To the Graduate Council:

I am submitting herewith a dissertation by Katie A. Roles entitled "Heat Capacity Studies of Solid Poly(amino acid)s." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of doctor of philosophy, with a major in chemistry.

Bernhard Wunderlich, Major Professor

We have read this dissertation
and recommend its acceptance:

Accepted for the Council:

Associate Vice Chancellor
and Dean of the Graduate School

HEAT CAPACITY STUDIES OF SOLID POLY(AMINO ACIDS)

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Katie A. Roles
May, 1991

For Jeff

Thanks for pushing me.

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ABSTRACT

Heat capacities of sixteen poly(amino acids), based on the twenty naturally occurring amino acids, and four copolymers of poly(amino acids) were analyzed using approximate group vibrations and fitting of the skeletal vibrations to a two parameter (Θ_1, Θ_3) Tarasov function. New experimental heat capacities were measured by differential scanning calorimetry in the temperature range 220 to 390 K. Good agreement between our experimental data and the calculated data was observed for all but two of the biopolymers, poly(L-methionine) and poly(L-serine). Previous investigations on the three simplest poly(amino acids) – polyglycine, poly(L-alanine), and poly(L-valine) showed agreement between calculation and reported experimental data for only limited, low temperature ranges. At higher temperatures, discrepancies of up to 55% existed between experiment and calculation. It is shown that systematic experimental errors plagued these earlier investigations. In fact, the most likely source of error in these earlier investigations was the presence of removable water. Recommended experimental data are revised on the basis of this investigation. Computed heat capacities are available for all the biopolymers studied in the solid state from 0 to 1000 K. For poly(L-serine) and poly(L-methionine), the lack of agreement between experiment and calculation is attributed to the presence of a broadened glass transition. For the remaining four poly(amino acids), attempts were made to calculate heat capacities based on the results of the sixteen that were measured.

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CHAPTER I

INTRODUCTION

The *ATHAS* (Advanced Thermal Analysis System) laboratory, under the direction of Professor Bernhard Wunderlich has had a long-time interest in conducting research on the thermal properties of linear macromolecules and in maintaining a critically evaluated data bank on these properties.[1] As a result of these interests, it has been possible to generate complete tables of the thermodynamic functions heat capacity, *Cp*, enthalpy, *H*, entropy, *S*, and Gibbs free energy, *G*. At present, data for over 150 solid linear macromolecules have been collected. The success of these efforts to fully describe the thermodynamic properties of synthetic macromolecules led to the consideration that a natural extension of this work should be the inclusion of the biological macromolecules. It was the goal of this research to lay the foundation for advanced thermal analysis of biological materials, starting with the poly(amino acids) and ultimately extending the work to proteins. Most recent research has suggested that thermodynamic functions play an important role in selecting the most favorable biological macromolecules for a given living system.[2]

Poly(amino acids) or homopolypeptides have long been considered useful models for the study of proteins for a number of reasons. First, they can be based on the twenty naturally occurring amino acids which make up the composition of all proteins. Like the amino acids, the homopolypeptides consist of a basic unit with

various substitutions depending on the particular amino acid. Unlike the amino acids, the poly(amino acids) are composed of a continuous repetition of this basic unit resulting in a polymeric form of the amino acid. This then leads to a second reason making them useful in the study of proteins. Like proteins, the poly(amino acids) are large polymers.

The first step in laying the foundation for the advanced thermal analysis of biological materials is the establishment of a data bank of heat capacities for the poly(amino acids) based on the common twenty amino acids. The next step is the verification of the copolymer rules established for synthetic polymers by the analysis of selected co-polymers, peptides, and ultimately proteins. As the data bank grows, the problems of order-disorder transitions, structure, and stability of systems containing proteins, in addition to other, low molecular mass components can be addressed. Ultimately, it is hoped to establish thermal analysis as an integral part of the analysis of biological materials as it is now in the thermal analysis of other polymeric materials.[3]

Such a massive undertaking is considered necessary, as a review of the literature reveals that most of the calorimetry of biological macromolecules has been concerned with the measurements of heats of transition, reaction, or dissolution.[4] There are only a few proteins for which heat capacities have been measured in aqueous solution or in the solid state. Furthermore, most of the available heat capacities are not precise enough to attempt to link them to structural features. One of the most compelling problems in protein chemistry today is the need for a

quantitative understanding and characterization of the interactions between proteins and water. The role water plays in biological macromolecules is of major concern in the food industry. A detailed understanding of the interactions between water and proteins, as well as between water and carbohydrates, lipids, and nucleic acids, is necessary for continued improvements in food preservation and in maintaining taste and texture.[5] This understanding is equally important in the field of medical research. Studies of intracellular water might provide insight into cell functions. Several studies have shown that the amount and relaxation of water in cells is dependent on the physiological state of the cells. Hazlewood et al.[6] have observed, for example, that the aging of tissues alters the NMR properties of water in the tissues. Damadian[7] found that water in malignant cells has longer NMR relaxation times than water in closely related normal tissue. The difficulty in these studies is that they have dealt with very large, complicated systems. It seems that to get to the heart of the matter, one must first begin with a complete knowledge of the simplest part. In the case of proteins, this simplest part is the poly(amino acid).

In regard to the poly(amino acids), a number of small studies have been conducted earlier on the heat capacities of the three simplest poly(amino acids): polyglycine[8-10], poly(L-alanine),[11-15] and poly(L-valine).[16] In this thesis, it will be shown however, that these studies were grossly in error.

In this thesis will be layed the foundation for the advanced thermal analysis of biological materials by presenting new recommended heat capacities for the three simplest poly(amino acids) based on new experimental work. In addition, for the

first time, experimental heat capacity data will be presented for thirteen other poly(amino acids) so that experimental data now exist for sixteen of the twenty poly(amino acids). In addition, the next step in extending the analysis to proteins will be taken by presenting experimental heat capacities for four copolymers of these poly(amino acids), thus verifying the copolymer rules established for synthetic polymers and leading the way for future extension to proteins. Furthermore, a complete understanding of any macroscopic property, in this case, the heat capacity, requires a link to its microscopic origin. In this thesis the discussion will go beyond the description of experimental studies and show that the heat capacity of biological materials can be linked to the vibrational spectrum, in the same manner as has been accomplished for other solid, linear polymers.[17] For fourteen of the poly(amino acids) and for the four copolymers, it will be shown that it is possible to calculate heat capacities based on the approximate individual vibrational spectra. For the additional two poly(amino acids), poly(L-serine) and poly(L-methionine), attempts to calculate heat capacities were unsuccessful for all but the lowest temperatures. It will be shown that the lack of success observed at higher temperatures can be attributed to the presence of a broadened glass transition.

The result of this research will thus be the establishment of a data bank for most poly(amino acids) based on the twenty naturally occurring amino acids. Verification of the copolymer rules established for synthetic polymers will make it possible in the future to extend the data bank to proteins and beyond. In addition, in the linking of the heat capacity to the vibrational spectrum, this research will

demonstrate that biological polymers can be treated in the same manner as other solid polymers.

I. LITERATURE REVIEW

IA. Structure

All poly(amino acids) consist of the same basic repeat unit with various substitutions. Poly(amino acids) based on the twenty naturally occurring amino acids have the (S) configuration at the α carbon and thus belong to the L series. Table 1 in Chapter II – Materials and Methods lists the twenty polyamino acids and their respective substitution group R.

Basic Repeat Unit $(C_\alpha HR-CO-NH-)_n$

The NH (imino) and CO (carbonyl) groups are known to interact with each other to give a partial double-bond character to the $C_\alpha N$ bond. Figure 1 illustrates the two resonance structures which lead to this partial double bond character. The result of this partial double bond character is that the conformation of each residue, that is the atoms starting from one α carbon to the next α carbon ($C_\alpha HR-CO-NH-C_\alpha HR$), is planar zigzag. Pauling, Corey, and Branson assigned bond lengths and angles to this peptide unit as early as 1951.[18] Figure 2 gives this information as it was later refined in 1953 by Pauling and Corey.[19] Note that the C–N distance of 13.2 nm and the C–O distance of 12.4 nm are representative of a

Figure 1 Resonance Structures of the Basic Repeat Unit.

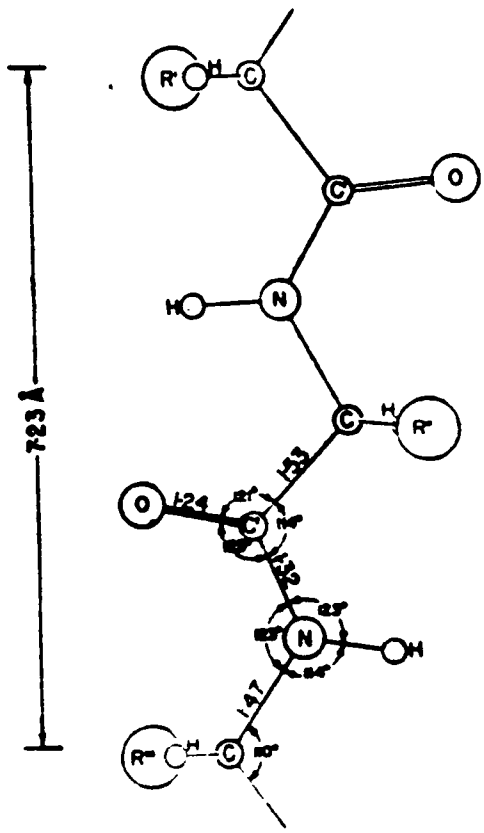

Figure 2 Bond Lengths and Angles of the Peptide Unit.[19] [Source: L. Pauling, R.B. Corey, and H.R. Branson *Nat'l Acad. Sci. USA* 37, 205 (1951).

nearly 50% double bond character.

Peptide units link together at the α carbon atoms when forming a polypeptide. The conformation of the peptide backbone is essentially characterized by two dihedral angles of rotation ϕ ($CNC_{\alpha}C$) and ψ($NC_{\alpha}CN$), shown in Figure 3.[20] The additional angle ω describes whether the peptide bond is in the cis or trans conformation. This is shown in Figure 4. It has been shown, however, that the most likely conformation of the peptide linkage is *trans*. As a result, the third angle ω is usually omitted when discussing the conformation. The *trans* conformation is favored over the *cis* conformation by roughly a little more than 8 kJ/mol.[20] The exception to this is poly(L-proline) for which the energy difference between the two conformations is much less. As a result, poly(L-proline) I is the only poly(amino acid) which favors the *cis* conformation.

Polyglycine is the simplest poly(amino acid), it's side group R being simply a single hydrogen atom. Polyglycine, like several of the other poly(amino acids) can be found in two energetically and sterically favorable forms. Polyglycine I (PGI) is a β-sheet or pleated structure. In such a conformation, the individual strands aggregate side by side, forming all possible hydrogen bonds between the CO^- and NH^+ groups of the peptide units. The chains are nearly fully extended. The result is the formation of sheets of parallel or antiparallel chains. The chain configuration is designated as 3*2/1.* In polyglycine II (PGII), all chains are parallel. The chains

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*The designation $n*p/q$ specifies the number (n) of skeletal atoms in the asymmetric unit of the chain and the number of such asymmetric units (p) per q turns of the helix in the crystallographic repeat unit.

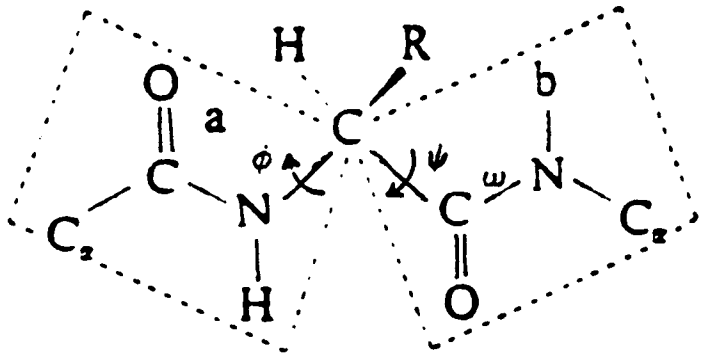

Figure 3 Dihedral Angles Characterizing the Peptide Unit.[20] [Source: F.A. Bovey and F.H. Winslow (eds.) *Macromolecules An Introduction to Polymer Science* Chapter 8, Academic Press, New York (1979).]

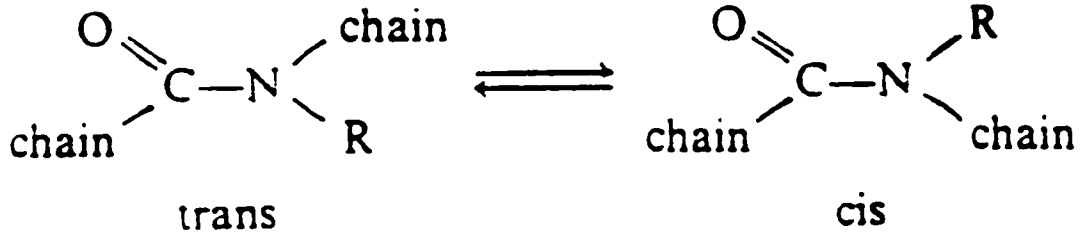

Figure 4 Cis and Trans Conformations of the Peptide Unit.[20] [Source: F.A. Bovey and F.H. Winslow (eds.) *Macromolecules An Introduction to Polymer Science* Chapter 8, Academic Press, New York (1979).]

are densely packed in a hexagonal array with each chain hydrogen bonded to each of its six neighbors. Figure 5, taken form the work of Crick and Rich,[21] illustrates the PGII structure. PGII is then designated as 3*3/1 helices with intermolecular hydrogen bonding rather than intramolecular hydrogen bonding.

Poly(L-alanine), for which R represents a methyl group, also occurs in two conformations. The α-poly(L-alanine) (α-PLA) consists of a closely packed array of right-handed helices of the type 3*47/13. Thus the repeating length of an α-helix is 47 residues in 13 turns. The direction of the peptide sequence of chains is random, some helices pointing up and some pointing down. Elliot and Malcolm[22] as well as Bamford and co-workers[23] point out that the packing of the α helices is governed largely by the methyl group contacts. The β-poly(L-alanine) (β-PLA) with a chain conformation of 3*2/1 can be thought of as sheets of parallel chains packed in an antiparallel fashion giving rise to an almost planar zig-zag configuration.

The structure of poly(L-proline), an imino poly(amino acid) has been studied in considerable detail. Two forms are found to exist, poly(L-proline) I (PRO I) and poly(L-proline) II (PRO II). The PRO I is a right-handed helix in which the peptide units favor the *cis* conformation over the *trans*. There are ten residues per every three turns of the helix. Figure 6, from the work of Traub and Shmueli,[24] illustrates this structure. The PRO II is a left-handed helix in which the peptide units are in the *trans* conformation. There are three residues per turn of the helix. The *trans* helix, unlike the *cis* helix, is considerably extended and packs into a hex-

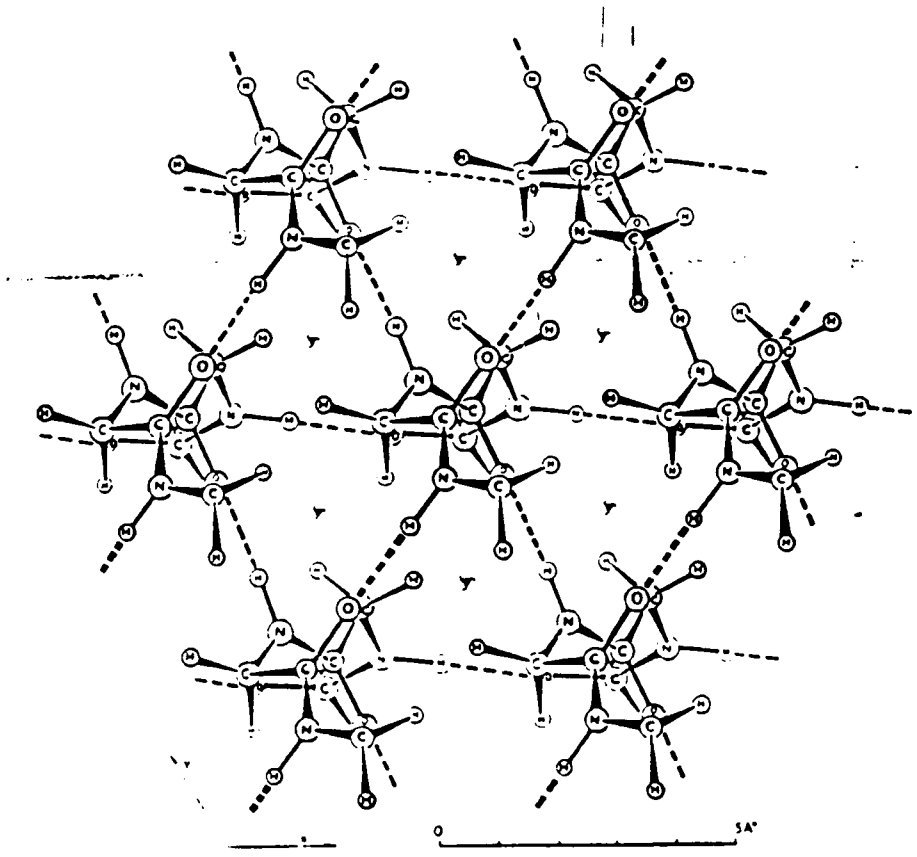

Figure 5 Structure of Polyglycine II.[21] [Source: F.H.C. Crick and A. Rich *Nature* 176, 780 (1955).]

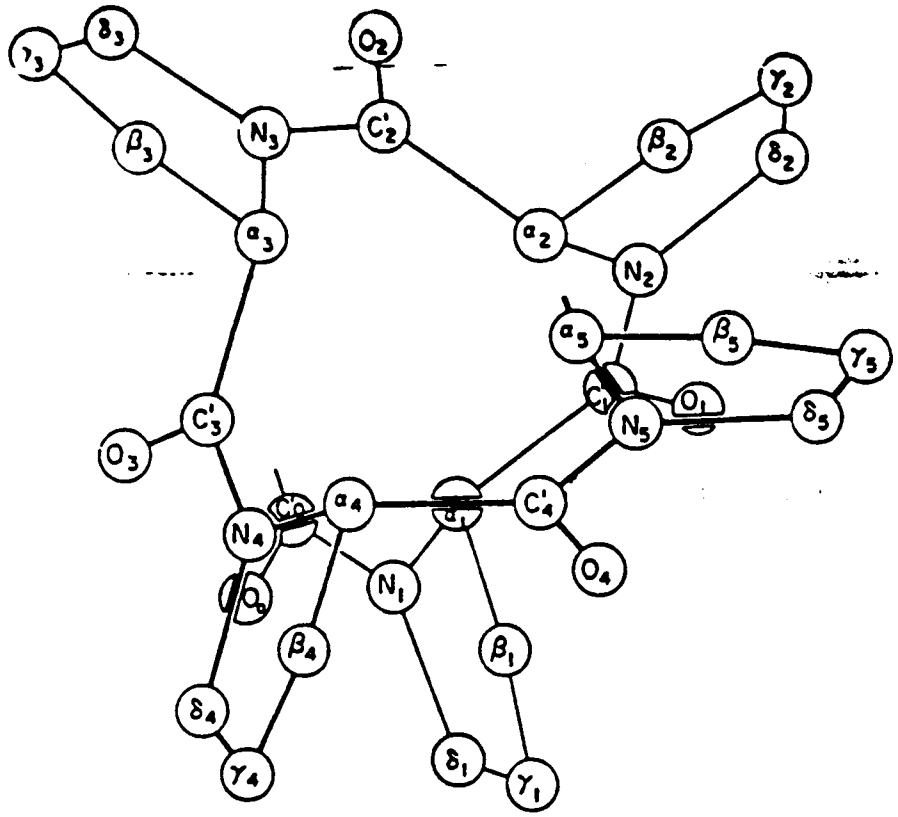

Figure 6 Structure of Poly(L–Proline) I.[24] [Source: W. Traub and U. Shmueli *Nature* 198, 1165 (1963).]

agonal lattice. The most interesting feature of the structure is the lack of any hydrogen bonding. Rather than hydrogen bonding, it is considered that the structure may be mainly stabilized by ring closure which locks rotation of the $N-C_\alpha$ bond and by the sterically unfavorable rotation of the $C_\alpha-C=O$ bond.[25]

For the remaining poly(amino acids) to be discussed, much less work has been done in terms of structural characterization than has been done for polyglycine, poly(L-alanine), and poly(L-proline). Poly(L-valine), R = $CH(CH_3)_2$, is found in the α-helix and β-sheet conformations. Yamashita and co-workers[26] report a right-handed α-helix with a chain conformation of 3*18/5. This 3*18/5 chain conformation is perhaps the best known poly(amino acid) conformation. It was first presented by Pauling, Corey, and Branson.[18] Figure 7,[20] below, illustrates a general example of the right-handed α-helix. The β-poly(L-valine) is composed of sheets of antiparallel chains.[26] (See Figure 8.[27]) Yamashita and Ashida[27] note that in the β-sheet conformation, the side group R of one residue overlaps with that of the opposite pointing or antiparallel chain. In addition, the NH group of one residue overlaps with the CO group of the chain opposite or antiparallel. This leads to a greater pleat angle than that observed for β-PLA.

For poly(L-leucine) two conformations are allowed, the α-helix and the β-sheet. The α-helix has been shown by Kawai and co-workers[28] to form a hexagonal lattice. It is considered the most stable conformation because it is not sterically unfavorable for the side group to form the α-helix. The chain conformation has yet to be worked out. The β-poly(L-leucine) (β-LEU) is an

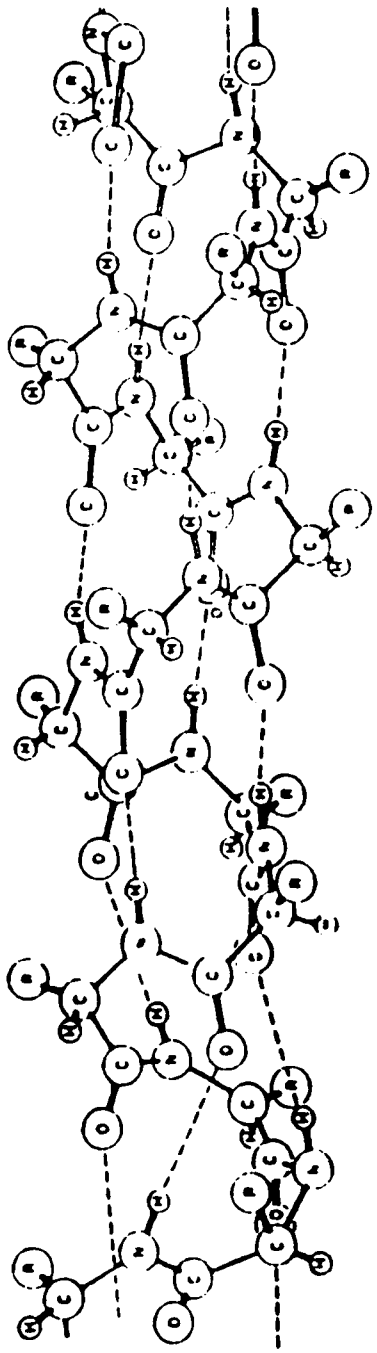

Figure 7 Right-Handed Helix Conformation.[20] [Source: F.A. Bovey and F.H. Winslow (eds.) *Macromolecules An Introduction to Polymer Science* Chapter 8, Academic Press, New York (1979).]

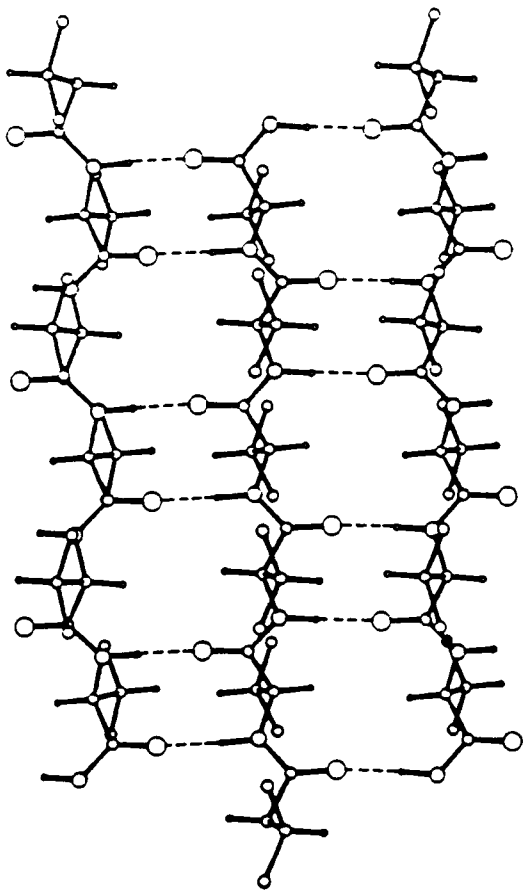

Figure 8 Structure of ß-Poly(L-Valine).[27] [Source: O. Yamashita and T. Ashida *Polymer Journal* 15(12), 899 (1983).]

arrangement of parallel chains packed in an antiparallel fashion which gives rise to an almost planar zig-zag conformation as in β-PLA and β-PLV.

Poly(L-methionine) is known to exist in the form of an α-helix. Colonna-Cesani and Premilat[29] suggest poly(L-methionine) packs into a hexagonal array. The chain conformation is given as 6*2/1.

Poly(L-histidine) hydrochloride has been shown by Oshima and Kumanotani[30] to form a helix with a chain conformation of the type 3*15/4. In this conformation, the CO group is found near the axis or interior while the NH group is found near the exterior. This is shown in Figure 9. The NH groups form strong hydrogen bonds with the Cl^- ions.

Poly(L-lysine) hydrobromide is found to exist in two forms, an α-helix and a β-sheet. Padden and co-workers[31] and Suwalsky and Llanos[32] have shown the α-helix to be a hexagonal array of lamellar crystals. The chain conformation has, however, yet to be worked out. The β-sheet conformation of poly(L-lysine)·HBr (β-LYS·HBr) is characterized by the typical antiparallel sheets packed in a parallel fashion. Suwalsky and Llanos[32] found that interpenetration of the side chains does not occur and suggest it is due to the steric hindrance of the Br^- ions. The most interesting observation of both research groups is the effect of humidity on the conformation. The β-sheet conformation is favored at low hydration levels while the α-helix is favored at high hydration levels. Studying both the hydrochloride and hydrobromide forms of poly(L-lysine), Suwalsky and Llanos[32] were able to conclude that the anions serve mainly in determining the water content at which a confor-

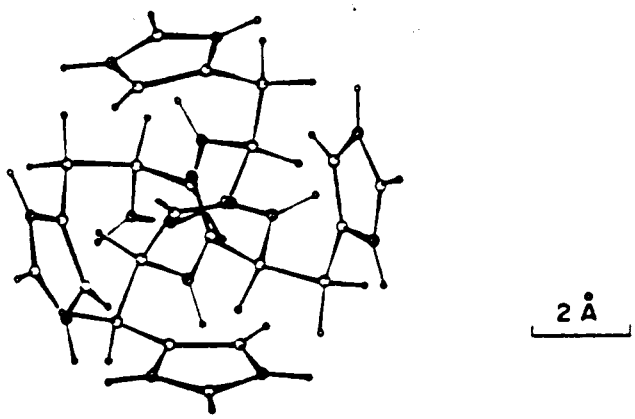

Figure 9 Structure of Poly(L-Histidine•HCl).[30] [Source: R. Oshima and J. Kumanotani *Macromolecules* 19, 938 (1986).]

mational change from the α-helix to the β-sheet is observed. They conclude that while the anions may affect the packing arrangement of the crystal, they do not affect the conformation.

Poly(L-glutamic acid) has been found to exist in three conformations, an α-helix, a β-sheet structure noted as β_1, and another β-sheet noted as β_2.[33] The α-helix is considered the most stable form at room temperature. As the temperature is increased, the α-helix is transformed to the β_1 structure. Further heating causes the β_1 to transform to the β_2 structure. Both β-sheet structures are of the antiparallel type. The difference between the two is the spacing between the pleated sheets, the β_2 structure being more tightly pleated than the β_1. Keith and co-workers[34] found that the three forms undergo crystallization with chain folding forming lamellar crystals.

Poly(L-arginine) hydrochloride is another poly(amino acid) whose conformation depends on the degree of hydration. Suwalsky and Traub[35] found that at low hydration levels the poly(amino acid) packs into a hexagonal array of rod-like units and assumes an α-helical conformation. They found from studies with space-filling models that "the observed intermolecular distances are consistent with interpenetrating and partially bent side chains. The side chains are folded back completely around the helix so that the molecules approximate smooth cylinders." At high hydration levels, the anitparallel β-sheet pleated structure is favored. The Cl^- ions are found to be roughly halfway between the pleated sheets.

The information discussed above represents the extent to which the structural

properties of the poly(amino acids) have been studied.

IB. Heat Capacities

In 1983, as part of the initial set up of the *ATHAS* data bank, the existing literature data on the heat capacities of poly(amino acids) were reviewed.[36] At that time literature data could only be found for the three simplest poly(amino acids): polyglycine,[8-10] poly(L-alanine),[11-15] and poly(L-valine).[16]

Finegold and Fanconi[9] were the first to measure the heat capacity of polyglycine. In 1975, using adiabatic calorimetry, they measured the heat capacity of a sample of (PGII) in the temperature range 2 to 20 K. Their sample was obtained from Sigma Chemical Company and then treated with a saturated solution of LiBr to precipitate PGII. No information regarding experimental uncertainty was provided. Much later, in 1981, Finegold and Kumar[8] extended this study to include PGI and higher temperature measurements. Heat capacity measurements were made on both PGI and PGII in the temperature range 150 to 375 K using a differential scanning calorimeter, the Mettler TA 2000B. Again samples were obtained from Sigma. Rather excessive pre-treatment was carried out to obtain samples predominantly consisting of PGI or PGII. After freeze drying, the samples were subjected to IR analysis and were determined to be "predominantly" PGI or PGII. An experimental uncertainty of 8% was claimed.

Poly(L-alanine) has been studied by two groups of researchers, Finegold and co-workers[11-13] and Daurel and co-workers.[14-15] In 1972 Finegold and Cude employed

heat pulse calorimetry to study α-poly(L-alanine) (α-PLA), β-poly(L-alanine) (β-PLA), and a random sample of the α and β forms of poly(L-alanine).[11-13] The α-PLA (MW = 106,000) and the β-PLA (MW = 5,650) were studied from 1.5 to 20 K. The results were fit to two-parameter Tarasov models below 10 K. Above 10 K, the experimental data rose sharply above that predicted by the chosen models. The random sample of PLA (MW= 19,000) was also studied using heat pulse calorimetry from 1.5 to 20 K. Contrary to the results for the α-PLA and β-PLA, they observed a fit to a two-parameter Tarasov model above 10 K. Below 10 K, the experimental data was much higher than that predicted by the chosen model.

Daurel and co-workers[14-15] also studied poly(L-alanine) in three forms, α, β, and mixed conformation. The α-PLA and β-PLA (note that the authors point out that only 85% of their samples are in the α or β conformation) were studied from 2 to 300 K using adiabatic calorimetry. Using heat capacity analysis similar to that developed at the ATHAS laboratory (described in Section II of the Introduction), they were able to fit their data only up to 100 K. An experimental uncertainty of 3% is claimed. The mixed sample (85% α-PLA, 15% β-PLA) of molecular weight 35,000 was studied over a very small temperature range 1.5 to 4 K using adiabatic calorimetry. Again, an experimental uncertainty of 3% is claimed.

Although many of the temperature ranges for which data was taken on PLA overlap, the results reported in each study are quite different from the other studies. The heat capacity measurements reported for α-PLA in the temperature range 2 to 20 K by Finegold and Cude[13] are on the average 33% higher than those reported by

Daurel et al.[14-15] For the β-PLA, the results of Finegold and Cude[13] in the same temperature range are on the average 39% higher than those of Daurel et al.[14-15]

The final study of heat capacity measurement on a poly(amino acid) was made by Daurel and co-workers[16] in 1976 on a sample of poly(L-valine) in the β conformation. Again, the method was adiabatic calorimetry and the temperature range was 2 to 300 K. Only at very low temperatures, below 10 K, was a fit to a two-parameter Tarasov model observed.

These studies represent the extent to which the heat capacities of the poly(amino acids) have been studied. Since our review of this data in 1983, no new results have been published. As we were interested in applying our computation method for calculating heat capacities from the vibrational spectra to biological materials, an initial effort[37] was made to calculate the heat capacities of polyglycine and poly(L-alanine) using the now well established *ATHAS* computation method outlined in Section II of the Introduction.

This initial effort to calculate heat capacities for polyglycine and poly(L-alanine) did not yield theta temperatures that would satisfactorily allow a calculation of heat capacities in agreement with experiment. For polyglycine in the helical conformation (PGII), a good fit was obtained only at low temperatures (1.6 to 20 K). For higher temperatures, errors of 25 to 35% were observed, the experimental heat capacities being seemingly much too high. For polyglycine in the β conformation (sheet, PGI), calculation of heat capacities were made from the low temperature fit of PGII. Still disagreement with the then available experimental data resulted in

errors ranging from 30 to 35%. Similarly, for α and β poly(L-alanine) (α-PLA and β-PLA) the calculated heat capacities varied significantly from those measured and reported in the literature, especially in the higher temperature range. Below 10 K, experimental data reported on both α-PLA and β-PLA could not be fitted well to the calculation. In the intermediate temperature range, the fit was better. From 60 to 160 K, the error was 2.0% for α-PLA. For β-PLA the error was 1.4% over the temperature range 40 to 110 K. At higher temperatures, the disagreement gradually increased again to as high as 50% at 300 K for α-PLA (again the experimental *C*p being higher than the calculated).

Several possible explanations for such large deviations were discussed earlier.[37] Initially it was considered that the deviation might indicate biological polymers could not be treated in the same manner as the corresponding nylons and other synthetic polymers. It was concluded, however, that the most likely source of the deviations were systematic errors in the experimental data,[37] a conclusion fully supported by the present work.

IC. Melting Transitions

It is generally understood that poly(amino acids) and proteins do not melt. Decomposition or denaturation occurs below the melting temperature for biological polymers. While the decomposition temperature for all amino acids has been studied thoroughly, only little information exists regarding this transition for the poly(amino acids). In 1981, Crighton and Findon[38] used the technique of differential thermal

analysis (Du Pont 900 DTA System) to study the decomposition of a number of proteins and poly(amino acids). For a "dry" sample of poly(glutamic acid)**, they observed decomposition at 250°C (523 K). In addition, they observed "an indication of an earlier transition" around 170°C (443 K). This "transition" was described only as being characterized by a change in heat capacity. Therefore, it may be possible that a glass transition exists for poly(glutamic acid) around 443 K.

For poly(asparagine) and poly(aspartic acid) peaks were also observed for "dry" samples. Poly(asparagine) showed two endotherms, one at 200°C (473 K) and a larger endothermic peak at 245°C (518 K). Poly(aspartic acid) showed similar behavior with an endothermic peak at 200°C (473 K) and again a larger peak at 250°C (523 K).

Later Crighton and Hole[39] studied "dry" samples of polyglycine, poly(L-glutamic acid), poly(L-aspartic acid) and poly(L-lysine•HBr) using the technique of differential thermogravimetry (DTG). Polyglycine I was observed to decompose around 250°C (523 K) while polyglycine II was observed to decompose around 270°C (543 K). Poly(L-glutamic acid) decomposed at 250°C (523 K). Poly(L-aspartic acid decomposed around 265°C (538 K), and poly(L-lysine)•HBr decomposed the earliest around 230°C (503 K).

Unfortunately, neither of these studies, which represent the extent of studies on the decomposition or "melting" of poly(amino acids), presented detailed

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**For all poly(amino acids) examined in this study, no evidence was given as to the conformation of the samples, L or D.

information regarding the nature of the samples nor detailed thermodynamic information. As a result, the information that they present can only considered preliminary. These studies also represent the extent of such studies on the decomposition ("melting") behavior of poly(amino acids).

CONCLUSIONS

The literature review presented above clearly demonstrates the need for reliable thermodynamic studies on the poly(amino acids). Only two studies have dealt with the decomposition temperature of a few of the poly(amino acids), and they cannot be considered to give reliable thermodynamic information. The more numerous heat capacity studies made on polyglycine and poly(L-alanine) are not only in conflict with each other, but also with our computed heat capacities.[37] Regarding the structural properties of the poly(amino acids), such information can be quite useful in understanding the thermodynamic behavior of these materials. Only polyglycine, poly(L-alanine), and poly(L-proline) had been studied in considerable detail. For the remaining poly(amino acids), further studies need to be conducted to collaborate and enhance the work that has been done.

In order to study the thermodynamic properties of the proteins, it is first necessary to lay a foundation of knowledge by addressing the thermodynamic properties of the poly(amino acids). This thesis will take the first necessary step in that direction by establishing a data bank for all poly(amino acids) based on the common twenty amino acids. This data bank will present new, reliable heat capacity

measurements for all available poly(amino acids) and a number of copolymers of the poly(amino acids). In addition, for each poly(amino acid) and copolymer, the measured heat capacity will be linked to the vibrational spectrum in the same way as has been established for other solid, linear macromolecules. For the copolymers, the copolymer rules established for synthetic polymers will be verified. Thus in this thesis it will be shown in two important ways, through the linking of the heat capacity to the vibrational spectrum and through verification of the copolymer rules, that biological polymers can be treated in the same manner as other solid polymers. This knowledge will allow the establishment of thermal analysis as an integral part of the analysis of biological macromolecules, much as it is for other polymers. Advanced thermal analysis can then be utilized to address such problems as order-disorder transitions, structure, decomposition, and the interactions between proteins and other low molecular mass components such as water.

II. INTERPRETATION OF THE HEAT CAPACITY

In the following sections the interpretation of the heat capacity of a solid in terms of its vibrational spectrum will be addressed. Section A will provide a historical survey of the development of an understanding of the heat capacity of a solid, including the application of this understanding to polymeric materials. Sections B and C will provide a detailed look at how in the *ATHAS* laboratory this knowledge to polymers is applied such that it becomes possible to calculate the heat capacity of

a solid polymer based on an approximate vibrational spectrum.

IIA. Heat Capacity Description

The first quantitative link of the heat capacity of a solid, which is a macroscopic property, to its microscopic cause, the vibrational motion, was established by Einstein.[40] He assumed that the entire crystal lattice vibrated at a single, characteristic frequency, giving:

$$C_v/NR = E(\Theta_E/T) = \frac{(\Theta_E/T)^2 \exp(\Theta_E/T)}{[\exp(\Theta_E/T) - 1]^2} \qquad (1)$$

where N is the number of moles of oscillators and Θ_E is a characteristic temperature ($h\nu/kT$). At the Θ-temperature, C_v has reached 92% of its full value, R. A representation of the Einstein model can be seen in Figure 10.[3] As shown, the entire frequency spectrum $\rho(\nu)$ concentrates in a single frequency ν_E.

This connection proved, however, to be too simple an approximation for even monatomic solids at low temperatures. Later, Debye[41-42] assumed, more correctly, that each atom vibrates over a range of frequencies and that the atoms do not vibrate independently of one another but, instead, are involved in coupled vibrations.

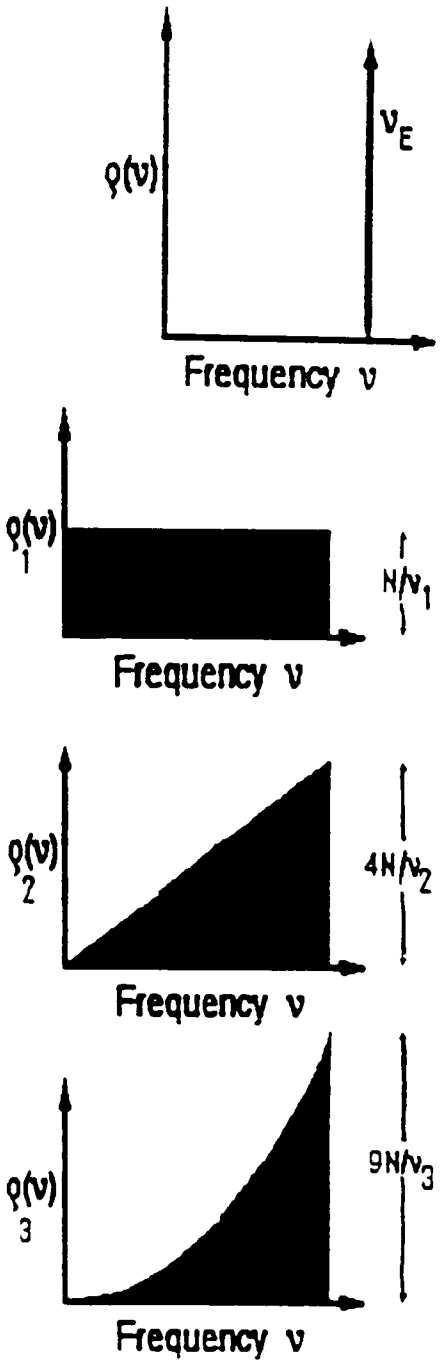


Figure 10 Frequency Distributions. From Top to Bottom: Einstein Distribution, One-Dimensional Frequency Distribution, Two-Dimensional Frequency Distribution, Three-Dimensional Frequency Distribution.[3] [Source: B. Wunderlich *Thermal Analysis* Academic Press, New York (1990.]

Thus for a three-dimensional structure:

$$C_v/RT = D_3(\Theta/T_3) = 3(T/\Theta_3)^3 \int_0^{(\Theta/T_3)} \frac{(\Theta/T)^4 \exp(\Theta/T)}{[\exp(\Theta/T) - 1]^2} \, d(\Theta/T) \qquad (2)$$

where Θ_D is the frequency at which the distribution reaches the number of degrees of freedom of the solid. For a three dimensional structure, the frequency distribution is quadratic as shown in Figure 10.[3] The maximum frequency at which $3N$, the total number of vibrators for N atoms, is reached is ν_3 or Θ_3. There are also one- and two-dimensional forms of the Debye function to describe the heat capacities of one-[43] and two-dimensional[44] structures, respectively.

$$C_v/NR = D_1(\Theta/T_1) = (T/\Theta_1) \int_0^{(\Theta/T_1)} \frac{(\Theta/T)^2 \exp(\Theta/T)}{[\exp(\Theta/T) - 1]^2} \, d(\Theta/T) \qquad (3)$$

$$C_v/NR = D_2(\Theta/T_2) = 2(T/\Theta_2)^2 \int_0^{(\Theta/T_2)} \frac{(\Theta/T)^3 \exp(\Theta/T)}{[\exp(\Theta/T) - 1]^2} \, d(\Theta/T) \qquad (4)$$

The one-dimensional Debye structure exhibits a frequency distribution that is constant over the entire range of frequencies, shown in Figure 10.[3] The two-dimensional Debye structure exhibits a frequency distribution that is linear, also shown in Figure 10[3]. For linear macromolecules, the three-dimensional Debye function has been found to hold only for crystals at very low temperatures, below 10 K.[45] Above 10 K, heat capacities of linear macromolecules are more complicated than this.

In making the connection between the heat capacity and the vibrational

motion for linear macromolecules above 10 K, it has proven useful to separate the vibrations into skeletal and group vibrations. The skeletal vibrations are of relatively low frequency, strongly coupled, and can be thought-of as the intra- and inter-molecular vibrations of the chain of beads with the appropriate masses. They dominate the heat capacity in the temperature region up to about 100 K. All efforts to calculate the intermolecular, skeletal vibrations from crystal structure and force constant data have failed in the past. Heat capacity measurements provide the best means for approximate evaluation of these low frequency vibrations. Recent work by Kanaya and co-workers[46] suggest however, that at least for crystalline polymers, the density of states can be described by the Debye model. The intramolecular skeletal vibrations are somewhat higher in frequency and can be assessed through isolated-chain, normal mode calculations. Tarasov[47-49] proposed to describe the skeletal heat capacities of a linear chain as the sum of two contributions, a three-dimensional Debye function for the intermolecular vibrations, and a one-dimensional Debye for the intramolecular vibrations.

$$C_v/NR = T(\Theta_1/T, \Theta_3/T) = D_1(\Theta_1/T) - (\Theta_3/\Theta_1)[D_1(\Theta_3/T) - D_3(\Theta_3/T)] \quad (5)$$

This equation has been shown to hold for most linear macromolecules. Its limits are reached when phenylene groups are included in the backbone chain, extensive branching exists, or alternating heavy and light mass backbone units occur.[17]

The group vibrations are higher in frequency than the skeletal vibrations and can be thought-of as the vibrations of the internal structure of the beads. They have a much narrower frequency distribution and can often be approximated by single

frequency Einstein-terms or by box distributions over small frequency ranges:

$$C_v/NR = B(\Theta_U/T, \Theta_L/T) = \frac{\Theta_U}{\Theta_U - \Theta_L}[D_1(\Theta_U/T) - (\Theta_L/\Theta_U)D_1(\Theta_L/T)] \quad (6)$$

where Θ_U and Θ_L are the upper and lower frequencies of the range.

IIB. Heat Capacity Analysis

Heat capacity analysis begins with an evaluation of the experimental crystalline and amorphous heat capacities over as wide a temperature range as possible. In the 10 to 100 K temperature range, heat capacity measurements are completely dominated by adiabatic calorimetry. Above 100 K, most measurements are made by differential scanning calorimetry.[17] The experimental heat capacity at constant pressure, C_p, is converted to C_v, the heat capacity at constant volume, using either the thermal expansivity (α) and the thermal compressibility (β) of the macromolecule:

$$C_p - C_v = \alpha^2 VT/\beta \quad (7)$$

or the semiempirical Nernst-Lindemann expression, when such data is not available:

$$C_p - C_v = 3RA_0(\text{new})\, C_p T/T_m^\circ \quad (8)$$

T_m° is the equilibrium melting temperature, and A_o is an approximately universal constant ($A_o = 3.9 \times 10^{-3}$ K mol/J).[51]

The total experimental C_v is then separated into the portion due to the group vibrations and the portion due to the skeletal vibrations.

$$C_v(\text{total}) = C_v(\text{skeletal}) + C_v(\text{group vibration}) \quad (9)$$

The heat capacity due to the group vibrations is calculated from an approximate spectrum of the group vibrations using information available from either normal mode calculations of isolated chains or attributed infrared and Raman spectra. If neither of these are available, it is often sufficient to substitute the vibrational spectrum of chemically identical groups of other macromolecules or even small molecules. Once the group vibrations have been collected, their contribution to the heat capacity is computed with the help of either single frequency Einstein terms [Eq. (1)] or box distributions of frequencies [Eq. (6)]. The total group vibration contribution to the heat capacity is then subtracted from the total experimental C_v, leaving the experimental heat capacity due to the skeletal vibrations. This remaining heat capacity is then fitted to the Tarasov function [Eq. (5)] at low temperatures to get Θ_3 and, at higher temperatures, to get Θ_1.

To summarize: With a table of group vibration frequencies, a limited range of heat capacity data (to arrive at the two Θ-temperatures) and the known number of skeletal vibrations, N, it becomes possible to calculate the heat capacity (either as C_v or C_p) of a solid macromolecule over a considerable temperature range (typically 0 to 1000 K, to cover the need to describe superheated states observed in flash pyrolysis and ablation). In addition, since group vibrations are affected little by their chemical environment, it becomes possible from the data on one polymer to calculate the heat capacity of another polymer of the same family. A further result of analyzing the heat capacities of a large body of macromolecules is that regularities

based on mass and intermolecular forces could be derived from lists of theta temperatures. The strict additivity of the heat capacity contributions of the group vibrations and the continuous change in Θ_1 with chemical composition led us to the development of addition schemes for heat capacities.[51-52] As long as the contributions of the backbone groupings that make up the polymer are known empirically, it is possible to estimate the heat capacity of unknown polymers and even of copolymers from these contributions.

IIC. Computer Programs for Data Analysis and Interpretation

At the *ATHAS* laboratory a number of computer programs have been developed which permit the evaluation of heat capacities from vibrational frequency spectra. These programs follow the general outline for heat capacity interpretation described in the previous sections. Central to the *ATHAS* heat capacity computation method is the evaluation of the Debye integrals which are of the type:

$$\mathrm{ANS} = \int_0^B \frac{X^n}{e^X - 1} dX \qquad (10)$$

These integrals cannot be solved in closed form. Note that B, the upper integral limit is (Θ/T).[53] Until recently, the *ATHAS* computation method used the DO1AHF function from the NAG library at the University of Tennessee VAXcluster to evaluate these integrals. This subroutine is based on the Patterson method which involves a family of quadrature rules which are extended over the entire interval of integration. The family of interlacing high precision rules was applied in sequence

to the integrand until two successive results are obtained which differ by less than a given interval.[37] Recently, however, in an effort to adapt the *ATHAS* computation method to a microcomputer, thereby making it more available to other laboratories, an approximate method of evaluation of the Debye functions was developed.[54] It was this adaptation of the computation method that was used for the calculations of heat capacities of the biological polymers reported in this thesis. Basically, the Debye integrals are solved by dividing them into several intervals and then fitting each of these by least squares techniques into either a polynomial or a polynomial logarithmic function.[54] Comparison of the older VAX programs to the newer microcomputer programs using the new technique for evaluation of the Debye integrals, illustrated that the new technique represents the functions well.[54]

The steps taken by the various *ATHAS* computer programs to calculate heat capacities from vibrational spectra are summarized below. First, the experimental heat capacity, C_p^{exp}, is converted to the experimental heat capacity at constant volume, C_v^{exp}, using the Nernst-Lindemann equation. The group vibration contribution to C_v^{exp} is then computed using a combination of single frequency Einstein terms and box distributions of frequencies. This total group vibration contribution to C_v^{exp} is then subtracted leaving the C_v^{exp} due to the skeletal vibrations. Using the known number of skeletal vibrations, this skeletal heat capacity is then fitted to the Tarasov function to arrive at the theta temperatures. Θ_3 describes this contribution at low temperatures (by fitting the low temperature C_v^{exp}) while Θ_1 describes this contribution at higher temperatures (by fitting the higher temperature

C_v^{exp}). The values for Θ_3 and Θ_1 are combined with the group vibration frequencies and the calculation then proceeds in reverse to the description above to give the calculated heat capacity at constant volume, C_v^{cal}. Using the Nernst-Lindemann equation, this is converted to the calculated heat capacity at constant pressure, C_p^{cal}.

CHAPTER II

EXPERIMENTAL DESIGN AND METHODS

I. MATERIALS

Of the twenty naturally occurring amino acids, only sixteen are available commercially in polymer form. As all naturally occurring amino acids have an (S) configuration at the α carbon, and thus belong to the L series — that is, the groups around the α carbon have the same configuration as in L-glyceraldehyde. As a result, all poly(amino acids) were purchased in this configuration. In addition to the homopolymers, four copolymers were studied. Each copolymer consisted of two of the sixteen amino acids. All the samples were obtained from Sigma Chemical Company. They were prepared by base-initiated polymerization of the corresponding N-carboxyanhydride (See Figure 11). The initiator is typically sodium methoxide or triethylamine.[55] As per the company's instructions, all samples were kept frozen and were packaged with a drying agent such as calcium chloride or silica gel.

All samples were in the solid state. Weight average molecular masses (MW) ranged from 5,300 to 560,000. This information was determined by Sigma Chemical Company through solution viscosity measurements and low angle light scattering (LALS). Regarding the physical appearance of the samples, all could be charac-

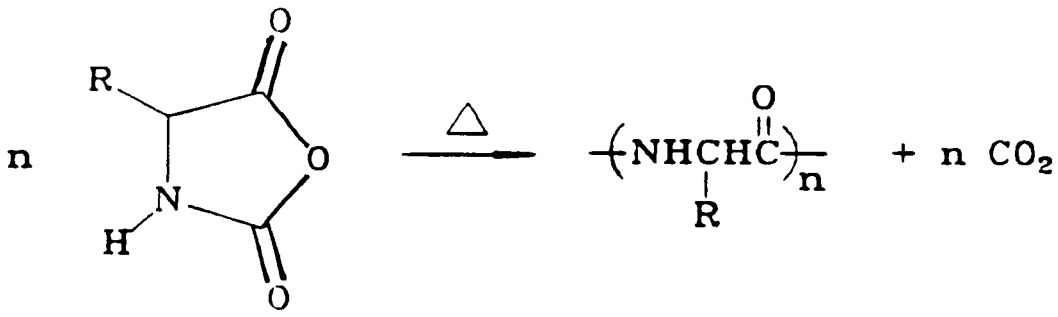


Figure 11 Preparation of Poly(amino Acids).

terized as either being a powder, crystal, or in a fluffy, cotton-like form. With the exception of the sequential copolymer poly(L-proline-glycine-proline), which was yellow in color, all samples were white in color. Due to their acidic or basic nature, several of the poly(amino acids) are available only as a salt, as this is their only stable form.

As previously noted, all poly(amino acids) consist of the same basic repeat unit with various substitutions.

Basic Repeat Unit (Backbone) $(C_{\alpha}HR-C_{\delta}O-NH-)_n$

Table 1 lists the sixteen homopolymers studied, the substitution group (R), the weight average molecular mass (MW), and the repeating unit molecular mass for each (mw) in g/mol. For those poly(amino acids) that are available only as salts, two substitution groups (R) are listed. The first is the free poly(amino acid), and the second is the salt which was studied.

Table 2 lists the four copolymers studied. The repeat unit of each of the copolymers consists of the listed poly(amino acids) in the order listed. Also noted are the molar ratios of each poly(amino acid) making up the copolymer, the weight average molecular masses (MW) determined by Sigma, and the average repeating unit molecular mass (mw) in g/mol.

TABLE 1

Homopolymers Studied

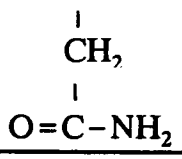
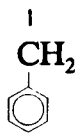
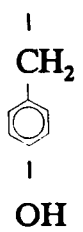
Homopolymer	Side Group R	MW	mw
Polyglycine (GLY)	$-H$	15,000	57.05
Poly(L-alanine) (ALA)	$-CH_3$	18,800	71.08
Poly(L-valine) (VAL)	$-CH(CH_3)_2$	7,230	99.13
Poly(L-leucine) (LEU)	$-CH_2CH(CH_3)_2$	150,000	113.16
Poly(L-serine) (SER)	$-CH_2OH$	6,000	87.08
Poly(L-asparatic acid) (ASP)	$-CH_2COOH$	42,500	137.07
•available as:	$-CH_2COO^-Na^+$		
Poly(L-glutamic acid) (GLU)	$-(CH_2)_2COOH$	74,000	151.10
•available as:	$-(CH_2)_2COO^-Na^+$		
Poly(L-asparagine) (ASN)		10,400	114.10
Poly(L-phenylalanine) (PHE)		23,000	147.18
Poly(L-tyrosine) (TYR)		125,000	163.18

TABLE 1 (Cont.)

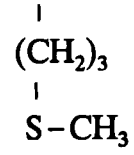
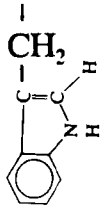
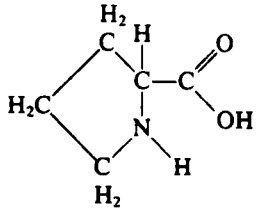
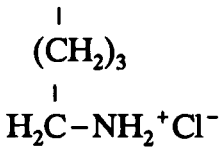
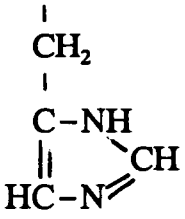
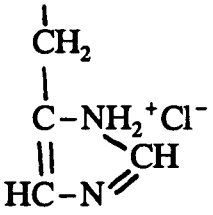
Homopolymer	Side Group R	MW	mw
Poly(L-methionine) (MET)		160,000	131.19
Poly(L-tryptophan) (TRP)		34,000	186.21
Poly(L-proline) (PRO)	 (complete structure)	44,000	97.18
Poly(L-lysine) (LYS) •available as:		560,000	209.09
Poly(L-histidine) (HIS)		49,000	137.14
•also available as HIS•HCl		23,100	173.60

TABLE 1 (Cont.)

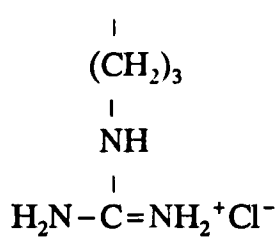
Homopolymer	Side Group R	MW	mw
Poly(L-arginine) (ARG) •available as:		139,200	192.65

TABLE 2

Copolymers Studied

Copolymer	Molar Ratios	MW	mw
Poly(L-lysine•HBr-alanine)	46/54	37,000	274.65
Poly(L-lysine•HBr-phenylalanine)	51/49	49,700	356.89
Poly(L-glutamic acid•Na-tyrosine)	50/50	30,000	314.27
Poly(L-proline-glycine-proline)	66/34	5,300	273.38

II. METHODS OF STUDY

Heat capacity measurements were carried out for the sixteen poly(amino acids) and four copolymers using a Perkin-Elmer Differential Scanning Calorimeter (DSC) Model 7. X-ray diffraction studies were made on two of the sixteen poly(amino acids) using a powder diffractometer located at Oak Ridge National Laboratory (ORNL). The following sections will provide an overview of the principles of differential scanning calorimetry and a description of the two instruments employed. As the focus of this work is on the measurement of heat capacity, most attention will be given to the calorimeter.

IIA. Calorimetry

IIAi. Overview of Differential Scanning Calorimetry

In differential scanning calorimetry, a sample and a reference calorimeter are enclosed in a constant temperature cavity (cell block). Inert gas (usually nitrogen) flows between the two symmetrically placed calorimeters. In close contact with each calorimeter is a platinum resistance thermometer, one to measure T_s (sample temperature) and one to measure T_r (reference temperature). Each calorimeter and its respective thermometer is also in close contact with a platinum resistance heater as schematically outline in Figure 12.[3] The programmer provides the average temperature amplifier with a voltage which is increased linearly with time. The average temperature amplifier compares T_s and T_r with the programmer signal and instructs the heaters to supply heat as necessary to their respective calorimeters so

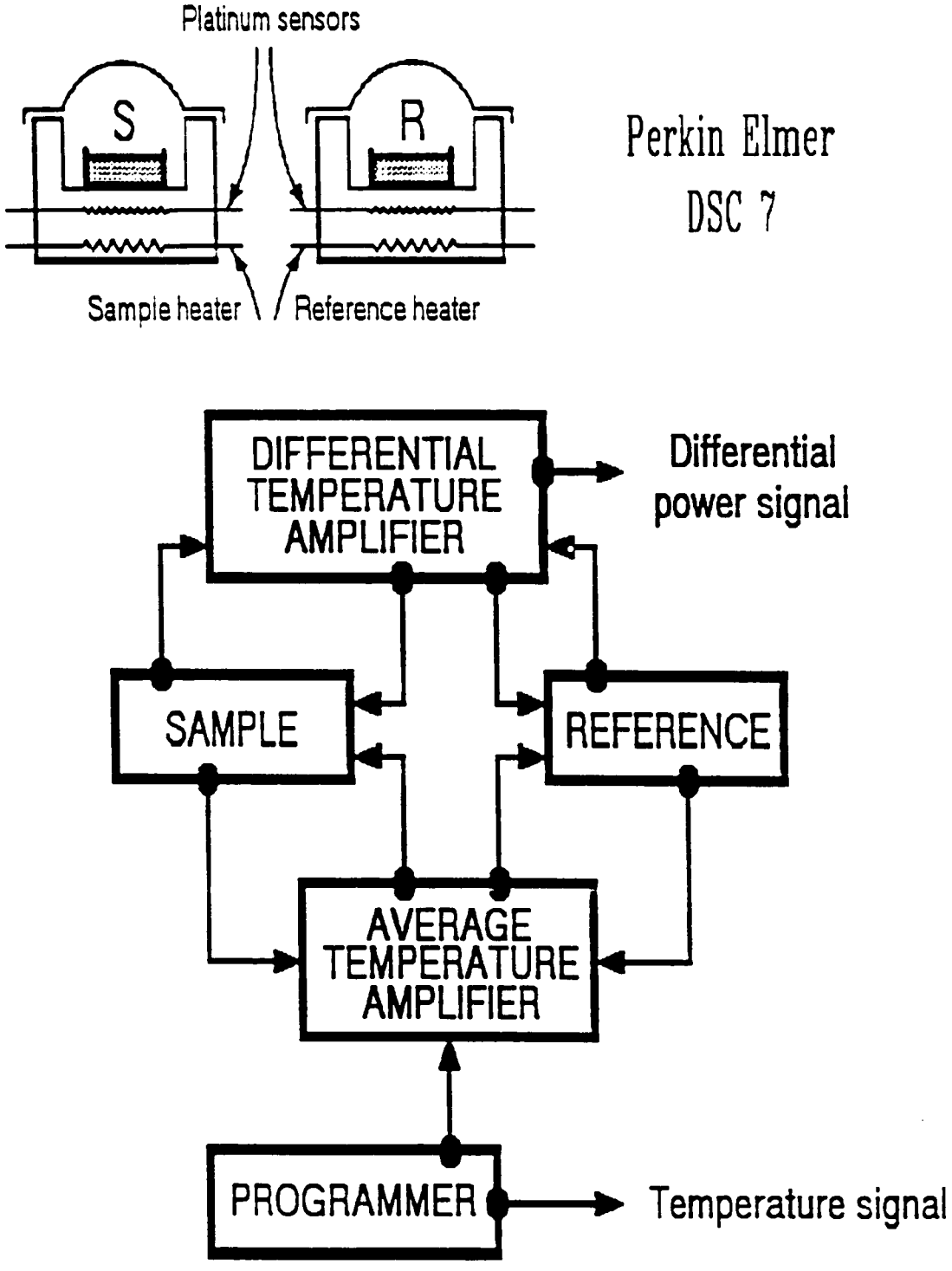


Figure 12 Schematic Outline of a Differential Scanning Calorimeter.[3] [Source: B. Wunderlich *Thermal Analysis* Academic Press, New York (1990).]

that the average temperature of the sample and the reference follow the programmer as closely as possible. The differential temperature amplifier also signals the heaters to supply heat as necessary when one calorimeter lags behind the other due to their different heat capacities. Thus, any thermally induced changes in the sample are recorded as differential heat flow versus temperature (or time).

IIAii. Description of The Perkin-Elmer DSC-7

The Perkin-Elmer DSC-7 operates along the principles described above. The two calorimeters are constructed of a platinum-iridium alloy. Thermally induced changes in the sample are recorded directly in energy units (milliwatts), thus providing a true electrical energy measurement of the peak area.

The temperature range of the instrument is 220 K to 725 K. For low temperature measurements, a mechanical refrigeration unit is employed (Perkin-Elmer Intracooler). In addition to providing a stable block temperature at low temperatures, the refrigeration unit is employed at ambient temperatures in order to get stable, reproducible isotherms. A minimum period of two hours of operation is needed to achieve a state of equilibrium so that experimental work can begin. This is judged as the time necessary for the differential heat flow signal to reach a constant value. A Perkin-Elmer dry-box assembly is added to the instrument in order to avoid signal instability due to drafts and periodic changes in room temperature. The dry box sits directly on top of the instrument, over the cell block containing the two calorimeters. Dry nitrogen gas is blown into the dry box assembly at a pressure

somewhat above ambient to avoid build-up of condensation on the sample block. In addition, dry nitrogen gas is allowed to flow inside the cell block, between the calorimeters, at a constant rate of 20 cm^3/min.

The instrument is interfaced with a Perkin-Elmer Model 7500 Professional Computer. This is a 32-bit microcomputer with a 10 MB Winchester hard disk. The computer uses the IDRIS operating system which is similar to UNIX. A Perkin-Elmer TAC 7 microprocessor controller links the computer to the calorimeter. An A/D converter gathers the measured data at a sampling period of 30 times per second. In this way no information is lost. A set of software for the computer is supplied by Perkin-Elmer which permits a variety of manipulations of the recorded data (plotted as heat flow versus temperature or time), calculation of heat capacity, and calculation of a number of peak parameters including peak temperature, onset temperature, peak height, peak area, and heat of fusion. The microcomputer operating system and the software supplied are proprietary to Perkin-Elmer. As a result very little information exists regarding their method of operation or the algorithms used for calculation of the heat capacity. Given that the heat capacity is proportional to the heat flow, the following equation is most likely utilized.

$$C_p = \frac{\text{Heat Flow}}{\text{Scan Rate}} \tag{11}$$

The maximum sensitivity of the instrument is 8μW. The RMS noise level is 0.002 mW. The calorimetric accuracy is better than $\pm 1.0\%$ as is the calorimetric precision. Temperature precision and accuracy are both ± 0.1 K. Heating and

cooling rates are 0.1 K/min to 500 K/min in 0.1 K increments.

IIAiii. Calibration

Calibration of the Perkin-Elmer DSC-7 first requires that the baseline be optimized. A baseline run consists of running two empty DSC sample pans (made of aluminum) of identical masses. Optimization of the baseline involves adjusting two controls, a balance control and a slope control. The balance control is used to minimize baseline curvature with sample holder temperature changes. The slope control is used to adjust the slope of the baseline. A heating run is carried out using the empty aluminum pans (reference pans) over the temperature range and at the heating rate of interest. Adjustment to the recorded baseline is made using the two controls. This process of running a baseline and then adjusting its slope and curvature is continued until the baseline is as free of curvature and negative or positive sloping as possible.

At this point it becomes possible to calibrate the instrument in terms of temperature (abscissa) and energy (area). Calibration is accomplished by running high purity standard materials with know temperature and energy of transition. Two standards are used for temperature calibration and one for energy calibration. The transition temperatures and enthalpy changes obtained from running these standards and the true values are then used by the Perkin-Elmer software calibration program to calibrate the instrument.

The two standards chosen for temperature calibration were indium (melting

transition temperature at 429.75 K) and naphthalene (melting transition temperature at 353.42 K). Both standards were obtained from the National Bureau of Standards and are accepted as standards in calorimetry. The energy (area) standard chosen was also indium. The enthalpy change corresponding to the transition at 429.75 K is 28.45 J/g. Once the instrument is calibrated, the calibration is checked periodically by running the indium sample and comparing the transition temperature and enthalpy change to the true values.

Over the two years of operation, the transition temperature and enthalpy change for the indium sample remained relatively constant. In all cases, when a temperature calibration was performed, it was done so only because of a need to replace the aluminum reference pans. Replacing the reference pans requires a re-optimization of the baseline. Optimization of the baseline, of course, requires that the temperature and enthalpy be re-calibrated. Although extreme care was taken in handling the aluminum reference pans and the platinum-iridium covers, scratches and dents are inevitable when an instrument is used so frequently and operated by more than one user. Such changes in conditions would cause shifts in the baseline slope and curvature which changed depending most commonly on the placement of the pans in the instrument. As a result, the pans were replaced approximately every six months, and once it was necessary to replace the platinum-iridium covers. Therefore, the calibration was repeated approximately every six months. It should be noted that the calibration over such a six month period was very stable. In the worst case, the indium transition temperature changed by 0.45% in a six month period.

Indium is used as an enthalpy standard only for initial, approximate heat capacity evaluation. Measurements on the well known heat capacity standard sapphire (Al_2O_3) found the heat capacity obtained using only the Perkin-Elmer software to be an average of 5% lower than the literature data. As a result, we consider it necessary to run a sapphire standard every time we make heat capacity measurements and correct the calculated heat capacity to the literature heat capacity.[56] A correction factor is then obtained for the sapphire standard at each temperature and is used to correct all sample heat capacity measurements according to the equation below.

$$C_p(\text{sample})^{\text{TRUE}} = \frac{C_p(\text{sapphire})^{\text{TRUE}} \times C_p(\text{sample})^{\text{MEASURED}}}{C_p(\text{sapphire})^{\text{MEASURED}}} \qquad (12)$$

IIAiv. Measurement of Heat Capacity

In order to obtain reproducible heat capacities using the Perkin-Elmer DSC-7, it thus becomes necessary to perform three consecutive runs per sample. These are a sample run, a baseline run, and a standard run. The baseline run consists of running two empty aluminum pans of equal weight, one in each calorimeter. For the sample run, the sample (enclosed in an aluminum pan) is run in one calorimeter and an empty pan in the other. Similarly in the standard run, a standard material (sapphire, in this case) is run along with an empty pan. In Figure 13,[3] an example of these three runs is shown.

In order to get reproducible heat capacity information on the sample, it is necessary to integrate the area under the three curves shown in Figure 13.

$$\text{Sample Run: } A_s = \int a_s dt \tag{13}$$

$$\text{Baseline Run: } A_r = \int a_r dt \tag{14}$$

$$\text{Sapphire Run: } A_c = \int a_c dt \tag{15}$$

An initial measurement of the sample's heat capacity is then found by subtracting the area under the baseline from the area under the sample.

$$\int_0^{t_f} C_p(\mathrm{S})dT = \overline{C_p}(\mathrm{S})\Delta T = (\mathrm{A_s} - \mathrm{A_r}) = [\mathrm{a_s}(T) - \mathrm{a_r}(T)] \tag{16}$$

Similarly, for the sapphire standard,

$$\int_0^{t_f} C_p(\mathrm{C})dT = \overline{C_p}(\mathrm{C})\Delta T = (\mathrm{A_c} - \mathrm{A_r}) = [\mathrm{a_c}(T) - \mathrm{a_r}(T)] \tag{17}$$

The final step is comparison of this measurement of sapphire's heat capacity to the literature data to obtain correction factors. The sample's heat capacity determined in Eq. (16) is then corrected for the sapphire standard according to Eq. (12). The Perkin-Elmer heat capacity software is used up to the point where it is corrected for the sapphire standard.

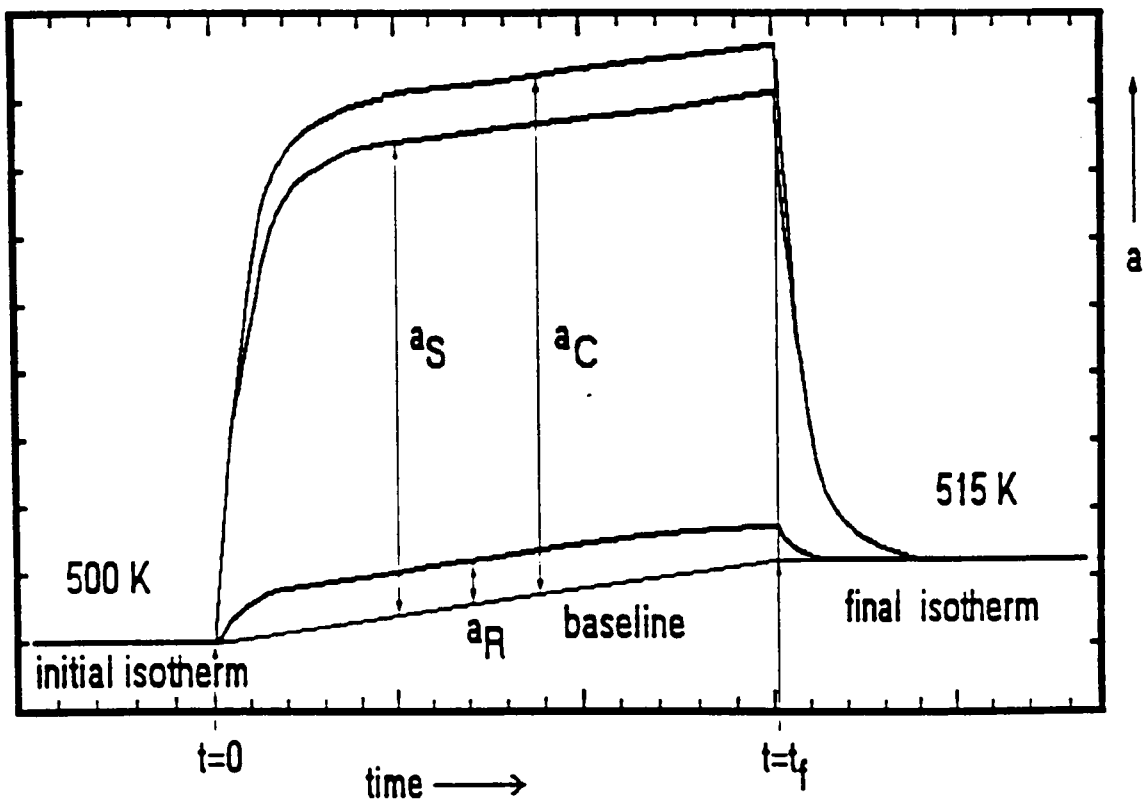


Figure 13 DSC Runs: Sample, Baseline, Standard. Sample (a_S), Baseline (a_R), Standard (a_C).[3] [Source: B. Wunderlich *Thermal Analysis* Academic Press, New York (1990).]

IIAv. Procedure

For all measurements on the poly(amino acids) and copolymers, sample weights ranged from 5 to 15 mg. All aluminum pans used for sample, baseline, and standard runs were within ±0.005 mg of the same weight, 25.300 mg. Weights of pans and samples were measured using a Cahn Electro-Balance which is capable of weighing within ±0.001 mg. As noted earlier, the weight averages molecular masses for all samples ranged from 5,300 to 560,000. Even at the low end of this range, the heat capacity already shows a negligible dependence on molecular mass.

All sample handling and preparation was carried out in a polyethylene glove bag inflated with a dry nitrogen atmosphere. This was considered necessary as these samples are notorious for picking up atmospheric moisture. As noted earlier, when not in use, all samples were kept frozen and packaged with a drying agent.

Each sample was placed in the DSC cell at room temperature, then cooled slowly (5 K/min) to 220 K and allowed to equilibrate. Again a state of thermal equilibrium was judged to have been achieved when the heat-flow signal remained constant over a period of time. Generally, a time period of twenty to thirty minutes was sufficient. An initial measurement from 220 K to 390 K at 10 K/min was performed to drive off any bulk water. The sample was held at 390 K until no further water loss was detected calorimetrically (steady baseline) and a steady state was achieved. The sample was then cooled slowly (1 K/min) to 220 K. A second measurement (220 K to 390 K) was performed next (after equilibration at 220 K). The sample was then removed from the DSC and placed over desiccant at room

temperature for two to three hours before a third heating run (220 K to 390 K) was performed. Again, for this third heating run, the sample was first cooled slowly (5 K/min) to 220 K and allowed to equilibrate. For each poly(amino acid and copolymer, this sequence of experimental runs was performed three times, thus resulting in twelve DSC runs per sample. The measured data reported for the poly(amino acids) and copolymers in Tables 3 – 8 are within 3% of the repeated data sets.

For each sample run, a corresponding baseline run with two empty pans and a sapphire standard run were performed. Care was taken to ensure that for all three runs, baseline, sample, and sapphire, similar initial and final isotherm levels were reached (typical allowable variation - less than 15% of maximum C_p signal).

IIB. X-ray diffraction

For a qualitative determination of the degree of crystallinity, an X-ray powder diffractometer was employed. The source of X-rays was a molybdenum target. The monochromator was adjusted such that only Kα radiation was accepted. The detector was a scintillation counter. The instrument was controlled by a microcomputer loaded with suitable software.

X-ray diffraction measurements were made on two of the poly(amino acid)s studied, poly(L-serine) and poly(L-methionine). Measurements were made in order to obtain an estimate of the two samples' degree of crystallinity. In order to do this, it was first necessary to run a background diffraction pattern. This consisted of

running a pattern with no sample in place, only the empty sample holder strip. The sample was then placed on the sample holder strip and another diffraction pattern was recorded. For the poly(L-serine), it was sufficient to spread a small amount of the powdered sample over the sample holder. For the poly(L-methionine) this was not possible as the sample was not in powder form, but rather in a cotton-like form. To prepare a sample for study, it was necessary to press the material into a pellet-like form. For each sample, the background pattern was subtracted from the sample pattern using the supplied software. Note that all measurements were performed under vacuum. Following the X-ray studies, DSC scans were repeated for the two poly(amino acids).

CHAPTER III

RESULTS

I. HEAT CAPACITY MEASUREMENTS

Figure 14 shows the heat capacity curves obtained for polyglycine. The initial heating run (run 1) shows a broad peak with a peak temperature of 363 K (90°). Run 2 refers to the second heating (after slow cooling). Notice that the broad peak has disappeared. We believe the peak observed in run 1 is due to the vaporization of water. It is well known that biological materials are notorious for containing significant quantities of water. In run 1, the sample is held at 390 K until all the water is driven off (steady baseline). The sample weight loss after run 1 was 0.45 mg or 3.9% of the total sample weight. Run 3 was performed two to three hours after run 1, and it appears that the sample has again picked up some atmospheric water, despite reasonable efforts to exclude moisture. A slight weight change was observed following run 3.

Heat capacity curves for all poly(amino acids) except one and for all co-polymers were similar in nature to those observed for polyglycine. The results for poly(L-alanine) are shown in Figure 15. The first heating run produced a broad peak with a corresponding peak temperature of 362 K (89°C). As in run 3 for polyglycine, run 3 for poly(L-alanine) indicated a slight uptake of water over a period of two to three hours.

