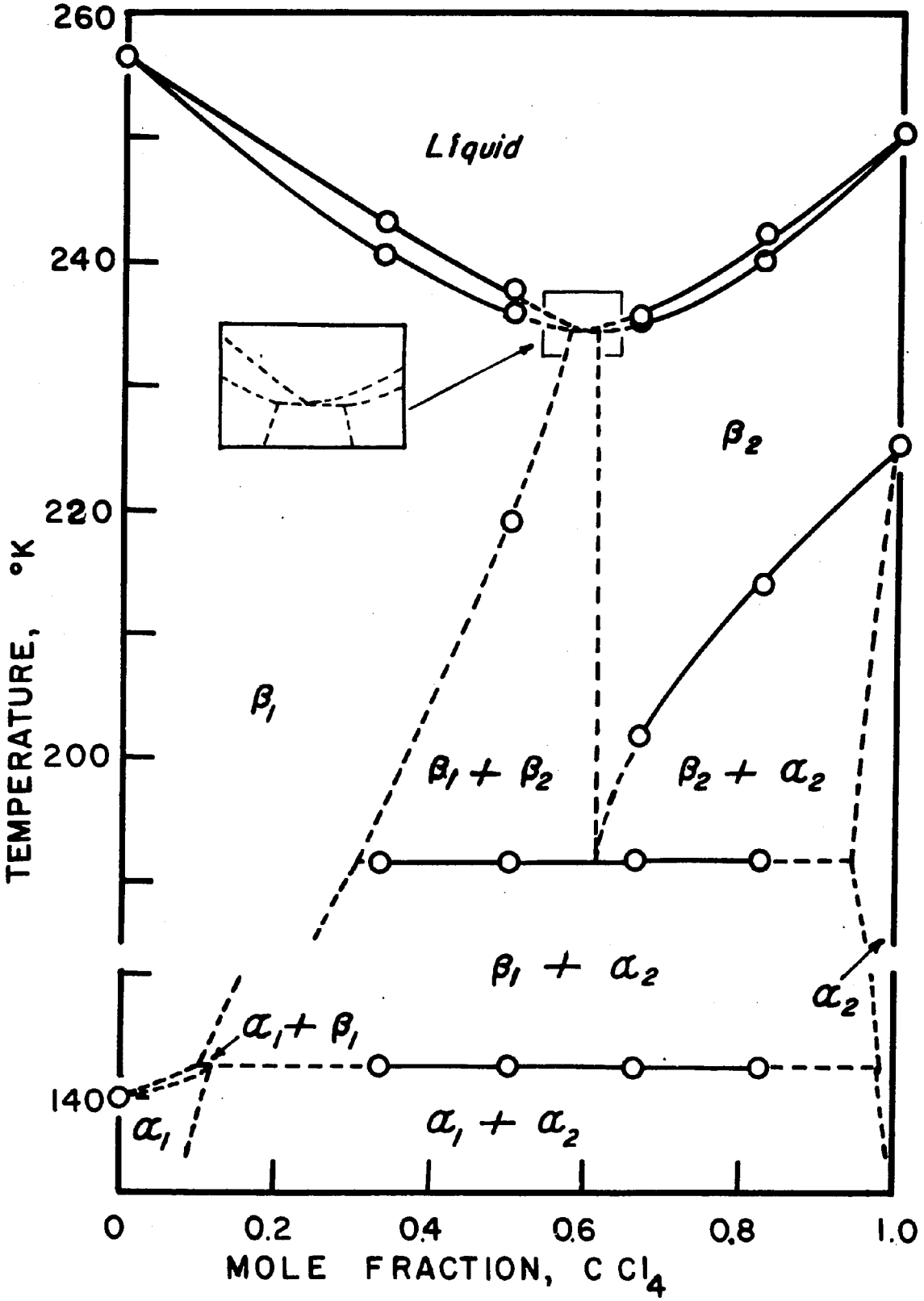

260
240
220
200
140
TEMPERATURE, °K
Liquid
β_2
β_1
$\beta_1 + \beta_2$
$\beta_2 + \alpha_2$
$\beta_1 + \alpha_2$
α_2
$\alpha_1 + \beta_1$
α_1
$\alpha_1 + \alpha_2$
0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION, CCl_4

