THERMODYNAMICS AND X-RAY STUDIES OF INDIUM-THALLIUM ALLOYS

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ABSTRACT

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In the present investigations x-ray and thermodynamic studies have been conducted for the In-Tl alloys in the composition range of 16.0 to 22.0 atom percent Tl. The thermodynamic studies result in direct determination of all thermodynamic parameters including the enthalpy and free energy of fcc to fct transformations for the above alloy compositions. From the results of x-ray investigation the lattice parameters of the low temperature phase (which is fct) have been determined for all alloy compositions. The enthalpy of phase transformation and the transformation temperatures bears a straight line relationship with the volume change. This seems to indicate that the strain free energy increases in the alloys containing larger percentage of Tl. This increase in strain free energy increases the non-chemical free energy change associated with the transformation. For the transformation to take place the chemical free energy change must overcome the non-chemical free energy change. This is obtained by increasing the degree of undercooling.

The free energy of mixing ΔFm^* curves show significant variation which have been interpreted in terms of short range order parameter.

ACKNOWLEDGEMENTS

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LIST OF SYMBOLS

SYMBOL	DEFINITION	UNITS OR REFERENCE
a/o	Atom percent	
°A	Angstrom	°A=10^{-8} cm.
a and c	Lattice parameters	°A
c/a	Axial ratio of crystal structure	
H_T	Enthalpy at temperature T	Calories per mole
H_{273}	Enthalpy at temperature 273°K	Calories per mole
Tl	Thallium	
In	Indium	
F_T	Free energy at temperature T	Calories per mole
F_{273}	Free energy at temperature 273°K	Calories per mole
$\int$	Integral sign	
ΔF^{m*}	Change in apparent free energy of mixing	Calories per mole
ΔH^{m*}	Change in apparent enthalpy of mixing	Calories per mole
ΔS^{m*}	Change in apparent entropy of mixing	Calories per mole per °K
ΔH^{m}_{T}	Enthalpy of mixing at temperature T	Calories per mole
ΔH^{Tl}_{T}	Enthalpy of Thallium at T°K	Calories per mole
ΔH^{In}_{T}	Enthalpy of Indium at T°K	Calories per mole

SYMBOL	DEFINITION	UNITS OR REFERENCE
N_{T1}	The mole fraction of T1	
N_{In}	The mole fraction of In	

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CHAPTER I

INTRODUCTION

The indium-thallium system has been extensively studied, particularly in relation to the fcc to fct martensitic transformation in the composition range of 16 to 25 atom percent Tl. However, the phase diagram is not completely established. From available informations Hansen[1] compiled a phase diagram shown in figure 1.

Lattice parameter measurements reported by Valentiner[2] for the alloys having compositions 5.9, 12.3, 19.4 and 27.3 atom percent Tl reveals that Tl additions cause the axial ratios of the fct lattice of In (c/a=1.075) to approach unity. According to Valentiner the alloy with 27.3 atom percent Tl is fcc with a=4.76A°, Makarov[3] clarifies that the tetragonal structure is stable up to about 25.0 atom percent Tl. Since no two phase region between both structures can be found, it is concluded that the transition fct → fcc is continuous.

Liquidus determined by Kurnakow and Puschin[4] indicate a peritectic equilibrium between the two primary solid solution at 180°C with the peritectic horizontal assumed to extend from about 45.5 to 56.0

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[1] Hansen, <u>Binary Phase Diagram</u>, 1968.

[2] S. Valentiner, Z. Metallkunde, <u>32</u>, 1940, p. 244-248.

[3] E.S. Makarov, Izvest Akad. Nauk, U.S.S.R., (Khim), 1950, p. 485-491.

[4] N. S. Kurnakow and N.A. Puschin, Zeit Anorg. Chem., <u>52</u>, 1907, p. 242-243.

atom percent Tl. Room temperature x-ray analysis of alloys with 30-100 atom percent Tl indicates that the fcc phase is present in the alloys containing up to at least 69 atom percent Tl and that alloys with 62-85 atom percent Tl are found to contain a bcc phase which co-exists with α phase between 62 and 69 atom percent Tl.

Klemm and Orlamünder suggest a tentative phase diagram, similar to that shown in figure 1. The two phase field extends from the region 38.5-58.0 atom-percent Tl at the peritectic temperature of 171°C to approximately 62-69 atom percent Tl at room temperature.

L. Guttman's[6] x-ray studies at 24°C confirms the gradual decrease of axial ratio of the pure In from c/a=1.075 to 1.023 at 22.24 atom percent Tl. The metallographic studies show the existence of a transformation from fct to fcc in indium rich solutions. From this investigation it is observed that there exist no two phase region separating the high temperature fcc phase to low temperature fct phase. All diffraction patterns at room temperature contain only lines from one structure or the other, never from both. It is concluded that the transformation fct $\rightleftarrows$ fcc was of the second order.

The conclusions of Guttman are criticized by A.H. Geisler and Martin[7] who point out that the experimental data presented by [6] is not sufficient to decide whether or not the transformation is first or second order. However, preference is given to the former.

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[5] W. Klemm and E. Orlamunder, Z. Amorg. Chem., 256, 1948, p. 242-243.

[6] L. Guttman, Trans. AIME, 188, 1950, p. 1472-1477.

[7] A.H. Geisler and D. L. Martin, Trans. AIME, 191, 1951, p. 1056-1057.

A diffusionless fcc → fct phase transformation is reported by Bowles, Barrett and Guttman.[8] The transformation takes place at approximately 105°C at 18.0 atom percent Tl and 25°C at 23.0 atom percent Tl using polycrystaline samples. Buckart and Read[9] investigate the transformation by using single crystals, to eliminate the transformation constraint imposed by adjoining grains. According to [9] the diffusionless transformation from cubic to tetragonal produces twin lamellae on {101} planes with sub-lamellae also on selected {101} planes. It progresses only with falling temperature, by the movement of the interface parallel to the main lamellae, and ceases when the cooling stops. They propose that the changes in orientation produced by the transformation is due to double shear mechanism. An analysis of the diffusionless transformation permits the complete determination of the transformation geometry from a knowledge of the lattice parameters of the phases involved. The application of stress to the specimen raises the transformation temperature on both heating and cooling. The transformation is found to be first order from the results of the dilatometer measurements.

Electrical resistivity studies of Stout and Guttman[10] in the composition range of 0 to 50 atom percent Tl, from the boiling point of helium to room temperature shows an anomalous behavior of the

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[8] J.S. Bowles, C.S. Barrett and Guttman, Trans. AIME, 188, 1950, p. 1478-1485.

[9] Bukart and Read, Trans. AIME, 197, 1953, p. 1516-1524.

[10] J.W. Stout and Lester Guttman, Physical Review, 88, 1952, p. 713-714.

resistivity. The specimen containing 30.0 atom percent Tl indicates that it undergoes a transformation from fcc to fct in the temperature interval 45-60°K. Such an assumption fit well an extra-polation of the composition-temperature curve of the cubic-tetragonal transformation found by Guttman.

Geisler[11] proposes that martensitic transformation in In-Tl system should be regarded as accompanied by strains. Basinski[12] summarizes these views by stating that the growth mechanism proposed by Geisler[11] for In-Tl is incorrect. The nucleation of the tetragonal phase may result from the formation of coherent platelets on {111} planes. The growth of such nuclei their twins might originally require thermal activation energy for individual atomic movements, but would degenerate into a shear process as soon as a critical size is reached. When the incomplete planes reaches a certain size, the transformation dislocation will glide with little or no thermal activation spreading the martensite structure over the whole atomic plane in contrast to the dislocation theory. The atom by atom theories require the formation of a new two-dimensional nucleus on each succeeding atomic plane. The kinetics of the transformations do not support this interpretation, particularly the formation of macroscopic regions of the homogeneous strain. The existence of macroscopic surface tilts is strong evidence that the characteristic reaction is the growth mechanism.

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[11] A.H. Geisler, Acta Met., 1, 1953, p. 260-281.

[12] Z.S. Basinski and J. W. Christain, Acta Met., 1, 1953, p. 759-761.

Basinski and Christain[12] report the transformation from fcc to fct in alloys containing approximately 18.5 atom percent Tl, using cine´-photograph and x-ray methods. After suitable annealing single crystal transforms by the migration of either a single or a double interface from one end of the specimen to the other end. In single interface transformations, a twinned tetragonal structure is produced in accordance with the double shear mechanism. Two types of double interface are observed to lead to a tetragonal single crystal. Each region of the crystal first transforms to twinned tetragonal. The kinetics of transformation observed are similar to those in gold-cadmium alloys.

There are two possible ways of distinguishing between the two mechanisms. First, a precise determination of the orientation of the plane of the sub-bands should permit one to distinguish between the {111} twinning planes of the tetragonal product assumed by the growth and twinning mechanism and {111} planes of second shear in the matrix distorted by the first shear. Such a determination has not yet been made. Secondly, a consideration of the stability of the twinned array is helpful in deciding whether it is necessary for the generation of the new structure or merely for accomodating the strain between the tetragonal product and the cubic parent phase.

Geisler[13] in his later research reports that the descriptions of the atom movements do not constitute the mechanism. The distinction between two mechanism is that the heterogeneous shear which causes microscopic surface tilts is regarded as part of the process in the

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[13] A. H. Geisler, Acta Met., 2, 1954, p. 639-642.

generation of the new crystallographic structure, at any particular point in or around the growing particle in the mechanism based on the growth with spontaneous deformation. Geisler supports the latter viewpoint. On this basis the characteristic of martensitic transformation is that it may be a shear product and not necessarily a product of shear.

The existence of a two phase region is reported by Moore, Graham, Williamson and Raynor[14] on the basis of diffractometer results. Further evidence is obtained from a Debye-Scherrer film of an alloy containing 22.5 atom percent Tl at 20°C, which shows three {400} reflections. These can be due to the co-existence of a cubic and tetragonal phase. If the transformation is of the second order, the chemical free energies of the two phases are regarded as equal, so that the two phases will co-exist in any relative proportions. The fact that there is a range of compositions and temperatures over which these phases exist is reproducible proportions, suggests either that the chemical free energies of the co-existing phases are not equal, or that the internal strain and surface energy factors are always reproducible. This later possibility is unlikely, on this evidence, therefore phase transformation appears to have first order characteristics. The diffusion must play an insignificant part in the mechanism of the transformation.

Basinski and Christain[15] discuss the crystallographic interpenetrating "main bands" observed in polycrystaline alloys after the cubic

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[14] A. Moore, J. Graham, G.K. Williamson and G.W. Raynor, Acta Met., 3, 1955, p. 579-589.

[15] Z.S. Basinski and J.W. Christain, Acta Met., 4, 1956, p. 371-378.

to tetragonal transformation. Experimental confirmation of the predicted twinning pattern for the case of a set of parallel bands crossed by a single interface is obtained. Cine´-photography shows that interpenetrating bands are probably not the result of growth from a common nucleus, but are merely a consequence of the ease with which one set of bands can accomodate the shear strain produced by another set. Bilby's[16] theory of surface dislocation provides a convenient description of the transformation patterns.

On the basis of determination of enthalpies of diffusionless martensitic transformation in In-Tl alloy 20.5 atom percent Tl and the determination of effect of tensile and compressive stresses on the transformation, Bredel[17] concludes that the stress dependence can be expressed by modified Clausius-Clapeyron equation showing the effect of hydraustatic pressure on M_S temperature.

Vaughan and Drickamer[18] studied the effect of pressure to several hundred K bars on the lattice parameters of In-Tl alloys. They report that the compressibilities are very close in shock wave values, but smaller than those of Bridgman[19] or Vereschangin[20] . Mayerhoff and

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[16] B.A. Bilby, Report of Bristol Conference on Defects in Crystalline Solids, 1954, (The Physical Society).

[17] B. Bredel, Zeit fur Metallkunde, 55, 1964, p. 117-122.

[18] R.W. Vaughan, H.G. Drickamer, J. Phys. Chem. Solids, 26, 1965, p. 1549-1553.

[19] Bridgman, P.W., Proc. Amer. Acad. Arts and Sci., 74, 1942, p. 425.

[20] Verschagin, L. f., Kabalkina, S.S. and Troitsha ia Z.V., Dokl. Akad. Nauk, USSR, 158, 1964, p. 1061.

Smith[21] report the phase diagram of the thallium rich region of the In-Tl system from atmospheric pressure to 5.5 K bars, primarily from electrical resistivity data obtained as a function of composition, temperature and pressure. Corroborative x-ray diffraction data are taken at atmospheric pressure. Extrapolation of the results of their investigation to high pressures indicates that a triple point occurs between three solid alltropes of Tl at 160°C and 35.8 K bars. The high pressure phase is continuous with the fcc phase observed at atmospheric pressure for Tl containing 40-77 atom percent In. The results indicate that the crystal structure of the high pressure allotroph of Tl is fcc. The remaining two phases in equilibrium at the triple point are continuous with the bcc high temperature phase observed for pure Tl at atmospheric pressure.

Luo, Hagen and Marriam[22] find that the samples containing 29 atom percent or less thallium are at least 95% and probably 99% or more transforms to the tetragonal phase at 3 °K. The samples containing 29-31 atom percent Tl can be two phase or they can be single phase tetragonal but severely strained.

Adler and Margolin[23] describe the experimental study of the behavior of the Tl rich portion of the system (50 to 98 atom percent Tl.) The pressure vs composition diagrams at room temperature, 90°

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[21] R.W. Mayerhoff and J.F. Smith, Acta Met., 11, 1963, p. 529-536.

[22] H.L. Luo, J. Hagen, and M.F. Merriam, Acta Met., 13, 1965, p. 1012-1013.

[23] R.N. Adler, H. Margolin, Acta Met., 14, 1966, p. 1645-1658.

and 135°C are interpreted from these results and combined in a P-T-x diagram. At 37 K bars and at room temperature thallium transforms from the hcp to fcc modifications. The addition of In to Tl lowers the pressure of this transition, thus suggesting the possibility that with sufficient addition of In, the fcc phase can be retained at ambient conditions. Miscibility gap formation in the fcc phase are suggested at the three temperatures studied. There is also an indication that another gap forms at temperature below those investigated. The existence of a peritectoid and monotectoid transformation at room temperature and at 90°C is indicated and the phase boundaries in P-x diagram with two quadruple points - one at 10°C and 6 K bar between four solid phases and the other slightly above atmospheric pressure at 180°C between three solid phases and a liquid.

Khayutin and Spichinetsky[24] show from microscopic examination of preliminary polished surfaces of specimens of In and In-Tl alloys containing Tl up to 40 atom percent that the In deforms plastically by slip and In-Tl alloys by twinning. The later effect attributes to the formation of Cottrell atmosphere on gliding dislocations, to a general reduction in the degree of lattice tetragonality and corresponding reduction in the energy for twin formation and to the segregation of Tl on twinning dislocation which leads to an additional reduction in the degree of tetragonality. Plastic deformation of In-Tl alloys with a martensitic structure promotes further progress of the martensitic transformation at a constant temperature.

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[24] Khayutin, S.G., Spichinetsky, E.S., Fizika Metallov i. Metalloredenie, 22, 1966, p. 432-437.

Pahlman and Smith[25] use the interferometric technique to determine the expansion behavior of In-Tl in the composition range 19-35 atom percent Tl and in the temperature range 4.2° to 360°K. Extensive data for four single crystals in this region, and supplementary data from five polycrystaline specimens indicate the existence of a narrow two phase region less than 0.5 atom percent in width, between the fcc and fct phase fields which is consistent with the fcc ⇄ fct transformation being first order. Two temperature regions of anomalous expansion are found for the fcc phase, one in the region 70°-100°K and other in the region 210°-230°K. These anomalies consist of inflections in the dimensional change as a function of temperature and reflect, respectively, maxima and minima in plots of the thermal co-efficients of expansion vs temperature.

Morton[26] measures the internal friction at strain amplitudes less than 10^{-5} in In rich In-Tl alloys and shows an amplitude dependent peak associated with the fcc-fct martensitic transformation. The peak is thermally activated when the transformation occurs near the melting point Tm, but not at lower temperatures. A mechanism is proposed for this relaxation, involving an interaction between twin boundaries and solute atoms whereby reordering of solute atom is affected in differently oriented tetragonal regions by twin boundary motion. Shear modulus measurements indicate abrupt changes at the transformation temperatures and positive temperature co-efficients of

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[25] J.E. Pahlman and J.F. Smith, J. Less Common Metals, 16, 1968, p. 397-405.

[26] M.E. DeMorton, Journal of Applied Physics, 40, 1969, p. 208-212.

modulus in the high temperature fcc phase; implying structural instability and an "entropy elastic" state. At 0.9 Tm, about 60% of the elasticity in a 19.5 atom percent Tl-In alloy arises from a change in vibrational entropy with extension. The results are consistent with the known crystallography of the transformation.

Sandig and Predel[27] investigate the atomic structure of liquid and solid of the In-Tl (40.0 atom percent Tl) by electric resistivity measurements at 20°C to 500°C. Anomalous resistivity increases in liquid attributes to bonding relations which lead to the formation of intermetallic phase in the solid state.

Khayutin[28] in his later investigation shows that on cooling indium alloys with 18 to 26 atom percent Tl undergo a martensitic transformation from fcc to fct lattice. As a result, there is formed a system of martensitic plates each of which has dual orientation in respect to its neighbors.

The In-Tl system is extensively investigated in the composition range of 16.0 atom percent Tl to 22.0 atom percent Tl[1-28]. The alloys in the above composition range undergoes fcc to fct transformation. It is pointed out by Guttman[6] from x-ray results that the fcc to fct transformation is a second order transformation. This particular investigation is criticized by Geisler and Martin[7] that there exist insufficient experimental data to indicate whether or not the transformation is first or second order. With the aid of

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[27] H. Sandig and Predel, Z. Metallkunde, 61, 1970, p. 387-394.

[28] S.G. Khayutin, Phys. Metals Metallography, 26, 1968, p. 165-166.

dilatometer measurements Buckart and Read[9] suggest that the phase transformation is of the first order. Moore, Graham, Williamson, and Raynor[14] on the basis of diffractometer study conclude that the reaction is of the first order and that the diffusion plays an insignificant role in the mechanism of transformation. Pahlman and Smith[23] report that there exist a narrow two phase region between the fcc and fct phase which is consistent with the fcc to fct transformation being first order reaction. This transformation for several alloy compositions are further studied by Bowles, Barrett and Guttman[8] , proposing a crystallographic mechanism for the above transformation involving a double shear.

Basinski and Christain[12] report that the single crystal transforms by migration of a single or double interface, starting at one end of the specimen and continuing to the other end. In single interface transformation the twinned tetragonal structure is produced according to double shear mechanism. There are certain similarities in the transformation kinetics of Au-Cd and In-Tl alloys. Bredel[17] determines the enthalpy of martensitic transformation in In-Tl alloy containing 20.5 atom percent Tl together with the effect of tensile and compressive stress on the phase transformation.

There has been no previous attempt to determine the thermodynamic properties including the enthalpy and entropy of the phase transformations in In-Tl alloys. In the present investigation attempts are made to determine the thermodynamic properties of In-Tl alloys in the composition range of 16.0 atom percent to 22.0 atom percent Tl in the temperature range of 300°K to 410°K. The enthalpy and tne entropy of the phase transformations and also the transformation temperatures are directly determined. The apparent free energy and the entropy of mixing are evaluated from the experimental results. X-ray studies are conducted to determine the changes in the lattice parameters with the changes in the composition of the alloys.

CHAPTER II

EXPERIMENTAL PROCEDURE AND RESULTS

Preparation of the Alloy

Pure indium (99.999%) and pure thallium (99.999%) were used to prepare the alloys. Thallium was carefully cleaned because of its oxidation characteristics. The weighed amount of In and Tl were capsuled under vacuum (10^{-6} mm of Hg) in quartz tubes, then homogenized and annealed at a temperature 50°C below the transformation depending on the alloy compositions. In this manner the following alloys were prepared.

In-Tl (16.0 atom percent Tl)
In-Tl (18.0 atom percent Tl)
In-Tl (19.0 atom percent Tl)
In-Tl (20.0 atom percent Tl)
In-Tl (21.0 atom percent Tl)
In-Tl (22.0 atom percent Tl)

Thermodynamic Investigations

A modified Olsen calorimeter (fig. 2) having an adiabatic jacket was used with nanovolt amplifiers and other electronic devices. The temperature measurement was carried out by thermopile and a quartz thermometer. The samples were heated to about 410°K and then capsuled in a copper jacket and allowed to cool in the calorimeter containing weighed amount of spectro quality isopropyl alcohol of known specific heat in the required temperature range. The increase in temperature of the calorimeter media was directly recorded as a function of sample temperature by a X-Y recorder.

X-ray Investigation

X-ray investigation was carried out on thin samples obtained from the samples used in thermodynamic studies. A Norelco diffractometer with copper target and nickel filter was used. Thus, the Bragg angle θ was obtained from which d values are calculated. The x-ray lines are then indexed. This procedure was followed in the case of one alloy composition which was 18.0 atom percent Tl (table 8). From these results certain {hkl} planes (namely {111}, {200}, {222}) were chosen to determine a and c. For further alloy compositions a and c values were determined from the d values of the above planes. There were changes in a and c values with increase in Tl addition. The changes in a and c values are shown in table 9 and figure 34. This x-ray investigation is carried out only for the low temperature phase at room temperature.