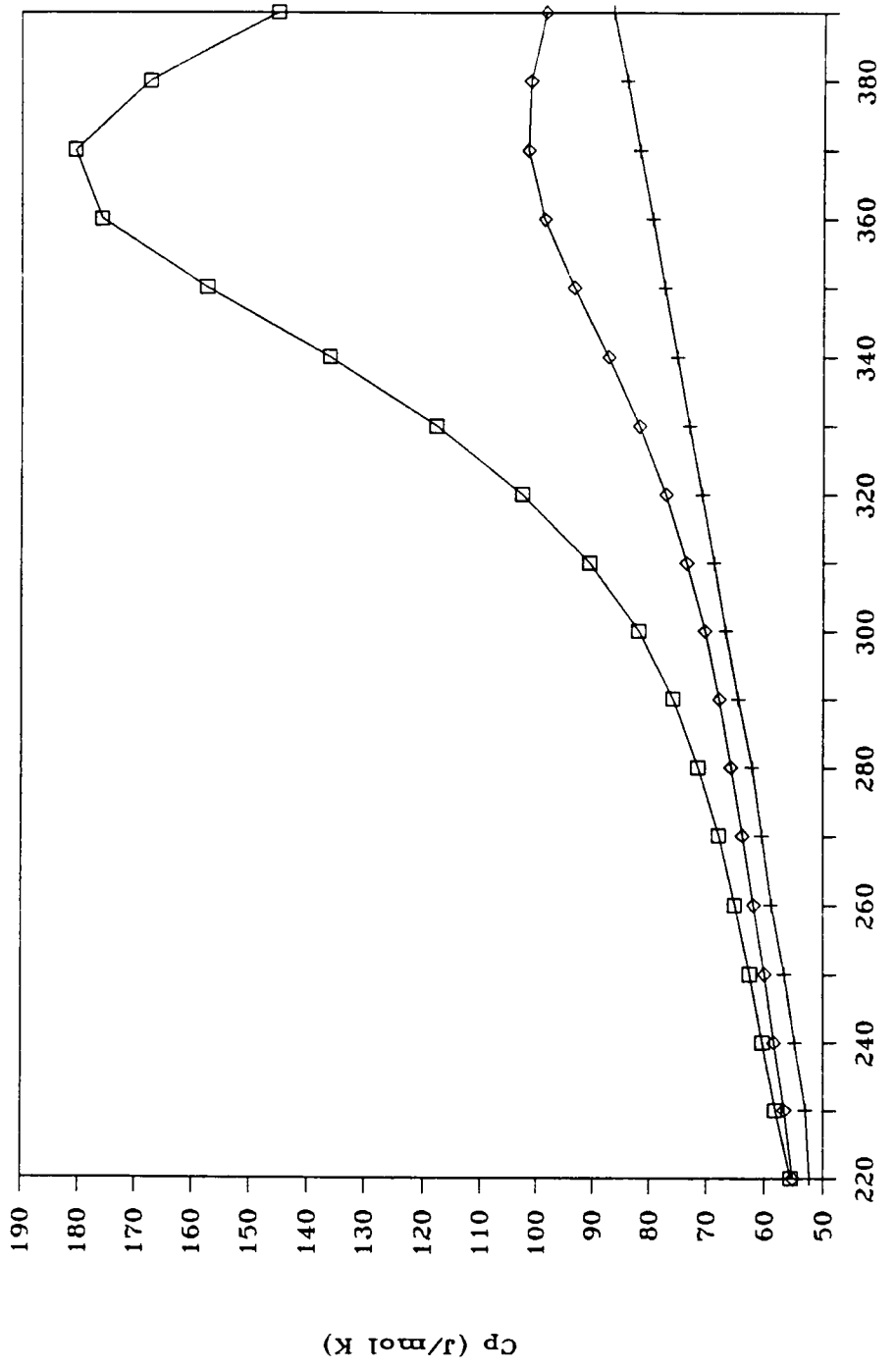


Figure 14 Measured Heat Capacities of Polyglycine. Top curve (□): DSC run 1. Bottom curve (+): DSC run 2. Center curve (◇): DSC run 3.

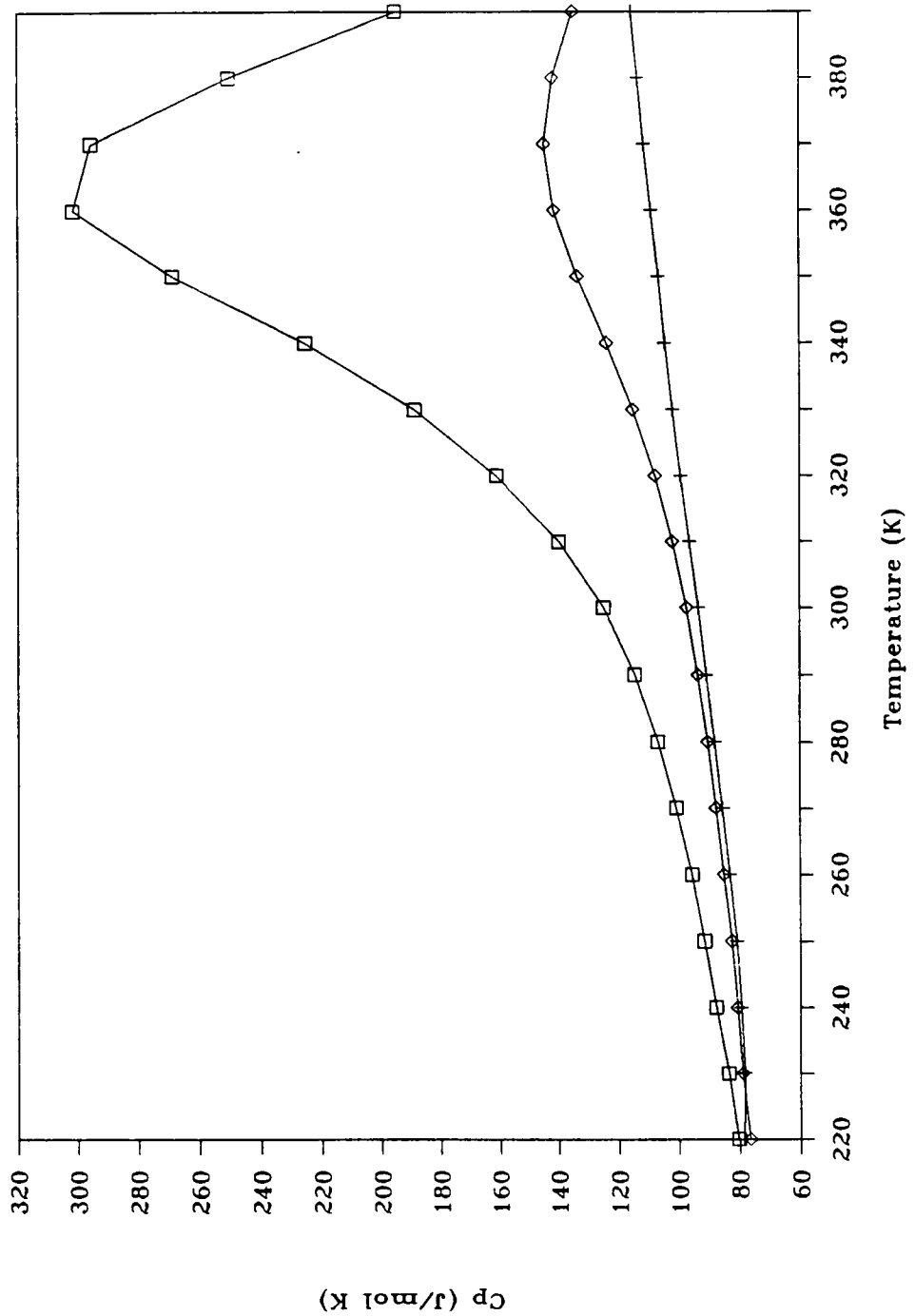


Figure 15 Measured Heat Capacities of Poly(L-alanine). Top curve (□): DSC run 1. Bottom curve (+): DSC run 2. Center curve (◇): DSC run 3.

Heat capacity curves for poly(L-valine) are shown in Figure 16. The peak temperature for run 1 was 355 K (82°C). Weight loss after this run was 0.25 mg or 3.0% of the total sample weight.

Figure 17 shows the heat capacity curves measured for poly(L-leucine). The peak temperature corresponding to run 1 was considerably lower than that previously observed for any other poly(amino acid), 323 K (50°C). The weight loss following run 1 was also considerably less than in the previous three samples, only 0.02 mg or 0.4% of the total weight.

Poly(L-serine) shown in Figure 18, exhibited a large, broad peak in run 1 with a corresponding peak temperature of 359 K (86°C). A significant weight loss of 0.74 mg or 5.3% of the total sample weight was observed. As in the previous samples, poly(L-serine) showed a slight uptake of water prior to run 3.

Poly(L-aspartic acid) sodium salt exhibited heat capacity curves as shown in Figure 19. Run 1 showed a rather high peak temperature of 377 K (104°C). A large weight loss of 0.84 mg or 7.3% of the total sample weight was observed.

The heat capacity results for poly(L-glutamic acid) sodium salt, which is identical to poly(L-aspartic acid) sodium salt except for an additional CH_2 group in the side chain, are shown in Figure 20. The observed peak temperature of 360 K (87°C) was much lower than that observed for poly(L-aspartic acid) sodium salt. The weight loss following run 1 was 0.37 mg or 9.9% of the total sample weight.

The results for poly(L-asparagine) are given in Figure 21. Run 1 again shows a broad peak with a corresponding peak temperature of 373 K (100°C). Again a

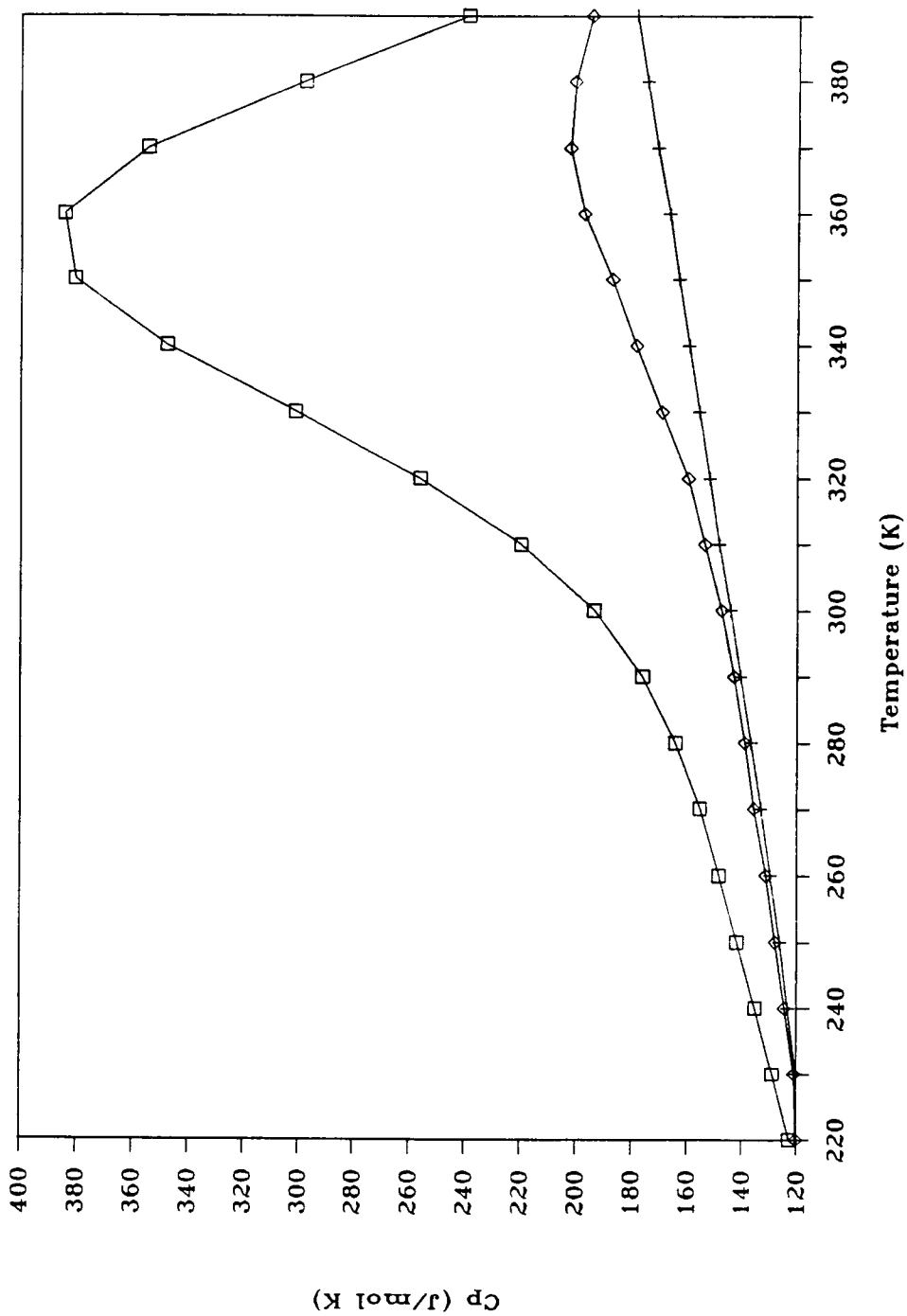


Figure 16 Measured Heat Capacities of Poly(L-valine). Top curve (□): DSC run 1. Bottom curve (+): DSC run 2. Center curve (◇): DSC run 3.

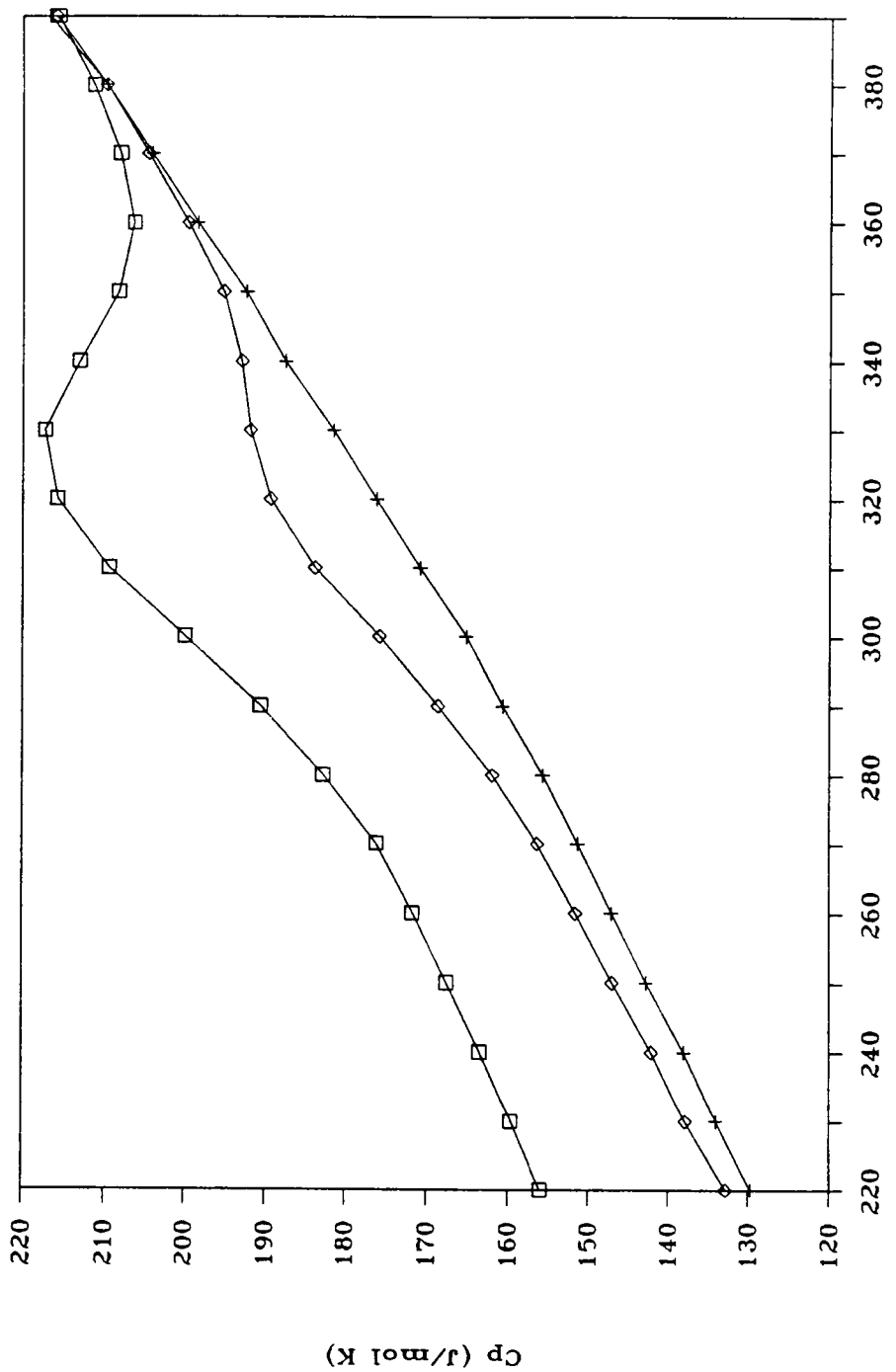


Figure 17 Measured Heat Capacities of Poly(L-leucine). Top curve (□): DSC run 1. Bottom curve (+): DSC run 2. Center curve (◇): DSC run 3.

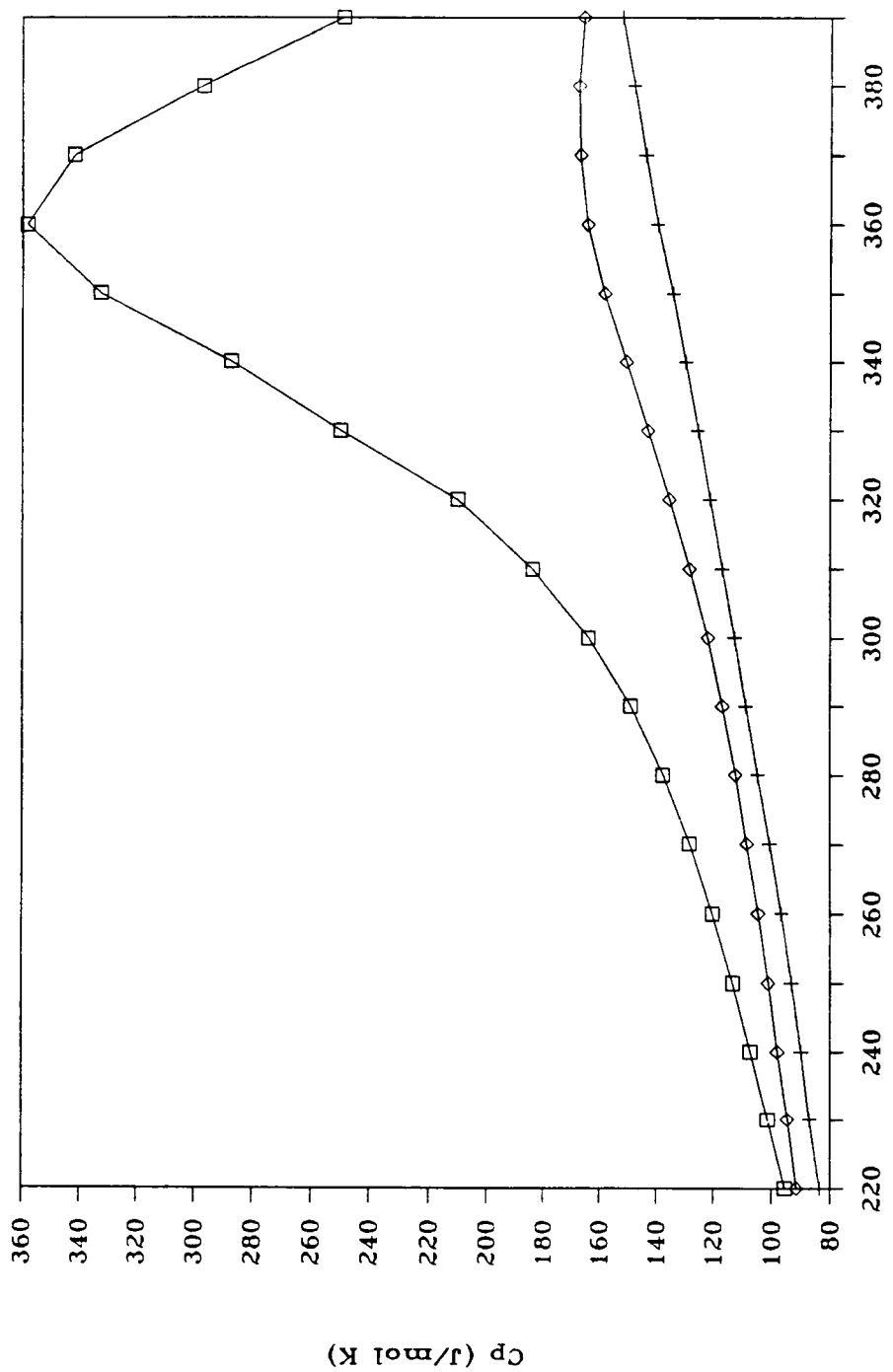


Figure 18 Measured Heat Capacities of Poly(L-serine). Top curve (□): DSC run 1. Bottom curve (+): DSC run 2. Center curve (◇): DSC run 3.

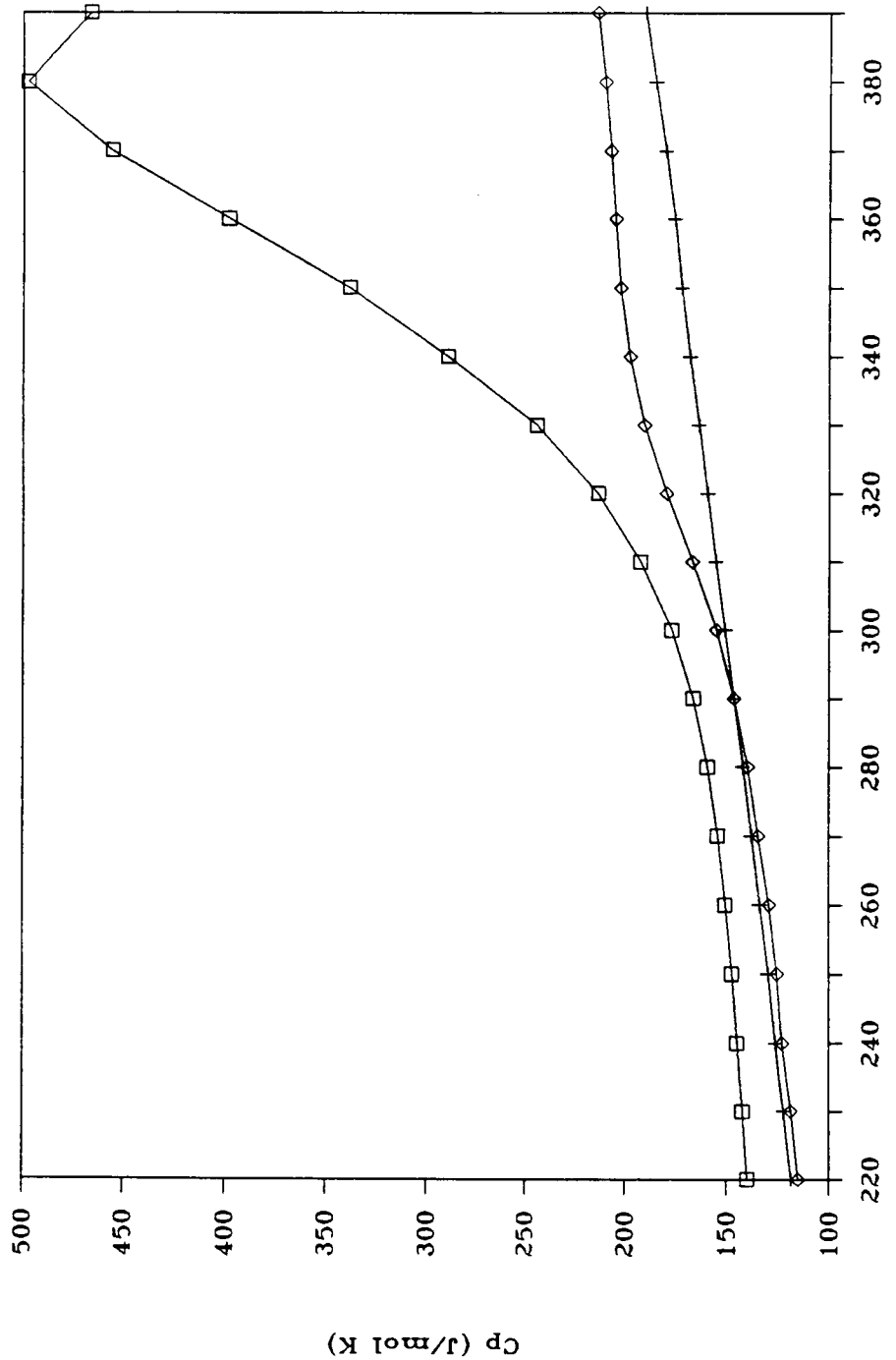


Figure 19 Measured Heat Capacities of Poly(L-aspartic acid•Na). Top curve (□): DSC run 1. Bottom curve (+): DSC run 2. Center curve (◇): DSC run 3.

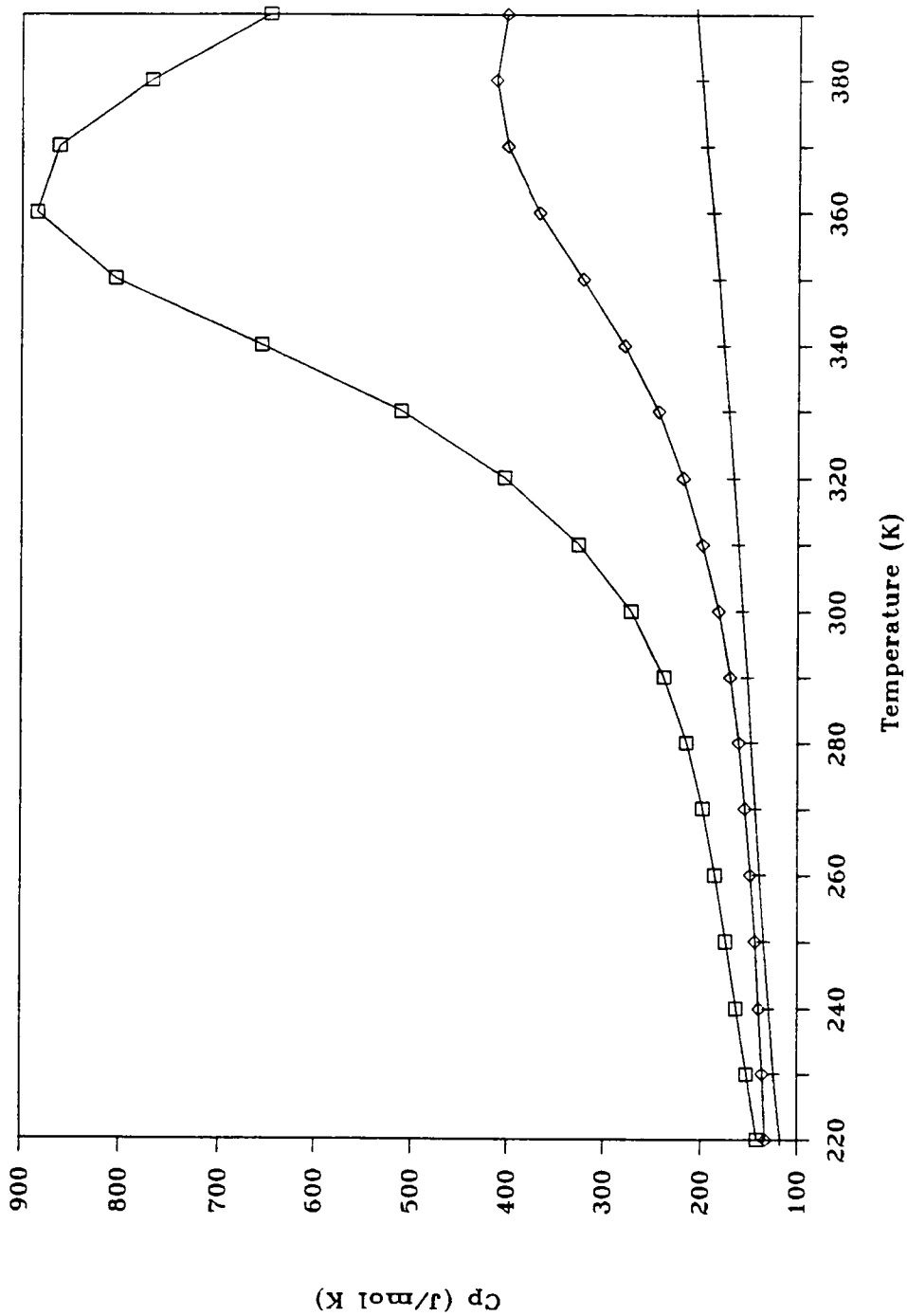


Figure 20 Measured Heat Capacities of Poly(L-glutamic acid•Na). Top curve (□): DSC run 1. Bottom curve (+): DSC run 2. Center curve (◇): DSC run 3.

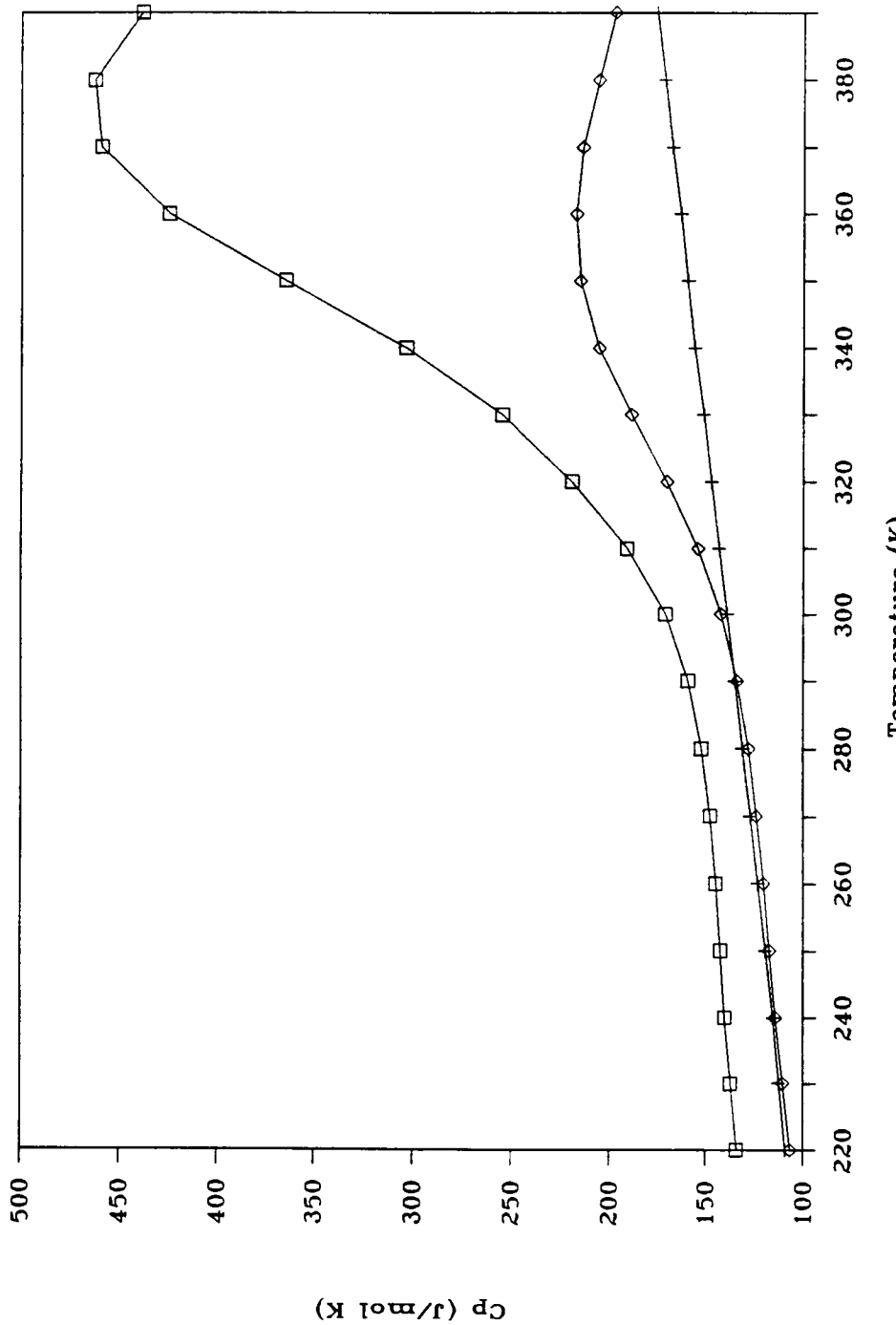


Figure 21 Measured Heat Capacities of Poly(L-asparagine). Top curve (□): DSC run 1. Bottom curve (+): DSC run 2. Center curve (◇): DSC run 3.

significant weight loss following run 1 was observed, 0.81 mg or 9.7% of the total sample weight.

Figure 22 shows the heat capacity curves obtained for poly(L-phenylalanine). Unlike any of the previous samples, poly(L-phenylalanine) exhibited two peaks in run 1, a small, very broad peak around 238 K (−35°C), and a much larger peak at 335 K (62°C). We believe both peaks can be attributed to water, the lower peak exhibiting the melting of water and the higher peak, the vaporization of water. Weight loss following run 1 was rather small, 0.07 mg or 0.7% of the sample's total weight.

Heat capacity results for poly(L-tyrosine) are shown in Figure 23. Poly(L-tyrosine) is identical to poly(L-phenylalanine) except for the addition of a CH_2 group in the side group. The peak in run 1 was sharper than those previously observed. The corresponding peak temperature was 339 K (66°C). Weight loss was rather high, 0.39 mg or 7.2% of the total sample weight.

Poly(L-methionine) exhibited rather unusual heat capacity curves as shown in Figure 24. Run 1, 2, and 3 are considerably different up to 360 K where they essentially become the same. It appears that run 1 began in the middle of a very broad peak extending over a large temperature range. This then disappears in run 2. The broad peak area appears again in run 3 but is less than in run 1. Only a small weight change was observed following run 1, 0.1 mg or 0.20% of the sample weight.

Results for poly(L-tryptophan) are given in Figure 25. The peak temperature

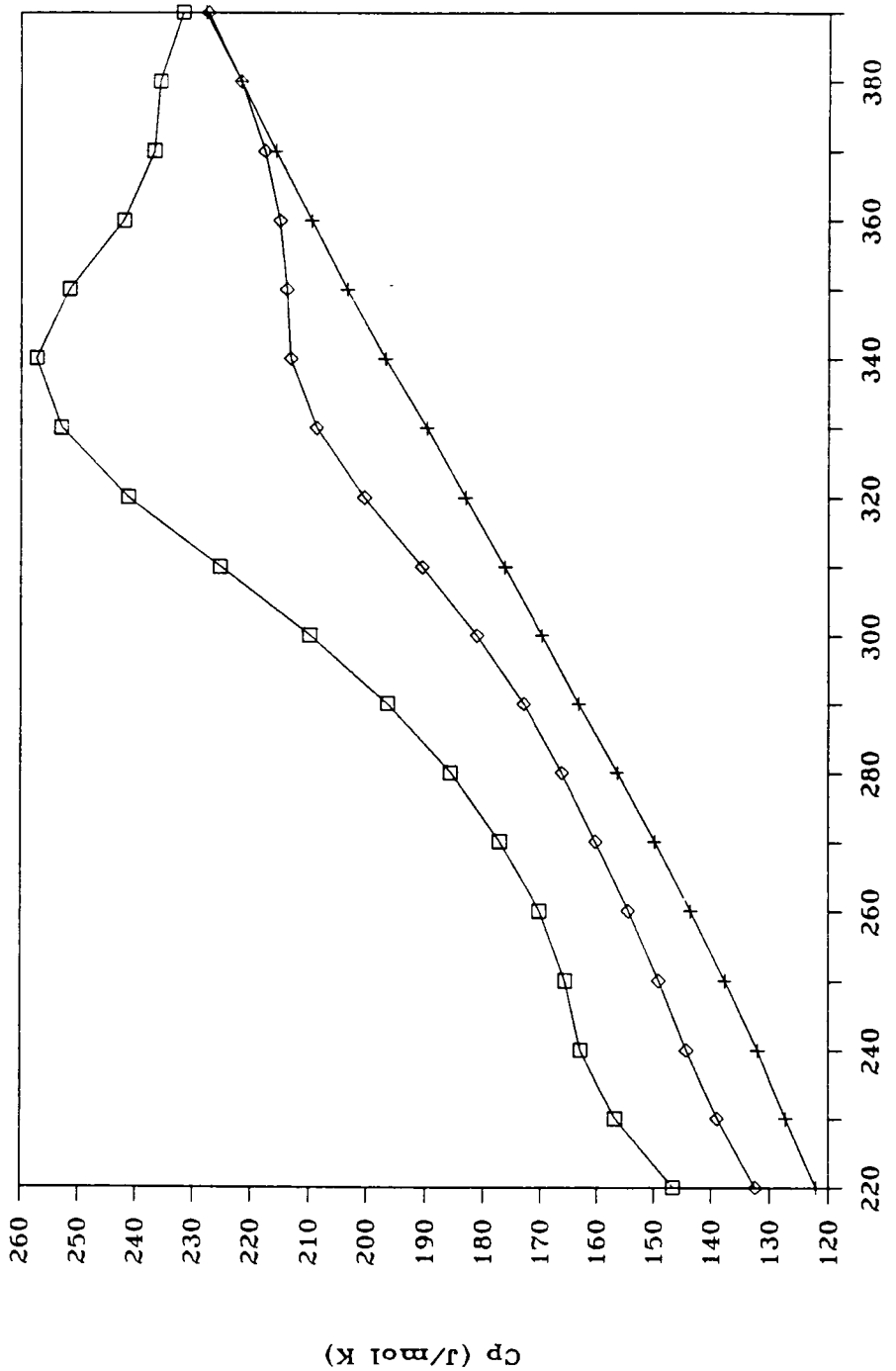


Figure 22 Measured Heat Capacities of Poly(L-phenylalanine). Top curve (□): DSC run 1. Bottom curve (+): DSC run 2. Center curve (◇): DSC run 3.

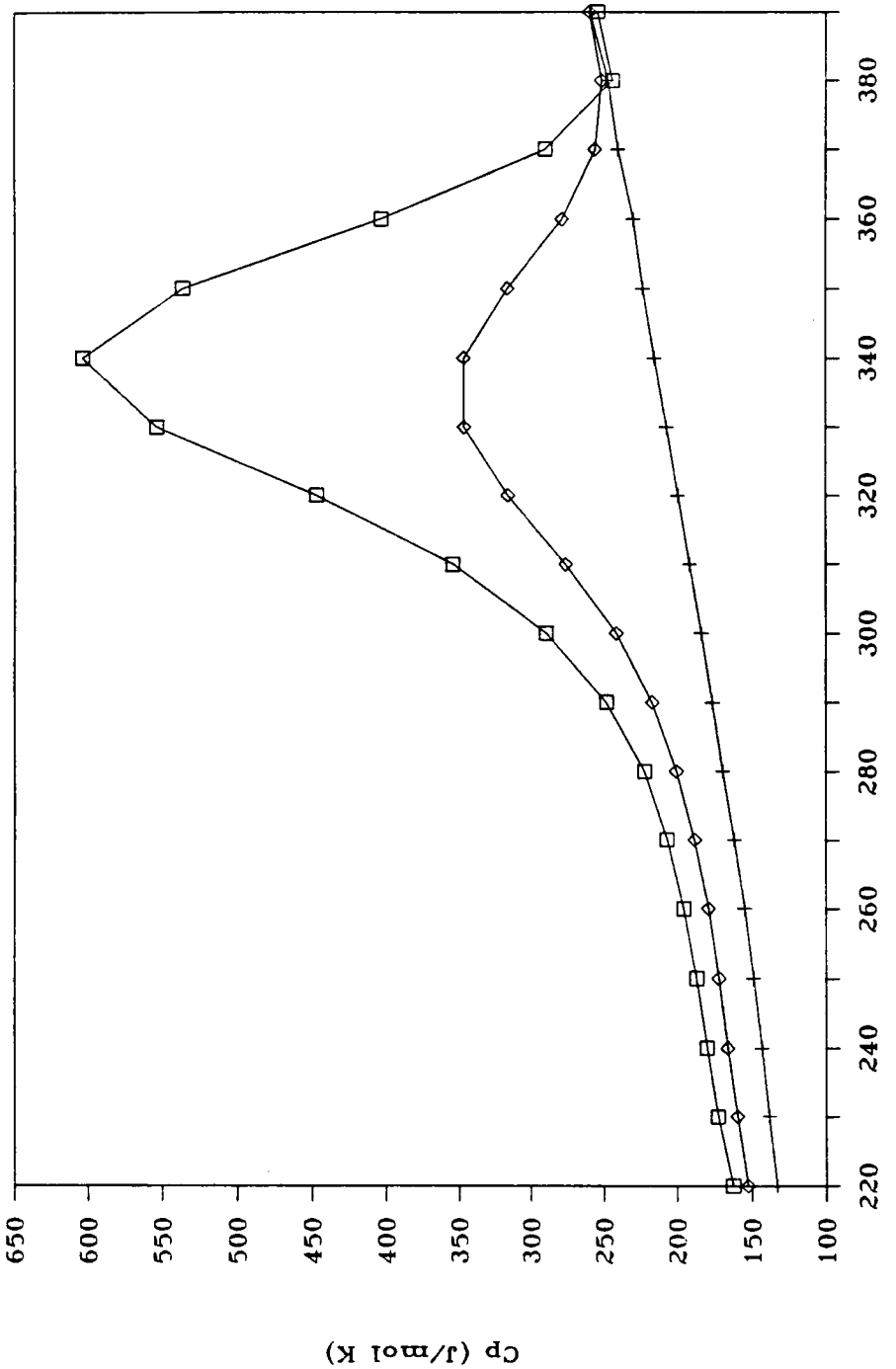


Figure 23 Measured Heat Capacities of Poly(L-tyrosine). Top curve (□): DSC run 1. Bottom curve (+): DSC run 2. Center curve (◇): DSC run 3.

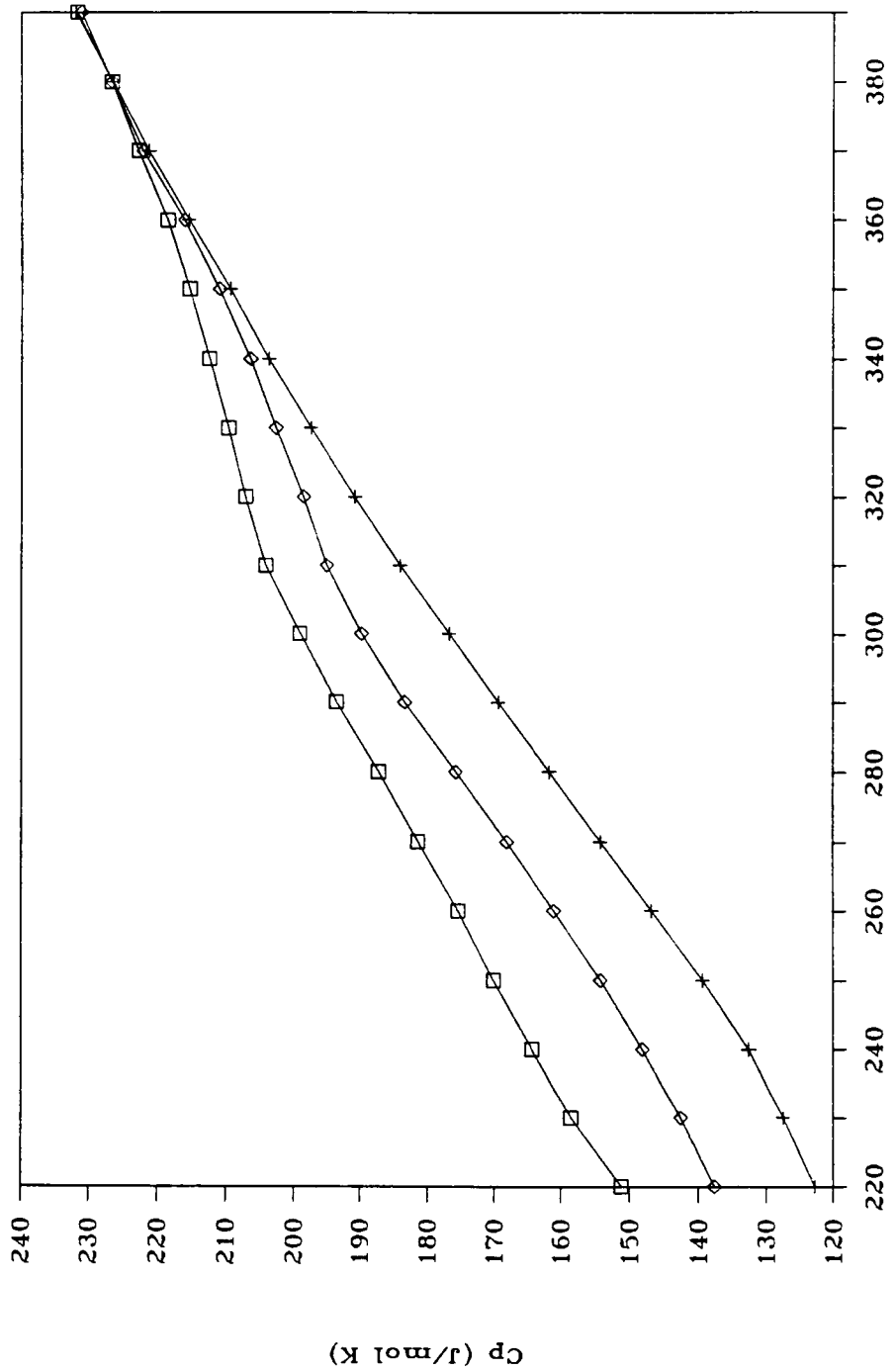


Figure 24 Measured Heat Capacities of Poly(L-methionine). Top curve (□): DSC run 1. Bottom curve (+): DSC run 2. Center curve (◇): DSC run 3.

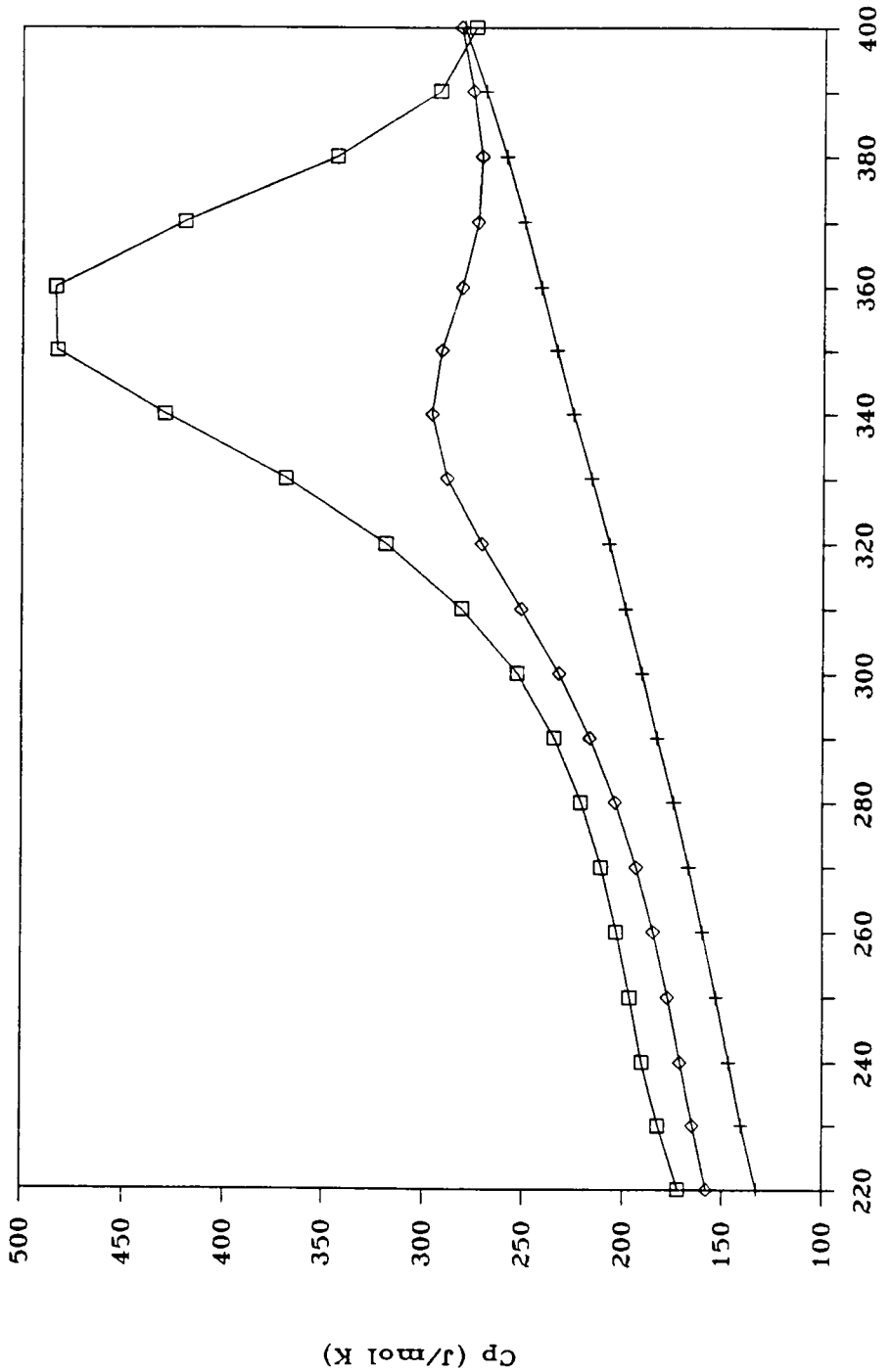


Figure 25 Measured Heat Capacities of Poly(L-tryptophan). Top curve (□): DSC run 1. Bottom curve (+): DSC run 2. Center curve (◇): DSC run 3.

corresponding to the peak observed in run 1 was 355 K (82°C). The sample lost 0.25 mg or 2.6% of its total weight during run 1.

Poly(L-proline) heat capacity results are shown in Figure 26. For the initial heating experiment, run 1, a peak temperature of 351 K (73°C) was observed. A weight loss of 0.28 mg was observed following run 1. This corresponds to 8.3% of the total sample weight.

Results for poly(L-lysine) hydrobromide are given in Figure 27. Run 1 exhibited a large, broad peak with a peak temperature of 367 K (94°C). Weight loss following run 1 was observed to be 0.3mg or 6.7% of the total weight.

The heat capacity results for poly(L-histidine) are given in Figure 28 while the results for poly(l-histidine)•HCl are given in Figure 29. Poly(L-histidine) exhibited a peak in run 1 with a corresponding peak temperature of 356 K (83°C). The sample lost 0.53 mg or 8.7% of its total weight during run 1. For poly(L-histidine)•HCl the peak temperature occurred at 357 K (84°C). Weight loss was 0.37 mg or 9.7% of the total sample weight.

The final poly(amino acid) measured was poly(L-arginine) hydrochloride. Its heat capacity results are given in Figure 30. For run 1, a peak temperature of 362 K (89°C) was observed. The sample lost 0.26 mg or 7.3% of its total weight during run 1.

Turning to the copolymers, the heat capacity results for poly(L-lysine)•HBr-alanine are shown in Figure 31. The peak temperature observed for run 1 (in Figure 31) was 361 K (88°C). During this run, the sample was observed to lose 0.29 mg or

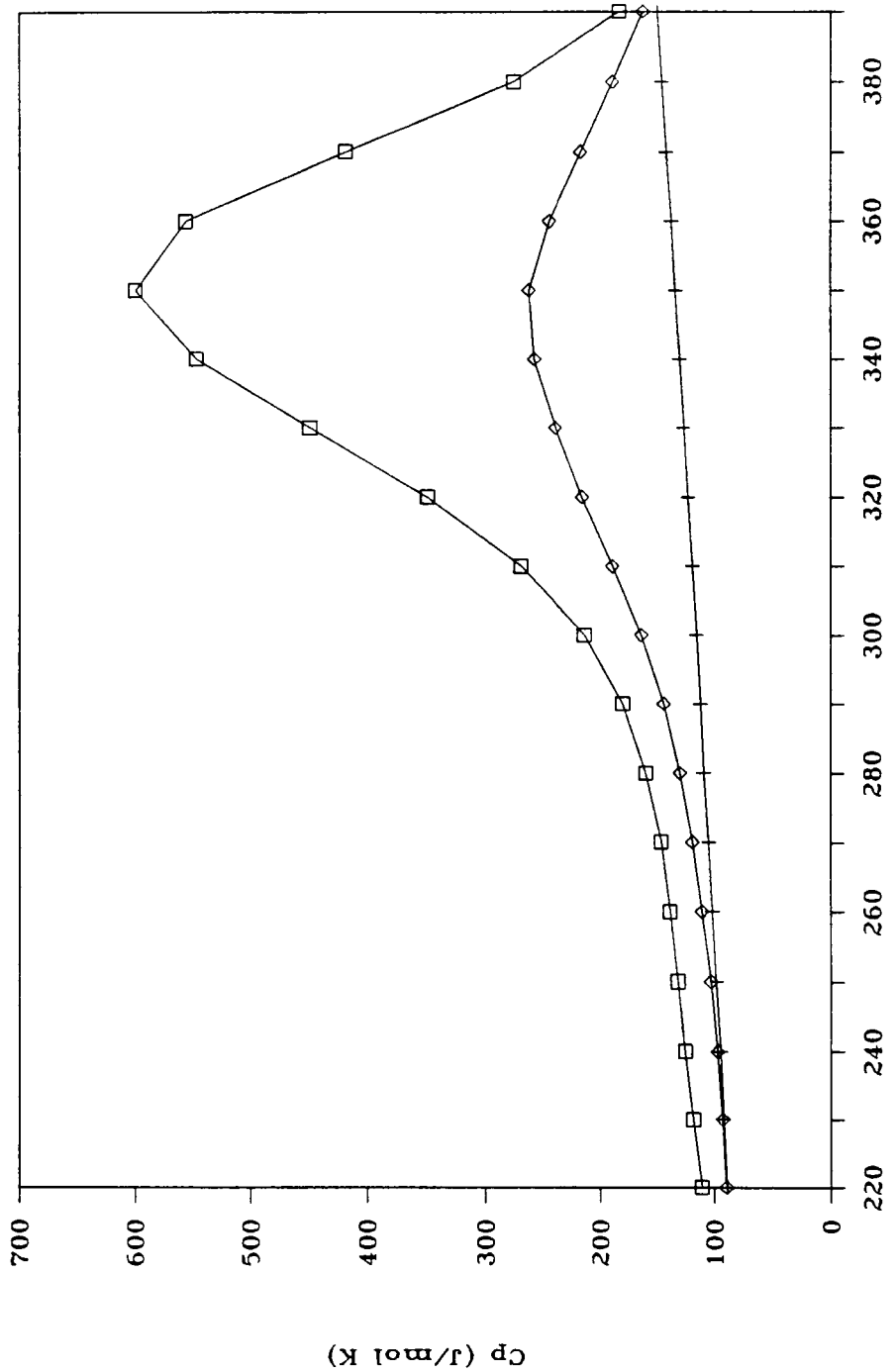


Figure 26 Measured Heat Capacities of Poly(L-proline). Top curve (□): DSC run 1. Bottom curve (+): DSC run 2. Center curve (◇): DSC run 3.

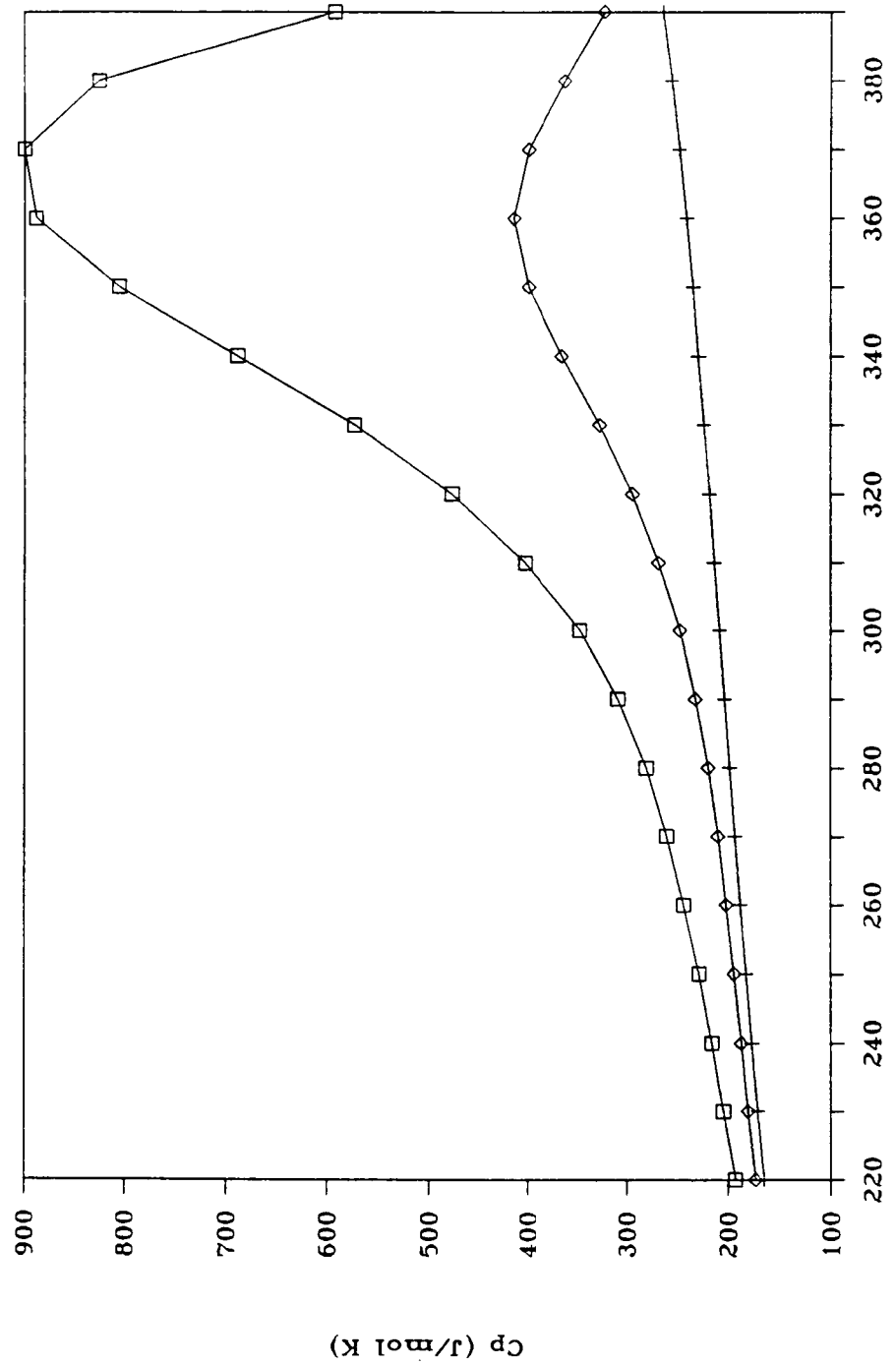


Figure 27 Measured Heat Capacities of Poly(L-lysine•HBr). Top curve (□): DSC run 1. Bottom curve (+): DSC run 2. Center curve (◇): DSC run 3.

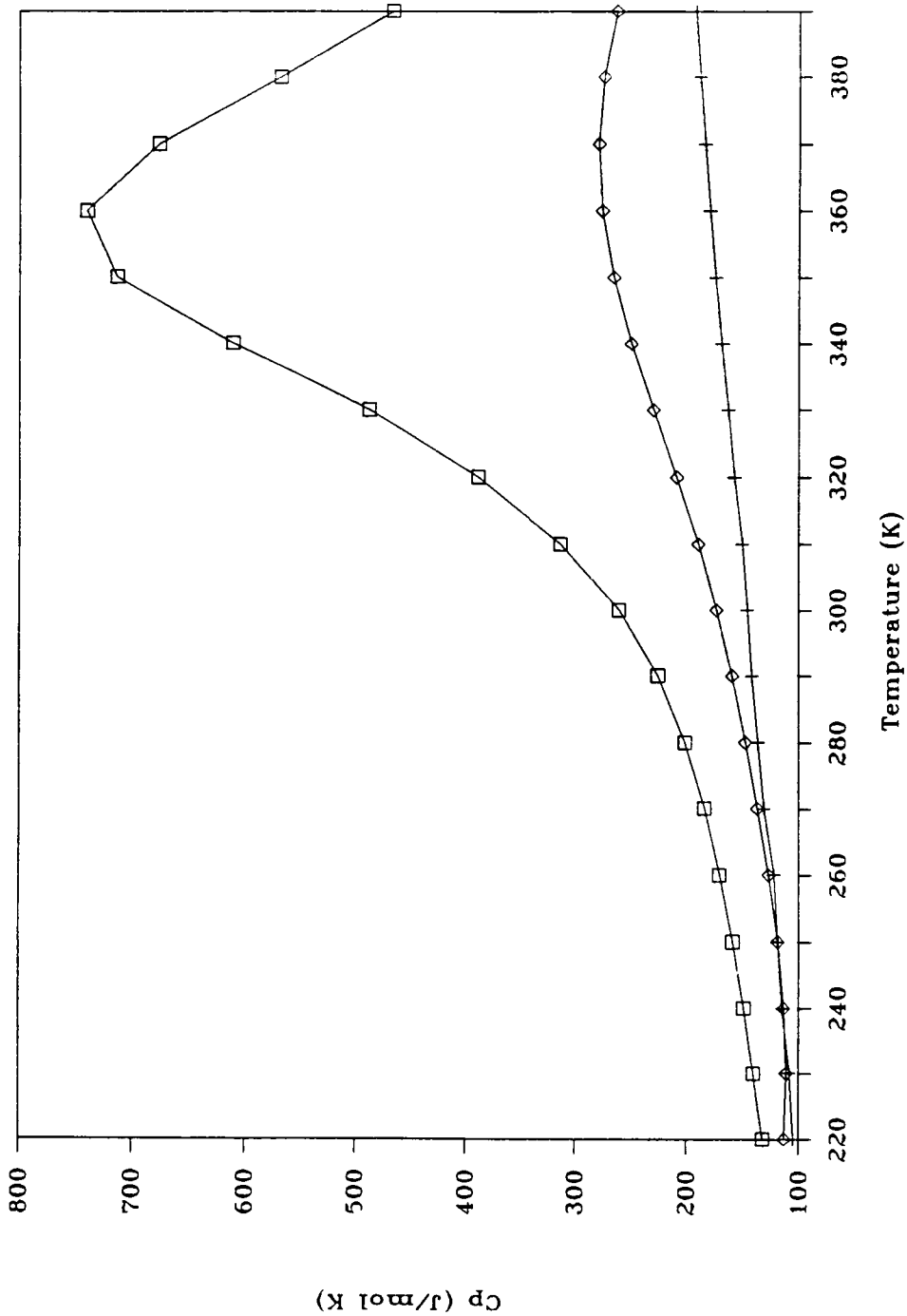


Figure 28 Measured Heat Capacities of Poly(L-histidine). Top curve (□): DSC run 1. Bottom curve (+): DSC run 2. Center curve (◇): DSC run 3.

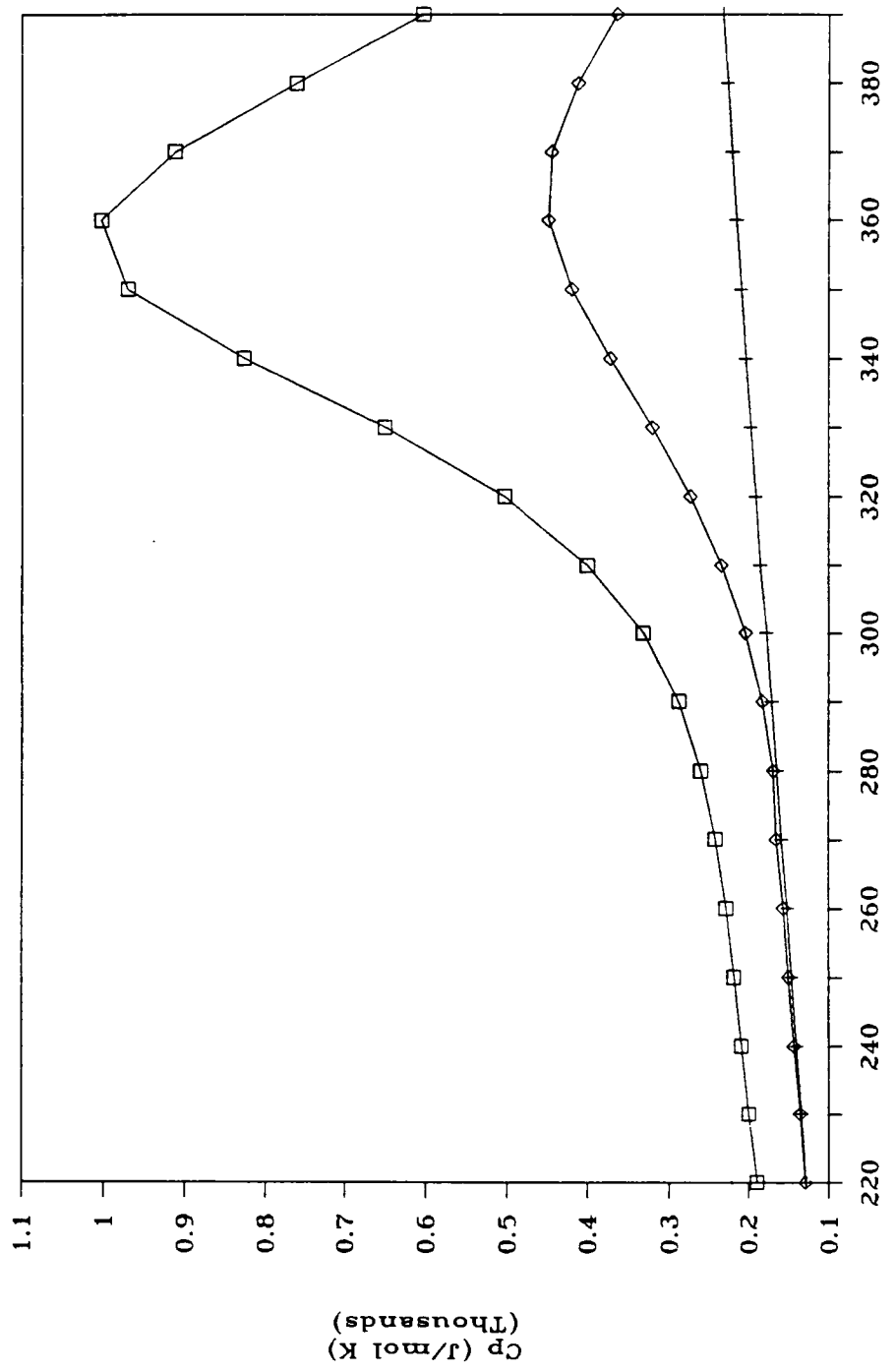


Figure 29 Measured Heat Capacities of Poly(L-histidine•HCl). Top curve (□): DSC run 1. Bottom curve (+): DSC run 2. Center curve (◇): DSC run 3.

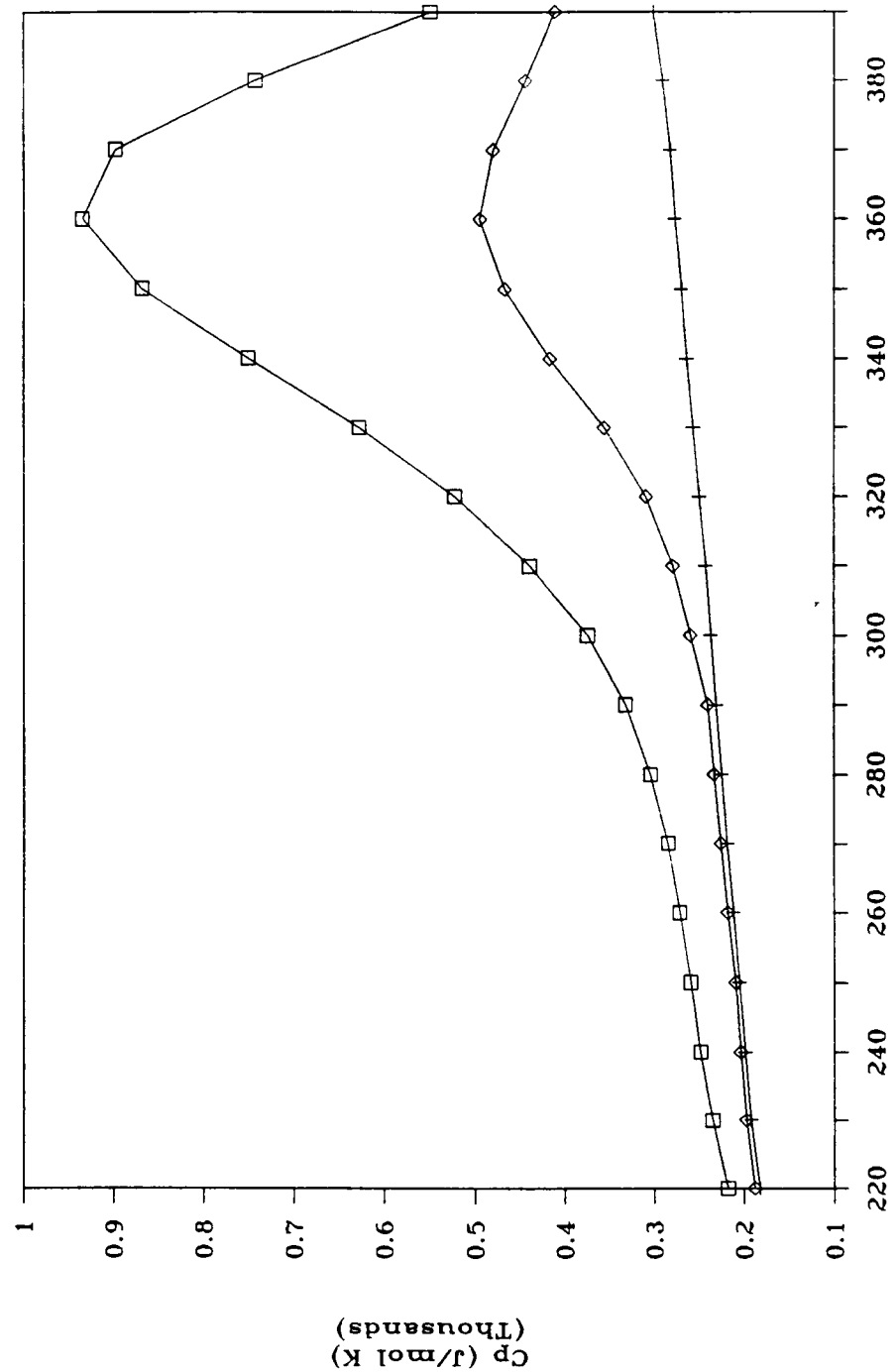


Figure 30 Measured Heat Capacities of Poly(L-arginine•HCl). Top curve (□): DSC run 1. Bottom curve (+): DSC run 2. Center curve (◇): DSC run 3.

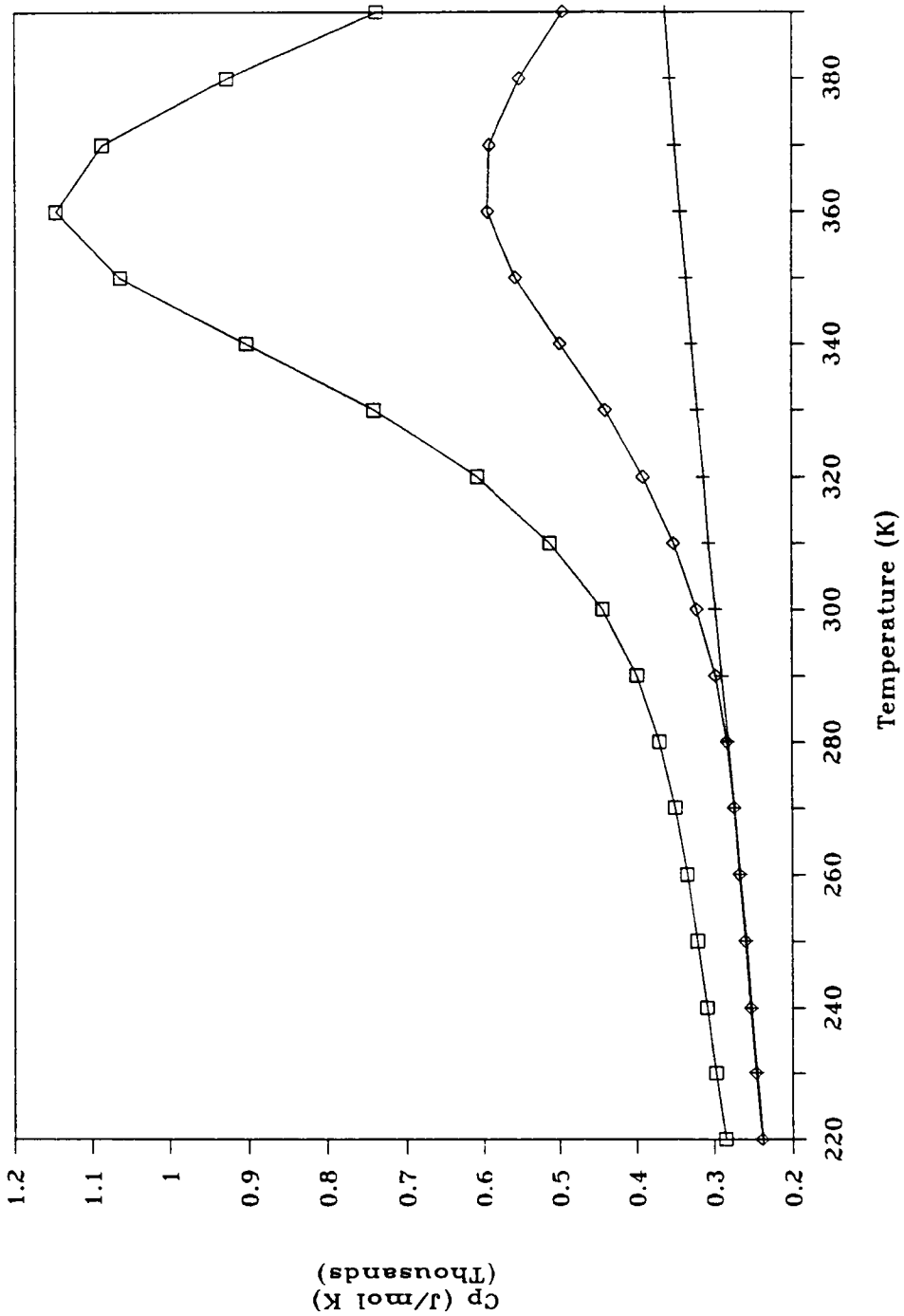


Figure 31 Measured Heat Capacities of Poly(L-lysine•HBr-alanine). Top curve (□): DSC run 1. Bottom curve (+): DSC run 2. Center curve (◇): DSC run 3.

5.6% of its total weight.

Heat capacity results for poly(L-lysine) • HBr-phenylalanine are given in Figure 32. The peak temperature observed for run 1 was 353 K (80°C). A weight loss of 0.22 mg or 5.1% of the sample weight was observed following run 1.

Poly(L-glutamic acid) sodium salt-tyrosine exhibited heat capacity curves as shown in Figure 33. The peak temperature corresponding to run 1 was 367 K (94°C). The sample lost 0.38 mg or 9.6% of its weight during run 1.

The final copolymer studied was poly(L-proline-glycine-proline), and its heat capacity curves are shown in Figure 34. Run 1 shows the large peak a bit sharper than in most of the samples. The peak temperature was 358 K (85°C). Weight loss noted following run 1 was 0.37 mg or 6.5% of the sample's total weight.

It is important to point out that for each of these samples, a slight uptake of water was noted between runs 2 and 3, corresponding to a time period of two to three hours. In each case, the sample lost this additional water during the third heating run (run 3), so that the sample weight following run 3 was the same as was noted following run 1. In addition, the smaller peak observed in run 3 for each sample was not always the same as was observed in run 1. In some cases, it was shifted to a slightly higher or lower temperature than observed in run 1.

Tables 3–8 list the measured heat capacities for run 2 (second heating run) from 230 to 390 K for the sixteen poly(amino acids) and four copolymers studied. For each poly(amino acid) and copolymer, the sequence of four runs, heat (run 1), cool, heat (run 2), and heat again (run 3), was repeated three times. The measured

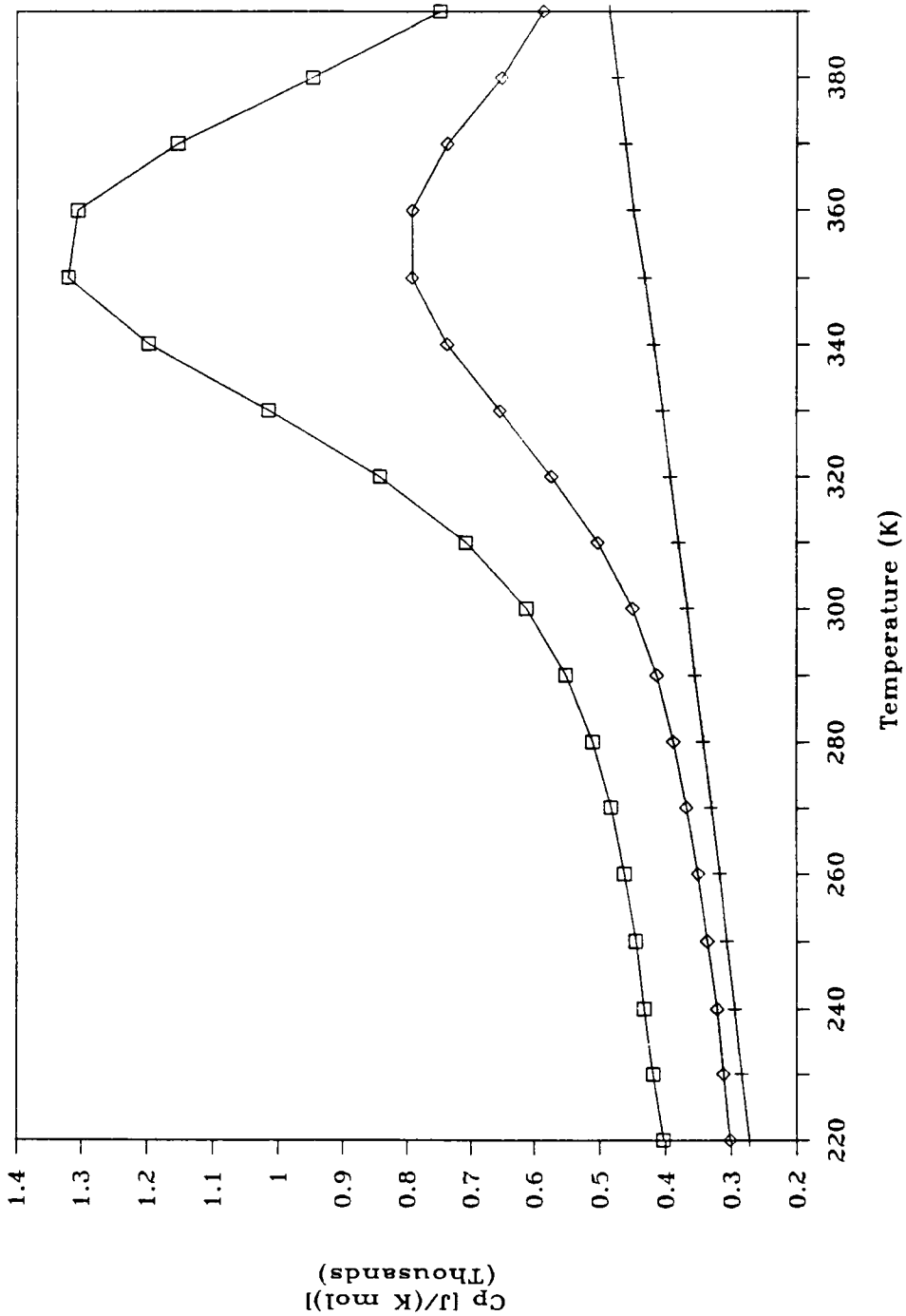


Figure 32 Measured Heat Capacities of Poly(L-lysine•HBr-phenylalanine). Top curve (□): DSC run 1. Bottom curve (+): DSC run 2. Center curve (◇): DSC run 3.