Figure XIV

tetrachloromethane-trimethylchloromethane[67]), nuclear magnetic resonance measurements (e.g., as on the systems cyclopentane-2,2-dimethylbutane[4] and 2,2-dimethylbutane-2,3-dimethylbutane[5]), and possibly other techniques would be desirable for a better understanding of this system.

APPENDIX I - DEFINITIONS

Mixing Functions

The increment on mixing of a relevant thermodynamic function is defined as the value of the function for the mixture minus the additive value of that function at the same temperature and pressure, i.e.,

$$G^{Mixing} = G_{Mixture,T,P} - (X_1 G_{1,T,P} + X_2 G_{2,T,P})$$

where G = the thermodynamic function,

X = mole fraction, and

1,2 refers to components 1 or 2 respectively.

Excess Functions

The excess functions are defined as the difference between the thermodynamic functions of mixing for an actual system and the value corresponding to that of a perfect solution at the same temperature, pressure, and composition; i.e.,

$$G^E = G^M_{actual} - G^M_{perfect}$$

where the superscript E refers to excess and M refers to mixing.

Perfect Solution

A solution is described as perfect if the Gibbs free energy of mixing takes the form:

$$G^{M}_{perfect} = RTX_1 \ln X_1 + RTX_2 \ln X_2$$

and the entropy of mixing takes the form:

$$S^{M}_{perfect} = - RX_1 \ln X_1 - RX_2 \ln X_2 \quad .$$

Therefore, in a perfect solution all thermodynamic functions of mixing except those containing the entropy are zero. And consequently, $H^E = H^M$ and $V^E = V^M$.

APPENDIX II - ADDITIONAL TABLES

TABLE A. ILLUSTRATION OF THE RELATIONS BETWEEN EXCESS FUNCTIONS AND INTERMOLECULAR FORCES APPLIED TO THE SMOOTH POTENTIAL CELL MODEL*

Assumptions made about intermolecular forces	Predicted excess functions
Geometric mean	
$E^{*}_{AB}{}^{2} = E^{*}_{AA}\, E^{*}_{BB}$	$G^E > 0$
$\theta = -\frac{d^2}{8}$	$H^E > 0$
	$V^E < 0$
	$S^E < 0$
Arithmetic mean	
$E^{*}_{AB} = \frac{E^{*}_{AA} + E^{*}_{BB}}{2}$	$G^E > 0$
$\theta = 0$	$H^E < 0$
	$V^E < 0$
Addition compound	
$E^{*}_{AB} \neq E^{*}_{AA} \approx E^{*}_{BB}$	$G^E < 0$
$d = 0$	$H^E < 0$
	$V^E < 0$
$\theta > 0$	$S^E < 0$
Interaction for BB much more important than AA or AB	
$E^{*}_{AA} \approx E^{*}_{AB} \ll E^{*}_{BB}$	$G^E > 0$
	$H^E > 0$
$\theta = -\frac{\lvert d \rvert}{2}$	$V^E > 0$

TABLE A (Cont.)

Interactions AB are of the order of BB, while AA is much smaller

$$E^*_{BB} \approx E^*_{AB} \gg E^*_{AA}$$

$$\theta = + \frac{|d|}{2}$$

$$G^E < 0$$
$$H^E < 0$$
$$V^E < 0$$

Prigogine's notation

d = the difference in the "depth" of interaction of molecules AA and BB

$$d = \frac{1}{E^*_{AA}} \left(E^*_{BB} - E^*_{AA} \right)$$

θ = the value of E^*_{AB} with respect to the arithmetic mean of E^*_{AA} and E^*_{BB}

$$\theta = \frac{1}{E^*_{AA}} \left(E^*_{AB} - \frac{E^*_{AA} + E^*_{BB}}{2} \right)$$

---

* Compiled from Prigogine, I., "The Molecular Theory of Solutions," North-Holland Publishing Company, Amsterdam, and Interscience Publishers, Inc., New York (1957).