CHAPTER III

DISCUSSION

In the thermodynamic investigations the experimental results consisted of the temperature of the calorimeter media as a function of temperature of the sample. From these data the enthalpy values are calculated using the following equation:

$$\Delta H = H_T - H_{273} = w.C_p.\Delta T$$

where, ΔH=the enthalpy change at temperature T with respect to the reference state at 273°K,

w=the weight of the isopropyl alcohol,

C_p=the specific heat of isopropyl alcohol, at the temperature of the calorimeter media,

ΔT= the temperature change of the calorimeter media.

The experimental results are then corrected for heat exchanged between the system and the surroundings. The corrected values of enthalpy for each alloy is obtained as a function of temperature (Table 2-7). From the experimental results, the enthalpy of phase transformation for each alloy composition is determined (Fig. 3-8).

The free energy values for each alloy composition is then calculated by using Gibb's Helmholz equation;

$$\frac{\partial\ (\Delta F_T)}{\partial\ (1/T)} = \Delta H$$

Thus,

$$\Delta F_T \text{ alloy} = T\left[\int_{273}^{T} \Delta H \text{ alloy}\ \partial\left(\frac{1}{T}\right)\right]$$

The free energies of the alloys are obtained by integrating ΔH vs $1/T$ curves (Fig. 9-14).

The free energy of mixing can be calculated from the knowledge of ΔH^m and ΔF^m for each alloy compositions at a given temperature by using the equation given by S. Ahmed[29].

$$\begin{aligned}\Delta F^m = {} & T_2 \frac{\Delta F^m}{T_1} + T_2 \left(\Delta H^m\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \\ & - T\int_{1/T_1}^{1/T_2} \left(H_{T_1}^{\text{alloy}} - H_{T_2}^{\text{alloy}}\right) \partial\left(\frac{1}{T}\right) \\ & - T N_{Tl} \int_{1/T_1}^{1/T_2} \left(H_{T_1}^{Tl} - H_{T_2}^{Tl}\right) \partial\left(\frac{1}{T}\right) \\ & - T N_{In} \int_{1/T_1}^{1/T_2} \left(H_{T_1}^{In} - H_{T_2}^{In}\right) \partial\left(\frac{1}{T}\right)\end{aligned}$$

Since values of ΔH^m and ΔF^m for these alloy compositions are not available in the literature, an apparent free energy of mixing ΔF^{m*} is calculated by using the following equation (Fig. 16 to 21).

$$\Delta F_T^{m*} = \Delta F_T^{\text{alloy}} - \left[N_{Tl}\Delta F_T^{Tl} + N_{In}\Delta F_T^{In}\right]$$

where, ΔF_T^{m*} = the apparent free energy of mixing at temperature T °K.

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[29] S. Ahmed, Private communications, papers to be published soon.

ΔF_T^{alloy} = the free energy of the alloy at T °K.

ΔF_T^{In} = the free energy of In at T °K.

ΔF_T^{Tl} = the free energy of Tl at T °K.

N_{In} = the mole fraction of In.

N_{Tl} = the mole fraction of Tl.

The apparent entropy of mixing is calculated from the ΔF^{m*} vs. temperature curves using the equation;

$$-\Delta S^{m*} = \frac{(\partial\ \Delta F^{m*})}{\partial\ (T)}$$

The results are shown in figure 23 to 28.

The thermodynamic properties have only been investigated between 300 °K to 410 °K. This limitation in temperature range was imposed by the phase diagram. The transformation temperature of these alloys range from 405 °K to 319 °K.

Indium-thallium alloys in the composition range of 16.0 atom percent Tl to 22.0 atom percent Tl undergo fcc to fct transformation on cooling. From the phase diagram the transformation temperature for 16.0 atom percent Tl is at about 405°K and that at 22.0 atom percent Tl is at 317°K. There exist certain controversy regarding the order of the phase transformation. It has been argued that the phase transformation is probably a first order transformation as discussed in the introduction.

The results of the present investigation indicates definitely that it is a first order reaction. The enthalpy of the transformation shows discontinuity at the transition temperature. It is also observed that such discontinuity occurs only at one temperature when the phase transforms from fcc to fct on cooling. This seems to indicate that a single phase region transforms to another single phase region at a definite temperature. This excludes the idea of existence of two phase region as suggested by other authors. The enthalpy of phase transformation and the transformation temperature as a function of alloy composition are shown in figure 32 and figure 33 respectively. The x-ray results (Fig. 34) indicate an increase in lattice parameter a and decrease in lattice parameter c of the low temperature structure with increase in the alloying addition of Tl. These changes in lattice parameters contribute to the volume change, which ultimately introduces some strain energy. It is significant to note that the transformation temperature monotonically decreases with increase in Tl content, whereas the enthalpy of phase transformation and the volume change increases with increase in Tl content. It is reasonable to believe that with the increase in the Tl content additional strain is introduced in the lattice. This additional strain increases the non-chemical free energy change. In order for the transformation to take place the chemical free energy change must overcome the non-chemical free energy change. Therefore, it becomes necessary to increase the chemical free energy change to compensate for the increase in non-chemical free energy change. This chemical free energy change is obtained by increasing the degree of undercooling which eventually decreases the transformation temperature. The amount of undercooling required is rather large compared to the chemical free energy change.

This is due to the shape of the free energy curve (fig. 15) of the two phases.

The x-ray results indicate that a increases and c decreases with Tl additions, thereby decreasing c/a ratio of the low temperature phase. The percent change in volume are calculated with respect to the volume of In-Tl alloy of 16.0 atom percent Tl. The transformation temperature as a function of $\Delta V/V_o$ indicates that at 16.0 atom percent Tl the transformation temperature should be 404°K which is also the experimental results. It is interesting to note that the enthalpy and the transformation temperature bears a straight line relationship with the percentage volume change. This seems to suggest that the changes in the transformation kinetics is essentially due to the change in strain energy arising from the volume change.

The transformation temperature on cooling, determined from experimental results agree well with the transformation temperature predicted by the phase diagram as shown in table 1. Additional experimental results suggest that the transformation temperature on heating is only one or two degrees greater. It appears that the equilibrium transformation temperature To is not much different from the transformation temperature T_C on cooling.

The variation in lattice parameters with composition seems to indicate that the bonding energies E_{AA}, E_{BB} and E_{AB} depends upon concentration, based on the fact that the molar volume of indium and thallium are almost the same. Furthermore, the experimental results indicate that the ΔH^{m*} is positive and increases with composition and temperature. This suggests that the bond energy E_{AA} and E_{BB} is less than the bond energy E_{AB} (i.e., $E_{AB} > (E_{AA} + E_{BB})/2$). This means that there is a preference of AA and BB bonds which represents a higher degree of order and smaller entropy of mixing. In the experimental results the entropy of mixing also decreases with concentration thereby indicating the formation of AA and BB bonds upon addition of thallium. Furthermore, the apparent free energy of mixing increases with the addition of thallium, thereby indicating also that the E_{AB} is greater than $(E_{AA} + E_{BB})/2$. Such interaction will increase the enthalpy of mixing but decrease the entropy of mixing at the same time with increase in Tl content.

The apparent free energy of mixing increases with temperature due to $T\Delta S^{m*}$ contribution. The ΔS^{m*} decreases with temperature (fig. 23-28) i.e., it becomes more negative, thereby increasing the $T\Delta S^{m*}$ contribution with temperature and composition. This makes ΔF^{m*} increase with temperature and concentration.

The geometry of a crystalline interface will change significantly at low temperature, since the atoms are not mobile and hence the interface will be expanded by creation of vacancies and the increased equilibrium separation of atoms and thereby changing the surface tension between the interface. The surface tension is a function of the crystallographic orientation of the boundary in solids. As a result there will exist the forces trying to shorten the boundaries in addition there may be angular forces attempting to cause the boundary to turn into a crystallographic orientation having lower energy. This reflects, in turn, the free energy change.

It is also observed that the high temperature fcc phase transforms into low temperature fct phase. The atoms of high temperature phase (fcc) tries to fit themselves into fct low temperature phase, which creates atom movements along the a and c axis. The boundaries may be considered to consist of regions of perfect fit and regions of misfit resulting in the formation of dislocation at the boundaries. This misfit of boundaries seems to increase with the increase in the Tl addition which in turn increases the enthalpy of mixing.

CHAPTER IV

CONCLUSION

The following conclusions can be drawn from the experimental results:

(1) The phase transformation is of the first order.

(2) The transformation temperature decreases and the enthalpy of transformation increases with increasing amount of Tl addition. This has been interpreted in terms of increase in the strain free-energy caused by distortions of the unit cell.

(3) The changes in unit cell have been studied in the x-ray investigation. The change in lattice parameters of In-Tl alloys introduces the strain in the lattice through distortions of the unit cell.

(4) The variation of enthalpy and transformation temperature bears a straight line relationship with the percentage volume change. This has been explained on the basis of strain free energy change.

(5) The apparent free energy of mixing, the entropy of mixing and the enthalpy of mixing has been interpreted in terms of short range order.

TABLE 1

THE COMPARISON OF TRANSFORMATION TEMPERATURES BETWEEN THE PHASE DIAGRAM AND THE EXPERIMENTAL RESULTS

Alloy Composition	T_o From The Phase Diagram	T_c From The Experimental Results
In-Tl (16.0 a/o Tl)	405	402.5
In-Tl (18.0 a/o Tl)	375	374
In-Tl (19.0 a/o Tl)	360.5	361
In-Tl (20.0 a/o Tl)	346	346.5
In-Tl (21.0 a/o Tl)	331	331
In-Tl (22.0 a/o Tl)	317	319.5

TABLE 2

TABLE OF ENTHALPY AND FREE ENERGY CHANGE In-Tl (16.0 ATOM PERCENT Tl)

T °K	ΔH Cal/mole	ΔF Cal/mole	T °K	ΔH Cal/mole	ΔF Cal/mole
273	0	0	390	1550	295
280	90	2.5	392	1590	304
290	228	7.5	393	1610	308.5
300	368	17.5	394	1631	314
310	510	31	395	1656	319
320	645	51	396	1680	324
330	778	75.5	397	1694	328
335	845	90	398	1733	334
340	910	105	399	1765	339
345	975	121	400	1800	344
350	1037	136	401	1834	348
355	1098	163.5	402.25	1904	356
360	1160	171	402.25	1927	356
365	1218	189.5	403	2000	360.5
370	1275	209	404	2060	366
375	1331	229	405	2170	372
380	1392	350.5	406	2290	379
385	1464	272	408.5	3270	400
388	1511	286			

TABLE 3

TABLE OF ENTHALPY AND FREE ENERGY CHANGE
In-Tl (18.0 ATOM PERCENT Tl)

T °K	ΔH Cal/mole	ΔF Cal/mole	T °K	ΔH Cal/mole	ΔF Cal/mole
273	0	0	369	1617	296
280	143	2.5	370	1628	300.5
285	246	6	371	1636	306
290	348	10.5	372	1645	312
295	453	17	373	1654	318
300	557	25	374	1662	324
305	668	36	374	1678	324
310	775	49	375	1692	329
315	870	55	376	1703	334
320	965	62.5	377	1714	339.5
325	1052	82	378	1722	344
330	1134	122.5	379	1734	348.5
335	1206	143	380	1744	355
340	1274	163.5	382	1767	366
345	1340	184	384	1789	376
350	1406	205.5	386	1811	388
355	1468	228	390	1862	410
360	1525	251	395	1938	439
363	1557	266	400	2030	467
366	1587	280.5	405	2200	496
367	1598	286	408.5	2620	520
368	1605	291			

TABLE 4

TABLE OF ENTHALPY AND FREE ENERGY CHANGE
In-Tl (19.0 ATOM PERCENT Tl)

T °K	ΔH Cal/mole	ΔF Cal/mole	T °K	ΔH Cal/mole	ΔF Cal/mole
273	0	0	358	1595	248
280	145	3	359	1610	253
285	253	7	360	1619	257
290	360	11	361	1628	263
295	472	18	361	1646.5	263
300	580	25	363	1668	272
310	790	49	364	1679	277
315	900	63	365	1686	282
320	1005	80	366	1697	287
325	1106	99	367	1710	292
330	1200	118	368	1720	298
335	1280	138	370	1742	309
340	1357	159	372	1768	320
345	1428	183	375	1802	337
348	1470	197	380	1865	365
350	1497	207	385	1940	395
352	1523	217	390	2030	426
353	1536	223	395	2162	466
354	1548	227	400	2380	493
355	1562	233	405	2740	528
356	1572	238	408	3310	554
357	1584	243			

TABLE 5

TABLE OF ENTHALPY AND FREE ENERGY CHANGE
In-Tl (20.0 ATOM PERCENT Tl)

T °K	ΔH Cal/mole	ΔF Cal/mole	T °K	ΔH Cal/mole	ΔF Cal/mole
273	0	0	345	1670	224
280	198	5	346.75	1692	233
285	325	9	346.75	1717	233
290	458	15	348	1730	239
295	592	23	349	1742	244
300	720	33	350	1754	251
305	844	46	351	1766	257
310	981	62	352	1780	263
315	1144	80	353	1791	269
320	1230	100	354	1803	275
325	1338	120	356	1828	287
327	1378	130	360	1875	302
330	1433	145	365	1940	342
332	1468	155	370	2004	374
334	1502	165	375	2065	407
336	1538	175	380	2126	440
338	1570	184	385	2190	475
339	1586	190	390	2257	510
340	1603	195	395	2326	546
341	1617	201	400	2400	581
342	1633	207	405	2483	618
343	1645	212	410	2575	657
344	1658	217	415	2680	698

TABLE 6

TABLE OF ENTHALPY AND FREE ENERGY CHANGE
In-Tl (21.0 ATOM PERCENT Tl)

T °K	ΔH Cal/mole	ΔF Cal/mole	T °K	ΔH Cal/mole	ΔF Cal/mole
273	0	0	333	1648	202
280	245	3	334	1662	207
285	445	9	335	1678	213
290	628	18	336	1692	219
295	810	31	337	1710	224
300	960	47	338	1720	230
305	1090	65	339	1740	236
310	1205	85	340	1750	242
315	1312	108	342	1780	254
318	1370	123	345	1820	272
320	1408	134	347	1848	284
322	1441	143	350	1885	303
323	1460	148	355	1948	335
324	1480	154	360	2000	366
325	1494	160	365	2058	399
326	1512	165	370	2112	432
327	1528	171	375	2168	466
328	1545	176	380	2228	501
329	1563	181	385	2298	536
330	1575	187	390	2390	571
331	1590	192	395	2465	609
331	1618	192	400	2910	654
332	1631	197	405	3490	684

TABLE 7

TABLE OF ENTHALPY AND FREE ENERGY CHANGE
In-Tl (22.0 ATOM PERCENT Tl)

T °K	ΔH Cal/mole	ΔF Cal/mole	T °K	ΔH Cal/mole	ΔF Cal/mole
273	0	0	319.5	1618	158
280	300	4	319.5	1654	158
285	530	11	321	1676	165
290	722	21	322	1692	170
293	850	29	323	1707	175
295	932	35	324	1725	180
298	1054	46	325	1741	186
300	1132	54	326	1758	192
303	1250	67	327	1778	198
306	1338	80	328	1795	205
308	1392	91	330	1830	216
310	1444	101	332	1870	228
312	1491	112	334	1909	242
313	1524	117	336	1948	255
314	1532	123	340	2038	282
315	1553	129	345	2180	318
316	1570	135	347	2265	333
317	1588	142	352.5	2700	373
318	1601	148			

TABLE 8

A CRYSTAL STRUCTURE DETERMINATION FOR THE LOW TEMPERATURE PHASE OF In-Tl ALLOY of 18.0 ATOM PERCENT Tl

Intensity	Bragg Angle 2θ	d Values	(hkl)
100	32.8167°	2.7289	(111)
21.67	37.333°	2.4085	(002)
23.75	38.65°	2.3295	(200)
16.67	54.53°	1.6828	(220)
8.34	64.166°	1.4513	(310)
10.84	65.667°	1.4218	(311)
8.34	68.667°	1.3668	(222)
6.25	89.7°	1.0931	(330)

Using Tetragonal Structure Equation

$$\frac{4\ \mathrm{Sin}^2\theta}{\lambda^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$$

(1) From (200) Plane.

$$\frac{4\ \mathrm{Sin}^2 19.325}{(1.54178)^2} = \frac{4}{a^2},\ a = 4.6589\ \mathrm{A}°$$

(2) From (111) Plane.

$$\frac{4\ \mathrm{Sin}^2\ 16.408}{(1.54178)^2} = \frac{2}{(4.6589)^2} + \frac{1}{C^2} \qquad C = 4.87169$$

(3) From (222) Plane.

$$\frac{4\ \mathrm{Sin}^2\ 34.33°}{(1.54178)^2} = \frac{8}{(4.6589)^2} + \frac{4}{C^2} \qquad C = 4.89815$$

TABLE 9

LATTICE PARAMETERS OF DIFFERENT ALLOY COMPOSITIONS

Composition	Lattice Parameter a in A°	Lattice Parameter c in A°	Volume of the Structure V in $(A°)^3$	% Volume Change $\Delta V/V_0$ X100
In-Tl (16.0 a/o Tl)	4.6505	4.894	105.843	0
In-Tl (18.0 a/o Tl)	4.663	4.881	106.1082	0.2505
In-Tl (19.0 a/o Tl)	4.6704	4.8705	106.2382	0.3733
In-Tl (20.0 a/o Tl)	4.679	4.86	106.3999	0.526
In-Tl (21.0 a/o Tl)	4.688	4.846	106.5019	0.6225
In-Tl (22.0 a/o Tl)	4.70	4.818	106.4296	0.554

TABLE 10

ENTHALPY OF PHASE TRANSFORMATION AND TRANSFORMATION TEMPERATURE FOR VARIOUS ALLOY COMPOSITIONS

Composition	Transformation Temperature T_C(°K)	ΔH_R (cal/mole)
In-Tl (16.0 a/o Tl)	402.5	22
In-Tl (18.0 a/o Tl)	374	16
In-Tl (19.0 a/o Tl)	361	18.5
In-Tl (20.0 a/o Tl)	346.5	25
In-Tl (21.0 a/o Tl)	331	29
In-Tl (22.0 a/o Tl)	319.5	36