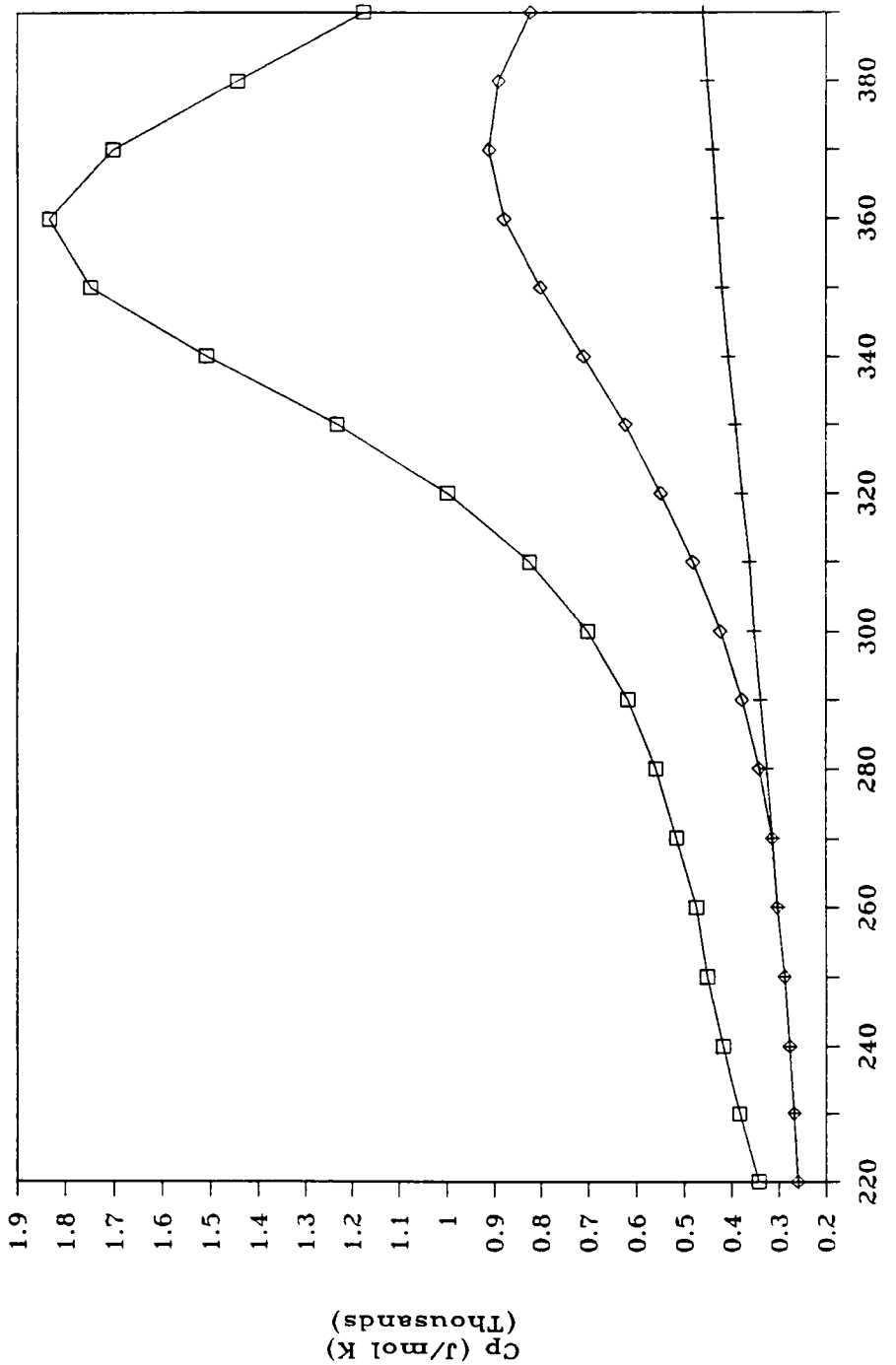


Figure 33 Measured Heat Capacities of Poly(L-glutamic acid•Na-tyrosine). Top curve (□): DSC run 1. Bottom curve (+): DSC run 2. Center curve (◇): DSC run 3.

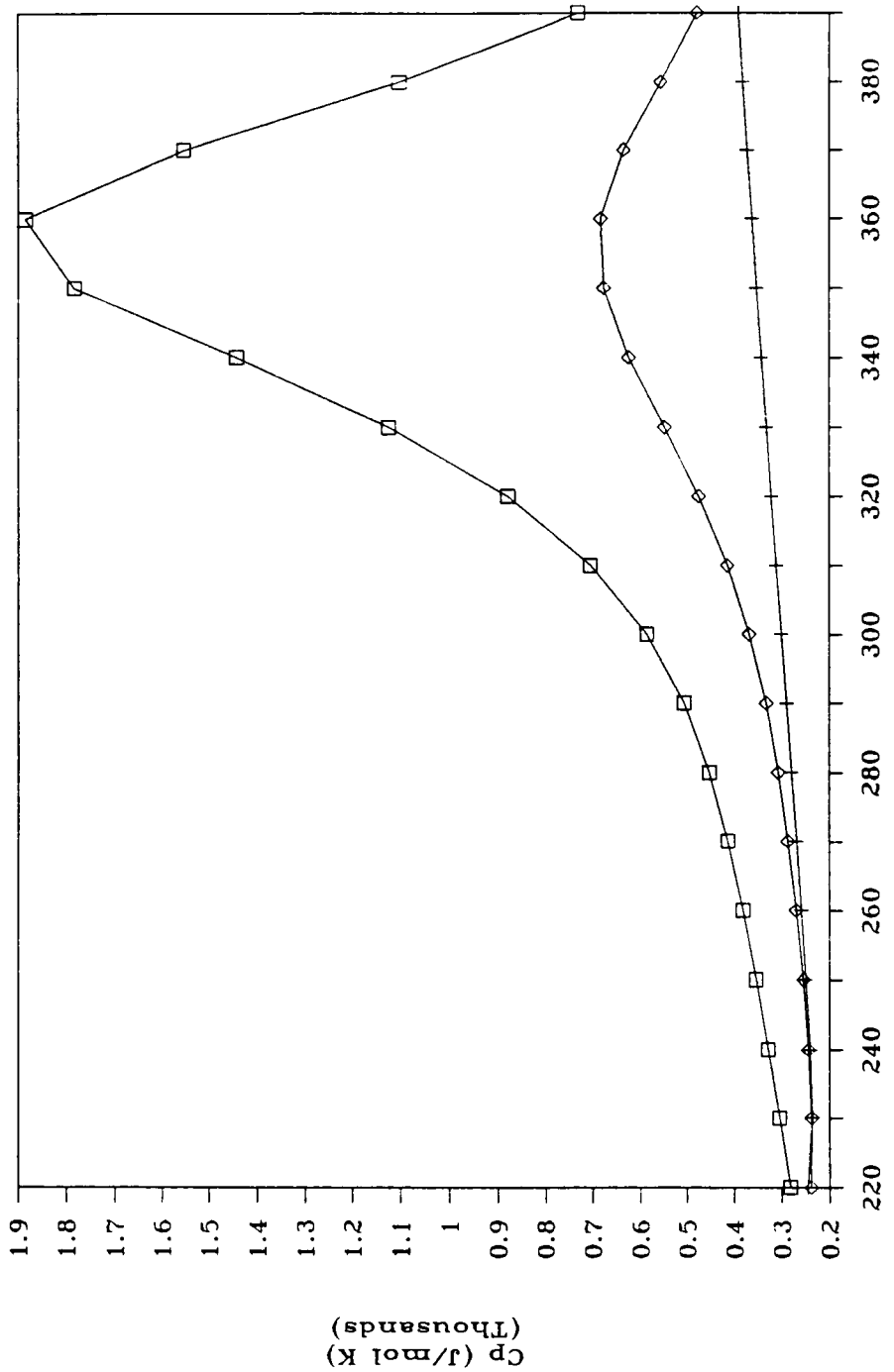


Figure 34 Measured Heat Capacities of Poly(L-proline-glycine-proline). Top curve (□): DSC run 1. Bottom curve (+): DSC run 2. Center curve (◇): DSC run 3.

TABLE 3

Experimental Heat Capacities of Poly(amino Acids)
I. GLY, ALA, VAL, LEU

Cp (J/mol K)

Temp (K)	GLY	ALA	VAL	LEU
220	51.79	77.12	117.5	132.8
230	53.00	78.33	120.2	137.8
240	54.80	79.40	123.1	142.1
250	56.60	80.96	126.2	147.0
260	58.80	83.09	129.6	151.6
270	60.50	85.51	133.0	156.3
280	62.20	88.07	136.8	161.9
290	64.58	90.70	140.6	168.6
300	66.75	93.47	144.2	175.8
310	68.80	96.24	148.4	183.8
320	70.86	99.08	152.0	189.4
330	73.02	101.8	155.9	191.9
340	75.19	104.4	159.6	193.0
350	77.36	106.5	163.3	195.2
360	79.53	108.8	166.7	199.6
370	81.75	111.2	170.9	204.6
380	84.09	113.3	174.8	209.8
390	86.49	115.3	178.6	215.9

TABLE 4

Experimental Heat Capacities of Poly(amino Acids)
II. Ser, ASP•Na, GLU•Na, ASN

Cp [J/(mol K)]

Temp (K)	SER	ASP•Na	GLU•Na	ASN
220	83.50	118.8	117.7	109.3
230	86.90	122.1	124.3	112.4
240	89.91	126.1	129.6	115.2
250	93.19	129.6	135.1	119.4
260	96.74	133.7	139.6	123.1
270	100.8	138.0	143.9	127.2
280	104.8	142.1	148.4	131.1
290	109.0	146.2	152.7	135.0
300	112.9	150.8	157.4	139.0
310	117.1	155.2	162.1	143.3
320	121.3	159.3	167.0	147.2
330	125.6	163.6	171.9	151.3
340	129.8	168.0	177.7	155.7
350	134.2	171.8	182.9	159.4
360	139.8	175.5	188.9	163.2
370	143.9	180.0	195.6	167.4
380	148.0	185.0	201.0	171.4
390	152.1	189.9	206.7	175.4

TABLE 5

Experimental Heat Capacities of Poly(amino Acids)
III. PHE, TYR, MET, TRP

Cp [J/(mol K)]

Temp (K)	PHE	TYR	MET	TRP
220	122.1	133.0	122.8	132.7
230	127.2	137.9	127.5	140.3
240	132.0	142.8	132.5	146.7
250	137.6	148.6	139.3	153.3
260	143.6	154.8	146.8	160.1
270	149.9	161.6	154.3	167.1
280	156.4	169.1	161.8	174.9
290	163.2	176.3	169.4	183.0
300	169.7	183.6	176.7	190.6
310	176.2	191.4	184.0	199.0
320	183.1	199.6	190.8	207.2
330	189.7	207.2	197.5	215.9
340	196.8	215.7	203.6	225.1
350	203.4	223.4	209.3	233.3
360	209.6	229.9	215.4	241.5
370	215.8	236.7	221.2	250.0
380	221.7	243.6	226.4	258.9
390	227.8	249.5	232.0	269.2

TABLE 6

Experimental Heat Capacities of Poly(amino Acids)
IV. PRO, LYS•HBr, HIS, HIS•HCl

Cp [J/(mol K)]

Temp (K)	PRO	LYS•HBr	HIS	HIS•HCl
220	89.2	165.1	104.8	127.9
230	92.56	171.1	108.4	133.8
240	95.34	176.8	114.4	139.9
250	98.60	182.7	119.6	145.9
260	102.4	188.3	124.7	151.9
270	105.5	193.5	131.0	158.8
280	109.1	198.6	136.0	164.8
290	112.2	203.4	141.5	170.7
300	115.7	208.5	147.9	177.6
310	119.2	213.6	153.3	185.5
320	122.9	218.2	160.2	191.1
330	126.6	223.7	166.0	197.2
340	130.5	229.5	171.7	203.1
350	134.2	234.5	177.4	208.9
360	137.7	240.9	182.4	214.9
370	141.9	247.9	187.1	220.8
380	146.0	255.3	192.1	226.5
390	149.6	263.9	197.9	232.5

TABLE 7

Experimental Heat Capacities of Poly(amino Acids)
V. ARG•HCl

Cp [J/(mol K)]

Temp (K)	ARG•HCl
220	186.4
230	192.1
240	198.6
250	204.9
260	211.8
270	218.1
280	224.3
290	230.3
300	236.3
310	242.3
320	249.0
330	256.0
340	263.5
350	269.6
360	276.6
370	282.0
380	290.4
390	298.0

TABLE 8

Experimental Heat Capacities of Copolymers of Poly(amino acids)

Cp [J/(K mol)]

Temp (K)	LYS•HBr-ALA	LYS•HBr-PHE	GLU•Na-TYR	PRO-GLY-PRO
220	237.9	272.7	258.9	223.3
230	245.2	284.6	267.7	231.9
240	251.8	294.6	277.4	240.4
250	258.5	306.5	288.4	249.3
260	266.2	317.6	303.0	259.4
270	273.4	330.4	313.7	268.6
280	281.6	342.5	325.9	279.0
290	289.8	354.9	339.2	289.7
300	297.5	366.5	353.2	300.1
310	305.9	380.2	362.9	310.5
320	313.2	392.3	378.6	321.2
330	321.0	403.5	392.2	331.8
340	328.2	416.9	406.8	342.6
350	335.0	431.6	420.5	352.4
360	342.7	447.6	430.7	362.8
370	349.9	460.0	440.7	372.7
380	356.4	472.7	452.3	382.5
390	363.1	485.4	461.8	392.2

heat capacities reported in Tables 3-8 for run 2 are within 3.0% of the repeated data sets for run 2.

II. HEAT CAPACITY CALCULATIONS

Section II of the Introduction described in detail the analysis of the heat capacity of a solid polymer in terms of its vibrational spectra. Essentially, it becomes possible with a table of group vibration frequencies, a limited range of heat capacity data (to arrive at the two Θ-temperatures), and the known number of skeletal vibrations, N, to calculate the heat capacity of a solid macromolecule over a large temperature range. For each of the poly(amino acids) and co-polymers for which heat capacity measurements were made, an effort has been made to repeat these results with calculation. The following sections will describe in detail how the heat capacity was linked to the vibrational spectra for each biological polymer studied.

IIA. Polyglycine

A new effort to calculate heat capacities for polyglycine has been undertaken. Since the low-temperature data fit for PGII was good[37], we combined this data set (1.4 to 20 K)[9-10] with our new data given in Table 3 on a mixed sample of polyglycine (230 to 390 K). For polyglycine, as well as all other biological polymers studied, the selection of the number of skeletal vibrations was done in a way consistent with the experience gained over the years in the *ATHAS* laboratory through the study of a

large number of solid macromolecules. For polyglycine, the substitution group on the backbone is simply a hydrogen atom

Polyglycine $(C_\alpha HR-C_\delta O-NH-)_n$

Six skeletal vibrations were then assumed, two for the CH group, two for CO group, and two for NH group. An equilibrium melting temperature of 555 K was extrapolated from higher nylons since no reliable data exists. For the final computation parameter, A_o, the universal value of 3.9 ± 2.4 x 10^{-3} K mol/J was taken. For polyglycine detailed dispersion curves of the vibrational spectrum do exist. The work of Singh and Gupta[57] on polyglycine II was chosen as the most reliable source of group vibration frequencies. Table 9 lists the group vibrations frequencies for polyglycine taken from this reference. The low temperature data fit (1.6 to 12 K) yielded a Debye temperature of 169.4 ± 2.3 K. The parameter Θ_1 was determined to be 750.3 ± 43.0 K, and the parameter Θ_3 was determined to be 80.6 ± 2.4 K for the temperature range 230 to 390 K. These theta temperatures fall outside the range of the previously determined theta temperatures (Θ_1 = 528.1 ± 34.9 K and Θ_3 = 96.4 ± 3.3 K).[37] When heat capacities are calculated with these new theta temperatures, a good fit is obtained for the entire range of the experiment (1.4 to 20 K and 230 to 390 K). This is shown in Figure 35. Table 10 lists these new calculated heat capacities for polyglycine from 0 to 1000 K. Comparison of the calculated and newly measured experimental heat capcities reveals a RMS deviation of 0.74%. The average deviation is −0.342%.

TABLE 9

Group Vibration Frequencies for Polyglycine[57] in Kelvin (hν/k), 1 K = 0.695 cm^{-1}

Approximate Vibrational Modes	Number of Vibrators	Frequency (K)
NH stretch	1.00	4737.0
CH_2 asym. stretch	1.00	4223.0
CH_2 sym. stretch	1.00	4093.0
Amide I	1.00	2370.0
Amide II	1.00	2233.0
CH_2 bend	1.00	2041.0
CH_2 wag	1.00	1982.0
Amide III	1.00	1840.0
CO stretch + $C_\alpha C$ stretch + CN stretch	1.00	1692.0 – 1700.7
Skeletal stretch	1.00	1471.9 – 1492.0
CH_2 rock	0.27 0.22 0.51	1301.0 – 1314.0 1291.0 – 1301.0 1291.0
Amide V	0.56 0.44	1118.0 – 1202.0 1151.0 – 1202.0
$C_\alpha C$ stretch + $C_\alpha C{=}O$ bend + NC_α stretch	0.50 0.50	1030.0 – 1109.0 1030.0 – 1097.0
Amide IV + Amide VI	0.54 0.46	971.0 – 1007.0 858.0 – 971.0
Amide VI + Amide V	1.00	830.0
	Total = 15 group vibrations	

Source: [57] R.D. Singh and V.D. Gupta *Spectrochimica Acta* 27A, 385 (1971).

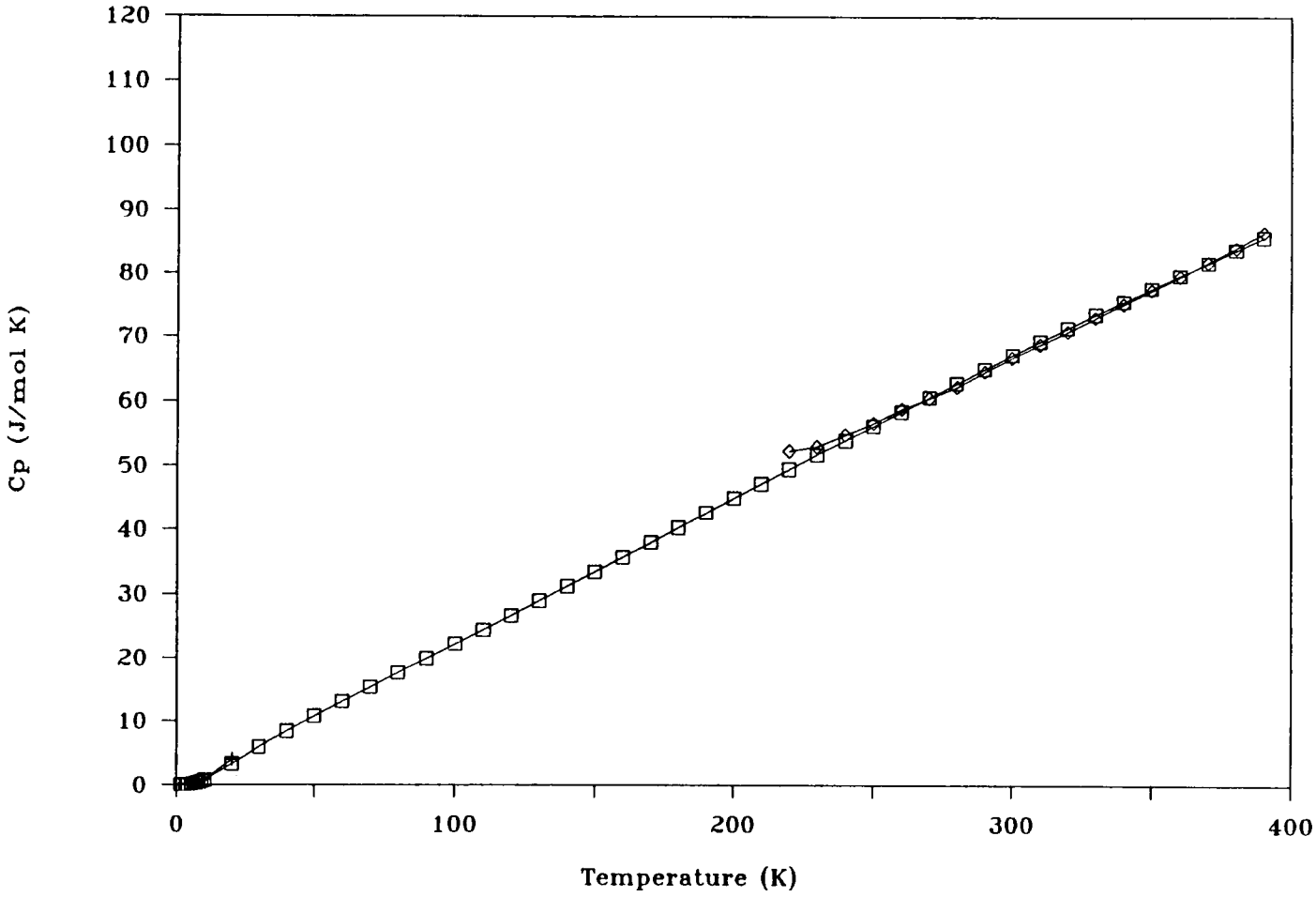


Figure 35 Heat Capacities of Polyglycine. Curve (□): New calculations. Curve (◇): New measurements. Curve (+): Previous measurements on polyglycine II.[9-10] [Sources: B. Fanconi and L. Finegold *Science* **190**, 458 (1975); L. Finegold and B. Fanconi *Conf. Int. Thermodyn. Chim. 4th* **2**, 117 (1975).]

TABLE 10

Calculated Heat Capacities of Polyglycine

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.000	0.000	0.000	0.000	0.000	0.000
0.60	0.000	0.000	0.000	0.000	0.000	0.000
0.70	0.000	0.000	0.000	0.000	0.000	0.000
0.80	0.000	0.000	0.000	0.000	0.000	0.000
0.90	0.001	0.000	0.000	0.000	0.001	0.001
1.00	0.001	0.000	0.000	0.000	0.001	0.001
1.20	0.001	0.000	0.000	0.000	0.001	0.001
1.40	0.002	0.000	0.000	0.000	0.002	0.002
1.60	0.003	0.000	0.000	0.000	0.003	0.003
1.80	0.005	0.000	0.000	0.000	0.005	0.005
2.00	0.006	0.000	0.000	0.000	0.006	0.006
3.00	0.022	0.000	0.000	0.000	0.022	0.022
4.00	0.051	0.000	0.000	0.000	0.051	0.051
5.00	0.100	0.000	0.000	0.000	0.100	0.100
6.00	0.172	0.000	0.000	0.000	0.172	0.172
7.00	0.272	0.000	0.000	0.000	0.272	0.272
8.00	0.400	0.000	0.000	0.000	0.400	0.401
9.00	0.558	0.000	0.000	0.000	0.558	0.559
10.00	0.744	0.000	0.000	0.000	0.744	0.745
15.00	1.943	0.000	0.000	0.000	1.943	1.948
20.00	3.302	0.000	0.000	0.000	3.302	3.314
25.00	4.637	0.000	0.000	0.000	4.637	4.658
30.00	5.917	0.000	0.000	0.000	5.917	5.949
40.00	8.340	0.000	0.000	0.000	8.340	8.399
50.00	10.658	0.000	0.000	0.000	10.658	10.753
60.00	12.918	0.002	0.000	0.002	12.920	13.059
70.00	15.148	0.008	0.000	0.008	15.157	15.347
80.00	17.339	0.028	0.017	0.045	17.384	17.635
90.00	19.469	0.070	0.036	0.107	19.576	19.895
100.00	21.526	0.144	0.084	0.229	21.755	22.150
110.00	23.496	0.255	0.199	0.454	23.950	24.431
120.00	25.372	0.406	0.352	0.758	26.130	26.704
130.00	27.128	0.596	0.588	1.184	28.311	28.988
140.00	28.767	0.823	0.876	1.699	30.467	31.253
150.00	30.281	1.083	1.251	2.334	32.616	33.521
160.00	31.676	1.373	1.700	3.073	34.749	35.783
170.00	32.962	1.689	2.227	3.916	36.878	38.048
180.00	34.148	2.030	2.876	4.906	39.054	40.371

TABLE 10 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	35.240	2.392	3.550	5.942	41.182	42.653
200.00	36.223	2.776	4.326	7.102	43.325	44.961
210.00	37.130	3.180	5.076	8.256	45.386	47.192
220.00	37.964	3.604	5.903	9.507	47.471	49.458
230.00	38.729	4.049	6.756	10.805	49.534	51.710
240.00	39.432	4.514	7.616	12.129	51.561	53.934
250.00	40.076	4.999	8.522	13.521	53.597	56.177
260.00	40.667	5.504	9.420	14.924	55.591	58.385
270.00	41.211	6.029	10.347	16.376	57.587	60.605
273.15	41.373	6.198	10.639	16.836	58.209	61.300
280.00	41.711	6.572	11.253	17.825	59.536	62.786
290.00	42.171	7.135	12.175	19.310	61.481	64.971
298.15	42.520	7.606	12.945	20.551	63.070	66.764
300.00	42.596	7.715	13.118	20.833	63.429	67.169
310.00	42.988	8.311	14.006	22.317	65.305	69.301
320.00	43.351	8.922	14.871	23.793	67.144	71.403
330.00	43.688	9.548	15.769	25.318	69.005	73.538
340.00	44.000	10.186	16.600	26.786	70.786	75.597
350.00	44.290	10.836	17.413	28.249	72.539	77.636
360.00	44.560	11.495	18.207	29.702	74.262	79.653
370.00	44.811	12.163	18.971	31.134	75.945	81.636
380.00	45.046	12.838	19.825	32.663	77.709	83.716
390.00	45.266	13.519	20.550	34.068	79.334	85.656
400.00	45.471	14.204	21.256	35.460	80.931	87.575
410.00	45.663	14.893	21.943	36.836	82.499	89.472
420.00	45.844	15.583	22.610	38.194	84.037	91.347
430.00	46.013	16.275	23.355	39.630	85.643	93.305
440.00	46.173	16.967	23.976	40.944	87.116	95.127
450.00	46.323	17.659	24.582	42.241	88.563	96.931
460.00	46.464	18.349	25.171	43.520	89.984	98.715
470.00	46.597	19.037	25.743	44.779	91.377	100.478
480.00	46.723	19.722	26.297	46.019	92.742	102.221
490.00	46.842	20.403	26.834	47.237	94.079	103.942
500.00	46.955	21.081	27.354	48.434	95.389	105.643
510.00	47.062	21.754	27.856	49.610	96.672	107.323
520.00	47.163	22.422	28.342	50.764	97.927	108.982
530.00	47.259	23.085	28.812	51.897	99.156	110.620
540.00	47.350	23.743	29.266	53.008	100.359	112.240
550.00	47.437	24.395	29.704	54.098	101.535	113.839
560.00	47.519	25.041	30.127	55.168	102.687	115.421
570.00	47.598	25.681	30.535	56.216	103.813	116.984
580.00	47.672	26.314	30.930	57.244	104.916	118.529
590.00	47.744	26.941	31.311	58.252	105.995	120.058
600.00	47.812	27.562	31.678	59.240	107.051	121.570

TABLE 10 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	47.877	28.175	32.033	60.209	108.085	123.067
620.00	47.939	28.783	32.376	61.159	109.097	124.549
630.00	47.998	29.383	32.708	62.090	110.088	126.017
640.00	48.054	29.977	33.028	63.004	111.059	127.471
650.00	48.109	30.563	33.337	63.900	112.009	128.912
660.00	48.161	31.143	33.636	64.779	112.940	130.341
670.00	48.211	31.716	33.924	65.641	113.851	131.758
680.00	48.258	32.283	34.204	66.486	114.745	133.164
690.00	48.304	32.842	34.474	67.316	115.620	134.559
700.00	48.348	33.395	34.735	68.130	116.478	135.945
710.00	48.390	33.941	34.987	68.928	117.319	137.321
720.00	48.431	34.480	35.232	69.712	118.143	138.689
730.00	48.470	35.013	35.469	70.481	118.951	140.049
740.00	48.507	35.539	35.698	71.236	119.744	141.401
750.00	48.544	36.058	35.919	71.978	120.521	142.747
760.00	48.572	36.571	36.134	72.705	121.278	144.079
770.00	48.606	37.077	36.342	73.420	122.026	145.412
780.00	48.638	37.577	36.544	74.121	122.759	146.740
790.00	48.669	38.071	36.740	74.810	123.479	148.063
800.00	48.699	38.558	36.929	75.487	124.186	149.382
810.00	48.727	39.039	37.113	76.152	124.879	150.697
820.00	48.755	39.513	37.292	76.805	125.560	152.010
830.00	48.782	39.982	37.465	77.446	126.228	153.320
840.00	48.807	40.444	37.633	78.077	126.884	154.628
850.00	48.832	40.900	37.796	78.696	127.528	155.935
860.00	48.856	41.351	37.957	79.308	128.164	157.245
870.00	48.879	41.795	38.111	79.906	128.785	158.550
880.00	48.902	42.234	38.260	80.494	129.396	159.857
890.00	48.923	42.666	38.406	81.072	129.995	161.164
900.00	48.944	43.093	38.547	81.640	130.584	162.472
910.00	48.964	43.514	38.684	82.198	131.163	163.783
920.00	48.984	43.930	38.817	82.747	131.731	165.097
930.00	49.003	44.340	38.947	83.287	132.290	166.414
940.00	49.021	44.745	39.073	83.818	132.839	167.735
950.00	49.039	45.144	39.196	84.340	133.379	169.060
960.00	49.056	45.538	39.316	84.853	133.910	170.391
970.00	49.073	45.926	39.432	85.358	134.431	171.729
980.00	49.089	46.309	39.556	85.865	134.955	173.086
990.00	49.105	46.687	39.667	86.354	135.459	174.438
1000.00	49.120	47.060	39.774	86.834	135.955	175.798

IIB. Poly(L-alanine)

Again, as with polyglycine, we have recalculated heat capacities for poly(L-alanine) using a combination of our measured data (reported in Table 3) and the data previously reported in the literature. For determination of the theta temperatures, several fits were made using a variety of combinations of the experimental data previously reported for both α-PLA and β-PLA. In the temperature range 60 to 90 K, good fits are observed for both the reported data on α-PLA and β-PLA. In fact, the fits are almost identical. Above 90 K, however, the previously measured data on β-PLA begins to show significant deviations from calculated results whereas the previously measured data on α-PLA fits reasonably to the calculated data up to about 160 K. Based on these observations, we have determined theta temperatures for our mixed sample of poly(L-alanine) (230 to 390 K) and the data reported by Daurel et al.[15] and Finegold and Cude[12] for α-PLA in the temperature range 60 to 160K. Nine skeletal vibrations were assumed. Since the backbone for all poly(amino acids) is the same, this gave six skeletal vibrations (as described for polyglycine). The additional three skeletal vibrations come from the substitution group R, which for poly(L-alanine) is a methyl group. Experience gained from work on polypropylene[58] led to the assignment of three skeletal vibrations for the methyl group. An equilibrium melting temperature of 573 K was chosen based on the value chosen for polyglycine and taking into consideration the added methyl group. Again the universal value for A_o was used. The group vibrations were taken from a detailed dispersion curve of the vibrational spectrum of α-PLA[59-60] (see Table

11). Fitting in the temperature ranges 60 to 150 K and 240 to 390 K resulted in a Θ_1 = 634.1 ± 33.3 K and a Θ_3 = 58.0 ± 1.5 K This new Θ_1 temperature falls within the range of the Θ_1 temperatures determined previously for α-PLA (626.6 ± 45.6 K) and β-PLA (632.7 ± 60.3 K). The Θ_3 falls outside the range of the Θ_3 previously determined for α-PLA (61.9 ± 2.4 K) and β-PLA (72.0 ± 3.5 K).

Calculation of heat capacities using these theta temperatures led to good agreement with both sets of experimental results, 60 to 160 K and 230 to 390 K (see Figure 36). Table 12 lists the newly calculated heat capacities for poly(L-alanine) from 0 to 1000 K. The RMS deviation between the calculated and the new experimental heat capacities is ± 0.879%. The average error is −0.142%.

IIC. Poly(L-valine)

For poly(L-valine) no prior calculations have been made using the *ATHAS* computation method. Unlike polyglycine and poly(L-alanine), detailed dispersion curves do not exist for poly(L-valine). This, however, is not a problem, however, as experience has shown that the group vibrations are, in most cases, not affected by their specific chemical environment. As a result, when either normal mode calculations of isolated chains or attributed infrared and Raman spectra are not available, it is often sufficient to substitute the vibrational spectrum of chemically identical groups of other macromolecules. As all poly(amino acids) consist of the same basic repeat unit with various substitutions, the group vibration spectrum for

TABLE 11

Group Vibrations Frequencies for Poly(L-Alanine)[59-60] in Kelvin ($h\nu/k$), 1 K = 0.695 cm^{-1}

Approximate Vibrational Modes	Number of Vibrators	Frequency (K)
NH stretch	1.00	4581.0
CH_3 asym. stretch	2(1.00)	4313.5
CH_3 sym. stretch	1.00	4230.0
$C_\alpha H$ stretch	1.00	4228.6
Amide I	1.00	2384.1 – 2387.0
Amide II	1.00	2217.0 – 2223.0
CH_3 asym. bend	2(1.00)	2103.5
CH_3 sym. bend	1.00	2000.0
Amide III	1.00	1910.7 – 1928.0
$HC_\alpha C_\beta$ bend + $HC_\alpha N$ bend	1.00	1883.4
$HC_\alpha C$ bend + $HC_\alpha C_\beta$ bend	1.00	1821.5 – 1856.0
CH_3 rock	2(1.00)	1679.0
$C_\alpha N$ stretch + $C_\alpha C$ stretch	0.27 0.73	1551.2 – 1574.3 1574.3 – 1613.1
$C_\alpha N$ stretch + $C_\alpha C$ stretch + CO stretch	0.44 0.31 0.25	1431.8 – 1466.3 1420.3 – 1431.8 1420.3 – 1424.6
$C_\alpha C_\beta$ stretch	1.00	1270.5 – 1310.7
Amide V + Amide VI	1.00	1082.0 – 1109.3
Amide IV + Amide V	0.44 0.56	946.9 – 985.7 946.9 – 1013.1
	Total = 21 group vibrations	

Sources: [59] B. Fanconi, E. W. Small, and W.L. Peticolas *Biopolymers* 10, 1277 (1971).
[60] M.V. Krishnan and V.D. Gupta *Chem. Phys. Lett.* 7(2), 285 (1970).

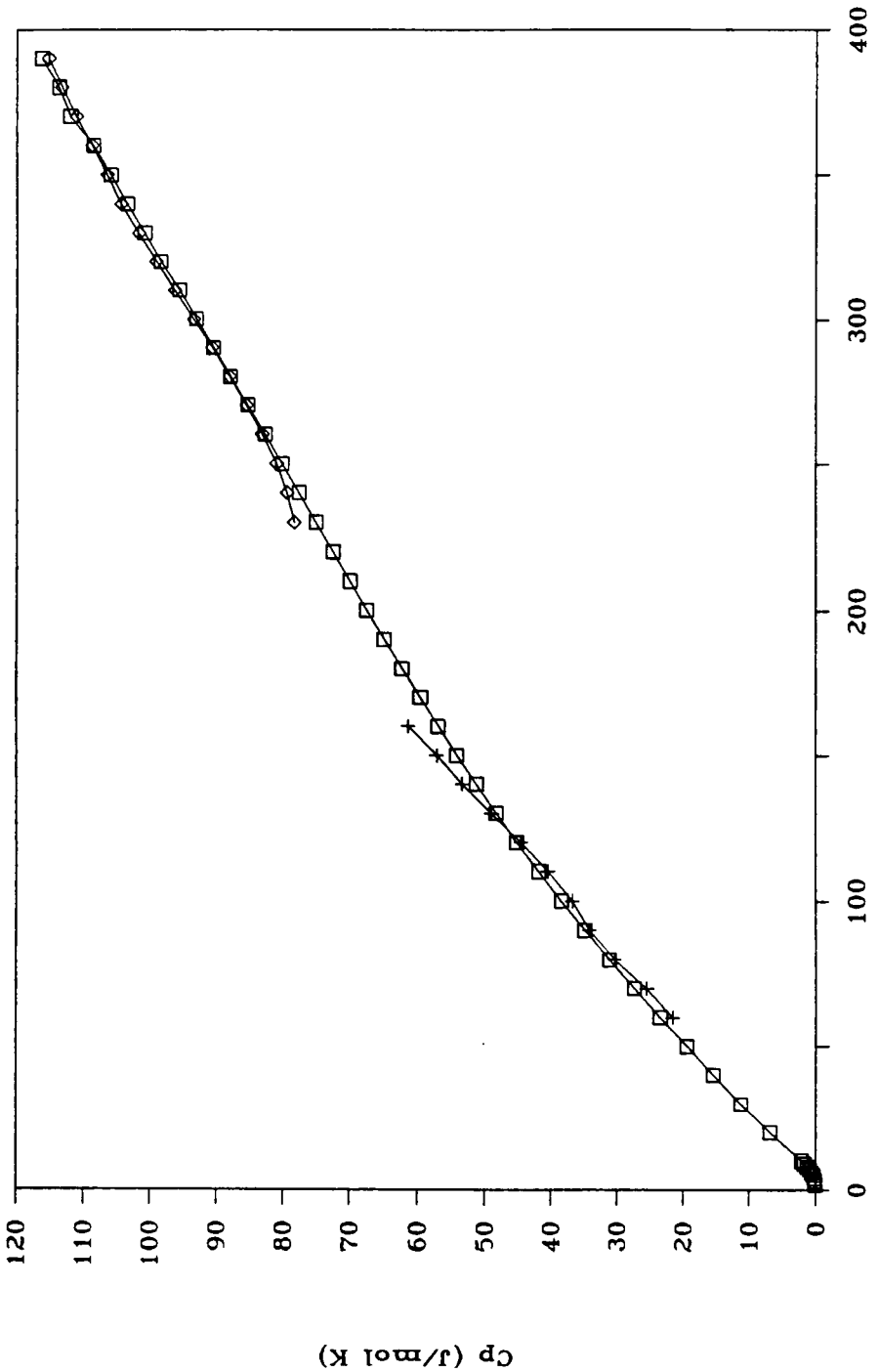


Figure 36 Heat Capacities of Poly(L-alanine). Curve (□): New calculations. Curve (◇): New measurements. Curve (+): Previous measurements on α-poly(L-alanine).[12,15] [Sources: L. Finegold and J.L. Cude *Biopolymers* **11**, 2483 (1972); M. Daurel, P. Delhaes, and E. Dupart *Biopolymers* **14**, 801 (1975).]

TABLE 12

Calculated Heat Capacities of Poly(L-Alanine)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.000	0.000	0.000	0.000	0.000	0.000
0.60	0.001	0.000	0.000	0.000	0.001	0.001
0.70	0.001	0.000	0.000	0.000	0.001	0.001
0.80	0.001	0.000	0.000	0.000	0.001	0.001
0.90	0.002	0.000	0.000	0.000	0.002	0.002
1.00	0.003	0.000	0.000	0.000	0.003	0.003
1.20	0.005	0.000	0.000	0.000	0.005	0.005
1.40	0.008	0.000	0.000	0.000	0.008	0.008
1.60	0.011	0.000	0.000	0.000	0.011	0.011
1.80	0.016	0.000	0.000	0.000	0.016	0.016
2.00	0.022	0.000	0.000	0.000	0.022	0.022
3.00	0.074	0.000	0.000	0.000	0.074	0.074
4.00	0.175	0.000	0.000	0.000	0.175	0.175
5.00	0.340	0.000	0.000	0.000	0.340	0.340
6.00	0.575	0.000	0.000	0.000	0.575	0.576
7.00	0.882	0.000	0.000	0.000	0.882	0.883
8.00	1.251	0.000	0.000	0.000	1.251	1.253
9.00	1.665	0.000	0.000	0.000	1.665	1.668
10.00	2.111	0.000	0.000	0.000	2.111	2.115
15.00	4.510	0.000	0.000	0.000	4.510	4.521
20.00	6.845	0.000	0.000	0.000	6.845	6.869
25.00	9.048	0.000	0.000	0.000	9.048	9.087
30.00	11.159	0.000	0.000	0.000	11.159	11.217
40.00	15.235	0.000	0.000	0.000	15.235	15.340
50.00	19.211	0.000	0.000	0.000	19.211	19.377
60.00	23.134	0.000	0.001	0.001	23.135	23.375
70.00	26.983	0.000	0.007	0.007	26.990	27.318
80.00	30.704	0.000	0.035	0.035	30.739	31.168
90.00	34.261	0.000	0.061	0.061	34.322	34.863
100.00	37.628	0.000	0.165	0.166	37.793	38.458
110.00	40.757	0.001	0.334	0.335	41.092	41.890
120.00	43.639	0.003	0.577	0.580	44.219	45.159
130.00	46.261	0.009	0.886	0.895	47.155	48.245
140.00	48.641	0.019	1.315	1.334	49.974	51.222
150.00	50.803	0.038	1.856	1.895	52.697	54.112
160.00	52.768	0.070	2.483	2.554	55.321	56.911
170.00	54.508	0.119	3.163	3.281	57.790	59.561
180.00	56.089	0.189	3.972	4.162	60.251	62.214

TABLE 12 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	57.520	0.286	4.864	5.149	62.670	64.833
200.00	58.813	0.412	5.807	6.219	65.032	67.404
210.00	59.980	0.573	6.792	7.365	67.345	69.934
220.00	61.034	0.771	7.861	8.632	69.666	72.483
230.00	61.988	1.008	9.011	10.019	72.007	75.063
240.00	62.853	1.285	10.181	11.466	74.319	77.623
250.00	63.638	1.604	11.367	12.971	76.609	80.170
260.00	64.353	1.962	12.602	14.564	78.917	82.747
270.00	65.004	2.361	13.782	16.143	81.147	85.252
273.15	65.197	2.495	14.181	16.676	81.873	86.069
280.00	65.599	2.798	15.109	17.907	83.506	87.905
290.00	66.144	3.271	16.341	19.612	85.756	90.453
298.15	66.554	3.683	17.349	21.031	87.585	92.534
300.00	66.643	3.779	17.577	21.356	88.000	93.006
310.00	67.103	4.318	18.831	23.149	90.252	95.579
320.00	67.526	4.887	20.332	25.219	92.745	98.419
330.00	67.916	5.482	21.446	26.927	94.844	100.852
340.00	68.277	6.100	22.687	28.787	97.064	103.425
350.00	68.612	6.740	23.917	30.657	99.268	105.993
360.00	68.922	7.398	25.185	32.583	101.505	108.607
370.00	69.210	8.072	27.239	35.312	104.522	112.070
380.00	69.478	8.760	27.626	36.386	105.864	113.749
390.00	69.728	9.460	28.799	38.259	107.987	116.277
400.00	69.962	10.169	30.027	40.196	110.157	118.867
410.00	70.180	10.885	31.219	42.104	112.284	121.424
420.00	70.384	11.608	32.347	43.955	114.339	123.914
430.00	70.576	12.335	33.454	45.789	116.365	126.386
440.00	70.755	13.065	34.540	47.605	118.361	128.836
450.00	70.924	13.798	35.601	49.399	120.323	131.263
460.00	71.083	14.531	36.656	51.187	122.271	133.685
470.00	71.233	15.264	37.746	53.010	124.243	136.148
480.00	71.374	15.996	38.710	54.707	126.081	138.474
490.00	71.508	16.727	39.789	56.516	128.024	140.929
500.00	71.634	17.456	40.726	58.182	129.815	143.230
510.00	71.753	18.182	41.643	59.825	131.578	145.511
520.00	71.866	18.905	42.541	61.446	133.312	147.772
530.00	71.973	19.624	43.418	63.042	135.015	150.012
540.00	72.074	20.340	44.273	64.613	136.687	152.230
550.00	72.170	21.051	45.108	66.159	138.330	154.427
560.00	72.262	21.759	46.021	67.780	140.042	156.715
570.00	72.349	22.461	46.809	69.270	141.619	158.864
580.00	72.432	23.159	47.579	70.738	143.170	160.997
590.00	72.511	23.852	48.331	72.184	144.694	163.112
600.00	72.586	24.540	49.167	73.707	146.293	165.324

TABLE 12 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	72.658	25.223	49.878	75.102	147.759	167.399
620.00	72.726	25.901	50.575	76.476	149.202	169.461
630.00	72.792	26.574	51.256	77.830	150.622	171.509
640.00	72.845	27.242	51.921	79.163	152.008	173.533
650.00	72.905	27.904	52.571	80.475	153.380	175.553
660.00	72.962	28.561	53.206	81.767	154.729	177.560
670.00	73.016	29.213	53.825	83.038	156.054	179.553
680.00	73.069	29.859	54.429	84.288	157.357	181.533
690.00	73.118	30.500	55.018	85.518	158.637	183.501
700.00	73.166	31.136	55.592	86.728	159.894	185.457
710.00	73.212	31.766	56.152	87.918	161.130	187.401
720.00	73.256	32.391	56.697	89.088	162.344	189.335
730.00	73.298	33.010	57.229	90.239	163.537	191.257
740.00	73.338	33.624	57.746	91.371	164.709	193.170
750.00	73.377	34.233	58.251	92.483	165.861	195.073
760.00	73.414	34.836	58.742	93.578	166.992	196.968
770.00	73.450	35.433	59.221	94.654	168.104	198.854
780.00	73.485	36.025	59.687	95.713	169.197	200.733
790.00	73.518	36.612	60.142	96.753	170.272	202.604
800.00	73.550	37.193	60.584	97.777	171.327	204.469
810.00	73.581	37.768	61.016	98.784	172.365	206.328
820.00	73.611	38.338	61.436	99.774	173.385	208.182
830.00	73.639	38.903	61.845	100.748	174.387	210.032
840.00	73.667	39.462	62.244	101.706	175.373	211.877
850.00	73.694	40.015	62.633	102.648	176.342	213.720
860.00	73.720	40.563	63.020	103.583	177.303	215.569
870.00	73.744	41.106	63.389	104.495	178.240	217.407
880.00	73.769	41.643	63.762	105.406	179.174	219.259
890.00	73.792	42.175	64.114	106.288	180.080	221.095
900.00	73.814	42.701	64.457	107.157	180.972	222.931
910.00	73.836	43.221	64.769	107.990	181.826	224.741
920.00	73.857	43.736	65.095	108.831	182.689	226.580
930.00	73.878	44.246	65.413	109.659	183.536	228.420
940.00	73.897	44.750	65.723	110.473	184.371	230.263
950.00	73.917	45.249	66.044	111.293	185.209	232.133
960.00	73.935	45.743	66.339	112.081	186.017	233.985
970.00	73.953	46.231	66.627	112.858	186.811	235.842
980.00	73.971	46.713	66.908	113.622	187.592	237.705
990.00	73.988	47.191	67.172	114.363	188.350	239.561
1000.00	74.004	47.663	67.440	115.103	189.107	241.439

the backbone of poly-l-valine can be constructed from the available group vibration information on polyglycine[57], poly-l-alanine[59-60]. Thus for the group vibration frequency spectrum of poly(L-valine), the information on polyglycine and poly(L-alanine) for the backbone (see Part A of Table 13) was combined with information on the $C(CH_3)_2-$ group from polyisobutylene (PIBUT)[61] (see Part B of Table 13), and information on the $-CH_3$ group from polypropylene (PP)[58] (see Part C of Table 13).

For calculations, 14 skeletal vibrations were chosen, $T_m°$ was guessed at as 573K, and the universal A_o value was used. The 14 skeletal vibrations come from the following groups: six for the backbone, as in polyglycine and poly(L-alanine); 3 for each methyl group, for a total of six; and two for the CH group. Regarding the value chosen for $T_m°$, no information exists for the equilibrium melting temperatures of most poly(amino acids) exists. As a result, the value chosen for poly(L-alanine) was also used for poly(L-valine). Again we combined our measured heat capacities with a selected set of the results reported by Daurel et al.[16] for the β conformation of poly(L-valine) (β-PLV). Fitting the low temperature heat capacities (2.0 to 6.0 K) resulted in a Debye temperature of 140.1 ± 2.1 K. A Θ_1 = 663.7 ± 44.2 K and a Θ_3 = 64.5 ± 2.2 K resulted from a fit using experimental heat capacities in the temperature range 40 to 60 K (Daurel et al.[16]) and 230 to 340 K (our data). Heat capacities calculated for poly-l-valine (reported in Table 14 from 0 to 1000 K) using these theta temperatures were observed to be in good agreement with our experimental results (230 to 390 K, reported in Table 3) and the experimental results

TABLE 13

Group Vibration Frequencies for Poly(Amino Acids) in Kelvin (hν/k), 1 K = 0.695 cm^{-1}

Assignment	# of Vibrators	Frequency (K)
A. From PG[57], PLA[59-60]		
NH stretch	1.00	4581.0 – 4764.0
Amide I	1.00	2346.7 – 2444.0
Amide II	1.00	2181.2 – 2233.0
Amide III	1.00	1771.2 – 1927.0
$C_\alpha H_\alpha$ stretch	1.00	4190.0 – 4229.2
$HC_\alpha C_\beta$ bend + $HC_\alpha N$ bend	1.00	1884.0
$HC_\alpha C_\delta$ bend + $HC_\alpha C_\beta$ bend	1.00	1741.0 – 1862.0
$C_\alpha N$ stretch + $C_\alpha C_\delta$ stretch	0.73 0.27	1574.0 – 1613.0 1551.0 – 1574.0
$C_\alpha N$ stretch + $C_\alpha NH$ bend	1.00	1517.0
Amide IV	0.20 0.59 0.21	740.0 – 751.0 616.0 – 740.0 596.0 – 616.0
Amide V	0.62 0.38	837.0 – 888.0 888.0
Amide VI	0.28 0.37 0.35	976.0 – 999.0 930.0 – 976.0 930.0
$C_\alpha C_\beta$ side stretch	1.00	1282.0 – 1324.0
B. From PIBUT[61]		
CH_3 asym. stretch	2(1.00)	4262.0
CH_3 asym. stretch	2(1.00)	4259.0
CH_3 sym. stretch	2(1.00)	4147.0
CH_3 asym. bend	2(1.00)	2107.0
CH_3 asym. bend	2(1.00)	2101.0

TABLE 13 (Cont.)

Assignment	# of Vibrators	Frequency (K)
B. From PIBUT[61] (cont.)		
CH_3 sym. bend	2(0.25)	1987.0
	2(0.38)	1973.0 – 1987.0
	2(0.37)	1973.0
C–CH_3 rock	4(1.00)	1164.0 – 1680.0
C–CH_3 stretch	2(1.00)	1164.0 – 1680.0
C. From PP[58]		
CH_3 asym. stretch	1.00	4262.0
CH_3 asym. stretch	1.00	4259.0
CH_2 asym. stretch	1.00	4213.0
CH stretch	1.00	4181.0
CH_3 sym. stretch	1.00	4147.0
CH_2 sym. stretch	1.00	4085.0
CH_3 asym. bend	1.00	2107.0
CH_3 asym. bend	1.00	2101.0
CH_2 bend	1.00	2094.0
CH_3 sym. bend	0.25	1987.0
	0.38	1973.0 – 1987.0
	0.37	1973.0
CH bend	0.42	1963.0 – 1973.0
	0.58	1966.0
CH bend	0.64	1944.0
	0.28	1916.0 – 1944.0
	0.08	1916.0
CH_2 wag	0.18	1876.0
	0.43	1842.0 – 1876.0
	0.39	1846.0
CH_2 twist (CH_3 rock)	0.33	1722.0 – 1791.0
	0.55	1695.0 – 1722.0
	0.12	1695.0

TABLE 13 (Cont.)

Assignment	# of Vibrators	Frequency (K)
C. From PP[58] (cont.)		
C–C chain stretch	0.16	1685.0
	0.84	1650.0 – 1685.0
$C–CH_3$ stretch	0.44	1568.0 – 1614.0
	0.56	1534.0 – 1614.0
CH_3 rock (+CH_2 wag)	0.55	1453.0 – 1521.0
	0.45	1453.0
CH_3 rock (+C–C chain stretch)	0.65	1361.0 – 1393.0
	0.21	1333.0 – 1361.0
	0.14	1336.0
CH_2 rock	0.52	1222.0 – 1295.0
	0.48	1289.0
C–C chain stretch	0.17	1197.0
	0.55	1167.0 – 1198.0
	0.28	1167.0
D. From PE[62]		
CH_2 asym. stretch	1.00	4148.0
CH_2 sym. stretch	1.00	4098.0
CH_2 bend	1.00	2075.0
CH_2 wag	0.65	1698.0 – 1977.0
	0.35	1977.0
CH_2 twist & rock	0.48	1690.0 – 1874.0
	0.52	1874.0
C–C stretch	0.34	1378.0 – 1638.0
	0.35	1378.0 – 1525.0
	0.31	1525.0
CH_2 rock & twist	0.04	1494.0
	0.59	1038.0 – 1494.0
	0.37	1079.0

TABLE 13 (Cont.)

Assignment	# of Vibrators	Frequency (K)
E. From PVA[63]		
O–H stretch	1.00	4306.0
O–H bend	1.00	1994.0
O–H rock	1.00	921.0
C–OH stretch	1.00	1577.0
C–OH bend	1.00	691.0
C–OH rock	1.00	590.0
F. From PIBA[61]		
C–OO stretch	1.00	1215.0
C=O stretch	1.00	2530.0
C–O stretch	1.00	1800.0
C=O in plane bend	1.00	980.0
C=O out of plane bend	1.00	840.0
G. From PEEK[64]		
C=O stretch	1.00	2498.0
C=O out of plane bend	1.00	1040.0
C=O in plane bend	1.00	693.0
H. From Propionamide[65] From Methylamine[66]		
NH_2 asym. stretch	1.00	4829.0
NH_2 sym. stretch	1.00	4657.0
NH_2 twist	1.00	1426.0
NH_2 wag	1.00	1164.0
NH_2 in plane bend	1.00	2333.0
NH_2 rock	1.00	1389.0 – 1594.0

TABLE 13 (Cont.)

Assignment	# of Vibrators	Frequency (K)
H. From Propionamide[65] From Methylamine[66] (cont.)		
C–N stretch	1.00	1502.0
I. From PVB[64]		
CH stretch	1.00	4408.0
CH stretch	1.00	4397.0
CH stretch	1.00	4388.0
CH stretch	1.00	4378.0
CH stretch	1.00	4371.0
C–C stretch	1.00	2298.0
C–C stretch	1.00	2281.0
CCH bend, C–C stretch	1.00	2161.0
CCH bend	1.00	2074.0
C–C stretch	1.00	1918.0
C–C stretch	1.00	1876.0
CCH bend	1.00	1739.0
CCH bend	1.00	1682.0
CCH bend, C–C stretch	1.00	1656.0
C–C stretch, CCH bend	1.00	1538.0
CCC bend, C–C stretch	1.00	1502.0
CCC bend, C–C stretch	1.00	1479.0
CH wag	1.00	1465.0
CH wag	1.00	1386.0
CH wag	1.00	1328.0
CH wag	1.00	1232.0
C–C stretch (C_6H_5–C)	0.23	1139.0
	0.32	1112.0 – 1139.0
	0.45	1112.0 – 1135.0

TABLE 13 (Cont.)

Assignment	# of Vibrators	Frequency (K)
I. From PVB[64] (cont.)		
CH wag, C_6H_5 wag	1.00	1097.0
CH wag	1.00	1010.0
CCC bend	1.00	904.0
CCC bend	0.31	846.0 – 862.0
	0.30	858.0 – 862.0
	0.35	858.0 – 902.0
Ring mode, coupled to the backbone chain	0.42	771.0 – 791.0
	0.32	771.0 – 800.0
	0.26	815.0
CCC bend C_6H_5-C)	0.31	633.0
	0.32	633.0 – 728.0
	0.37	728.0
C–C torsion	1.00	584.0
CCC rock (C_6H_5-C)	0.16	435.0 – 451.0
	0.39	451.0 – 546.0
	0.45	546.0
J. From PMA[61]		
CH_3 asym. stretch	1.00	4262.0
CH_3 asym. stretch	1.00	4259.0
CH_3 sym. stretch	1.00	4213.0
CH_3 asym. bend	1.00	2107.0
CH_3 asym. bend	1.00	2101.0
CH_3 sym. bend	0.25	1987.0
	0.37	1973.0
	0.42	1963.0 – 1973.0
CH_3 rock	0.55	1453.0 – 1521.0
	0.45	1453.0
CH_3 rock	0.65	1361.0 – 1393.0
	0.21	1333.0 – 1361.0
	0.14	1336.0

TABLE 13 (Cont.)

Assignment	# of Vibrators	Frequency (K)
J. From PMA[61] (cont.)		
CH_3–C stretch	0.44 0.56	1568.0 – 1614.0 1534.0 – 1614.0
K. From Cross[67]		
C–S stretch	1.00	820.1 – 1014.4
L. From Indole[68]		
C–N stretch	2(1.00)	1502.0
NH stretch	1.00	4028.8 – 4460.4
NH in plane bend	1.00	1689.2 – 1788.5
NH out of plane bend	1.00	1343.9
CH stretch	1.00	4460.4 – 4522.3
CH in plane bend	1.00	1513.7 – 1581.3
CH out of plane bend	1.00	1059.0 – 1201.4
C=C stretch	1.00	2384.1
CCC bend	1.00	2217.3 – 2263.3
CCC bend	1.00	2143.9
NCC bend	1.00	2086.3
CNC bend	1.00	1640.3 – 1903.6
CCN bend	1.00	1286.3 – 1343.9
M. From PRO[25,69]		
C=O bend	1.00	1083.4
C=O bend	1.00	1204.3
$C_\beta C_\gamma$ ring stretch	1.00	1236.0 – 1316.5
$C_\gamma C_\nu$ ring stretch	1.00	1331.0 – 1407.2
$C_\alpha C_\beta$ ring stretch	1.00	1558.3

TABLE 13 (Cont.)

Assignment	# of Vibrators	Frequency (K)
N. From Small Molecules[67,70-71]		
NH_3^+ stretch	1.00	4719.4
NH_3^+ stretch	1.00	4532.4 - 4820.1
NH_3^+ stretch	1.00	4359.7 - 4503.6
NH_3^+ bend	1.00	2287.8 - 2316.5
NH_3^+ bend	1.00	2136.7 - 2230.2
NH_3^+ rock	2(1.00)	1151.1
NH_3^+ bend	1.00	1870.5
C-N stretch	1.00	1502.0
O. From Imidazole[72]		
CH stretch	2(1.00)	4460.4 - 4522.3
CH in plane bend	1.00	1812.9
CH in plane bend	1.00	1513.7 - 1581.3
CH out of plane bend	1.00	1329.5
CH out of plane bend	1.00	1059.4 - 1201.4
NH stretch	1.00	4028.8
NH in plane bend	1.00	1788.5
NH out of plane bend	1.00	1343.9
Ring stretch	1.00	2217.3 - 2263.3
Ring stretch	2(1.00)	2086.3 - 2143.9
Ring stretch	1.00	1812.9 - 1903.6
Ring stretch	1.00	1640.3 - 1647.5
Ring bend (in plane)	1.00	1343.9
Ring bend (in plane)	1.00	1286.3
Ring bend (out plane)	1.00	945.3
Ring bend (out plane)	1.00	890.6

TABLE 13 (Cont.)

Assignment	# of Vibrators	Frequency (K)
P. From PCP[63]		
$C-CH_2$	1.00	1378.0 – 1638.0
Q. From Small Molecules[67,70-71]		
NH_2^+ sym. stretch	1.00	3237.4 – 3884.9
NH_2^+ asym. stretch	1.00	3237.4 – 3884.9
NH_2^+ bend	2(1.00)	2244.6 – 2330.9
NH_2^+ rock	2(1.00)	1151.0
R. From Small Molecules[67,70-71]		
NH stretch	1.00	4748.2 – 5036.0
NH bend	2(1.00)	2230.2 – 2374.1
C–N stretch	2(1.00)	1502.0
S. From Small Molecules[67,70-71]		
C=N stretch	1.00	2302.2

Sources:
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TABLE 14

Calculated Heat Capacities of Poly(L-Valine)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.000	0.000	0.000	0.000	0.000	0.000
0.60	0.001	0.000	0.000	0.000	0.001	0.001
0.70	0.001	0.000	0.000	0.000	0.001	0.001
0.80	0.002	0.000	0.000	0.000	0.002	0.002
0.90	0.002	0.000	0.000	0.000	0.002	0.002
1.00	0.003	0.000	0.000	0.000	0.003	0.003
1.20	0.006	0.000	0.000	0.000	0.006	0.006
1.40	0.009	0.000	0.000	0.000	0.009	0.009
1.60	0.013	0.000	0.000	0.000	0.013	0.013
1.80	0.019	0.000	0.000	0.000	0.019	0.019
2.00	0.026	0.000	0.000	0.000	0.026	0.026
3.00	0.089	0.000	0.000	0.000	0.089	0.089
4.00	0.210	0.000	0.000	0.000	0.210	0.210
5.00	0.410	0.000	0.000	0.000	0.410	0.410
6.00	0.701	0.000	0.000	0.000	0.701	0.702
7.00	1.089	0.000	0.000	0.000	1.089	1.090
8.00	1.569	0.000	0.000	0.000	1.569	1.571
9.00	2.129	0.000	0.000	0.000	2.129	2.132
10.00	2.747	0.000	0.000	0.000	2.747	2.752
15.00	6.249	0.000	0.000	0.000	6.249	6.265
20.00	9.784	0.000	0.000	0.000	9.784	9.818
25.00	13.144	0.000	0.000	0.000	13.144	13.200
30.00	16.348	0.000	0.000	0.000	16.348	16.432
40.00	22.490	0.000	0.000	0.000	22.491	22.645
50.00	28.453	0.000	0.004	0.004	28.457	28.703
60.00	34.317	0.000	0.008	0.008	34.325	34.682
70.00	40.088	0.002	0.059	0.061	40.149	40.638
80.00	45.697	0.009	0.161	0.170	45.868	46.508
90.00	51.087	0.026	0.333	0.359	51.446	52.257
100.00	56.218	0.058	0.606	0.664	56.883	57.882
110.00	61.063	0.110	0.937	1.047	62.110	63.315
120.00	65.524	0.187	1.400	1.587	67.111	68.537
130.00	69.635	0.289	1.944	2.233	71.867	73.527
140.00	73.385	0.419	2.655	3.074	76.459	78.368
150.00	76.804	0.579	3.423	4.002	80.806	82.976
160.00	79.925	0.769	4.377	5.146	85.072	87.517
170.00	82.755	0.992	5.378	6.370	89.125	91.857
180.00	85.290	1.249	6.537	7.786	93.075	96.108

TABLE 14 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	87.600	1.544	7.773	9.316	96.916	100.262
200.00	89.699	1.879	9.108	10.987	100.686	104.358
210.00	91.603	2.256	10.519	12.775	104.378	108.391
220.00	93.331	2.678	12.165	14.842	108.173	112.547
230.00	94.899	3.146	13.739	16.886	111.785	116.528
240.00	96.324	3.663	15.465	19.128	115.451	120.583
250.00	97.621	4.227	17.282	21.509	119.130	124.667
260.00	98.803	4.840	19.150	23.990	122.793	128.752
270.00	99.883	5.500	21.009	26.510	126.393	132.787
273.15	100.204	5.718	21.616	27.333	127.537	134.073
280.00	100.872	6.206	22.902	29.108	129.980	136.827
290.00	101.778	6.956	24.844	31.801	133.579	140.895
298.15	102.461	7.599	26.518	34.117	136.578	144.294
300.00	102.610	7.749	26.818	34.566	137.176	144.980
310.00	103.376	8.580	28.918	37.497	140.873	149.188
320.00	104.082	9.447	30.929	40.377	144.459	153.296
330.00	104.735	10.348	33.158	43.507	148.242	157.632
340.00	105.338	11.280	34.969	46.248	151.587	161.521
350.00	105.898	12.238	36.970	49.208	155.106	165.614
360.00	106.418	13.221	38.937	52.158	158.576	169.671
370.00	106.901	14.225	40.993	55.217	162.118	173.825
380.00	107.351	15.247	42.845	58.092	165.443	177.765
390.00	107.770	16.286	44.763	61.048	168.819	181.778
400.00	108.162	17.337	46.776	64.113	172.276	185.898
410.00	108.529	18.400	48.646	67.046	175.575	189.866
420.00	108.872	19.471	50.510	69.981	178.854	193.832
430.00	109.195	20.549	52.288	72.838	182.032	197.708
440.00	109.497	21.633	54.046	75.679	185.176	201.565
450.00	109.782	22.720	55.809	78.529	188.311	205.432
460.00	110.049	23.809	57.552	81.361	191.411	209.280
470.00	110.302	24.899	59.256	84.155	194.456	213.088
480.00	110.540	25.989	60.889	86.878	197.417	216.823
490.00	110.764	27.077	62.522	89.599	200.363	220.560
500.00	110.977	28.163	64.190	92.353	203.329	224.340
510.00	111.178	29.246	65.704	94.950	206.127	227.954
520.00	111.368	30.325	67.189	97.514	208.882	231.540
530.00	111.549	31.400	68.644	100.044	211.593	235.096
540.00	111.720	32.470	70.068	102.538	214.258	238.621
550.00	111.883	33.535	71.469	105.004	216.886	242.125
560.00	112.037	34.594	72.919	107.513	219.551	245.689
570.00	112.184	35.647	74.245	109.891	222.076	249.118
580.00	112.324	36.693	75.541	112.234	224.558	252.519
590.00	112.458	37.733	76.806	114.539	226.996	255.890
600.00	112.585	38.765	78.091	116.856	229.441	259.288

TABLE 14 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	112.706	39.791	79.339	119.130	231.837	262.652
620.00	112.822	40.809	80.536	121.345	234.167	265.962
630.00	112.933	41.819	81.689	123.508	236.441	269.229
640.00	113.039	42.822	82.816	125.638	238.677	272.474
650.00	113.140	43.817	83.918	127.735	240.875	275.696
660.00	113.237	44.804	84.995	129.799	243.036	278.896
670.00	113.316	45.783	86.047	131.830	245.146	282.060
680.00	113.405	46.754	87.075	133.828	247.233	285.218
690.00	113.489	47.716	88.078	135.795	249.284	288.357
700.00	113.571	48.671	89.297	137.968	251.538	291.753
710.00	113.649	49.616	90.036	139.653	253.301	294.601
720.00	113.723	50.554	90.981	141.535	255.258	297.697
730.00	113.795	51.483	91.905	143.387	257.182	300.776
740.00	113.864	52.403	92.817	145.220	259.083	303.852
750.00	113.930	53.315	93.698	147.013	260.943	306.902
760.00	113.993	54.218	94.546	148.764	262.758	309.923
770.00	114.055	55.112	95.447	150.559	264.613	313.016
780.00	114.113	55.998	96.277	152.275	266.388	316.038
790.00	114.170	56.875	97.091	153.966	268.136	319.052
800.00	114.224	57.743	97.830	155.573	269.797	321.987
810.00	114.277	58.602	98.606	157.208	271.485	324.980
820.00	114.327	59.453	99.365	158.818	273.146	327.965
830.00	114.376	60.295	100.107	160.402	274.778	330.943
840.00	114.423	61.128	100.843	161.971	276.394	333.926
850.00	114.469	61.952	101.553	163.505	277.974	336.893
860.00	114.513	62.767	102.247	165.014	279.527	339.856
870.00	114.555	63.574	102.926	166.500	281.055	342.815
880.00	114.596	64.372	103.590	167.962	282.558	345.772
890.00	114.636	65.161	104.229	169.390	284.026	348.715
900.00	114.674	65.941	104.865	170.806	285.480	351.671
910.00	114.711	66.713	105.486	172.199	286.910	354.627
920.00	114.747	67.476	106.094	173.570	288.317	357.586
930.00	114.782	68.230	106.697	174.927	289.708	360.556
940.00	114.815	68.975	107.279	176.255	291.070	363.522
950.00	114.848	69.712	107.849	177.561	292.410	366.493
960.00	114.880	70.441	108.407	178.848	293.728	369.471
970.00	114.910	71.160	108.953	180.114	295.024	372.457
980.00	114.940	71.872	109.494	181.366	296.306	375.459
990.00	114.969	72.575	110.018	182.592	297.561	378.465
1000.00	114.997	73.269	110.517	183.786	298.783	381.465

reported by Daurel et al.[16] in limited temperature ranges (2.0 to 6.0 K and 40 to 60 K). The results are shown in Figure 37. The RMS deviation between the calculated and the new experimental heat capacities is 1.18%. The average deviation is +0.061%.

For poly(L-valine), we now recommend our experimental heat capacities in the temperature range 230 to 390 K and the heat capacities reported by Daurel et al.[16] in the temperature ranges 2 to 10 K and 40 to 60 K as more reliable experimental heat capacities for a random sample poly(L-valine). Recommended theta temperatures are 663.7 ± 44.2 K for Θ_1 and 64.5 ± 2.2 K for Θ_3.

IID. Poly(L-leucine)

For poly(L-leucine) and the remaining poly(amino acids) studied, no prior heat capacity measurements can be found in the literature. As a result, we are not only reporting experimental heat capacity data for the first time, but also making the first attempt to link this macroscopic property to its microscopic origin, the vibrational spectrum. Like poly(L-valine), neither normal mode calculations nor infrared or Raman spectra are available for poly(L-leucine). The same is true for the remaining poly(amino acids). Therefore the vibrational spectra for poly(L-leucine) and the remaining poly(amino acids) will be constructed from available group vibration information on polyglycine and poly(L-alanine) to make up the backbone repeat unit and on information from other chemically similar groups from other macromolecules as was done in the case of poly(L-valine).

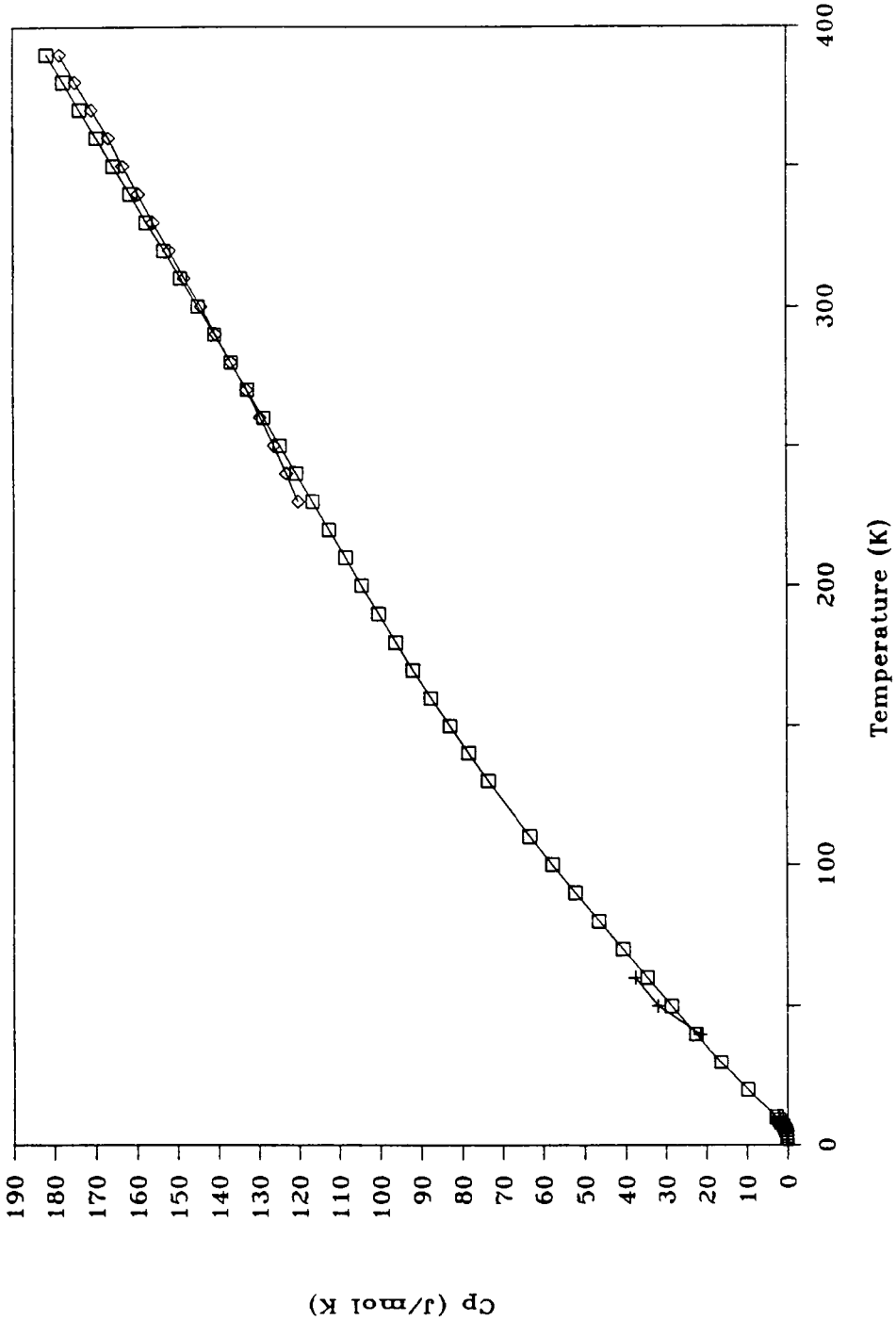


Figure 37 Heat Capacities of Poly(L-valine). Curve (□): New calculations. Curve (◇): New measurements. Curve (+): Previous measurements on ß-poly(L-valine).[16] [Source: M. Daurel, P. Delhaes, and E. Dupart *Biopolymers* **15**, 415 (1976).]

For the calculation of heat capacities, the group vibrational spectrum for poly(L-leucine) was constructed from the group vibration information from two sources. As in poly(L-valine), the backbone was taken from polyglycine and poly(L-alanine), part A of Table 13. The side group R was constructed in two parts by using the CH_2-CH-CH_3 group from polypropylene (Part C of Table 13) and the CH_3 group from polypropylene (Part C of Table 13). The number of skeletal vibrations was taken as sixteen: six from the backbone, three from each methyl group in the side chain for a total of six, two for the CH_2 group (from experience with polyethylene[62]), and two for the CH group. As the total number of vibrational modes for solid poly(L-leucine) is 57 (3N = 3*19 = 57), this left 41 group vibrations. Again T_m^o was taken as 573 for the reasons stated earlier for poly(L-valine), and the universal value for A_o was used.

Fitting the experimental heat capacities in the temperature range 220 to 390 K resulted in a Θ_1 = 624.5 ± 14.3 K. No Θ_3-temperature could be determined as the experimental heat capacities did not go to low enough temperatures. Θ_3 represents the intermolecular skeletal vibrations which dominate the heat capacity only up to 100 K. As a result, a value of 68.0 K was chosen for Θ_3. This represents the average of the Θ_3 values determined from the low temperature results of polyglycine, poly(L-alanine), and poly(L-valine). Heat capacities calculated for poly(L-leucine) using these Θ-temperatures are reported in Table 15 from 0 to 1000 K. Again good agreement between calculated and experimental heat capacities (reported in Table 3) was observed for the entire temperature range (230 to 390 K).