TABLE B. SOME BINARY SYSTEMS OF PLASTIC CRYSTALS

SYSTEM	REFERENCES FOR PHASE DIAGRAM DATA	REFERENCES FOR OTHER MIXING DATA
Argon-Krypton	68,69	70,71,72
Methane-Krypton	73,74	75
Methane-Tetrafluoromethane	76	75
Methane-Hydrogen Sulfide	77	
Tetrachloromethane-Tetrabromomethane	78,79	
Tetrachloromethane-Cyclohexane	7,8	6,80,81,82
Tetrachloromethane-Tetrahydrofuran	83	
Tetrachloromethane-Trimethylchloromethane	67,84	11
2,2-Dimethylbutane-2,3-Dimethylbutane	2,5	
Cyclopentane-2,2-Dimethylbutane	2,3,4	
d and l-Camphoroxime	85,86	
2,2,3,3-Tetramethylbutane -2,2,3-Trimethylbutane	87	
Perfluorocyclohexane-Cyclohexane	24	
Tetramethylmethane-Tetrachloromethane	This Research	10,11

TABLE C. COMPARISON OF EXCESS FUNCTIONS CALCULATED BY CELL MODEL WITH EXPERIMENT*
(X = 0.5; Units: cal, gram-mole solution, °K, cm^3)

SYSTEM	TEMP.	H^E		TS^E		G^E		V^E	
		EXP.	CALC.	EXP.	CALC.	EXP.	CALC.	EXP.	CALC.
Cyclohexane + Benzene	298	190±10	100±30	115±10	30±15	76±1	70±15	0.65±.01	0.4±.2
Cyclohexane + CCl_4	298	37± 4	25± 5	20± 5	8± 2	17±1	17± 3	0.16±.01	0.1±.05
Benzene + CCl_4	298	26± 2	25±10	7± 3	8± 4	19±1	17± 6	0.01±.01	0.1±.1
Benzene + CS_2	298	135±15	150	72±20	50	63±5	100	0.75±.05	0.7
$SiCl_4$ + CCl_4	298	33± 3	25	13± 7	7	20±4	17	0.02±.01	0.05
Cyclohexane + CMe_4	273	----	32± 5	----	- 8± 3	44±5	40± 8	-1.00±.2	-0.2±.1
CCl_4 + CMe_4	273	74± 3	55±10	- 2± 6	- 5± 5	76±3	60±15	-0.5 ±.1	-0.2±.1
Benzene + CMe_4	273	----	120±30	----	10±10	135±5	110±20	-0.5 ±.1	-0.2±.1

* From A. Englert-Chwoles, Thesis (1955)

TABLE D. THERMODYNAMIC FUNCTIONS OF TETRAMETHYLMETHANE AND TETRACHLOROMETHANE
(Units: cal, gram-mole, °K)