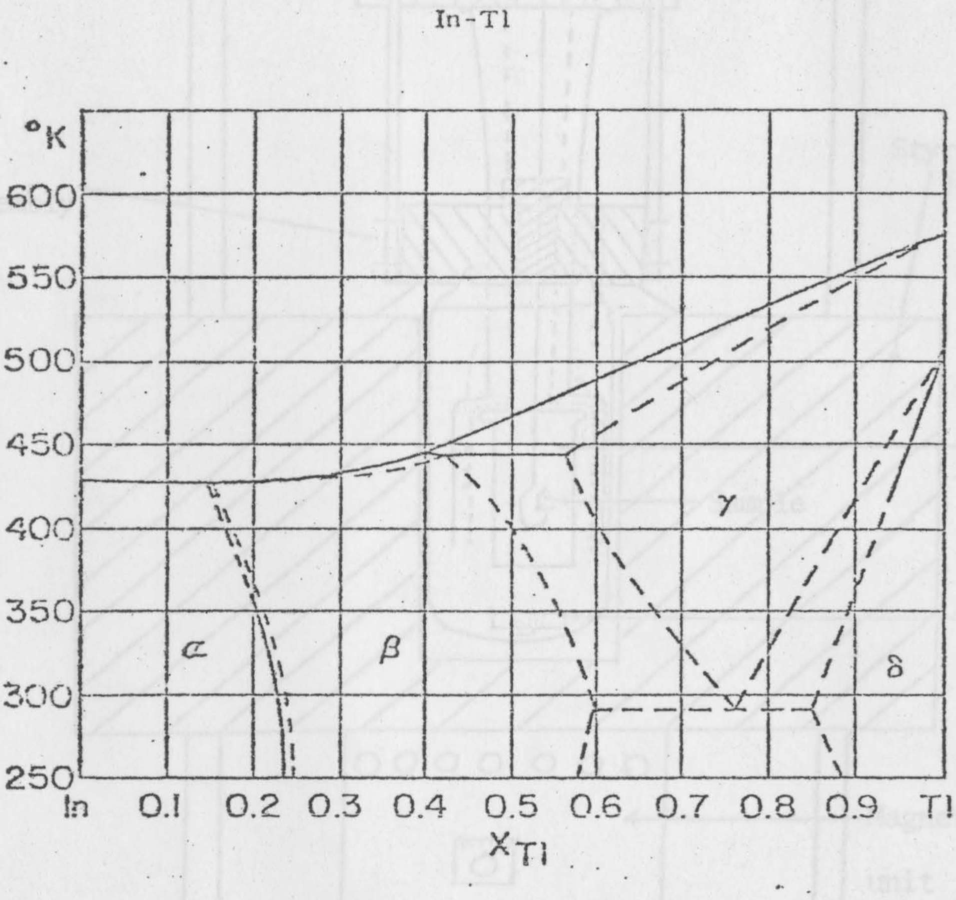

Figure 1. The Phase Diagram

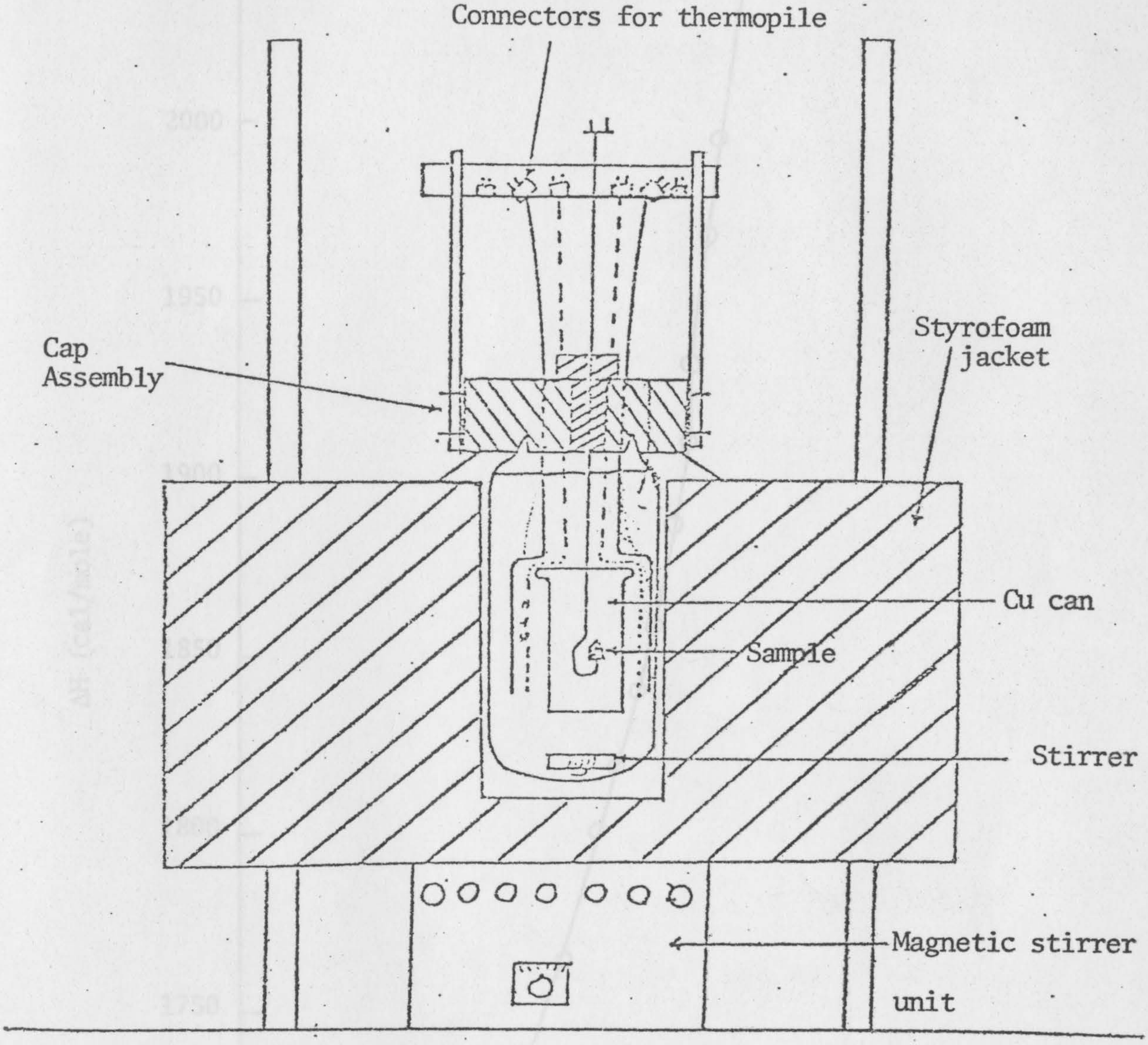

Figure 2. Modified Olsen Calorimeter

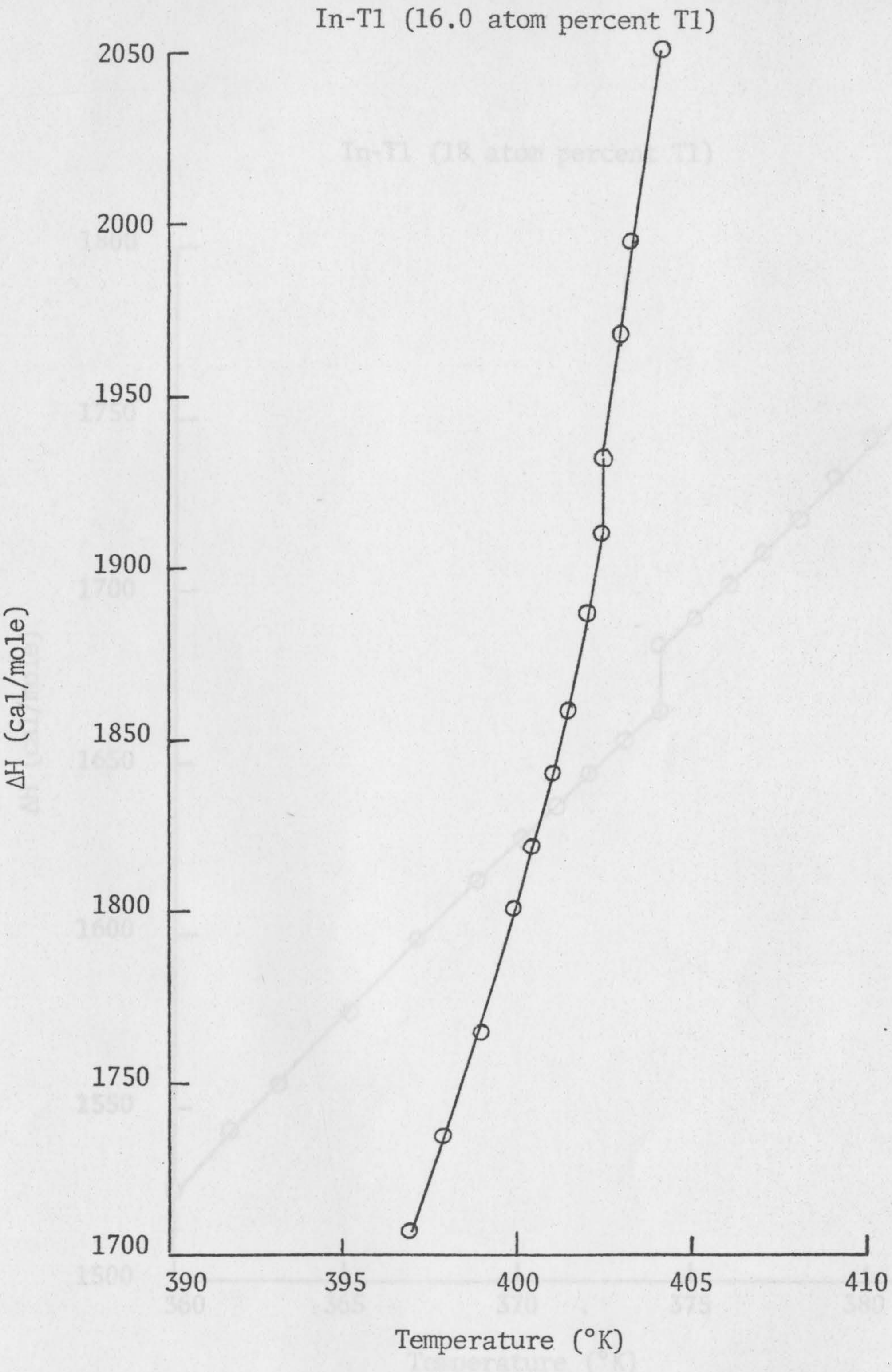

Figure 3. Enthalpy As A Function Of Temperature

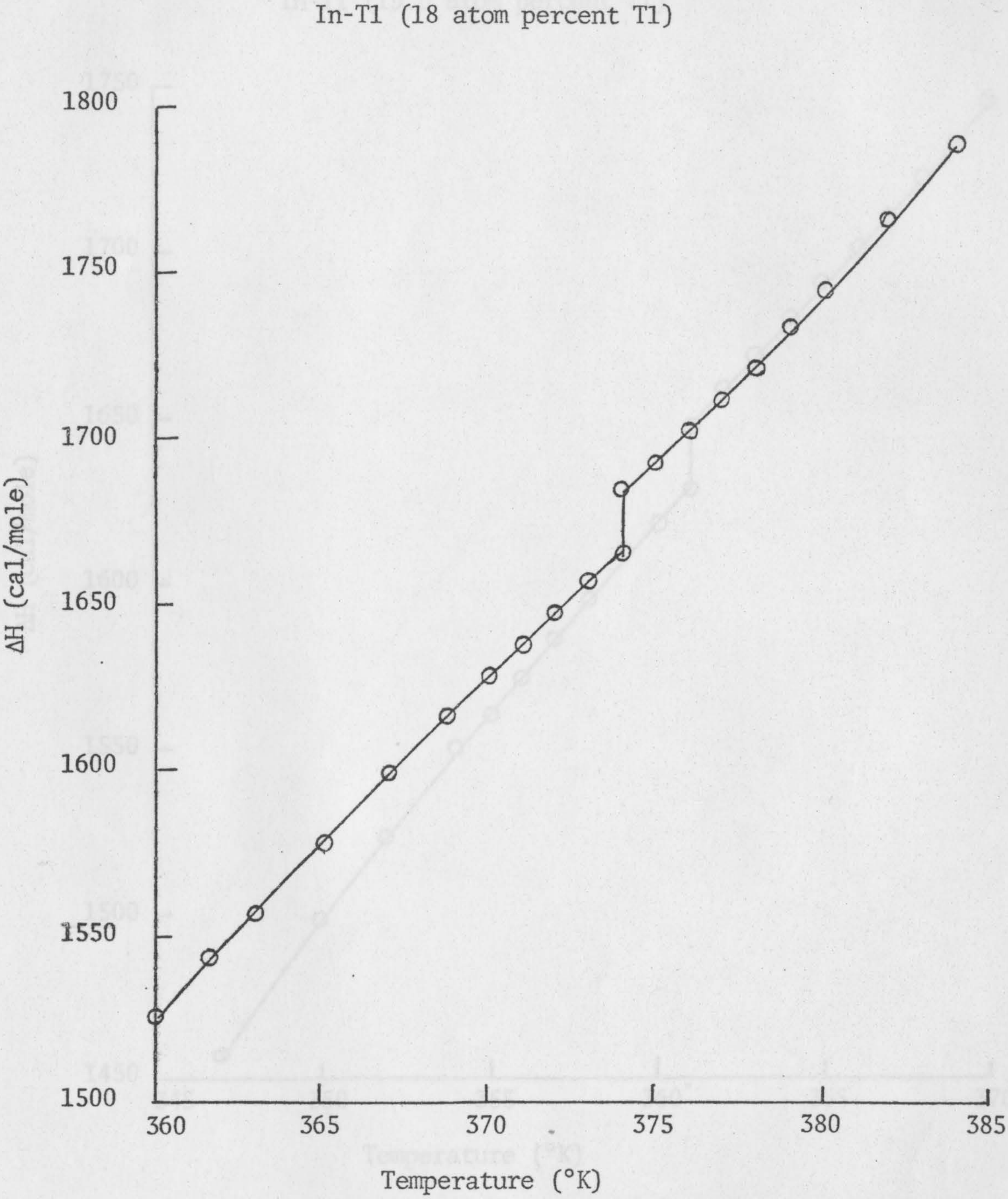

Figure 4. Enthalpy As A Function Of Temperature

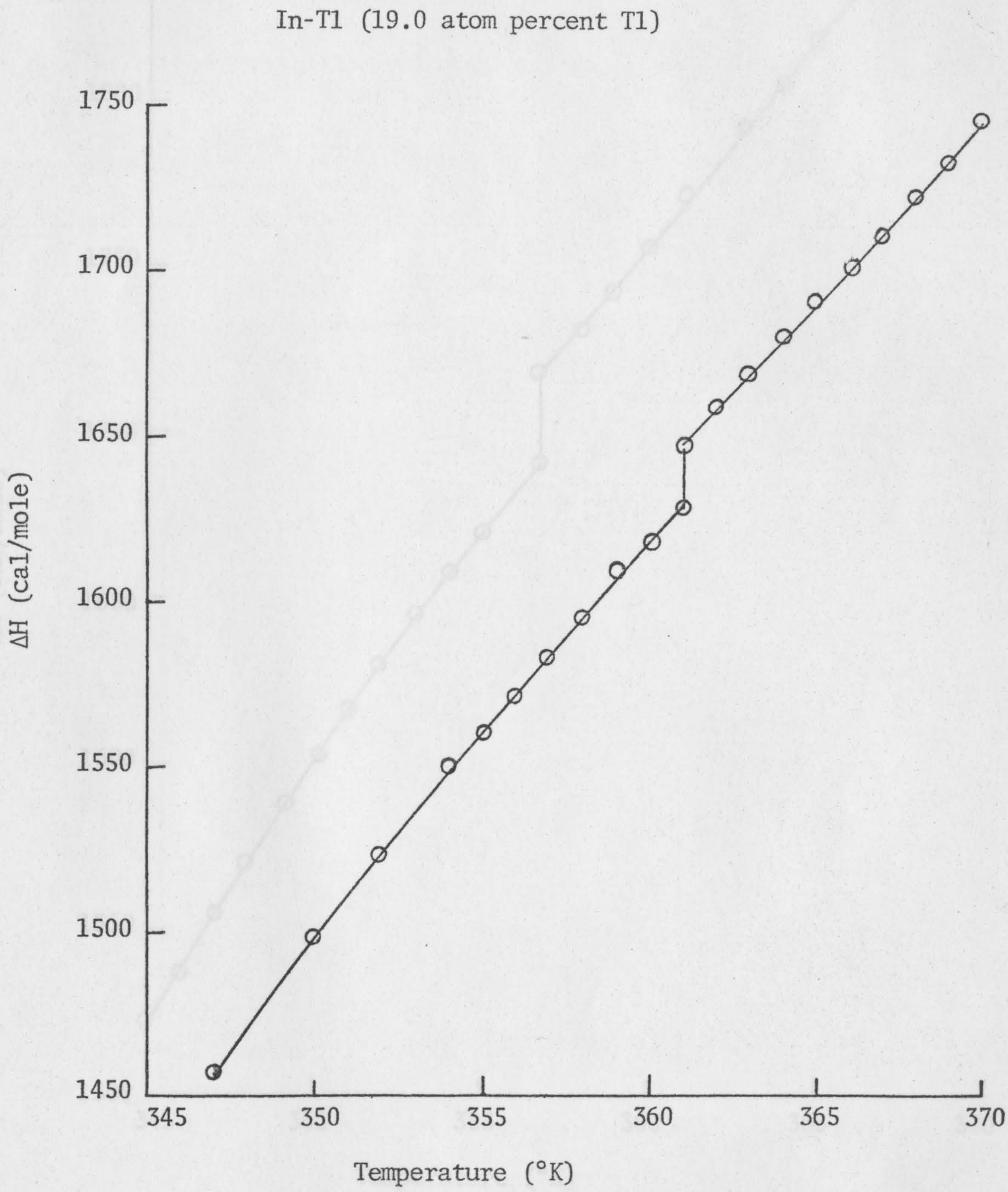

Figure 5. Enthalpy As A Function Of Temperature

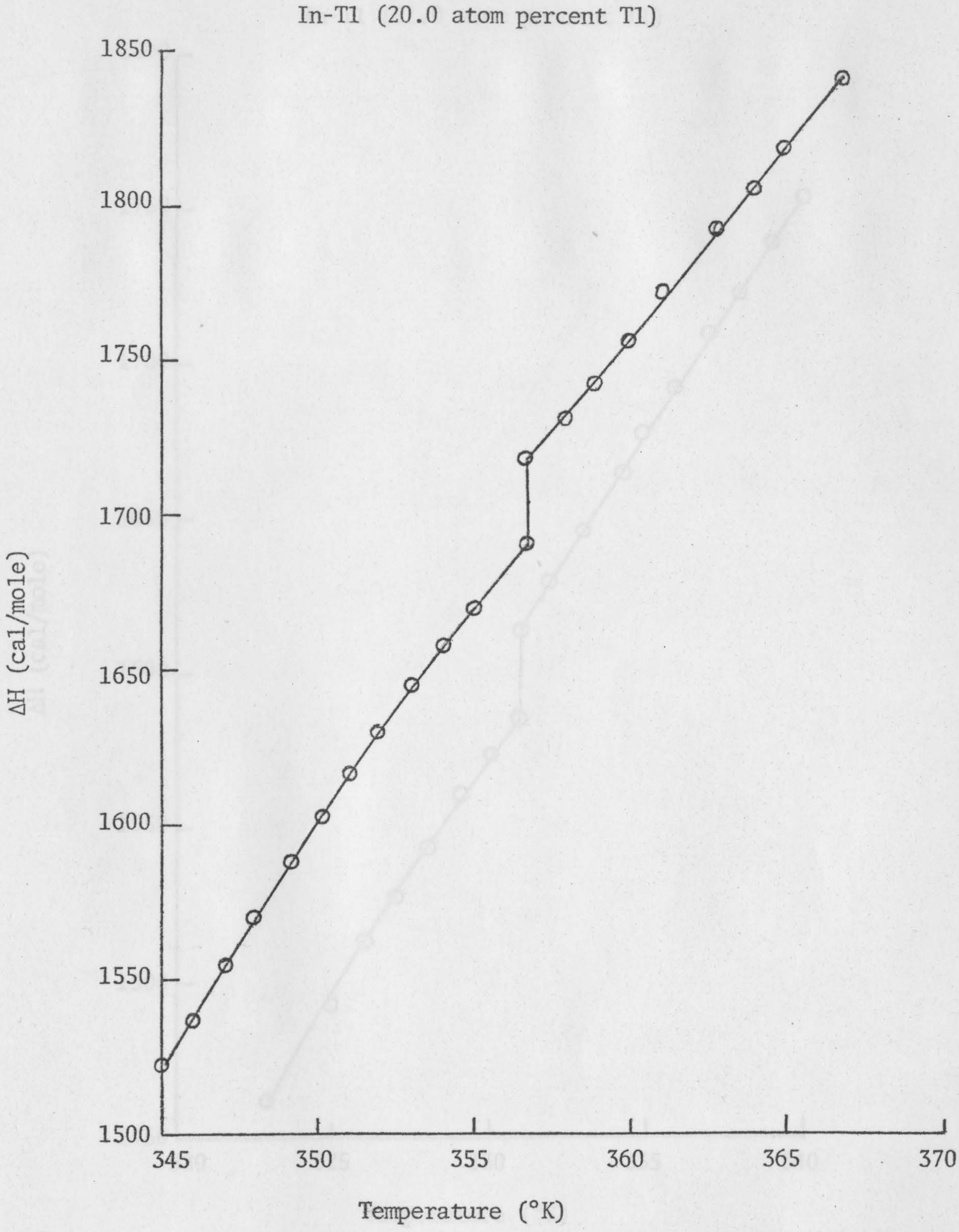

Figure 6. Enthalpy As A Function Of Temperature