TABLE 15

Calculated Heat Capacities of Poly(L-Leucine)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.000	0.000	0.000	0.000	0.000	0.000
0.60	0.001	0.000	0.000	0.000	0.001	0.001
0.70	0.001	0.000	0.000	0.000	0.001	0.001
0.80	0.002	0.000	0.000	0.000	0.002	0.002
0.90	0.003	0.000	0.000	0.000	0.003	0.003
1.00	0.004	0.000	0.000	0.000	0.004	0.004
1.20	0.006	0.000	0.000	0.000	0.006	0.006
1.40	0.010	0.000	0.000	0.000	0.010	0.010
1.60	0.015	0.000	0.000	0.000	0.015	0.015
1.80	0.021	0.000	0.000	0.000	0.021	0.021
2.00	0.029	0.000	0.000	0.000	0.029	0.029
3.00	0.097	0.000	0.000	0.000	0.097	0.097
4.00	0.230	0.000	0.000	0.000	0.230	0.230
5.00	0.448	0.000	0.000	0.000	0.448	0.448
6.00	0.770	0.000	0.000	0.000	0.770	0.771
7.00	1.201	0.000	0.000	0.000	1.201	1.202
8.00	1.742	0.000	0.000	0.000	1.742	1.745
9.00	2.383	0.000	0.000	0.000	2.383	2.386
10.00	3.102	0.000	0.000	0.000	3.102	3.108
15.00	7.289	0.000	0.000	0.000	7.289	7.308
20.00	11.613	0.000	0.000	0.000	11.613	11.653
25.00	15.745	0.000	0.000	0.000	15.745	15.813
30.00	19.683	0.000	0.000	0.000	19.683	19.784
40.00	27.204	0.000	0.000	0.000	27.204	27.391
50.00	34.471	0.000	0.004	0.004	34.476	34.773
60.00	41.610	0.000	0.008	0.008	41.618	42.050
70.00	48.575	0.003	0.060	0.062	48.638	49.230
80.00	55.289	0.010	0.160	0.170	55.459	56.234
90.00	61.686	0.028	0.324	0.353	62.039	63.017
100.00	67.723	0.065	0.621	0.686	68.409	69.612
110.00	73.308	0.129	0.923	1.052	74.360	75.803
120.00	78.434	0.227	1.367	1.594	80.027	81.728
130.00	83.084	0.367	1.891	2.258	85.343	87.314
140.00	87.300	0.556	2.546	3.103	90.403	92.660
150.00	91.125	0.800	3.251	4.051	95.176	97.732
160.00	94.573	1.104	4.145	5.250	99.823	102.693
170.00	97.644	1.474	5.090	6.563	104.207	107.402
180.00	100.426	1.912	6.197	8.110	108.535	112.072

TABLE 15 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	102.937	2.424	7.387	9.811	112.748	116.641
200.00	105.201	3.011	8.643	11.654	116.856	121.118
210.00	107.243	3.675	10.011	13.686	120.929	125.578
220.00	109.085	4.417	11.570	15.987	125.072	130.129
230.00	110.751	5.237	13.207	18.443	129.194	134.676
240.00	112.259	6.132	14.771	20.904	133.163	139.081
250.00	113.627	7.102	16.612	23.714	137.342	143.725
260.00	114.871	8.143	18.464	26.607	141.479	148.344
270.00	116.005	9.252	20.304	29.556	145.561	152.925
273.15	116.341	9.615	20.920	30.534	146.875	154.402
280.00	117.040	10.424	22.371	32.795	149.834	157.727
290.00	117.987	11.655	24.326	35.981	153.968	162.401
298.15	118.700	12.698	26.059	38.758	157.458	166.354
300.00	118.855	12.940	26.352	39.292	158.147	167.144
310.00	119.653	14.274	28.586	42.860	162.514	172.106
320.00	120.388	15.652	30.665	46.316	166.705	176.903
330.00	121.066	17.068	32.890	49.958	171.024	181.858
340.00	121.693	18.519	34.926	53.444	175.137	186.615
350.00	122.273	19.998	37.158	57.156	179.429	191.584
360.00	122.811	21.503	39.215	60.718	183.529	196.370
370.00	123.311	23.028	41.393	64.421	187.732	201.288
380.00	123.776	24.569	43.405	67.973	191.749	206.030
390.00	124.209	26.123	45.456	71.579	195.788	210.818
400.00	124.614	27.687	47.659	75.345	199.959	215.770
410.00	124.992	29.257	49.699	78.956	203.948	220.549
420.00	125.346	30.831	51.690	82.520	207.867	225.275
430.00	125.678	32.406	53.676	86.082	211.760	229.996
440.00	125.989	33.980	55.615	89.595	215.585	234.665
450.00	126.282	35.552	57.544	93.096	219.378	239.324
460.00	126.557	37.120	59.437	96.556	223.114	243.943
470.00	126.817	38.681	61.337	100.018	226.835	248.569
480.00	127.061	40.236	63.124	103.360	230.421	253.071
490.00	127.292	41.782	64.914	106.697	233.989	257.576
500.00	127.510	43.320	66.745	110.065	237.575	262.124
510.00	127.716	44.847	68.420	113.267	240.984	266.501
520.00	127.912	46.365	70.066	116.430	244.342	270.846
530.00	128.097	47.871	71.682	119.552	247.649	275.157
540.00	128.272	49.365	73.265	122.630	250.903	279.433
550.00	128.439	50.848	74.824	125.672	254.111	283.682
560.00	128.597	52.318	76.431	128.749	257.346	287.985
570.00	128.748	53.776	77.910	131.686	260.434	292.147
580.00	128.891	55.221	79.358	134.579	263.470	296.276
590.00	129.028	56.653	80.772	137.425	266.453	300.368
600.00	129.158	58.073	82.202	140.275	269.433	304.483

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	129.282	59.479	83.594	143.073	272.355	308.556
620.00	129.401	60.872	84.931	145.803	275.203	312.571
630.00	129.498	62.252	86.220	148.473	277.971	316.518
640.00	129.606	63.619	87.482	151.101	280.707	320.455
650.00	129.709	64.973	88.714	153.687	283.396	324.364
660.00	129.807	66.313	89.919	156.232	286.039	328.245
670.00	129.901	67.640	91.096	158.736	288.637	332.100
680.00	129.991	68.954	92.245	161.199	291.190	335.929
690.00	130.077	70.255	93.367	163.623	293.699	339.734
700.00	130.159	71.543	94.703	166.246	296.405	343.793
710.00	130.238	72.817	95.554	168.371	298.609	347.296
720.00	130.314	74.079	96.609	170.687	301.001	351.045
730.00	130.387	75.327	97.639	172.966	303.353	354.773
740.00	130.456	76.562	98.655	175.217	305.674	358.493
750.00	130.523	77.784	99.639	177.423	307.946	362.184
760.00	130.588	78.993	100.586	179.579	310.167	365.843
770.00	130.650	80.190	101.583	181.772	312.422	369.570
780.00	130.709	81.373	102.507	183.880	314.589	373.223
790.00	130.767	82.543	103.413	185.956	316.723	376.865
800.00	130.822	83.701	104.241	187.942	318.764	380.426
810.00	130.875	84.846	105.104	189.950	320.825	384.042
820.00	130.927	85.978	105.948	191.926	322.852	387.647
830.00	130.976	87.097	106.772	193.870	324.846	391.244
840.00	131.024	88.204	107.589	195.793	326.817	394.844
850.00	131.070	89.298	108.377	197.675	328.745	398.426
860.00	131.114	90.380	109.147	199.527	330.642	402.002
870.00	131.157	91.449	109.901	201.350	332.508	405.574
880.00	131.199	92.506	110.638	203.144	334.343	409.142
890.00	131.239	93.551	111.348	204.898	336.137	412.695
900.00	131.278	94.583	112.052	206.635	337.913	416.261
910.00	131.316	95.603	112.741	208.344	339.659	419.826
920.00	131.352	96.611	113.415	210.026	341.378	423.394
930.00	131.387	97.607	114.081	211.688	343.075	426.974
940.00	131.421	98.590	114.726	213.317	344.738	430.549
950.00	131.455	99.562	115.357	214.919	346.374	434.130
960.00	131.487	100.522	115.975	216.497	347.984	437.718
970.00	131.518	101.471	116.579	218.050	349.567	441.316
980.00	131.548	102.407	117.174	219.582	351.130	444.929
990.00	131.577	103.333	117.753	221.086	352.663	448.549
1000.00	131.605	104.246	118.308	222.555	354.160	452.167

The results are shown in Figure 38. Comparison of the calculated results to the experimental results reveals a RMS deviation of ± 1.07% and an average deviation of 0.09%.

IIE. Poly(L-serine)

Construction of the group vibrational spectrum of poly(L-serine) consisted of putting together the backbone information gained from polyglycine and poly(L-alanine) (given in Part A of Table 13), the information on a CH_2 group gained from experience on polyethylene (Part D of Table 13), and the information on an OH group which was taken from poly(vinyl alcohol)[63] (PVA), given in part E of Table 13. For the skeletal vibrations, again six were taken for the backbone, and two were taken for the CH_2 group. None were taken for the OH group based on the experience with PVA.[63] Thus for poly(L-serine), with a total of 33 vibrational modes (3N = 3*11), eight were assigned as skeletal and 25 as group vibations.

Again for the calculations, an equilbrium melting temperature of 573 K and the universal value for A_o were used. When an attempt was made to calculate a Θ_1-temperature, success was met only in the temperature range 220 to 280 K. Above 280 K, the skeletal Cv was higher than the Dulong-Petit limit, a clearly impossible result, and no values for Θ_1 could be determined.

A second attempt to calculate a Θ_1-temperature was made, this time taking ten as the number of skeletal vibrations, rather than eight. Two of the six group vibrations for the OH group taken from PVA are quite low in frequency. Being so

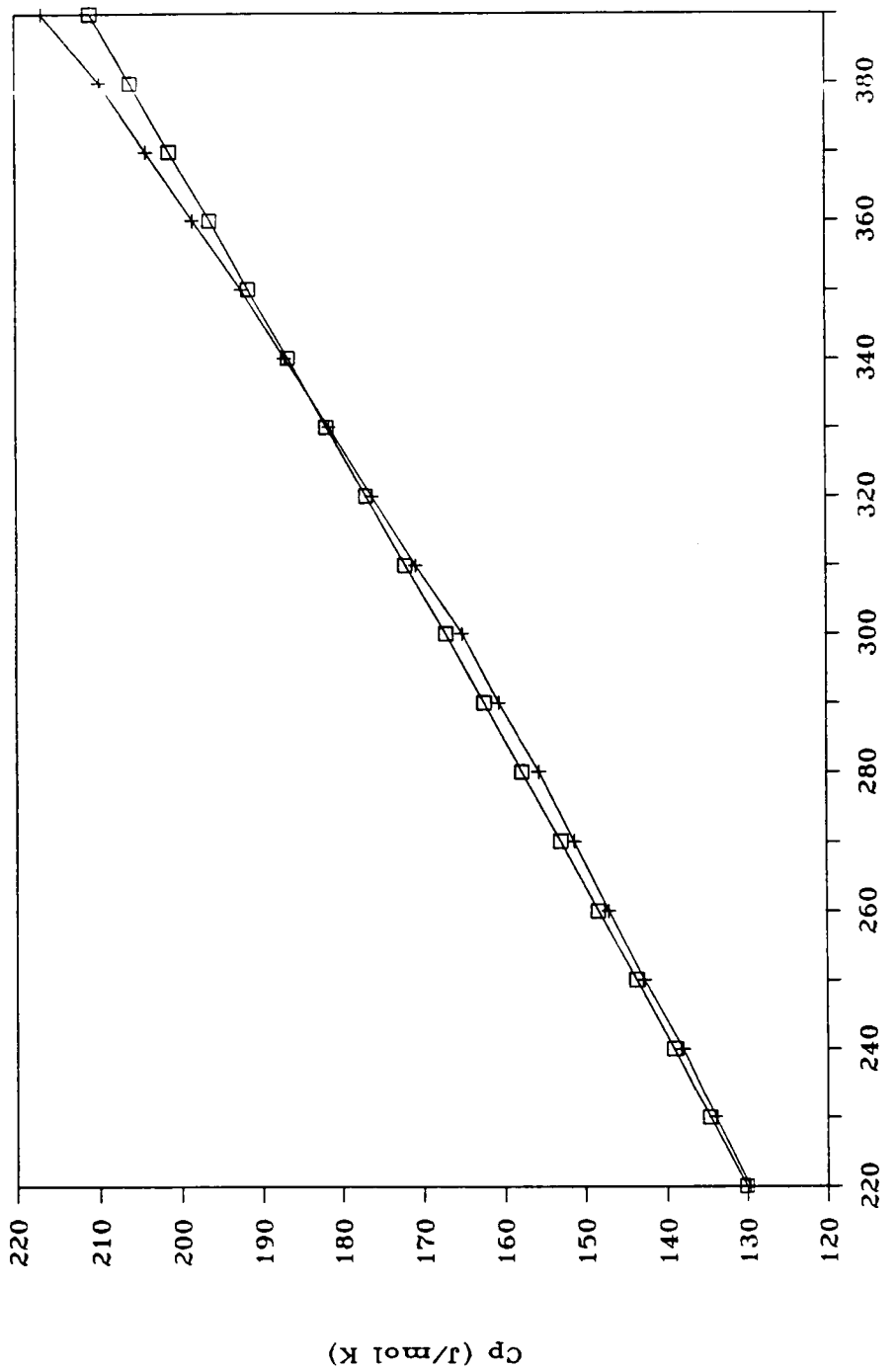


Figure 38 Heat Capacities of Poly(L-leucine). Curve (□): Calculations. Curve (+): Measurements.

low in frequency, it becomes possible that they may be better taken as skeletal modes rather than group modes. These two modes are the C-OH bend at 691 K and the C-OH rock at 590 K. Thus for this new calculation, the number of skeletal vibrations was ten, the number of group vibrations 23. The same values for $T_m°$ and A_o were used. Slightly better results were observed. Values for Θ_1 could be determined from 220 to 310 K. Above 310 K, the skeletal C_v was higher than the Dulong-Petit limit, and no values for Θ_1 could be determined. Using a value of 685.3 K ± 5.4 K for Θ_1, determined from the temperature range 220 K to 230 K, heat capacities were calculated for poly(L-serine) from 0 to 1000 K and are listed in Table 16. Figure 39 shows the comparison of the calculated heat capacities to the experimental heat capacities (listed in Table 4). Agreement was observed only for the lower temperatures, 220 to 280 K. The RMS deviation between the calculated and experimental heat capacities is ± 1.06% in this temperature range. Since the experimental heat capacities were consistently higher than the calculated heat capacities above 280 K, and in fact seemed to exhibit a very broad positive curvature, an x-ray diffraction study was performed to determine the degree of crystallinity of the sample. The information resulting from such a study would, as a first step, allow one to determine if the poly(L-serine) might be undergoing a very broad glass transition beginning around room temperature. The results are given in Section III.

TABLE 16

Calculated Heat Capacities of Poly(L-Serine)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.000	0.000	0.000	0.000	0.000	0.000
0.60	0.000	0.000	0.000	0.000	0.000	0.000
0.70	0.001	0.000	0.000	0.000	0.001	0.001
0.80	0.001	0.000	0.000	0.000	0.001	0.001
0.90	0.001	0.000	0.000	0.000	0.001	0.001
1.00	0.002	0.000	0.000	0.000	0.002	0.002
1.20	0.004	0.000	0.000	0.000	0.004	0.004
1.40	0.006	0.000	0.000	0.000	0.006	0.006
1.60	0.008	0.000	0.000	0.000	0.008	0.008
1.80	0.012	0.000	0.000	0.000	0.012	0.012
2.00	0.016	0.000	0.000	0.000	0.016	0.016
3.00	0.055	0.000	0.000	0.000	0.055	0.055
4.00	0.131	0.000	0.000	0.000	0.131	0.131
5.00	0.255	0.000	0.000	0.000	0.255	0.255
6.00	0.438	0.000	0.000	0.000	0.438	0.439
7.00	0.684	0.000	0.000	0.000	0.684	0.685
8.00	0.992	0.000	0.000	0.000	0.992	0.994
9.00	1.357	0.000	0.000	0.000	1.357	1.359
10.00	1.767	0.000	0.000	0.000	1.767	1.770
15.00	4.152	0.000	0.000	0.000	4.152	4.162
20.00	6.614	0.000	0.000	0.000	6.614	6.637
25.00	8.968	0.000	0.000	0.000	8.968	9.006
30.00	11.210	0.000	0.000	0.000	11.210	11.268
40.00	15.494	0.000	0.000	0.000	15.495	15.601
50.00	19.644	0.000	0.004	0.004	19.648	19.818
60.00	23.710	0.001	0.008	0.008	23.718	23.965
70.00	27.723	0.005	0.060	0.065	27.788	28.127
80.00	31.636	0.021	0.161	0.182	31.818	32.263
90.00	35.410	0.060	0.326	0.386	35.797	36.361
100.00	39.017	0.136	0.591	0.727	39.745	40.443
110.00	42.437	0.263	0.912	1.175	43.611	44.458
120.00	45.618	0.448	1.346	1.794	47.413	48.420
130.00	48.565	0.698	1.841	2.539	51.104	52.285
140.00	51.264	1.015	2.454	3.469	54.732	56.099
150.00	53.731	1.398	3.056	4.454	58.185	59.747
160.00	55.989	1.845	3.810	5.655	61.643	63.415
170.00	58.057	2.352	4.554	6.906	64.962	66.954
180.00	59.912	2.916	5.406	8.322	68.234	70.457

TABLE 16 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	61.600	3.532	6.285	9.816	71.417	73.882
200.00	63.141	4.197	7.176	11.372	74.514	77.232
210.00	64.544	4.907	8.101	13.008	77.552	80.534
220.00	65.821	5.659	9.195	14.854	80.675	83.937
230.00	66.983	6.450	10.158	16.608	83.591	87.137
240.00	68.041	7.275	11.219	18.494	86.535	90.381
250.00	69.006	8.131	12.321	20.452	89.458	93.616
260.00	69.887	9.016	13.436	22.452	92.338	96.819
270.00	70.692	9.925	14.513	24.438	95.130	99.943
273.15	70.932	10.216	14.867	25.083	96.015	100.935
280.00	71.431	10.855	15.639	26.494	97.925	103.083
290.00	72.108	11.803	16.792	28.595	100.703	106.219
298.15	72.620	12.587	17.790	30.377	102.997	108.816
300.00	72.731	12.766	17.935	30.701	103.432	109.316
310.00	73.305	13.740	19.206	32.946	106.252	112.523
320.00	73.835	14.723	20.347	35.070	108.905	115.567
330.00	74.325	15.712	21.545	37.257	111.582	118.650
340.00	74.778	16.705	22.754	39.459	114.237	121.723
350.00	75.198	17.698	23.928	41.627	116.825	124.739
360.00	75.589	18.691	25.076	43.766	119.355	127.706
370.00	75.952	19.680	26.319	45.999	121.951	130.758
380.00	76.291	20.665	27.365	48.030	124.321	133.580
390.00	76.607	21.643	28.484	50.127	126.734	136.463
400.00	76.902	22.613	29.708	52.322	129.224	139.442
410.00	77.179	23.575	30.800	54.375	131.553	142.261
420.00	77.437	24.526	31.883	56.410	133.847	145.056
430.00	77.680	25.467	32.958	58.425	136.106	147.826
440.00	77.909	26.397	34.033	60.429	138.338	150.582
450.00	78.123	27.314	35.125	62.439	140.562	153.342
460.00	78.325	28.219	36.211	64.429	142.755	156.082
470.00	78.516	29.110	37.275	66.385	144.901	158.785
480.00	78.695	29.989	38.283	68.272	146.967	161.414
490.00	78.865	30.854	39.264	70.118	148.984	164.002
500.00	79.026	31.706	40.217	71.923	150.949	166.547
510.00	79.178	32.545	41.149	73.693	152.871	169.058
520.00	79.322	33.370	42.066	75.435	154.757	171.543
530.00	79.458	34.181	42.967	77.148	156.606	174.001
540.00	79.588	34.979	43.851	78.830	158.418	176.431
550.00	79.711	35.764	44.727	80.491	160.201	178.844
560.00	79.828	36.536	45.667	82.203	162.030	181.321
570.00	79.939	37.295	46.496	83.791	163.730	183.667
580.00	80.045	38.041	47.310	85.352	165.397	185.991
590.00	80.146	38.775	48.108	86.883	167.029	188.290
600.00	80.242	39.497	48.939	88.435	168.677	190.620

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	80.334	40.206	49.746	89.953	170.287	192.921
620.00	80.422	40.904	50.515	91.419	171.841	195.174
630.00	80.506	41.590	51.253	92.843	173.349	197.388
640.00	80.586	42.265	51.979	94.243	174.829	199.585
650.00	80.662	42.928	52.691	95.619	176.281	201.765
660.00	80.736	43.581	53.389	96.970	177.706	203.927
670.00	80.806	44.222	54.075	98.297	179.103	206.073
680.00	80.874	44.854	54.747	99.601	180.474	208.203
690.00	80.928	45.475	55.406	100.881	181.809	210.306
700.00	80.990	46.086	56.291	102.377	183.367	212.683
710.00	81.050	46.687	56.705	103.392	184.441	214.514
720.00	81.106	47.278	57.335	104.613	185.720	216.597
730.00	81.161	47.860	57.953	105.813	186.974	218.667
740.00	81.213	48.432	58.569	107.001	188.215	220.738
750.00	81.264	48.996	59.163	108.159	189.422	222.785
760.00	81.312	49.550	59.732	109.282	190.594	224.806
770.00	81.358	50.096	60.361	110.457	191.816	226.902
780.00	81.403	50.633	60.928	111.561	192.964	228.929
790.00	81.446	51.162	61.487	112.649	194.095	230.951
800.00	81.488	51.682	61.978	113.659	195.147	232.897
810.00	81.528	52.194	62.513	114.707	196.235	234.901
820.00	81.566	52.698	63.038	115.736	197.302	236.900
830.00	81.603	53.194	63.552	116.747	198.350	238.893
840.00	81.639	53.683	64.067	117.750	199.389	240.892
850.00	81.674	54.164	64.562	118.726	200.399	242.876
860.00	81.707	54.638	65.047	119.684	201.391	244.856
870.00	81.739	55.104	65.522	120.626	202.366	246.834
880.00	81.771	55.563	65.989	121.552	203.322	248.809
890.00	81.801	56.015	66.435	122.450	204.251	250.771
900.00	81.830	56.460	66.884	123.343	205.173	252.744
910.00	81.858	56.898	67.323	124.221	206.079	254.718
920.00	81.885	57.330	67.754	125.083	206.969	256.693
930.00	81.912	57.755	68.183	125.938	207.850	258.679
940.00	81.937	58.173	68.598	126.771	208.708	260.659
950.00	81.962	58.585	69.004	127.589	209.551	262.642
960.00	81.986	58.991	69.402	128.393	210.379	264.630
970.00	82.010	59.390	69.793	129.183	211.193	266.623
980.00	82.032	59.784	70.180	129.964	211.996	268.628
990.00	82.054	60.172	70.556	130.728	212.782	270.635
1000.00	82.075	60.553	70.913	131.467	213.542	272.636

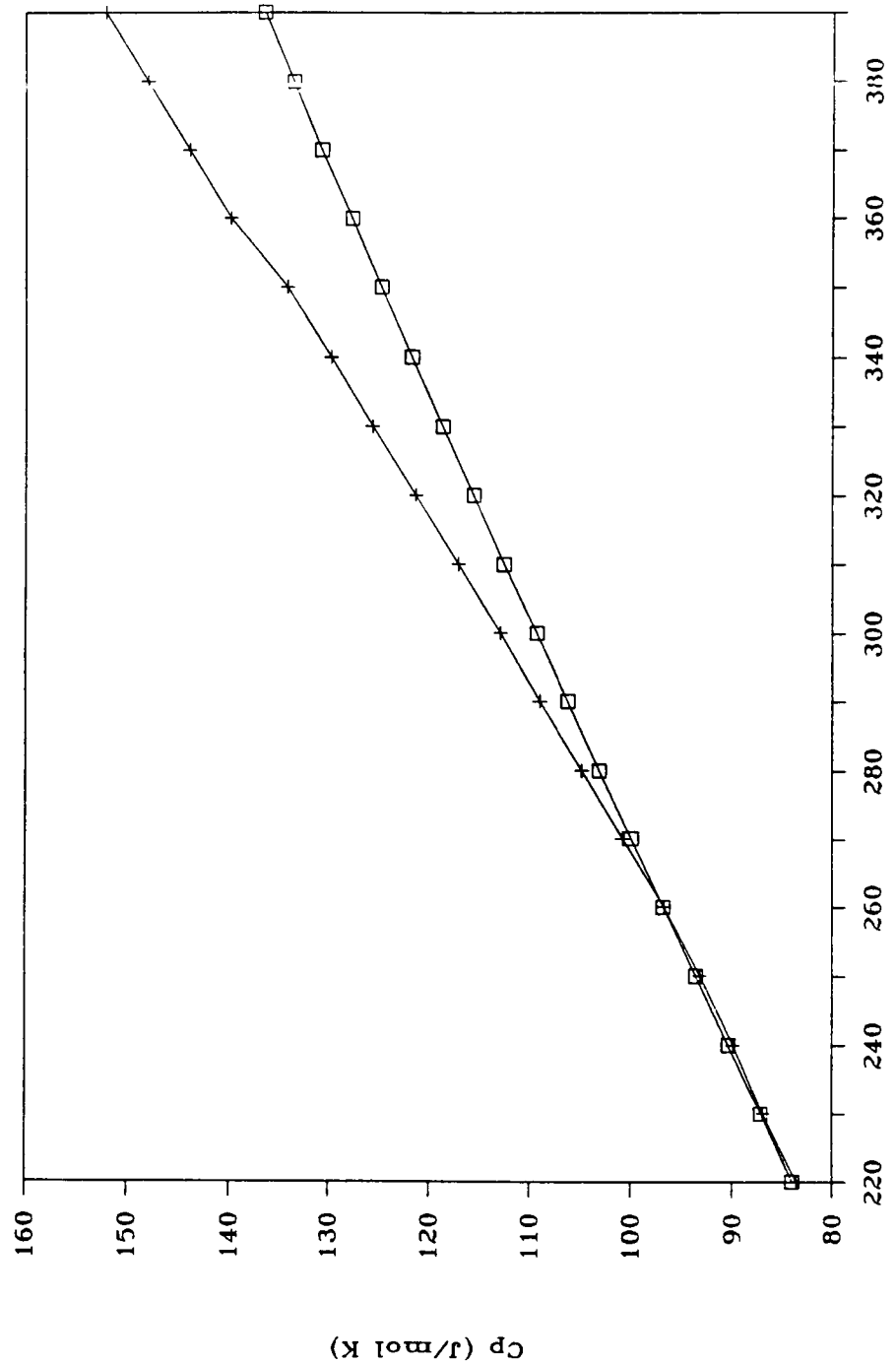


Figure 39 Heat Capacities of Poly(L-serine). Curve (□): Calculations. Curve (+): Measurements.

IIF. Poly(L-aspartic acid) sodium salt

Poly(L-aspartic acid) is not available in its free from due to its instability. As a result, studies were made on the sodium salt of poly(L-aspartic acid). The group vibrational spectrum constructed consisted of the backbone chain which was put together with vibrational data on polyglycine and poly(L-alanine) (See Part A of Table 13), the CH_2 group from polyethylene (Part D of Table 13), and the COO^- group from polyisobutyl acrylate[61] (PIBA), given in Part F of Table 13. A total of fourteen skeletal vibrations were taken, six for the backbone, two for the CH_2 group, three for the COO^- group (from experience with PIBA[61]), and three for the Na^+ atom. Thus the vibrational spectrum for poly(L-aspartic acid) consisted of fourteen skeletal vibrations and twenty-five group vibrations, for a total of thirty-nine vibrational modes (3N = 3*13).

For calculations, $T_m°$ was again taken as 573 K and A_o was taken as 3.9×10^{-3} K mol/J, the universal value. Note that these values for $T_m°$ and A_o will be used for all the following poly(amino acid) heat capacity calculations. Fitting of the experimental heat capacities in the temperature range 220 to 290 K led to a Θ_1-temperature of 597.02 ± 12.13 K. Again using a value of 68.0 K for Θ_3 in the calculations, heat capacities for poly(L-aspartic acid) sodium salt were calculated from 0 to 1000 K and are reported in Table 17. Good agreement between calculated and experimental heat capacities (given in Table 4) was observed for the entire temperature range (230 to 390 K). The results are shown in Figure 40. The RMS deviation is ± 0.852% and the average deviation is 0.33%.

TABLE 17

Calculated Heat Capacities of Poly(L-Aspartic Acid) Sodium Salt

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.000	0.000	0.000	0.000	0.000	0.000
0.60	0.001	0.000	0.000	0.000	0.001	0.001
0.70	0.001	0.000	0.000	0.000	0.001	0.001
0.80	0.002	0.000	0.000	0.000	0.002	0.002
0.90	0.002	0.000	0.000	0.000	0.002	0.002
1.00	0.003	0.000	0.000	0.000	0.003	0.003
1.20	0.005	0.000	0.000	0.000	0.005	0.005
1.40	0.008	0.000	0.000	0.000	0.008	0.008
1.60	0.012	0.000	0.000	0.000	0.012	0.012
1.80	0.018	0.000	0.000	0.000	0.018	0.018
2.00	0.024	0.000	0.000	0.000	0.024	0.024
3.00	0.082	0.000	0.000	0.000	0.082	0.082
4.00	0.194	0.000	0.000	0.000	0.194	0.194
5.00	0.377	0.000	0.000	0.000	0.377	0.378
6.00	0.649	0.000	0.000	0.000	0.649	0.650
7.00	1.013	0.000	0.000	0.000	1.013	1.014
8.00	1.469	0.000	0.000	0.000	1.469	1.471
9.00	2.009	0.000	0.000	0.000	2.009	2.013
10.00	2.616	0.000	0.000	0.000	2.616	2.621
15.00	6.148	0.000	0.000	0.000	6.148	6.164
20.00	9.794	0.000	0.000	0.000	9.794	9.828
25.00	13.280	0.000	0.000	0.000	13.280	13.336
30.00	16.600	0.000	0.000	0.000	16.600	16.686
40.00	22.944	0.000	0.000	0.000	22.944	23.102
50.00	29.077	0.000	0.004	0.004	29.082	29.333
60.00	35.102	0.002	0.008	0.010	35.112	35.477
70.00	41.009	0.012	0.060	0.071	41.080	41.580
80.00	46.729	0.043	0.161	0.204	46.933	47.588
90.00	52.206	0.117	0.326	0.444	52.650	53.480
100.00	57.402	0.260	0.589	0.849	58.251	59.275
110.00	62.255	0.493	0.918	1.411	63.666	64.902
120.00	66.748	0.835	1.352	2.187	68.935	70.400
130.00	70.846	1.298	1.847	3.144	73.991	75.700
140.00	74.575	1.884	2.467	4.351	78.926	80.897
150.00	77.968	2.593	3.084	5.677	83.645	85.890
160.00	81.059	3.418	3.860	7.278	88.337	90.876
170.00	83.825	4.350	4.632	8.983	92.807	95.652
180.00	86.323	5.380	5.520	10.900	97.223	100.390

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	88.591	6.496	6.439	12.935	101.526	105.031
200.00	90.644	7.687	7.377	15.064	105.709	109.565
210.00	92.503	8.942	8.355	17.298	109.801	114.022
220.00	94.185	10.252	9.508	19.760	113.945	118.552
230.00	95.710	11.607	10.546	22.153	117.863	122.864
240.00	97.093	12.998	11.682	24.680	121.773	127.186
250.00	98.350	14.419	12.870	27.288	125.639	131.478
260.00	99.495	15.861	14.071	29.932	129.428	135.708
270.00	100.540	17.319	15.247	32.567	133.107	139.841
273.15	100.850	17.781	15.629	33.410	134.260	141.140
280.00	101.495	18.788	16.470	35.258	136.754	143.957
290.00	102.370	20.262	17.726	37.988	140.358	148.046
298.15	103.030	21.464	18.808	40.272	143.302	151.398
300.00	103.174	21.737	18.972	40.709	143.883	152.068
310.00	103.912	23.209	20.345	43.554	147.467	156.171
320.00	104.593	24.675	21.587	46.262	150.855	160.084
330.00	105.222	26.131	22.885	49.016	154.238	164.008
340.00	105.803	27.576	24.192	51.768	157.571	167.897
350.00	106.342	29.006	25.468	54.474	160.815	171.709
360.00	106.841	30.420	26.723	57.143	163.985	175.458
370.00	107.306	31.816	28.072	59.888	167.194	179.268
380.00	107.739	33.193	29.224	62.417	170.155	182.828
390.00	108.142	34.549	30.441	64.990	173.132	186.422
400.00	108.519	35.884	31.759	67.644	176.162	190.092
410.00	108.871	37.197	32.946	70.143	179.014	193.585
420.00	109.201	38.487	34.118	72.604	181.805	197.030
430.00	109.510	39.753	35.280	75.034	184.544	200.435
440.00	109.800	40.996	36.442	77.438	187.239	203.810
450.00	110.073	42.216	37.620	79.835	189.908	207.175
460.00	110.330	43.411	38.789	82.200	192.530	210.504
470.00	110.572	44.583	39.935	84.518	195.090	213.783
480.00	110.800	45.731	41.023	86.754	197.554	216.973
490.00	111.016	46.855	42.083	88.938	199.954	220.110
500.00	111.219	47.957	43.111	91.068	202.288	223.191
510.00	111.412	49.035	44.117	93.152	204.564	226.225
520.00	111.595	50.090	45.106	95.196	206.791	229.222
530.00	111.768	51.124	46.077	97.200	208.968	232.179
540.00	111.932	52.135	47.028	99.163	211.095	235.098
550.00	112.087	53.125	47.969	101.094	213.182	237.989
560.00	112.236	54.093	48.973	103.066	215.302	240.935
570.00	112.376	55.041	49.864	104.904	217.281	243.739
580.00	112.510	55.969	50.737	106.706	219.216	246.512
590.00	112.638	56.876	51.592	108.468	221.106	249.250
600.00	112.760	57.765	52.479	110.243	223.003	252.013

TABLE 17 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	112.876	58.634	53.341	111.974	224.851	254.737
620.00	112.987	59.485	54.162	113.646	226.633	257.406
630.00	113.093	60.318	54.951	115.268	228.361	260.029
640.00	113.194	61.133	55.725	116.857	230.052	262.627
650.00	113.277	61.931	56.484	118.415	231.692	265.185
660.00	113.370	62.712	57.229	119.940	233.310	267.736
670.00	113.458	63.477	57.958	121.435	234.893	270.263
680.00	113.543	64.226	58.673	122.899	236.442	272.769
690.00	113.624	64.959	59.374	124.333	237.956	275.254
700.00	113.701	65.677	60.299	125.975	239.677	277.995
710.00	113.775	66.380	60.752	127.132	240.908	280.187
720.00	113.847	67.069	61.420	128.489	242.336	282.626
730.00	113.915	67.744	62.075	129.819	243.734	285.048
740.00	113.981	68.405	62.726	131.131	245.112	287.466
750.00	114.044	69.053	63.355	132.407	246.451	289.858
760.00	114.104	69.687	63.957	133.644	247.749	292.220
770.00	114.163	70.309	64.619	134.928	249.090	294.654
780.00	114.219	70.919	65.217	136.136	250.355	297.016
790.00	114.273	71.516	65.806	137.323	251.595	299.370
800.00	114.325	72.102	66.326	138.428	252.753	301.646
810.00	114.375	72.676	66.890	139.566	253.941	303.978
820.00	114.423	73.238	67.443	140.681	255.104	306.303
830.00	114.470	73.790	67.985	141.775	256.244	308.620
840.00	114.514	74.331	68.526	142.857	257.371	310.944
850.00	114.558	74.862	69.046	143.907	258.465	313.250
860.00	114.600	75.382	69.556	144.938	259.537	315.551
870.00	114.640	75.892	70.056	145.948	260.588	317.850
880.00	114.679	76.393	70.545	146.938	261.617	320.146
890.00	114.717	76.884	71.015	147.898	262.615	322.428
900.00	114.754	77.365	71.485	148.850	263.604	324.723
910.00	114.789	77.838	71.946	149.784	264.573	327.018
920.00	114.823	78.302	72.398	150.699	265.523	329.315
930.00	114.856	78.757	72.848	151.605	266.461	331.624
940.00	114.888	79.203	73.282	152.485	267.374	333.927
950.00	114.920	79.642	73.707	153.349	268.269	336.236
960.00	114.950	80.072	74.125	154.196	269.146	338.551
970.00	114.979	80.494	74.534	155.028	270.007	340.873
980.00	115.007	80.908	74.939	155.847	270.855	343.209
990.00	115.035	81.315	75.332	156.647	271.682	345.550
1000.00	115.062	81.715	75.706	157.421	272.482	347.887

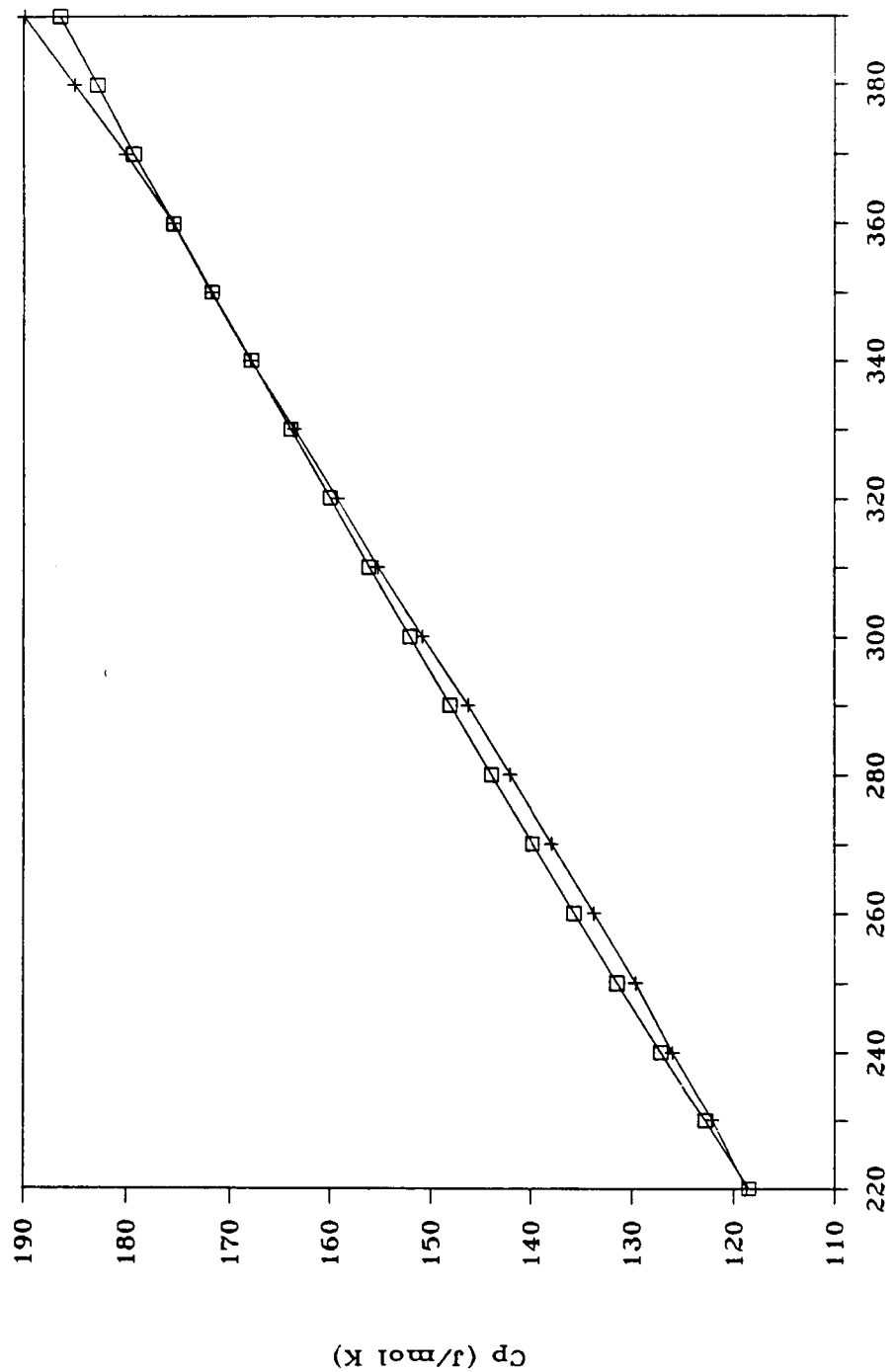


Figure 40 Heat Capacities of Poly(L-aspartic acid•Na). Curve (□): Calculations. Curve (+): Measurements.

IIG. Poly(L-glutamic acid) sodium salt

Like poly(L-aspartic acid), poly(L-glutamic acid) is available only as a sodium salt. The constructed group vibrational spectrum was the same as that for poly(L-aspartic acid) except that an additional CH_2 group was added. Parts A, D (taken twice), and F of Table 13 were put together to construct the group vibrational spectrum. The number of skeletal vibrations therefore increased by two due to the additional CH_2 group. Thus the vibrational spectrum consisted of sixteen skeletal modes and thirty-two group modes for a total of forty-eight modes (3N = 3*16).

Fitting of the experimental heat capacities (given in Table 4) from 280 to 350 K resulted in a Θ_1-temperature of 906.9 ± 23.3 K. Using the chosen value of 68.0 K for Θ_3 and this value for Θ_1, heat capacities were calculated from 0 to 1000 K and are listed in Table 18. Again good agreement between experiment and calculation was observed, as is shown in Figure 41. The RMS deviation is ± 1.127% for the entire temperature range of experiment. The average deviation is 0.420%

IIH. Poly(L-asparagine)

Poly(L-asparagine) is the third and final acidic poly(amino acid) studied. Construction of the group vibrational spectrum consisted of putting together four chemical groups. These four groups were the backbone or repeat unit constructed from polyglycine and poly(L-alanine) (see Part A of Table 13), the CH_2 group from polyethylene (see Part D of Table 13), the C=O group from poly(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene)[64] (PEEK)

TABLE 18

Calculated Heat Capacities of Poly(L-Glutamic Acid) Sodium Salt

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.000	0.000	0.000	0.000	0.000	0.000
0.60	0.001	0.000	0.000	0.000	0.001	0.001
0.70	0.001	0.000	0.000	0.000	0.001	0.001
0.80	0.001	0.000	0.000	0.000	0.001	0.001
0.90	0.002	0.000	0.000	0.000	0.002	0.002
1.00	0.002	0.000	0.000	0.000	0.002	0.002
1.20	0.004	0.000	0.000	0.000	0.004	0.004
1.40	0.007	0.000	0.000	0.000	0.007	0.007
1.60	0.010	0.000	0.000	0.000	0.010	0.010
1.80	0.014	0.000	0.000	0.000	0.014	0.014
2.00	0.020	0.000	0.000	0.000	0.020	0.020
3.00	0.067	0.000	0.000	0.000	0.067	0.067
4.00	0.158	0.000	0.000	0.000	0.158	0.158
5.00	0.308	0.000	0.000	0.000	0.308	0.308
6.00	0.530	0.000	0.000	0.000	0.530	0.531
7.00	0.827	0.000	0.000	0.000	0.827	0.828
8.00	1.200	0.000	0.000	0.000	1.200	1.201
9.00	1.641	0.000	0.000	0.000	1.641	1.643
10.00	2.136	0.000	0.000	0.000	2.136	2.140
15.00	5.019	0.000	0.000	0.000	5.019	5.032
20.00	7.997	0.000	0.000	0.000	7.997	8.024
25.00	10.842	0.000	0.000	0.000	10.842	10.888
30.00	13.553	0.000	0.000	0.000	13.553	13.623
40.00	18.733	0.000	0.000	0.000	18.733	18.862
50.00	23.747	0.000	0.004	0.004	23.751	23.956
60.00	28.683	0.002	0.008	0.010	28.693	28.991
70.00	33.568	0.012	0.060	0.072	33.640	34.049
80.00	38.424	0.044	0.162	0.205	38.629	39.169
90.00	43.246	0.120	0.328	0.448	43.694	44.383
100.00	47.993	0.267	0.593	0.860	48.854	49.712
110.00	52.635	0.509	0.928	1.438	54.073	55.122
120.00	57.146	0.867	1.371	2.238	59.383	60.645
130.00	61.505	1.352	1.887	3.238	64.744	66.239
140.00	65.699	1.969	2.537	4.507	70.205	71.958
150.00	69.716	2.719	3.186	5.905	75.621	77.652
160.00	73.482	3.596	4.005	7.601	81.083	83.414
170.00	77.049	4.590	4.836	9.426	86.475	89.126
180.00	80.387	5.694	5.800	11.493	91.881	94.874

TABLE 18 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	83.509	6.895	6.810	13.705	97.213	100.569
200.00	86.426	8.183	7.854	16.037	102.463	106.200
210.00	89.154	9.547	8.954	18.501	107.655	111.793
220.00	91.707	10.978	10.241	21.219	112.926	117.491
230.00	94.086	12.465	11.427	23.892	117.978	122.984
240.00	96.262	14.002	12.721	26.723	122.985	128.451
250.00	98.299	15.580	14.072	29.651	127.950	133.897
260.00	100.200	17.191	15.446	32.637	132.837	139.283
270.00	101.972	18.829	16.806	35.635	137.608	144.570
273.15	102.505	19.350	17.247	36.596	139.101	146.230
280.00	103.623	20.488	18.218	38.706	142.329	149.826
290.00	105.160	22.163	19.689	41.852	147.012	155.065
298.15	106.334	23.536	20.941	44.477	150.811	159.331
300.00	106.591	23.848	21.145	44.993	151.584	160.208
310.00	107.924	25.539	22.737	48.277	156.201	165.421
320.00	109.167	27.232	24.194	51.427	160.594	170.418
330.00	110.326	28.923	25.713	54.636	164.962	175.412
340.00	111.409	30.609	27.251	57.860	169.268	180.361
350.00	112.420	32.286	28.757	61.043	173.463	185.214
360.00	113.366	33.952	30.242	64.194	177.560	189.984
370.00	114.252	35.605	31.819	67.424	181.676	194.795
380.00	115.082	37.242	33.194	70.436	185.518	199.335
390.00	115.861	38.863	34.628	73.491	189.352	203.888
400.00	116.592	40.465	36.162	76.626	193.218	208.497
410.00	117.280	42.046	37.559	79.605	196.885	212.911
420.00	117.927	43.607	38.937	82.545	200.472	217.260
430.00	118.537	45.147	40.310	85.456	203.993	221.560
440.00	119.111	46.663	41.688	88.351	207.463	225.825
450.00	119.654	48.157	43.077	91.235	210.889	230.062
460.00	120.166	49.628	44.455	94.083	214.249	234.250
470.00	120.651	51.075	45.807	96.882	217.533	238.376
480.00	121.110	52.498	47.086	99.584	220.694	242.387
490.00	121.544	53.898	48.334	102.232	223.776	246.333
500.00	121.956	55.274	49.546	104.820	226.776	250.210
510.00	122.347	56.627	50.726	107.353	229.700	254.022
520.00	122.718	57.956	51.887	109.843	232.561	257.786
530.00	123.071	59.262	53.027	112.288	235.359	261.502
540.00	123.406	60.545	54.144	114.689	238.095	265.169
550.00	123.725	61.805	55.248	117.053	240.779	268.798
560.00	124.030	63.044	56.411	119.454	243.484	272.472
570.00	124.320	64.260	57.457	121.717	246.036	275.996
580.00	124.596	65.455	58.482	123.937	248.533	279.479
590.00	124.860	66.628	59.485	126.114	250.974	282.919
600.00	125.112	67.781	60.516	128.297	253.410	286.375

TABLE 18 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	125.353	68.914	61.519	130.432	255.786	289.784
620.00	125.584	70.026	62.477	132.503	258.087	293.130
630.00	125.805	71.119	63.399	134.518	260.322	296.422
640.00	126.016	72.192	64.303	136.495	262.511	299.683
650.00	126.218	73.247	65.188	138.435	264.653	302.912
660.00	126.412	74.283	66.055	140.339	266.751	306.111
670.00	126.598	75.302	66.904	142.206	268.804	309.281
680.00	126.777	76.302	67.736	144.037	270.814	312.423
690.00	126.948	77.285	68.549	145.834	272.782	315.538
700.00	127.113	78.251	69.583	147.834	274.947	318.904
710.00	127.272	79.200	70.143	149.344	276.615	321.716
720.00	127.424	80.134	70.915	151.048	278.472	324.770
730.00	127.570	81.051	71.670	152.721	280.291	327.803
740.00	127.712	81.952	72.419	154.371	282.083	330.826
750.00	127.847	82.838	73.143	155.981	283.828	333.819
760.00	127.978	83.709	73.838	157.547	285.525	336.777
770.00	128.104	84.565	74.589	159.155	287.259	339.804
780.00	128.226	85.407	75.275	160.682	288.908	342.755
790.00	128.343	86.235	75.950	162.184	290.528	345.695
800.00	128.457	87.048	76.552	163.601	292.057	348.553
810.00	128.566	87.848	77.197	165.045	293.611	351.465
820.00	128.672	88.635	77.828	166.463	295.134	354.366
830.00	128.774	89.408	78.446	167.854	296.628	357.258
840.00	128.872	90.169	79.061	169.229	298.102	360.152
850.00	128.968	90.917	79.653	170.570	299.537	363.027
860.00	129.060	91.653	80.233	171.885	300.945	365.896
870.00	129.149	92.376	80.801	173.177	302.326	368.760
880.00	129.235	93.087	81.357	174.445	303.680	371.620
890.00	129.319	93.787	81.891	175.679	304.998	374.464
900.00	129.400	94.475	82.425	176.900	306.300	377.319
910.00	129.463	95.152	82.947	178.100	307.563	380.154
920.00	129.539	95.818	83.459	179.277	308.816	383.010
930.00	129.612	96.473	83.967	180.441	310.053	385.876
940.00	129.683	97.118	84.458	181.576	311.259	388.737
950.00	129.752	97.751	84.939	182.691	312.443	391.603
960.00	129.819	98.375	85.411	183.786	313.605	394.474
970.00	129.884	98.988	85.872	184.861	314.745	397.353
980.00	129.947	99.592	86.329	185.921	315.868	400.247
990.00	130.008	100.186	86.772	186.958	316.966	403.146
1000.00	130.067	100.770	87.195	187.965	318.032	406.041

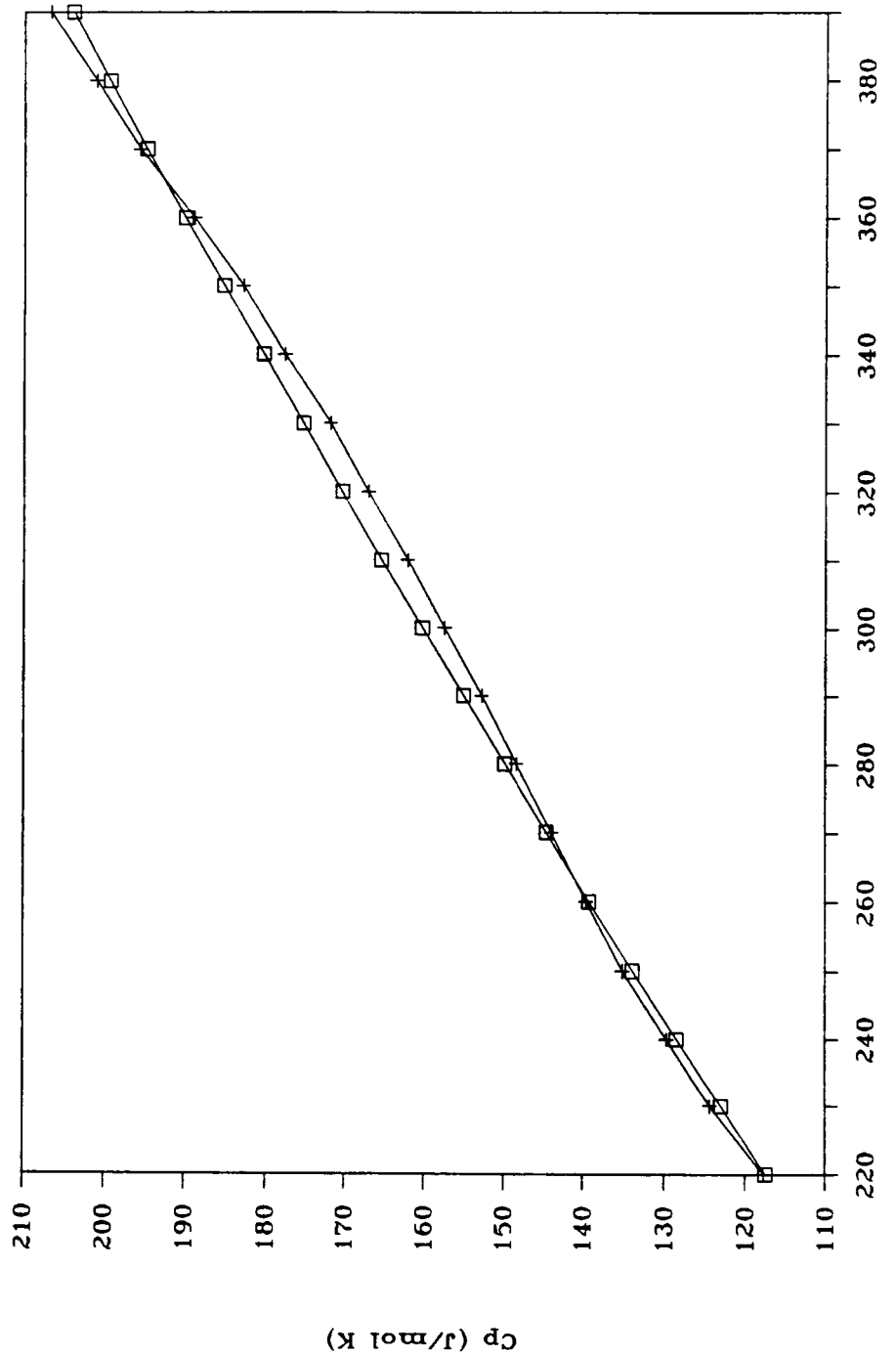


Figure 41 Heat Capacities of Poly(L-glutamic acid•Na). Curve (□): Calculations. Curve (+): Measurements.

(see Part G of Table 13), and the NH_2 group. Information on the group vibrations of the NH_2 group were taken from information on propionamide[65] and methylamine.[66] These vibrations are given in Part H of Table 13. A total of twelve skeletal vibrations were taken; six for the backbone, two for the CH_2 group, two for the C=O group (from experience with PEEK), and two for the NH_2 group. As a result, the vibrational spectrum of poly(L-asparagine) consisted of twelve skeletal modes and thiry group modes for a total of forty-two vibrational modes (3N = 3*14).

Fitting the experimental heat capacities (listed in Table 4) in the temperature range 230 to 390 K resulted in a Θ_1-temperature of 568.8 ± 18.2 K. Using this value and the chosen value for Θ_3, heat capacities were calculated form 0 to 1000 K and are given in Table 19. Excellent agreement between calculation and experiment was observed as is shown in Figure 42. The RMS deviation is ± 0.767%, and the average deviation is −0.01%.

III. Poly(L-phenylalalanine)

Poly(L-phenylalanine) is one of the two aromatic poly(amino acids). As there are a total of twenty atoms making up poly(L-phenylalanine), there are sixty vibrational modes to be accounted for (3N = 3*20). Forty-nine of these are the group vibrations which are easily constructed from the data available on the backbone (Part A of Table 13), the CH_2 group of polyethylene (Part D of Table 13), and the phenyl group of phenylene containing polymers such as the polybenzoates[64]

TABLE 19

Calculated Heat Capacities of Poly(L-Asparagine)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.000	0.000	0.000	0.000	0.000	0.000
0.60	0.001	0.000	0.000	0.000	0.001	0.001
0.70	0.001	0.000	0.000	0.000	0.001	0.001
0.80	0.002	0.000	0.000	0.000	0.002	0.002
0.90	0.003	0.000	0.000	0.000	0.003	0.003
1.00	0.003	0.000	0.000	0.000	0.003	0.003
1.20	0.006	0.000	0.000	0.000	0.006	0.006
1.40	0.010	0.000	0.000	0.000	0.010	0.010
1.60	0.014	0.000	0.000	0.000	0.014	0.014
1.80	0.020	0.000	0.000	0.000	0.020	0.020
2.00	0.028	0.000	0.000	0.000	0.028	0.028
3.00	0.094	0.000	0.000	0.000	0.094	0.094
4.00	0.222	0.000	0.000	0.000	0.222	0.222
5.00	0.432	0.000	0.000	0.000	0.432	0.433
6.00	0.738	0.000	0.000	0.000	0.738	0.738
7.00	1.142	0.000	0.000	0.000	1.142	1.143
8.00	1.640	0.000	0.000	0.000	1.640	1.642
9.00	2.215	0.000	0.000	0.000	2.215	2.218
10.00	2.845	0.000	0.000	0.000	2.845	2.850
15.00	6.369	0.000	0.000	0.000	6.369	6.386
20.00	9.891	0.000	0.000	0.000	9.891	9.925
25.00	13.229	0.000	0.000	0.000	13.229	13.286
30.00	16.416	0.000	0.000	0.000	16.416	16.500
40.00	22.535	0.000	0.000	0.000	22.535	22.691
50.00	28.472	0.002	0.004	0.006	28.477	28.723
60.00	34.288	0.011	0.008	0.019	34.307	34.664
70.00	39.899	0.044	0.060	0.104	40.003	40.490
80.00	45.241	0.122	0.161	0.283	45.524	46.160
90.00	50.265	0.267	0.326	0.593	50.858	51.660
100.00	54.894	0.496	0.588	1.084	55.977	56.961
110.00	59.104	0.822	0.918	1.740	60.843	62.024
120.00	62.887	1.252	1.354	2.606	65.493	66.884
130.00	66.284	1.788	1.848	3.637	69.920	71.536
140.00	69.338	2.430	2.471	4.902	74.239	76.093
150.00	72.036	3.174	3.093	6.267	78.303	80.405
160.00	74.440	4.013	3.877	7.891	82.330	84.697
170.00	76.592	4.943	4.661	9.604	86.195	88.838
180.00	78.512	5.955	5.562	11.517	90.029	92.963

TABLE 19 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	80.227	7.042	6.498	13.540	93.767	97.004
200.00	81.759	8.196	7.455	15.651	97.410	100.963
210.00	83.129	9.410	8.454	17.865	100.994	104.877
220.00	84.358	10.677	9.631	20.308	104.666	108.898
230.00	85.463	11.989	10.685	22.673	108.137	112.725
240.00	86.459	13.339	11.864	25.203	111.663	116.626
250.00	87.359	14.723	13.085	27.808	115.167	120.520
260.00	88.175	16.133	14.333	30.466	118.641	124.398
270.00	88.915	17.564	15.537	33.100	122.016	128.189
273.15	89.135	18.018	15.936	33.954	123.089	129.397
280.00	89.590	19.011	16.808	35.819	125.409	132.015
290.00	90.205	20.470	18.108	38.578	128.784	135.838
298.15	90.668	21.664	19.227	40.891	131.560	138.992
300.00	90.769	21.936	19.399	41.335	132.104	139.619
310.00	91.285	23.405	20.818	44.223	135.508	143.506
320.00	91.760	24.875	22.104	46.979	138.739	147.226
330.00	92.197	26.341	23.446	49.787	141.984	150.978
340.00	92.600	27.800	24.798	52.598	145.198	154.714
350.00	92.973	29.252	26.112	55.364	148.337	158.386
360.00	93.319	30.692	27.415	58.107	151.425	162.020
370.00	93.639	32.120	28.809	60.929	154.568	165.730
380.00	93.937	33.533	30.006	63.539	157.476	169.204
390.00	94.214	34.930	31.273	66.203	160.417	172.732
400.00	94.473	36.311	32.646	68.957	163.430	176.352
410.00	94.715	37.673	33.865	71.538	166.252	179.785
420.00	94.940	39.016	35.076	74.092	169.032	183.188
430.00	95.152	40.340	36.277	76.618	171.769	186.561
440.00	95.350	41.644	37.478	79.122	174.472	189.914
450.00	95.537	42.928	38.694	81.622	177.158	193.265
460.00	95.712	44.191	39.901	84.092	179.804	196.589
470.00	95.876	45.434	41.084	86.518	182.394	199.870
480.00	96.032	46.655	42.209	88.864	184.896	203.070
490.00	96.178	47.856	43.303	91.160	187.338	206.222
500.00	96.317	49.037	44.367	93.403	189.720	209.324
510.00	96.447	50.197	45.406	95.603	192.050	212.386
520.00	96.571	51.336	46.428	97.764	194.335	215.415
530.00	96.688	52.456	47.430	99.887	196.575	218.410
540.00	96.799	53.557	48.413	101.970	198.769	221.371
550.00	96.905	54.637	49.384	104.022	200.926	224.308
560.00	97.005	55.699	50.417	106.116	203.121	227.304
570.00	97.088	56.742	51.336	108.078	205.166	230.150
580.00	97.179	57.767	52.237	110.004	207.183	232.980
590.00	97.265	58.775	53.118	111.893	209.157	235.780
600.00	97.346	59.764	54.030	113.794	211.141	238.607

TABLE 19 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	97.424	60.737	54.917	115.654	213.078	241.400
620.00	97.498	61.692	55.762	117.455	214.952	244.139
630.00	97.568	62.632	56.575	119.206	216.774	246.836
640.00	97.635	63.555	57.371	120.926	218.562	249.510
650.00	97.700	64.463	58.153	122.615	220.315	252.164
660.00	97.761	65.355	58.918	124.273	222.034	254.796
670.00	97.819	66.233	59.669	125.901	223.721	257.409
680.00	97.876	67.095	60.404	127.499	225.375	260.002
690.00	97.929	67.944	61.124	129.068	226.997	262.576
700.00	97.981	68.779	62.067	130.846	228.826	265.410
710.00	98.030	69.600	62.539	132.139	230.169	267.697
720.00	98.077	70.408	63.224	133.632	231.709	270.232
730.00	98.122	71.203	63.896	135.099	233.221	272.754
740.00	98.166	71.985	64.564	136.548	234.714	275.272
750.00	98.208	72.754	65.208	137.963	236.171	277.767
760.00	98.248	73.512	65.826	139.338	237.586	280.233
770.00	98.287	74.258	66.503	140.760	239.047	282.773
780.00	98.324	74.991	67.116	142.107	240.431	285.243
790.00	98.360	75.714	67.719	143.433	241.793	287.707
800.00	98.394	76.425	68.253	144.678	243.072	290.093
810.00	98.427	77.125	68.831	145.956	244.383	292.538
820.00	98.459	77.815	69.396	147.211	245.671	294.976
830.00	98.490	78.494	69.951	148.445	246.935	297.408
840.00	98.520	79.163	70.504	149.666	248.186	299.847
850.00	98.549	79.821	71.036	150.857	249.406	302.270
860.00	98.577	80.470	71.557	152.027	250.604	304.689
870.00	98.603	81.109	72.068	153.177	251.780	307.107
880.00	98.629	81.738	72.569	154.307	252.936	309.523
890.00	98.654	82.357	73.049	155.406	254.061	311.925
900.00	98.679	82.968	73.530	156.498	255.176	314.341
910.00	98.702	83.569	74.001	157.570	256.272	316.758
920.00	98.725	84.162	74.462	158.624	257.349	319.177
930.00	98.747	84.746	74.922	159.667	258.414	321.609
940.00	98.768	85.321	75.365	160.686	259.454	324.036
950.00	98.789	85.888	75.800	161.687	260.476	326.469
960.00	98.809	86.446	76.226	162.672	261.480	328.909
970.00	98.828	86.996	76.643	163.639	262.468	331.356
980.00	98.847	87.538	77.057	164.595	263.442	333.817
990.00	98.865	88.072	77.458	165.531	264.396	336.283
1000.00	98.883	88.599	77.840	166.439	265.322	338.745

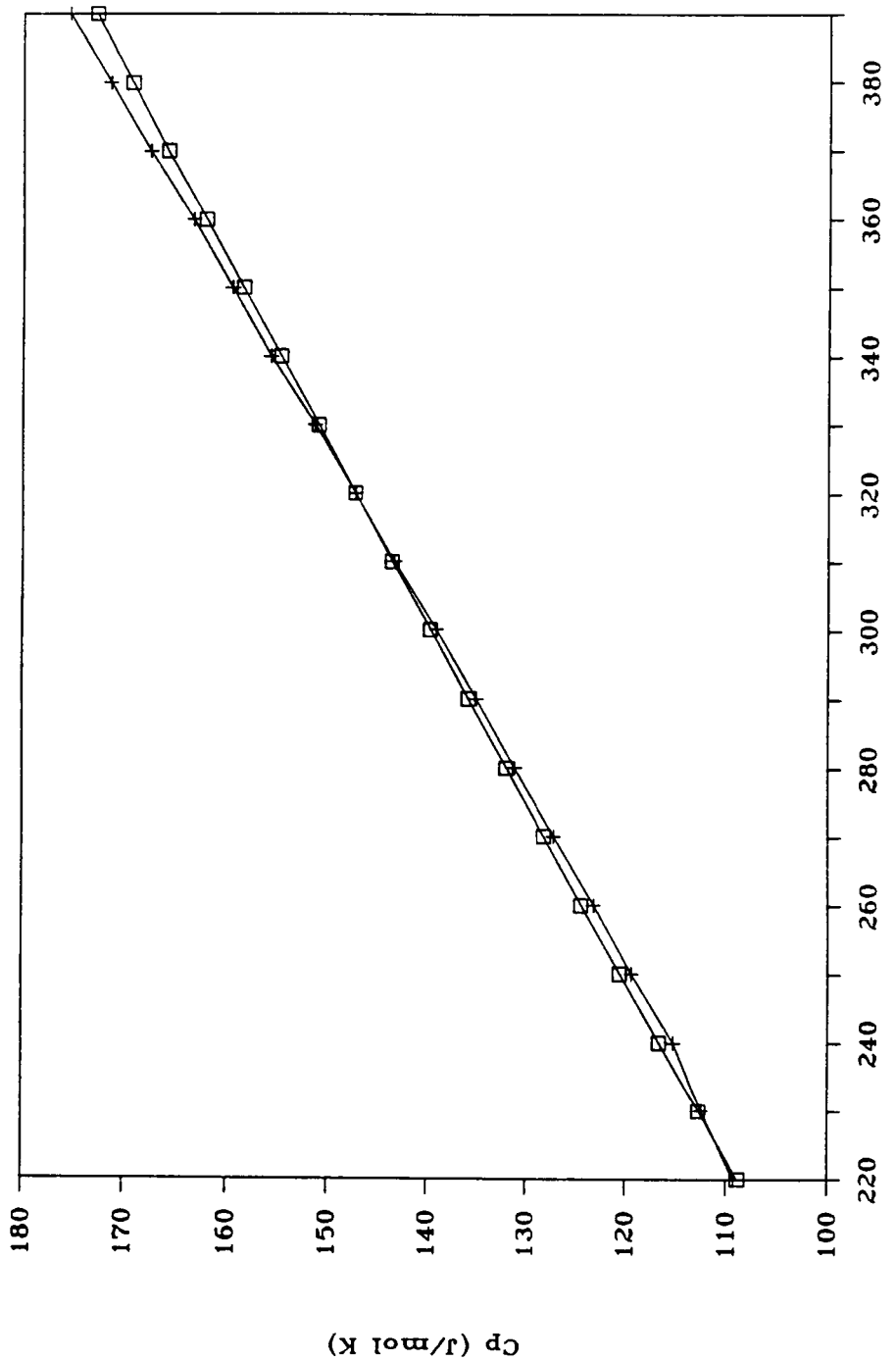


Figure 42 Heat Capacities of Poly(L-asparagine). Curve (□): Calculations. Curve (+): Measurements.

(Part I of Table 13). The group vibrations of these groups are put together to give the group vibrational spectrum of poly(L-phenylalanine). The eleven skeletal vibrations result from taking six for the backbone, two for the CH_2 group, and three for the phenyl group. Assigning three skeletal modes to the phenyl group resulted from experience gained working with other phenyl containing polymers.

Fitting the experimental heat capacities (given in Table 5) in the temperature range 220 to 320 K resulted in a Θ_1-temperature of 609.7 ± 29.5 K. Calculation of heat capacities using this value for Θ_1 and 68.0 K for Θ_3 resulted in the data given in Table 20. Comparison of the calculated results to the experimental results in the temperature range 220 to 390 K shows good agreement as shown in Figure 43. The RMS deviation observed between the calculated and the experimental heat capacities is ±1.538%. The average deviation is 0.847%

IIJ. Poly(L-tyrosine)

Poly(L-tyrosine), also an aromatic poly(amino acid) is quite similiar to poly(L-phenylalanine). The only difference is the addition of an OH group on the phenyl group. Thus construction of the group vibrational spectrum of poly(L-tyrosine) is quite similiar to that of poly(L-phenylalanine). The group vibrations are taken from the backbone unit constructed from experimental data on polyglycine and poly(L-alanine) (Part A of Table 13), the CH_2 group of polyethylene (Part D of Table 13), the phenyl group of the phenyl containing polymers (Part I of Table 13), and the OH group from poly(vinyl alcohol) (PVA) (Part E of Table 13).

TABLE 20

Calculated Heat Capacities of Poly(L-Phenylalanine)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.000	0.000	0.000	0.000	0.000	0.000
0.60	0.001	0.000	0.000	0.000	0.001	0.001
0.70	0.001	0.000	0.000	0.000	0.001	0.001
0.80	0.001	0.000	0.000	0.000	0.001	0.001
0.90	0.002	0.000	0.000	0.000	0.002	0.002
1.00	0.003	0.000	0.000	0.000	0.003	0.003
1.20	0.004	0.000	0.000	0.000	0.004	0.004
1.40	0.007	0.000	0.000	0.000	0.007	0.007
1.60	0.010	0.000	0.000	0.000	0.010	0.010
1.80	0.015	0.000	0.000	0.000	0.015	0.015
2.00	0.020	0.000	0.000	0.000	0.020	0.020
3.00	0.068	0.000	0.000	0.000	0.068	0.068
4.00	0.162	0.000	0.000	0.000	0.162	0.162
5.00	0.315	0.000	0.000	0.000	0.315	0.315
6.00	0.542	0.000	0.000	0.000	0.542	0.543
7.00	0.846	0.000	0.000	0.000	0.846	0.847
8.00	1.227	0.000	0.000	0.000	1.227	1.228
9.00	1.678	0.000	0.000	0.000	1.678	1.680
10.00	2.185	0.000	0.000	0.000	2.185	2.188
15.00	5.133	0.000	0.000	0.000	5.133	5.146
20.00	8.178	0.000	0.000	0.000	8.178	8.206
25.00	11.088	0.000	0.000	0.000	11.088	11.135
30.00	13.860	0.000	0.000	0.000	13.861	13.932
40.00	19.157	0.002	0.005	0.007	19.164	19.295
50.00	24.273	0.019	0.037	0.056	24.329	24.539
60.00	29.294	0.093	0.126	0.219	29.514	29.821
70.00	34.179	0.276	0.318	0.594	34.773	35.197
80.00	38.873	0.616	0.640	1.255	40.128	40.688
90.00	43.329	1.139	1.187	2.326	45.655	46.375
100.00	47.520	1.856	1.889	3.745	51.266	52.167
110.00	51.368	2.769	2.731	5.499	56.867	57.971
120.00	54.882	3.871	3.771	7.642	62.524	63.853
130.00	58.062	5.157	4.976	10.133	68.195	69.770
140.00	60.937	6.619	6.272	12.891	73.829	75.672
150.00	63.542	8.252	7.683	15.935	79.477	81.611
160.00	65.860	10.049	9.237	19.286	85.146	87.594
170.00	67.940	12.002	10.806	22.808	90.748	93.530
180.00	69.817	14.106	12.468	26.574	96.391	99.531

TABLE 20 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	71.505	16.353	14.145	30.498	102.003	105.524
200.00	73.024	18.732	15.893	34.626	107.649	111.576
210.00	74.390	21.235	17.579	38.815	113.204	117.556
220.00	75.620	23.851	19.488	43.338	118.959	123.769
230.00	76.731	26.568	21.191	47.759	124.490	129.773
240.00	77.736	29.375	22.952	52.328	130.063	135.844
250.00	78.646	32.260	24.733	56.992	135.638	141.943
260.00	79.473	35.210	26.499	61.709	141.182	148.033
270.00	80.226	38.214	28.199	66.413	146.639	154.058
273.15	80.449	39.170	28.743	67.913	148.362	155.965
280.00	80.913	41.261	29.919	71.180	152.093	160.104
290.00	81.541	44.339	31.707	76.046	157.587	166.218
298.15	82.013	46.864	33.143	80.006	162.020	171.174
300.00	82.116	47.438	33.385	80.823	162.939	172.209
310.00	82.645	50.549	35.169	85.718	168.362	178.300
320.00	83.131	53.662	36.800	90.461	173.593	184.212
330.00	83.580	56.769	38.465	95.234	178.814	190.141
340.00	83.994	59.863	40.119	99.982	183.976	196.033
350.00	84.378	62.937	41.717	104.654	189.031	201.837
360.00	84.733	65.986	43.265	109.251	193.984	207.557
370.00	85.064	69.003	44.889	113.892	198.956	213.323
380.00	85.371	71.985	46.298	118.283	203.654	218.822
390.00	85.657	74.928	47.759	122.688	208.345	224.339
400.00	85.924	77.829	49.309	127.138	213.062	229.909
410.00	86.174	80.684	50.710	131.394	217.568	235.277
420.00	86.408	83.492	52.086	135.578	221.986	240.576
430.00	86.626	86.251	53.439	139.690	226.317	245.806
440.00	86.832	88.960	54.783	143.743	230.574	250.982
450.00	87.025	91.617	56.126	147.744	234.768	256.113
460.00	87.206	94.223	57.449	151.671	238.878	261.178
470.00	87.377	96.776	58.740	155.516	242.893	266.166
480.00	87.538	99.277	59.965	159.241	246.780	271.037
490.00	87.690	101.725	61.152	162.878	250.568	275.826
500.00	87.834	104.122	62.302	166.424	254.258	280.531
510.00	87.970	106.468	63.421	169.888	257.858	285.163
520.00	88.099	108.762	64.516	173.279	261.377	289.729
530.00	88.220	111.007	65.588	176.595	264.815	294.230
540.00	88.336	113.203	66.635	179.838	268.174	298.668
550.00	88.446	115.350	67.664	183.014	271.460	303.049
560.00	88.550	117.450	68.753	186.203	274.753	307.464
570.00	88.649	119.504	69.724	189.228	277.877	311.714
580.00	88.743	121.512	70.674	192.186	280.930	315.909
590.00	88.833	123.476	71.602	195.079	283.912	320.050
600.00	88.919	125.398	72.557	197.955	286.874	324.192

TABLE 20 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	88.990	127.277	73.485	200.761	289.751	328.264
620.00	89.068	129.115	74.368	203.483	292.550	332.273
630.00	89.142	130.913	75.216	206.129	295.271	336.218
640.00	89.212	132.672	76.049	208.721	297.934	340.122
650.00	89.280	134.394	76.862	211.256	300.536	343.982
660.00	89.344	136.079	77.658	213.737	303.081	347.802
670.00	89.406	137.728	78.437	216.165	305.571	351.584
680.00	89.465	139.342	79.200	218.542	308.006	355.329
690.00	89.521	140.922	79.945	220.868	310.389	359.039
700.00	89.575	142.470	80.913	223.383	312.958	362.992
710.00	89.627	143.985	81.408	225.393	315.020	366.383
720.00	89.677	145.470	82.115	227.585	317.262	370.009
730.00	89.724	146.924	82.806	229.730	319.454	373.604
740.00	89.770	148.349	83.493	231.842	321.612	377.186
750.00	89.814	149.745	84.157	233.902	323.716	380.731
760.00	89.856	151.113	84.793	235.906	325.762	384.237
770.00	89.897	152.454	85.486	237.940	327.837	387.805
780.00	89.936	153.769	86.140	239.909	329.845	391.322
790.00	89.974	155.058	86.760	241.818	331.791	394.794
800.00	90.010	156.322	87.284	243.606	333.616	398.151
810.00	90.045	157.562	87.876	245.437	335.482	401.587
820.00	90.078	158.777	88.455	247.233	337.311	405.008
830.00	90.111	159.970	89.023	248.993	339.104	408.416
840.00	90.142	161.140	89.589	250.729	340.871	411.824
850.00	90.172	162.289	90.149	252.438	342.610	415.230
860.00	90.202	163.415	90.752	254.167	344.369	418.692
870.00	90.230	164.521	91.195	255.716	345.946	421.965
880.00	90.257	165.607	91.707	257.313	347.570	425.329
890.00	90.283	166.672	92.197	258.870	349.153	428.676
900.00	90.309	167.719	92.688	260.407	350.715	432.032
910.00	90.334	168.746	93.162	261.907	352.241	435.378
920.00	90.358	169.754	93.632	263.387	353.744	438.732
930.00	90.381	170.745	94.101	264.846	355.227	442.097
940.00	90.403	171.718	94.553	266.271	356.674	445.456
950.00	90.425	172.674	94.996	267.669	358.094	448.819
960.00	90.446	173.612	95.429	269.042	359.487	452.189
970.00	90.466	174.535	95.854	270.389	360.855	455.566
980.00	90.486	175.441	96.275	271.716	362.202	458.958
990.00	90.505	176.331	96.684	273.015	363.520	462.357
1000.00	90.524	177.206	97.072	274.278	364.802	465.754

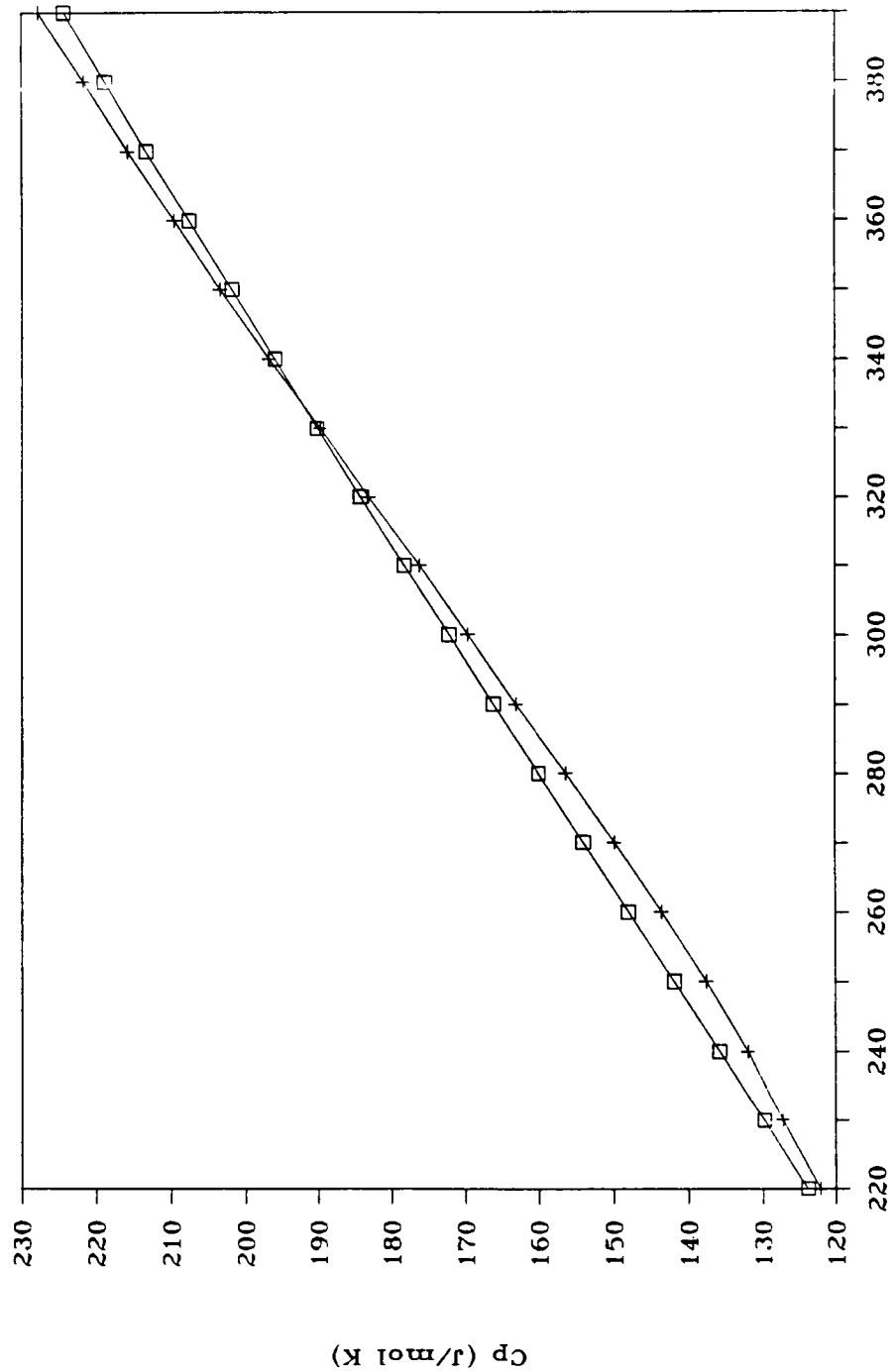


Figure 43 Heat Capacities of Poly(L-phenylalanine). Curve (□): Calculations. Curve (+): Measurements.