T	C_p	$S° - S°_0$	$H° - H°_0$	$-(F° - H°_0)/T$
		Tetramethylmethane*		
15	2.198	0.778	8.83	0.200
20	3.960	1.661	24.22	0.451
25	5.538	2.720	48.09	0.797
30	6.802	3.846	79.06	1.212
35	7.834	4.974	115.72	1.668
40	8.735	6.080	157.17	2.151
45	9.495	7.154	202.80	2.647
50	10.19	8.191	252.02	3.150
60	11.55	10.169	360.73	4.157
70	12.92	12.055	483.31	5.151
80	14.46	13.884	620.4	6.129
90	15.99	15.675	772.6	7.090
100	17.60	17.442	940.5	8.037
110	19.35	19.200	1125.1	8.972
120	21.33	20.967	1328.3	9.898
130	23.56	22.761	1552.5	10.818
135	24.74	23.672	1673.3	11.277
150	24.84	30.679	2661.3	12.938
180	26.86	35.390	3437.3	16.294
200	28.12	38.285	3987.0	18.350
230	30.39	42.362	4862.9	21.219
245	31.77	44.325	5329.1	22.573
250	32.23	44.971	5489.1	23.015
260	36.24	49.327	6604.6	23.925
270	37.86	50.716	6972.6	24.892
280	38.45	52.095	7351.7	25.839
273.15	37.70	51.15	7091	25.19

TABLE D (Cont.)

Tetrachloromethane**

20	5.002	1.872	25.82	0.582
25	6.756	3.186	55.42	0.969
30	8.078	4.541	92.66	1.452
35	9.087	5.865	135.68	1.988
40	9.878	7.132	183.17	2.553
45	10.52	8.334	234.22	3.129
50	11.08	9.472	288.24	3.707
60	12.06	11.579	404.0	4.846
70	13.01	13.509	529.3	5.948
80	13.99	15.310	664.3	7.006
90	15.01	17.016	809.3	8.025
100	16.01	18.650	964.4	9.006
110	16.98	20.222	1129.4	9.955
120	17.88	21.739	1303.8	10.874
130	18.72	23.203	1486.8	11.766
135	19.11	23.917	1581.4	12.203
150	20.26	25.991	1876.8	13.479
180	22.76	29.898	2520.9	15.893
200	24.76	32.398	2995.7	17.419
230	27.97	40.945	4883.4	19.712
245	29.30	42.753	5312.8	21.068
250	29.75	43.349	5460.4	21.508
260	31.16	46.969	6372.3	22.461
270	31.24	48.147	6684.3	23.390
280	31.33	49.284	6997.1	24.295
290	31.41	50.385	7310.8	25.176
300	31.49	51.451	7625.3	26.034
273.15	31.27	48.51	6783	23.68
298.15	31.48	51.26	7567	25.88

* Calculated by integrating Aston and Messerly's heat capacity data, cf., reference 18.

**Calculated by integrating Hicks et al.'s heat capacity data, cf., reference 19.

APPENDIX III - THERMAL HISTORY OF RUNS

The following account of the thermal history of runs is given is chronological order. (Cf. Table III.)

The N_{CCl_4} = 0.501 (1-1) Mixture

The N_{CCl_4} = 0.501 mixture was the first composition of the system tetramethylmethane-tetrachloromethane studied in this investigation. It also was the first sample to be measured in the new Mark II cryostat and the first one on which automatic adiabatic shield control was used in low temperature calorimetry in this laboratory. Therefore, there were a large number of experimental runs made during the experimental heat capacity determination of this composition. About the first one-third of the total runs made (i.e., Series I through VI, and Series XII) involved experimentation and testing (i.e., cooling rates, automatic shield control settings, and sensitivity of automatic shield control). The thermal histories of all the runs of this composition are summarized below.

Series I (160 to 190°K, cf. Table III) was made after loading the calorimeter into the cryostat and cooling from room temperature to about 160°K. For this series the calorimeter was cooled at the "contacted-to-can" position over a period of about 20 hours. (At the conclusion of Series I,

the automatic shield control went out of control, i.e., caused by running into the unexpected transition at 191.6°K.) Before the runs of Series II were made, the calorimeter was heated to 229°K (just below fusion), held there for about three hours, and cooled at the "can" position for 14 hours to about 180°K. The first three runs of Series II are believed to be made in an undercooled phase (180 to 205°K); Runs A and B through Transition III and fusion and a series of runs in the liquid range to about 297°K were then made. Series III (241 to 294°K) was made after cooling at the maximum rate from 297 to 241°K (remaining in the liquid range) over a period of about two and a half hours.