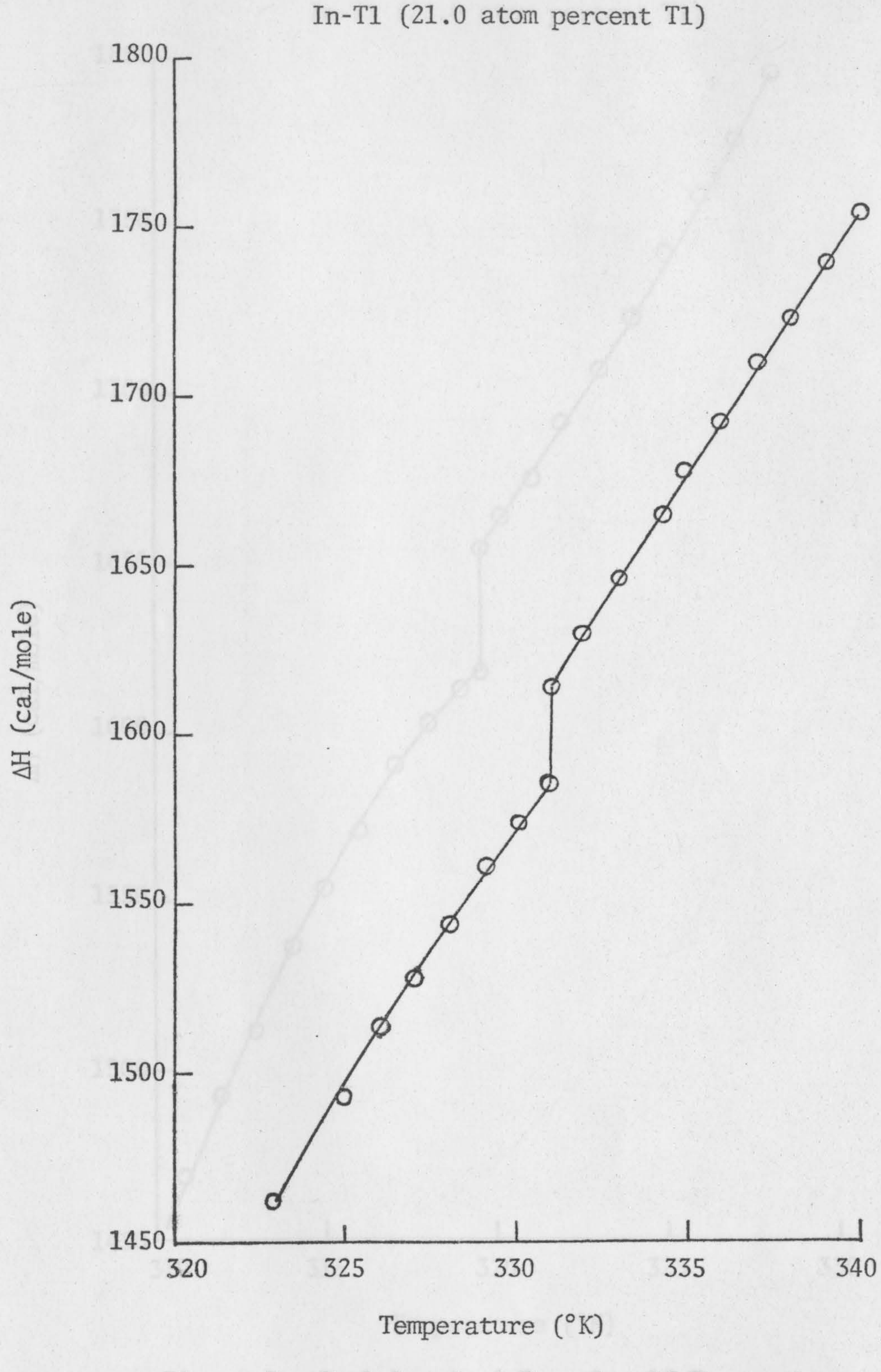

Figure 7. Enthalpy As A Function Of Temperature

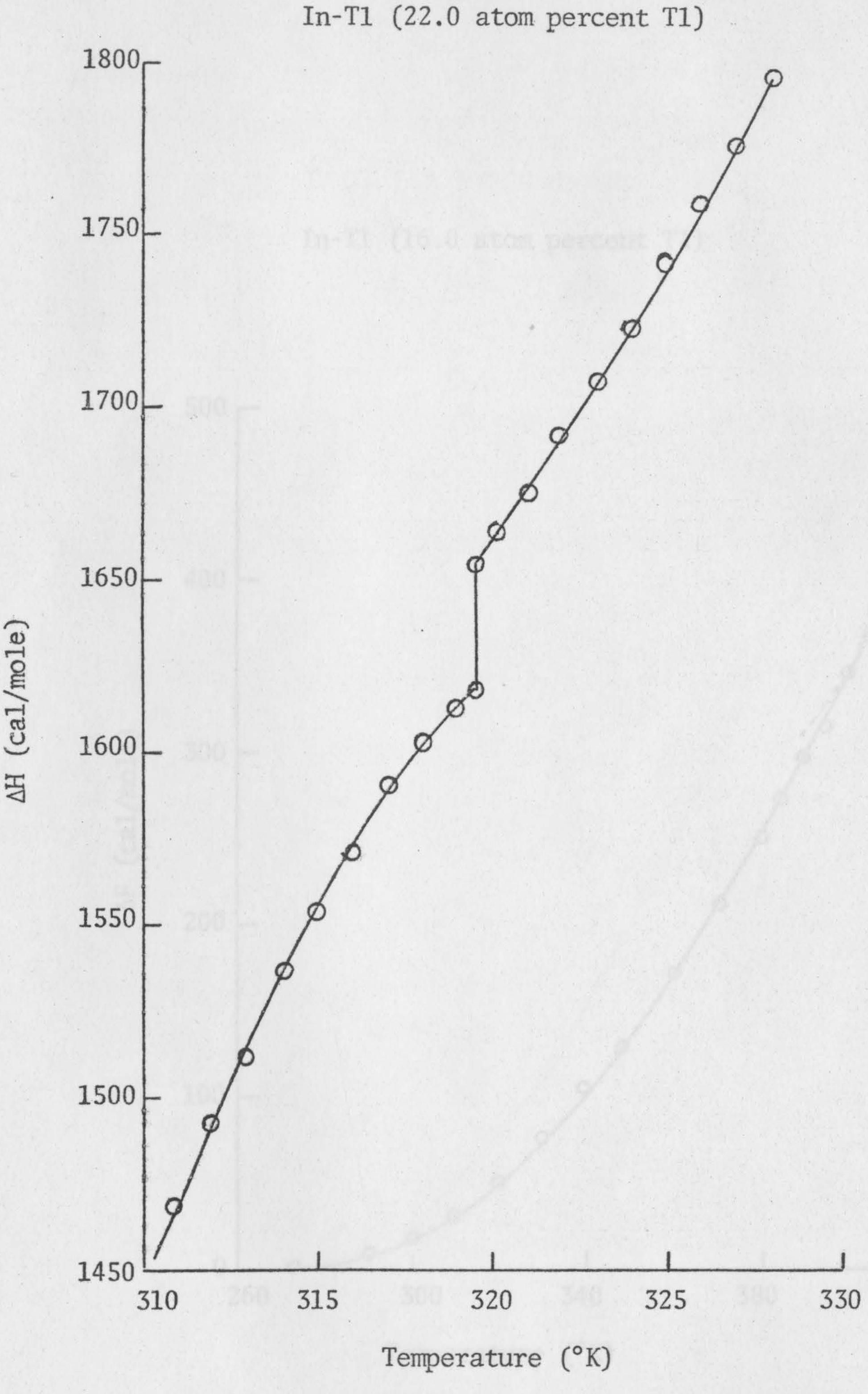

Figure 8. Enthalpy As A Function Of Temperature

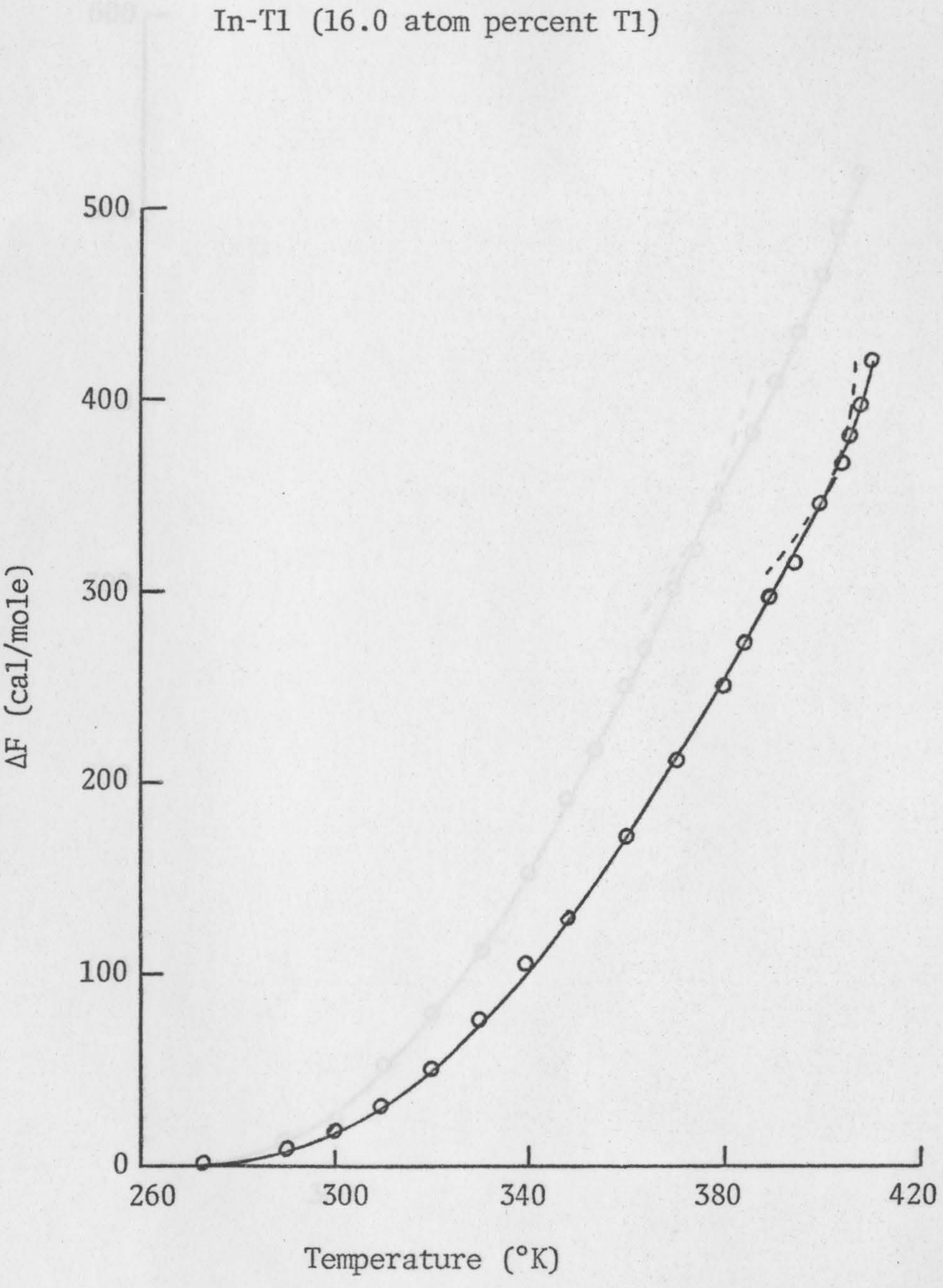

Figure 9. Free Energy As A Function Of Temperature

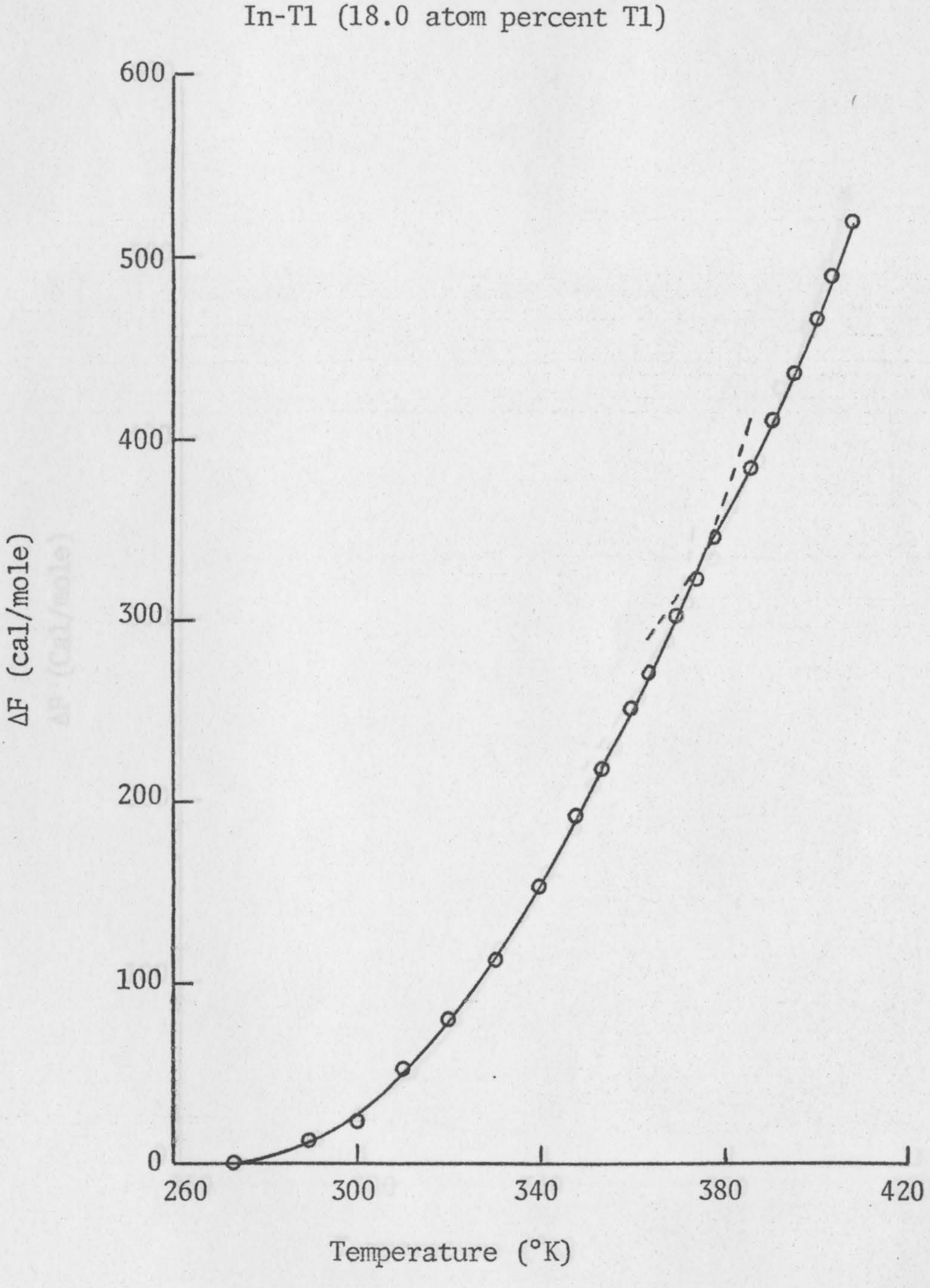

Figure 10. Free Energy As A Function Of Temperature

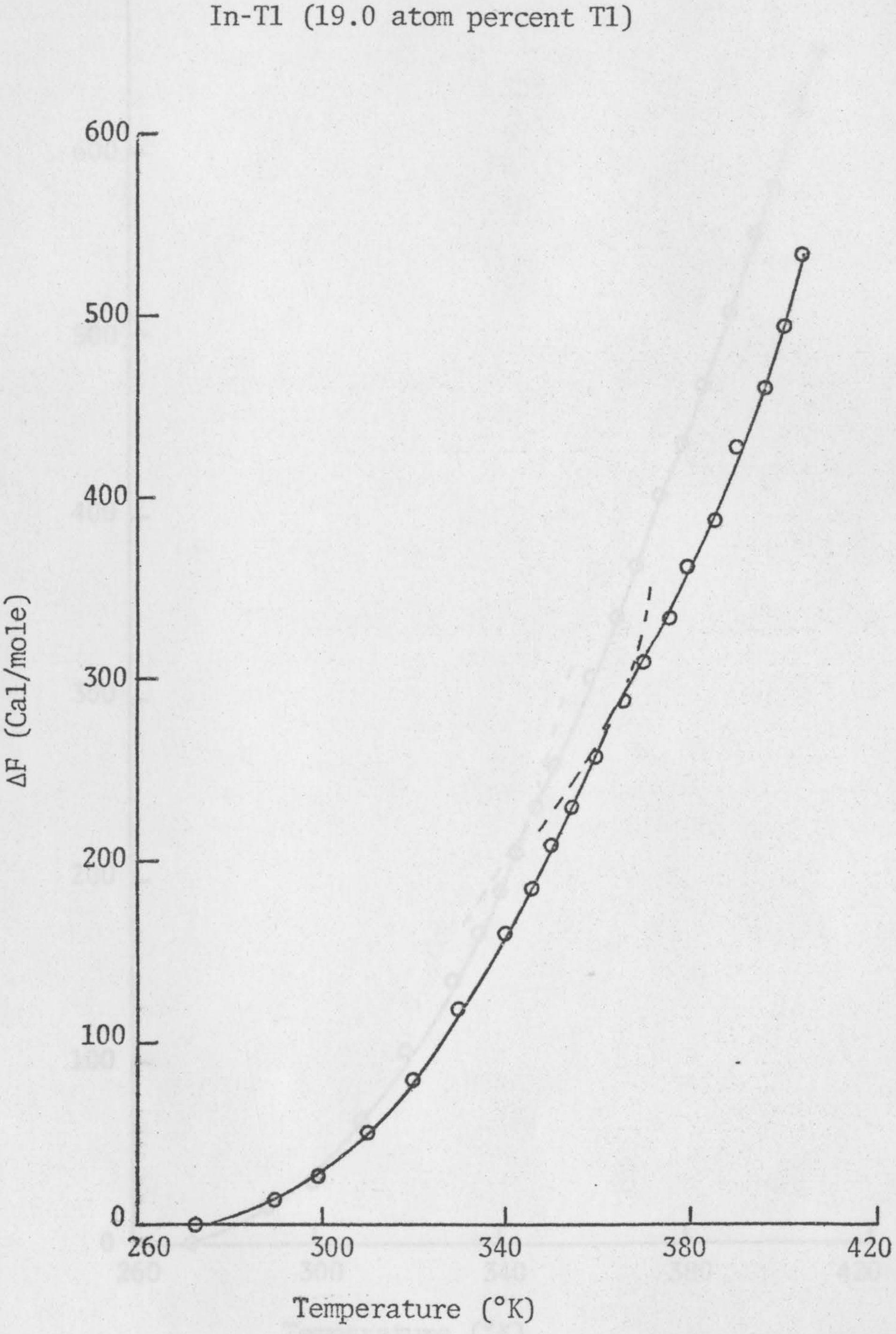

Figure 11. Free Energy As A Function Of Temperature

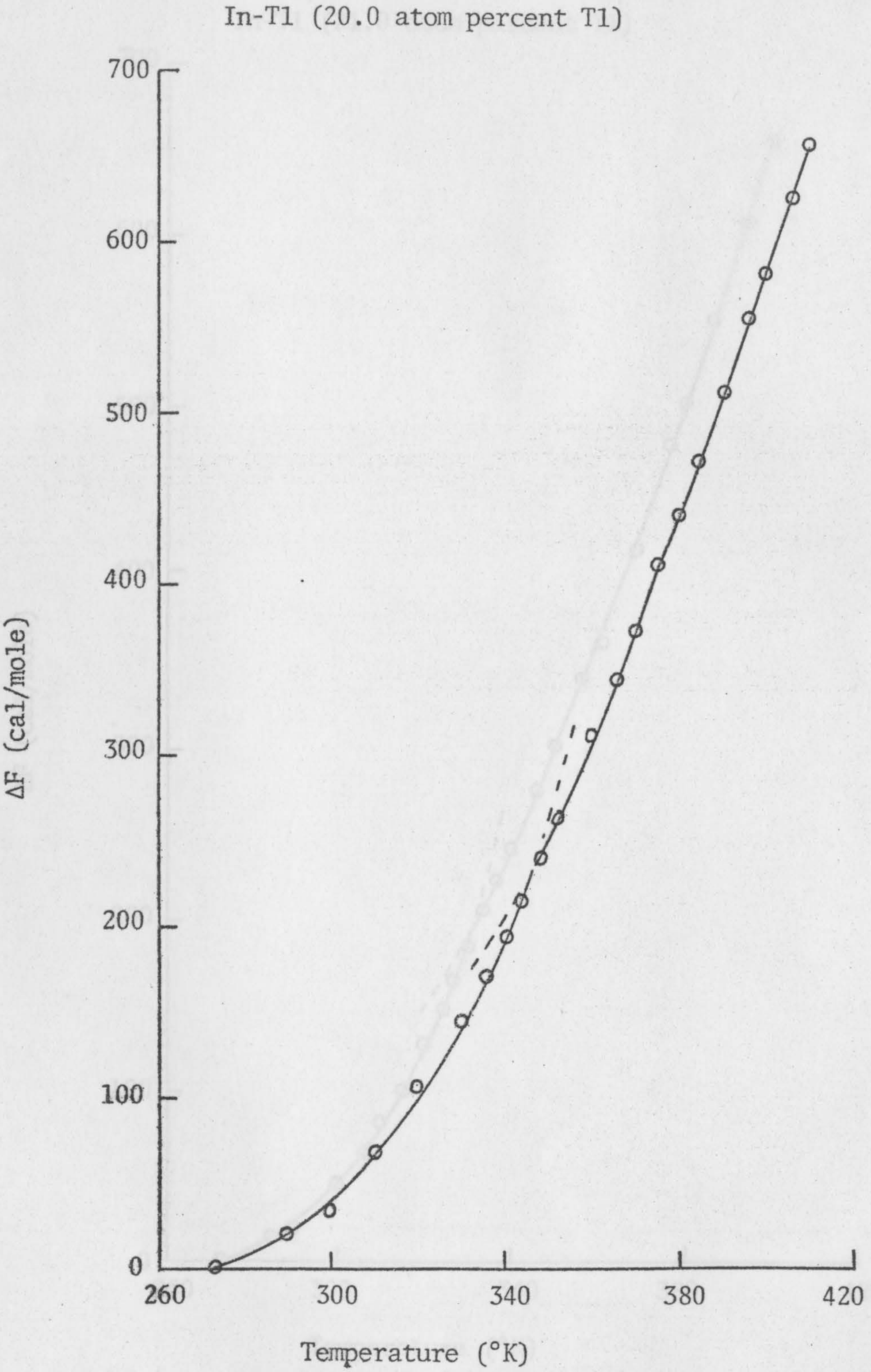