For the phenyl group, it becomes necessary to eliminate three of the thirty group vibrations to accomodate the addition of the OH group. These omitted modes are the CH stretch at 4378.0 K, the CCH bend at 1682.0 K, and the CH wag at 1232.0 K. Thus the group vibrational modes, totaling fifty are taken as follows: thirteen from the backbone, six from the CH_2 group, twenty-seven from the phenyl group, and four from the OH group. For the thirteen skeletal vibrations, six come from the backbone, two from the CH_2 group, three from the phenyl group, and two from the OH group. (Note, as in one calculation for poly(L-serine), the two lowest frequency vibrations of the OH group were taken as skeletal vibrations due to their low frequencies. The same has been done for poly(l-tyrosine).

For heat capacity calculation, the experimental heat capacities (listed in Table 5) in the temperature range 220 to 310 K were fitted to a Tarasov function resulting in a Θ_1-temperature of 728.5 ± 35.0 K. Taking this and the usual value for Θ_3, heat capacities were calculated for poly(L-tyrosine) from 0 to 1000 K. The results are given in Table 21. Figure 44 shows that good agreement between the calculated and experimental results was observed. The RMS deviation is ± 1.818%, and the average deviation is 0.60%.

IIK. Poly(L-methionine)

Poly(L-methionine) is one of the two sulfur containing poly(amino acids). Construction of the group vibrational spectrum consisted of taking the backbone repeat unit (Part A of Table 13), two CH_2 groups from polyethylene (Part D of Table

TABLE 21

Calculated Heat Capacities of Poly(L-Tyrosine)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.000	0.000	0.000	0.000	0.000	0.000
0.60	0.001	0.000	0.000	0.000	0.001	0.001
0.70	0.001	0.000	0.000	0.000	0.001	0.001
0.80	0.001	0.000	0.000	0.000	0.001	0.001
0.90	0.002	0.000	0.000	0.000	0.002	0.002
1.00	0.003	0.000	0.000	0.000	0.003	0.003
1.20	0.004	0.000	0.000	0.000	0.004	0.004
1.40	0.007	0.000	0.000	0.000	0.007	0.007
1.60	0.010	0.000	0.000	0.000	0.010	0.010
1.80	0.015	0.000	0.000	0.000	0.015	0.015
2.00	0.020	0.000	0.000	0.000	0.020	0.020
3.00	0.068	0.000	0.000	0.000	0.068	0.068
4.00	0.160	0.000	0.000	0.000	0.160	0.160
5.00	0.312	0.000	0.000	0.000	0.312	0.312
6.00	0.536	0.000	0.000	0.000	0.536	0.537
7.00	0.836	0.000	0.000	0.000	0.836	0.837
8.00	1.213	0.000	0.000	0.000	1.213	1.215
9.00	1.659	0.000	0.000	0.000	1.659	1.662
10.00	2.161	0.000	0.000	0.000	2.161	2.164
15.00	5.077	0.000	0.000	0.000	5.077	5.090
20.00	8.089	0.000	0.000	0.000	8.089	8.116
25.00	10.967	0.000	0.000	0.000	10.967	11.014
30.00	13.709	0.000	0.000	0.000	13.709	13.780
40.00	18.948	0.002	0.005	0.007	18.955	19.085
50.00	24.019	0.018	0.037	0.055	24.074	24.282
60.00	28.999	0.086	0.126	0.212	29.211	29.515
70.00	33.926	0.254	0.318	0.572	34.498	34.918
80.00	38.765	0.568	0.640	1.208	39.972	40.531
90.00	43.465	1.058	1.187	2.246	45.710	46.431
100.00	47.990	1.744	1.889	3.633	51.623	52.531
110.00	52.313	2.635	2.731	5.365	57.678	58.798
120.00	56.416	3.732	3.771	7.503	63.918	65.276
130.00	60.223	5.034	4.976	10.010	70.233	71.855
140.00	63.763	6.537	6.272	12.809	76.571	78.483
150.00	67.021	8.233	7.683	15.916	82.937	85.164
160.00	70.015	10.117	9.237	19.354	89.369	91.939
170.00	72.770	12.179	10.805	22.984	95.754	98.689
180.00	75.306	14.411	12.468	26.878	102.184	105.514

TABLE 21 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	77.600	16.803	14.145	30.948	108.547	112.295
200.00	79.692	19.345	15.893	35.239	114.931	119.123
210.00	81.614	22.027	17.579	39.607	121.221	125.881
220.00	83.374	24.838	19.488	44.325	127.700	132.863
230.00	84.985	27.765	21.191	48.956	133.941	139.624
240.00	86.459	30.797	22.952	53.749	140.209	146.440
250.00	87.809	33.921	24.733	58.654	146.462	153.270
260.00	89.045	37.125	26.499	63.624	152.669	160.078
270.00	90.179	40.397	28.199	68.596	158.775	166.808
273.15	90.517	41.440	28.743	70.182	160.700	168.935
280.00	91.221	43.725	29.919	73.644	164.865	173.550
290.00	92.180	47.096	31.707	78.803	170.983	180.349
298.15	92.905	49.869	33.143	83.011	175.917	185.856
300.00	93.063	50.501	33.385	83.886	176.949	187.016
310.00	93.879	53.928	35.169	89.096	182.975	193.775
320.00	94.632	57.367	36.799	94.167	188.799	200.349
330.00	95.330	60.810	38.465	99.275	194.605	206.932
340.00	95.977	64.248	40.119	104.367	200.344	213.474
350.00	96.577	67.674	41.716	109.390	205.968	219.920
360.00	97.136	71.080	43.265	114.345	211.481	226.278
370.00	97.656	74.460	44.889	119.349	217.006	232.677
380.00	98.142	77.810	46.297	124.107	222.249	238.802
390.00	98.595	81.124	47.759	128.883	227.478	244.941
400.00	99.019	84.398	49.309	133.707	232.726	251.128
410.00	99.417	87.629	50.709	138.338	237.754	257.107
420.00	99.789	90.813	52.086	142.899	242.688	263.012
430.00	100.139	93.950	53.439	147.388	247.527	268.843
440.00	100.467	97.035	54.782	151.818	252.285	274.614
450.00	100.777	100.069	56.126	156.195	256.971	280.335
460.00	101.068	103.049	57.448	160.498	261.566	285.984
470.00	101.343	105.976	58.740	164.716	266.059	291.551
480.00	101.602	108.848	59.964	168.812	270.415	296.996
490.00	101.848	111.666	61.152	172.817	274.665	302.352
500.00	102.080	114.429	62.301	176.729	278.809	307.620
510.00	102.299	117.137	63.420	180.557	282.856	312.808
520.00	102.508	119.791	64.516	184.307	286.815	317.925
530.00	102.705	122.392	65.587	187.979	290.684	322.973
540.00	102.893	124.940	66.634	191.574	294.467	327.950
550.00	103.071	127.435	67.663	195.099	298.169	332.867
560.00	103.240	129.880	68.752	198.632	301.872	337.811
570.00	103.402	132.273	69.723	201.996	305.398	342.586
580.00	103.555	134.617	70.674	205.291	308.846	347.302
590.00	103.702	136.913	71.601	208.514	312.216	351.956
600.00	103.841	139.161	72.556	211.717	315.559	356.609

TABLE 21 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	103.975	141.362	73.484	214.846	318.821	361.198
620.00	104.102	143.518	74.367	217.885	321.987	365.707
630.00	104.224	145.630	75.215	220.845	325.069	370.148
640.00	104.340	147.698	76.048	223.746	328.086	374.543
650.00	104.452	149.723	76.862	226.585	331.036	378.891
660.00	104.558	151.707	77.658	229.365	333.923	383.195
670.00	104.661	153.651	78.437	232.088	336.748	387.456
680.00	104.759	155.556	79.199	234.754	339.513	391.676
690.00	104.853	157.422	79.944	237.366	342.219	395.858
700.00	104.943	159.250	80.912	240.162	345.105	400.279
710.00	105.030	161.043	81.407	242.450	347.479	404.134
720.00	105.113	162.799	82.115	244.914	350.027	408.221
730.00	105.180	164.521	82.805	247.326	352.506	412.258
740.00	105.257	166.209	83.492	249.702	354.959	416.295
750.00	105.331	167.865	84.156	252.020	357.351	420.291
760.00	105.402	169.488	84.792	254.279	359.681	424.244
770.00	105.470	171.079	85.485	256.565	362.035	428.258
780.00	105.535	172.640	86.139	258.780	364.315	432.217
790.00	105.599	174.172	86.759	260.931	366.529	436.129
800.00	105.659	175.674	87.283	262.957	368.616	439.922
810.00	105.718	177.148	87.875	265.023	370.741	443.793
820.00	105.774	178.594	88.455	267.048	372.823	447.647
830.00	105.829	180.013	89.022	269.035	374.864	451.485
840.00	105.881	181.405	89.588	270.993	376.875	455.322
850.00	105.932	182.772	90.148	272.920	378.853	459.154
860.00	105.981	184.114	90.751	274.865	380.846	463.042
870.00	106.028	185.431	91.194	276.625	382.654	466.739
880.00	106.074	186.724	91.706	278.430	384.504	470.525
890.00	106.118	187.994	92.196	280.190	386.309	474.294
900.00	106.161	189.240	92.687	281.928	388.089	478.070
910.00	106.203	190.465	93.161	283.626	389.828	481.836
920.00	106.243	191.667	93.632	285.299	391.541	485.610
930.00	106.281	192.848	94.100	286.948	393.229	489.393
940.00	106.319	194.008	94.552	288.560	394.879	493.170
950.00	106.355	195.147	94.995	290.142	396.497	496.952
960.00	106.390	196.267	95.429	291.695	398.086	500.740
970.00	106.425	197.366	95.854	293.220	399.645	504.537
980.00	106.458	198.447	96.274	294.721	401.179	508.348
990.00	106.490	199.509	96.683	296.192	402.682	512.167
1000.00	106.521	200.552	97.071	297.624	404.145	515.984

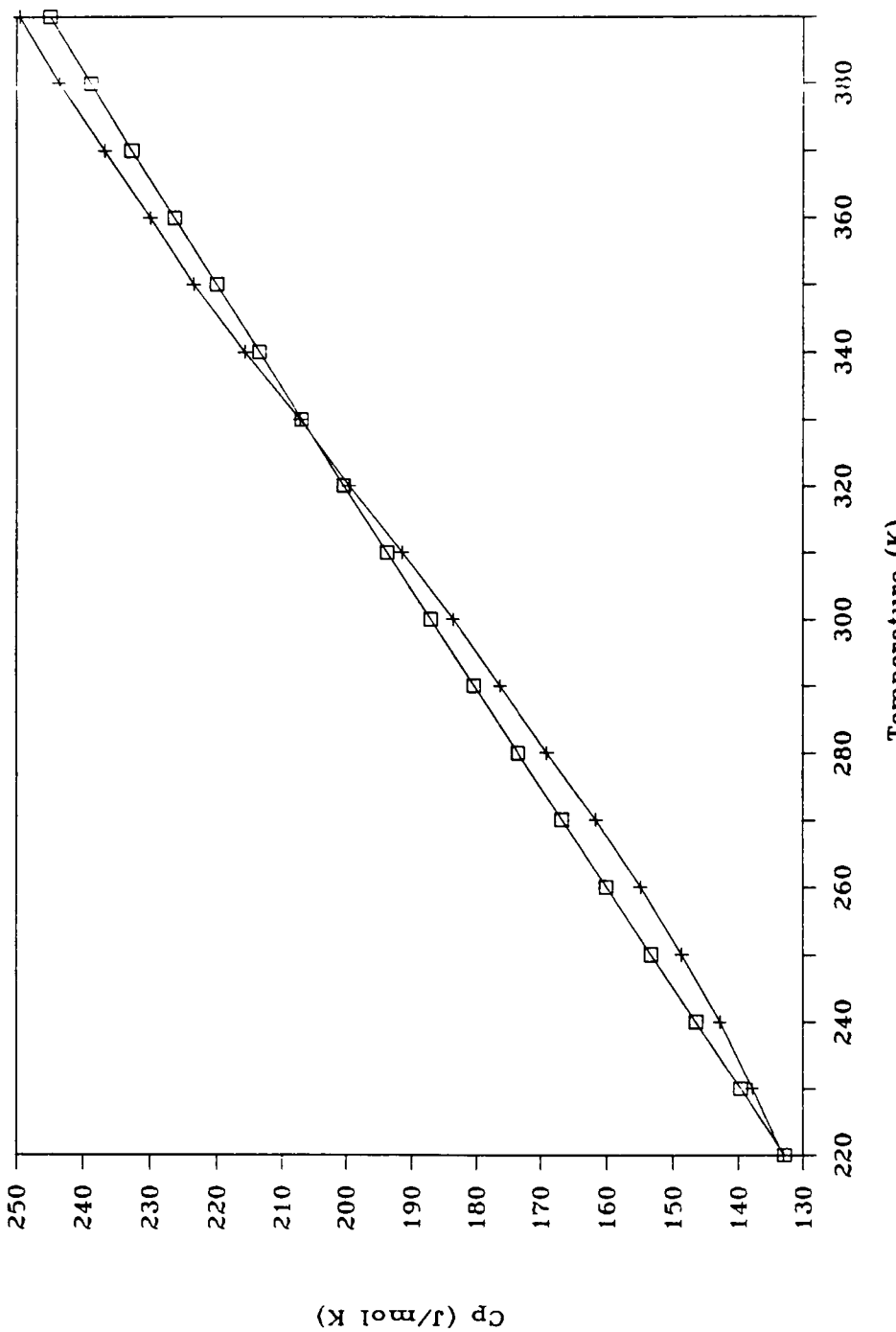


Figure 44 Heat Capacities of Poly(L-tyrosine). Curve (□): Calculations. Curve (+): Measurements.

13, taken twice), a CH_3 group from poly(methyl acrylate)[61] (PMA) (Part J of Table 13), and a C-S stretching vibration (taken twice) from literature data on a number of small molecules[67] (see Part K of Table 13). For the skeletal vibrations, the backbone contributed six, each CH_2 group contributed two for a total of four, the methyl group contributed three, and the carbon-sulfur group contributed two, one for each C−S bond. This gave a total of fifteen skeletal vibrations.

Calculation began by fitting the experimental heat capacities to determine a value for Θ_1. The resulting Θ_1-temperatures looked reasonable up to 260 K. From 260 to 300 K, they began to fall off rapidly until at 310 K and above, the skeletal Cv became higher than the Dulong-Petit limit. All attempts to get better results for Θ_1 by changing the number of skeletal and group vibrations were unsuccessful and actually produced worse Θ_1 temperatures. Using a Θ_1 of 691.3 K ± 4.6 K (determined from 220 to 230 K), heat capacities were calculated for poly(L-methionine) and are given in Table 22. Figure 45 shows both the calculated and experimental heat capacities (listed in Table 5). A reasonable fit was achieved only in the temperature range 220 to 250 K. The RMS deviation was ± 0.962% in this temperature range. Above 250 K, the measured heat capacities were considerably higher than those calculated, and as in the case of poly(L-serine) seemed to suggest the possibility of a very broad glass transition beginning below room temperature. Based on these results, an x-ray diffraction study was made to determine the degree of crystallinity of the poly(L-methionine), and hence the possibility of a glass transition. The results are reported in Section III.

TABLE 22

Calculated Heat Capacities of Poly(L-Methionine)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.000	0.000	0.000	0.000	0.000	0.000
0.60	0.001	0.000	0.000	0.000	0.001	0.001
0.70	0.001	0.000	0.000	0.000	0.001	0.001
0.80	0.002	0.000	0.000	0.000	0.002	0.002
0.90	0.002	0.000	0.000	0.000	0.002	0.002
1.00	0.003	0.000	0.000	0.000	0.003	0.003
1.20	0.005	0.000	0.000	0.000	0.005	0.005
1.40	0.008	0.000	0.000	0.000	0.008	0.008
1.60	0.012	0.000	0.000	0.000	0.012	0.012
1.80	0.018	0.000	0.000	0.000	0.018	0.018
2.00	0.024	0.000	0.000	0.000	0.024	0.024
3.00	0.082	0.000	0.000	0.000	0.082	0.082
4.00	0.195	0.000	0.000	0.000	0.195	0.195
5.00	0.379	0.000	0.000	0.000	0.379	0.379
6.00	0.652	0.000	0.000	0.000	0.652	0.653
7.00	1.017	0.000	0.000	0.000	1.017	1.018
8.00	1.475	0.000	0.000	0.000	1.475	1.477
9.00	2.018	0.000	0.000	0.000	2.018	2.021
10.00	2.627	0.000	0.000	0.000	2.627	2.632
15.00	6.173	0.000	0.000	0.000	6.173	6.189
20.00	9.835	0.000	0.000	0.000	9.835	9.869
25.00	13.335	0.000	0.000	0.000	13.335	13.392
30.00	16.670	0.000	0.000	0.000	16.670	16.755
40.00	23.040	0.000	0.000	0.000	23.040	23.199
50.00	29.212	0.000	0.004	0.004	29.217	29.469
60.00	35.257	0.000	0.006	0.007	35.264	35.630
70.00	41.229	0.003	0.071	0.074	41.302	41.805
80.00	47.058	0.011	0.181	0.192	47.251	47.910
90.00	52.686	0.032	0.394	0.425	53.111	53.949
100.00	58.070	0.074	0.771	0.845	58.915	59.951
110.00	63.181	0.146	1.252	1.398	64.579	65.832
120.00	67.947	0.255	1.885	2.140	70.088	71.577
130.00	72.370	0.409	2.651	3.061	75.431	77.173
140.00	76.424	0.612	3.633	4.245	80.669	82.683
150.00	80.135	0.868	4.680	5.548	85.683	87.984
160.00	83.532	1.179	5.966	7.145	90.677	93.283
170.00	86.645	1.547	7.306	8.854	95.499	98.426
180.00	89.453	1.975	8.834	10.809	100.263	103.529

TABLE 22 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	92.000	2.463	10.426	12.889	104.888	108.509
200.00	94.327	3.012	12.061	15.073	109.400	113.390
210.00	96.448	3.622	13.769	17.391	113.840	118.216
220.00	98.380	4.293	15.691	19.984	118.364	123.149
230.00	100.140	5.024	17.585	22.609	122.748	127.957
240.00	101.743	5.813	19.484	25.297	127.040	132.687
250.00	103.206	6.659	21.539	28.198	131.404	137.511
260.00	104.542	7.558	23.555	31.113	135.656	142.239
270.00	105.765	8.509	25.562	34.071	139.836	146.911
273.15	106.129	8.818	26.205	35.024	141.153	148.386
280.00	106.886	9.507	27.615	37.122	144.009	151.594
290.00	107.915	10.549	29.719	40.268	148.183	156.300
298.15	108.692	11.428	31.476	42.904	151.596	160.161
300.00	108.862	11.631	31.790	43.421	152.283	160.946
310.00	109.734	12.750	33.987	46.737	156.471	165.706
320.00	110.539	13.900	36.029	49.929	160.468	170.285
330.00	111.283	15.079	38.121	53.199	164.482	174.901
340.00	111.972	16.282	40.229	56.511	168.482	179.524
350.00	112.611	17.506	42.343	59.849	172.460	184.143
360.00	113.205	18.747	44.346	63.093	176.298	188.634
370.00	113.758	20.002	46.442	66.444	180.202	193.215
380.00	114.273	21.268	48.339	69.607	183.880	197.575
390.00	114.754	22.543	50.258	72.800	187.554	201.952
400.00	115.203	23.823	52.254	76.077	191.280	206.405
410.00	115.624	25.106	54.102	79.208	194.832	210.691
420.00	116.018	26.391	55.917	82.308	198.326	214.935
430.00	116.387	27.675	57.713	85.388	201.775	219.151
440.00	116.735	28.957	59.500	88.458	205.192	223.353
450.00	117.062	30.236	61.285	91.521	208.583	227.547
460.00	117.369	31.509	63.045	94.554	211.923	231.708
470.00	117.659	32.777	64.765	97.542	215.202	235.821
480.00	117.933	34.038	66.400	100.438	218.371	239.836
490.00	118.191	35.291	67.990	103.282	221.473	243.798
500.00	118.436	36.536	69.575	106.111	224.547	247.750
510.00	118.667	37.772	71.072	108.844	227.511	251.602
520.00	118.887	38.998	72.540	111.538	230.425	255.419
530.00	119.095	40.215	73.977	114.192	233.287	259.200
540.00	119.292	41.421	75.383	116.805	236.096	262.943
550.00	119.479	42.617	76.765	119.383	238.862	266.658
560.00	119.657	43.803	78.197	122.000	241.657	270.428
570.00	119.827	44.977	79.504	124.481	244.308	274.057
580.00	119.988	46.141	80.781	126.922	246.910	277.654
590.00	120.142	47.294	82.027	129.321	249.463	281.216
600.00	120.289	48.435	83.293	131.728	252.017	284.801

TABLE 22 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	120.429	49.566	84.523	134.088	254.517	288.348
620.00	120.563	50.685	85.701	136.385	256.948	291.837
630.00	120.690	51.793	86.835	138.628	259.318	295.279
640.00	120.813	52.890	87.944	140.834	261.647	298.696
650.00	120.929	53.975	89.028	143.004	263.933	302.087
660.00	121.041	55.050	90.088	145.137	266.179	305.454
670.00	121.149	56.113	91.122	147.235	268.384	308.797
680.00	121.251	57.165	92.133	149.298	270.550	312.117
690.00	121.350	58.206	93.121	151.327	272.676	315.416
700.00	121.430	59.236	94.329	153.565	274.994	318.959
710.00	121.520	60.255	95.046	155.301	276.821	321.955
720.00	121.607	61.263	95.975	157.238	278.845	325.205
730.00	121.690	62.260	96.883	159.143	280.833	328.436
740.00	121.770	63.246	97.780	161.026	282.796	331.662
750.00	121.847	64.221	98.647	162.868	284.715	334.861
760.00	121.920	65.185	99.481	164.666	286.587	338.030
770.00	121.991	66.139	100.367	166.506	288.497	341.269
780.00	122.060	67.082	101.183	168.265	290.325	344.436
790.00	122.125	68.014	101.984	169.998	292.124	347.595
800.00	122.189	68.936	102.710	171.645	293.834	350.674
810.00	122.250	69.847	103.473	173.320	295.569	353.810
820.00	122.308	70.747	104.220	174.967	297.275	356.937
830.00	122.365	71.637	104.958	176.595	298.960	360.067
840.00	122.420	72.517	105.682	178.198	300.618	363.193
850.00	122.473	73.386	106.380	179.766	302.239	366.301
860.00	122.524	74.245	107.063	181.308	303.831	369.405
870.00	122.573	75.093	107.731	182.825	305.397	372.506
880.00	122.620	75.932	108.385	184.317	306.937	375.605
890.00	122.666	76.760	109.013	185.774	308.440	378.690
900.00	122.711	77.579	109.639	187.217	309.928	381.788
910.00	122.754	78.387	110.251	188.638	311.392	384.887
920.00	122.796	79.185	110.849	190.035	312.830	387.988
930.00	122.836	79.974	111.442	191.416	314.252	391.102
940.00	122.875	80.753	112.016	192.769	315.644	394.212
950.00	122.913	81.522	112.577	194.099	317.012	397.329
960.00	122.950	82.281	113.126	195.408	318.357	400.452
970.00	122.985	83.031	113.664	196.696	319.681	403.585
980.00	123.020	83.772	114.195	197.967	320.986	406.733
990.00	123.053	84.503	114.711	199.214	322.267	409.888
1000.00	123.086	85.224	115.204	200.428	323.514	413.040

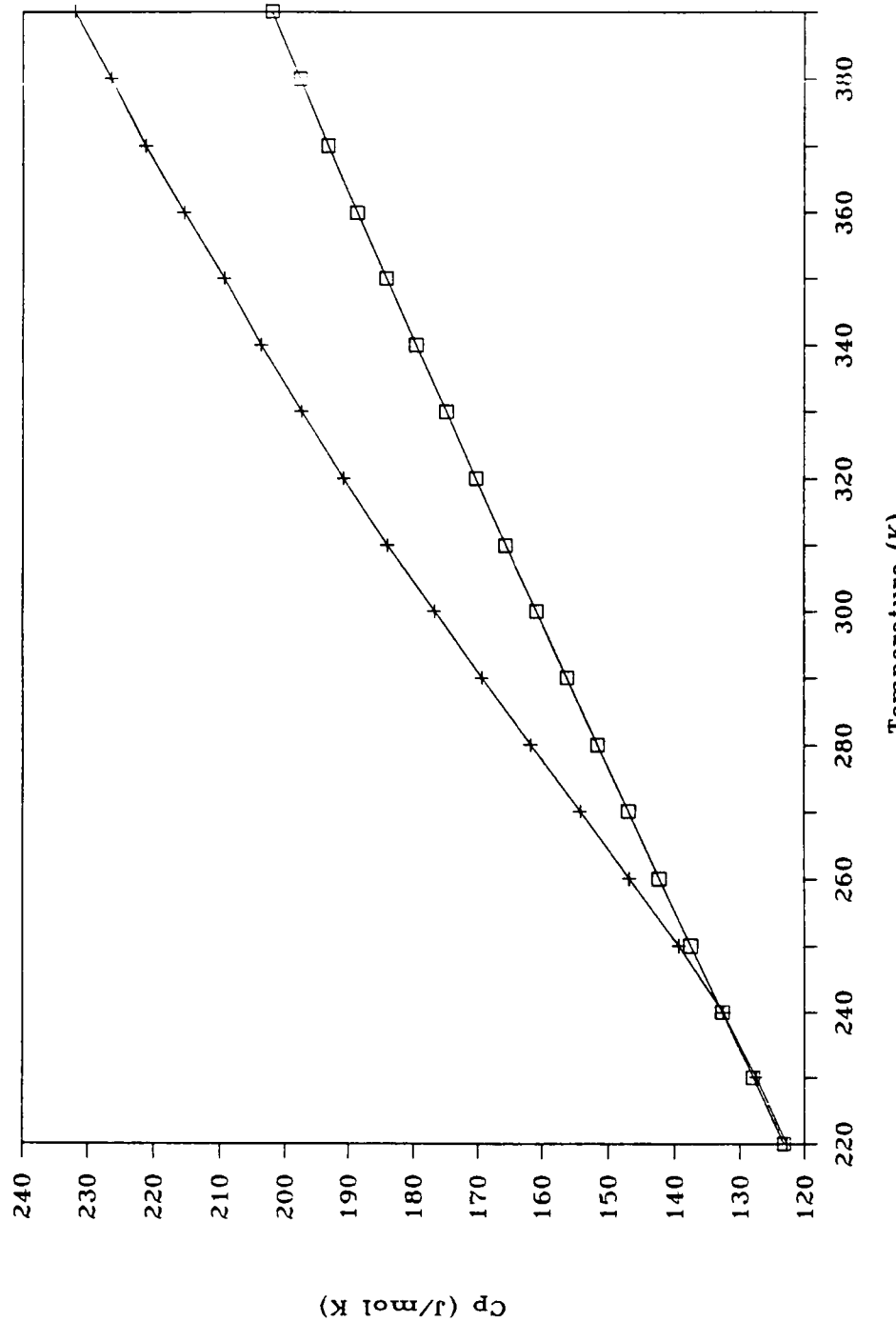


Figure 45 Heat Capacities of Poly(L-methionine). Curve (□): Calculations. Curve (+): Measurements.

IIL. Poly(L-tryptophan)

Poly(L-tryptophan) has one of the most complicated side groups fo the poly(amino acids). It consists of a CH_2 group and two ring groups, a five-membered ring and a six-membered phenyl ring. As a result, poly(L-tryptophan) has a rather involved group vibrational spectrum. Construction of the group vibrational spectrum involved taking the backbone repeat unit (Part A of Table 13), the CH_2 group from polyethylene (Part D of Table 13), the phenyl group from phenyl containing polymers (Part I of Table 13), and the five membered ring from a similiar small molecule, indole[68] (Part L Table 13). Skeletal vibrations totaled thirteen, six for the backbone, two for the CH_2 group, three for the phenyl group, and two for the five membered ring. Thus for poly(L-tryptophan), there were a total of seventy-two vibrational modes (3N = 3*24)), thirteen of which were skeletal and sixty-nine of which were group.

For the heat capacity calculations the experimental heat capacities (given in Table 5) were best fitted in the temperature range 250 to 310 K. This yielded a Θ_1 of 793.2 ± 12.6 K. Taking this and the usual value for Θ_3, heat capacities were calculated in the temperature range 0 to 1000 K. The results are given in Table 23. A comparison of the calculated and the experimental results showes good agreement. This can be seen in Figure 46. This comparison yielded a RMS deviation was ± 1.513%. The average deviation is 0.912%.

TABLE 23

Calculated Heat Capacities of Poly(L-Tryptophan)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.000	0.000	0.000	0.000	0.000	0.000
0.60	0.000	0.000	0.000	0.000	0.000	0.000
0.70	0.001	0.000	0.000	0.000	0.001	0.001
0.80	0.001	0.000	0.000	0.000	0.001	0.001
0.90	0.002	0.000	0.000	0.000	0.002	0.002
1.00	0.002	0.000	0.000	0.000	0.002	0.002
1.20	0.004	0.000	0.000	0.000	0.004	0.004
1.40	0.006	0.000	0.000	0.000	0.006	0.006
1.60	0.009	0.000	0.000	0.000	0.009	0.009
1.80	0.013	0.000	0.000	0.000	0.013	0.013
2.00	0.018	0.000	0.000	0.000	0.018	0.018
3.00	0.062	0.000	0.000	0.000	0.062	0.062
4.00	0.147	0.000	0.000	0.000	0.147	0.147
5.00	0.286	0.000	0.000	0.000	0.286	0.287
6.00	0.492	0.000	0.000	0.000	0.492	0.493
7.00	0.768	0.000	0.000	0.000	0.768	0.769
8.00	1.114	0.000	0.000	0.000	1.114	1.116
9.00	1.524	0.000	0.000	0.000	1.524	1.526
10.00	1.984	0.000	0.000	0.000	1.984	1.988
15.00	4.663	0.000	0.000	0.000	4.663	4.675
20.00	7.429	0.000	0.000	0.000	7.429	7.454
25.00	10.072	0.000	0.000	0.000	10.072	10.116
30.00	12.591	0.000	0.000	0.000	12.591	12.656
40.00	17.403	0.002	0.005	0.007	17.410	17.530
50.00	22.061	0.019	0.037	0.056	22.117	22.308
60.00	26.643	0.093	0.126	0.219	26.862	27.142
70.00	31.173	0.276	0.318	0.594	31.768	32.154
80.00	35.662	0.616	0.642	1.259	36.921	37.436
90.00	40.063	1.142	1.196	2.338	42.401	43.069
100.00	44.340	1.865	1.911	3.776	48.116	48.962
110.00	48.466	2.790	2.756	5.546	54.012	55.061
120.00	52.422	3.916	3.853	7.769	60.190	61.469
130.00	56.191	5.239	5.144	10.383	66.574	68.112
140.00	59.711	6.758	6.540	13.298	73.009	74.832
150.00	63.009	8.471	8.088	16.559	79.569	81.705
160.00	66.067	10.376	9.830	20.206	86.273	88.753
170.00	68.897	12.469	11.634	24.104	93.001	95.852
180.00	71.517	14.747	13.599	28.346	99.864	103.118

TABLE 23 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	73.945	17.204	15.623	32.827	106.773	110.459
200.00	76.195	19.832	17.776	37.609	113.804	117.955
210.00	78.225	22.623	19.889	42.512	120.737	125.379
220.00	80.107	25.566	22.337	47.903	128.010	133.186
230.00	81.847	28.649	24.531	53.179	135.026	140.755
240.00	83.451	31.859	26.855	58.714	142.165	148.484
250.00	84.930	35.184	29.218	64.401	149.331	156.272
260.00	86.293	38.609	31.647	70.256	156.548	164.145
270.00	87.549	42.120	33.944	76.064	163.613	171.891
273.15	87.925	43.242	34.698	77.940	165.865	174.365
280.00	88.709	45.704	36.352	82.056	170.765	179.760
290.00	89.780	49.348	38.871	88.219	177.999	187.748
298.15	90.593	52.352	40.861	93.213	183.806	194.190
300.00	90.770	53.038	41.239	94.276	185.046	195.574
310.00	91.687	56.762	43.736	100.498	192.184	203.528
320.00	92.536	60.509	46.025	106.533	199.070	211.248
330.00	93.325	64.267	48.498	112.765	206.090	219.145
340.00	94.057	68.028	50.899	118.927	212.985	226.943
350.00	94.739	71.782	53.185	124.967	219.706	234.590
360.00	95.375	75.521	55.418	130.940	226.315	242.150
370.00	95.968	79.238	57.721	136.959	232.927	249.748
380.00	96.522	82.926	59.794	142.720	239.242	257.061
390.00	97.040	86.579	61.974	148.553	245.593	264.446
400.00	97.525	90.193	64.215	154.408	251.934	271.854
410.00	97.980	93.763	66.251	160.014	257.994	278.995
420.00	98.408	97.286	68.264	165.551	263.958	286.064
430.00	98.809	100.759	70.268	171.027	269.836	293.073
440.00	99.187	104.178	72.270	176.448	275.635	300.031
450.00	99.544	107.543	74.260	181.803	281.347	306.926
460.00	99.879	110.851	76.181	187.031	286.910	313.695
470.00	100.196	114.101	78.062	192.163	292.360	320.372
480.00	100.496	117.293	79.868	197.160	297.656	326.915
490.00	100.779	120.426	81.614	202.039	302.818	333.343
500.00	101.047	123.499	83.313	206.812	307.859	339.672
510.00	101.301	126.513	84.973	211.487	312.788	345.909
520.00	101.542	129.468	86.600	216.068	317.611	352.062
530.00	101.771	132.365	88.192	220.557	322.328	358.131
540.00	101.989	135.203	89.749	224.952	326.941	364.117
550.00	102.195	137.984	91.277	229.261	331.456	370.027
560.00	102.392	140.708	92.855	233.563	335.954	375.952
570.00	102.579	143.376	94.304	237.680	340.259	381.692
580.00	102.758	145.988	95.722	241.711	344.468	387.359
590.00	102.928	148.547	97.107	245.654	348.582	392.951
600.00	103.090	151.053	98.510	249.563	352.653	398.528

TABLE 23 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	103.245	153.507	99.874	253.381	356.627	404.029
620.00	103.394	155.910	101.185	257.095	360.489	409.436
630.00	103.535	158.263	102.452	260.715	364.250	414.763
640.00	103.671	160.567	103.694	264.261	367.932	420.032
650.00	103.801	162.824	104.907	267.731	371.532	425.241
660.00	103.925	165.035	106.095	271.129	375.054	430.395
670.00	104.044	167.199	107.257	274.456	378.501	435.495
680.00	104.159	169.320	108.417	277.737	381.896	440.571
690.00	104.268	171.397	109.534	280.931	385.200	445.576
700.00	104.374	173.432	110.867	284.299	388.673	450.812
710.00	104.475	175.426	111.721	287.147	391.622	455.475
720.00	104.572	177.379	112.783	290.162	394.734	460.362
730.00	104.666	179.294	113.821	293.115	397.781	465.207
740.00	104.756	181.170	114.852	296.022	400.777	470.031
750.00	104.842	183.009	115.998	299.007	403.849	474.978
760.00	104.926	184.811	116.817	301.628	406.553	479.531
770.00	105.006	186.578	117.843	304.421	409.427	484.319
780.00	105.084	188.310	118.825	307.134	412.218	489.048
790.00	105.158	190.008	119.766	309.774	414.932	493.723
800.00	105.217	191.674	120.606	312.279	417.497	498.258
810.00	105.287	193.307	121.508	314.815	420.102	502.880
820.00	105.354	194.909	122.393	317.301	422.655	507.480
830.00	105.418	196.480	123.260	319.740	425.158	512.059
840.00	105.480	198.021	124.120	322.141	427.621	516.631
850.00	105.540	199.533	124.969	324.502	430.042	521.194
860.00	105.598	201.016	125.856	326.873	432.471	525.808
870.00	105.654	202.472	126.578	329.050	434.704	530.227
880.00	105.708	203.901	127.364	331.265	436.973	534.732
890.00	105.760	205.302	128.124	333.426	439.187	539.215
900.00	105.811	206.678	128.879	335.557	441.368	543.703
910.00	105.860	208.029	129.613	337.642	443.501	548.177
920.00	105.907	209.355	130.339	339.693	445.601	552.657
930.00	105.953	210.656	131.058	341.714	447.667	557.144
940.00	105.997	211.934	131.756	343.690	449.688	561.622
950.00	106.040	213.189	132.441	345.630	451.671	566.104
960.00	106.082	214.421	133.113	347.534	453.616	570.590
970.00	106.123	215.631	133.772	349.403	455.526	575.084
980.00	106.162	216.819	134.423	351.242	457.404	579.592
990.00	106.200	217.986	135.057	353.043	459.243	584.107
1000.00	106.237	219.133	135.668	354.800	461.037	588.620

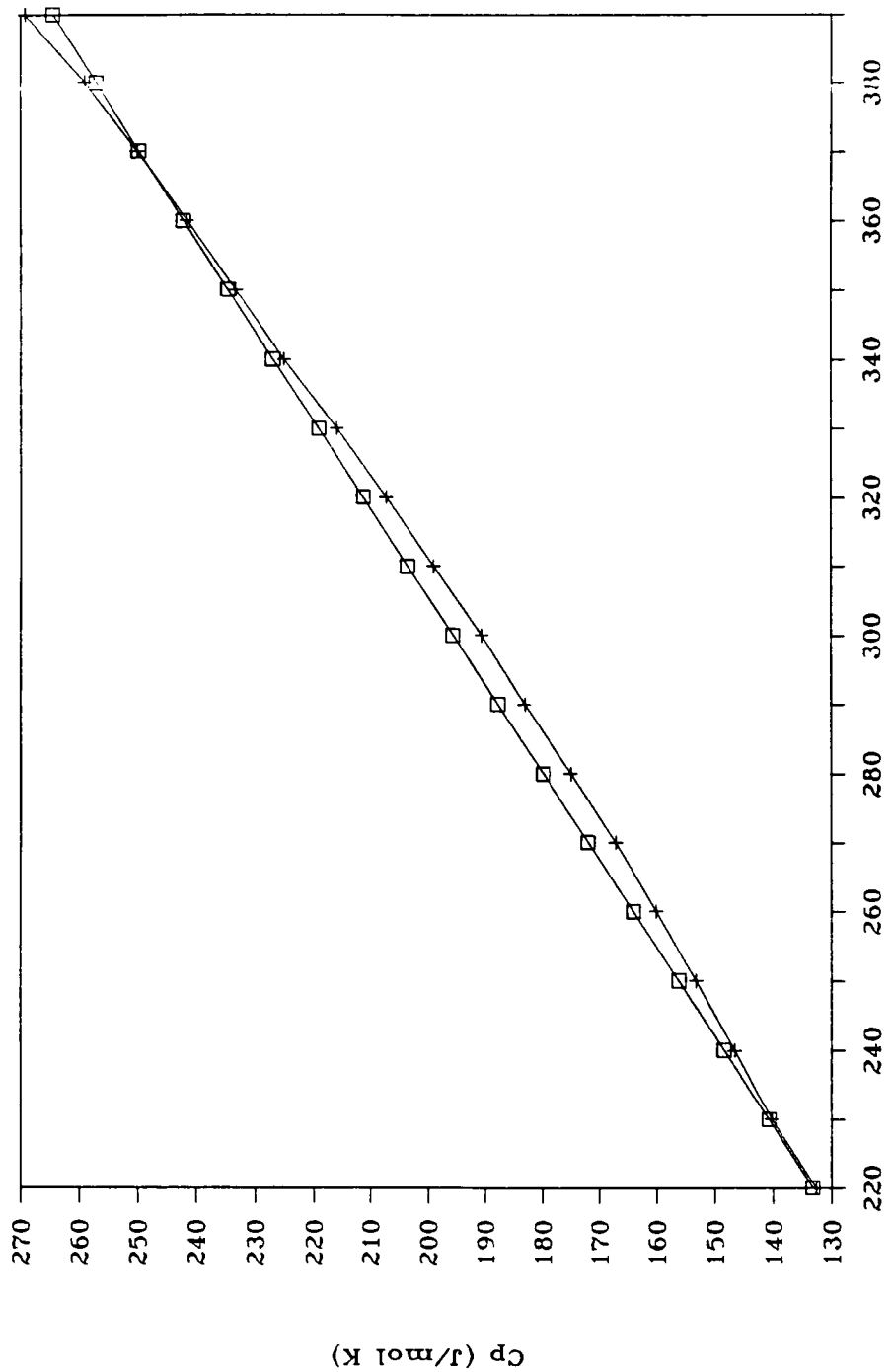


Figure 46 Heat Capacities of Poly(L-tryptophan). Curve (□): Calculations. Curve (+): Measurements.

IIM. Poly(L-proline)

Poly(L-proline) is, like poly(L-tryptophan), considered a heterocyclic poly(amino acid). Construction of its group vibrational spectrum is aided by two dispersion curve studies done by Gupta and Gupta[69] and Gupta and co-workers.[25] The spectrum was thus constructed by taking parts of the backbone repeat unit (Part A of Table 13), information on the CH_2 group from polyethylene (Part D of Table 13), the CH group from polypropylene (Part C of Table 13), and information on poly(L-proline) taken from the work in the literature[25,69] (Part M of Table 13). The total number of vibrational modes for poly(L-proline) is forty-two (3N = 3*14), thirty-one are taken as group vibrations, and eleven are considered skeletal vibrations. This is according to the literature work of Gupta and Gupta[69] and Gupta and co-workers.[25] They point out that all the C-C and C-N bending vibrations are considered heavily coupled and are therefore taken as skeletal modes.

Fitting the experimental heat capacities (given in Table 6) in the temperature range 270 to 390 K resulted in a Θ_1-temperature of 690.5 ± 46.3 K. Calculations using this value for Θ_1 and 68.0 K for Θ_3 led to the results given in Table 24. Agreement with experiment was good. This can be seen in Figure 47. The RMS deviation is ± 1.783%, and the average deviation is 0.47%.

IIN. Poly(L-lysine) hydrobromide

Poly(L-lysine) is one of the basic poly(amino acids). For its stability, it must be purchased as poly(L-lysine) hydrobromide. Construction of its group vibrational

TABLE 24

Calculated Heat Capacities of Poly(L-Proline)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.000	0.000	0.000	0.000	0.000	0.000
0.60	0.000	0.000	0.000	0.000	0.000	0.000
0.70	0.001	0.000	0.000	0.000	0.001	0.001
0.80	0.001	0.000	0.000	0.000	0.001	0.001
0.90	0.002	0.000	0.000	0.000	0.002	0.002
1.00	0.002	0.000	0.000	0.000	0.002	0.002
1.20	0.004	0.000	0.000	0.000	0.004	0.004
1.40	0.006	0.000	0.000	0.000	0.006	0.006
1.60	0.009	0.000	0.000	0.000	0.009	0.009
1.80	0.013	0.000	0.000	0.000	0.013	0.013
2.00	0.018	0.000	0.000	0.000	0.018	0.018
3.00	0.060	0.000	0.000	0.000	0.060	0.060
4.00	0.143	0.000	0.000	0.000	0.143	0.143
5.00	0.278	0.000	0.000	0.000	0.278	0.279
6.00	0.479	0.000	0.000	0.000	0.479	0.479
7.00	0.747	0.000	0.000	0.000	0.747	0.748
8.00	1.083	0.000	0.000	0.000	1.083	1.085
9.00	1.481	0.000	0.000	0.000	1.481	1.484
10.00	1.929	0.000	0.000	0.000	1.929	1.932
15.00	4.532	0.000	0.000	0.000	4.532	4.544
20.00	7.221	0.000	0.000	0.000	7.221	7.246
25.00	9.790	0.000	0.000	0.000	9.790	9.832
30.00	12.239	0.000	0.000	0.000	12.239	12.302
40.00	16.916	0.000	0.000	0.000	16.916	17.032
50.00	21.447	0.000	0.000	0.000	21.447	21.632
60.00	25.885	0.000	0.000	0.000	25.885	26.155
70.00	30.269	0.001	0.000	0.001	30.270	30.639
80.00	34.548	0.005	0.003	0.008	34.556	35.039
90.00	38.679	0.018	0.003	0.020	38.699	39.309
100.00	42.630	0.049	0.026	0.075	42.704	43.455
110.00	46.379	0.111	0.057	0.168	46.547	47.450
120.00	49.875	0.216	0.111	0.327	50.202	51.269
130.00	53.118	0.377	0.209	0.586	53.705	54.945
140.00	56.091	0.603	0.394	0.998	57.089	58.514
150.00	58.811	0.903	0.667	1.570	60.381	62.002
160.00	61.301	1.280	1.020	2.299	63.601	65.429
170.00	63.583	1.737	1.471	3.208	66.791	68.838
180.00	65.640	2.274	2.076	4.350	69.990	72.270

TABLE 24 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	67.506	2.890	2.754	5.644	73.150	75.675
200.00	69.211	3.583	3.543	7.125	76.336	79.121
210.00	70.765	4.350	4.474	8.823	79.589	82.648
220.00	72.180	5.187	5.459	10.645	82.826	86.174
230.00	73.469	6.090	6.625	12.716	86.184	89.841
240.00	74.643	7.055	7.892	14.948	89.591	93.573
250.00	75.714	8.078	9.231	17.309	93.023	97.347
260.00	76.693	9.153	10.707	19.860	96.553	101.239
270.00	77.588	10.276	12.125	22.401	99.989	105.048
273.15	77.855	10.639	12.610	23.248	101.103	106.284
280.00	78.409	11.441	13.673	25.115	103.524	108.977
290.00	79.162	12.645	15.315	27.960	107.122	112.990
298.15	79.731	13.650	16.636	30.286	110.018	116.234
300.00	79.855	13.882	16.867	30.749	110.604	116.897
310.00	80.494	15.147	18.602	33.749	114.242	120.985
320.00	81.083	16.436	20.322	36.758	117.841	125.050
330.00	81.628	17.745	21.986	39.731	121.359	129.046
340.00	82.132	19.071	23.685	42.755	124.887	133.072
350.00	82.600	20.408	25.402	45.810	128.410	137.109
360.00	83.035	21.755	27.135	48.890	131.924	141.155
370.00	83.439	23.107	28.856	51.963	135.402	145.180
380.00	83.816	24.462	30.550	55.012	138.829	149.169
390.00	84.168	25.818	32.263	58.080	142.249	153.168
400.00	84.497	27.171	33.970	61.141	145.638	157.154
410.00	84.805	28.521	35.503	64.024	148.829	160.944
420.00	85.093	29.866	37.074	66.939	152.032	164.765
430.00	85.364	31.203	38.646	69.848	155.212	168.579
440.00	85.618	32.531	40.228	72.759	158.378	172.395
450.00	85.857	33.850	41.783	75.633	161.490	176.173
460.00	86.083	35.158	43.309	78.467	164.550	179.911
470.00	86.295	36.455	44.813	81.268	167.562	183.617
480.00	86.495	37.740	46.243	83.983	170.478	187.236
490.00	86.684	39.012	47.706	86.717	173.402	190.881
500.00	86.863	40.271	49.112	89.383	176.246	194.458
510.00	87.033	41.516	50.443	91.959	178.991	197.945
520.00	87.193	42.748	51.748	94.496	181.689	201.397
530.00	87.345	43.966	53.026	96.992	184.337	204.813
540.00	87.490	45.170	54.277	99.447	186.936	208.193
550.00	87.627	46.360	55.499	101.859	189.486	211.536
560.00	87.757	47.535	56.693	104.228	191.985	214.842
570.00	87.881	48.697	57.857	106.554	194.435	218.112
580.00	87.999	49.844	58.993	108.837	196.837	221.345
590.00	88.112	50.978	60.097	111.075	199.187	224.541
600.00	88.219	52.098	61.216	113.314	201.533	227.750

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	88.322	53.203	62.306	115.509	203.831	230.924
620.00	88.420	54.295	63.348	117.643	206.062	234.042
630.00	88.513	55.374	64.344	119.717	208.231	237.107
640.00	88.602	56.439	65.316	121.754	210.357	240.144
650.00	88.688	57.490	66.264	123.754	212.442	243.153
660.00	88.770	58.528	67.189	125.717	214.487	246.135
670.00	88.848	59.554	68.090	127.644	216.492	249.092
680.00	88.924	60.566	68.969	129.535	218.459	252.023
690.00	88.996	61.565	69.826	131.392	220.387	254.931
700.00	89.054	62.552	70.900	133.452	222.506	258.079
710.00	89.120	63.526	71.496	135.022	224.142	260.687
720.00	89.184	64.488	72.300	136.787	225.971	263.540
730.00	89.244	65.437	73.083	138.520	227.765	266.372
740.00	89.303	66.374	73.848	140.222	229.525	269.186
750.00	89.359	67.299	74.593	141.892	231.252	271.981
760.00	89.413	68.212	75.320	143.533	232.946	274.760
770.00	89.465	69.114	76.029	145.143	234.608	277.522
780.00	89.515	70.003	76.721	146.724	236.239	280.270
790.00	89.563	70.881	77.396	148.277	237.840	283.003
800.00	89.609	71.748	78.053	149.801	239.411	285.723
810.00	89.654	72.603	78.695	151.299	240.952	288.431
820.00	89.697	73.447	79.321	152.769	242.466	291.127
830.00	89.738	74.280	79.932	154.212	243.951	293.814
840.00	89.778	75.102	80.528	155.630	245.409	296.491
850.00	89.817	75.914	81.109	157.023	246.840	299.160
860.00	89.854	76.714	81.677	158.391	248.245	301.822
870.00	89.890	77.504	82.231	159.734	249.625	304.478
880.00	89.925	78.283	82.771	161.054	250.979	307.128
890.00	89.959	79.052	83.299	162.351	252.309	309.775
900.00	89.991	79.810	83.814	163.624	253.616	312.419
910.00	90.023	80.558	84.317	164.876	254.899	315.060
920.00	90.053	81.296	84.809	166.105	256.159	317.701
930.00	90.083	82.025	85.289	167.313	257.396	320.342
940.00	90.111	82.743	85.757	168.500	258.612	322.984
950.00	90.139	83.451	86.216	169.667	259.806	325.629
960.00	90.166	84.150	86.663	170.813	260.979	328.278
970.00	90.192	84.840	87.100	171.940	262.132	330.932
980.00	90.217	85.519	87.528	173.047	263.265	333.592
990.00	90.242	86.190	87.946	174.136	264.378	336.259
1000.00	90.266	86.851	88.354	175.206	265.471	338.935

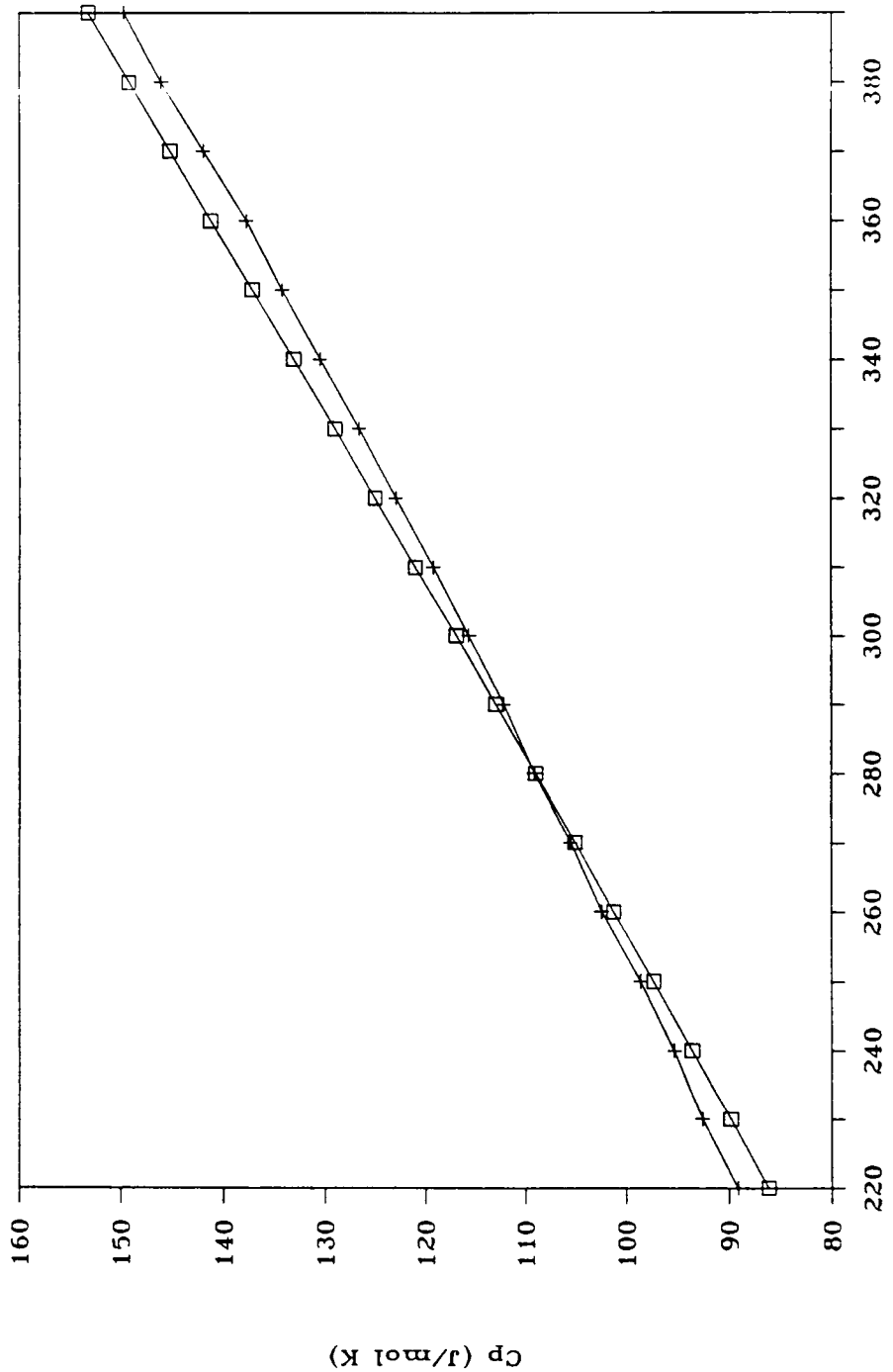


Figure 47 Heat Capacities of Poly(L-proline). Curve (□): Calculations. Curve (+): Measurements.

specturm begins by taking the backbone unit, given in Part A of Table 13. To this the group vibration information on four CH_2 groups from polyethylene (Part D of Table 13, taken four times) is added. The final group vibrations needed are those for the NH_3^+ group. These were taken from information on a number of small, low molecular weight compounds[67,70-71] (Part N of Table 13). For the skeletal vibrations, six are taken for the backbone, two are taken for each CH_2 group resulting in a total of eight, three are taken for the NH_3^+ group which is treated similiarly to the CH_3 group, and three are taken for the bromine atom. Thus for poly(L-lysine)•HBr, there are a total of twenty skeletal vibrations and forty-nine group vibrations.

For the calculation of heat capcity, a fit of the experimental heat capacites (listed in Table 6) in the temperature range 230 to 390 K resulted in a Θ_1-temperature of 636.3 ± 46.7 K. Using this and 68.0 for Θ_3, heat capacities were calculated form 0 to 1000 K and are reported in Table 25. Figure 48 shows the comparison of the calculated heat capacties to those measured in the temperature range 220 to 390 K. The RMS deviation is ± 1.24%, and the average deviation is 0.20%.

IIO. Poly(L-histidine)

Poly(L-histidine) is available commercially in two forms, as the free poly(amino acid) and as poly(L-histidine) hydrochloride. For both samples, heat capacity measurements and calculations were carried out. Construction of the group vibrational spectrum of poly(L-histidine) is done by putting together the group

TABLE 25

Calculated Heat Capacities of Poly(L-Lysine) Hydrobromide

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.001	0.000	0.000	0.000	0.001	0.001
0.60	0.001	0.000	0.000	0.000	0.001	0.001
0.70	0.002	0.000	0.000	0.000	0.002	0.002
0.80	0.002	0.000	0.000	0.000	0.002	0.002
0.90	0.003	0.000	0.000	0.000	0.003	0.003
1.00	0.004	0.000	0.000	0.000	0.004	0.004
1.20	0.008	0.000	0.000	0.000	0.008	0.008
1.40	0.012	0.000	0.000	0.000	0.012	0.012
1.60	0.018	0.000	0.000	0.000	0.018	0.018
1.80	0.026	0.000	0.000	0.000	0.026	0.026
2.00	0.035	0.000	0.000	0.000	0.035	0.035
3.00	0.119	0.000	0.000	0.000	0.119	0.119
4.00	0.282	0.000	0.000	0.000	0.282	0.282
5.00	0.549	0.000	0.000	0.000	0.549	0.549
6.00	0.944	0.000	0.000	0.000	0.944	0.945
7.00	1.473	0.000	0.000	0.000	1.473	1.475
8.00	2.137	0.000	0.000	0.000	2.137	2.140
9.00	2.923	0.000	0.000	0.000	2.923	2.927
10.00	3.806	0.000	0.000	0.000	3.806	3.812
15.00	8.942	0.000	0.000	0.000	8.942	8.965
20.00	14.247	0.000	0.000	0.000	14.247	14.295
25.00	19.316	0.000	0.000	0.000	19.316	19.399
30.00	24.146	0.000	0.000	0.000	24.146	24.271
40.00	33.373	0.000	0.000	0.000	33.374	33.603
50.00	42.292	0.000	0.004	0.004	42.296	42.661
60.00	51.053	0.000	0.008	0.008	51.061	51.592
70.00	59.623	0.003	0.060	0.064	59.687	60.413
80.00	67.903	0.015	0.163	0.178	68.081	69.032
90.00	75.813	0.045	0.332	0.377	76.191	77.392
100.00	83.298	0.111	0.598	0.709	84.007	85.484
110.00	90.259	0.231	0.960	1.192	91.451	93.225
120.00	96.674	0.425	1.420	1.845	98.519	100.612
130.00	102.510	0.709	1.979	2.689	105.198	107.629
140.00	107.809	1.098	2.706	3.803	111.613	114.400
150.00	112.625	1.600	3.449	5.049	117.674	120.833
160.00	117.009	2.223	4.415	6.638	123.647	127.201
170.00	120.886	2.970	5.425	8.395	129.281	133.245
180.00	124.412	3.840	6.601	10.441	134.853	139.246

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	127.603	4.833	7.872	12.705	140.308	145.152
200.00	130.487	5.945	9.230	15.175	145.662	150.975
210.00	133.092	7.172	10.693	17.865	150.956	156.760
220.00	135.446	8.507	12.390	20.898	156.344	162.665
230.00	137.577	9.945	14.052	23.997	161.574	168.429
240.00	139.508	11.477	15.853	27.330	166.838	174.254
250.00	141.262	13.097	17.752	30.849	172.111	180.111
260.00	142.858	14.797	19.703	34.500	177.358	185.965
270.00	144.313	16.567	21.696	38.263	182.576	191.813
273.15	144.745	17.139	22.331	39.469	184.214	193.655
280.00	145.643	18.401	23.752	42.153	187.796	197.688
290.00	146.860	20.291	25.943	46.233	193.093	203.670
298.15	147.777	21.866	27.774	49.639	197.417	208.570
300.00	147.977	22.227	28.111	50.338	198.315	209.598
310.00	149.004	24.204	30.444	54.648	203.651	215.672
320.00	149.949	26.213	32.632	58.845	208.794	221.568
330.00	150.822	28.248	34.917	63.165	213.987	227.542
340.00	151.629	30.303	37.233	67.537	219.166	233.529
350.00	152.377	32.372	39.535	71.907	224.284	239.478
360.00	153.070	34.450	41.875	76.324	229.395	245.445
370.00	153.714	36.531	44.271	80.802	234.517	251.452
380.00	154.314	38.612	46.410	85.022	239.337	257.162
390.00	154.873	40.689	48.666	89.354	244.228	262.976
400.00	155.396	42.757	51.008	93.765	249.161	268.862
410.00	155.884	44.816	53.214	98.030	253.914	274.582
420.00	156.341	46.861	55.385	102.246	258.586	280.242
430.00	156.769	48.891	57.557	106.448	263.217	285.884
440.00	157.171	50.903	59.751	110.654	267.825	291.529
450.00	157.549	52.897	61.945	114.843	272.392	297.157
460.00	157.905	54.871	64.118	118.989	276.894	302.744
470.00	158.240	56.824	66.259	123.084	281.323	308.278
480.00	158.555	58.755	68.294	127.050	285.605	313.679
490.00	158.854	60.664	70.290	130.954	289.808	319.021
500.00	159.135	62.550	72.236	134.787	293.922	324.294
510.00	159.402	64.413	74.128	138.541	297.943	329.492
520.00	159.655	66.252	75.990	142.242	301.897	334.644
530.00	159.894	68.068	77.821	145.889	305.783	339.748
540.00	160.121	69.861	79.628	149.489	309.610	344.816
550.00	160.336	71.630	81.442	153.072	313.409	349.880
560.00	160.541	73.376	83.307	156.683	317.224	354.992
570.00	160.736	75.099	84.996	160.095	320.831	359.899
580.00	160.921	76.800	86.756	163.556	324.477	364.879
590.00	161.098	78.477	88.378	166.856	327.953	369.697
600.00	161.266	80.133	90.021	170.154	331.420	374.533

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	161.427	81.766	91.628	173.394	334.820	379.324
620.00	161.580	83.378	93.181	176.559	338.139	384.052
630.00	161.726	84.968	94.690	179.658	341.384	388.726
640.00	161.847	86.538	96.171	182.708	344.555	393.344
650.00	161.980	88.086	97.624	185.710	347.690	397.952
660.00	162.108	89.614	99.050	188.664	350.771	402.528
670.00	162.229	91.122	100.447	191.569	353.799	407.073
680.00	162.346	92.610	101.817	194.427	356.773	411.588
690.00	162.458	94.078	103.160	197.238	359.696	416.074
700.00	162.564	95.528	104.714	200.241	362.806	420.809
710.00	162.667	96.958	105.784	202.742	365.409	424.987
720.00	162.765	98.369	107.057	205.426	368.191	429.405
730.00	162.859	99.762	108.373	208.135	370.994	433.880
740.00	162.950	101.137	109.613	210.750	373.700	438.274
750.00	163.037	102.494	110.824	213.317	376.354	442.640
760.00	163.120	103.833	111.961	215.793	378.913	446.929
770.00	163.201	105.154	113.183	218.337	381.537	451.328
780.00	163.278	106.458	114.333	220.791	384.069	455.652
790.00	163.352	107.745	115.465	223.210	386.562	459.966
800.00	163.424	109.015	116.519	225.534	388.959	464.200
810.00	163.493	110.269	117.570	227.839	391.332	468.442
820.00	163.560	111.506	118.635	230.141	393.701	472.715
830.00	163.624	112.727	119.680	232.407	396.031	476.979
840.00	163.686	113.932	120.714	234.646	398.332	481.245
850.00	163.746	115.121	121.718	236.839	400.584	485.492
860.00	163.803	116.294	122.702	238.996	402.800	489.733
870.00	163.859	117.452	123.667	241.119	404.978	493.969
880.00	163.913	118.594	124.613	243.208	407.121	498.202
890.00	163.965	119.722	125.530	245.252	409.217	502.420
900.00	164.016	120.834	126.440	247.274	411.289	506.650
910.00	164.064	121.932	127.331	249.263	413.327	510.881
920.00	164.112	123.015	128.205	251.220	415.331	515.115
930.00	164.157	124.083	129.069	253.152	417.310	519.362
940.00	164.202	125.137	129.910	255.047	419.249	523.606
950.00	164.244	126.177	130.734	256.911	421.156	527.858
960.00	164.286	127.203	131.542	258.745	423.031	532.119
970.00	164.326	128.216	132.334	260.550	424.877	536.391
980.00	164.365	129.214	133.116	262.330	426.696	540.681
990.00	164.403	130.200	133.879	264.078	428.482	544.981
1000.00	164.440	131.172	134.615	265.786	430.226	549.283

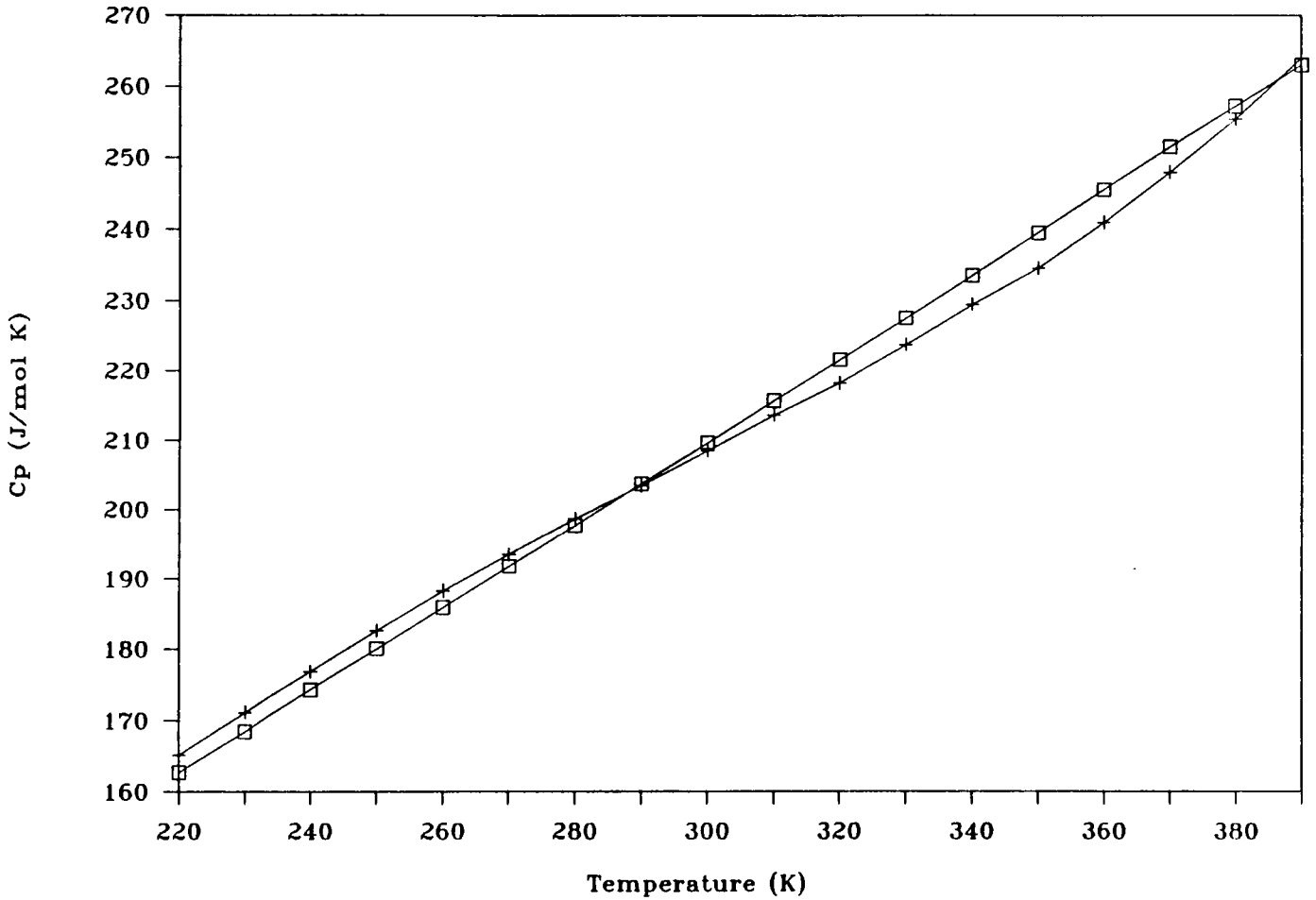


Figure 48 Heat Capacities of Poly(L-lysine•HBr). Curve (□): Calculations. Curve (+): Measurements.

vibration information on the backbone unit (Part A of Table 13), a CH_2 group from polyethylene (Part D of Table 13), and a five-membered ring[72] (Part O of Table 13). In addition the C-CH_2 stretch was taken from polycyclopentene[63] (PCP) (Part P of Table 13). The five-membered ring is not difficult to access, as it is the same five-membered ring that makes up the small compound imidazole[72] (see Part O of Table 13). And fortunately, a complete assignment of the infrared vibrations of imidazole has been preciously worked out. For the skeletal vibrations, six are taken for the backbone unit, two for the CH_2 group, and five for the imidazole group. Thus poly(L-hisdidine) is composed of thirteen skeletal vibrations and thirty-eight group vibrations.

Fitting the experimental heat capacities (given in Table 6) in the temperature range 230 to 310 K resulted in a Θ_1-temperature of 801.2 ± 34.0 K. Combining this with the general value for Θ_3, heat capacity calculations were carried out. The results are listed in Table 26. Good agreement between experiment and calculation was observed as seen in Figure 49. The RMS deviation is ± 1.26%, and the average deviation is 0.76%.

IIP. Poly(L-histidine) hydrochloride

Construction of the group vibrational spectrum of poly(l-histidine)•HCl was similiar to that of poly(L-histidine). The backbone unit (Part A of Table 13) was put together with a CH_2 group from polyethylene (Part D of Table 13), and a C−CH_2 stretch from polycyclopentene (Part P of Table 13). The five-membered ring taken

TABLE 26

Calculated Heat Capacities of Poly(L-Histidine)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.000	0.000	0.000	0.000	0.000	0.000
0.60	0.001	0.000	0.000	0.000	0.001	0.001
0.70	0.001	0.000	0.000	0.000	0.001	0.001
0.80	0.002	0.000	0.000	0.000	0.002	0.002
0.90	0.002	0.000	0.000	0.000	0.002	0.002
1.00	0.003	0.000	0.000	0.000	0.003	0.003
1.20	0.005	0.000	0.000	0.000	0.005	0.005
1.40	0.008	0.000	0.000	0.000	0.008	0.008
1.60	0.012	0.000	0.000	0.000	0.012	0.012
1.80	0.018	0.000	0.000	0.000	0.018	0.018
2.00	0.024	0.000	0.000	0.000	0.024	0.024
3.00	0.081	0.000	0.000	0.000	0.081	0.081
4.00	0.193	0.000	0.000	0.000	0.193	0.193
5.00	0.375	0.000	0.000	0.000	0.375	0.376
6.00	0.646	0.000	0.000	0.000	0.646	0.646
7.00	1.007	0.000	0.000	0.000	1.007	1.008
8.00	1.461	0.000	0.000	0.000	1.461	1.463
9.00	1.999	0.000	0.000	0.000	1.999	2.002
10.00	2.602	0.000	0.000	0.000	2.602	2.607
15.00	6.114	0.000	0.000	0.000	6.114	6.130
20.00	9.741	0.000	0.000	0.000	9.741	9.775
25.00	13.207	0.000	0.000	0.000	13.207	13.264
30.00	16.510	0.000	0.000	0.000	16.510	16.595
40.00	22.820	0.000	0.000	0.000	22.820	22.977
50.00	28.927	0.000	0.004	0.004	28.931	29.181
60.00	34.926	0.000	0.009	0.009	34.935	35.298
70.00	40.864	0.003	0.084	0.087	40.951	41.450
80.00	46.710	0.012	0.176	0.189	46.899	47.553
90.00	52.402	0.037	0.391	0.428	52.830	53.663
100.00	57.896	0.090	0.771	0.862	58.757	59.790
110.00	63.158	0.186	1.238	1.424	64.582	65.835
120.00	68.165	0.338	1.950	2.289	70.454	71.951
130.00	72.844	0.560	2.742	3.302	76.145	77.904
140.00	77.208	0.861	3.800	4.661	81.869	83.913
150.00	81.235	1.247	4.955	6.202	87.437	89.785
160.00	84.943	1.722	6.383	8.105	93.048	95.723
170.00	88.360	2.286	7.990	10.276	98.635	101.659
180.00	91.509	2.936	9.729	12.665	104.174	107.568

TABLE 26 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	94.396	3.668	11.581	15.249	109.645	113.430
200.00	97.004	4.476	13.539	18.016	115.020	119.215
210.00	99.408	5.356	15.582	20.937	120.345	124.972
220.00	101.616	6.298	17.995	24.293	125.909	130.999
230.00	103.641	7.297	20.265	27.562	131.203	136.770
240.00	105.497	8.346	22.792	31.138	136.636	142.709
250.00	107.199	9.437	25.313	34.750	141.949	148.547
260.00	108.761	10.563	27.964	38.527	147.288	154.436
270.00	110.196	11.719	30.536	42.255	152.451	160.164
273.15	110.623	12.088	31.374	43.463	154.086	161.982
280.00	111.515	12.898	33.266	46.164	157.679	165.985
290.00	112.730	14.095	36.035	50.130	162.859	171.780
298.15	113.649	15.079	38.359	53.438	167.087	176.528
300.00	113.850	15.304	38.806	54.109	167.959	177.514
310.00	114.884	16.520	41.744	58.264	173.149	183.369
320.00	115.841	17.740	44.381	62.121	177.962	188.850
330.00	116.728	18.960	47.415	66.374	183.102	194.701
340.00	117.550	20.176	50.340	70.516	188.066	200.391
350.00	118.314	21.385	53.289	74.674	192.988	206.061
360.00	119.025	22.584	55.939	78.523	197.548	211.371
370.00	119.688	23.772	58.940	82.712	202.400	217.016
380.00	120.306	24.947	61.671	86.618	206.924	222.335
390.00	120.884	26.106	64.422	90.528	211.411	227.640
400.00	121.424	27.248	67.361	94.609	216.033	233.115
410.00	121.930	28.372	70.110	98.482	220.413	238.354
420.00	122.405	29.478	72.913	102.392	224.797	243.623
430.00	122.851	30.565	75.591	106.156	229.007	248.728
440.00	123.271	31.632	78.252	109.883	233.154	253.789
450.00	123.665	32.678	80.909	113.587	237.252	258.823
460.00	124.037	33.704	83.554	117.257	241.295	263.821
470.00	124.388	34.709	86.177	120.886	245.274	268.775
480.00	124.720	35.693	88.713	124.407	249.127	273.615
490.00	125.033	36.657	91.158	127.815	252.849	278.337
500.00	125.329	37.601	93.550	131.151	256.480	282.983
510.00	125.610	38.524	95.896	134.420	260.030	287.564
520.00	125.876	39.427	98.200	137.628	263.504	292.086
530.00	126.129	40.311	100.531	140.842	266.971	296.625
540.00	126.369	41.175	102.899	144.074	270.443	301.194
550.00	126.596	42.020	105.083	147.103	273.700	305.550
560.00	126.813	42.847	107.331	150.178	276.991	309.968
570.00	127.019	43.656	109.559	153.215	280.234	314.358
580.00	127.216	44.446	111.713	156.159	283.375	318.659
590.00	127.403	45.220	113.800	159.019	286.422	322.880
600.00	127.582	45.976	115.846	161.822	289.404	327.051

TABLE 26 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	127.752	46.716	117.856	164.572	292.325	331.180
620.00	127.915	47.440	119.814	167.253	295.169	335.247
630.00	128.071	48.148	121.725	169.873	297.944	339.261
640.00	128.220	48.840	123.608	172.448	300.669	343.244
650.00	128.363	49.518	125.434	174.953	303.315	347.163
660.00	128.499	50.181	127.254	177.435	305.935	351.076
670.00	128.630	50.831	129.041	179.872	308.502	354.956
680.00	128.756	51.466	130.796	182.262	311.018	358.803
690.00	128.876	52.088	132.519	184.607	313.483	362.618
700.00	128.992	52.697	134.447	187.145	316.137	366.679
710.00	129.103	53.294	135.887	189.181	318.284	370.179
720.00	129.209	53.878	137.524	191.402	320.612	373.915
730.00	129.312	54.450	139.130	193.580	322.892	377.624
740.00	129.411	55.011	140.714	195.725	325.136	381.318
750.00	129.490	55.560	142.597	198.156	327.646	385.354
760.00	129.581	56.098	143.804	199.902	329.483	388.626
770.00	129.668	56.625	145.366	201.991	331.660	392.327
780.00	129.753	57.142	146.849	203.991	333.744	395.947
790.00	129.834	57.648	148.307	205.955	335.789	399.551
800.00	129.912	58.145	149.679	207.824	337.736	403.068
810.00	129.987	58.632	151.073	209.705	339.692	406.627
820.00	130.060	59.109	152.459	211.568	341.628	410.191
830.00	130.130	59.577	153.818	213.395	343.525	413.741
840.00	130.197	60.036	155.161	215.197	345.395	417.289
850.00	130.262	60.486	156.469	216.955	347.217	420.814
860.00	130.325	60.928	157.751	218.679	349.004	424.327
870.00	130.386	61.361	159.009	220.370	350.756	427.833
880.00	130.445	61.786	160.243	222.030	352.475	431.330
890.00	130.502	62.204	161.444	223.647	354.149	434.809
900.00	130.557	62.613	162.664	225.277	355.834	438.337
910.00	130.610	63.015	163.831	226.846	357.455	441.823
920.00	130.661	63.409	164.976	228.385	359.046	445.308
930.00	130.711	63.796	166.108	229.904	360.615	448.803
940.00	130.759	64.176	167.212	231.388	362.147	452.291
950.00	130.806	64.549	168.262	232.811	363.617	455.741
960.00	130.851	64.915	169.326	234.242	365.093	459.239
970.00	130.895	65.275	170.372	235.646	366.541	462.745
980.00	130.938	65.628	171.399	237.027	367.965	466.261
990.00	130.979	65.975	172.395	238.370	369.349	469.771
1000.00	131.019	66.315	173.362	239.677	370.696	473.279

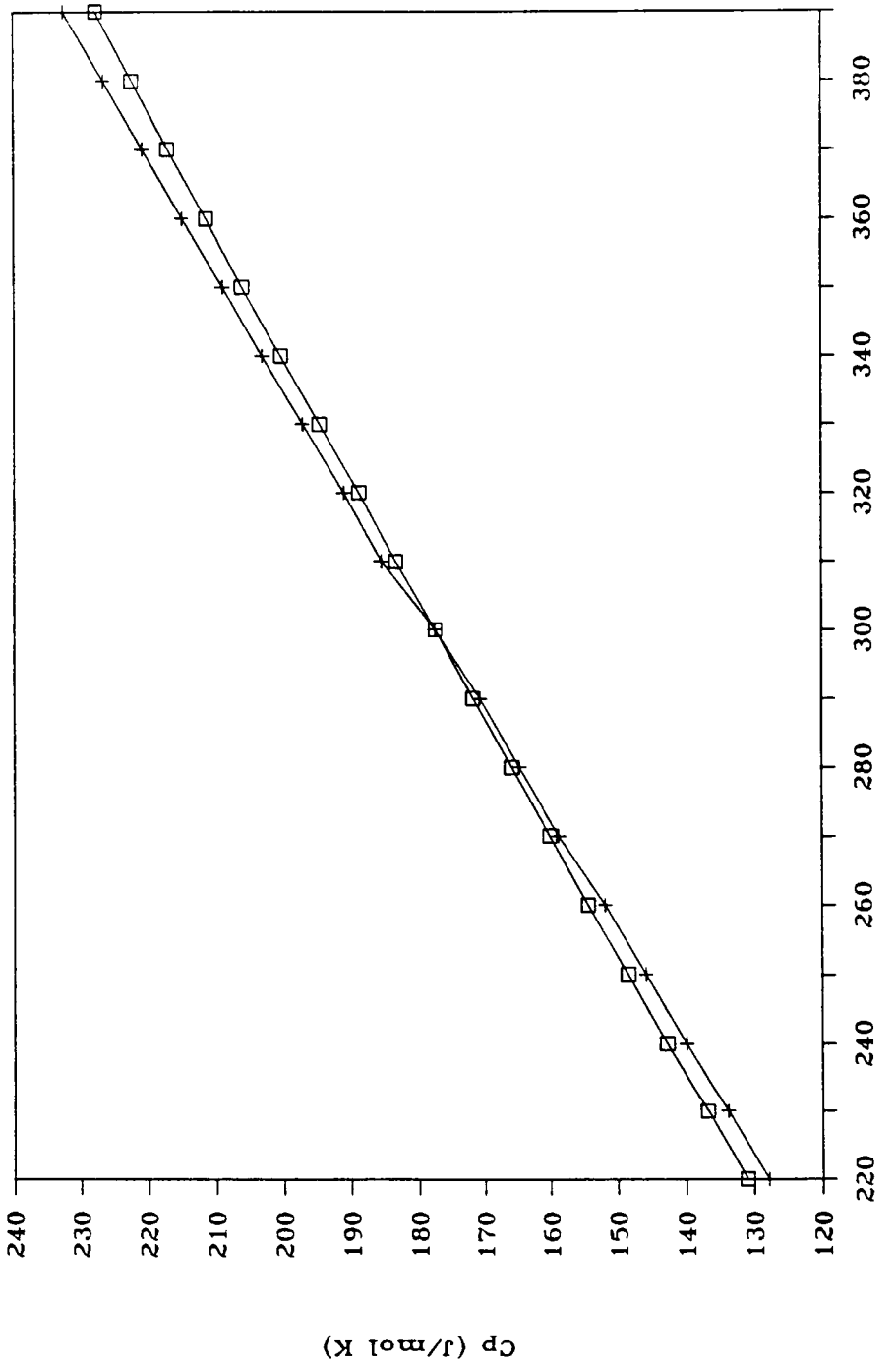


Figure 49 Heat Capacities of Poly(L-histidine). Curve (□): Calculations. Curve (+): Measurements.

from imidazole was modified by replacing the three NH vibrations with six vibrations for the NH_2 group (Part Q of Table 13). For the skeletal vibrations, six were taken for the backbone unit, two for the CH_2 group, eight for the ring group, and three for the chlorine atom.