Series IV (133 to 185°K) was made after cooling from 294 to 133°K (at "can" position) over a period of about 40 hours. It included Runs C through Transition I and some runs in the region between Transitions I and II. After this (due to loss of shield control) the calorimeter and sample were heated to 225°K, held at that temperature overnight (about 15 hours), and cooled (at "can") to about 175°K (about 23 hours). Then, Series V runs through Transitions II (Runs D) and III (Runs E) and fusion (Runs F) were made from 175 to 247°K.

Runs of Series VI (129 to 146°K) (Runs G) were made after cooling from 247 to 235°K at the "operate" position, and then cooling at "shield" to 129°K (total cooling period about 82 hours). After Series VI was made, electrical leaks developed in the Mark II cryostat. Therefore, the cryostat

had to be disassembled, repaired, reassembled, and tested. After testing, the calorimeter and sample were cooled at the "shield" position from room temperature to about 122°K over a period of 5.5 days.

It is desirable to have a continuous series of runs through all the transitions (I,* II,* III,* and fusion) but at the beginning of Transition II, Series VII (Runs I), unexpected shield control trouble overheated the calorimeter and sample beyond Transition II; therefore, Series VIII was made after cooling again (to 179°K). The runs of this series covered Transitions II and III (Runs J and K) and a ΔH of fusion run (Run L) through fusion.

After Series VIII, the calorimeter and sample were cooled in the optimum procedure described on page 24 (i.e., cooled at "operate" position to about 180°K, then at "contacted-to-shield" position to 138°K over a period of 5.5 days and finally at the maximum rate to the desired temperature).

Series IX (69 to 76°K), X (62 to 133°K), and Series XI (65 to 104°K) were made while testing the sensitivity of the automatic shield control. At the conclusion of Series XI the calorimeter and sample were cooled to the liquid helium temperature region. Series XII (13 runs, Runs M) were made from 4.4 to 18.6°K; these runs (the results of which are not reported) are considered as test runs to determine the optimum shield control settings for operation in the liquid helium temperature region.

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* Based on consecutive numbers with increasing temperature.

Series XIII (8.5 to 18.7°K) was made with manual shield control as a check of the reliability of the automatic shield control in this temperature region. Series XIV was made after cooling again to 4.6°K using automatic shield control. Series XV consisted of an enthalpy-type run (Run N) from about 14.7 to 24.5°K to cover the overlap of the previous series and regular heat capacity runs up to 64.2°K. Series XVI contained two regular heat capacity runs for check in the overlap, a long enthalpy-type run (Run O) across the region which has been covered in Series X and XI, a regular heat capacity check run just before Transition I, and a ΔH of transition run (Run P) across Transition I.

Series XVII is a continuation of Series XVI with some overlap. This series started at 149°K with an enthalpy-type run (Run Q), a ΔH of transition run (Run S), a series of runs (Runs T) through Transition III, and finally a ΔH of fusion run (Run U). The final series, Series XVIII, was made after cooling from the liquid region to just below fusion (231°K). It contained a series of runs (Runs V) through fusion and runs in the liquid range ending at about 305°K.

The N_{CCl_4} = 0.334 (2-1) Mixture

The N_{CCl_4} = 0.334 mixture was the second composition of this system studied. The sample was cooled at the "operate" position from room temperature to 163°K over a period of about four days (89 hours); then it was cooled at the "shield"

position to 127°K (21 hours); and finally, it was cooled at the maximum rate to about 70°K. At this point an attempt to add liquid helium and cool to the liquid helium temperature region failed, due to either an air or an ice plug in the helium transfer line. Therefore, Series I was started at about 75°K. It contained a series of regular heat capacity runs in the region below Transition I; Runs A through Transition I; a series of runs in the region between Transitions I and II; Runs B through Transition II; a series of small ΔT runs in the region between Transition II and fusion (region where Transition III appeared in the previous composition); and finally, a series of runs (Runs C) through fusion into the liquid range up to about 254°K.