Figure 12. Free Energy As A Function Of Temperature

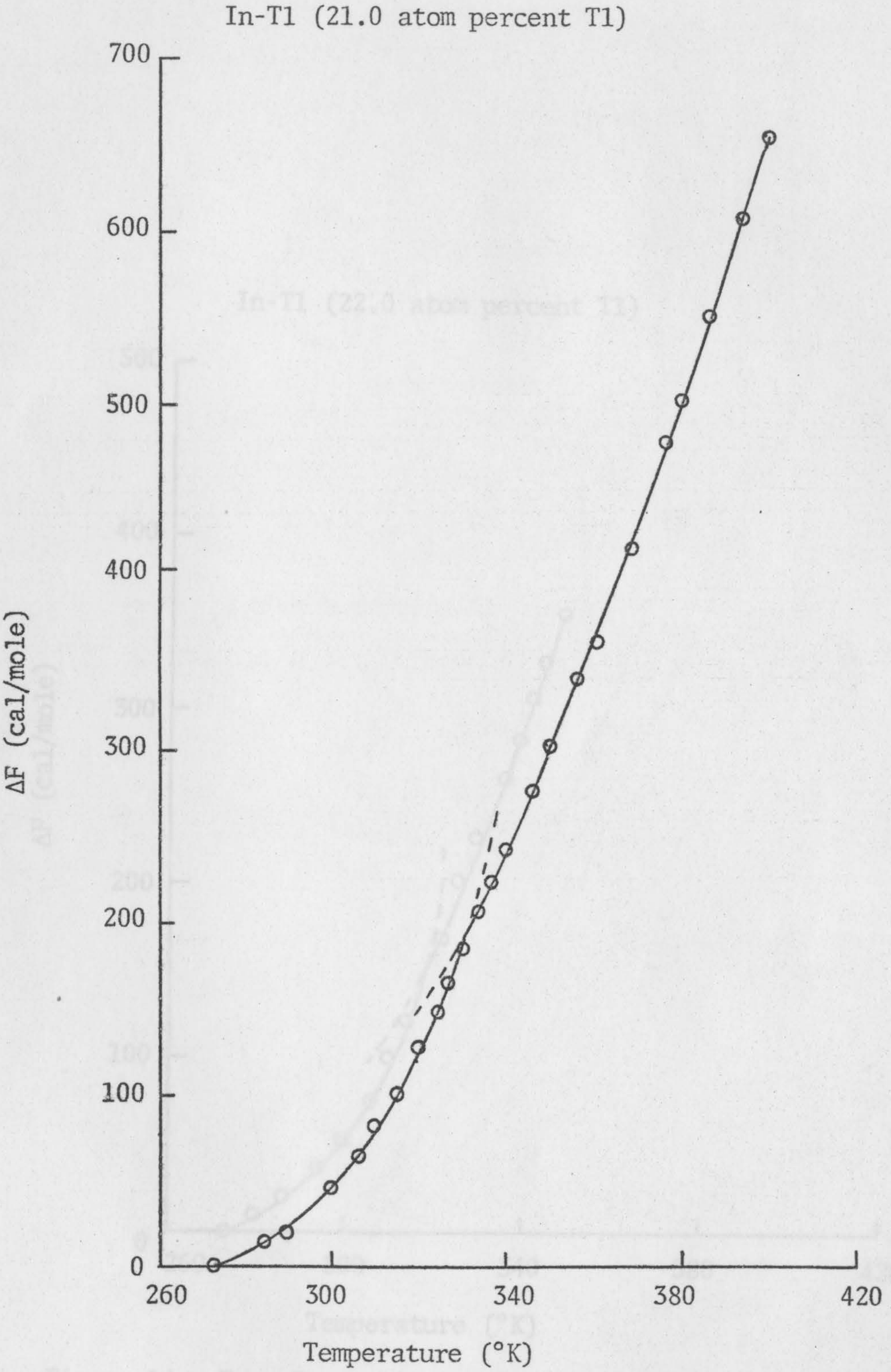

Figure 13. The Free Energy As A Function Of Temperature

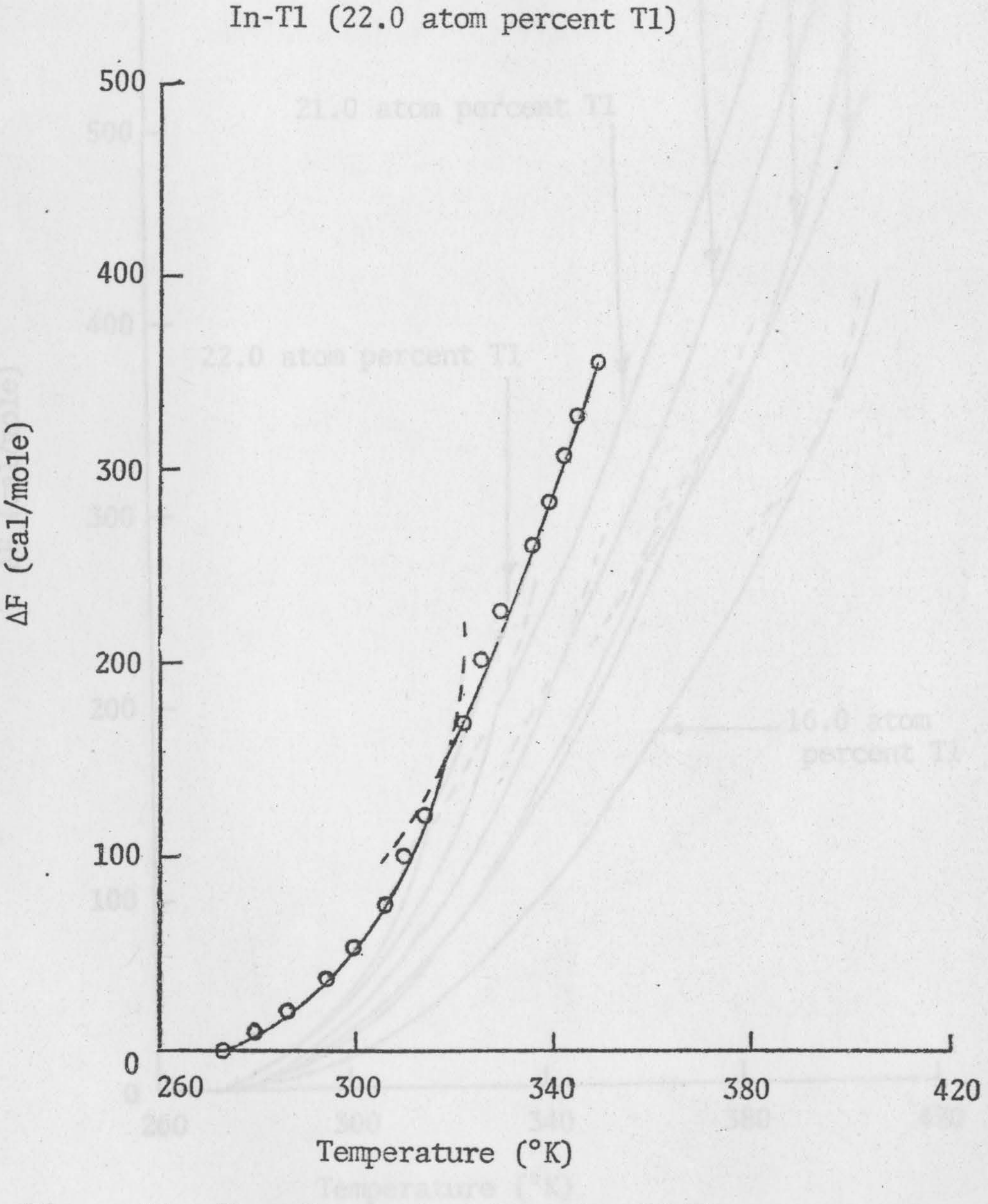

Figure 14. Free Energy As A Function Of Temperature

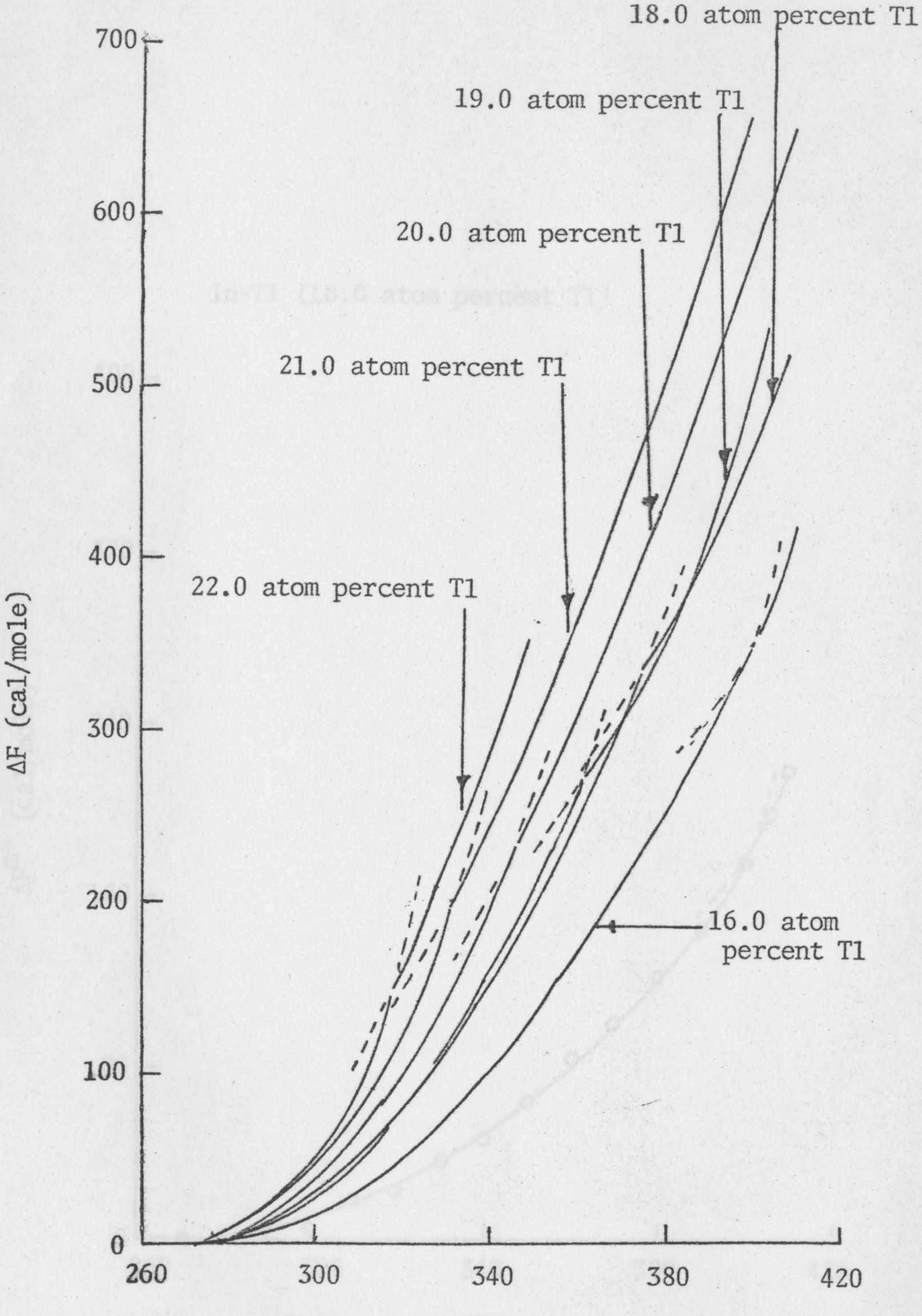

Figure 15. Free Energy As A Function Of Temperature For Various Alloy Compositions.

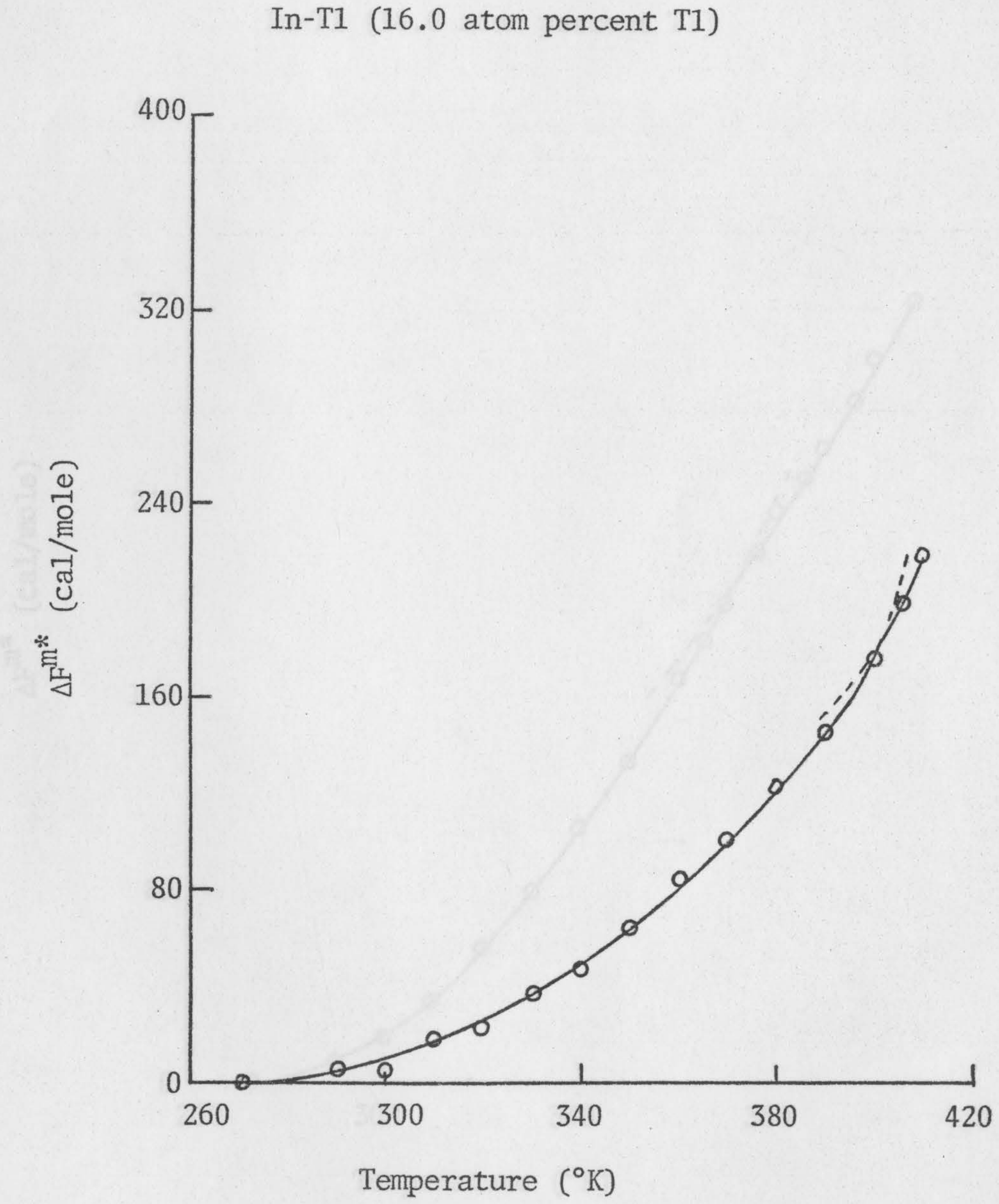

Figure 16. Apparent Free Energy Of Mixing As A Function Of Temperature.