Fitting the experimental heat capacities (given in Table 6) in the temperature range 220 to 260 K resulted in a Θ_1-temperature of 744.5 ± 23.4 K. Combining this with the general value for Θ_3, heat capacities were calculated and are listed in Table 27. Figure 50 illustrated that good agreement between experiment and calculation was observed. The RMS deviation is ± 1.48%, and the average deviation is −0.06%.

IIQ. Poly(L-arginine) hydrochloride

Poly(L-arginine) hydrochloride is the final poly(amino acid) for which both heat capacity measurements and calculations were performed. Poly(L-arginine) has a relatively long side group R. Its group vibrational spectrum, however, is easily constructed from information on small groups. For the specturm, the backbone unit group vibrations (Part A of Table 13) are first needed. To these vibrations are added the group vibrations of three CH_2 groups (polyethylene) (Part D of Table 13, taken three times), the vibrations of an NH group which were taken from a number of small molecules[67,70-71] (see Part R of Table 13), the vibrations of a $C-NH_2$ group which were taken from information on propionamide[65] and methylamine[66] (Part H of Table 13), the vibrations of an NH_2^+ group which were taken from information on a number of small molecules[67,70-71] (Part Q of Table 13), and a C=N stretching

TABLE 27

Calculated Heat Capacities of Poly(L-Histidine) Hydrochloride

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.000	0.000	0.000	0.000	0.000	0.000
0.60	0.000	0.000	0.000	0.000	0.000	0.000
0.70	0.001	0.000	0.000	0.000	0.001	0.001
0.80	0.001	0.000	0.000	0.000	0.001	0.001
0.90	0.002	0.000	0.000	0.000	0.002	0.002
1.00	0.002	0.000	0.000	0.000	0.002	0.002
1.20	0.004	0.000	0.000	0.000	0.004	0.004
1.40	0.006	0.000	0.000	0.000	0.006	0.006
1.60	0.009	0.000	0.000	0.000	0.009	0.009
1.80	0.013	0.000	0.000	0.000	0.013	0.013
2.00	0.018	0.000	0.000	0.000	0.018	0.018
3.00	0.061	0.000	0.000	0.000	0.061	0.061
4.00	0.146	0.000	0.000	0.000	0.146	0.146
5.00	0.283	0.000	0.000	0.000	0.283	0.284
6.00	0.488	0.000	0.000	0.000	0.488	0.488
7.00	0.760	0.000	0.000	0.000	0.760	0.761
8.00	1.103	0.000	0.000	0.000	1.103	1.105
9.00	1.509	0.000	0.000	0.000	1.509	1.511
10.00	1.965	0.000	0.000	0.000	1.965	1.968
15.00	4.616	0.000	0.000	0.000	4.616	4.628
20.00	7.355	0.000	0.000	0.000	7.355	7.380
25.00	9.972	0.000	0.000	0.000	9.972	10.014
30.00	12.465	0.000	0.000	0.000	12.465	12.529
40.00	17.229	0.000	0.000	0.000	17.229	17.348
50.00	21.840	0.000	0.004	0.004	21.845	22.033
60.00	26.378	0.000	0.009	0.009	26.387	26.662
70.00	30.862	0.003	0.084	0.087	30.949	31.326
80.00	35.310	0.010	0.176	0.187	35.497	35.993
90.00	39.675	0.030	0.391	0.421	40.096	40.728
100.00	43.922	0.070	0.771	0.842	44.763	45.550
110.00	48.023	0.140	1.238	1.378	49.401	50.360
120.00	51.959	0.248	1.951	2.199	54.158	55.308
130.00	55.714	0.404	2.742	3.146	58.859	60.219
140.00	59.231	0.614	3.799	4.414	63.644	65.234
150.00	62.532	0.885	4.954	5.839	68.371	70.207
160.00	65.595	1.222	6.381	7.603	73.197	75.302
170.00	68.432	1.626	7.959	9.585	78.018	80.410
180.00	71.062	2.101	9.712	11.813	82.875	85.575

TABLE 27 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	73.499	2.647	11.571	14.218	87.716	90.745
200.00	75.761	3.262	13.526	16.788	92.549	95.925
210.00	77.812	3.946	15.557	19.503	97.315	101.057
220.00	79.706	4.695	17.950	22.645	102.352	106.490
230.00	81.459	5.505	20.193	25.698	107.157	111.704
240.00	83.078	6.372	22.685	29.057	112.135	117.119
250.00	84.572	7.292	25.156	32.448	117.020	122.459
260.00	85.949	8.259	27.751	36.010	121.959	127.878
270.00	87.220	9.268	30.261	39.529	126.750	133.162
273.15	87.600	9.593	31.078	40.672	128.272	134.845
280.00	88.394	10.313	32.915	43.228	131.622	138.555
290.00	89.478	11.389	35.613	47.002	136.481	143.956
298.15	90.302	12.286	37.871	50.157	140.459	148.394
300.00	90.481	12.492	38.302	50.794	141.275	149.312
310.00	91.410	13.616	41.147	54.763	146.174	154.801
320.00	92.272	14.756	43.681	58.437	150.709	159.929
330.00	93.071	15.909	46.601	62.510	155.581	165.437
340.00	93.815	17.070	49.403	66.473	160.288	170.792
350.00	94.507	18.236	52.218	70.454	164.960	176.135
360.00	95.151	19.402	54.726	74.128	169.279	181.124
370.00	95.753	20.567	57.574	78.142	173.895	186.453
380.00	96.316	21.728	60.014	81.743	178.059	191.320
390.00	96.842	22.882	62.671	85.553	182.395	196.397
400.00	97.335	24.028	65.395	89.423	186.759	201.526
410.00	97.798	25.163	67.922	93.085	190.882	206.420
420.00	98.232	26.287	70.496	96.783	195.014	211.346
430.00	98.640	27.397	72.939	100.336	198.976	216.111
440.00	99.024	28.493	75.361	103.854	202.878	220.834
450.00	99.386	29.574	77.775	107.349	206.735	225.532
460.00	99.727	30.640	80.174	110.813	210.541	230.196
470.00	100.050	31.689	82.549	114.238	214.288	234.819
480.00	100.354	32.722	84.834	117.557	217.911	239.331
490.00	100.642	33.739	87.027	120.765	221.408	243.726
500.00	100.915	34.738	89.165	123.903	224.818	248.049
510.00	101.174	35.720	91.256	126.976	228.150	252.309
520.00	101.419	36.685	93.306	129.991	231.410	256.511
530.00	101.652	37.633	95.381	133.015	234.666	260.732
540.00	101.873	38.565	97.471	136.036	237.909	264.961
550.00	102.083	39.479	99.395	138.875	240.958	268.998
560.00	102.283	40.377	101.382	141.759	244.042	273.097
570.00	102.474	41.259	103.299	144.559	247.032	277.113
580.00	102.655	42.125	105.098	147.223	249.878	280.992
590.00	102.828	42.975	106.862	149.836	252.665	284.825
600.00	102.994	43.809	108.640	152.449	255.443	288.672

TABLE 27 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	103.152	44.628	110.376	155.005	258.156	292.470
620.00	103.303	45.433	112.054	157.487	260.789	296.200
630.00	103.447	46.222	113.683	159.905	263.351	299.872
640.00	103.585	46.997	115.279	162.276	265.861	303.507
650.00	103.717	47.758	116.842	164.601	268.318	307.106
660.00	103.844	48.506	118.374	166.880	270.723	310.669
670.00	103.965	49.240	119.874	169.113	273.079	314.199
680.00	104.082	49.960	121.342	171.303	275.384	317.695
690.00	104.193	50.668	122.780	173.448	277.641	321.158
700.00	104.301	51.363	124.425	175.788	280.089	324.867
710.00	104.404	52.046	125.583	177.629	282.033	328.017
720.00	104.503	52.717	126.941	179.657	284.160	331.404
730.00	104.598	53.376	128.270	181.645	286.243	334.763
740.00	104.690	54.023	129.581	183.603	288.293	338.109
750.00	104.778	54.659	131.192	185.851	290.629	341.817
760.00	104.863	55.284	132.132	187.416	292.278	344.743
770.00	104.945	55.898	133.429	189.327	294.272	348.100
780.00	105.023	56.501	134.651	191.152	296.176	351.377
790.00	105.100	57.094	135.851	192.945	298.044	354.639
800.00	105.173	57.677	136.968	194.645	299.818	357.815
810.00	105.231	58.250	138.118	196.367	301.598	361.026
820.00	105.299	58.813	139.244	198.056	303.355	364.237
830.00	105.365	59.366	140.347	199.713	305.078	367.435
840.00	105.428	59.910	141.437	201.348	306.776	370.632
850.00	105.489	60.445	142.496	202.941	308.431	373.805
860.00	105.548	60.971	143.534	204.504	310.053	376.969
870.00	105.605	61.488	144.550	206.038	311.643	380.124
880.00	105.661	61.996	145.546	207.542	313.202	383.272
890.00	105.714	62.496	146.511	209.006	314.720	386.401
900.00	105.766	62.987	147.499	210.486	316.251	389.577
910.00	105.815	63.471	148.436	211.906	317.722	392.711
920.00	105.864	63.946	149.354	213.300	319.164	395.843
930.00	105.910	64.413	150.261	214.675	320.585	398.984
940.00	105.956	64.873	151.144	216.017	321.973	402.117
950.00	106.000	65.325	151.975	217.300	323.300	405.209
960.00	106.042	65.770	152.823	218.592	324.634	408.348
970.00	106.083	66.207	153.653	219.861	325.944	411.492
980.00	106.123	66.637	154.472	221.109	327.233	414.648
990.00	106.162	67.060	155.271	222.331	328.493	417.807
1000.00	106.200	67.477	156.042	223.519	329.719	420.962

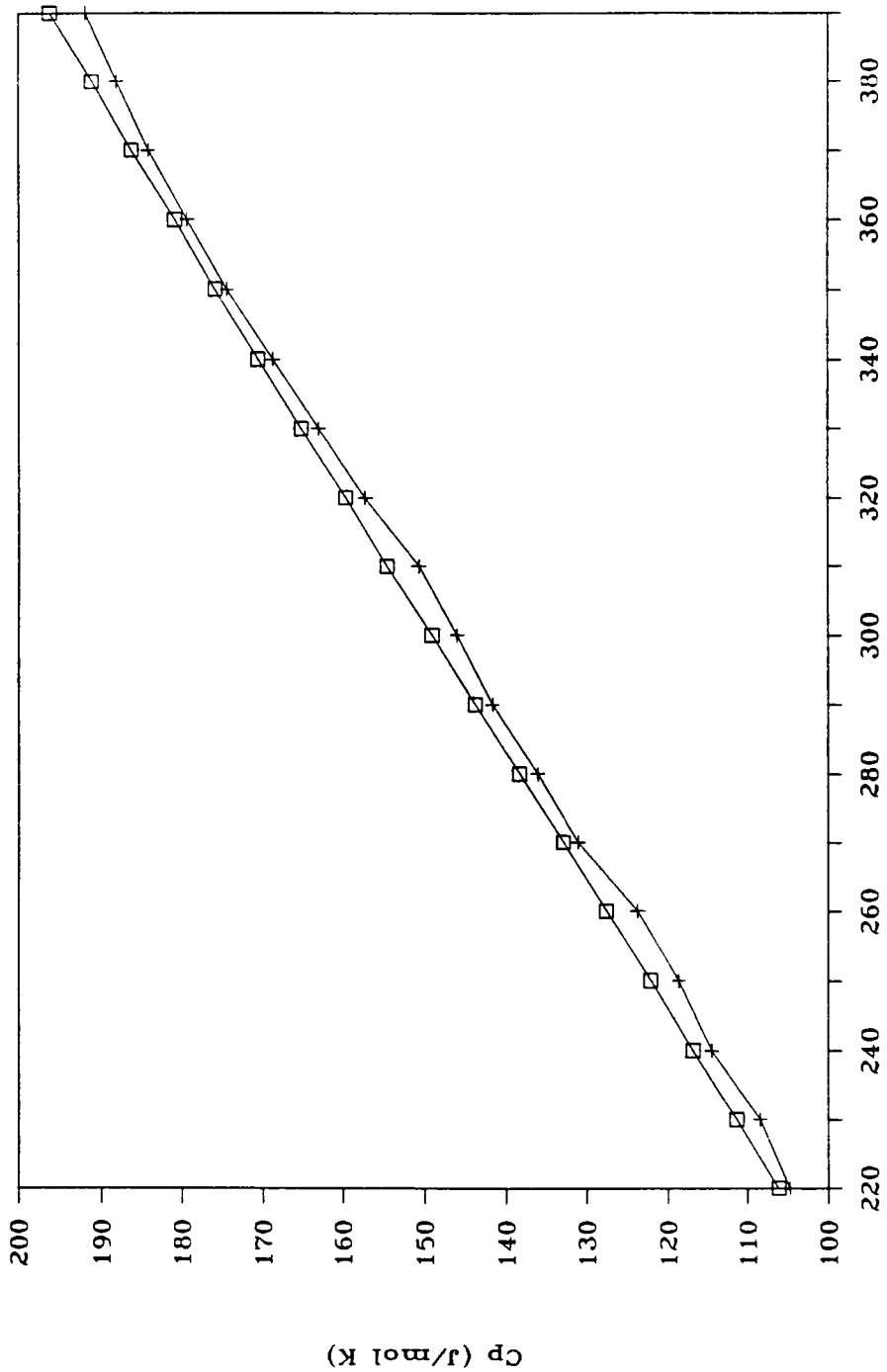


Figure 50 Heat Capacities of Poly(L-histidine•HCl). Curve (□): Calculations. Curve (+): Measurements.

vibration, also taken from information on a number of small molecules (see Part S of Table 13). Twenty-three skeletal vibrations are taken for the calculations; six for the backbone, two for each CH_2 group for a total of six, two for the NH group, two for the NH_2 group (treated similarily to CH_2), two for the NH_2^+ group (treated similarily to CH_2), two for the C=N group, and finally three for the Cl^- ion.

Fitting the experimental heat capacities (listed in Table 7) in the temperature range 220 to 330 K resulted in a Θ_1-temperature of 609.5 ± 14.4 K. Using this and 68.0 K for Θ_3, heat capacities were calculated form 0 to 1000 K and are listed in Table 28. Excellent agreement between experiment and calculation was observed as is seen in Figure 51. The RMS deviation was ± 0.443%; the average deviation 0.30%.

IIR. Poly(L-lysine • HBr)-alanine

Poly(L-lysine • HBr)-alanine is a copolymer whose repeat unit consists of one poly(L-lysine) • HBr and one poly(L-alanine). Construction of a group vibrational spectrum for a copolymer is made easy by the fact that the group vibrational spectrum of each of its parts has already been constructed. Thus, all that is necessary is a combination of the two spectra. For poly(L-lysine • HBr)-alanine, this requires combining Table 11 with Parts A, D, and N of Table 13. Similarily, determining the number of skeletal vibrations simply requires adding the number of skeletal vibrations for the two homopolymers making up the copolymer. Poly(L-lysine) • HBr has twenty skeletal vibrations, poly(L-alanine) nine. Thus the number of skeletal

TABLE 28

Calculated Heat Capacities of Poly(L-Arginine) Hydrochloride

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.001	0.000	0.000	0.000	0.001	0.001
0.60	0.001	0.000	0.000	0.000	0.001	0.001
0.70	0.002	0.000	0.000	0.000	0.002	0.002
0.80	0.003	0.000	0.000	0.000	0.003	0.003
0.90	0.004	0.000	0.000	0.000	0.004	0.004
1.00	0.005	0.000	0.000	0.000	0.005	0.005
1.20	0.009	0.000	0.000	0.000	0.009	0.009
1.40	0.015	0.000	0.000	0.000	0.015	0.015
1.60	0.022	0.000	0.000	0.000	0.022	0.022
1.80	0.031	0.000	0.000	0.000	0.031	0.031
2.00	0.042	0.000	0.000	0.000	0.042	0.042
3.00	0.143	0.000	0.000	0.000	0.143	0.143
4.00	0.338	0.000	0.000	0.000	0.338	0.339
5.00	0.659	0.000	0.000	0.000	0.659	0.660
6.00	1.134	0.000	0.000	0.000	1.134	1.135
7.00	1.769	0.000	0.000	0.000	1.769	1.771
8.00	2.566	0.000	0.000	0.000	2.566	2.569
9.00	3.509	0.000	0.000	0.000	3.509	3.514
10.00	4.569	0.000	0.000	0.000	4.569	4.577
15.00	10.735	0.000	0.000	0.000	10.735	10.763
20.00	17.103	0.000	0.000	0.000	17.103	17.162
25.00	23.189	0.000	0.000	0.000	23.189	23.289
30.00	28.988	0.000	0.000	0.000	28.988	29.138
40.00	40.065	0.000	0.000	0.000	40.065	40.341
50.00	50.765	0.000	0.004	0.004	50.769	51.208
60.00	61.268	0.000	0.008	0.008	61.276	61.913
70.00	71.484	0.003	0.060	0.063	71.548	72.419
80.00	81.299	0.015	0.162	0.177	81.476	82.614
90.00	90.618	0.046	0.331	0.377	90.995	92.430
100.00	99.383	0.116	0.592	0.708	100.091	101.850
110.00	107.427	0.245	0.950	1.194	108.622	110.730
120.00	114.776	0.458	1.403	1.860	116.636	119.114
130.00	121.424	0.776	1.941	2.717	124.141	127.009
140.00	127.436	1.220	2.640	3.860	131.296	134.574
150.00	132.880	1.804	3.357	5.161	138.041	141.747
160.00	137.727	2.538	4.252	6.789	144.516	148.671
170.00	142.076	3.427	5.288	8.716	150.791	155.414
180.00	145.998	4.474	6.383	10.857	156.855	161.966

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	149.528	5.676	7.570	13.246	162.774	168.393
200.00	152.701	7.028	8.839	15.867	168.568	174.717
210.00	155.557	8.522	10.208	18.730	174.287	180.988
220.00	158.130	10.150	11.809	21.959	180.089	187.370
230.00	160.451	11.901	13.361	25.262	185.714	193.594
240.00	162.551	13.765	15.076	28.841	191.392	199.899
250.00	164.454	15.729	16.888	32.617	197.071	206.231
260.00	166.182	17.783	18.761	36.544	202.726	212.564
270.00	167.755	19.915	20.652	40.567	208.322	218.862
273.15	168.222	20.601	21.265	41.866	210.088	220.854
280.00	169.191	22.114	22.637	44.751	213.942	225.211
290.00	170.504	24.370	24.719	49.089	219.593	231.621
298.15	171.492	26.243	26.477	52.719	224.211	236.879
300.00	171.707	26.672	26.797	53.469	225.176	237.986
310.00	172.812	29.011	29.040	58.051	230.863	244.489
320.00	173.828	31.378	31.158	62.537	236.365	250.825
330.00	174.766	33.766	33.357	67.122	241.888	257.211
340.00	175.632	36.166	35.587	71.753	247.385	263.597
350.00	176.433	38.573	37.822	76.395	252.828	269.956
360.00	177.177	40.980	40.082	81.063	258.239	276.308
370.00	177.867	43.383	42.420	85.802	263.669	282.710
380.00	178.509	45.775	44.776	90.551	269.060	289.099
390.00	179.107	48.154	46.935	95.089	274.196	295.245
400.00	179.666	50.515	49.250	99.765	279.431	301.526
410.00	180.187	52.856	51.486	104.342	284.529	307.689
420.00	180.675	55.174	53.703	108.878	289.553	313.802
430.00	181.133	57.467	55.925	113.393	294.526	319.889
440.00	181.562	59.733	58.165	117.899	299.461	325.965
450.00	181.966	61.971	60.414	122.385	304.351	332.022
460.00	182.345	64.180	62.647	126.827	309.171	338.034
470.00	182.702	66.358	64.851	131.209	313.911	343.988
480.00	183.039	68.504	66.965	135.470	318.509	349.817
490.00	183.357	70.620	69.042	139.662	323.019	355.580
500.00	183.657	72.704	71.075	143.779	327.436	361.271
510.00	183.941	74.756	73.060	147.816	331.757	366.887
520.00	184.210	76.776	75.019	151.795	336.005	372.451
530.00	184.464	78.765	76.947	155.712	340.176	377.962
540.00	184.706	80.722	78.866	159.588	344.294	383.444
550.00	184.935	82.649	80.743	163.391	348.327	388.861
560.00	185.153	84.544	82.664	167.208	352.361	394.312
570.00	185.360	86.409	84.568	170.978	356.338	399.729
580.00	185.557	88.245	86.484	174.729	360.287	405.147
590.00	185.745	90.051	88.336	178.387	364.132	410.480
600.00	185.924	91.828	90.137	181.965	367.889	415.746

TABLE 28 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	186.072	93.576	91.868	185.444	371.517	420.898
620.00	186.235	95.297	93.554	188.851	375.086	426.016
630.00	186.390	96.991	95.202	192.193	378.583	431.083
640.00	186.537	98.658	96.829	195.487	382.024	436.119
650.00	186.678	100.298	98.407	198.705	385.383	441.094
660.00	186.813	101.913	99.984	201.897	388.710	446.065
670.00	186.942	103.502	101.535	205.038	391.980	451.004
680.00	187.065	105.067	103.061	208.128	395.193	455.911
690.00	187.183	106.608	104.560	211.168	398.350	460.788
700.00	187.296	108.125	106.270	214.395	401.691	465.911
710.00	187.404	109.618	107.497	217.116	404.520	470.475
720.00	187.508	111.089	108.926	220.015	407.523	475.277
730.00	187.607	112.538	110.329	222.866	410.474	480.052
740.00	187.703	113.964	111.715	225.679	413.382	484.813
750.00	187.795	115.369	113.066	228.435	416.230	489.540
760.00	187.883	116.753	114.378	231.131	419.014	494.228
770.00	187.968	118.116	115.737	233.852	421.820	498.979
780.00	188.050	119.458	117.019	236.478	424.528	503.651
790.00	188.128	120.781	118.281	239.062	427.190	508.308
800.00	188.204	122.084	119.500	241.584	429.788	512.927
810.00	188.277	123.368	120.710	244.078	432.355	517.549
820.00	188.347	124.633	121.918	246.551	434.898	522.181
830.00	188.415	125.879	123.104	248.983	437.399	526.802
840.00	188.481	127.107	124.241	251.348	439.829	531.380
850.00	188.544	128.317	125.382	253.699	442.243	535.981
860.00	188.605	129.509	126.502	256.011	444.616	540.574
870.00	188.664	130.683	127.601	258.285	446.948	545.162
880.00	188.721	131.841	128.680	260.521	449.242	549.746
890.00	188.776	132.982	129.728	262.709	451.485	554.315
900.00	188.829	134.106	130.767	264.873	453.702	558.896
910.00	188.881	135.213	131.787	267.000	455.881	563.479
920.00	188.931	136.305	132.788	269.093	458.024	568.065
930.00	188.979	137.381	133.779	271.160	460.138	572.665
940.00	189.026	138.441	134.744	273.185	462.211	577.263
950.00	189.071	139.486	135.693	275.178	464.249	581.870
960.00	189.115	140.516	136.624	277.140	466.255	586.488
970.00	189.158	141.531	137.539	279.069	468.227	591.119
980.00	189.199	142.531	138.439	280.970	470.168	595.767
990.00	189.239	143.517	139.310	282.826	472.065	600.415
1000.00	189.278	144.488	140.154	284.642	473.920	605.068

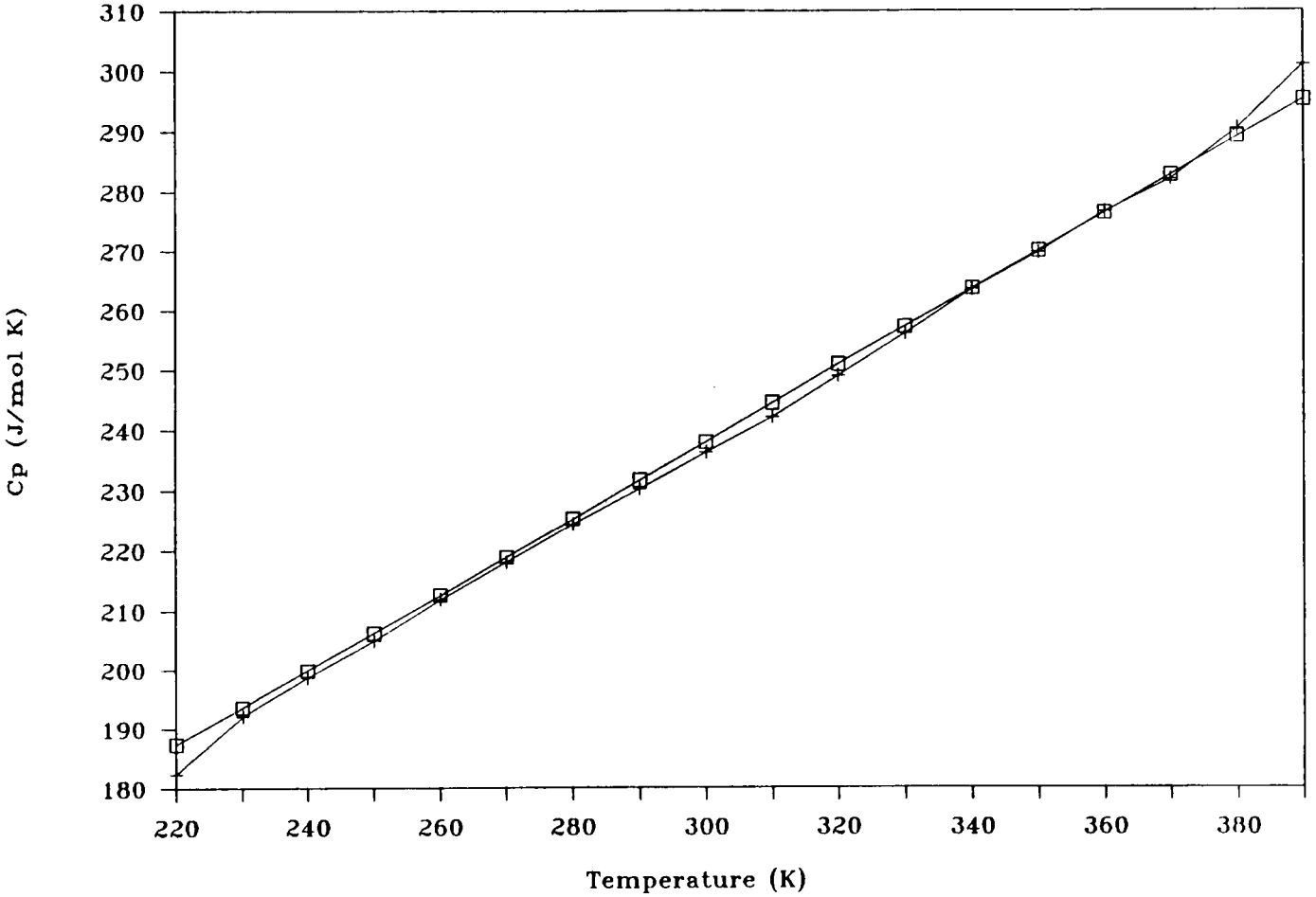


Figure 51 Heat Capacities of Poly(L-arginine•HCl). Curve (□): Calculations. Curve (+): Measurements.

vibrations for the copolymer becomes twenty-nine.

Calculation of heat capacity is carried out for a copolymer in the same manner as for a homopolymer. Like for the homopolymers, an equilbrium melting temperature of 573 K and the universal value for A_o were chosen as computation parameters for the copolymers. Again, no information regarding the equilbrium melting temperature nor the expansivity or compressibility of the copolymers exists. Fitting the experimental data (listed in Table 8) in the temperature range 240 to 340 K resulted in a Θ_1-temperature of 656.3 ± 33.3 K. Again, since low-temperature heat capacities do not exist for the copolymers, it is not possible to determine a Θ_3-temperature for each. As a result, the value of 68.0 K (average of Θ_3-temperatures of PG, PLA, PLV) will be used for the computations. Calculating heat capacities using these Θ-temperatures resulted in the data in Table 29. Figure 52 shows the comparison of calculated heat capacities to the experimental heat capacities. The RMS deviation is ± 1.01%; the average deviation −0.49%.

IIS. Poly(L-lysine • HBr)-phenylalanine

As in the copolymer above, the group vibrational spectrum of poly(L-lysine • HBr)-phenylalanine is constructed by taking the group vibrational spectra of its parts, poly(L-lysine) • HBr and poly(L-phenylalanine). Thus Parts A, D, and N of Table 13 were combined for poly(L-lysine) • HBr and Parts A, D, and I of Table 13 were combined for poly(L-phenylalanine). The number of skeletal vibrations becomes thirty-one, taking twenty for poly(L-lysine) • HBr and eleven for

TABLE 29

Calculated Heat Capacities of Poly(L-Lysine•HBr-Alanine)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.001	0.000	0.000	0.000	0.001	0.001
0.60	0.002	0.000	0.000	0.000	0.002	0.002
0.70	0.003	0.000	0.000	0.000	0.003	0.003
0.80	0.004	0.000	0.000	0.000	0.004	0.004
0.90	0.005	0.000	0.000	0.000	0.005	0.005
1.00	0.007	0.000	0.000	0.000	0.007	0.007
1.20	0.013	0.000	0.000	0.000	0.013	0.013
1.40	0.020	0.000	0.000	0.000	0.020	0.020
1.60	0.031	0.000	0.000	0.000	0.031	0.031
1.80	0.043	0.000	0.000	0.000	0.043	0.043
2.00	0.060	0.000	0.000	0.000	0.060	0.060
3.00	0.201	0.000	0.000	0.000	0.201	0.201
4.00	0.477	0.000	0.000	0.000	0.477	0.477
5.00	0.929	0.000	0.000	0.000	0.929	0.930
6.00	1.583	0.000	0.000	0.000	1.583	1.584
7.00	2.447	0.000	0.000	0.000	2.447	2.450
8.00	3.507	0.000	0.000	0.000	3.507	3.512
9.00	4.727	0.000	0.000	0.000	4.727	4.734
10.00	6.056	0.000	0.000	0.000	6.056	6.066
15.00	13.458	0.000	0.000	0.000	13.458	13.493
20.00	20.818	0.000	0.000	0.000	20.818	20.890
25.00	27.788	0.000	0.000	0.000	27.788	27.907
30.00	34.445	0.000	0.000	0.000	34.445	34.622
40.00	47.241	0.000	0.000	0.000	47.241	47.566
50.00	59.687	0.000	0.004	0.004	59.692	60.207
60.00	71.947	0.000	0.009	0.009	71.956	72.705
70.00	84.004	0.003	0.067	0.070	84.074	85.098
80.00	95.712	0.013	0.198	0.211	95.923	97.262
90.00	106.948	0.041	0.393	0.434	107.382	109.075
100.00	117.631	0.100	0.763	0.863	118.494	120.577
110.00	127.636	0.207	1.283	1.490	129.126	131.632
120.00	136.938	0.379	1.996	2.375	139.312	142.272
130.00	145.437	0.632	2.859	3.491	148.928	152.369
140.00	153.182	0.979	4.004	4.984	158.166	162.115
150.00	160.238	1.434	5.275	6.709	166.946	171.429
160.00	166.672	2.005	6.832	8.836	175.508	180.554
170.00	172.470	2.697	8.491	11.189	183.659	189.289
180.00	177.685	3.517	10.462	13.979	191.663	197.908

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	182.429	4.465	12.596	17.061	199.490	206.377
200.00	186.733	5.542	14.858	20.400	207.132	214.688
210.00	190.632	6.746	17.254	24.000	214.632	222.884
220.00	194.167	8.074	19.956	28.030	222.197	231.181
230.00	197.372	9.521	22.671	32.192	229.564	239.304
240.00	200.283	11.081	25.557	36.639	236.922	247.452
250.00	202.931	12.748	28.526	41.275	244.205	255.556
260.00	205.343	14.514	31.611	46.125	251.468	263.672
270.00	207.546	16.371	34.639	51.010	258.556	271.637
273.15	208.200	16.973	35.632	52.605	260.805	274.171
280.00	209.561	18.310	37.888	56.198	265.759	279.758
290.00	211.407	20.324	41.168	61.492	272.899	287.847
298.15	212.800	22.014	43.886	65.900	278.699	294.445
300.00	213.103	22.403	44.424	66.827	279.930	295.855
310.00	214.663	24.540	47.856	72.395	287.058	304.001
320.00	216.101	26.725	51.391	78.116	294.217	312.216
330.00	217.429	28.953	54.608	83.561	300.990	320.056
340.00	218.657	31.215	57.992	89.207	307.864	328.040
350.00	219.796	33.505	61.331	94.835	314.631	335.945
360.00	220.853	35.816	64.670	100.486	321.339	343.822
370.00	221.835	38.143	68.913	107.056	328.891	352.642
380.00	222.750	40.481	71.273	111.754	334.504	359.418
390.00	223.603	42.825	74.472	117.297	340.901	367.070
400.00	224.400	45.172	77.820	122.992	347.392	374.861
410.00	225.146	47.517	80.969	128.486	353.632	382.417
420.00	225.844	49.858	84.015	133.873	359.717	389.841
430.00	226.499	52.191	87.041	139.232	365.731	397.226
440.00	227.113	54.515	90.064	144.579	371.693	404.590
450.00	227.691	56.828	93.064	149.892	377.583	411.912
460.00	228.235	59.128	96.036	155.163	383.398	419.190
470.00	228.747	61.413	99.010	160.423	389.171	426.459
480.00	229.231	63.683	101.754	165.437	394.668	433.462
490.00	229.687	65.936	104.574	170.510	400.197	440.539
500.00	230.119	68.173	107.205	175.378	405.496	447.398
510.00	230.527	70.392	109.763	180.154	410.681	454.168
520.00	230.914	72.593	112.273	184.866	415.779	460.879
530.00	231.280	74.776	114.733	189.508	420.788	467.528
540.00	231.628	76.940	117.140	194.081	425.708	474.115
550.00	231.958	79.086	119.503	198.589	430.547	480.650
560.00	232.272	81.214	121.994	203.207	435.479	487.326
570.00	232.571	83.323	124.232	207.555	440.125	493.719
580.00	232.855	85.413	126.423	211.836	444.690	500.060
590.00	233.125	87.485	128.562	216.047	449.172	506.345
600.00	233.384	89.539	130.802	220.341	453.724	512.748

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	233.630	91.574	132.880	224.454	458.084	518.972
620.00	233.865	93.592	134.889	228.480	462.345	525.123
630.00	234.090	95.591	136.836	232.427	466.517	531.211
640.00	234.304	97.573	138.740	236.313	470.618	537.258
650.00	234.510	99.537	140.601	240.138	474.648	543.263
660.00	234.678	101.484	142.419	243.902	478.580	549.196
670.00	234.866	103.413	144.194	247.607	482.472	555.123
680.00	235.045	105.324	145.928	251.252	486.297	561.013
690.00	235.217	107.219	147.620	254.839	490.056	566.867
700.00	235.382	109.096	149.510	258.606	493.988	572.964
710.00	235.540	110.956	150.903	261.859	497.399	578.498
720.00	235.691	112.799	152.486	265.285	500.976	584.267
730.00	235.836	114.626	154.031	268.657	504.493	590.008
740.00	235.976	116.435	155.549	271.984	507.959	595.733
750.00	236.110	118.227	157.021	275.248	511.358	601.422
760.00	236.238	120.003	158.444	278.447	514.685	607.072
770.00	236.362	121.762	159.904	281.666	518.028	612.785
780.00	236.481	123.504	161.280	284.784	521.265	618.419
790.00	236.596	125.229	162.627	287.856	524.452	624.039
800.00	236.706	126.938	163.883	290.822	527.528	629.574
810.00	236.813	128.630	165.165	293.795	530.608	635.161
820.00	236.915	130.306	166.416	296.722	533.637	640.735
830.00	237.014	131.965	167.638	299.602	536.616	646.299
840.00	237.109	133.607	168.841	302.447	539.557	651.867
850.00	237.202	135.233	170.006	305.238	542.440	657.416
860.00	237.290	136.842	171.152	307.994	545.284	662.969
870.00	237.376	138.435	172.264	310.698	548.075	668.510
880.00	237.459	140.011	173.363	313.374	550.833	674.066
890.00	237.540	141.571	174.414	315.985	553.524	679.594
900.00	237.617	143.115	175.451	318.565	556.183	685.138
910.00	237.692	144.642	176.442	321.084	558.776	690.660
920.00	237.765	146.153	177.432	323.585	561.350	696.215
930.00	237.836	147.647	178.407	326.054	563.890	701.789
940.00	237.904	149.126	179.353	328.479	566.382	707.364
950.00	237.970	150.588	180.296	330.884	568.854	712.976
960.00	238.034	152.035	181.200	333.234	571.268	718.581
970.00	238.096	153.465	182.084	335.549	573.645	724.205
980.00	238.156	154.879	182.953	337.832	575.988	729.854
990.00	238.215	156.278	183.787	340.065	578.280	735.508
1000.00	238.271	157.660	184.603	342.263	580.534	741.186

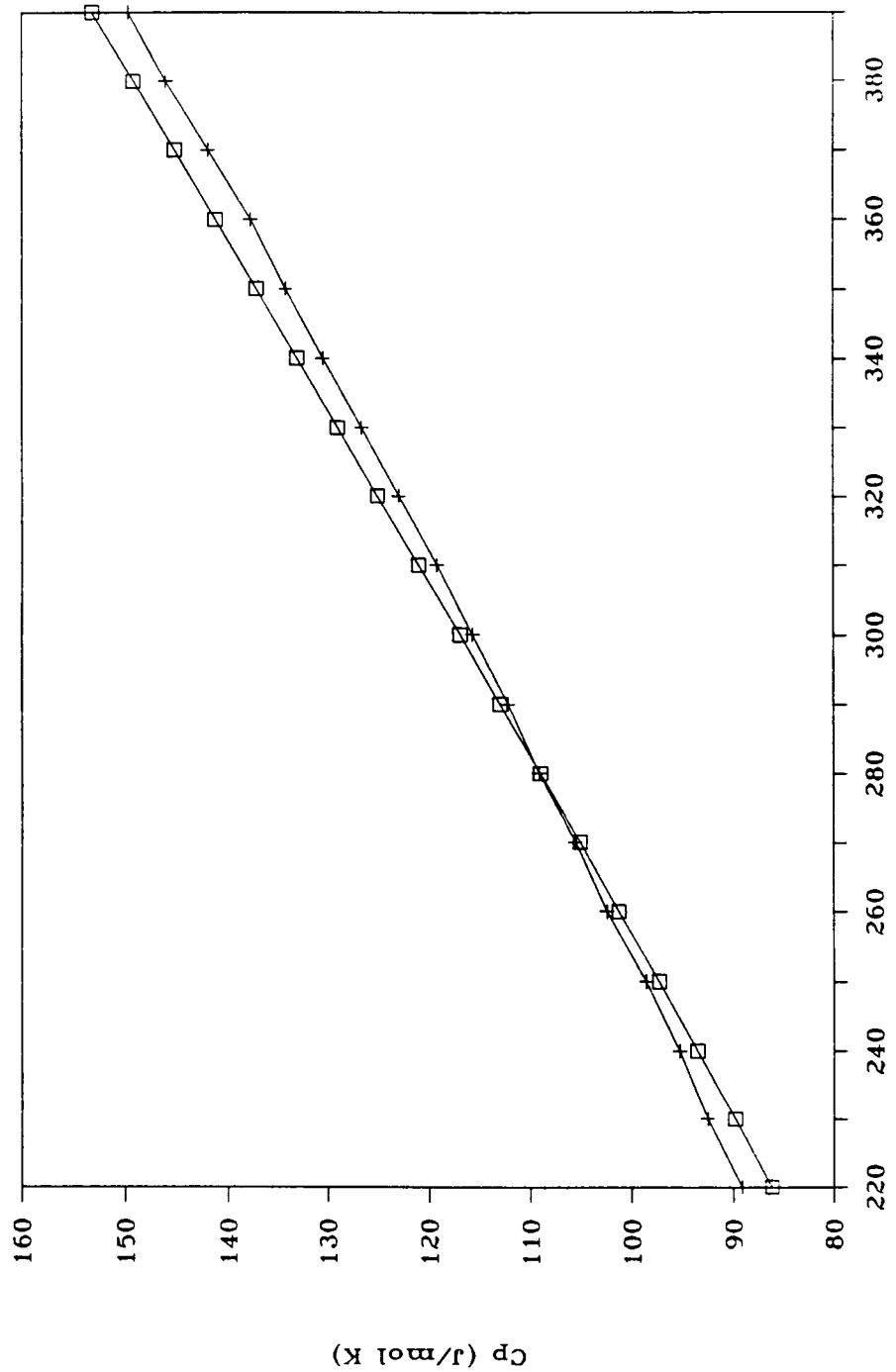


Figure 52 Heat Capacities of Poly(L-lysine•HBr-alanine). Curve (□): Calculations. Curve (+): Measurements.

poly(L-phenylalanine).

Fitting the experimental heat capacities (given in Table 8) in the temperature range 230 to 380 K resulted in a Θ_1-temperature of 756.9 ± 20.6 K. Taking this and 68.0 K for Θ_3, heat capacities were calculated from 0 to 1000 K (see Table 30). Upon comparison of the calculated and the experimental heat capacities, good agreement is observed for the entire temperature range (see Figure 53). The RMS deviations is ± 0.756%; the average deviation 0.41%.

IIT. Poly(L-glutamic acid • Na)-tyrosine

For poly(L-glutamic acid • Na)-tyrosine, the group vibrational spectrum is constructed by taking the constructed spectrum of poly(L-glutamic acid) • Na (Parts A, D, and F of Table 13) and combining it with the constructed spectrum of poly(L-tyrosine) (Parts A, D, E and I of Table 13). The number of skeletal vibrations is taken as twenty-nine by adding the sixteen of poly(L-glutamic acid) • Na to the thirteen of poly(L-tyrosine).

Fitting the experimental heat capacities (given in Table 8) in the temperature range 220 to 280 K resulted in a Θ_1-temperature of 744.0 ± 26.5 K. Heat capacities were then calculated with this Θ_1-temperautre and a Θ_3-temperature of 68.0 K, resulting in the data in Table 31. Comparison of the calculated and the experimental heat capacities is shown in Figure 54. The RMS deviation between the calculated and experimental heat capacities is ± 1.54%. The average deviation is 0.06%.

TABLE 30

Calculated Heat Capacities of Poly(L-Lysine•HBr-Phenylalanine)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.001	0.000	0.000	0.000	0.001	0.001
0.60	0.001	0.000	0.000	0.000	0.001	0.001
0.70	0.002	0.000	0.000	0.000	0.002	0.002
0.80	0.003	0.000	0.000	0.000	0.003	0.003
0.90	0.004	0.000	0.000	0.000	0.004	0.004
1.00	0.006	0.000	0.000	0.000	0.006	0.006
1.20	0.010	0.000	0.000	0.000	0.010	0.010
1.40	0.016	0.000	0.000	0.000	0.016	0.016
1.60	0.024	0.000	0.000	0.000	0.024	0.024
1.80	0.033	0.000	0.000	0.000	0.033	0.033
2.00	0.046	0.000	0.000	0.000	0.046	0.046
3.00	0.155	0.000	0.000	0.000	0.155	0.155
4.00	0.367	0.000	0.000	0.000	0.367	0.368
5.00	0.715	0.000	0.000	0.000	0.715	0.716
6.00	1.231	0.000	0.000	0.000	1.231	1.232
7.00	1.920	0.000	0.000	0.000	1.920	1.922
8.00	2.785	0.000	0.000	0.000	2.785	2.789
9.00	3.809	0.000	0.000	0.000	3.809	3.815
10.00	4.959	0.000	0.000	0.000	4.959	4.967
15.00	11.652	0.000	0.000	0.000	11.652	11.682
20.00	18.564	0.000	0.000	0.000	18.564	18.627
25.00	25.170	0.000	0.000	0.000	25.170	25.277
30.00	31.464	0.000	0.000	0.000	31.464	31.626
40.00	43.487	0.002	0.005	0.007	43.495	43.794
50.00	55.127	0.018	0.041	0.059	55.186	55.662
60.00	66.563	0.086	0.134	0.220	66.783	67.477
70.00	77.883	0.255	0.378	0.633	78.516	79.472
80.00	89.047	0.572	0.803	1.375	90.421	91.684
90.00	99.937	1.074	1.520	2.593	102.530	104.146
100.00	110.467	1.790	2.487	4.277	114.744	116.761
110.00	120.573	2.745	3.691	6.436	127.009	129.474
120.00	130.209	3.958	5.191	9.149	139.357	142.318
130.00	139.250	5.447	6.955	12.402	151.652	155.155
140.00	147.714	7.223	8.978	16.200	163.914	168.006
150.00	155.536	9.294	11.132	20.426	175.962	180.687
160.00	162.753	11.664	13.652	25.316	188.069	193.476
170.00	169.408	14.332	16.231	30.563	199.971	206.102
180.00	175.551	17.294	19.068	36.362	211.913	218.818

TABLE 30 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	181.236	20.539	22.016	42.556	223.792	231.518
200.00	186.335	24.058	25.123	49.182	235.516	244.107
210.00	191.045	27.836	28.272	56.108	247.153	256.655
220.00	195.381	31.856	31.878	63.734	259.116	269.592
230.00	199.366	36.101	35.243	71.344	270.710	282.196
240.00	203.024	40.550	38.806	79.356	282.380	294.931
250.00	206.382	45.184	42.485	87.669	294.051	307.719
260.00	209.467	49.981	46.203	96.184	305.651	320.484
270.00	212.304	54.922	49.895	104.816	317.120	333.164
273.15	213.149	56.504	51.074	107.578	320.727	337.163
280.00	214.914	59.984	53.671	113.655	328.569	345.876
290.00	217.319	65.148	57.650	122.797	340.117	358.746
298.15	219.141	69.418	60.916	130.334	349.476	369.220
300.00	219.539	70.394	61.496	131.890	351.429	371.422
310.00	221.590	75.704	65.613	141.317	362.907	384.327
320.00	223.488	81.061	69.432	150.493	373.981	396.860
330.00	225.247	86.449	73.382	159.830	385.078	409.471
340.00	226.880	91.852	77.352	169.204	396.084	422.042
350.00	228.398	97.257	81.252	178.509	406.907	434.471
360.00	229.810	102.652	85.140	187.792	417.603	446.822
370.00	231.127	108.027	89.160	197.187	428.314	459.245
380.00	232.356	113.370	92.708	206.078	438.434	471.089
390.00	233.505	118.675	96.425	215.100	448.605	483.042
400.00	234.580	123.933	100.317	224.250	458.830	495.110
410.00	235.588	129.138	103.924	233.062	468.649	506.796
420.00	236.533	134.285	107.471	241.755	478.288	518.343
430.00	237.421	139.369	110.997	250.366	487.786	529.792
440.00	238.256	144.387	114.534	258.921	497.177	541.180
450.00	239.042	149.336	118.072	267.408	506.450	552.496
460.00	239.783	154.214	121.567	275.781	515.564	563.695
470.00	240.482	159.018	125.000	284.018	524.500	574.755
480.00	241.143	163.748	128.259	292.008	533.150	585.557
490.00	241.767	168.404	131.442	299.845	541.612	596.209
500.00	242.358	172.983	134.538	307.521	549.879	606.700
510.00	242.917	177.488	137.548	315.036	557.953	617.035
520.00	243.448	181.917	140.506	322.423	565.871	627.251
530.00	243.951	186.272	143.409	329.681	573.632	637.349
540.00	244.429	190.553	146.263	336.816	581.245	647.338
550.00	244.883	194.761	149.106	343.866	588.750	657.262
560.00	245.316	198.896	152.060	350.956	596.272	667.261
570.00	245.727	202.961	154.720	357.681	603.408	676.885
580.00	246.119	206.956	157.430	364.387	610.506	686.522
590.00	246.493	210.883	159.981	370.863	617.356	695.937
600.00	246.849	214.742	162.578	377.320	624.170	705.366

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	247.190	218.535	165.112	383.648	630.837	714.688
620.00	247.515	222.264	167.549	389.813	637.328	723.865
630.00	247.826	225.930	169.906	395.835	643.661	732.921
640.00	248.123	229.533	172.220	401.753	649.876	741.900
650.00	248.408	233.076	174.486	407.562	655.970	750.798
660.00	248.681	236.559	176.708	413.267	661.948	759.621
670.00	248.942	239.985	178.885	418.869	667.812	768.371
680.00	249.193	243.354	181.017	424.370	673.563	777.050
690.00	249.433	246.667	183.105	429.772	679.205	785.663
700.00	249.664	249.925	185.627	435.552	685.216	794.764
710.00	249.886	253.131	187.192	440.323	690.208	802.744
720.00	250.099	256.284	189.172	445.456	695.555	811.196
730.00	250.303	259.386	191.178	450.564	700.868	819.670
740.00	250.500	262.439	193.107	455.545	706.045	828.048
750.00	250.690	265.442	194.980	460.422	711.112	836.359
760.00	250.842	268.397	196.753	465.150	715.992	844.515
770.00	251.017	271.306	198.669	469.975	720.992	852.875
780.00	251.186	274.168	200.473	474.641	725.827	861.108
790.00	251.348	276.986	202.224	479.210	730.559	869.283
800.00	251.505	279.759	203.803	483.562	735.066	877.259
810.00	251.655	282.488	205.446	487.934	739.589	885.321
820.00	251.801	285.176	207.091	492.266	744.067	893.398
830.00	251.941	287.821	208.703	496.523	748.464	901.449
840.00	252.076	290.425	210.302	500.727	752.803	909.501
850.00	252.206	292.989	211.867	504.856	757.062	917.529
860.00	252.332	295.514	213.454	508.968	761.300	925.606
870.00	252.454	297.999	214.862	512.861	765.315	933.488
880.00	252.572	300.447	216.320	516.767	769.338	941.455
890.00	252.685	302.857	217.727	520.584	773.270	949.388
900.00	252.795	305.230	219.128	524.358	777.153	957.342
910.00	252.901	307.567	220.493	528.060	780.962	965.286
920.00	253.004	309.869	221.838	531.706	784.711	973.239
930.00	253.104	312.135	223.170	535.306	788.410	981.214
940.00	253.201	314.368	224.462	538.830	792.031	989.180
950.00	253.294	316.566	225.729	542.296	795.590	997.157
960.00	253.385	318.732	226.971	545.703	799.088	1005.149
970.00	253.473	320.864	228.189	549.053	802.526	1013.159
980.00	253.558	322.965	229.391	552.356	805.914	1021.201
990.00	253.641	325.034	230.562	555.596	809.236	1029.259
1000.00	253.721	327.072	231.687	558.758	812.479	1037.317

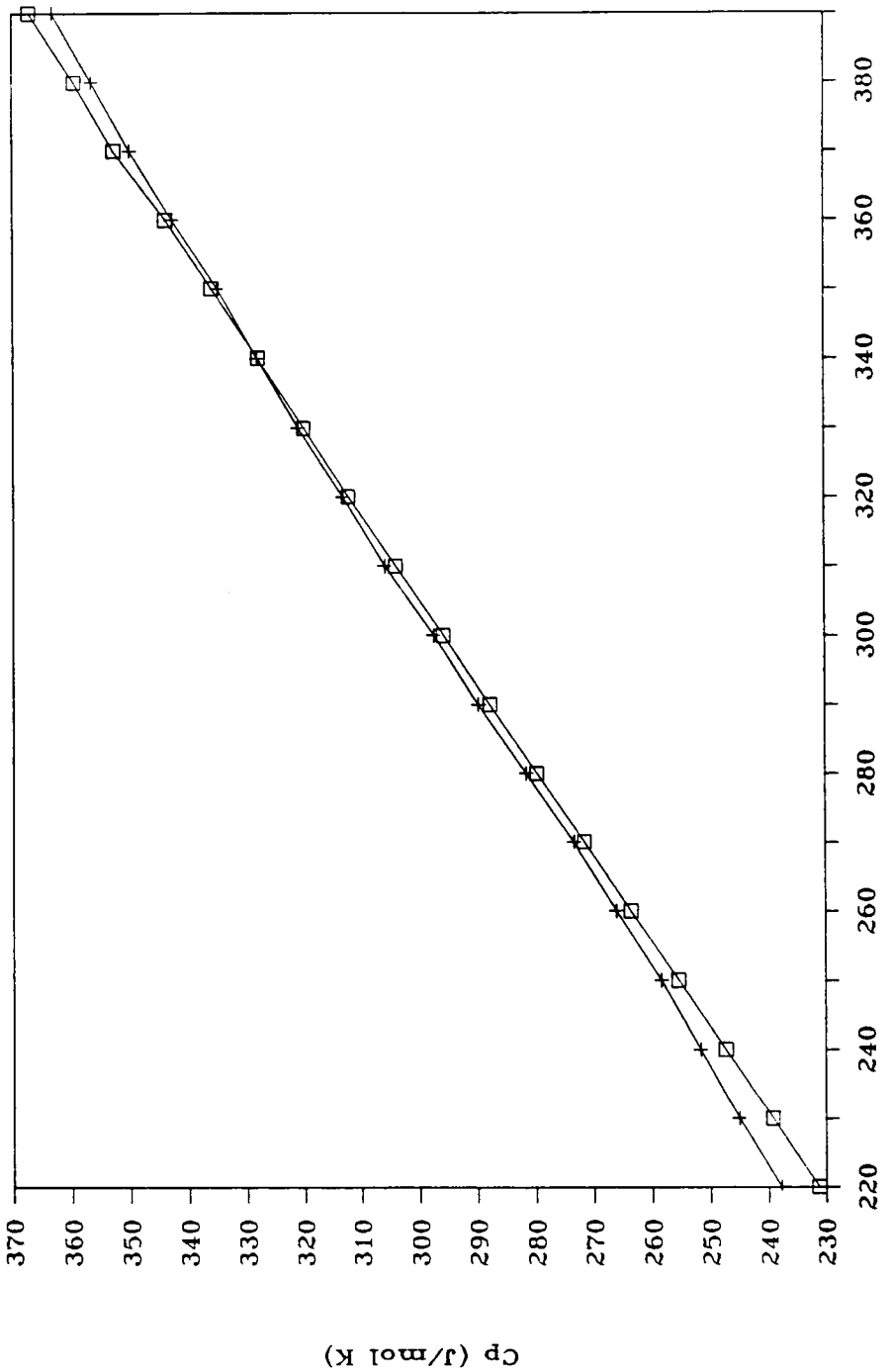


Figure 53 Heat Capacities of Poly(L-lysine•HBr-phenylalanine). Curve (□): Calculations. Curve (+): Measurements.

TABLE 31

Calculated Heat Capacities of Poly(L-Glutamic Acid•Na-Tyrosine)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.001	0.000	0.000	0.000	0.001	0.001
0.60	0.001	0.000	0.000	0.000	0.001	0.001
0.70	0.002	0.000	0.000	0.000	0.002	0.002
0.80	0.003	0.000	0.000	0.000	0.003	0.003
0.90	0.004	0.000	0.000	0.000	0.004	0.004
1.00	0.005	0.000	0.000	0.000	0.005	0.005
1.20	0.009	0.000	0.000	0.000	0.009	0.009
1.40	0.015	0.000	0.000	0.000	0.015	0.015
1.60	0.022	0.000	0.000	0.000	0.022	0.022
1.80	0.032	0.000	0.000	0.000	0.032	0.032
2.00	0.044	0.000	0.000	0.000	0.044	0.044
3.00	0.147	0.000	0.000	0.000	0.147	0.148
4.00	0.350	0.000	0.000	0.000	0.350	0.350
5.00	0.681	0.000	0.000	0.000	0.681	0.681
6.00	1.171	0.000	0.000	0.000	1.171	1.172
7.00	1.827	0.000	0.000	0.000	1.827	1.829
8.00	2.651	0.000	0.000	0.000	2.651	2.654
9.00	3.625	0.000	0.000	0.000	3.625	3.630
10.00	4.720	0.000	0.000	0.000	4.720	4.728
15.00	11.090	0.000	0.000	0.000	11.090	11.118
20.00	17.668	0.000	0.000	0.000	17.668	17.728
25.00	23.955	0.000	0.000	0.000	23.955	24.057
30.00	29.945	0.000	0.000	0.000	29.945	30.099
40.00	41.388	0.002	0.005	0.007	41.395	41.680
50.00	52.465	0.018	0.041	0.059	52.525	52.978
60.00	63.346	0.088	0.134	0.222	63.568	64.229
70.00	74.116	0.266	0.378	0.644	74.760	75.670
80.00	84.717	0.612	0.801	1.413	86.130	87.333
90.00	95.039	1.178	1.515	2.694	97.733	99.274
100.00	105.001	2.011	2.482	4.494	109.495	111.419
110.00	114.542	3.144	3.659	6.803	121.345	123.700
120.00	123.620	4.598	5.142	9.740	133.361	136.194
130.00	132.100	6.386	6.863	13.248	145.349	148.706
140.00	140.011	8.506	8.809	17.315	157.326	161.255
150.00	147.308	10.952	10.869	21.822	169.130	173.671
160.00	154.029	13.712	13.243	26.955	180.984	186.187
170.00	160.219	16.769	15.641	32.410	192.630	198.535
180.00	165.927	20.104	18.267	38.372	204.298	210.955

TABLE 31 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	171.155	23.698	20.955	44.652	215.807	223.257
200.00	175.881	27.528	23.748	51.276	227.157	235.443
210.00	180.236	31.574	26.533	58.107	238.343	247.506
220.00	184.235	35.815	29.729	65.544	249.779	259.878
230.00	187.903	40.231	32.617	72.848	260.751	271.815
240.00	191.266	44.799	35.673	80.472	271.738	283.816
250.00	194.349	49.501	38.804	88.305	282.653	295.791
260.00	197.177	54.316	41.945	96.261	293.438	307.678
270.00	199.775	59.226	45.005	104.231	304.006	319.387
273.15	200.549	60.789	45.989	106.779	307.328	323.077
280.00	202.164	64.213	48.137	112.350	314.514	331.081
290.00	204.364	69.259	51.396	120.655	325.019	342.822
298.15	206.029	73.405	54.084	127.488	333.517	352.360
300.00	206.392	74.349	54.529	128.878	335.270	354.344
310.00	208.265	79.467	57.906	137.373	345.638	366.040
320.00	209.998	84.600	60.994	145.593	355.591	377.345
330.00	211.603	89.734	64.177	153.911	365.514	388.668
340.00	213.092	94.857	67.370	162.227	375.319	399.916
350.00	214.476	99.960	70.473	170.433	384.909	410.983
360.00	215.763	105.032	73.507	178.539	394.302	421.891
370.00	216.963	110.065	76.708	186.773	403.736	432.891
380.00	218.082	115.052	79.491	194.543	412.625	443.357
390.00	219.128	119.987	82.387	202.374	421.502	453.859
400.00	220.106	124.862	85.471	210.333	430.440	464.475
410.00	221.023	129.675	88.268	217.943	438.966	474.697
420.00	221.883	134.421	91.023	225.444	447.327	484.789
430.00	222.691	139.096	93.748	232.845	455.535	494.764
440.00	223.450	143.699	96.470	240.169	463.619	504.652
450.00	224.165	148.226	99.203	247.430	471.594	514.471
460.00	224.838	152.677	101.903	254.581	479.419	524.175
470.00	225.474	157.051	104.547	261.598	487.071	533.740
480.00	226.073	161.347	107.050	268.397	494.470	543.075
490.00	226.641	165.564	109.485	275.049	501.690	552.261
500.00	227.177	169.703	111.847	281.550	508.727	561.296
510.00	227.685	173.764	114.146	287.910	515.595	570.191
520.00	228.167	177.747	116.402	294.150	522.317	578.973
530.00	228.624	181.654	118.614	300.268	528.892	587.639
540.00	229.058	185.485	120.779	306.263	535.322	596.193
550.00	229.471	189.241	122.911	312.152	541.623	604.651
560.00	229.863	192.923	125.163	318.086	547.949	613.185
570.00	230.236	196.533	127.180	323.713	553.950	621.404
580.00	230.592	200.072	129.156	329.228	559.820	629.525
590.00	230.931	203.541	131.086	334.627	565.559	637.546
600.00	231.255	206.942	133.072	340.014	571.269	645.584

TABLE 31 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	231.564	210.276	135.002	345.278	576.842	653.515
620.00	231.859	213.544	136.844	350.388	582.247	661.305
630.00	232.141	216.748	138.614	355.363	587.503	668.976
640.00	232.411	219.890	140.351	360.241	592.651	676.572
650.00	232.669	222.970	142.050	365.020	597.689	684.091
660.00	232.916	225.991	143.713	369.704	602.620	691.538
670.00	233.153	228.953	145.341	374.294	607.447	698.916
680.00	233.380	231.858	146.934	378.792	612.172	706.227
690.00	233.598	234.707	148.493	383.200	616.798	713.475
700.00	233.807	237.502	150.495	387.997	621.804	721.214
710.00	234.008	240.243	151.550	391.793	625.802	727.836
720.00	234.201	242.933	153.030	395.962	630.164	734.933
730.00	234.387	245.572	154.475	400.047	634.434	741.975
740.00	234.565	248.161	155.912	404.073	638.639	748.993
750.00	234.709	250.703	157.299	408.001	642.710	755.910
760.00	234.874	253.197	158.630	411.826	646.700	762.784
770.00	235.032	255.645	160.075	415.719	650.751	769.786
780.00	235.185	258.047	161.415	419.462	654.647	776.660
790.00	235.332	260.406	162.709	423.115	658.446	783.477
800.00	235.473	262.722	163.835	426.557	662.030	790.095
810.00	235.609	264.996	165.072	430.068	665.677	796.845
820.00	235.740	267.229	166.282	433.511	669.251	803.567
830.00	235.867	269.421	167.468	436.889	672.756	810.266
840.00	235.989	271.574	168.648	440.223	676.212	816.967
850.00	236.107	273.689	169.801	443.490	679.598	823.645
860.00	236.221	275.767	170.984	446.751	682.972	830.373
870.00	236.331	277.807	171.995	449.802	686.133	836.906
880.00	236.438	279.812	173.063	452.875	689.312	843.525
890.00	236.540	281.781	174.088	455.869	692.409	850.111
900.00	236.640	283.716	175.112	458.828	695.468	856.718
910.00	236.736	285.617	176.108	461.725	698.461	863.313
920.00	236.829	287.485	177.091	464.576	701.405	869.918
930.00	236.919	289.321	178.068	467.389	704.308	876.545
940.00	237.006	291.125	179.010	470.136	707.142	883.161
950.00	237.091	292.899	179.934	472.833	709.924	889.787
960.00	237.173	294.642	180.839	475.481	712.654	896.426
970.00	237.252	296.355	181.726	478.081	715.333	903.081
980.00	237.330	298.039	182.603	480.642	717.972	909.767
990.00	237.404	299.694	183.455	483.150	720.554	916.465
1000.00	237.477	301.322	184.266	485.589	723.065	923.160

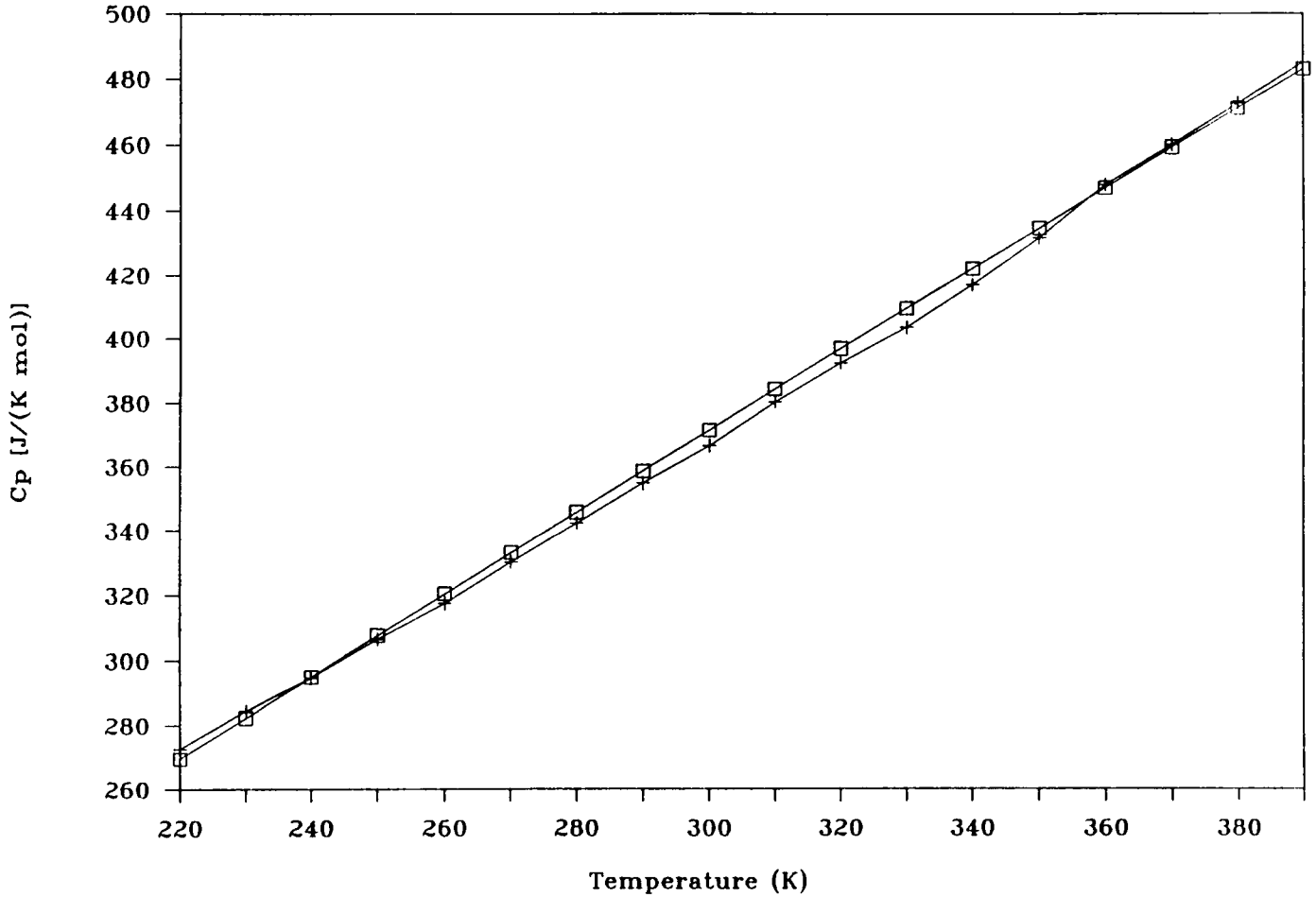


Figure 54 Heat Capacities of Poly(L-glutamic acid•Na-tyrosine). Curve (□): Calculations. Curve (+): Measurements.

IIU. Poly(L-proline-glycine-proline)

Poly(L-proline-glycine-proline) is a sequential copolymer whose repeat unit consists of poly(L-proline) followed by polyglycine followed by poly(L-proline). Again, its group vibrational spectrum is easily constructed by simply putting together the constructed spectrum of poly(L-proline) twice (Parts A, C, D, and M of Table 13) and the constructed spectrum of polyglycine (Table 9). The skeletal vibrations total twenty-eight. Poly(L-proline) has eleven skeletal vibrations which are counted twice to make twenty-two, and polyglycine has six skeletal vibrations.

Fitting the experimental heat capacities (listed in Table 8) in the temperature range 220 to 260 K resulted in a Θ_1-temperature of 698.6 ± 13.0 K. Using this and a Θ_3-temperature of 68.0 K, heat capacities were calculated from 0 to 1000 K and are given in Table 32. As shown in Figure 55, the agreement between experiment and calculation was excellent. The RMS deviation is ± 0.382%; the average deviation 0.18%.

CONCLUSIONS

Table 33 provides a summary of heat capacity calculation parameters and results. For each homopolymer and copolymer studied, listed are the value for Θ_3, the number of skeletal vibrations, the number of group vibrations, and the observed RMS deviation between calculated and experimental heat capacities.