At the conclusion of Series I the diffusion pump was turned off; the vacuum in the cryostat was broken with helium gas; and the plug in the helium line was removed by heating. After the removal of the plug the calorimeter and sample were cooled again (at "operate" from room temperature to 169°K, then at "shield" to about 135°K, and finally, at the maximum rate to about 63°K). At about 63°K the nitrogen in the helium refrigerant tank was boiled off and replaced by liquid helium. Series II was started at about 9°K (about 26 hours after the addition of liquid helium). Regular heat capacity runs were made with manual shield control from 9 to 49°K. Series III over the region of 44 to 82°K was made with automatic shield control.

Then, the calorimeter and sample were heated to 135°K

and Runs D of Series IV were made through Transition I. At about 145°K, the sample and calorimeter were contacted to "shield" and cooled overnight (15 hours) to about 138°K, and then Runs E of Series V were made. The runs of Series V are believed to be made in a partly undercooled phase (i.e., calorimeter self-warming yielded large, positive drifts). After Series V (149°K), the calorimeter and sample were again contacted to "shield" and cooled overnight (16 hours) to 139°K, and the ΔH of transition run (Run F) of Series VI was made. This run also began in a partly undercooled phase (large positive fore-drift and larger than calculated ΔT for run). After this run the calorimeter and sample were again cooled at the "shield" position overnight to 139°K, and since there were still signs of undercooling, it was cooled further at the maximum rate to 132°K before Series VII was started.

Series VII contained a regular heat capacity run in the region below Transition I; a ΔH of transition run (Run G) across Transition I; an enthalpy-type run (Run H) in the region between Transitions I and II; a ΔH of transition run (Run I) across Transition II; an enthalpy-type run (Run J) across the region between Transition II and fusion; and finally, a series of constant energy runs (Runs K) through fusion to about 245°K. Then the calorimeter and sample were cooled at "operate" overnight (9 hours) to 231°K. The final series, Series VIII, consisted of a ΔH of fusion run (Run L) through fusion and a series of runs in the liquid range to about 300°K.

The N_{CCl_4} = 0.666 (1-2) Mixture

The third composition of this system studied by low temperature calorimetry was the N_{CCl_4} = 0.666 mixture. The sample of this composition was cooled all the way down to the liquid helium temperature region before any measurements were made. The sample was cooled at "operate" from room temperature to 140°K over a period of about 6 days (141 hours), then cooled at "shield" position to 135°K (19 hours), at "can" position to 125°K (92 hours), and finally, at "maximum" to about 66°K (22 hours). Then, 26 hours after the subsequent addition of liquid helium, the calorimeter and sample reached a temperature of about 10.2°K.

Series I was started at about 10.2°K (the cooling rate for this sample at this temperature seemed to be almost zero and since there was no apparent anomaly at low temperatures for this system, it was therefore decided to start measurements at this temperature rather than wait for the customary starting temperature of about 4.5°K). The runs of Series I were made with manual shield control. At the conclusion of Series I (39°K) the sample was cooled at the "shield" position to provide some overlap before the start of the next series.

Before Series II was started, the calorimeter and sample were heated for a few minutes (i.e., a few degrees). It was intended to start this series with about two runs overlap, but during the energy input of the first run

"oscillations" in the energy readings [i.e., unsteady heater current (I_H) and heater potential (E_H) readings] developed. Therefore, the run was stopped, and tests were made to try to find the cause of oscillation. Finally, after the "oscillations" disappeared, Series II was started at 37°K and continued to 73°K with manual shield control.