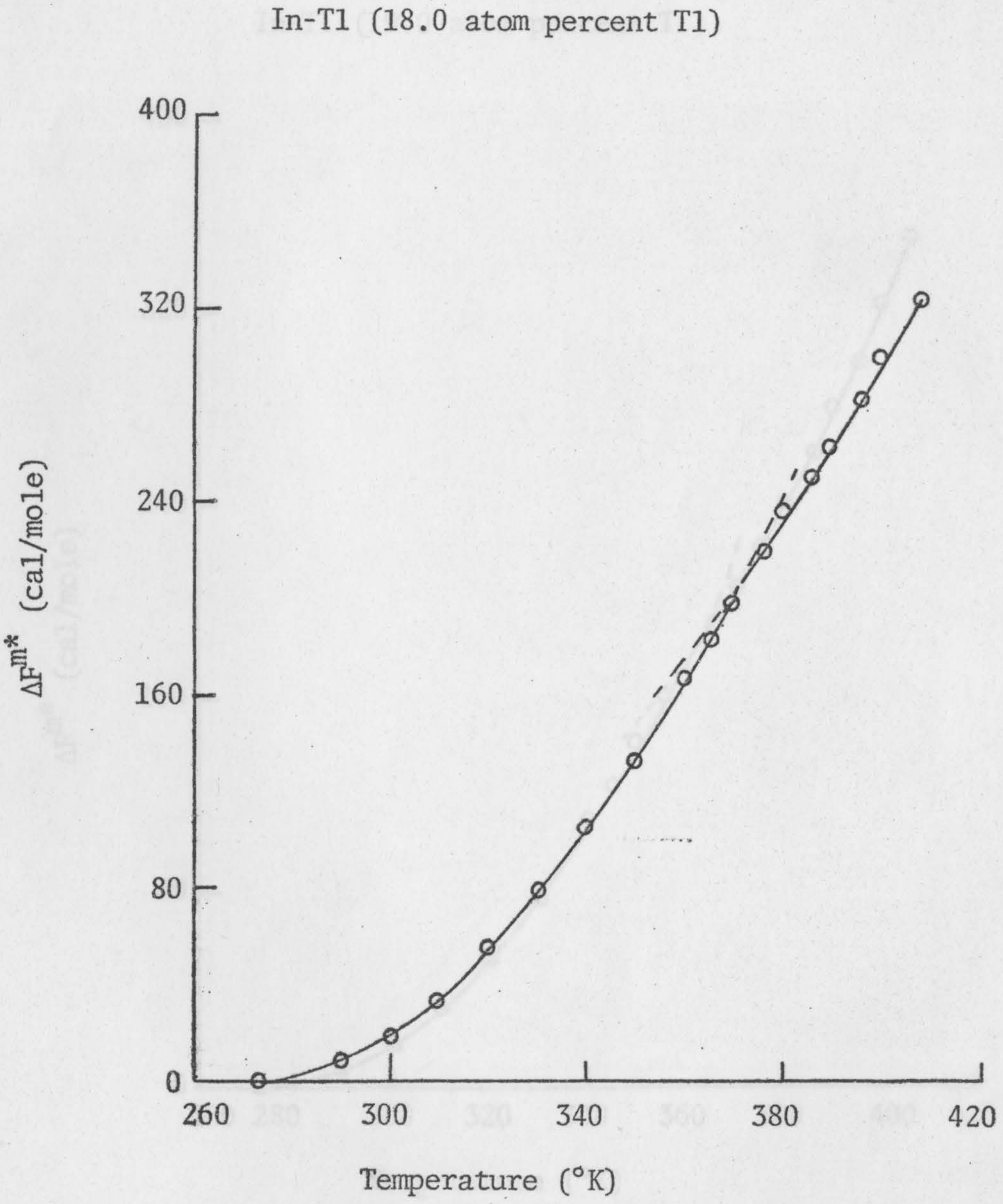

Figure 17. The Apparent Free Energy Of Mixing As A Function Of Temperature

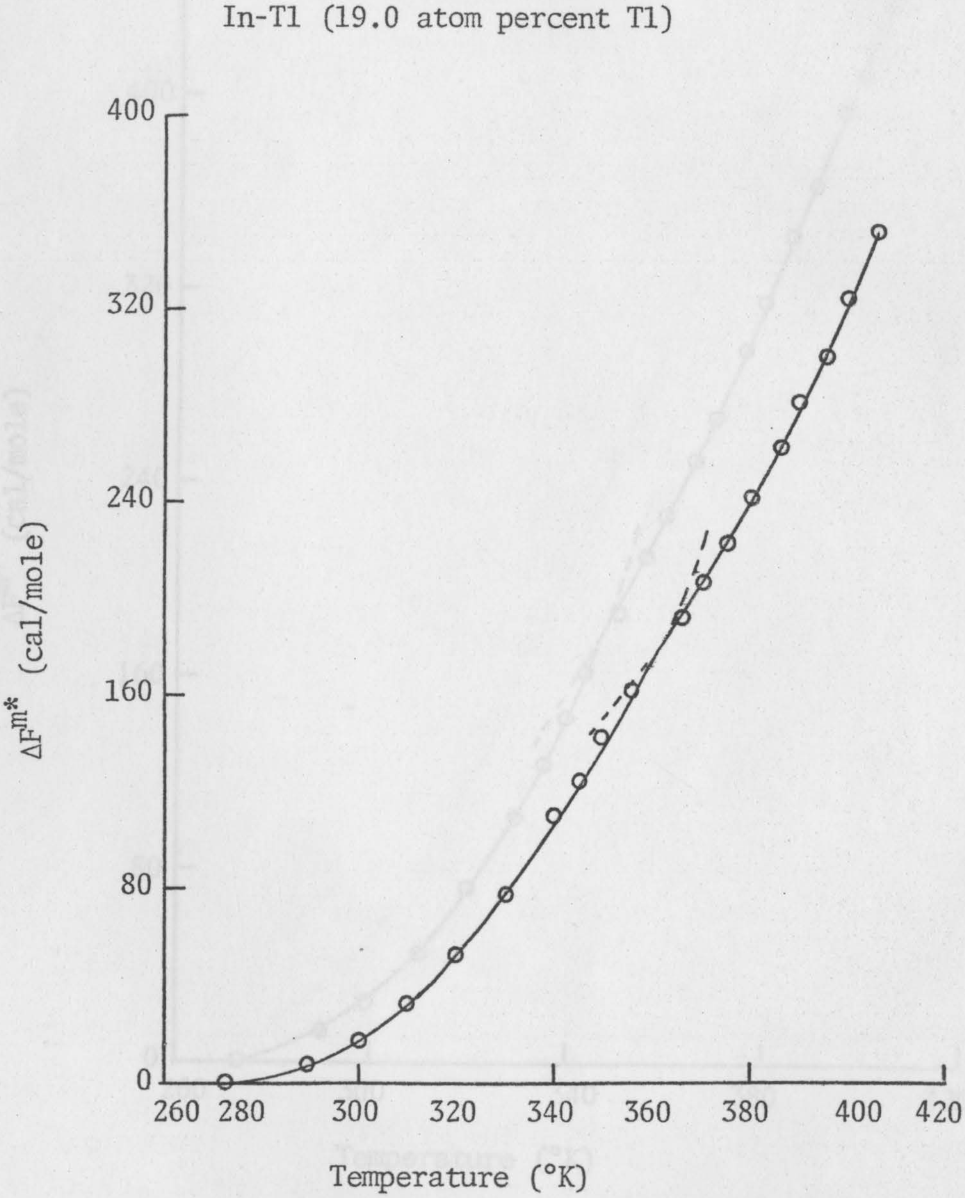

Figure 18. The Apparent Free Energy Of Mixing As A Function Of Temperature

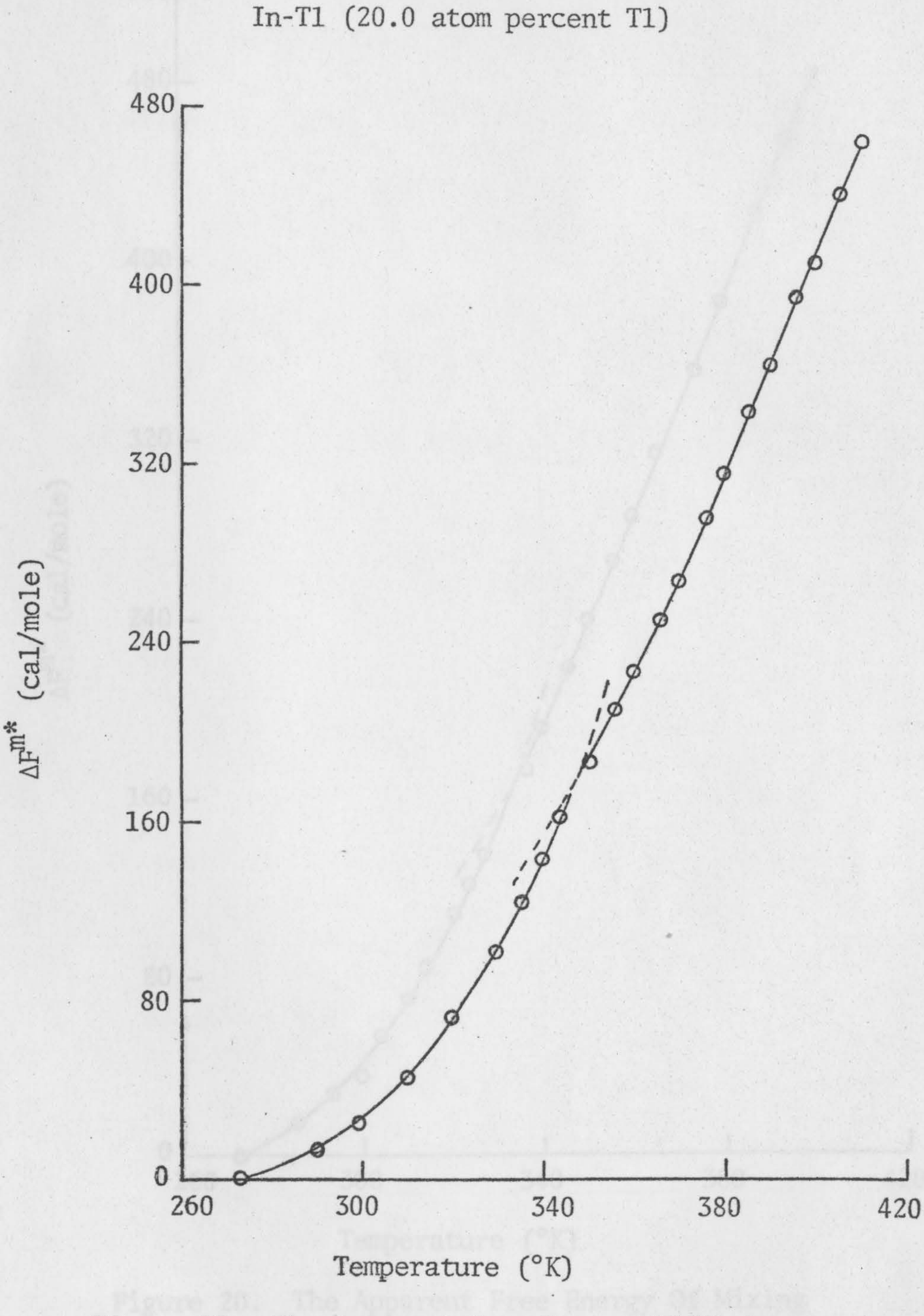

Figure 19. The Apparent Free Energy Of Mixing As A Function Of Temperature.

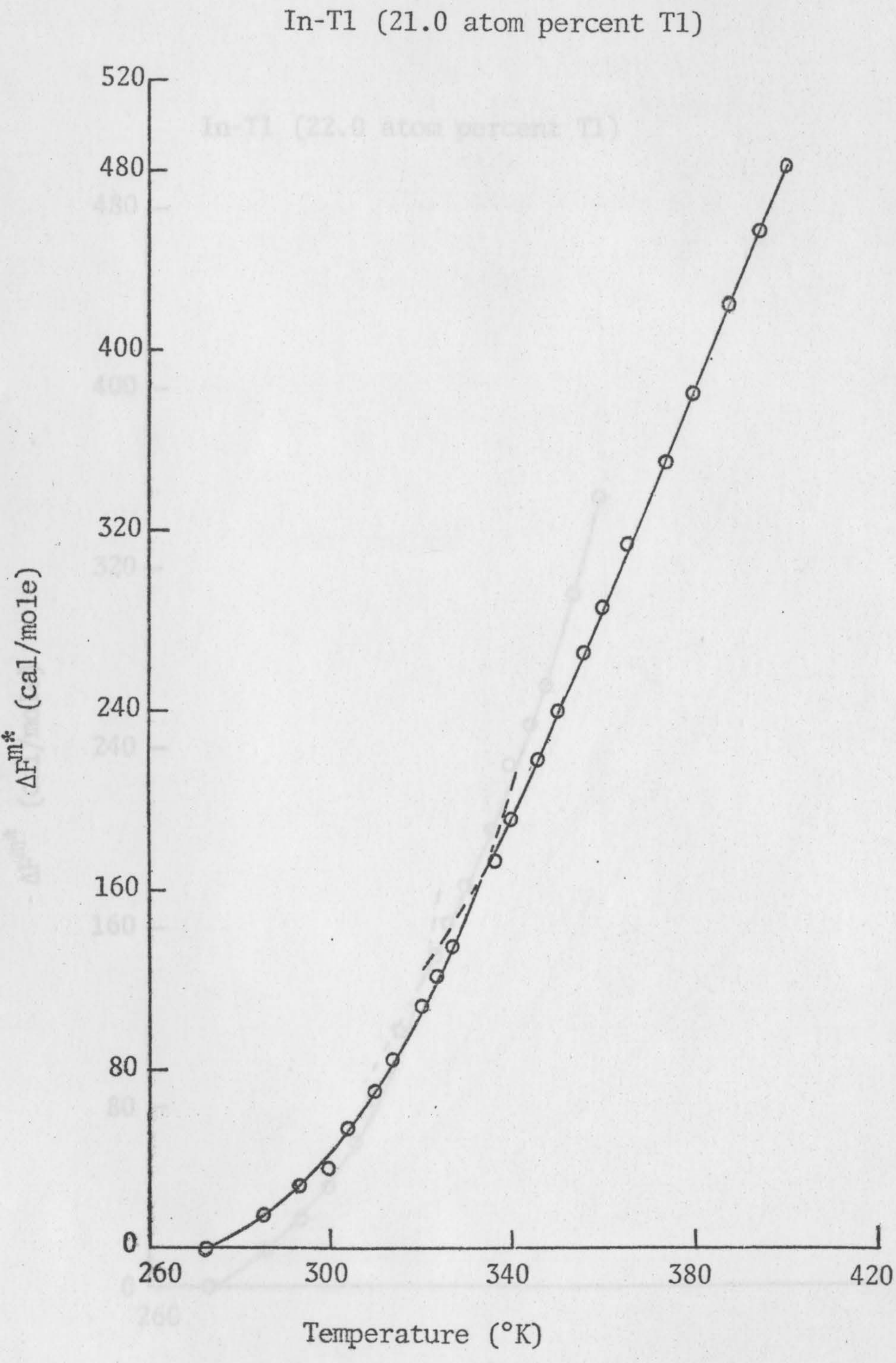

Figure 20. The Apparent Free Energy Of Mixing As A Function Of Temperature.

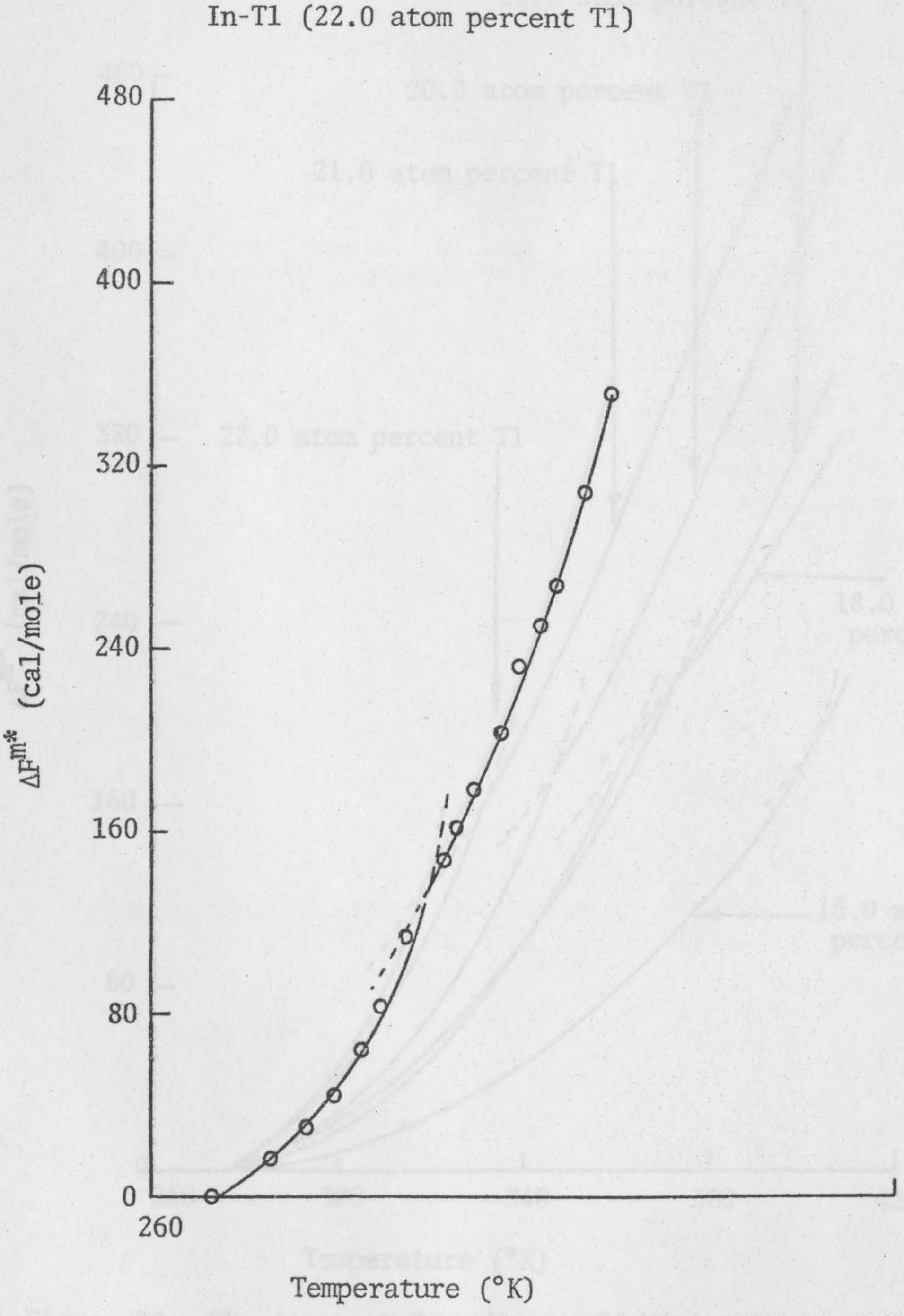

Figure 21. The Apparent Free Energy Of Mixing As A Function Of Temperature.

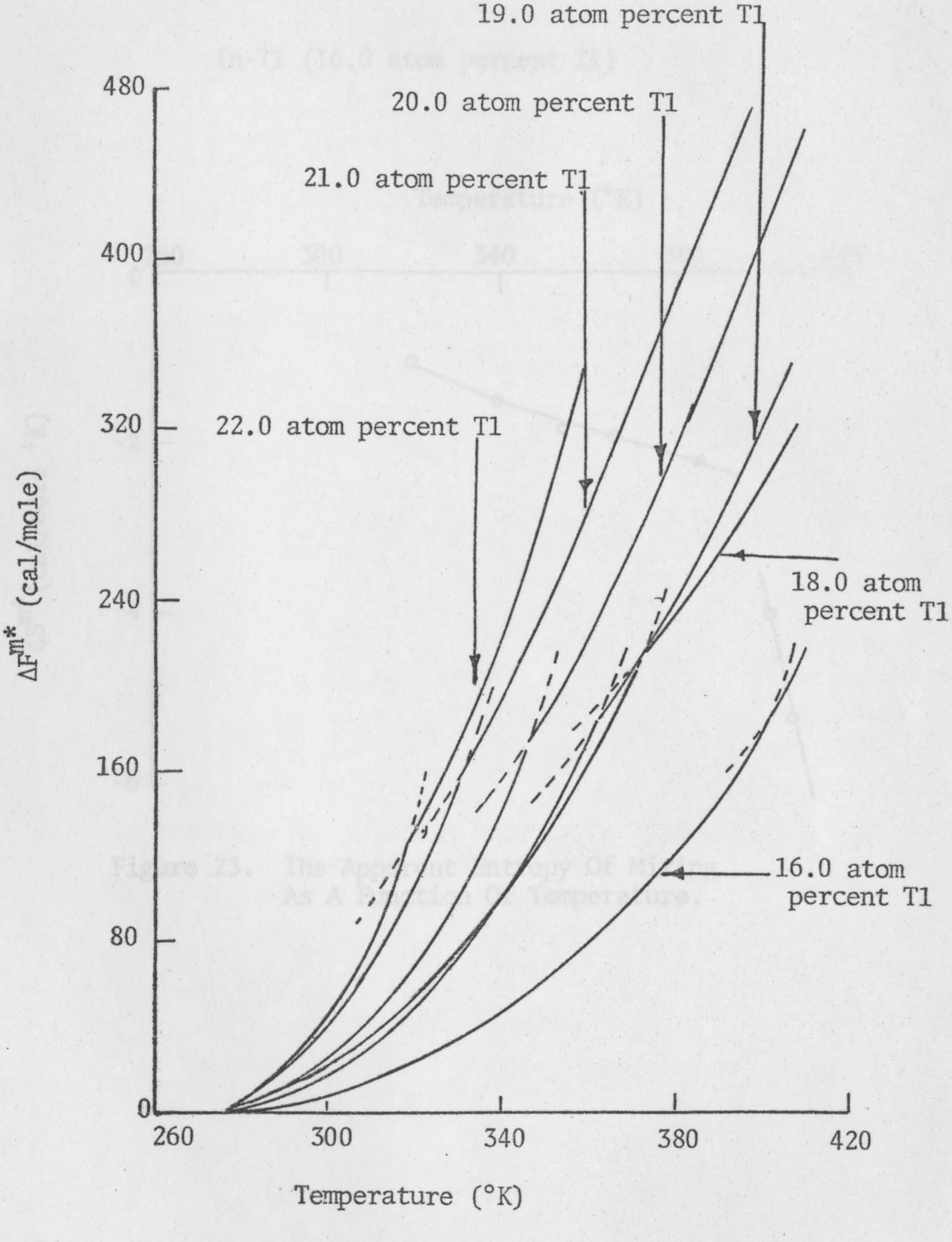

Figure 22. The Apparent Free Energy Of Mixing As A Function Of Temperature For Various Alloy Compositions.

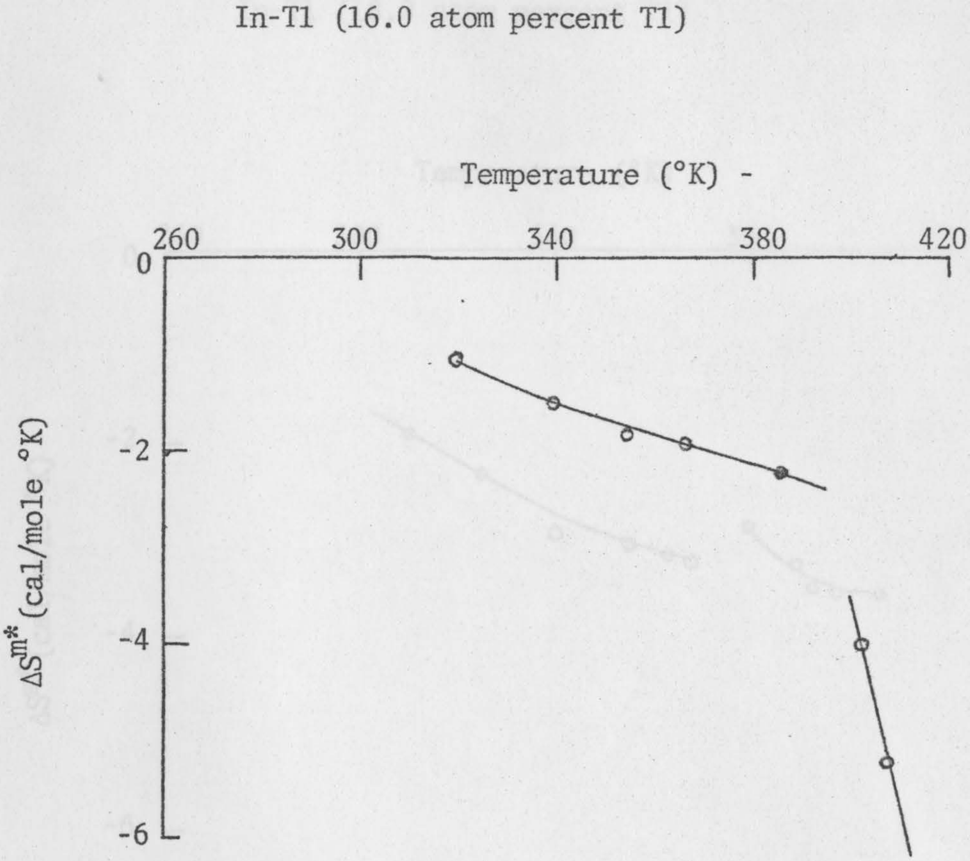

Figure 23. The Apparent Entropy Of Mixing As A Function Of Temperature.