TABLE 32

Calculated Heat Capacities of Poly(L-Proline-Glycine-Proline)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.001	0.000	0.000	0.000	0.001	0.001
0.60	0.001	0.000	0.000	0.000	0.001	0.001
0.70	0.002	0.000	0.000	0.000	0.002	0.002
0.80	0.003	0.000	0.000	0.000	0.003	0.003
0.90	0.005	0.000	0.000	0.000	0.005	0.005
1.00	0.007	0.000	0.000	0.000	0.007	0.007
1.20	0.012	0.000	0.000	0.000	0.012	0.012
1.40	0.019	0.000	0.000	0.000	0.019	0.019
1.60	0.028	0.000	0.000	0.000	0.028	0.028
1.80	0.039	0.000	0.000	0.000	0.039	0.039
2.00	0.054	0.000	0.000	0.000	0.054	0.054
3.00	0.182	0.000	0.000	0.000	0.182	0.182
4.00	0.432	0.000	0.000	0.000	0.432	0.433
5.00	0.842	0.000	0.000	0.000	0.842	0.843
6.00	1.435	0.000	0.000	0.000	1.435	1.437
7.00	2.219	0.000	0.000	0.000	2.219	2.222
8.00	3.181	0.000	0.000	0.000	3.181	3.185
9.00	4.287	0.000	0.000	0.000	4.287	4.294
10.00	5.493	0.000	0.000	0.000	5.493	5.502
15.00	12.207	0.000	0.000	0.000	12.207	12.238
20.00	18.883	0.000	0.000	0.000	18.883	18.947
25.00	25.204	0.000	0.000	0.000	25.204	25.312
30.00	31.242	0.000	0.000	0.000	31.242	31.403
40.00	42.849	0.000	0.000	0.000	42.849	43.144
50.00	54.166	0.000	0.000	0.000	54.167	54.634
60.00	65.272	0.002	0.000	0.002	65.274	65.953
70.00	76.274	0.010	0.000	0.010	76.284	77.213
80.00	87.038	0.038	0.023	0.061	87.099	88.315
90.00	97.451	0.106	0.041	0.147	97.598	99.136
100.00	107.429	0.242	0.136	0.378	107.807	109.703
110.00	116.916	0.477	0.313	0.789	117.705	119.989
120.00	125.790	0.838	0.574	1.412	127.202	129.904
130.00	134.044	1.350	1.006	2.356	136.400	139.551
140.00	141.622	2.030	1.665	3.694	145.316	148.945
150.00	148.565	2.889	2.585	5.474	154.038	158.175
160.00	154.926	3.933	3.739	7.672	162.598	167.272
170.00	160.760	5.163	5.169	10.332	171.092	176.337
180.00	166.056	6.577	7.028	13.605	179.661	185.515

TABLE 32 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	170.837	8.172	9.058	17.230	188.067	194.559
200.00	175.215	9.941	11.411	21.353	196.568	203.738
210.00	179.211	11.879	14.024	25.903	205.114	213.000
220.00	182.855	13.978	16.820	30.798	213.653	222.291
230.00	186.176	16.229	20.006	36.236	222.412	231.849
240.00	189.205	18.625	23.400	42.025	231.230	241.507
250.00	191.970	21.155	26.984	48.139	240.109	251.269
260.00	194.498	23.810	30.834	54.644	249.142	261.232
270.00	196.812	26.580	34.597	61.177	257.989	271.042
273.15	197.500	27.475	35.858	63.333	260.833	274.200
280.00	198.934	29.455	38.600	68.055	266.989	281.052
290.00	200.883	32.424	42.805	75.229	276.112	291.236
298.15	202.355	34.907	46.217	81.123	283.479	299.495
300.00	202.676	35.478	46.852	82.330	285.006	301.220
310.00	204.329	38.604	51.210	89.815	294.143	311.505
320.00	205.854	41.795	55.515	97.309	303.164	321.710
330.00	207.266	45.039	59.741	104.780	312.045	331.812
340.00	208.573	48.328	63.970	112.297	320.870	341.898
350.00	209.786	51.652	68.217	119.869	329.654	351.986
360.00	210.913	55.005	72.477	127.482	338.394	362.071
370.00	211.962	58.377	76.683	135.060	347.021	372.081
380.00	212.939	61.762	80.925	142.687	355.627	382.114
390.00	213.852	65.154	85.075	150.229	364.081	392.030
400.00	214.705	68.547	89.196	157.742	372.448	401.898
410.00	215.504	71.935	92.949	164.885	380.389	411.351
420.00	216.252	75.315	96.757	172.072	388.324	420.844
430.00	216.955	78.681	100.647	179.327	396.282	430.407
440.00	217.615	82.030	104.433	186.463	404.077	439.841
450.00	218.235	85.359	108.148	193.507	411.742	449.177
460.00	218.820	88.665	111.789	200.454	419.274	458.416
470.00	219.371	91.947	115.368	207.314	426.685	467.568
480.00	219.891	95.201	118.784	213.985	433.876	476.525
490.00	220.382	98.426	122.246	220.672	441.054	485.514
500.00	220.847	101.622	125.578	227.200	448.047	494.345
510.00	221.287	104.786	128.742	233.528	454.815	502.975
520.00	221.704	107.918	131.838	239.756	461.460	511.515
530.00	222.099	111.017	134.865	245.882	467.981	519.963
540.00	222.474	114.082	137.820	251.902	474.377	528.318
550.00	222.831	117.114	140.703	257.817	480.647	536.580
560.00	223.170	120.111	143.512	263.624	486.793	544.749
570.00	223.492	123.074	146.250	269.324	492.816	552.827
580.00	223.799	126.003	148.915	274.918	498.717	560.814
590.00	224.092	128.897	151.505	280.402	504.494	568.709
600.00	224.371	131.757	154.111	285.867	510.238	576.613

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	224.637	134.582	156.645	291.227	515.864	584.432
620.00	224.891	137.373	159.072	296.445	521.336	592.124
630.00	225.134	140.130	161.395	301.526	526.660	599.694
640.00	225.367	142.854	163.659	306.513	531.880	607.195
650.00	225.589	145.544	165.865	311.408	536.997	614.626
660.00	225.802	148.200	168.013	316.213	542.015	621.991
670.00	226.006	150.824	170.105	320.929	546.935	629.292
680.00	226.201	153.414	172.143	325.557	551.758	636.531
690.00	226.389	155.973	174.127	330.099	556.488	643.712
700.00	226.541	158.499	176.538	335.036	561.578	651.359
710.00	226.714	160.993	177.980	338.972	565.686	657.919
720.00	226.879	163.455	179.831	343.287	570.166	664.960
730.00	227.038	165.887	181.635	347.522	574.560	671.951
740.00	227.190	168.287	183.393	351.680	578.870	678.897
750.00	227.336	170.656	185.106	355.763	583.099	685.799
760.00	227.477	172.996	186.775	359.771	587.248	692.660
770.00	227.612	175.305	188.402	363.706	591.318	699.482
780.00	227.742	177.584	189.986	367.570	595.312	706.267
790.00	227.867	179.834	191.531	371.365	599.232	713.019
800.00	227.988	182.054	193.036	375.090	603.078	719.739
810.00	228.104	184.245	194.504	378.749	606.853	726.430
820.00	228.216	186.408	195.934	382.342	610.558	733.095
830.00	228.324	188.543	197.329	385.871	614.195	739.736
840.00	228.428	190.649	198.688	389.338	617.766	746.355
850.00	228.529	192.728	200.014	392.742	621.271	752.955
860.00	228.626	194.779	201.311	396.090	624.716	759.544
870.00	228.720	196.803	202.572	399.375	628.095	766.114
880.00	228.810	198.799	203.803	402.602	631.413	772.673
890.00	228.898	200.770	205.004	405.773	634.671	779.223
900.00	228.983	202.713	206.175	408.889	637.872	785.767
910.00	229.065	204.631	207.319	411.950	641.015	792.308
920.00	229.144	206.523	208.435	414.958	644.102	798.849
930.00	229.221	208.389	209.525	417.914	647.135	805.391
940.00	229.296	210.230	210.589	420.819	650.115	811.938
950.00	229.368	212.047	211.628	423.674	653.042	818.494
960.00	229.438	213.838	212.642	426.480	655.918	825.060
970.00	229.505	215.605	213.633	429.239	658.744	831.639
980.00	229.571	217.348	214.612	431.960	661.531	838.249
990.00	229.635	219.067	215.559	434.626	664.261	844.866
1000.00	229.697	220.762	216.484	437.246	666.943	851.506

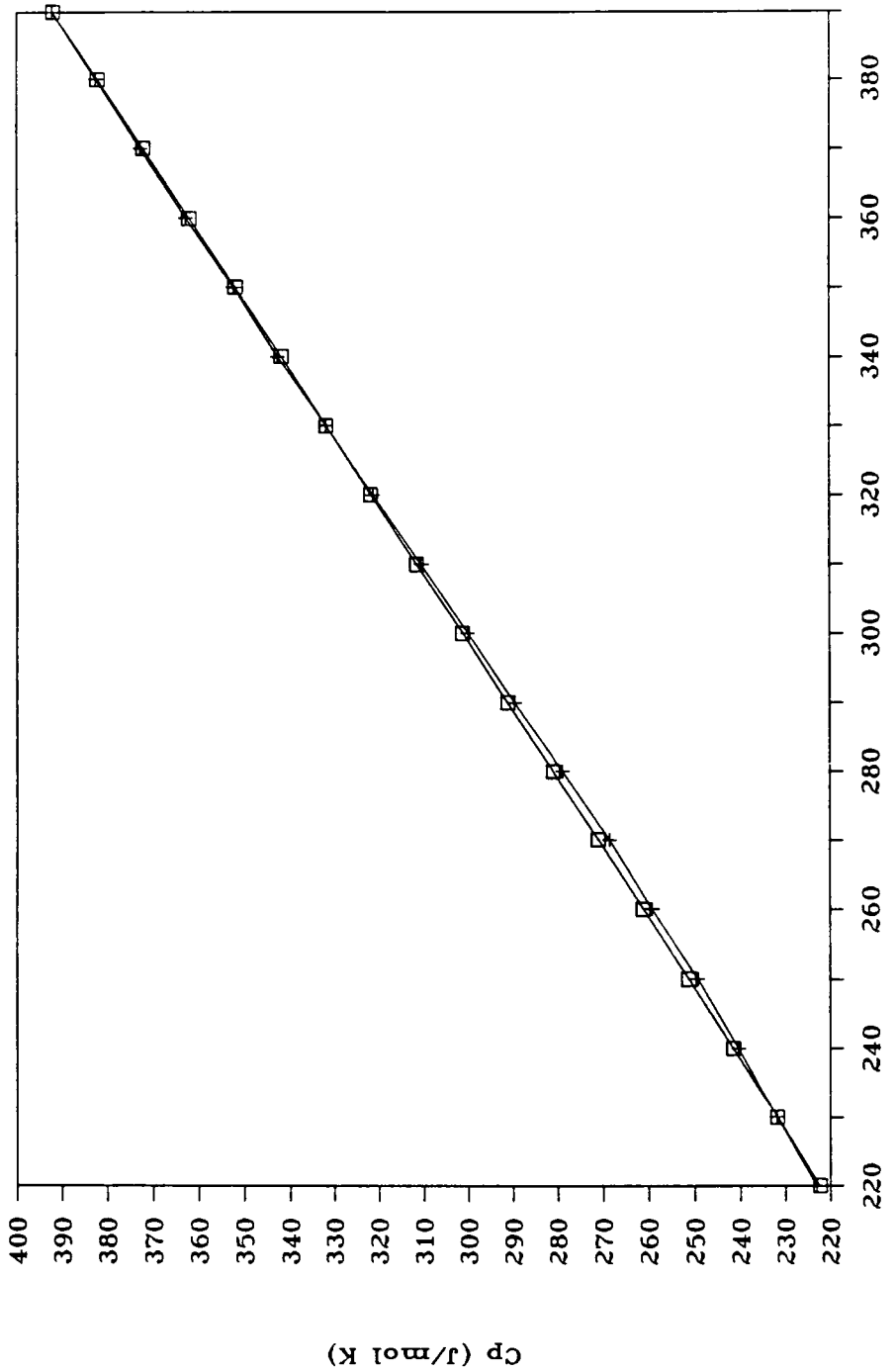


Figure 55 Heat Capacities of Poly(L-proline-glycine-proline). Curve (□): Calculations. Curve (+): Measurements.

TABLE 33

Heat Capacity Calculation Parameters/Results

Biopolymer	Θ_1	Skeletal	Group	RMS Error
GLY	750.3	6	15	0.74%
ALA	634.1	9	21	0.88%
VAL	663.7	14	37	1.18%
LEU	624.5	16	41	1.07%
ASP•Na	597.0	14	25	0.85%
GLU•Na	906.9	16	32	1.13%
ASN	568.8	12	30	0.77%
PHE	609.7	11	49	1.54%
TYR	728.5	13	50	1.82%
TRP	793.2	13	69	1.51%
PRO	690.5	11	31	1.78%
LYS•HBr	636.3	20	49	1.24%
HIS	808.0	13	38	0.86%
HIS•HCl	744.5	19	38	1.48%
ARG•HCl	609.5	23	52	0.44%
LYS•HBr-ALA	656.3	29	70	1.01%
LYS•HBr-PHE	756.9	31	98	0.76%
GLU•Na-TYR	744.0	29	82	1.54%
PRO-GLY-PRO	698.6	28	77	0.38%

III. X-RAY DIFFRACTION RESULTS

Figure 56 shows the X-ray powder diffractometer results obtained for poly(L-serine). Figure 57 shows the results for poly(L-methionine). In both cases the backbround diffraction pattern has been subtracted. For interpretation of the results, Dr. Anton Habenschuss and Dr. Alfred Narten of Oak Ridge National Laboratory were consulted. As shown in Figure 56, the poly(L-serine) does exhibit a few Bragg peaks indicating some degree of order. However, it was estimated that the degree of crystallinity for this poly(amino acid) was no more than 15%. The poly(L-methionine) pattern, on the other hand, does not give any indication of Bragg peaks. The pattern is typical, however, for an amorphous polymer. As a result, the poly(L-methionine) was determined to mostly amorphous. It is quite possible that the poly(L-methionine) could have some crystallinity associated with it, on the order of 1-5%. As a result, we cannot label it 100% amorphous. Following the X-ray diffraction studies, the two poly(amino acid) samples were again subjected to DSC analysis to determine, if any, the effects of the X-ray beams on the samples. For both poly(L-serine) and poly(L-methionine), the resulting heat capacities that were measured following the X-ray studies were within 3.0% of the heat capacities measured prior to the X-ray studies. It can therefore be concluded that the X-rays had no adverse effects on the two poly(amino acids).

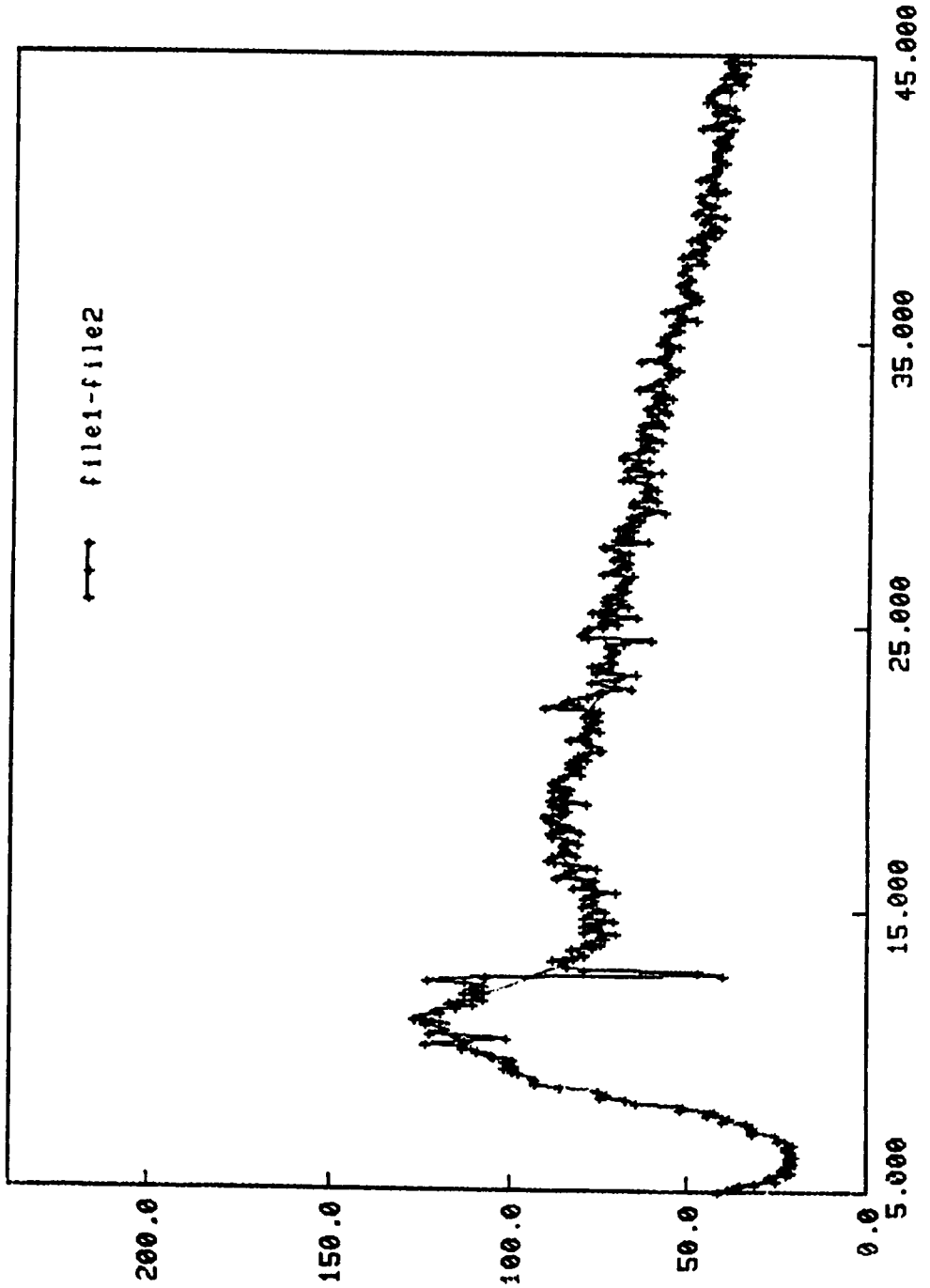


Figure 57 X-ray Powder Diffraction of Poly(L-methionine).

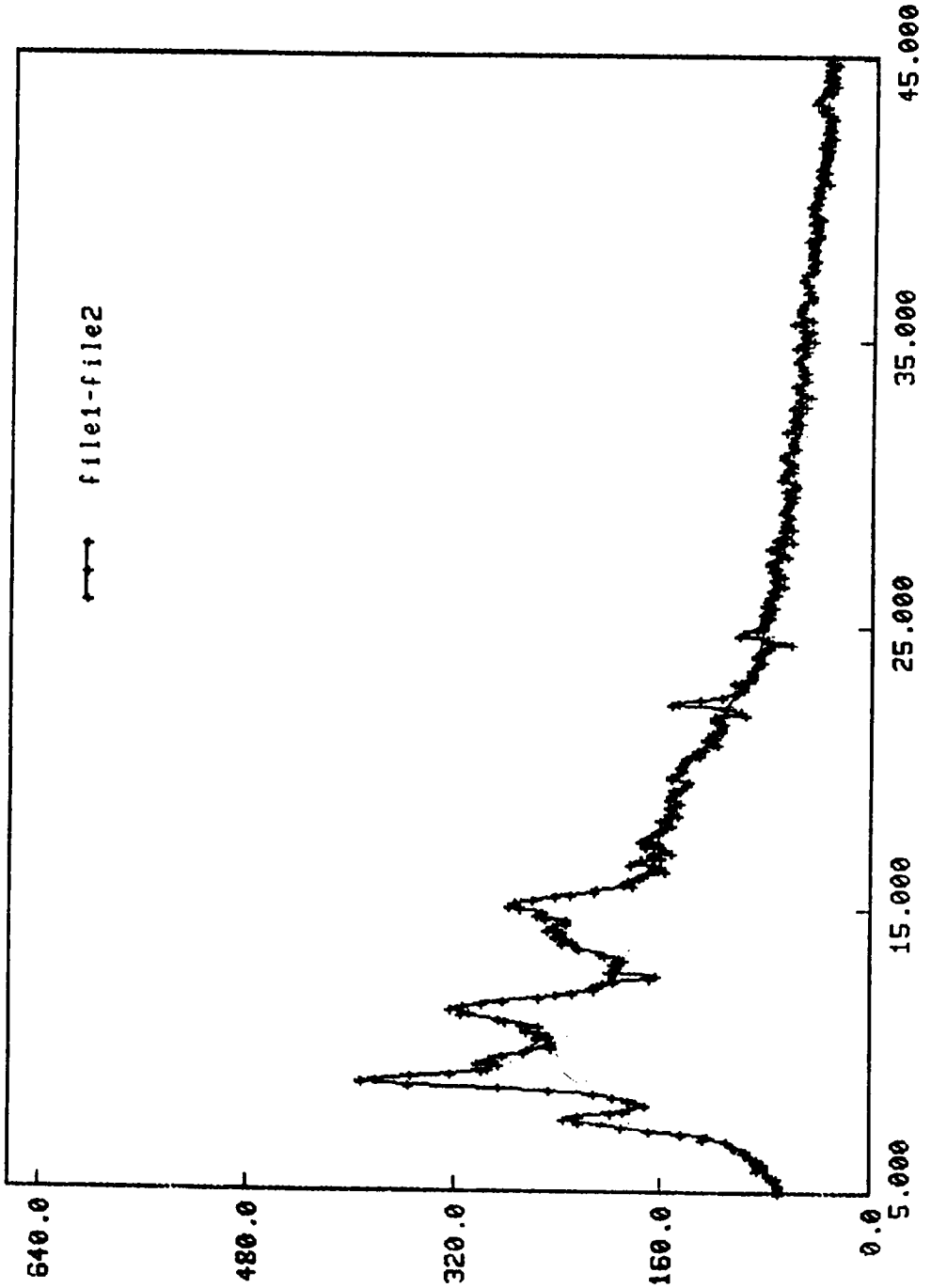


Figure 56 X-ray Powder Diffraction of Poly(L-serine).

CHAPTER IV

DISCUSSIONS

I. COMPARISON OF MEASURED HEAT CAPACITIES TO LITERATURE

Polyglycine, poly(L-alanine), and poly(L-valine) are the three simplest poly(amino acids). They are also the only three poly(amino acids) for which prior heat capacity measurements have been reported in the literature. The newly measured results for these three homopolymers are compared in this section to the results reported in the literature.

First it is important to point out that the newly measured data reflect samples of mixed crystal forms, whereas the literature data are reported for samples in a specific conformation. The fact that we are comparing a mixed sample to samples of specific conformation is not considered to cause significant problems. It is not even possible to prepare a sample that is 100% of one conformation. Although the authors of the literature work on polyglycine comment that their samples are "predominantly" PGI or PGII, absolute analysis of the sample is not provided. For poly(L-alanine) where analysis has been provided by the authors, the samples were reported to be 85% α-PLA or 85% β-PLA. Second, when heat capacities are calculated for different conformations, differences between the results are negligible. For polyglycine, the RMS deviation between the calculated heat capacities for PGI and PGII is only 0.74%, a value less than the experimental uncertainty, and

insignificant when compared to the RMS deviations observed between these calculated results and the experimental data in the literature. In the temperature range of 150 to 370 K, the RMS deviation of the experiment was 33.9% for PGI and 28.4% for PGII. If a comparison of the newly measured data of mixed conformation samples to these same calculated data is made, the RMS deviation decreases to 5.55% (when comparing to PGII). Even this more acceptable error has been improved upon as has been shown in Section II of Chapter III.

A similar comparison of results can be made for poly(L-alanine). When heat capacities are calculated for α-PLA and β-PLA using the literature data and spectra, the RMS deviation observed between the two is only 0.62% in the temperature range 150 to 390 K. The RMS deviation between these calculated results and the experiments reported in the literature, is 31.47% for α-PLA and 43.99% for β-PLA in the temperature range 150 to 300 K. Again, the RMS deviation between the newly measured heat capacities on the random sample and this calculated data on α-PLA is only 1.16% and only 1.50% upon comparison to β-PLA (temperature range 220 to 390 K). As a result, we consider that the comparison of our newly measured data on mixed samples to those of specific conformation to be reasonable.

Figure 58 illustrates the comparison of the newly measured heat capacities for polyglycine in a mixed form (Curve B) to the literature results for PGII (Curve C).[9-10] In addition, the newly calculated results for heat capacity are shown (Curve A). As mentioned in Chapter III, the fit of the literature data from 1.4 to 20 K for

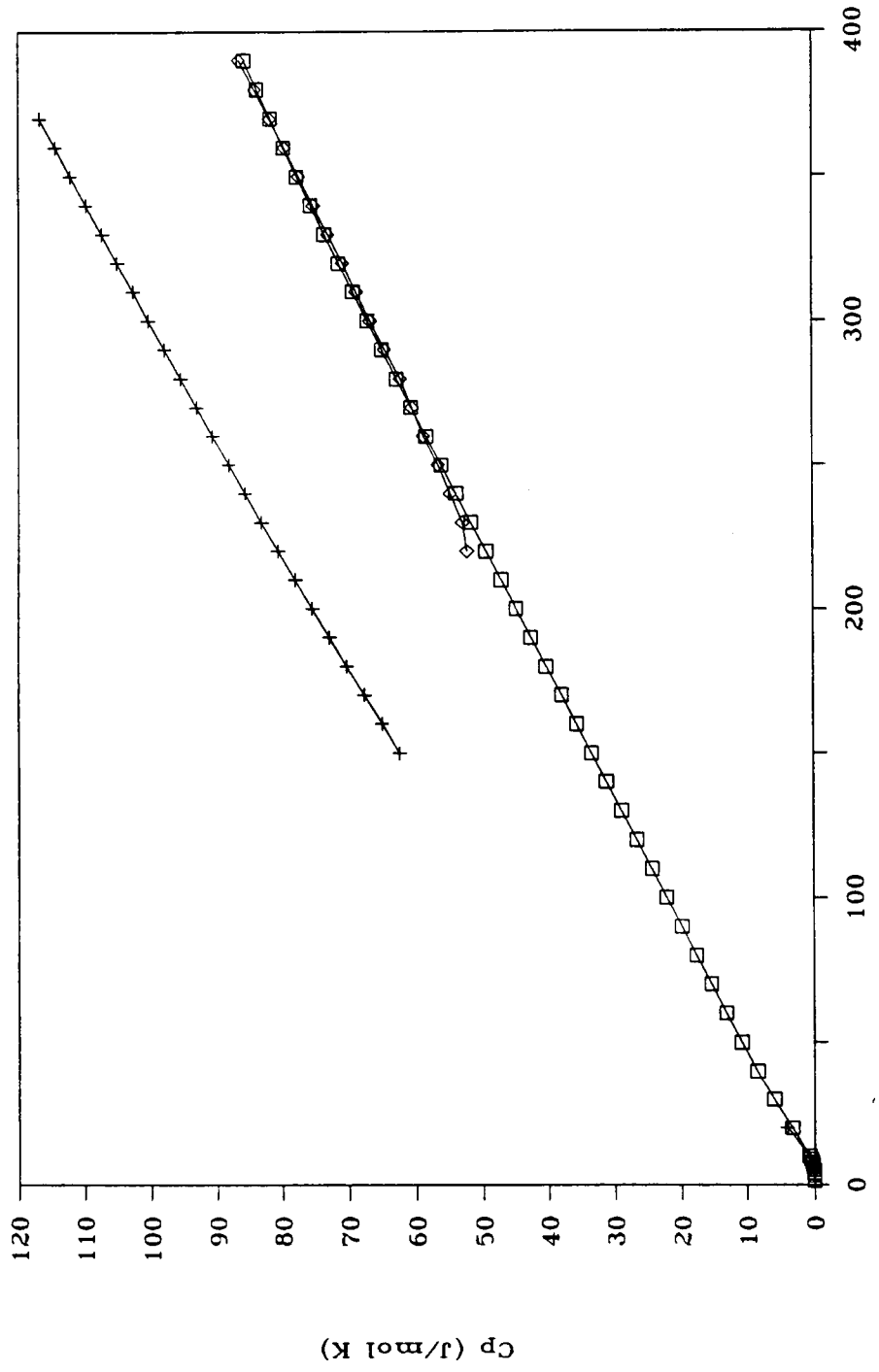


Figure 58 Comparison of Heat Capacities of Polyglycine. Curve (□): New calculations. Curve (◇): New measurements. Curve (+): Previous measurements on polyglycine II.[8-10] [Sources: L. Finegold and P.K. Kumar *Thermochimica Acta* **48**, 51 (1981); B. Fanconi and L. Finegold *Science* **190**, 458 (1975); B. Fanconi and L. Finegold *Conf. Int. Thermodyn. Chim. 4th* **2**, 117 (1975).]

PGII was good. The great discrepancies between the literature data and the newly measured data as well as the newly calculated data are seen in the temperature range 220 to 370 K. Consistently, the literature data is higher than the calculated data and the newly measured data. Also noted earlier, the RMS deviation between the newly calculated data and the newly measured data is only 0.74% (220 to 390 K).

Based on these results, we selected our experimental data in the temperature range 220 to 390 K and the data reported by Finegold and Fanconi[9-10] for PGII in the temperature range 1.4 to 20 K as "recommended experimental heat capacities" for a mixed sample of polyglycine.*** The theta temperatures based on these experiments are 750.3 ± 43.0 K for Θ_1 and 80.6 ± 2.4 K for Θ_3. Samples of specific conformation should deviate, at least at higher temperature, only insignificantly from the recommended data.

A similar comparison of results for poly(L-alanine) can be seen in Figure 59. Again the large discrepancies between the newly measured and calculated data on a mixed sample of poly(L-alanine) and the literature data on α-PLA can be seen. The literature data only show reasonable agreement with calculation up to 160 K. Above 160 K, the literature data are consistently higher than either the calculated data or the newly measured data. However, the newly measured data show good agreement with the calculation over the entire range of measurement, the RMS deviation being only 0.88%. Based on these results, use our experimental data in the

*** The term "recommended heat capacity" is used for the critically reviewed *ATHAS* data bank.

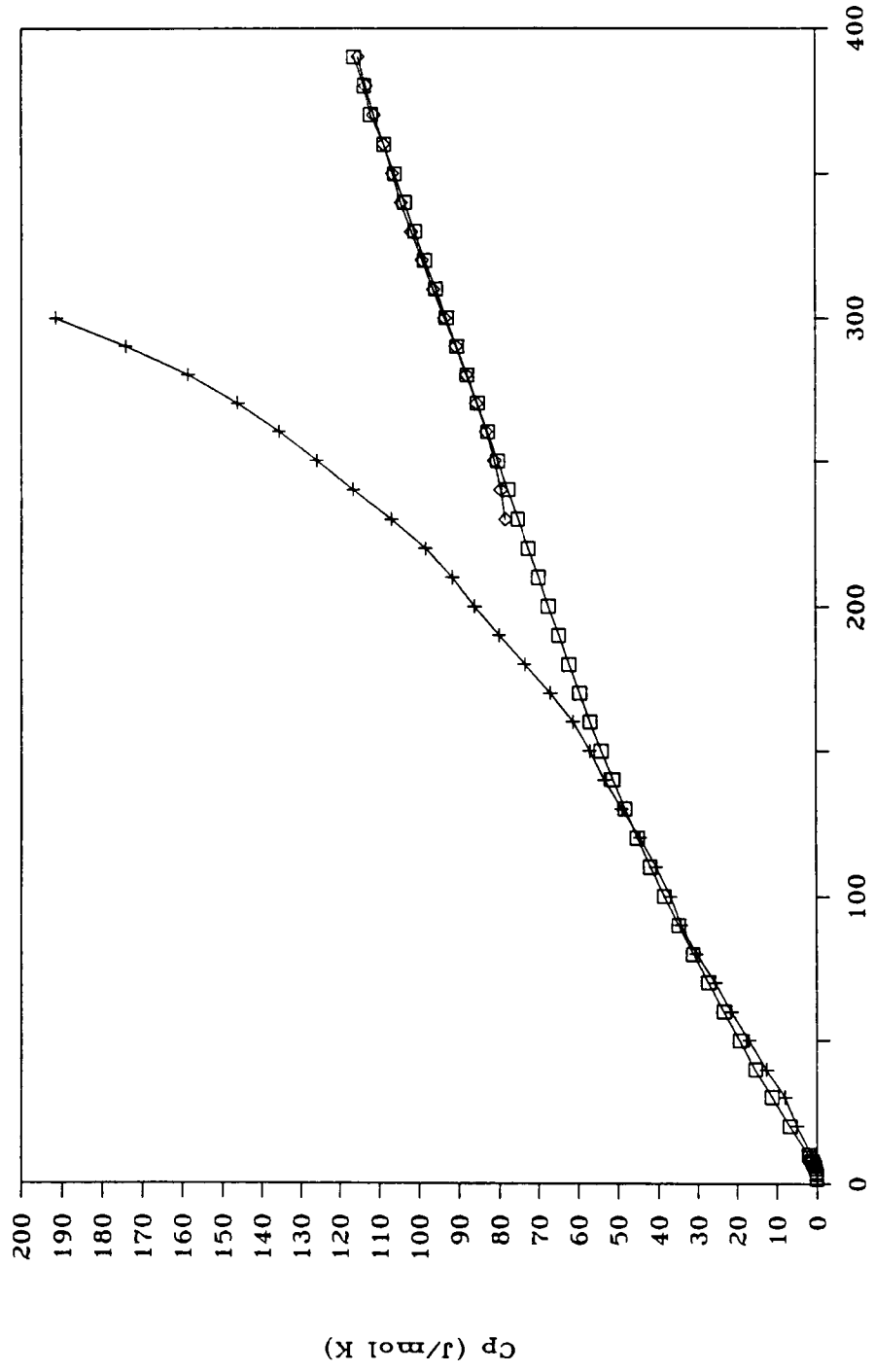


Figure 59 Comparison of Heat Capacities of Poly(L-alanine). Curve (□): New calculations. Curve (◇): New measurements. Curve (+): Previous measurements on α-poly(L-alanine).[12,15] [Sources: L. Finegold and J.L. Cude *Biopolymers* **11**, 2483 (1972); M. Daurel, P. Delhaes, and E. Dupart *Biopolymers* **14**, 801 (1975).]

temperature range 220 to 390 K and the data reported by Daurel et al.[15] and Finegold and Cude[12] for α-PLA in the temperature range 60 to 160 K as more recommended experimental heat capacity for a random sample of poly(L-alanine). The corresponding theta temperatures are 634.1 ± 33.3 K for Θ_1 and 58.0 ± 1.5 K for Θ_3.

Finally, the comparison of the newly measured and calculated data on poly(L-valine) in mixed form to the previously reported data on β-PLV can be seen in Figure 60. For poly(L-valine), the agreement observed between the literature data nd the calculated data covers an even smaller temperature range than was observed for either polyglycine or poly(L-alanine). On the other hand, the RMS deviation between the newly measured data and the calculated data is only 1.18% (220 to 390 K). We use the newly measured experimental data in the temperature range 220 to 390 K and the data reported by Daurel et al.[16] on β-PLV in the limited temperature ranges 2 to 10 K and 40 to 60 K as more recommended experimental heat capacity data for a sample of random conformation poly(L-valine). The corresponding theta temperatures are 663 ± 44.2 K for Θ_1 and 64.5 ± 2.2 K for Θ_3.

Figure 61 shows the deviations of the newly measured data form the calculated data for polyglycine, poly(L-alanine), and poly(L-valine). The literature data for these three homopolymers seem to be plagued by systematic experimental errors. As the authors of the literature data did not provide detailed experimental procedures for their measurement of heat capacity, only speculation on the source

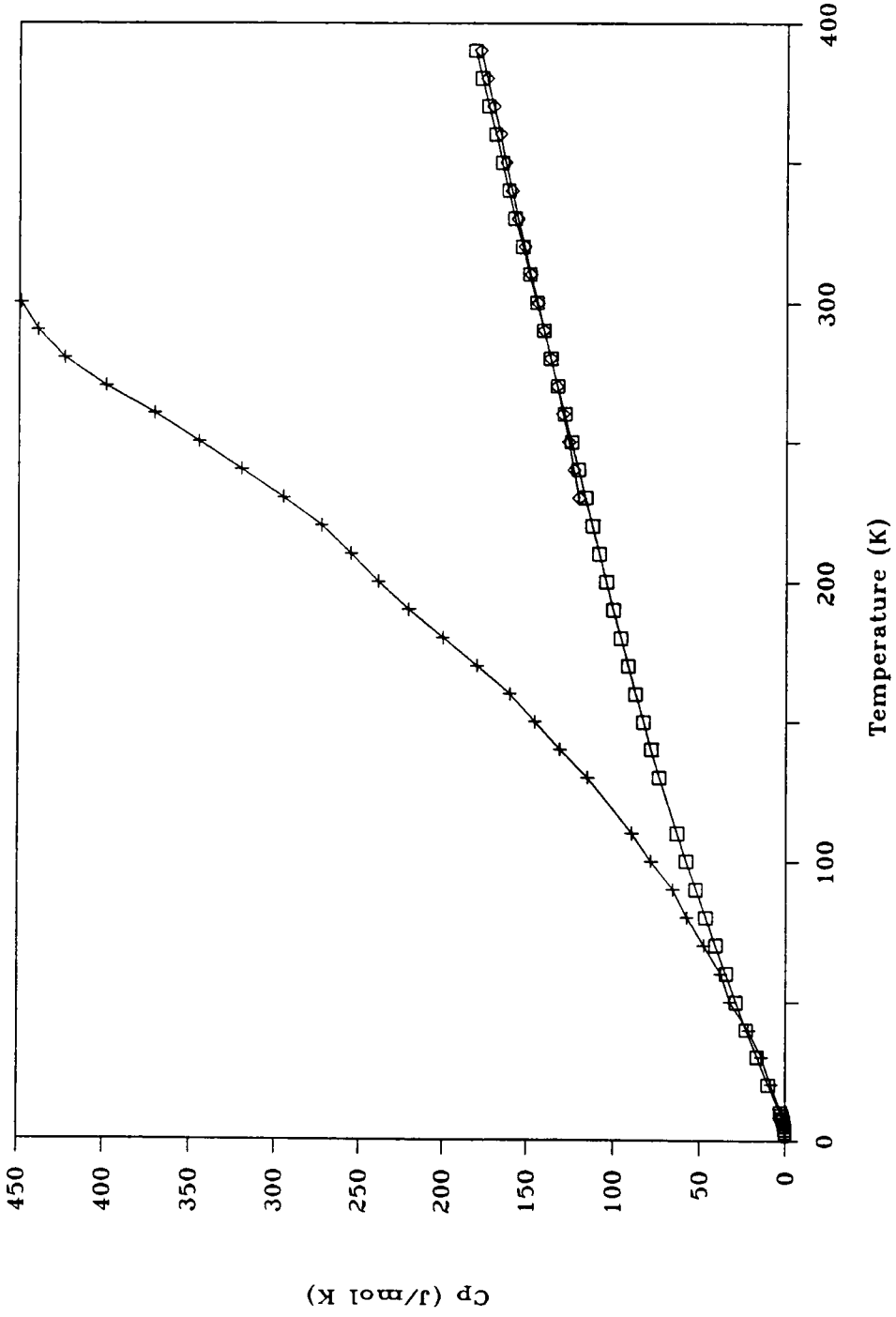


Figure 60 Comparison of Heat Capacities of Poly(L-valine). Curve (□): New calculations. Curve (◇): New measurements. Curve (+): Previous measurements on β-poly(L-valine).[16] [Source: M. Daurel, P. Delhaes, and E. Dupart *Biopolymers* **15**, 415 (1976).]

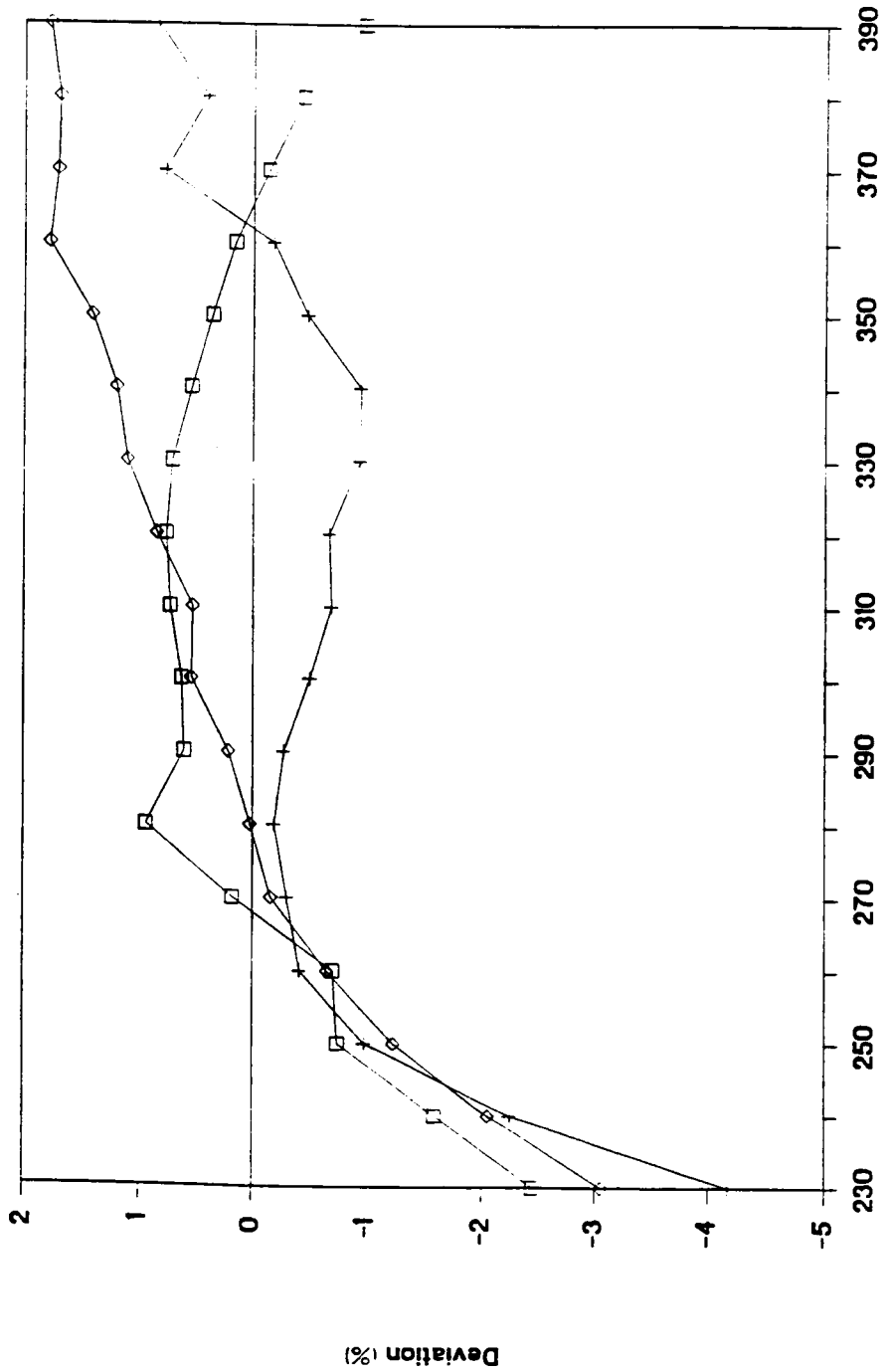


Figure 61 Deviations of Calculated Heat Capacities from Experimental Heat Capacities – GLY, ALA, VAL. $[(C_p^{calc} - C_p^{exp})/C_p^{exp}]$. Curve A (□): Polyglycine. Curve B (+): Poly(L-alanine). Curve C (◇): Poly(L-valine).

of such errors is possible. One of the most likely sources of such errors is water content. As noted earlier, biological polymers are notorious for containing significant quantities of water and must be handled carefully not only to remove any free water, but also to prevent later uptake of atmospheric water. The literature data for all three poly(amino acids) show consistently positive deviations from the calculated data. This additional measured heat capacity could very well be due to the presence of water. The effect of water content on experimental heat capacities of these biological polymers will be discussed in more detail in the following section.

II. EXAMINATION OF WATER CONTENT

IIA. Effect on Heat Capacities

In Section I of Chapter III, the results of the heat capacity measurements for all nineteen poly(amino acids) and copolymers are given. For each of the samples studied, the initial DSC run produced a curve containing a fairly broad peak. After this initial heating to 390 K (120°C), the peak was observed to disappear. As stated in Section I of Chapter III, we believe the peaks observed in the initial heating runs can be attributed to the vaporization of water. In each case, the sample weight was observed to be less following the initial run. When the sample was left at room temperature in a desiccator for a period of several hours, the sample weight was observed to increase slightly, and a smaller, but similar broad peak was again observed upon heating the sample to 390 K.

In an attempt to quantify our belief that the observed peaks can be attributed to the vaporization of water, some calculations were necessary. Assuming that for each sample the weight loss observed following the initial heating run is due to a loss of water, then one can calculate the heat of vaporization of this lost water in joules by simply multiplying the weight loss by the true heat of vaporization of water at 100°C and atmospheric pressure. As an example, the polyglycine was observed to lose 0.45 mg following the initial heating, resulting in a heat of vaporization of 1.02 J.

$$\Delta H_{vap}\ H_2O\ (J) = \Delta H_{vap}\ H_2O\ (J/g) \times \text{Weight of } H_2O\ (g) \qquad (18)$$

$$\Delta H_{vap}\text{mass} = 2259\ J/g \times 0.45\ mg = 1.02\ J \qquad (19)$$

We will call this heat of vaporization, the mass heat of vaporization, ΔH_{vap}mass. It is the heat of vaporization determined assuming the weight loss is solely due to water evaporation. This mass heat of vaporization of water must then be compared to the heat of vaporization calculated from the heat capacity curves. For each sample, the second heating run was subtracted from the first or initial heating run. This resulted in the heat capacity due solely to the water assuming the partial molar heat of evaporation is equal to the heat of evaporation of pure water. The area of this curve was then integrated resulting in the C_p heat of vaporization of water, $\Delta H_{vap}C_p$. For polyglycine, the integration resulted in:

$$\Delta H_{vap}\ H_2O = 7.8552 \times 10^{-2}\ \frac{J}{g(gly)} \qquad (20)$$

Multiplying by the weight of polyglycine gives the C_p heat of vaporization of water in joules.

$$\Delta H_{vap} C_p = 7.8552 \times 10^{-2}\ \frac{J}{g(gly)} \times 11.08\ mg\ gly = 0.8704\ J \qquad (21)$$

A comparison of the mass and the C_p heats of vaporization reveals the C_p heat of vaporization to be 14.7% lower than the mass heat of vaporization. A similar set of calculations were carried out for each of the remaining poly(amino acids) and copolymers. The results are given in Table 34. In each case, the percent difference reflects the degree to which the C_p heat of vaporization was lower than the mass heat of vaporization.

In discussing the results, it is important to point out that for most of the poly(amino acids) and copolymers, the entire peak observed in the initial heating run was not recorded. Consider, for example, Figures 14, 15, and 16 in Chapter III. The water peak is most fully recorded in the case of poly(L-valine) (Figure 16), less so in the case of poly(L-alanine) (Figure 15) and even less so in the case of polyglycine (Figure 14). In cases such as these, before the C_p heat of vaporization was determined, an attempt was made to extrapolate the heat capacity curves for runs 1 and 2 until they coincided. It is interesting to note that for these three poly(amino acids), the difference between the C_p and mass heats of vaporization becomes less

TABLE 34

Water Results for the Biolpolymers

Biopolymer	ΔH_{vap}mass (J)	$\Delta H_{vap}C_p$ (J)	% Difference
GLY	0.8704	1.02	14.67
ALA	0.848	0.904	6.195
VAL	0.597	0.599	0.334
LEU	0.034	0.045	24.44
SER	1.437	1.672	14.06
ASP•Na	1.524	2.114	27.91
GLU•Na	0.7506	0.8426	10.92
ASN	1.410	1.911	26.22
PHE	0.1372	0.1581	13.22
TYR	0.865	0.890	2.80
TRP	0.4752	0.574	17.21
PRO	0.6027	0.657	8.26
LYS•HBr	0.7911	0.856	7.58
HIS	1.140	1.20	5.36
HIS•HCl	0.7338	0.8268	12.59
ARG•HCl	0.5919	0.594	0.353
LYS•HBr–ALA	0.6305	0.664	5.04
LYS•HBr–PHE	0.4979	0.504	1.21
GLU•Na–TYR	0.6225	0.867	28.20
PRO–GLY–PRO	1.252	1.46	14.25

as the peak is recorded more fully; thus as fewer data points need to be extrapolated in order to resolve the water peak.

For poly(L-leucine), the peak is fully recorded (Figure 17 Chapter III), the percent difference between the mass and C_p heats of vaporization is 24.4%. This large difference may be in part attributed to the fact that we are looking at a fairly large difference between two small numbers, ΔH_{vap} exp = 0.045 J and ΔH_{vap} obs = 0.034 J. The two small numbers arise from the relatively smaller observed water peak (compared to the majority of samples studied) and the corresponding very small loss in weight, only 0.02 mg.

For poly(L-serine), the difference of 14% is quite reasonable considering the degree to which the peak is recorded (Figure 18). The degree of peak recording and percent difference in the heats of vaporization are similar to the results observed for polyglycine.

The results for the three acidic poly(amino acids), poly(aspartic acid)•Na (Figure 19), poly(L-glutamic acid)•Na (Figure 20), and poly(L-asparagine) (Figure 21) are not surprising either based on the degree of recording of the water peak. All three of these samples were observed to lose a considerable amount of weight following the initial heat runs. For poly(L-aspartic acid)•Na and poly(L-asparagine), the water peak is only partly recorded. This leads to a rather extensive amount of extrapolation and the not surprisingly high differences between the two heats of vaporization. The water peak is more fully resolved for poly(L-glutamic acid)•Na, and as a result, the C_p heat of vaporization is much closer in value to the mass heat

of vaporization.

Poly(L-phenylalanine) (Figure 22) was the only poly(amino acid) to exhibit two peaks, one for the vaporization of water and one for the fusion of water. Due to the relatively small and broad nature of the fusion peak, it was not possible to determine the heat of fusion. Considering the recording of the vaporization peak, a slightly better agreement between the C_p and mass heats of vaporization might have been expected, although a difference of 13.2% is not large and not out of line with the general results observed for all the samples.

The C_p heat of vaporization of poly(L-tyrosine) (Figure 23) was only 2.80% lower than the mass heat of vaporization. Note that the peak is completely recorded in the temperature range of measurement. Poly(L-methionine) (Figure 24), on the other hand is very difficult to interpret. The extreme broadness of the peak did not permit an C_p heat of vaporization to be determined. Based on the weight loss, the expected heat of vaporization is 0.032 J.

For the remaining poly(amino acids) and copolymers, with the exception of poly(L-glutamic acid • Na-tyrosine), the agreement between the C_p and mass heats of vaporization are all quite good and reasonable, ranging from 0.353% to 14.2%. For poly(L-glutamic acid • Na-tyrosine), a rather high difference of 28.20% was observed.

Taking a look at these results as a whole, one can conclude that the peaks observed in the initial heating runs can be largely attributed to the presence of removable water. The average difference between the mass and C_p heats of vaporization for the 20 samples for which an observed heat of vaporization was

determined, is only 12.0%. Considering the fact that some extrapolation of the peaks was necessary in the majority of cases and extensive extrapolation was necessary in a few of the cases, this does not seem to be an unreasonable difference. In addition, the mass heats of vaporization were determined using the heat of vaporization of pure water at 100°C and atmospheric pressure. None of the samples studied exhibited a water peak temperature of 100°C, and the C_p heats of vaporization were determined over rather broad temperature ranges. Furthermore, the partial molar heat of evaporation may well be higher than the heat of evaporation. As a result, the differences calculated reflect a difference or error over a large temperature range. A 12.0% error over a temperature range of 130° (the minimum case) is rather insignificant. For these reasons, we attribute the peaks observed in the initial heating runs to the presence of removable water. It is important to point out that although for most of the samples the water peak was not completely recorded, we are confident that the water removed (as reflected in the weight loss following the initial heating run) represents the total amount of removable water. In each case, the sample was held at 390 K (120°) for a period of time no less than 20 minutes. As mentioned in Chapter III, the sample was held at 390 K until the baseline remained steady (indicating the end of water evaporation). The samples were then held an additional 10 minutes at 390 K to achieve a state of equilibrium before a cooling run was started. Furthermore, the weight observed following run 3 (third heating run after the sample was left at room temperature in a desiccator for several hours was within 0.50% of the weight observed following run 1 (the initial heating run).

This study has an important impact on the results presented in the previous section, Section I of Chapter IV. It now seems almost certain that the differences observed between the literature data on polyglycine,[9-10] poly(L-alanine),[12,15] and poly(L-valine)[16] can be attributed to the presence of water that was not removed prior to the measurements. The results of this section have shown how important it is to consider the water content when making any thermodynamic measurement on these biological polymers. As an aside, it has been further shown that desiccants such as calcium chloride and silica gel are not preventing these materials from absorbing some atmospheric water at room temperature. Most importantly, these results have shown that good thermodynamic data can be obtained once the water has been removed from biological polymers.

IIB. Effect on Peak Temperatures

For the 21 samples studied, the peak temperatures for the water vaporization peaks ranged from 323 K (50°C) to 377 K (104°C). For 80% of the samples, the vaporization peak ranged between 353 K (80°C) and 377 K (104°C). The fusion peak of water observed for poly(L-phenylalanine) occurred at 238 K (-35°C), 35 degrees lower than the fusion temperature of pure water at atmospheric pressure. The fact that for all but one of the samples studied, the vaporization peak occurred at a slightly higher or lower temperature than what would be expected for pure water is not unusual, considering that we are dealing with biological polymers. Proteins have been found to influence the structure and physical properties of their solvent water.

Calorimetry studies on protein-water systems including work on such proteins as β-lactoglobulin,[73] egg albumin,[74] lysozyme,[75] and α-lactalbumin[76] have shown water fusion peak temperatures and heats of fusion to be in some cases less and in other cases more than those observed for ordinary water. Vaporization peak temperatures and heats of vaporization were not discussed for these systems as the protein denatured before the vaporization of water could be observed.

III. HEAT CAPACITIES OF COPOLYMERS - ADDITIVITY

Now that the foundation for the advanced thermal analysis of biological materials has been layed through the establishment of a data bank for the heat capacities of the poly(amino acids) based on the common twenty amino acids, the next step is the verification of the copolymer rules established for synthetic polymers. Regarding heat capacity measurements, the trend observed for the synthetic copolymers is that heat capacities are additive with respect to composition in both the solid and liquid states above 50 K.[51-52] Thus the heat capacity of a copolymer, AB, is composed of the heat capacities of polymers A and B:

$$C_p = C_p(\mathrm{A}) + C_p(\mathrm{B}) \qquad (22)$$

In the crystalline and amorphous solid states of matter, the heat capacity is dominated almost completely by vibrational motions. As a result, and as discussed in Chapter I, we are able to calculate heat capacities of solids and amorphous

polymers based on their vibrational spectra. To suggest that heat capacities of solid polymers are additive therefore suggests that the vibrational spectra must be approximately additive. As shown in Chapter I, we characterize vibrational frequencies by their Θ-temperatures. At the temperature Θ K, a particular vibrational frequency has reached 92% of its total excitation relative to the heat capacity. In other words, we can say that above this Θ-temperature, the contribution of this particular frequency to the heat capacity remains essentially the same (R). The heat capacity then depends solely on the number of vibrators. Remember that we divide the vibrational frequencies of linear macromolecules into two types, group and skeletal. By their nature, group vibrations are largely independent of their chemical environment and therefore additive. The skeletal vibrations are further subdivided into inter- and intra-molecular vibrations. The intermolecular vibrations, characterized by Θ_3 and important mainly at low temperatures, are observed to be nonadditive, thus restricting the additivity to at least above 50 K. The intramolecular vibrations, characterized by Θ_1 and important at higher temperatures, are more closely additive. Consider that the frequency of a vibration is given by its force constant and mass.

$$\nu = \sqrt{\frac{k}{m}} \tag{23}$$

Mass is additive, and for similar backbone polymers force constants can be considered roughly the same (and therefore additive). As a result, above 50 K

additivity of solid heat capacities of polymers is frequently observed provided frequency and number of vibrators do not change for different molecular structures made up of the same basic units.[51-52] For the copolymers of the poly(amino acids), these conditions are met, and therefore, additivity is expected.

In order to verify this copolymer rule of heat capacity additivity for the biological polymers, heat capacity measurements were made on four copolymers of the poly(amino acids) studied. These four copolymers are listed in Table 2 in Chapter 2. For each copolymer, the measured heat capacities of the poly(amino acids) making up the copolymer were added together with respect to the molar ratios of each present in the copolymer. These resulting heat capacities were then compared to the heat capacities measured for that copolymer. Figure 62 shows these results for the copolymer poly(L-lysine • HBr-alanine). The squares (□) represent the measured heat capacities for poly(L-lysine) • HBr, while the crosses (+) represent the measured heat capacities for poly(L-alanine). The diamonds (◇) represent the heat capacities determined by adding the measured heat capacities for the two poly(amino acids) with respect to molar ratios. Finally, the triangles (△) represent the heat capacities measured for the copolymer poly(l-lysine • HBr-alanine). The graph makes it quite clear that for this copolymer of two poly(amino acids), the heat capacities of the individual polymers are indeed additive. The RMS deviation between the added copolymer heat capacities and the measured copolymer heat capacities is ±1.89% over the entire range of the experiment (220 to 390 K).

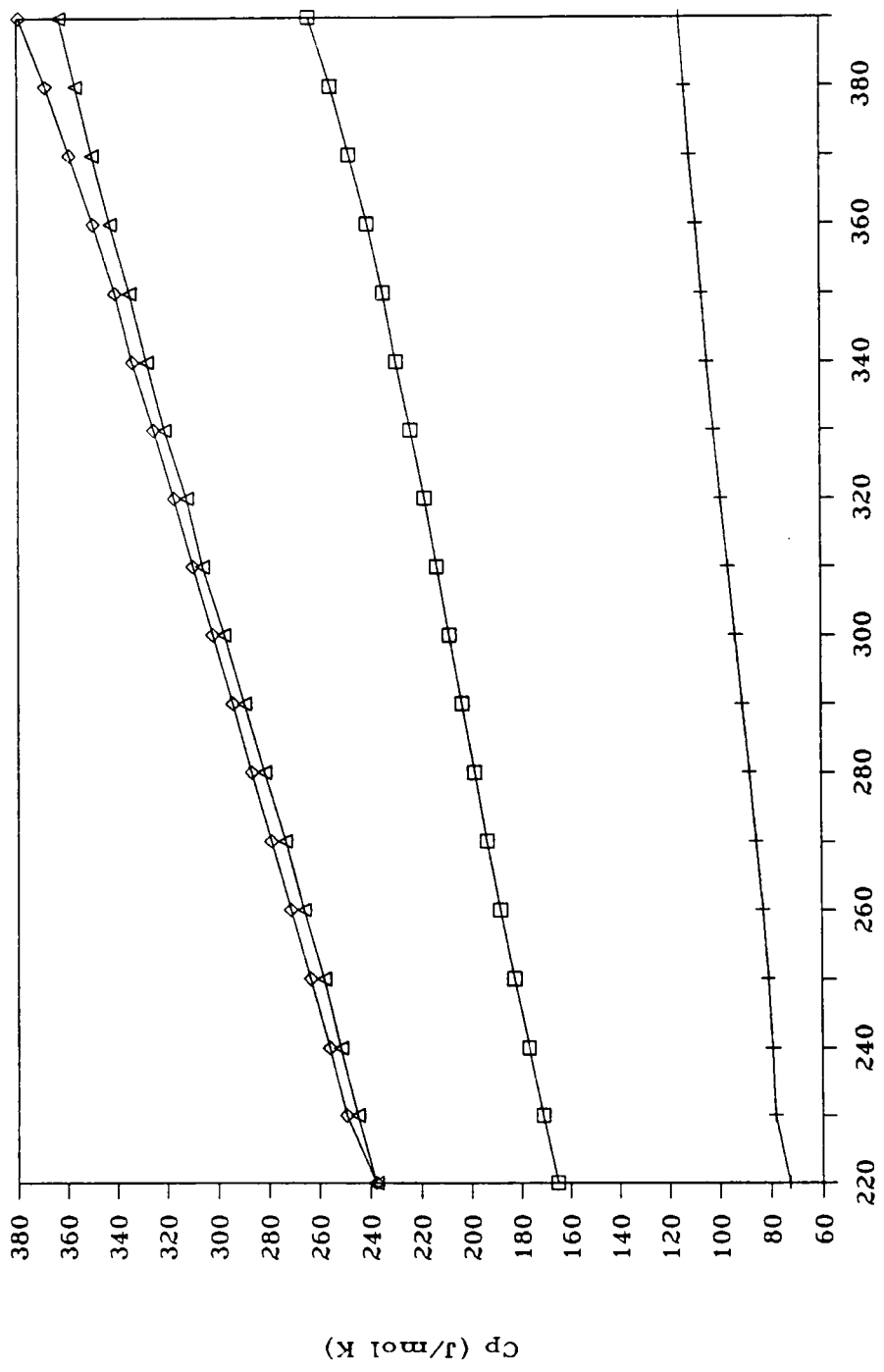


Figure 62 Copolymer Additivity Results – LYS•HBr–ALA. Curve A (□): Heat Capacities of Poly(L-lysine•HBr). Curve B (+): Heat Capacities of Poly(L-alanine). Curve C (◇): Added heat capacities of poly(L-lysine•HBr) and Poly(L-alanine), i.e. Curve A (□) + Curve B (+). Curve D (△): Measured heat capacities of the copolymer, Poly(L-lysine•HBr-alanine).

Figure 63 illustrates the copolymer calculation for poly(l-lysine•HBr-phenylalanine). Again the measured heat capacities for the two poly(amino acids), in this case poly(L-lysine)•HBr and poly(L-phenylalanine), were added together with respect to molar ratios. Comparison of the added copolymer heat capacities to the measured copolymer heat capacities reveals an RMS deviation of ±3.07%.

The results for the copolymer poly(L-glutamic acid•Na-tyrosine) is shown in Figure 64. When the measured heat capacities of poly(L-glutamic acid)•Na were added to the measured heat capacities of poly(L-tyrosine), the heat capacities represented by the diamonds (◇) resulted. Upon comparison to the measured heat capacities for the copolymer to those determined by addition, an RMS deviation of ±2.58% was observed.

The final copolymer studied was the sequential copolymer poly(l-proline-glycine-proline). The measured heat capacities of poly(L-proline) were added to the measured heat capacities for polyglycine. The resulting added heat capacities were then compared to the measured heat capacities for the copolymer as shown in Figure 65. The RMS deviation between added and measured heat capacities was ±1.63%.

The results of these four copolymers verify that the copolymer addition rule of heat capacities observed for synthetic polymers can similarly be extended to the biological polymers. Although the work of this thesis does not extend beyond heat

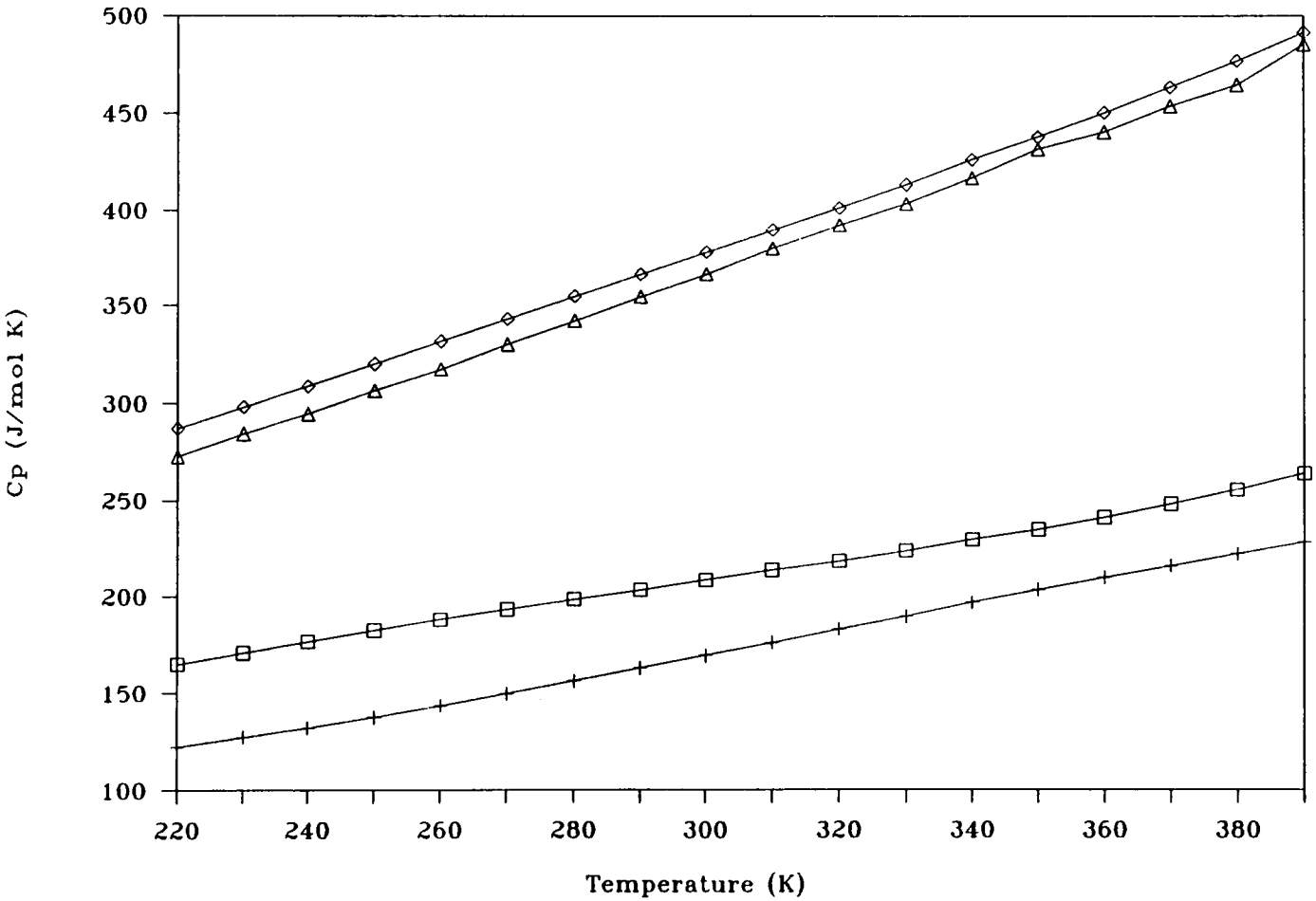


Figure 63 Copolymer Additivity Results – LYS•HBr–PHE. Curve A (□): Heat Capacities of Poly(L-lysine•HBr). Curve B (+): Heat Capacities of Poly(L-phenylalanine). Curve C (◇): Added heat capacities of poly(L-lysine•HBr) and Poly(L-phenylalanine), i.e. Curve A (□) + Curve B (+). Curve D (△): Measured heat capacities of the copolymer, Poly(L-lysine•HBr-phenylalanine).

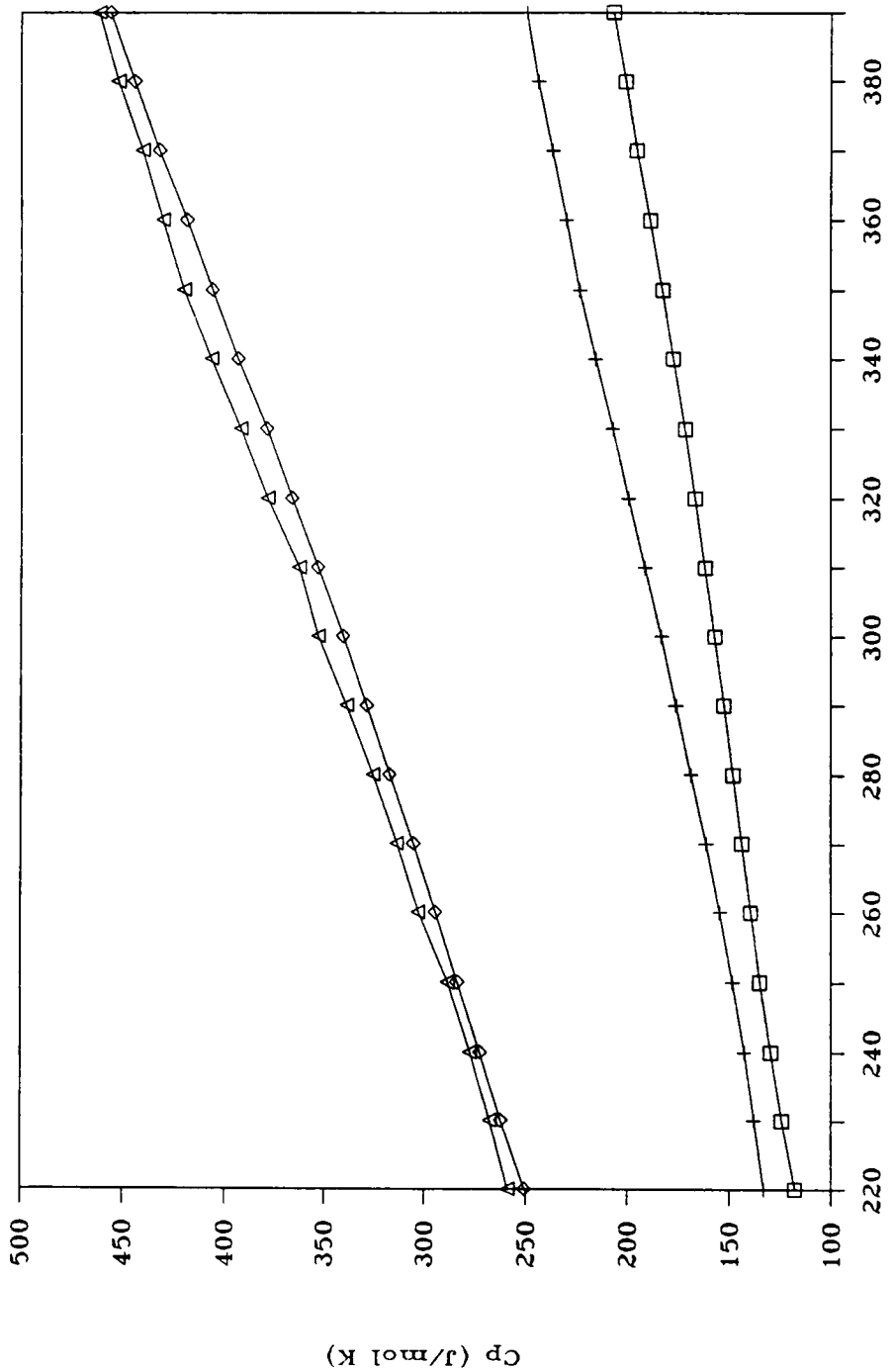


Figure 64 Copolymer Additivity Results – GLU•Na–TYR. Curve A (□): Heat Capacities of Poly(L-glutamic acid•Na). Curve B (+): Heat Capacities of Poly(L-tyrosine). Curve C (◇): Added heat capacities of poly(L-glutamic acid•Na) and Poly(L-tyrosine), i.e. Curve A (□) + Curve B (+). Curve D (△): Measured heat capacities of the copolymer, Poly(L-glutamic acid•Na-tyrosine).

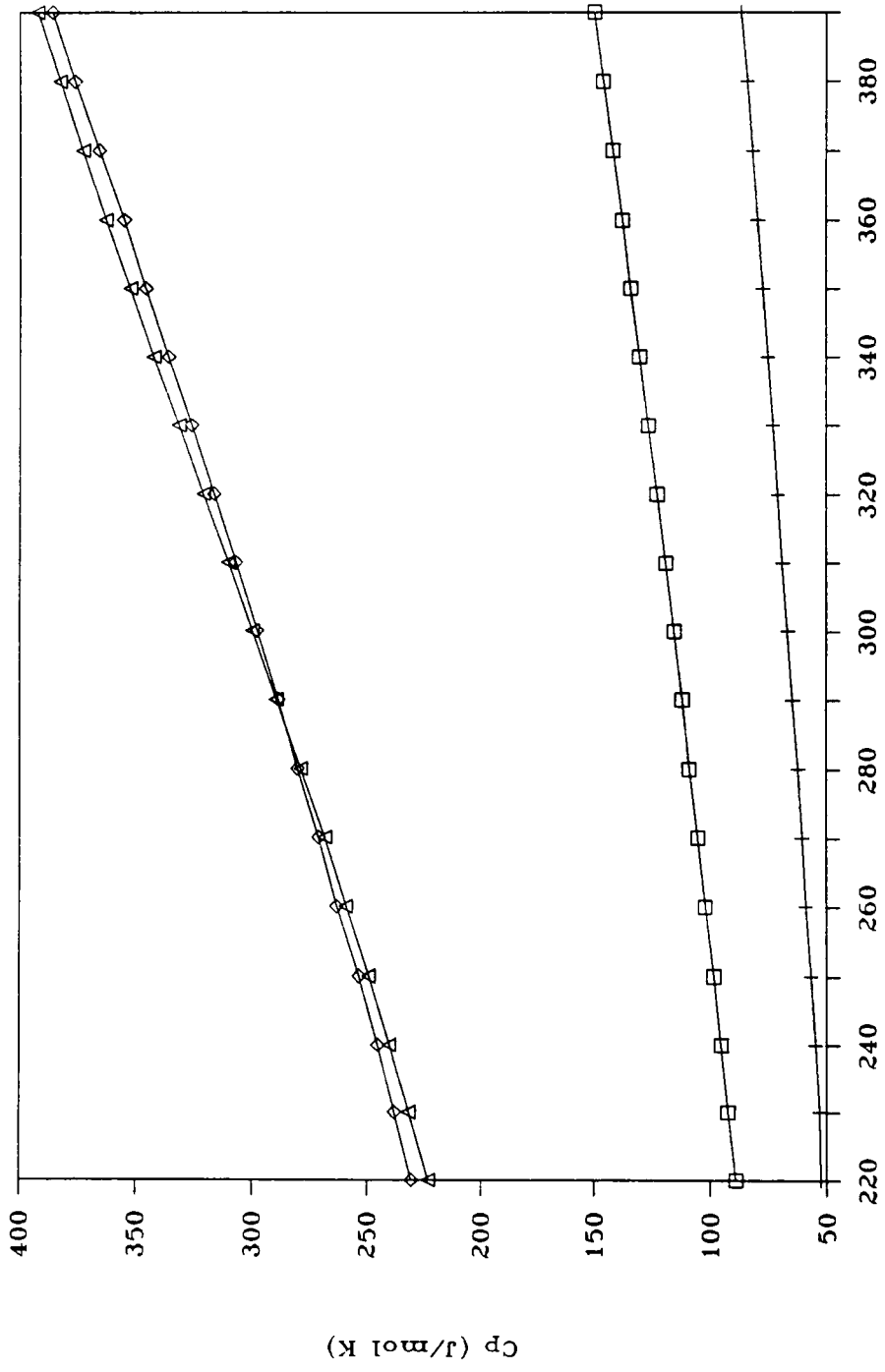


Figure 65 Copolymer Additivity Results – PRO-GLY-PRO. Curve A (□): Heat Capacities of Poly(L-proline). Curve B (+): Heat Capacities of Polyglycine. Curve C (◇): Added heat capacities of poly(L-proline) and Polyglycine, i.e. Curve A (□) + Curve B (+). Curve D (△): Measured heat capacities of the copolymer, Poly(L-proline-glycine-proline).

capacity measurements for copolymers, the next logical step would be verification of this rule for peptides and ultimately proteins. The success of applying his copolymer rule to biological polymers is further proof that the advanced thermal analyses developed for synthetic linear macromolecules can be extended to include the biological polymers.

IV. CALCULATION OF HEAT CAPACITY

For all the poly(amino acids) and copolymers for which heat capacity measurements were made, the agreement between calculation and measurement was quite good over the entire range of the experiment. Exceptions to this were poly(L-serine) and poly(L-methionine) for which agreement between calculation and measurement was achieved over only a limited range of the experiment. A discussion of the cause of the deviations observed at higher temperatures is given in Section V. Overall though, the skeletal heat capacities of the poly(amino acids) and copolymers were successfully fitted to the two parameter (Θ_1, Θ_3) Tarasov function. It was therefore possible to calculate heat capacities for all the polymers studied from 0 to 1000 K. Again it is necessary to point out that this temperature range goes well beyond the stability of the biopolymer. Calculations over such a considerable temperature range are necessary to cover the possible need to describe superheated states observed in flash pyrolysis and ablation. The overwhelming agreement observed between calculation and measurement for these biopolymers leads us to

conclude that the *ATHAS* method for computing heat capacities from vibrational spectra can well be extended to include the biological polymers.

Although agreement was observed between calculation and measurement, it is important to discuss a few aspects of the calculations. As pointed out in Chapter 3, information from normal mode calculations of isolated chains or attributed infrared and Raman spectra on the group vibration spectrum is available for only the two simplest poly(amino acids) - polyglycine and poly(L-alanine). As a result, for the remaining poly(amino acids) and copolymers, the group vibrational spectrum had to be constructed from other sources. For each of these biopolymers, the spectra were constructed in essentially two parts. The first part for each was the same, the backbone unit for which vibrational information was taken from polyglycine and poly(L-alanine). The second part, the construction of each side group, required taking the vibrational information available on chemically identical group of other macromolecules or even small molecules. The majority of this information came form the *ATHAS* data bank where vibrational information has been collected for over 150 linear macromolecules. Having to rely on constructed spectra to calculate the group vibration contribution to the heat capacity does not pose any difficulties, as the group vibrations are known to be essentially unaffected by their chemical environment and therefore transferable from one molecule to another.

When constructing the group vibration spectra for these biopolymers, it becomes necessary to take into consideration another important aspect of the heat capacity calculation, the number of skeletal vibrations, N. For each of the

biopolymers, we were interested in calculating the heat capacity of the solid. For a solid, the heat capacity is essentially entirely composed of vibrational motion. For every atom *n*, there are 3*n* degrees of freedom thus three vibrational modes. In the case of poly(L-valine), there are 16 atoms and therefore 48 vibrational modes total. The determination of how many of these are skeletal modes (*N*) was done in a manner consistent with previous studies in the *ATHAS* laboratory. The experience gained in the *ATHAS* laboratory over many years from the calculation of heat capacities of over 150 macromolecules has led to some general rules of thumb. One such rule is that two skeletal vibrations are assigned to every C=O, NH, CH, and CH_2 group. For CH_3- groups, as in the case of poly(L-valine) where two methyl groups are involved, each group is assigned three skeletal modes, this is according to the experience gained from work on polypropylene. This led to the assignment of 14 skeletal vibrations. For the majority of the poly(amino acids) and copolymers studied, the number of skeletal modes assigned to each is based on an accumulation of knowledge gained from work on other macromolecules. The chlorine and bromine anions and the sodium cation found in several of the polymers studied represent a separate case, as no polymer contained in the *ATHAS* data bank contains either an anion or cation. As a result, in assigning these species three skeletal vibrations and zero group vibrations, it was necessary to go back to the early days of trial and error. For the chlorine and bromine anions, an educated guess would be the assignment of the three vibrational modes as skeletal. Skeletal modes, as discussed earlier, are of relatively low frequency. Since frequency is inversely

proportional to the square root of mass,

$$\nu = \sqrt{\frac{k}{m}} \tag{24}$$

one sees that the larger the mass, the smaller or lower the frequency. Both the chlorine and bromine anions are relatively large. It is quite reasonable then to assume that their vibrational frequencies are relatively low and can thus be considered skeletal. The agreement observed when comparing experimental and calculated heat capacities for poly(amino acids) containing a bromine or chlorine anion indicated that such an assignment is reasonable. While the sodium cation is not as massive as either the bromine or chlorine anion, as a first guess, its vibrational modes were also assigned all skeletal. Again the agreement observed between calculation and measurement for the two sodium containing poly(amino acids) and one sodium containing copolymer suggests that such an assignment is reasonable and correct.

In discussing the assignment of three skeletal vibrations to the bromine and chlorine anions and the sodium atom, it is important to remember that the skeletal vibrations are described by the two-parameter (Θ_3, Θ_1) Tarasov equation which was given in Chapter I. Elements and salts are characterized by three-dimensional Debye functions. By assigning the anions and cation as skeletal vibrations, we are essentially "throwing in" three additional skeletal vibrations to the Θ_1 portion of the Tarasov equation. This is because we do not have the low temperature heat capacity data

necessary to determine a three-dimensional Debye function, Θ_3. Remember that due to the lack of low temperature heat capacity data for all but the three simplest poly(amino acids), we assumed a value of Θ_3 for the remaining poly(amino acids) based on an average of the Θ_3-temperatures of polyglycine, poly(L-alanine), and poly(L-valine). Taking a look at a list of Θ_3 temperatures for some compounds and elements (see Table 35), it is evident that the values are higher than the chosen value of 68.0 K used in the calculation of heat capacities for the poly(amino acids). It is quite likely that the chosen Θ_3-temperature of 68.0 K is more incorrect for the poly(amino acids) containing anions or cations than it is for those that do not. For this reason, it would be desirable to have low temperature heat capacity data for a more accurate determination of Θ_3. It should be stressed though, that over the temperature range of the experimental heat capacity data (220 to 390 K), a change in the chosen Θ_3-temperature from 68.0 K to 250 K does not appreciatively change the calculated heat capacities. This can be explained by the fact that at higher temperatures, the three-dimensional vibrators are essentially completely excited and contribute a constant amount to the heat capacity. The Θ_3 vibrators are most important in the temperature range 30 to 200 K. The one-dimensional Debye function becomes important at higher temperatures. This point is further made by a comparison the the determined Θ_1-temperatures for poly(L-histidine) and poly(L-histidine)•HCl. Essentially the two Θ_1-temperatures are the same even though the poly(L-histidine)•HCl is assigned three more skeletal vibrators than the poly(L-histidine). We would expect these two poly(amino acids) to have rather different Θ_3-

TABLE 35

Debye Temperatures of Compounds/Elements

Compound/Element	θ in K at $\theta/2$
NaCl	280
Cl_2	115
Na	150
KBr	180
KCl	230

temperatures. Again, low temperature heat capacity studies of all the poly(amino acids) would be useful and informative.