Series III was started at about 70°K with automatic shield control. This series contained: a series of regular heat capacity runs in the region below the first transition; a series of runs (Runs A) through Transition I; a series of runs in the region between Transitions I and II; a series of runs (Runs B) through Transitions II and III; several runs in the region between Transition III and fusion (i.e., plastically crystalline region); and finally, a series of approximately constant energy runs through fusion to 244°K. Throughout Series III at the start of Runs A, there were some "oscillations" in I_H and E_H readings during energy inputs. in most cases the "oscillations" were small and since all the runs through the transition region were made with the same current and essentially the same length of time of energy input, corrections in the energy readings were made by extrapolation. Therefore, the series was continued to the liquid range.

After the last run of Series III cooling was started again (first at "operate" to 136°K over about 5.5 days, then at "shield" until about 131°K. Series IV (131 to 153°K) consisted of a check run in the region just below Transition

I and a series of runs (Runs D) through Transition I. Before Series V was started, the calorimeter and sample were cooled at "operate" until 132°K (64 hours). Series V (132 to 206°K) contained a regular heat capacity run for checking; a ΔH of transition run (Run E) across Transition I; an enthalpy-type run (Run F) across the region between Transitions I and II; a long ΔH of transition run (Run G) across Transitions II and III; and an additional run to ascertain that the sample was completely out of Transition III. For a check of the magnitudes of Transitions II and III the sample was cooled again (at "operate" over 35 hours) to about 186°K. Then the following runs of Series VI were made: Run H across Transition II; Run I across Transition III; Run J across the plastically crystalline region; and Run K through fusion.

Finally the sample was cooled below fusion, and Series VII was made. This series included a ΔH of fusion run (Run L) and a series of runs in the liquid range to 304°K.

The N_{CCl_4} = 0.826 (1-5) mixture

The final composition of the system tetramethylmethane-tetrachloromethane studied was the N_{CCl_4} = 0.826 mixture. The calorimeter and sample were cooled at "operate" from room temperature to about 184°K (three days); then at "shield" to 138°K (19 hours); and at "maximum" to 72°K (35 hours). Liquid helium was then added. After 35 hours the calorimeter and sample cooled to about 5°K. Series I was made with

manual shield control from 5.2 to 33.4°K. Before Series II (29 to 61°K) was started, the calorimeter and sample were heated from about 24 to 29°K. Manual shield control was used for the runs of Series II.

Series III was made with automatic shield control and a few degrees overlap in temperature. This series included: a series of runs in the region below Transition I; two runs (Runs A) across Transition I; a series of runs in the region between Transitions I and II; a ΔH of transition run (Run B) across Transition III; a few runs in the region just below fusion; a series of runs (Runs D) through fusion; and finally, a few runs in the liquid region.

After Series III the calorimeter and sample were cooled at "operate" to 182°K (60 hours); then cooled at "shield" to 140°K (30 hours); and at "maximum" to 136°K (4 hours). Before the start of Series IV it was found that the sample had undercooled (i.e., calorimeter self-warming gave a large positive drift). Therefore, the calorimeter and sample were heated to above the first transition to 149°K and cooled at "shield" to about 124°K (35 hours). Then the calorimeter and sample were heated from 124 to about 126°K, and Series IV was made. Series IV included a regular heat capacity run in the region below Transition I and a series of runs (Runs E) across Transition I.

After Series IV the calorimeter and sample were cooled at "shield" to 133°K (17 hours) and heated from about 133 to 136°K. Series V (136 to 299°K) consisted of a ΔH of

transition run (Run F) across Transition I; an enthalpy-type run (Run G) in the region above Transition I; a series of small ΔT runs in the region between Transitions I and II (some small anomalous heat capacity behavior is apparent in this region, i.e., 168 to 175°K); an enthalpy-type run (Run H) just below Transition II; a series of runs (Runs I) across Transition II; a ΔH of transition run (Run J) across Transition III; an enthalpy-type run (Run J) across the plastically crystalline region; a ΔH of fusion run (Run L) through fusion; and finally, a series of runs in the liquid region to 299°K.

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