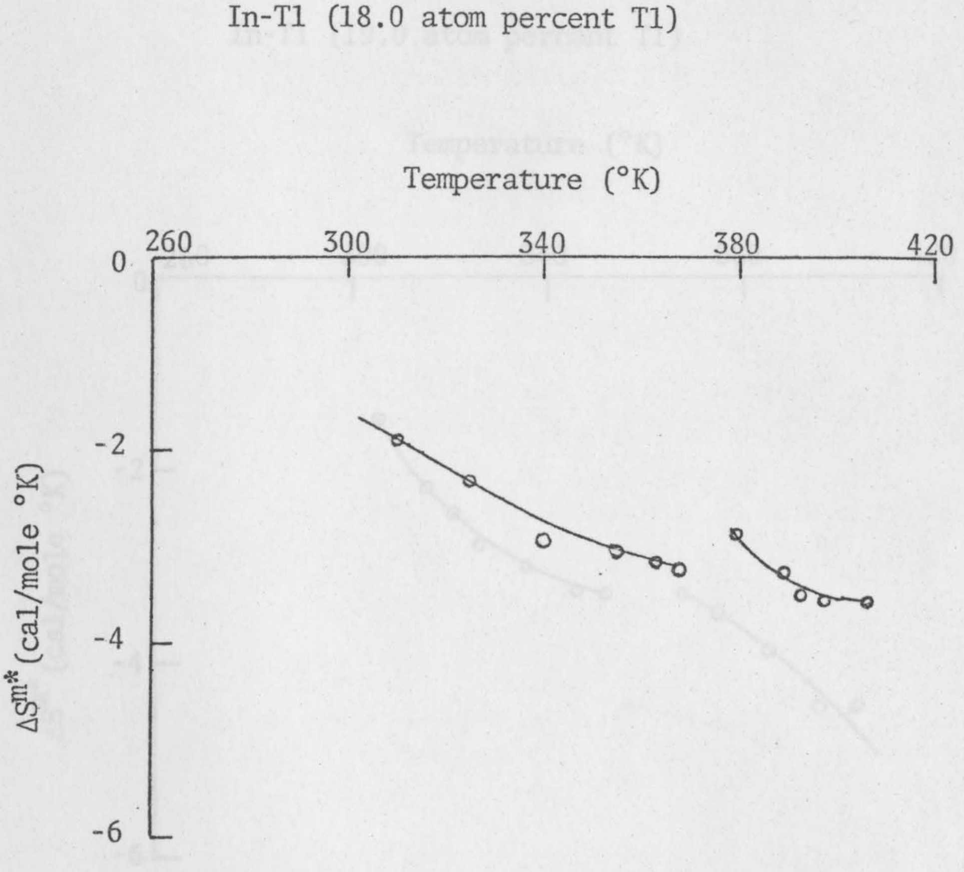

Figure 24. The Apparent Entropy Of Mixing As A Function Of Temperature.

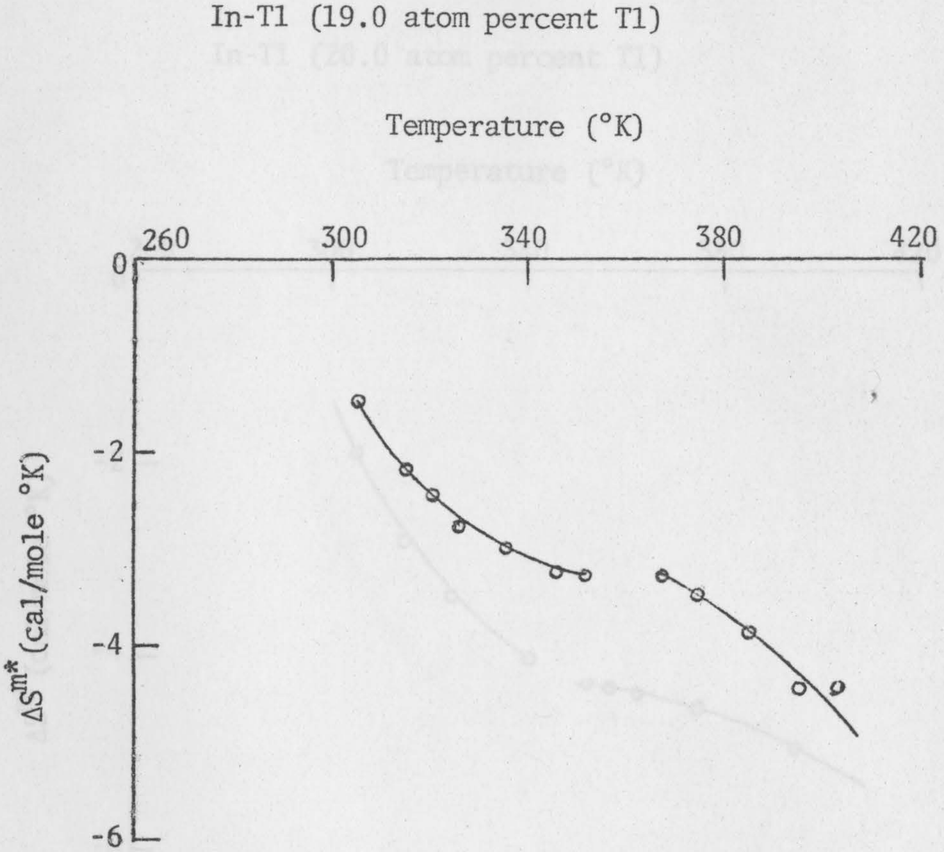

Figure 25. The Apparent Entropy Of Mixing As A Function Of Temperature.

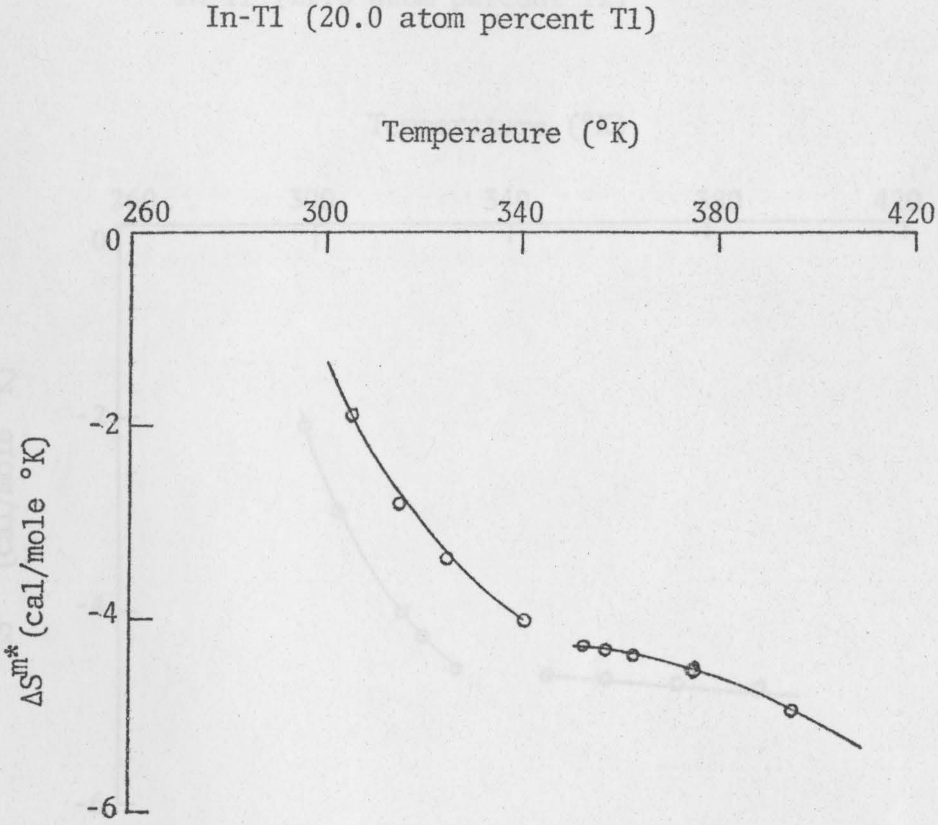

Figure 26. The Apparent Entropy Of Mixing As A Function Of Temperature.

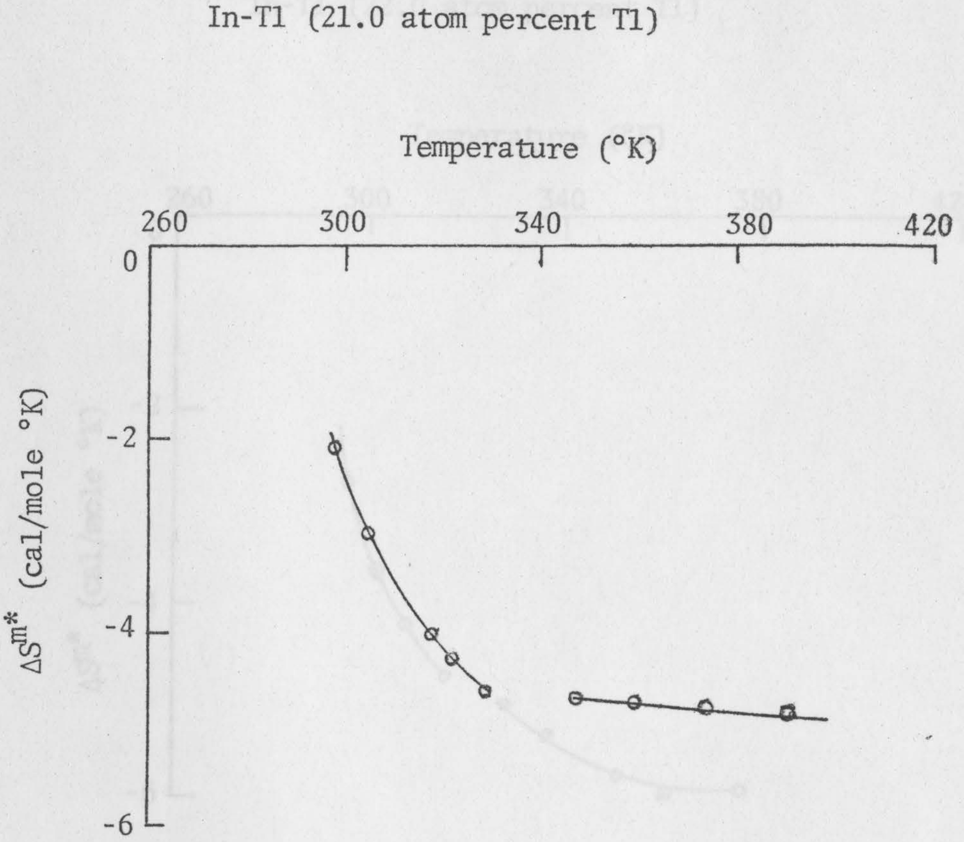

Figure 27. The Apparent Entropy Of Mixing As A Function Of Temperature.

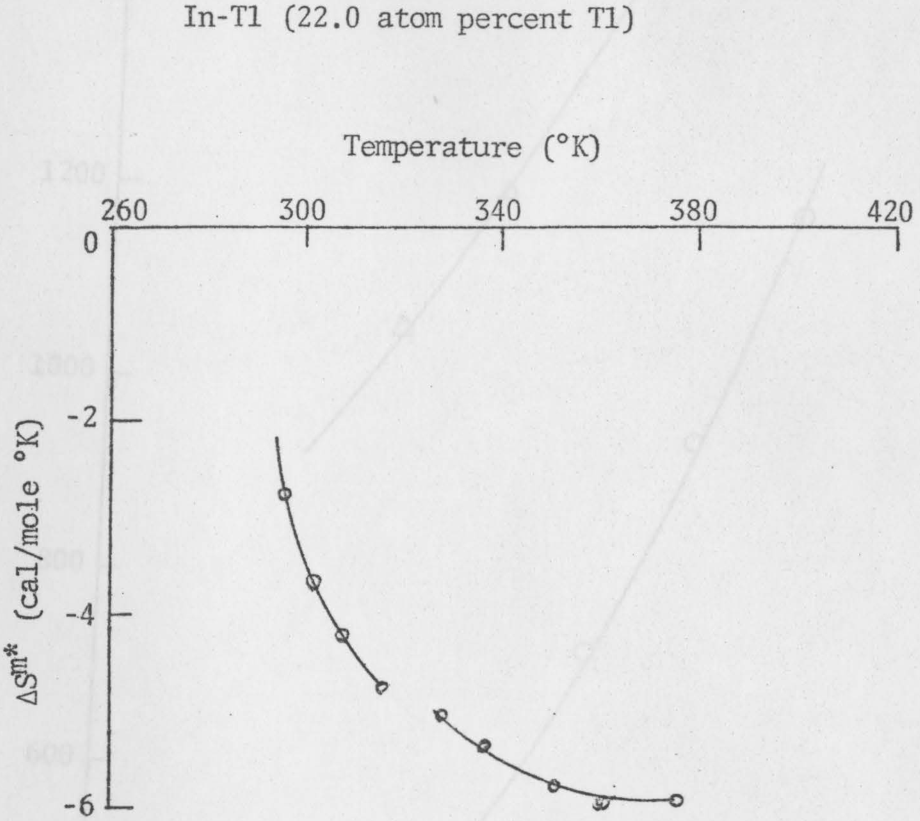

Figure 28. The Apparent Entropy Of Mixing As A Function Of Temperature.

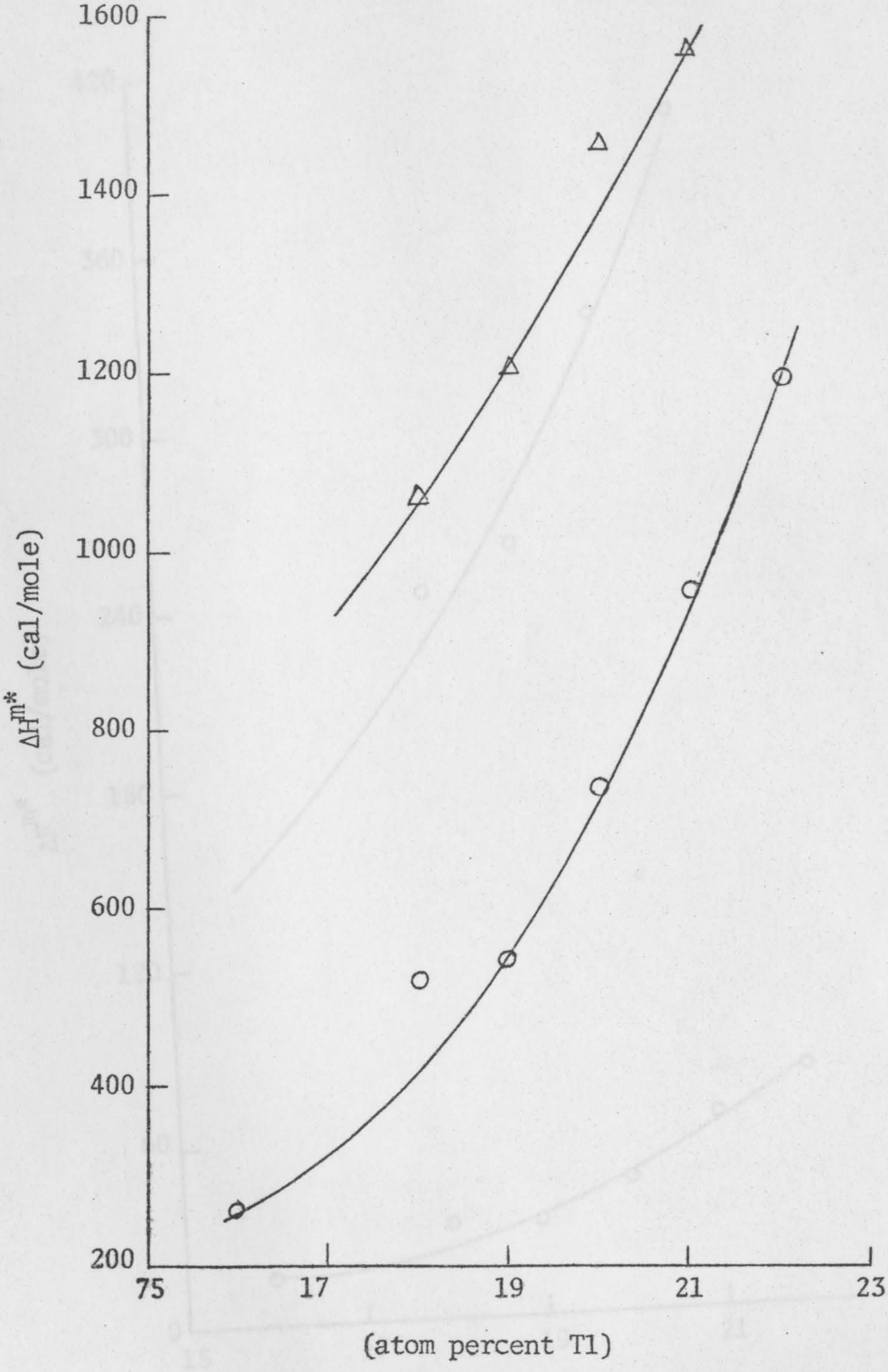

Figure 29. Apparent Enthalpy Of Mixing As A Function Of Alloy Composition.

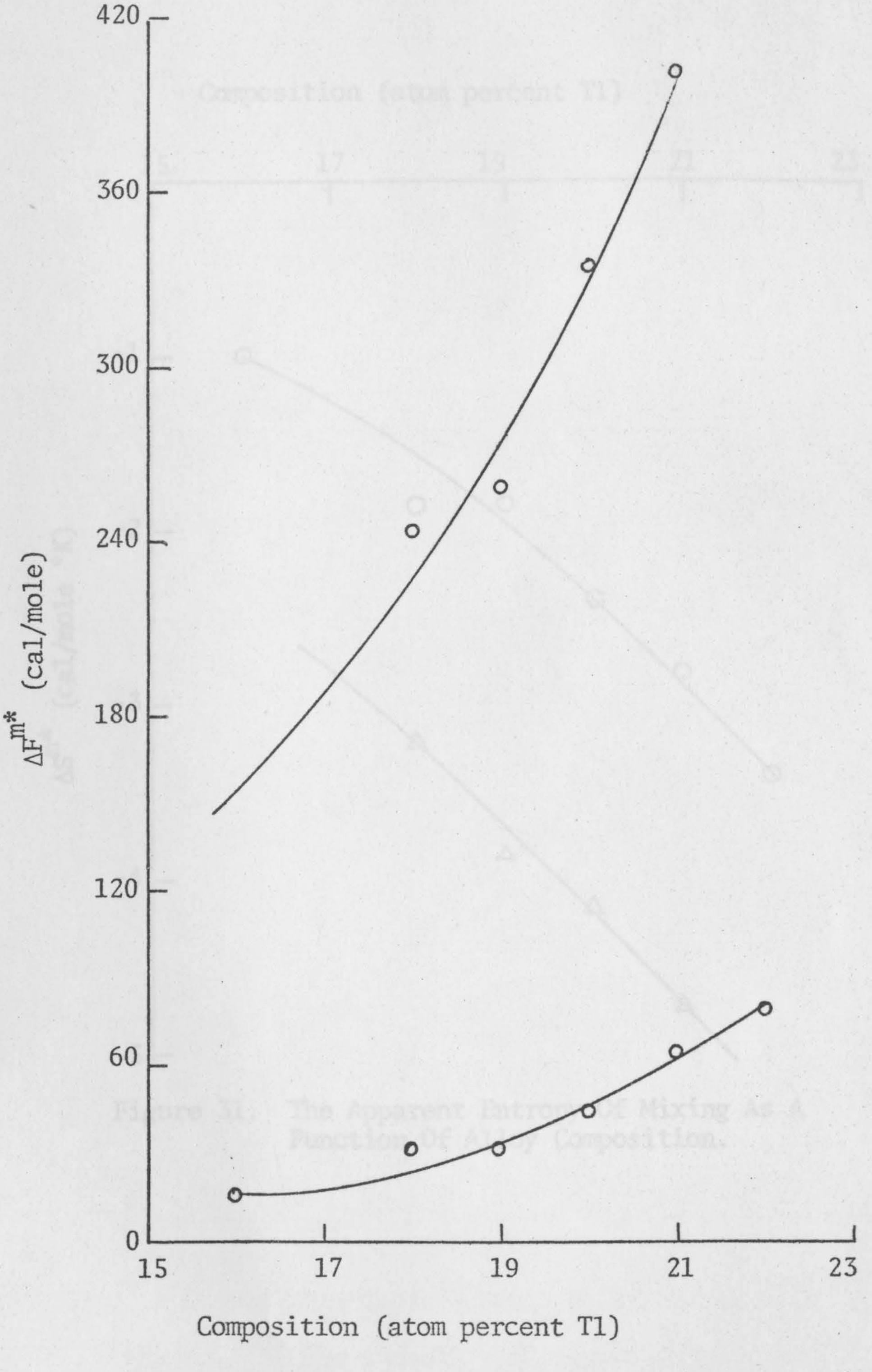

Figure 30. The Apparent Free Energy Of Mixing As A Function Of Alloy Composition.

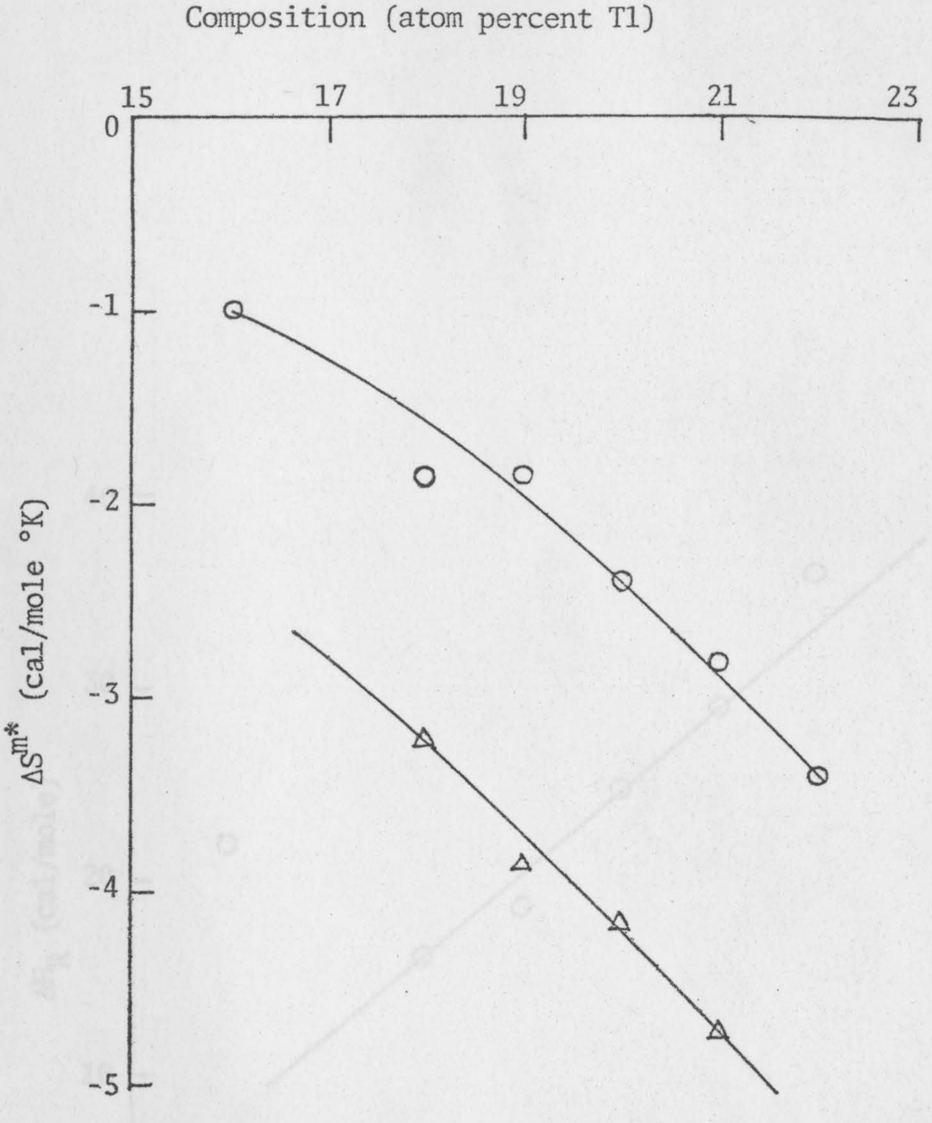

Figure 31. The Apparent Entropy Of Mixing As A Function Of Alloy Composition.

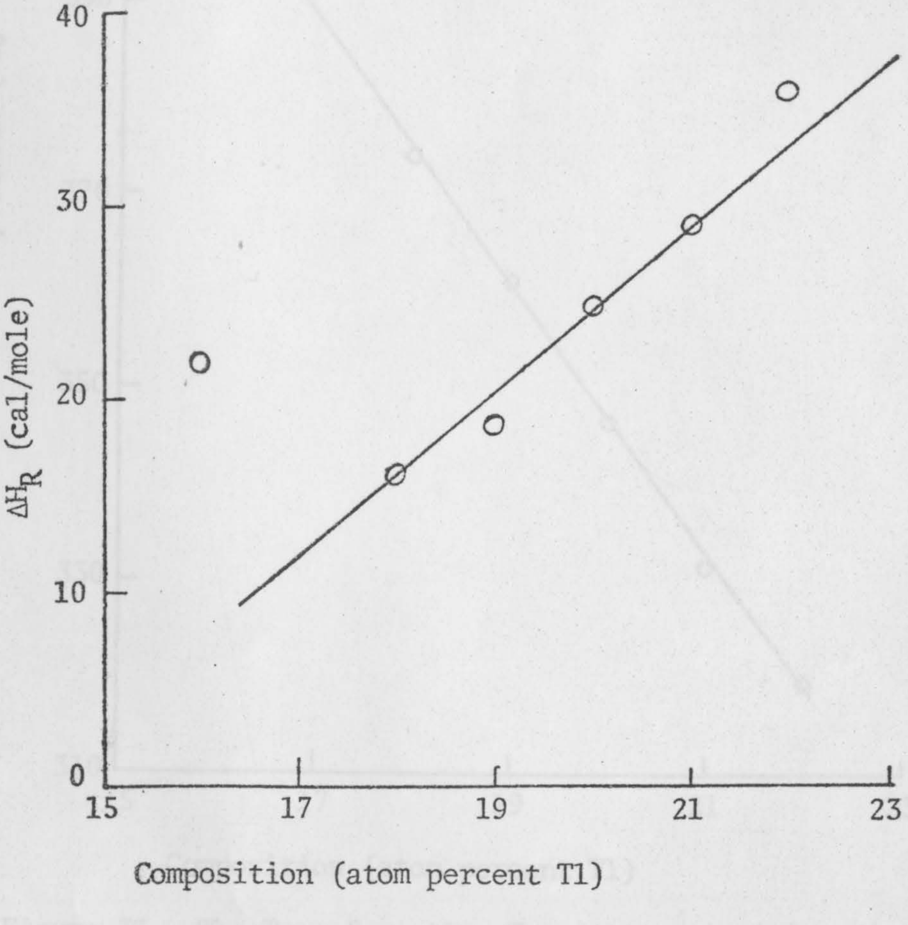

Figure 32. Enthalpy Of Transformation As A Function Of Alloy Composition.

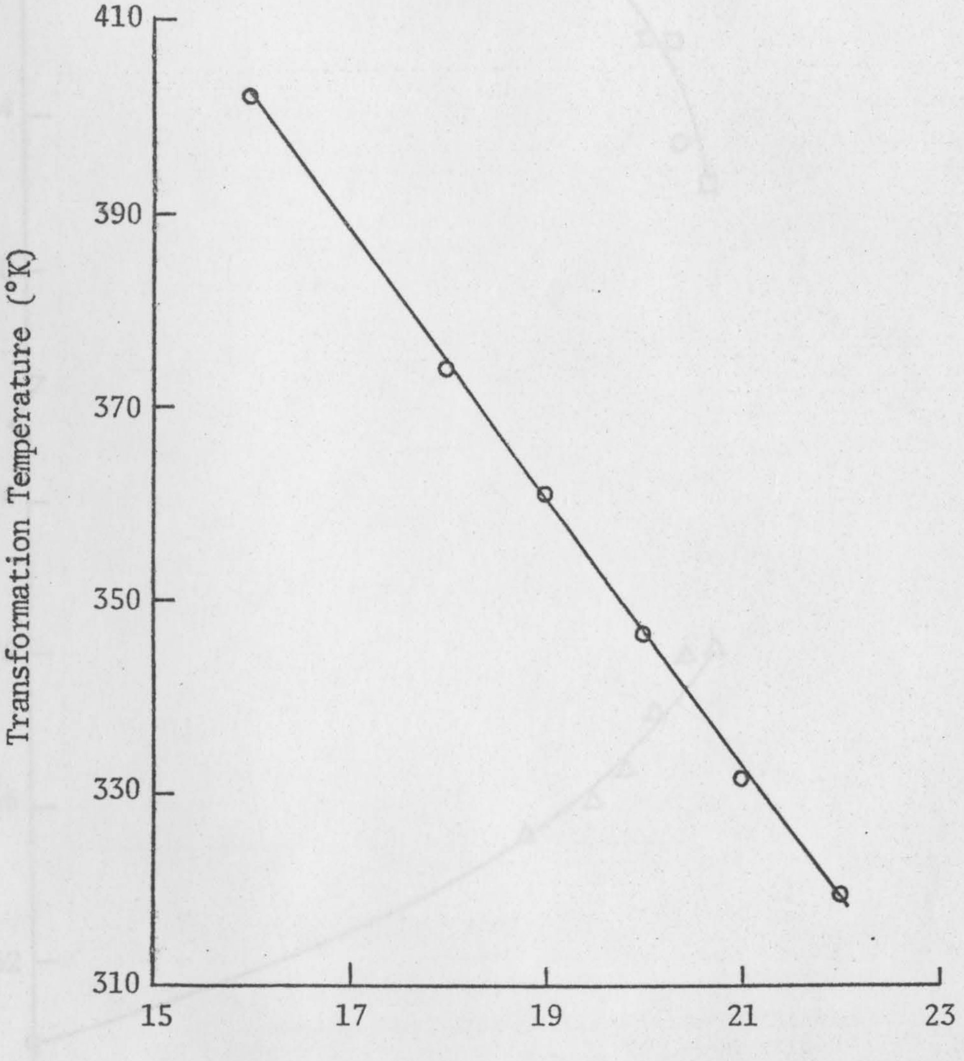

Figure 33. The Transformation Temperature As A Function Of Alloy Composition.

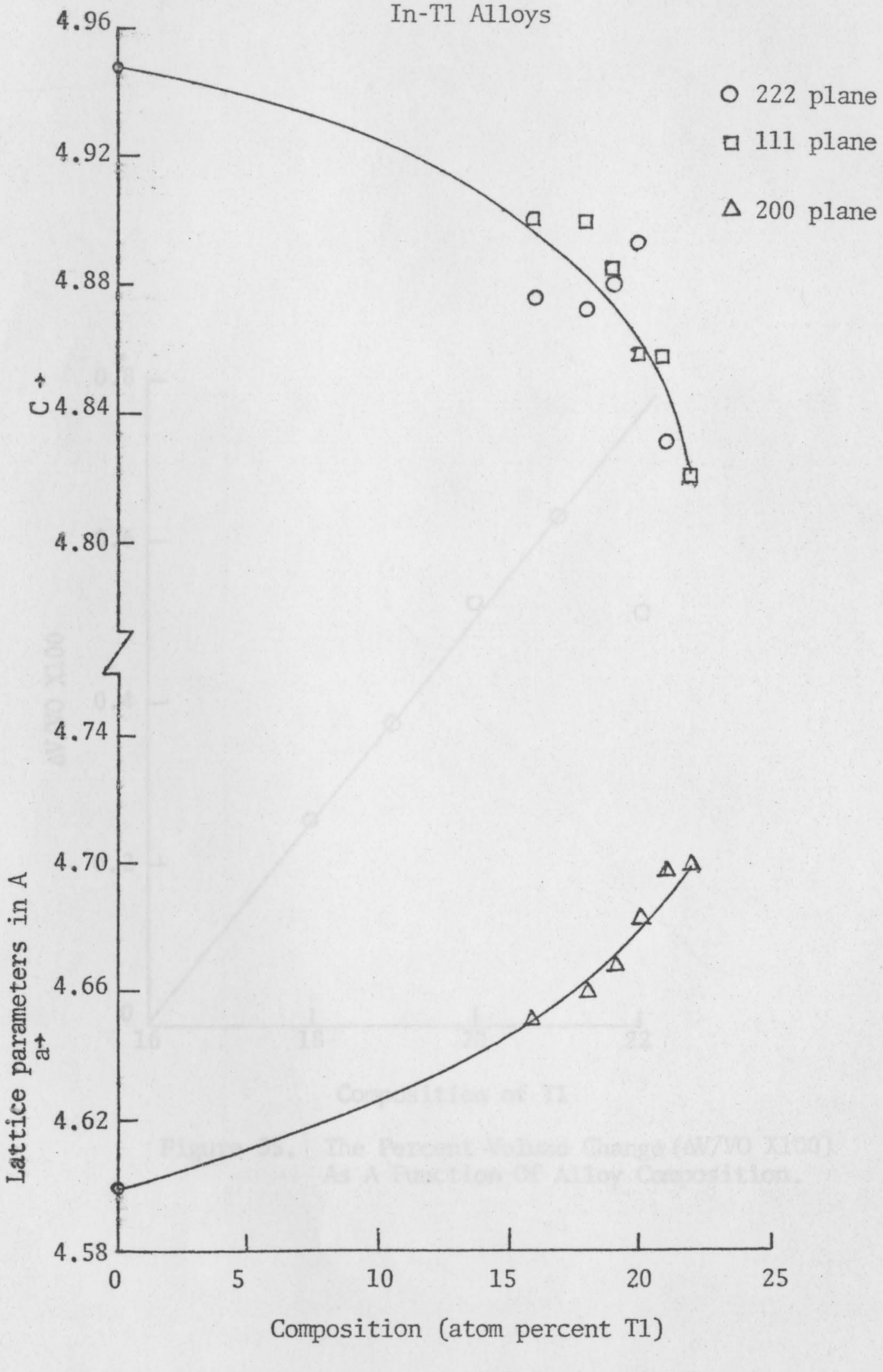

Figure 34. Lattice Parameters As A Function Of Alloy Composition.

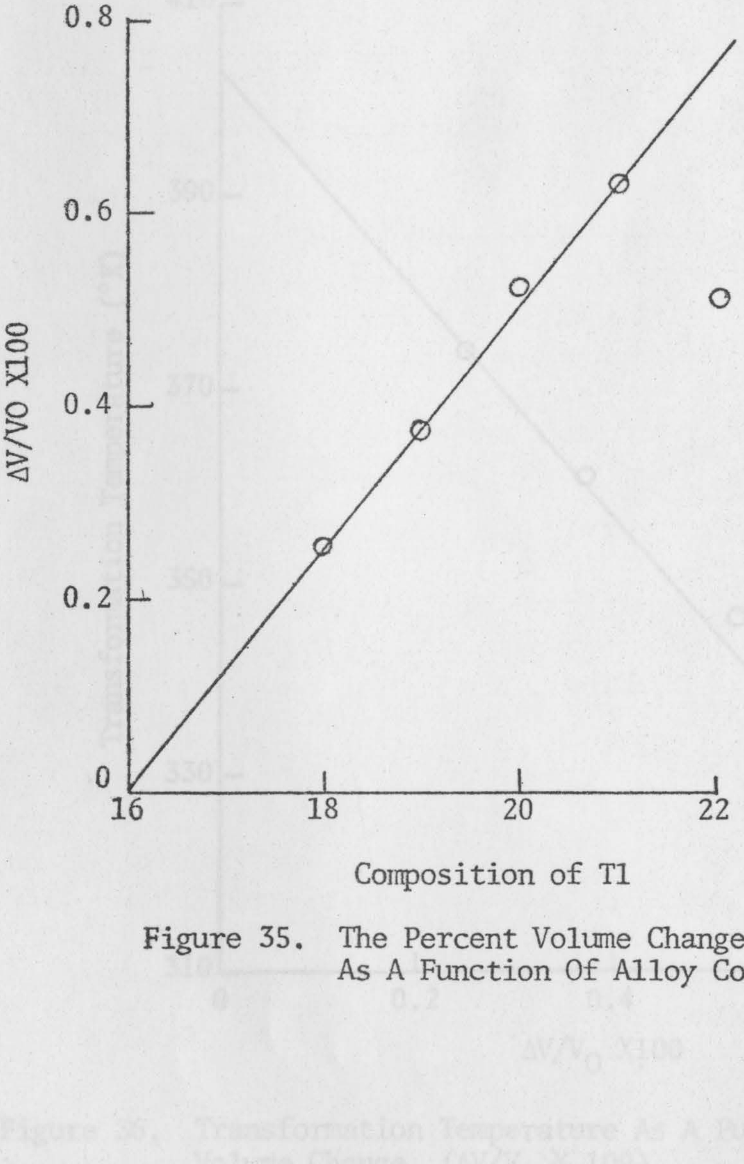

Figure 35. The Percent Volume Change (ΔV/VO X100) As A Function Of Alloy Composition.

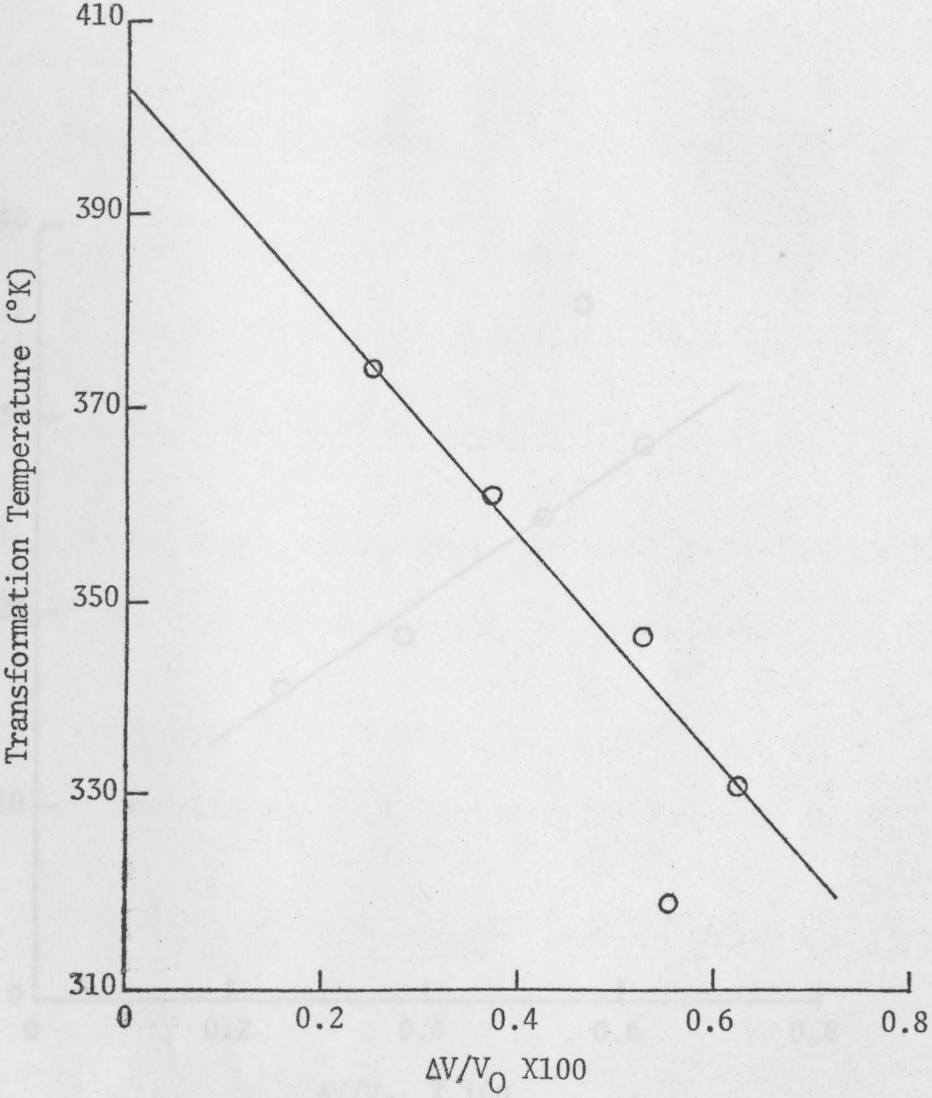

Figure 36. Transformation Temperature As A Function Of Percent Volume Change ($\Delta V/V_O$ X 100)

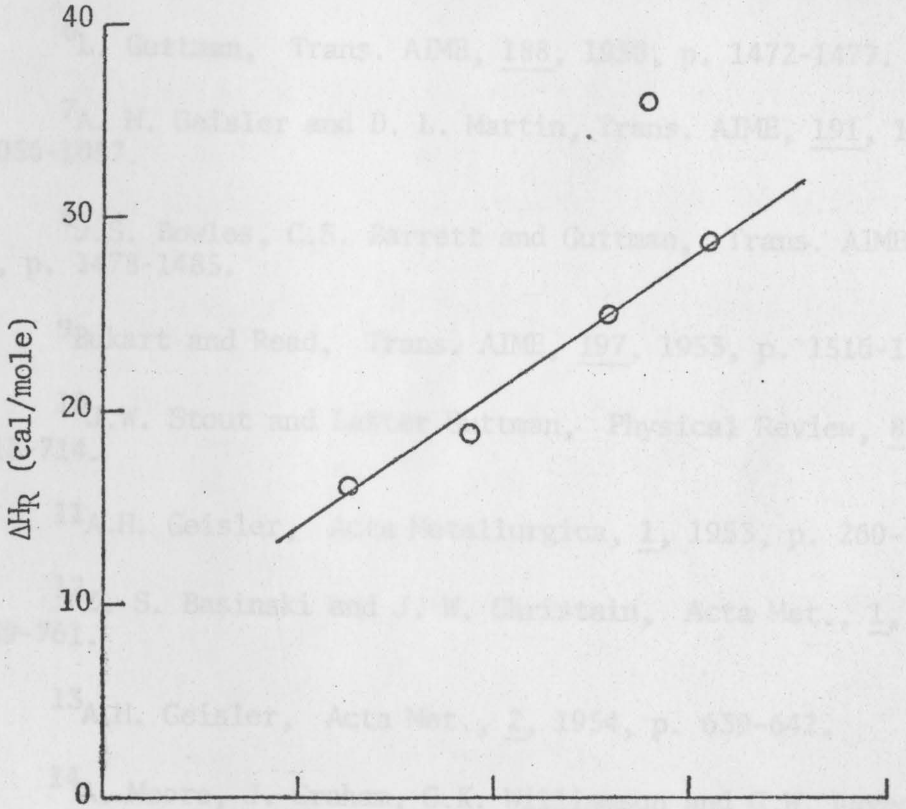

Figure 37. The Enthalpy Of Transformation As A Function Of Percent Volume Change ($\Delta V/V_O$ X 100)

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