Two other important parameters in the calculation of heat capacity are the constant A_o and the equilibrium melting temperature T_m^o. Both are necessary in the conversion of heat capacity at constant pressure, C_p, to the heat capacity at constant volume, C_v. They become important when expansivity and compressibility data are not available. In such a situation, the Nernst-Lindemann equation must be employed. For all the poly(amino acids) and copolymers studied, expansivity and compressibility data have not yet been measured. Thus the Nernst-Lindemann equation was employed. The Nernst-Lindemann equation was originally derived for relatively heavy, monatomic solids. For solid linear macromolecules, only those vibrations associated with the heavy atoms (C, N, O, etc.) were originally considered to contribute to the heat capacity and thus lead to the choice of a value of A_o. A value for A_o was determined by putting together expansivity, compressibility, and heat capacity data for a number of solid polymers.[77] Later, the need to consider that at higher temperatures, vibrations such as C-H, N-H, or O-H stretching and bending contribute to the heat capacity. A simple measure of the number of vibrators excited at any given temperature is given by:

$$C_v = 3nR \tag{25}$$

In Eq. (25), n is the average number of excited vibrators. Taking this into consideration, a new temperature dependent value for the constant A_o was arrived

at in the *ATHAS* laboratory by evaluation experimental thermal expansivity, isothermal compressibility, and heat capacity data for 22 solid polymers. An average value of $(3.9 \pm 2.4) \times 10^{-3}$ (K mol)/J was obtained.[50] This average value has been found to be quite acceptable as a universal constant when it is not possible to calculate A_o due to a lack of expansivity and compressibility data.[50] For all heat capacity calculations, this universal constant was employed. While this universal constant can vary between 1.5×10^{-3} and 6.3×10^{-3} (K mol)/J, the success observed when comparing the calculated and measured heat capacities for the biopolymers studied suggests, however, that it was not necessary to use this constant as another fitting parameter.

Assignment of the equilibrium melting temperature for each of the poly(amino acids) and copolymers involves a considerable amount of guessing. Since polyglycine is the first member of the polyamide or nylon family, its equilibrium melting temperature was extrapolated from known information on the other polyamides by assuming that the change of $T_m°$ with the number of CH_2 groups is linear. A value of 555 K for $T_m°$ was determined. For poly(L-alanine), this value of 555 K was increased to 573 K to take into account the addition of a methyl group. For the remaining poly(amino acids) and copolymers this value of 573 K for $T_m°$ was used in the heat capacity calculations. It is worthwhile to point out that in the DTG studies carried out on a number of the poly(amino acids), decomposition was observed to occur for all between 503 K and 543 K. Thus the values used for the equilibrium melting temperatures are presumably quite reasonable. This is

supported by the agreement observed between the calculated and experimental heat capacities for the biopolymers studied. It is also important to note that $T_m°$ is rather insignificant in the C_p-C_v conversion, and plays no role in the C_v that is calculated. At 300 K the difference between C_p and C_v is about 5%. An error as large as 100 K in $T_m°$ would cause an error of only 1% in the calculated C_p.

The successes that was met in calculating heat capacities for the poly(amino acids) and copolymers are proof that the *ATHAS* method for computing heat capacities for solid linear macromolecules from vibrational spectra information can be extended to include the biological macromolecules. It would have been reasonable to assume that some difficulties might have been encountered in the calculations due to hydrogen bonding which plays such an important role in biological macromolecules. The effects of hydrogen bonding are considerably limited in the *ATHAS* computation method by the fact that the analysis of the vibrational frequencies is mostly concerned with an isolated chain model. The *ATHAS* laboratory has long recognized, however, that heat capacities are little effected by small changes in the vibrational frequencies of single bonds used for calculation. Rather, heat capacities are more effected by the overall degree of excitation of the vibrational modes.[51-52] Molecular dynamics simulations of polyethylene-like crystals have revealed that when the normal mode approximation breaks-down and heat capacities can no longer be described by a simple harmonic oscillator model such as is the Tarasov model, the heat capacities calculated with this simple harmonic oscillator model still agree well with the measured heat capacities.[78] As a result, it

becomes clear that heat capacities are little effected by specific details of the vibrational spectra. This is further evidence that using group vibrational frequencies from similar chemical groups in other macromolecules and small molecules to construct a vibrational spectrum for a polymer for which no such information is available is quite justified.

It is important at this point to make a comment concerning the deviations observed between the calculated and measured heat capacities. Figure 61, shown earlier, presented a graph of the deviations observed for the first three poly(amino acids) - polyglycine, poly(L-alanine), and poly(L-valine). Similar deviations of the newly measured data from the calculated data are observed for the remaining poly(amino acids) and copolymers, with the exception of poly(L-serine) and poly(L-methionine) which will be discussed separately. As in the cases of polyglycine, poly(L-alanine), and poly(L-valine), it is evident that the errors observed are not systematic.

V. COMPARISON OF Θ_1-TEMPERATURES

It is worthwhile to take a look at the determined Θ_1-temperatures for the poly(amino acids) and copolymers as a whole. A table of Θ_1-temperatures along with the number of skeletal and group vibrations was given in Chapter III (Table 33). The Θ_1-temperatures are seen to range from approximately 600 K to 900 K. Looking at the list of Θ_1-temperatures, they all tend to cluster around the range 630 K and 750

K with a few exceptions. No significant variations are observed. If one takes a look at the theta-temperatures determined for over 150 linear macromolecules (*ATHAS* data bank), it is observed that in the same structural group, Θ_1 is usually inversely proportional to the mass of the group. In other words, the Θ_1-temperatures are observed to decrease as the mass increases for polymers of the same structural group. The following is a discussion of the observed changes in Θ_1 with change in poly(amino acid) side group for a few of the poly (amino acids). At times, observations also include those made by comparing Θ_1-temperatures for other polymers. This information can be found in the *ATHAS* data bank.

Polyglycine is the simplest nylon, nylon 2. As a result, it is interesting to compare it to the other nylons. For nylon 6, Θ_1 is 544 K, and for nylon 11, it is 420 K. Thus we see that as the repeat group becomes larger, the Θ_1-temperature decreases. One would expect the Θ_1-temperature of polyglycine then to be higher than that of nylon 6. At 750 K, it is. On going from polyglycine to poly(L-alanine), the side group H is replaced by a CH_3. A decrease in Θ_1 is expected and is observed. Similarily on going from poly(L-valine) to poly(L-leucine), a CH_2 group is added, and one would expect a lower value of Θ_1 which is what is observed. However this is not the case on going from poly(L-aspartic acid•Na) to poly(L-glutamic acid•Na) where again a CH_2 group is added to the side group. Poly(L-tyrosine) is identical to poly(L-phenylalanine) with the exception of an added OH group on the phenyl group. Here the Θ_1-temperature is observed to increase with the addition of the OH group. This is not expected based on the increase in mass alone. For the remaining poly(amino

acids) where the side groups become more complicated, it is not as easy to compare Θ_1-temperatures. It is also important to remember that frequency is not just affected by mass but also by force constants.

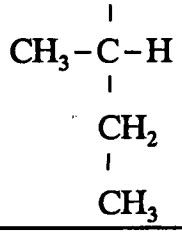
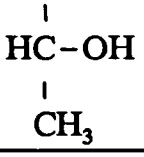
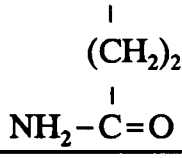
VA. Prediction of Heat Capacities Based on Θ_1-Temperatures

Based on this table of Θ_1-temperatures (Table 33), it is worthwhile to attempt to calculate heat capacties for the four poly(amino acids) which could not be purchased commercially – poly(L-leucine), poly(L-threonine), poly(L-glutamine), and poly(L-cysteine). The side groups of these poly(amino acids) are provided in Table 36.

Poly(L-isoleucine) has the same side group as poly(L-leucine). The only difference is the arrangement of the side group in the structure. Based on this different arrangement, it is necessary to construct the vibrational spectrum differently than was done for poly(L-leucine). For poly(L-isoleucine), the side group consisted of the backbone group from polyglycine and poly(L-alanine) (Table 13 Part A), two CH_3 groups from polypropylene (Table 13 Part C), a CH group from polypropylene (Table 13 Part C) and a CH_2 group from polyethylene (Table 13 Part D). As in poly(L-leucine), 16 skeletal vibrations were taken and the remaining 41 vibrations were assigned as being group. For poly(L-leucine), the determined Θ_1-temperature was 624.5 K. As the structural arrangement of poly(L-isoleucine) is different, one would expect a different value for Θ_1. Attempts were made to determine this difference by looking at other linear macromolecules for which Θ_1-temperatures have

TABLE 36

Side Groups of Four Poly(amino acids)

Poly(amino acid)	Side Group R
Poly(L-isoleucine) (ILE)	
Poly(L-threonine) (THR)	
Poly(L-glutamine) (GLN)	
Poly(L-cysteine) (CYS)	CH_2SH

been determined. The *ATHAS* data bank of this information did not, however, provide insight into this expected change in Θ_1. As a result, heat capacites for poly(L-isoleucine) were calculated using the Θ_1-temperature of poly(L-leucine). For poly(L-isoleucine) and the following three poly(amino acids), the value of Θ_3 was taken as 68.0, and $T_m°$ was taken as 573 K. The results of the calculation are given in Table 37. Essentially there is no difference in these calculated heat capacities from those calculated for poly(L-leucine). As a result, for poly(L-isoleucine), heat capacity measurements would be very useful. Although it is not available commercially, it would be worthwhile to have it specially prepared for heat capacity analysis.

Poly(L-threonine) is similiar to poly(L-serine). For calculation of heat capacities for poly(L-threonine), the vibrational spectrum was constructed by taking the backbone group (Part A Table 13), the OH group (Part E of Table 13), a CH group from polypropylene (Part C Table 13), and a CH_3 group (Part J Table 13). The number of skeletal vibrations was taken as 13 leaving 29 group vibrations. As in poly(L-serine), the two lowest frequency vibrations of the OH group were taken as skeletal rather than group. This was done based on the experience with poly(L-serine) and the fact that in order to use the Θ_1-temperature of poly(L-serine) as the basis for guessing a Θ_1-temperature for poly(L-threonine), it is necessary that the number of skeltal vibrations, N, be chosen in the same consistent manner. Essentially the difference between poly(L-threonine) and poly(L-serine) is the addition of a CH_3 group. To guess a likely value for Θ_1, it was necessary to consider

TABLE 37

Calculated Heat Capacities of Poly(L-isoleucine)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.000	0.000	0.000	0.000	0.000	0.000
0.60	0.001	0.000	0.000	0.000	0.001	0.001
0.70	0.001	0.000	0.000	0.000	0.001	0.001
0.80	0.002	0.000	0.000	0.000	0.002	0.002
0.90	0.003	0.000	0.000	0.000	0.003	0.003
1.00	0.004	0.000	0.000	0.000	0.004	0.004
1.20	0.006	0.000	0.000	0.000	0.006	0.006
1.40	0.010	0.000	0.000	0.000	0.010	0.010
1.60	0.015	0.000	0.000	0.000	0.015	0.015
1.80	0.021	0.000	0.000	0.000	0.021	0.021
2.00	0.029	0.000	0.000	0.000	0.029	0.029
3.00	0.097	0.000	0.000	0.000	0.097	0.097
4.00	0.230	0.000	0.000	0.000	0.230	0.230
5.00	0.448	0.000	0.000	0.000	0.448	0.448
6.00	0.770	0.000	0.000	0.000	0.770	0.771
7.00	1.201	0.000	0.000	0.000	1.201	1.202
8.00	1.742	0.000	0.000	0.000	1.742	1.745
9.00	2.383	0.000	0.000	0.000	2.383	2.386
10.00	3.102	0.000	0.000	0.000	3.102	3.108
15.00	7.289	0.000	0.000	0.000	7.289	7.308
20.00	11.613	0.000	0.000	0.000	11.613	11.653
25.00	15.745	0.000	0.000	0.000	15.745	15.813
30.00	19.683	0.000	0.000	0.000	19.683	19.784
40.00	27.204	0.000	0.000	0.000	27.204	27.391
50.00	34.471	0.000	0.004	0.004	34.476	34.773
60.00	41.610	0.000	0.008	0.008	41.618	42.050
70.00	48.575	0.003	0.060	0.063	48.638	49.230
80.00	55.289	0.010	0.161	0.171	55.460	56.235
90.00	61.686	0.029	0.328	0.357	62.043	63.021
100.00	67.723	0.067	0.622	0.689	68.412	69.615
110.00	73.308	0.132	0.936	1.067	74.375	75.819
120.00	78.434	0.230	1.396	1.625	80.059	81.760
130.00	83.084	0.367	1.898	2.265	85.350	87.321
140.00	87.300	0.550	2.580	3.130	90.430	92.688
150.00	91.125	0.784	3.311	4.095	95.220	97.777
160.00	94.573	1.072	4.230	5.302	99.875	102.747
170.00	97.644	1.419	5.201	6.620	104.264	107.460
180.00	100.426	1.830	6.340	8.170	108.596	112.134

TABLE 37 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	102.937	2.306	7.564	9.871	112.808	116.702
200.00	105.201	2.853	8.858	11.711	116.912	121.176
210.00	107.243	3.471	10.240	13.711	120.954	125.604
220.00	109.085	4.162	11.844	16.007	125.092	130.150
230.00	110.751	4.927	13.526	18.454	129.205	134.687
240.00	112.259	5.766	15.133	20.899	133.158	139.077
250.00	113.627	6.677	17.020	23.697	137.324	143.707
260.00	114.871	7.657	18.917	26.574	141.445	148.309
270.00	116.005	8.704	20.815	29.520	145.524	152.887
273.15	116.341	9.048	21.444	30.492	146.833	154.357
280.00	117.040	9.815	22.831	32.646	149.686	157.571
290.00	117.987	10.985	24.896	35.881	153.867	162.295
298.15	118.700	11.980	26.643	38.622	157.323	166.211
300.00	118.855	12.210	26.959	39.169	158.024	167.014
310.00	119.653	13.485	29.152	42.638	162.291	171.870
320.00	120.388	14.806	31.257	46.063	166.451	176.634
330.00	121.066	16.167	33.357	49.524	170.590	181.397
340.00	121.693	17.564	35.535	53.099	174.791	186.246
350.00	122.273	18.992	37.787	56.779	179.052	191.181
360.00	122.811	20.447	39.865	60.312	183.123	195.936
370.00	123.311	21.925	42.063	63.988	187.298	200.824
380.00	123.776	23.422	44.092	67.513	191.289	205.536
390.00	124.209	24.933	46.154	71.087	195.296	210.288
400.00	124.614	26.456	48.366	74.822	199.436	215.205
410.00	124.992	27.988	50.419	78.407	203.399	219.955
420.00	125.346	29.525	52.372	81.898	207.244	224.600
430.00	125.678	31.066	54.312	85.378	211.056	229.231
440.00	125.989	32.608	56.242	88.850	214.840	233.854
450.00	126.282	34.149	58.178	92.327	218.609	238.485
460.00	126.557	35.688	60.093	95.780	222.338	243.094
470.00	126.817	37.222	61.969	99.191	226.008	247.663
480.00	127.061	38.751	63.764	102.514	229.575	252.142
490.00	127.292	40.273	65.558	105.830	233.123	256.622
500.00	127.510	41.787	67.391	109.178	236.688	261.146
510.00	127.716	43.293	69.057	112.350	240.067	265.487
520.00	127.912	44.790	70.694	115.484	243.396	269.797
530.00	128.097	46.277	72.301	118.577	246.674	274.074
540.00	128.272	47.753	73.874	121.627	249.899	278.315
550.00	128.439	49.218	75.423	124.641	253.080	282.531
560.00	128.597	50.673	77.019	127.692	256.289	286.802
570.00	128.748	52.115	78.487	130.603	259.351	290.932
580.00	128.891	53.546	79.925	133.471	262.362	295.030
590.00	129.028	54.965	81.328	136.293	265.320	299.092
600.00	129.158	56.372	82.747	139.119	268.277	303.177

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	129.282	57.766	84.128	141.894	271.177	307.221
620.00	129.401	59.148	85.454	144.602	274.003	311.207
630.00	129.498	60.517	86.733	147.251	276.749	315.127
640.00	129.606	61.874	87.984	149.858	279.464	319.036
650.00	129.709	63.218	89.206	152.424	282.133	322.918
660.00	129.807	64.550	90.400	154.950	284.757	326.774
670.00	129.901	65.868	91.567	157.435	287.336	330.603
680.00	129.991	67.174	92.706	159.881	289.871	334.408
690.00	130.077	68.467	93.819	162.286	292.363	338.188
700.00	130.159	69.748	95.144	164.891	295.051	342.222
710.00	130.238	71.015	95.986	167.001	297.240	345.703
720.00	130.314	72.270	97.032	169.302	299.616	349.429
730.00	130.387	73.512	98.053	171.565	301.952	353.135
740.00	130.456	74.742	99.060	173.802	304.259	356.834
750.00	130.523	75.958	100.035	175.994	306.517	360.503
760.00	130.588	77.162	100.974	178.136	308.724	364.140
770.00	130.650	78.354	101.962	180.316	310.965	367.847
780.00	130.709	79.532	102.878	182.410	313.120	371.479
790.00	130.767	80.698	103.776	184.474	315.241	375.101
800.00	130.822	81.852	104.596	186.447	317.269	378.643
810.00	130.875	82.993	105.451	188.444	319.319	382.239
820.00	130.927	84.121	106.288	190.409	321.335	385.826
830.00	130.976	85.237	107.105	192.342	323.318	389.403
840.00	131.024	86.340	107.914	194.254	325.278	392.985
850.00	131.070	87.431	108.695	196.126	327.196	396.549
860.00	131.114	88.510	109.459	197.969	329.083	400.107
870.00	131.157	89.576	110.205	199.782	330.939	403.660
880.00	131.199	90.630	110.936	201.566	332.765	407.211
890.00	131.239	91.672	111.639	203.311	334.550	410.747
900.00	131.278	92.702	112.337	205.039	336.317	414.295
910.00	131.316	93.719	113.020	206.739	338.055	417.843
920.00	131.352	94.725	113.688	208.413	339.765	421.394
930.00	131.387	95.719	114.348	210.067	341.454	424.956
940.00	131.421	96.700	114.988	211.688	343.109	428.515
950.00	131.455	97.670	115.613	213.283	344.738	432.079
960.00	131.487	98.629	116.225	214.853	346.340	435.651
970.00	131.518	99.575	116.824	216.399	347.917	439.232
980.00	131.548	100.510	117.414	217.924	349.472	442.828
990.00	131.577	101.434	117.988	219.422	350.999	446.432
1000.00	131.605	102.346	118.538	220.884	352.489	450.034

what effect the addition of a CH_3 group has had on Θ_1 for other polymers. On going from polyglycine to poly(L-alanine) the H is replaced by a CH_3. The change in Θ_1 is an decrease of 116 K. On going from poly(L-alanine) to poly(L-valine), where a CH_3 and H are added to a CH_3 in the side group, the change in Θ_1 is an increase of 29.6 K. On going from polypropylene to polyisobutylene, the addition of a CH_3 causes an increase in Θ_1 by 136 K. Rather arbitrarily, a value of 655.7 K was assigned for Θ_1 for poly(L-threonine). This represents the value of Θ_1 for poly(L-serine) minus 29.6 K. The results of the calculation are given in Table 38.

Poly(L-glutamine) is identical to poly(L-asparagine) with the exception of an additional CH_2 in the side chain. For heat capacity calculations, its vibrational spectrum was constructed of the backbone group (Part A Table 13), two CH_2 groups (Part D Table 13), a C=O group (Part G Table 13), and an NH_2 group (Part H Table 13). This vibrational spectrum is the same as that constructed for poly(L-asparagine) with the exception of an additional CH_2 group. The number of skeletal vibrations was increased from 12 to 14 to account for the additional CH_2 group. If one examines the effect of an additional CH_2 group on Θ_1 for a number of polymers in the *ATHAS* data bank, a wide number of changes are observed, both increases and decreases in Θ_1 with an added CH_2 group. As a result, for calculation purposes, a value of 529.6 K was used for Θ_1. This value represents the Θ_1-temperature of poly(L-asparagine) (568.8 K) minus 39.2 K, the change in Θ_1 on going from poly(L-valine) to poly(L-leucine) where a CH_2 group is added. The results of the calculation are given in Table 39.

TABLE 38

Calculated Heat Capacities of Poly(L-threonine)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.000	0.000	0.000	0.000	0.000	0.000
0.60	0.001	0.000	0.000	0.000	0.001	0.001
0.70	0.001	0.000	0.000	0.000	0.001	0.001
0.80	0.001	0.000	0.000	0.000	0.001	0.001
0.90	0.002	0.000	0.000	0.000	0.002	0.002
1.00	0.003	0.000	0.000	0.000	0.003	0.003
1.20	0.005	0.000	0.000	0.000	0.005	0.005
1.40	0.008	0.000	0.000	0.000	0.008	0.008
1.60	0.011	0.000	0.000	0.000	0.011	0.011
1.80	0.016	0.000	0.000	0.000	0.016	0.016
2.00	0.022	0.000	0.000	0.000	0.022	0.022
3.00	0.075	0.000	0.000	0.000	0.075	0.075
4.00	0.178	0.000	0.000	0.000	0.178	0.178
5.00	0.346	0.000	0.000	0.000	0.346	0.347
6.00	0.596	0.000	0.000	0.000	0.596	0.596
7.00	0.929	0.000	0.000	0.000	0.929	0.930
8.00	1.348	0.000	0.000	0.000	1.348	1.350
9.00	1.844	0.000	0.000	0.000	1.844	1.847
10.00	2.401	0.000	0.000	0.000	2.401	2.405
15.00	5.641	0.000	0.000	0.000	5.641	5.655
20.00	8.987	0.000	0.000	0.000	8.987	9.017
25.00	12.184	0.000	0.000	0.000	12.184	12.237
30.00	15.231	0.000	0.000	0.000	15.231	15.310
40.00	21.052	0.000	0.000	0.000	21.052	21.197
50.00	26.681	0.000	0.004	0.004	26.685	26.916
60.00	32.209	0.001	0.008	0.008	32.217	32.552
70.00	37.637	0.005	0.060	0.065	37.702	38.161
80.00	42.901	0.020	0.160	0.181	43.081	43.683
90.00	47.950	0.058	0.325	0.383	48.332	49.094
100.00	52.747	0.130	0.603	0.733	53.480	54.420
110.00	57.238	0.248	0.911	1.159	58.397	59.530
120.00	61.411	0.422	1.349	1.771	63.182	64.524
130.00	65.223	0.656	1.826	2.483	67.706	69.270
140.00	68.696	0.954	2.443	3.396	72.092	73.893
150.00	71.860	1.315	3.071	4.385	76.245	78.292
160.00	74.745	1.739	3.851	5.590	80.334	82.644
170.00	77.342	2.224	4.637	6.861	84.204	86.785
180.00	79.680	2.771	5.541	8.312	87.992	90.859

TABLE 38 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	81.806	3.377	6.485	9.862	91.668	94.832
200.00	83.734	4.040	7.454	11.493	95.228	98.701
210.00	85.481	4.759	8.468	13.227	98.709	102.503
220.00	87.065	5.533	9.663	15.196	102.261	106.395
230.00	88.500	6.359	10.813	17.172	105.673	110.156
240.00	89.804	7.235	11.966	19.201	109.005	113.850
250.00	90.990	8.158	13.269	21.428	112.418	117.643
260.00	92.071	9.126	14.577	23.702	115.773	121.391
270.00	93.057	10.134	15.850	25.984	119.041	125.064
273.15	93.350	10.459	16.275	26.735	120.085	126.239
280.00	93.959	11.179	17.205	28.384	122.344	128.788
290.00	94.786	12.259	18.569	30.827	125.613	132.494
298.15	95.410	13.160	19.749	32.909	128.319	135.569
300.00	95.546	13.367	19.935	33.302	128.848	136.178
310.00	96.244	14.502	21.422	35.924	132.169	139.970
320.00	96.888	15.659	22.827	38.486	135.374	143.656
330.00	97.483	16.835	24.220	41.055	138.537	147.313
340.00	98.033	18.025	25.670	43.695	141.728	151.016
350.00	98.542	19.227	27.140	46.368	144.910	154.727
360.00	99.016	20.438	28.508	48.946	147.962	158.314
370.00	99.456	21.654	29.987	51.641	151.097	162.008
380.00	99.865	22.873	31.289	54.162	154.027	165.499
390.00	100.247	24.093	32.652	56.745	156.992	169.044
400.00	100.604	25.311	34.148	59.459	160.063	172.720
410.00	100.938	26.526	35.501	62.027	162.964	176.229
420.00	101.250	27.734	36.808	64.542	165.792	179.677
430.00	101.543	28.937	38.100	67.036	168.580	183.097
440.00	101.819	30.130	39.381	69.511	171.329	186.493
450.00	102.077	31.315	40.677	71.992	174.070	189.896
460.00	102.321	32.489	41.965	74.454	176.775	193.278
470.00	102.550	33.652	43.225	76.877	179.427	196.619
480.00	102.767	34.803	44.427	79.230	181.997	199.886
490.00	102.971	35.942	45.640	81.582	184.553	203.157
500.00	103.164	37.068	46.866	83.934	187.098	206.432
510.00	103.347	38.181	47.988	86.168	189.515	209.583
520.00	103.520	39.280	49.091	88.371	191.891	212.705
530.00	103.684	40.366	50.175	90.541	194.225	215.799
540.00	103.840	41.439	51.238	92.677	196.516	218.862
550.00	103.988	42.497	52.289	94.786	198.774	221.905
560.00	104.128	43.542	53.401	96.943	201.071	225.009
570.00	104.262	44.573	54.397	98.970	203.232	227.980
580.00	104.389	45.590	55.375	100.966	205.354	230.924
590.00	104.510	46.594	56.332	102.926	207.436	233.839
600.00	104.626	47.585	57.317	104.902	209.528	236.784

TABLE 38 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	104.736	48.562	58.276	106.838	211.574	239.696
620.00	104.841	49.526	59.192	108.718	213.559	242.556
630.00	104.942	50.477	60.074	110.550	215.492	245.375
640.00	105.038	51.415	60.938	112.353	217.390	248.173
650.00	105.130	52.340	61.785	114.125	219.255	250.950
660.00	105.205	53.253	62.615	115.868	221.073	253.693
670.00	105.289	54.153	63.428	117.581	222.870	256.430
680.00	105.369	55.041	64.225	119.266	224.635	259.149
690.00	105.446	55.918	65.004	120.922	226.368	261.849
700.00	105.520	56.782	66.006	122.788	228.308	264.808
710.00	105.591	57.635	66.534	124.169	229.759	267.221
720.00	105.658	58.476	67.275	125.751	231.409	269.883
730.00	105.723	59.305	68.001	127.306	233.030	272.530
740.00	105.786	60.124	68.721	128.845	234.631	275.174
750.00	105.846	60.932	69.417	130.348	236.194	277.794
760.00	105.903	61.728	70.084	131.813	237.716	280.386
770.00	105.959	62.514	70.810	133.324	239.282	283.052
780.00	106.012	63.289	71.470	134.759	240.771	285.647
790.00	106.063	64.054	72.120	136.174	242.237	288.235
800.00	106.113	64.808	72.698	137.507	243.620	290.746
810.00	106.160	65.553	73.319	138.872	245.033	293.315
820.00	106.206	66.287	73.928	140.215	246.421	295.877
830.00	106.251	67.011	74.524	141.535	247.785	298.432
840.00	106.293	67.726	75.117	142.843	249.136	300.994
850.00	106.334	68.431	75.689	144.119	250.454	303.540
860.00	106.374	69.126	76.248	145.374	251.749	306.082
870.00	106.413	69.812	76.797	146.609	253.021	308.621
880.00	106.450	70.488	77.334	147.822	254.272	311.158
890.00	106.486	71.156	77.850	149.005	255.491	313.681
900.00	106.521	71.814	78.365	150.179	256.700	316.218
910.00	106.554	72.463	78.870	151.333	257.887	318.754
920.00	106.587	73.104	79.364	152.468	259.055	321.293
930.00	106.618	73.735	79.856	153.592	260.210	323.844
940.00	106.649	74.359	80.331	154.690	261.338	326.390
950.00	106.678	74.973	80.796	155.769	262.448	328.940
960.00	106.707	75.579	81.252	156.831	263.538	331.497
970.00	106.735	76.177	81.699	157.876	264.611	334.061
980.00	106.762	76.767	82.141	158.908	265.669	336.639
990.00	106.788	77.348	82.570	159.918	266.706	339.221
1000.00	106.813	77.922	82.979	160.901	267.714	341.799

TABLE 39

Calculated Heat Capacities of Poly(L-glutamine)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.000	0.000	0.000	0.000	0.000	0.000
0.60	0.001	0.000	0.000	0.000	0.001	0.001
0.70	0.001	0.000	0.000	0.000	0.001	0.001
0.80	0.002	0.000	0.000	0.000	0.002	0.002
0.90	0.003	0.000	0.000	0.000	0.003	0.003
1.00	0.004	0.000	0.000	0.000	0.004	0.004
1.20	0.006	0.000	0.000	0.000	0.006	0.006
1.40	0.010	0.000	0.000	0.000	0.010	0.010
1.60	0.015	0.000	0.000	0.000	0.015	0.015
1.80	0.022	0.000	0.000	0.000	0.022	0.022
2.00	0.030	0.000	0.000	0.000	0.030	0.030
3.00	0.100	0.000	0.000	0.000	0.100	0.100
4.00	0.237	0.000	0.000	0.000	0.237	0.237
5.00	0.462	0.000	0.000	0.000	0.462	0.462
6.00	0.794	0.000	0.000	0.000	0.794	0.795
7.00	1.239	0.000	0.000	0.000	1.239	1.240
8.00	1.798	0.000	0.000	0.000	1.798	1.800
9.00	2.458	0.000	0.000	0.000	2.458	2.462
10.00	3.201	0.000	0.000	0.000	3.201	3.206
15.00	7.521	0.000	0.000	0.000	7.521	7.540
20.00	11.982	0.000	0.000	0.000	11.982	12.023
25.00	16.246	0.000	0.000	0.000	16.246	16.315
30.00	20.309	0.000	0.000	0.000	20.309	20.413
40.00	28.064	0.000	0.000	0.000	28.065	28.258
50.00	35.547	0.002	0.004	0.006	35.553	35.860
60.00	42.800	0.011	0.008	0.019	42.819	43.264
70.00	49.713	0.044	0.060	0.104	49.817	50.424
80.00	56.216	0.123	0.162	0.285	56.501	57.290
90.00	62.221	0.270	0.329	0.598	62.819	63.809
100.00	67.674	0.504	0.588	1.092	68.765	69.974
110.00	72.539	0.839	0.940	1.779	74.318	75.760
120.00	76.871	1.286	1.383	2.669	79.540	81.230
130.00	80.734	1.848	1.901	3.749	84.482	86.434
140.00	84.121	2.527	2.569	5.096	89.217	91.444
150.00	87.113	3.321	3.253	6.573	93.686	96.202
160.00	89.768	4.225	4.123	8.348	98.116	100.936
170.00	92.117	5.236	5.021	10.257	102.374	105.513
180.00	94.197	6.346	6.069	12.415	106.612	110.085

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	96.041	7.549	7.177	14.727	110.767	114.591
200.00	97.678	8.838	8.335	17.174	114.852	119.041
210.00	99.137	10.206	9.562	19.768	118.905	123.476
220.00	100.440	11.645	10.991	22.635	123.075	128.051
230.00	101.607	13.147	12.341	25.488	127.095	132.488
240.00	102.656	14.707	13.829	28.535	131.191	137.022
250.00	103.601	16.316	15.385	31.701	135.302	141.591
260.00	104.456	17.968	16.979	34.947	139.403	146.168
270.00	105.231	19.657	18.564	38.222	143.452	150.710
273.15	105.460	20.196	19.077	39.273	144.733	152.150
280.00	105.935	21.377	20.218	41.595	147.530	155.301
290.00	106.577	23.120	21.940	45.061	151.637	159.943
298.15	107.058	24.556	23.396	47.952	155.010	163.768
300.00	107.163	24.883	23.646	48.529	155.692	164.549
310.00	107.700	26.660	25.488	52.148	159.848	169.283
320.00	108.192	28.446	27.193	55.639	163.831	173.854
330.00	108.646	30.237	28.955	59.192	167.838	178.470
340.00	109.063	32.029	30.733	62.762	171.826	183.086
350.00	109.449	33.818	32.480	66.299	175.748	187.654
360.00	109.806	35.601	34.229	69.830	179.637	192.206
370.00	110.137	37.376	36.064	73.440	183.577	196.834
380.00	110.445	39.139	37.693	76.832	187.277	201.225
390.00	110.731	40.888	39.374	80.262	190.993	205.655
400.00	110.998	42.622	41.151	83.773	194.770	210.171
410.00	111.246	44.339	42.771	87.110	198.356	214.502
420.00	111.479	46.037	44.365	90.402	201.881	218.788
430.00	111.696	47.715	45.952	93.668	205.364	223.049
440.00	111.900	49.373	47.543	96.916	208.817	227.298
450.00	112.092	51.010	49.142	100.152	212.243	231.540
460.00	112.272	52.624	50.725	103.349	215.621	235.750
470.00	112.441	54.216	52.278	106.494	218.935	239.912
480.00	112.600	55.786	53.754	109.539	222.140	243.975
490.00	112.750	57.333	55.193	112.526	225.276	247.985
500.00	112.892	58.857	56.592	115.449	228.341	251.936
510.00	113.026	60.358	57.954	118.311	231.338	255.834
520.00	113.153	61.836	59.291	121.127	234.280	259.692
530.00	113.259	63.292	60.602	123.893	237.153	263.495
540.00	113.373	64.725	61.886	126.610	239.983	267.272
550.00	113.480	66.136	63.150	129.286	242.766	271.017
560.00	113.582	67.525	64.469	131.994	245.576	274.813
570.00	113.679	68.893	65.666	134.559	248.237	278.465
580.00	113.770	70.239	66.838	137.077	250.847	282.081
590.00	113.857	71.565	67.982	139.547	253.404	285.659
600.00	113.940	72.870	69.150	142.020	255.960	289.257

TABLE 39 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	114.019	74.155	70.286	144.441	258.459	292.813
620.00	114.094	75.420	71.372	146.793	260.886	296.309
630.00	114.165	76.666	72.419	149.085	263.250	299.756
640.00	114.233	77.893	73.443	151.336	265.569	303.174
650.00	114.298	79.101	74.445	153.546	267.845	306.564
660.00	114.360	80.291	75.425	155.716	270.077	309.927
670.00	114.420	81.463	76.384	157.847	272.266	313.264
680.00	114.477	82.617	77.320	159.938	274.415	316.576
690.00	114.531	83.755	78.236	161.991	276.522	319.864
700.00	114.583	84.875	79.370	164.245	278.828	323.405
710.00	114.633	85.979	80.026	166.005	280.638	326.395
720.00	114.681	87.066	80.891	167.957	282.638	329.628
730.00	114.727	88.137	81.737	169.874	284.601	332.843
740.00	114.771	89.193	82.573	171.766	286.537	336.050
750.00	114.814	90.233	83.382	173.615	288.429	339.229
760.00	114.854	91.258	84.159	175.417	290.272	342.376
770.00	114.894	92.269	84.990	177.259	292.152	345.593
780.00	114.931	93.264	85.754	179.018	293.949	348.736
790.00	114.968	94.246	86.503	180.749	295.716	351.869
800.00	115.003	95.213	87.179	182.392	297.394	354.923
810.00	115.036	96.166	87.894	184.060	299.097	358.032
820.00	115.069	97.106	88.593	185.700	300.768	361.131
830.00	115.100	98.032	89.278	187.310	302.411	364.223
840.00	115.130	98.946	89.958	188.903	304.034	367.319
850.00	115.160	99.846	90.613	190.459	305.618	370.397
860.00	115.188	100.733	91.254	191.987	307.175	373.470
870.00	115.215	101.608	91.882	193.489	308.704	376.540
880.00	115.241	102.470	92.496	194.966	310.207	379.607
890.00	115.267	103.320	93.086	196.406	311.673	382.659
900.00	115.291	104.158	93.674	197.832	313.124	385.724
910.00	115.315	104.985	94.250	199.234	314.550	388.790
920.00	115.338	105.799	94.813	200.612	315.951	391.858
930.00	115.361	106.602	95.372	201.974	317.335	394.938
940.00	115.382	107.394	95.912	203.306	318.688	398.015
950.00	115.403	108.175	96.440	204.615	320.018	401.097
960.00	115.424	108.944	96.958	205.902	321.326	404.186
970.00	115.443	109.703	97.465	207.168	322.611	407.285
980.00	115.462	110.451	97.965	208.417	323.879	410.398
990.00	115.481	111.189	98.452	209.641	325.122	413.519
1000.00	115.499	111.916	98.917	210.832	326.331	416.637

The final poly(amino acid) for which heat capacity measurements were not made is poly(L-cysteine). The vibrational spectrum of poly(L-cysteine) was constructed of the backbone (Part A Table 13), a CH_2 group (Part D Table 13), and the vibrations of a SH group taken from studies on methyl and ethyl mercaptan.[79] The group vibrations of the SH group are listed in Table 40. Poly(L-cysteine) is very similiar to poly(L-serine). In poly(L-cysteine), the side group is a CH_2SH group whereas in poly(L-serine), the side group is a CH_2OH group. As in poly(L-serine), two skeletal modes were assigned to the OH group, thus resulting in 10 total skeletal vibrations and 23 group vibrations. A value of 674.3 K was assumed for Θ_1. This was based on the value of Θ_1 for poly(L-serine) (685.3 K) minus 11 K, the change in Θ_1 upon going from poly(thio-1,4-phenylene) to poly(oxy-1,4-phenylene). The results of the calculation are given in Table 41.

The results of these four attempts to calculate heat capacities for the poly(amino acids) for which heat capacity measurements were not available are clearly not to be taken too seriously. As first guesses, they will do, but it is evident from the difficulty and rather arbitrary nature in assigning a value for Θ_1 that heat capacity measurements are necessary so that more precise and correct calculations can be carried out. Since these poly(amino acids) are not available commercially, they would have to be specially prepared. Such an effort seems necessary.

TABLE 40

Group Vibrations Frequencies of SH[79]
in Kelvin (hν/k), 1 K = 0.695 cm^{-1}

Assignment	# of Vibrators	Frequency
SH stretch	1.00	3705.0
SH bend	1.00	1155.4 – 1251.8
SH bend	1.00	863.3
C–SH stretch	1.00	820.1 – 1014.4

Source: [79] L.M. Sverdlov *Vibrational Spectra of Polyatomic Molecules*. Wiley, New York (1973).

TABLE 41

Calculated Heat Capacities of Poly(L-cysteine)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
0.10	0.000	0.000	0.000	0.000	0.000	0.000
0.20	0.000	0.000	0.000	0.000	0.000	0.000
0.30	0.000	0.000	0.000	0.000	0.000	0.000
0.40	0.000	0.000	0.000	0.000	0.000	0.000
0.50	0.000	0.000	0.000	0.000	0.000	0.000
0.60	0.000	0.000	0.000	0.000	0.000	0.000
0.70	0.001	0.000	0.000	0.000	0.001	0.001
0.80	0.001	0.000	0.000	0.000	0.001	0.001
0.90	0.002	0.000	0.000	0.000	0.002	0.002
1.00	0.002	0.000	0.000	0.000	0.002	0.002
1.20	0.004	0.000	0.000	0.000	0.004	0.004
1.40	0.006	0.000	0.000	0.000	0.006	0.006
1.60	0.009	0.000	0.000	0.000	0.009	0.009
1.80	0.012	0.000	0.000	0.000	0.012	0.012
2.00	0.017	0.000	0.000	0.000	0.017	0.017
3.00	0.056	0.000	0.000	0.000	0.056	0.056
4.00	0.133	0.000	0.000	0.000	0.133	0.133
5.00	0.259	0.000	0.000	0.000	0.259	0.259
6.00	0.446	0.000	0.000	0.000	0.446	0.446
7.00	0.695	0.000	0.000	0.000	0.695	0.696
8.00	1.008	0.000	0.000	0.000	1.008	1.010
9.00	1.379	0.000	0.000	0.000	1.379	1.381
10.00	1.796	0.000	0.000	0.000	1.796	1.799
15.00	4.219	0.000	0.000	0.000	4.219	4.230
20.00	6.722	0.000	0.000	0.000	6.722	6.745
25.00	9.114	0.000	0.000	0.000	9.114	9.153
30.00	11.393	0.000	0.000	0.000	11.393	11.452
40.00	15.747	0.000	0.000	0.000	15.747	15.856
50.00	19.961	0.000	0.004	0.004	19.966	20.138
60.00	24.095	0.000	0.008	0.008	24.103	24.354
70.00	28.168	0.002	0.060	0.062	28.230	28.574
80.00	32.131	0.009	0.160	0.169	32.301	32.752
90.00	35.946	0.026	0.324	0.350	36.297	36.869
100.00	39.584	0.058	0.587	0.645	40.229	40.937
110.00	43.026	0.110	0.903	1.013	44.039	44.894
120.00	46.213	0.186	1.328	1.514	47.727	48.741
130.00	49.155	0.288	1.805	2.092	51.248	52.431
140.00	51.845	0.416	2.392	2.808	54.653	56.017
150.00	54.300	0.571	2.961	3.532	57.832	59.385
160.00	56.544	0.753	3.674	4.427	60.971	62.724
170.00	58.596	0.961	4.371	5.332	63.928	65.888
180.00	60.423	1.196	5.164	6.360	66.783	68.959

TABLE 41 (Cont.)

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
190.00	62.092	1.457	5.977	7.434	69.526	71.926
200.00	63.613	1.744	6.793	8.537	72.150	74.781
210.00	64.994	2.056	7.637	9.692	74.687	77.558
220.00	66.250	2.392	8.643	11.035	77.285	80.409
230.00	67.391	2.754	9.513	12.266	79.657	83.037
240.00	68.428	3.138	10.476	13.614	82.042	85.689
250.00	69.374	3.545	11.481	15.026	84.400	88.323
260.00	70.236	3.973	12.496	16.469	86.706	90.913
270.00	71.025	4.421	13.468	17.889	88.914	93.412
273.15	71.259	4.566	13.789	18.355	89.614	94.206
280.00	71.747	4.887	14.490	19.376	91.123	95.923
290.00	72.409	5.369	15.540	20.909	93.318	98.429
298.15	72.909	5.772	16.455	22.228	95.137	100.512
300.00	73.018	5.865	16.582	22.447	95.465	100.896
310.00	73.578	6.374	17.753	24.127	97.705	103.472
320.00	74.095	6.895	18.795	25.689	99.784	105.889
330.00	74.573	7.424	19.896	27.320	101.893	108.347
340.00	75.015	7.961	21.010	28.971	103.986	110.800
350.00	75.424	8.504	22.090	30.595	106.019	113.201
360.00	75.805	9.052	23.145	32.197	108.002	115.559
370.00	76.159	9.602	24.298	33.900	110.059	118.007
380.00	76.489	10.155	25.258	35.412	111.901	120.236
390.00	76.797	10.708	26.294	37.002	113.799	122.535
400.00	77.084	11.260	27.438	38.699	115.783	124.938
410.00	77.353	11.812	28.451	40.262	117.616	127.189
420.00	77.605	12.361	29.458	41.818	119.424	129.425
430.00	77.842	12.907	30.458	43.365	121.207	131.644
440.00	78.064	13.449	31.461	44.910	122.974	133.858
450.00	78.273	13.987	32.484	46.471	124.744	136.085
460.00	78.469	14.521	33.503	48.023	126.492	138.301
470.00	78.654	15.049	34.502	49.551	128.205	140.489
480.00	78.829	15.572	35.447	51.019	129.848	142.612
490.00	78.994	16.090	36.368	52.457	131.452	144.702
500.00	79.150	16.601	37.263	53.864	133.014	146.759
510.00	79.298	17.106	38.139	55.245	134.543	148.789
520.00	79.438	17.605	39.002	56.607	136.044	150.801
530.00	79.570	18.098	39.851	57.948	137.519	152.794
540.00	79.696	18.584	40.685	59.269	138.965	154.767
550.00	79.816	19.064	41.512	60.576	140.391	156.729
560.00	79.929	19.537	42.406	61.943	141.872	158.763
570.00	80.038	20.003	43.190	63.194	143.231	160.672
580.00	80.140	20.463	43.962	64.425	144.565	162.566
590.00	80.239	20.917	44.717	65.634	145.873	164.440
600.00	80.332	21.364	45.508	66.872	147.204	166.354

Temp (K)	Skeletal (J/mol K)	Einstein (J/mol K)	Box Dist. (J/mol K)	Group (J/mol K)	Cv (J/mol K)	Cp (J/mol K)
610.00	80.421	21.805	46.277	68.082	148.504	168.243
620.00	80.506	22.240	47.009	69.249	149.755	170.089
630.00	80.588	22.668	47.712	70.379	150.967	171.903
640.00	80.666	23.090	48.402	71.492	152.158	173.703
650.00	80.740	23.506	49.081	72.586	153.327	175.491
660.00	80.811	23.915	49.747	73.663	154.474	177.267
670.00	80.880	24.319	50.402	74.721	155.600	179.031
680.00	80.935	24.717	51.044	75.761	156.696	180.771
690.00	80.998	25.109	51.674	76.783	157.781	182.511
700.00	81.058	25.495	52.530	78.025	159.083	184.516
710.00	81.115	25.876	52.918	78.794	159.909	185.981
720.00	81.170	26.251	53.522	79.773	160.943	187.701
730.00	81.223	26.621	54.114	80.735	161.958	189.411
740.00	81.274	26.985	54.706	81.690	162.964	191.124
750.00	81.322	27.343	55.276	82.619	163.942	192.817
760.00	81.369	27.697	55.822	83.519	164.888	194.486
770.00	81.414	28.045	56.429	84.474	165.888	196.233
780.00	81.458	28.388	56.975	85.363	166.821	197.913
790.00	81.499	28.726	57.513	86.239	167.738	199.590
800.00	81.540	29.059	57.983	87.042	168.582	201.193
810.00	81.578	29.387	58.499	87.886	169.465	202.857
820.00	81.616	29.711	59.005	88.716	170.331	204.516
830.00	81.651	30.029	59.501	89.530	171.182	206.171
840.00	81.686	30.343	59.998	90.341	172.027	207.835
850.00	81.720	30.652	60.475	91.128	172.847	209.484
860.00	81.752	30.957	60.944	91.901	173.653	211.131
870.00	81.783	31.257	61.403	92.660	174.443	212.776
880.00	81.814	31.553	61.853	93.406	175.220	214.420
890.00	81.843	31.844	62.285	94.129	175.972	216.050
900.00	81.871	32.131	62.718	94.849	176.720	217.694
910.00	81.898	32.414	63.143	95.557	177.455	219.338
920.00	81.925	32.692	63.560	96.252	178.177	220.984
930.00	81.950	32.967	63.976	96.942	178.893	222.641
940.00	81.975	33.237	64.377	97.614	179.589	224.291
950.00	81.999	33.503	64.770	98.273	180.273	225.946
960.00	82.022	33.766	65.156	98.922	180.944	227.604
970.00	82.045	34.024	65.534	99.559	181.604	229.268
980.00	82.067	34.279	65.910	100.189	182.256	230.942
990.00	82.088	34.530	66.274	100.804	182.892	232.619
1000.00	82.109	34.777	66.620	101.397	183.506	234.287

VB. Prediction of Copolymer Θ_1-Temperatures

In Section III, the additivity of heat capacities was discussed by comparing the heat capacities measured for the copolymers and the heat capacities measured for the homopolymers making up the copolymers. For the four copolymers studied, the copolymer heat capacity additivity rule was observed to hold for the poly(amino acids). Along these lines, it is interesting to compare the Θ_1-temperatures of the copolymers and the hompolymers making up the copolymers (see Table 33).

For poly(L-lysine•HBr-alanine), Θ_1 is 656.3 ± 33.3 K. For poly(L-lysine•HBr), Θ_1 is 636.3 ± 46.7 K and for poly(L-alanine), Θ_1 is 634.1 K ± 33.3 K. An average of these two Θ_1-temperatures is 635.2 K. This is well within the range of Θ_1 for the copolymer.

For poly(L-lysine•HBr-phenylanine), Θ_1 is 756.9 ± 20.6 K. For the homopolymers making up the copolymer, Θ_1 is 636.3 ± 46.7 K for poly(L-lysine•HBr) and 609.7 ± 29.5 K for poly(L-phenylalanine). The average of these two values is 623.0 K. Even at the extreme ranges of the Θ_1-temperatures for the two homopolymers, the average Θ_1-temperature is still approximately 74 K lower than the extreme low range of Θ_1 of the copolymer.

Poly(L-glutamic acid•Na-tyrosine) has a Θ_1-temperature of 744.0 ± 26.5 K. Poly(L-glutamic acid•Na) has a Θ_1-temperature of 906.9 ± 23.3 K while for poly(L-tyrosine), Θ_1 is 728.5 ± 35.0 K. The average of the two homopolymer theta-temperatures is 817.7 K. Taking the low end range values for the theta-temperatures of the homopolymers, the average is 788.0 K, quite close to the high end range of the

copolymer, 770.5 K.

For poly(L-proline-glycine-proline), Θ_1 is 698.6 K ± 13.0 K. For poly(L-proline), Θ_1 is 690.5 ± 46.3 K, and Θ_1 is 750.3 ± 43.0 K for polyglycine). The average of these theta temperatures, taken in correct proportion, is 710.4 K. This is within the range of Θ_1 for the copolymer.

With the exception of poly(L-lysine • HBr-phenylalanine), it appears that these initial heat capacity studies indicate that the Θ_1-temperature of a copolymer of poly(amino acids) can be determined from an average of the Θ_1-temperatures of the hompolymers making up the copolymer. Such knowledge would be particularily useful in the prediction of protein heat capacities, however, many additional copolymers and peptides would need to be studied before any such general conclusions could be satisfactorily drawn.

VI. POLY(L-METHIONINE) AND POLY(L-SERINE)

As first noted in Chapter III, when heat capacities were calculated for poly(L-methionine) and poly(L-serine), agreement with the experimental heat capacities was observed only at the lowest temperature of comparison. For poly(L-methionine), good agreement between calculation and experiment was observed only from 220 to 250 K. The observed RMS deviation for this temperature range was ±0.67%. Between 220 and 240 K, the RMS deviation was only ±0.09%. In fact, for this temperature range (220 to 240 K), the experimental heat capacities fall essentially

on top of those calculated. Please refer to Figure 45. At approximately 260 K, the experimental heat capacity begins to rise above that calculated. The rise is rather sharp and does not show any signs of decreasing in the temperature range of the experiment. For poly(L-serine), similar results are observed (refer to Figure 39). Again rather excellent agreement between the calculated and experimental heat capacities is observed at only the lowest temperatures, 220 to 280 K. For this temperature range the RMS deviation is ±0.72%. As was the case with poly(L-methionine), the lowest experimental heat capacities (220 to 260 K) fall essentially on top of those calculated. At 280 K, the experimental heat capacities begin to rise above those calculated. The rise becomes even sharper at approximately 360 K. Again, at the end of the experimental range of heat capacities, the positive deviations from the calculated heat capacities do not show any signs of decreasing. Both poly(amino acids) thus exhibit experimental heat capacities that deviate increasingly (positively) with temperature from the calculated heat capacities above a certain, low temperature. The remainder of this section will be devoted a discussion of the probable cause for these observed deviations.

At first glance, based on the previous observations made with these biological polymers, one might consider that these positive deviations in heat capacity may be due to sample water that has yet to be removed. Such a possibility can, however, be ruled out. First, these observed experimental heat capacities for poly(L-methionine) and poly(L-serine) are repeatable. As was the case with all the other poly(amino acids), these two samples were subjected to three sets of three heating runs. (This

is described in Chapter II.) In each set of heating experiments, the second heating runs (run used for comparison to the calculated heat capacities) were reproducible to ±3.0%. Once the water was removed in the first heating runs, the sample weight and heat capacities remained essentially the same for the second heating runs. If water were present, one would see weight changes and a diminishment of the positive deviations as the sample was continuously taken through successive heating runs. Second, for poly(L-serine), the difference between ΔH_{vap}mass and $\Delta H_{vap}C_p$ was determined to be only 14.0% in Section IA, Chapter IV. This is not a significant difference considering the degree to which the water peak was resolved and the large temperature range (130 degrees) this error covers. Thus we are further confident that the sample heat capacities taken from the second heating run are free of any interfering water content. Thirdly, the experimental heat capacities of both samples are observed to be in complete agreement with the calculated heat capacities over the small, low temperature ranges. One would expect a positive deviation in the experimental heat capacities even at the low temperature range of the experiment if water were involved. This, however, is not the case. For these reasons, we do not believe the positive deviations of the experimental heat capacities from those calculated can be attributed to water content. Rather, we believe these deviations can be attributed to the existence of a broad glass transition in both poly(amino acids).

A literature search reveals only one study examining glass transitions in poly(amino acid) type biological polymers. This study, performed by Pezzin and co-

workers,[80] is very interesting to the cases at hand. Using differential scanning calorimetry, Pezzin and co-workers observed slightly broadened glass transitions for a number of homopolymers of poly(α-amino acids) as well as copolymers of poly(α-amino acids). The glass transitions occurred over the temperature range 303 to 333 K (30 to 60°C). Such a study gives confidence to the suggestion that a glass transition occurring in poly(L-serine) and poly(L-methionine) can account for the elevated experimental heat capacities.

It is important at this point to briefly discuss glass transitions. Glass transitions are not as easy to detect calorimetrically as are melting or evaporation transitions. The reason for this is that a glass transition is not accompanied by a measurable heat of transition, and therefore, there is no entropy of transition. A glass transition is detected by a sudden increase or jump in the heat capacity. This is illustrated in Figure 66.[3] The increase in the heat capacity generally occurs over a temperature range of 5 to 20 K.[3] In semicrystalline polymers, the crystals are considered to separate into microphases. These microphases hinder the molecular motion at the glass transition and cause a broader distribution of relaxation times. This is observed calorimetrically as a broadening of the glass transition. If the polymer is cooled more slowly, better crystallization occurs, and the transition is even further broadened. Such observations has been made for a number of polymers such as poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (PEEK)[81] and poly(thio-1,4-phenylene).[82] For some semicrystalline polymers, the broadening of the glass transition has been observed to be accompanied by a ΔC_p lower than that ex-

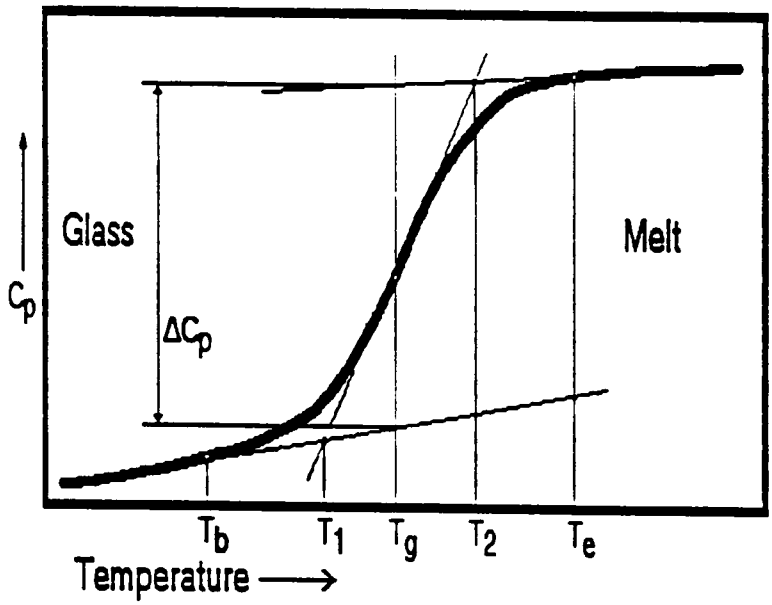


Figure 66 Example of Glass Transition.[3] [Source: B. Wunderlich *Thermal Analysis* Academic Press, New York (1990).]

pected based on the polymer's degree of crystallinity,[3] where ΔC_p refers to the change in heat capacity at the glass transition. Empirically, ΔC_p has been observed to be approximately 11 J/(mol K) for every mole of small mobile units or beads.[83] A decreased ΔC_p is considered an indication that the mobility of the amorphous portion of the polymer is hindered to the point that it has the lower heat capacity of the glass rather than the higher heat capacity of the liquid.[3] Figure 67 shows an example a glass transition broadening for the copolymer poly(1,4-oxybenzoate-co-2,6-oxynapthoate).[3]

As pointed out above, glass transitions are detected by an jump in the heat capacity. This occurs over a fairly broad temperature range to begin with (5 to 20 K) without increased broadening. From the heat capacity curves for poly(L-methionine) and poly(L-serine) (Figures 45 and 39), the possibility that a broad glass transition is in progress is thus probable.

Since broadened glass transitions are often characteristic of semicrystalline polymers, the X-ray powder diffractometer studies described in Chapter II were carried out to determine the degree of crystallinity of the two samples - poly(L-methionine) and poly(L-serine). To restate the results of these studies which were given in Chapter III, the poly(L-serine) was estimated to be 15 to 30% crystalline and the poly(L-methionine) was estimated to be mostly amorphous with some small degree of crystallinity (1-5%) possible. The results of these studies are a first suggestion that the deviations observed between the experimental and calculated heat capacities may be, in fact, attributable to broadened glass transitions.

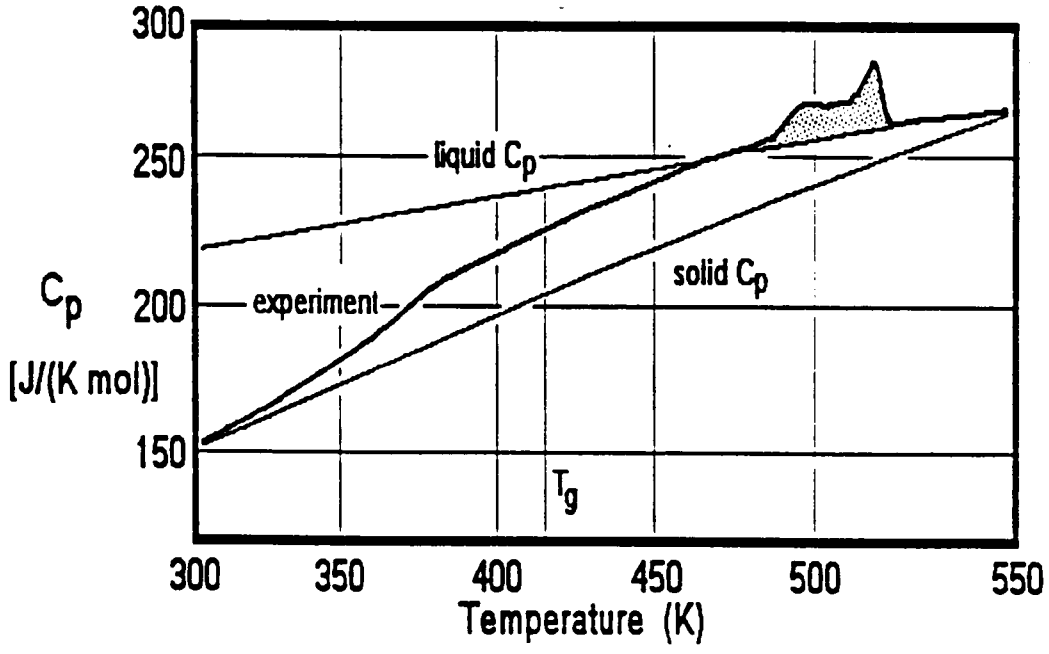


Figure 67 Glass Transition Broadening in a Copolymer.[3] [Source: B. Wunderlich *Thermal Analysis* Academic Press, New York (1990).]

Following this work, some qualitative experiments were performed. The results of these experiments suggest that in all probability, a broadened glass transition can explain the increased heat capacities measured for poly(L-methionine) and poly(L-serine). Referring to Figures 45 and 39, the increase in heat capacity begins as early as 260 K for poly(L-methionine), while for poly(L-serine), the increase is somewhat later at 280 to 290 K. For both samples, however, the transition is well in progress at room temperature, 298 K (25°C). It is important at this point to discuss the physical nature of the two samples. The poly(L-methionine) sample can be characterized as consisting of rather stiff branch-like pieces at 253 K (-20°C). At room temperature, the pieces become sticky and softer and can easily be finger molded into any shape. These physical observations as to the nature of the polymer at different temperatures further suggests we are dealing with a material that could be characterized as glass-like below room temperature and much less so at room temperature (i.e., the glass transition to the more mobile melt is in progress at room temperature). Little can be inferred from the poly(L-serine) sample though as it is observed to be a powder both at 253 K(-20°C) and 290 K 25°C).

A very simple but nevertheless information important experiment was performed on both samples in an attempt to get further evidence that a broad glass transition is in progress at room temperature. A small sample of poly(L-methionine) was finger shaped into a ball at room temperature and then pressed into a flat rectangular-like piece approximately two millimeters in thickness. A set of DSC heating runs were performed on a small piece of the sample to determine if the

pressing had affected the sample. No change in heat capacity was observed to within ±3.0%. The dried sample was then placed over drying agent and left inside a freezer at 253 K (−20°C) for 24 hours. An attempt was then made to cut the cold sample suing an Exacto-knife. No cut could be made. The sample was extremely hard and brittle at this temperature. The poly(L-methionine) sample as then moved to a refrigerator at 278 K (5°C) and left for 24 hours. Another attempt was made to cut the cold sample. This time a cut could be made rather easily. In addition, the sample was observed to be rather pliable. Similar observations were made at room temperature. These results further suggest that the poly(L-methionine) is undergoing a broad glass transition beginning at approximately 260 K (−13°C). At 253 K (−20°C), the sample is hard and brittle suggesting it is below the glass transition. At this temperature, the measured heat capacities fit well those calculated. At 278 K (5°C), the sample has become soft and pliable and can be easily cut, suggesting a more mobile state of matter. At this temperature, the measured heat capacity has begun to deviate significantly from the calculated heat capacity. To summarize, the results imply that at 253 K (−20°C), the poly(L-methionine) is below the glass transition, but at 278 K (5°C), it is not.

A similar experiment was carried out with the poly(L-serine) sample. The sample, however, is a powder and no physical changes were observed on movement of the sample from freezer to refrigerator to room temperature. It is important to point out that when both samples were brought to room temperature under a dry nitrogen gas atmosphere (after the freezing and refrigeration), no appreciable change

in sample weight was noted. In other words, the samples did not pick up moisture in the freezer or refrigerator. It appears that after drying the samples in the DSC, they do not pick up atmospheric moisture unless left at room temperature in an air atmosphere for a significant length of time (two to three hours).

The next qualitative study involved observation of changes in the two samples during heating. Dried samples of both poly(amino acids) were placed in open aluminum pans in a DuPont Differential Thermal Analyser (DTA) and heated from room temperature to 673 K (400°C). Again the poly(L-methionine) sample that was used was a piece of the pressed material described earlier. Prior to placing the poly(L-methionine) sample in the DTA, two cuts in the sample were made. The first was a rather superficial cut or scratch across the surface, the second a deep cut through the entire thickness of the sample. Upon heating, the scratch became less and less viable until it was no longer visible at 473 K (200°C). The deep cut also began to "heal" itself as the sample was heated and the mobility of the molecules increased. At 573 K (300°C), the cut was no longer viable. Slightly below 623 K (350°C), the sample began to blacken. By 623 K (350°C), the sample had completely decomposed (turned black). The weight loss following decomposition was 34.5% of the total sample weight prior to heating. The fact that the poly(L-methionine) sample "healed" itself upon heating further suggests increased mobility of the molecules brought on by a glass transition. Regarding the poly(L-serine) powder sample, the initial physical observations involved changes in sample color with heating. At 473 K (200°C) the sample began to turn yellow. It changed to a

brownish-yellow at 523 K (250°C) and then to orange-yellow at 548 K (275°C). At 573 K (300°C), it began to decompose. The weight loss following decomposition was 22.9% of the total sample weight prior to heating. A second heating of a new dried sample of poly(L-serine) revealed that the powdery material began to exhibit stickiness at approximately 323 K (50°C). The physical observation of the powder becoming more mobile (stickiness) upon heating suggests the likelihood of a glass transition. As a side note, it is important to point out that the decomposition temperatures measured here are not out of line with the temperatures used for in the conversion of C_p to C_v and vice-versa.

As a final step in analyzing the experimentally observed increase in heat capacities for poly(L-methionine) and poly(L-serine), the liquid heat capacities for both polymers were calculated and compared to the experimentally measured heat capacities of the solid and the calculated heat capacities of the solid. As mentioned in Section III of Chapter IV, heat capacities have been shown to be additive for solids from 60 K up to the glass transition. The accuracy of prediction is typically to within ±5.0%. Indeed, this thesis, it has been shown that over the range of experiment (220 to 390 K), the heat capacities of the copolymers of the poly(amino acids) can be predicted to within ± 3.0% based on additivity of the individual poly(amino acids) making up the copolymer. In 1979, analysis of the linear macromolecules contained in the *ATHAS* data bank revealed that molten or liquid polymer heat capacities are also additive,[83] this despite the fact that while liquid heat capacities are still largely due to vibrational contributions, there is an additional heat

capacity contribution resulting from longer range motion and conformational motion.[52] Observations have shown that as long as the change in heat capacity at the glass transition is empirically additive in terms of small groups of atoms, liquid heat capacities are additive in terms of these small groups. For both poly(L-methionine) and poly(L-serine), the liquid heat capacities were calculated by use of an addition scheme where the heat capacity contribution of small groups of atoms has been determined. These contributions were taken either from experimentally determined heat capacities or from linear equations shown to represent the heat capacity of a particular atom or group of atoms. For both poly(amino acids), these liquid heat capacities were calculated in two different ways (using different small groups of atoms) and comparisons have been made.

For poly(L-methionine), the contributions of the amide group and the CH_2 group were taken from recent liquid studies on the aliphatic polyamides.[85] The sulfur atom was taken from work on polymers containing phenylene and naphthalene groups [specifically, poly(thio-1,4-phenylene)].[86] For the CH_3 group, it was necessary to subtract the experimentally determined heat capacity contribution of C_6H_4[54] from the experimentally determined heat capacity contribution of a C_6H_4 group with two methyl groups attached.[52] Finally, the contribution of the CH group was determined by subtracting the liquid heat capacity contribution of a methyl group (as determined above) from the liquid heat capacity contribution of a $CHCH_3$ group.[52] These heat capacity contributions were then added together to give the calculated heat capacity of liquid poly(L-methionine). Figure 68 shows the results. The calculated liquid heat

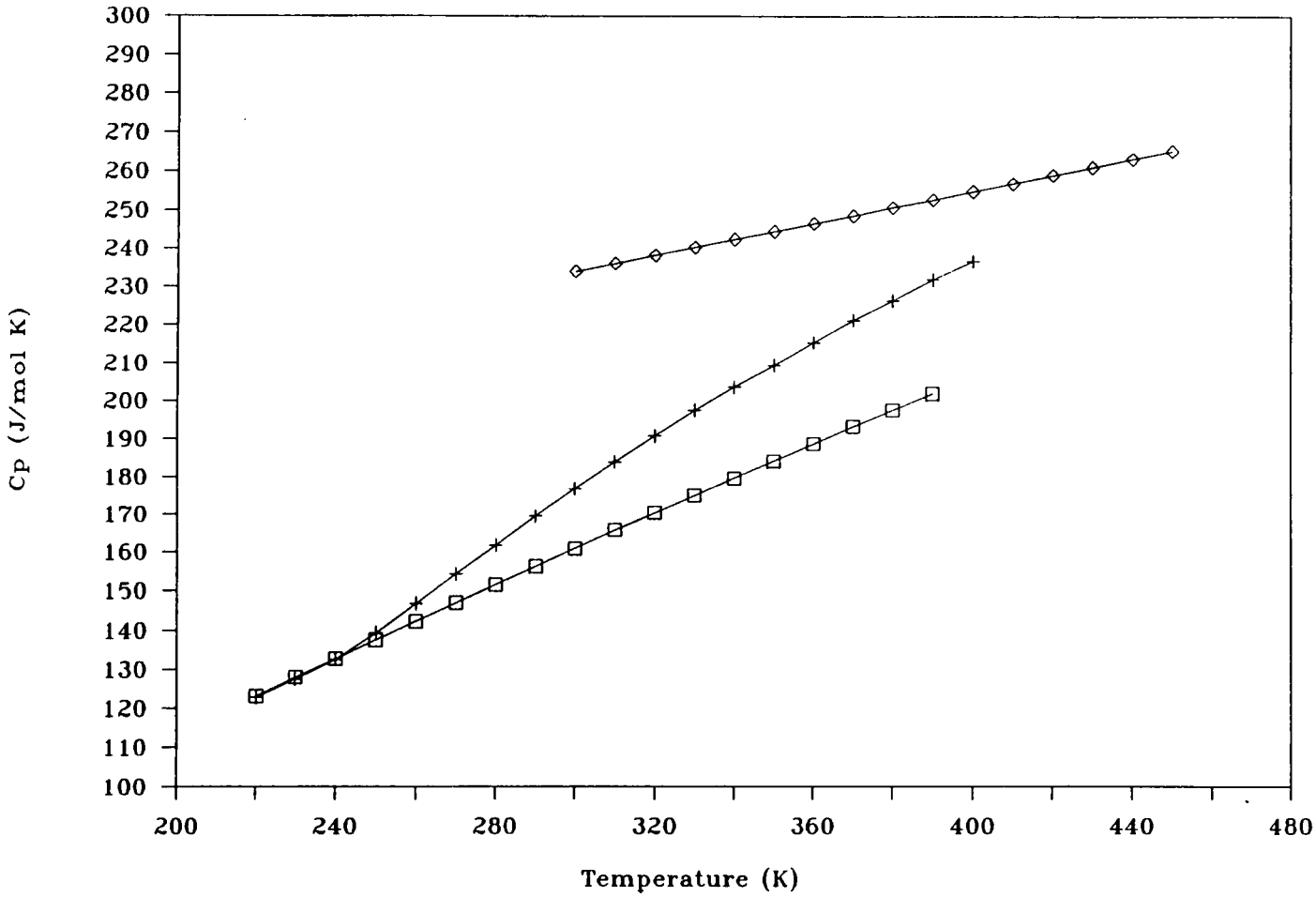


Figure 68 Liquid Heat Capacities of Poly(L-methionine). Bottom curve (□): Calculated heat capacities of the solid. Center curve (+): Measured heat capacites of the solid. Top curve (◇): Calculated heat capacites of the liquid.

capacities are plotted along with the experimental and calculated solid heat capacities. A second calculation was performed using a different choice of groups. For this calculation, again the amide contribution was taken form the recent work on aliphatic polyamides,[85] and the sulfur group was taken from work on polymers containing phenylene and naphthalene groups.[86] The heat capacity contribution of the remainder of the poly(L-methionine) molecule - $CH_3CH_2CH_2CH$ was taken by subtracting a CH_2 group[85] from the experimentally determined liquid heat capacities of polypentene.[87] For the two calculations, the liquid heat capacities differed by only ± 1.02% for the temperature range 300 to 450 K. Such close agreement between the two calculated results further shows the validity of such a scheme in determining the liquid heat capacity of an unknown polymer, in this case poly(L-methionine).

For poly(L-serine), the heat capacity contributions of the amide group were as before taken from work on the liquid aliphatic polyamides.[85] The CH group was taken as before by subtracting the heat capacity contribution determined for the CH_3 group (outlined above) from the contribution of the $CHCH_3$ group. No information on the contribution of the OH group can be obtained as the liquid heat capacities of poly(vinyl alcohol) have not been determined. As a result the heat capacity contribution of the CH_2O group, taken from work on liquid aliphatic polyoxides,[87] was used for the contribution of the CH_2OH group. These heat capacity contributions were added resulting in the calculated heat capacity shown in Figure 69. Along with this calculated liquid heat capacity are plotted the solid experimental and solid calculated heat capacities. A second calculation was performed for com-

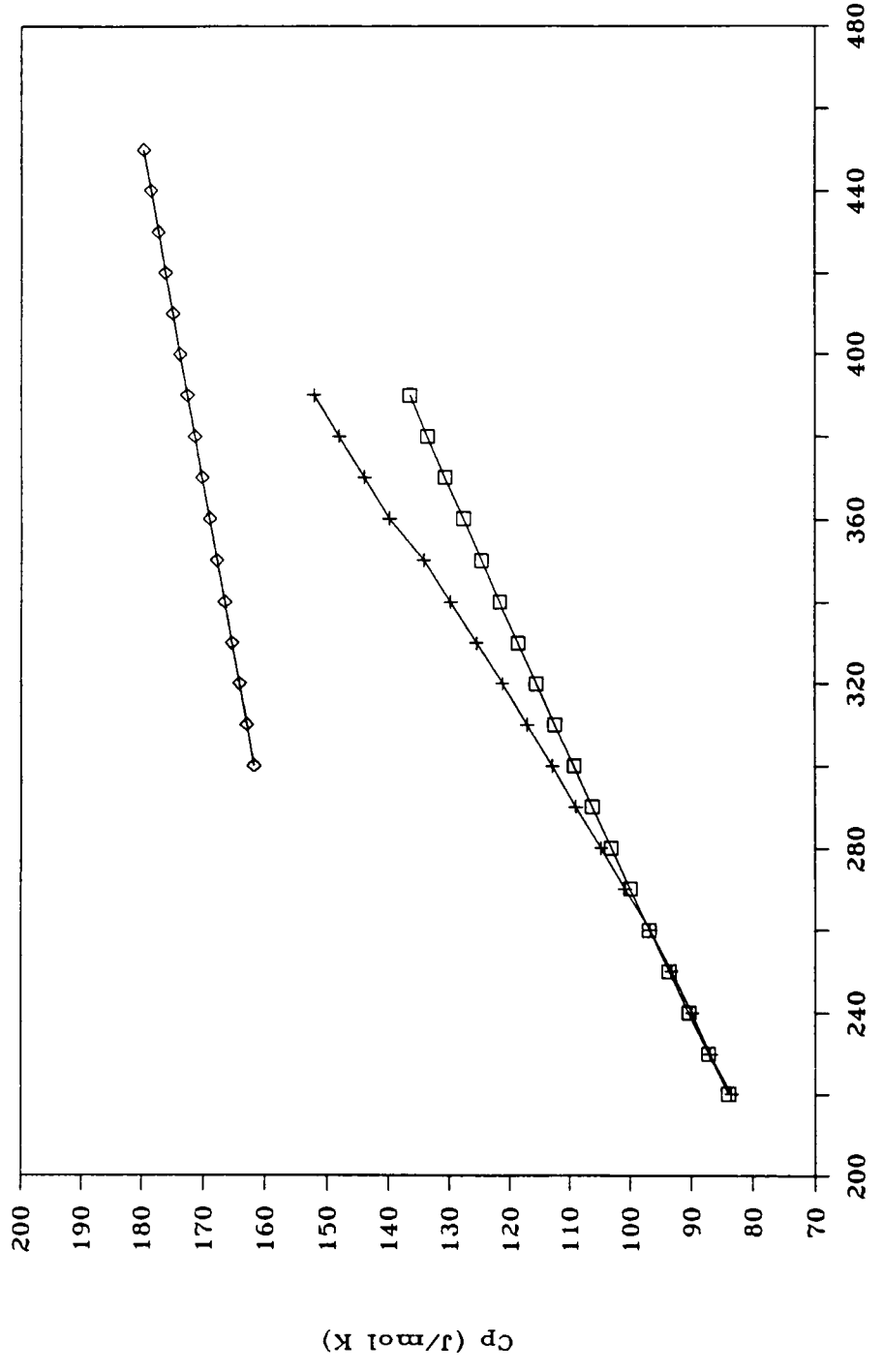


Figure 69 Liquid Heat Capacities of Poly(L-serine). Bottom curve (□): Calculated heat capacities of the solid. Center curve (+): Measured heat capacites of the solid. Top curve (◇): Calculated heat capacites of the liquid.

parison. In this, again the amide group contribution was taken from the polyamides.[85] The CH_2CH group contribution was determined by subtracting the contribution of a CH_3 group from the experimentally determined liquid heat capacities of polypropylene.[89] Finally, the oxygen atom heat capacity contribution was taken from work on polymers containing oxygen atoms.[86] Heat capacities calculated using these two different sets of group contributions were the same to within ±0.5% over the temperature range 300 to 450 K. Again this confirms the validity of such addition schemes.

Referring to Figure 68, we see that the difference between the calculated heat capacity for the solid poly(L-methionine) and the calculated liquid heat capacity is 50.8 J/(mol K). For the temperature range 300 to 390 K, the average of these differences is 61.7 J/(mol K). Earlier it was pointed out that for glass transitions in amorphous polymers, it has been empirically observed that the jump in heat capacity is often 11 J/(mol K) of mobile units or beads. That is every mole of mobile units or beads contributes 11 J/(mol K) to ΔC_p at the glass transition. For poly(L-methionine), one would expect the number of mobile units or beads to be four or five, thus giving a ΔC_p value of 44 J/(mol K) or 55 J(mol K) respectively. Taking the number of beads as five thus can easily account for the ΔC_p shown in Figure 68. Such a comparison is rather convincing proof that the calculated liquid heat capacities are indeed correct. It is important to point out here that Pezzin and co-workers were able to account for the ΔC_p observed for a number of poly(α-amino acids) using Wunderlich's rule[83] of 11 J/(mol K) per mole of beads and counting

beads as we have done for poly(L-methionine). Now, if one considers the difference between the experimental heat capacity for the solid poly(L-methionine) and the calculated heat capacity for the liquid poly(L-methionine) at 390 K, a value of 20.77 J/(mol K) is determined. For the temperature range 300 to 390 K, the average of these differences is 37.68 J/mol K. This means that the ΔC_p that is observed experimentally is approximately one-half to one-third of the ΔC_p that is expected. Looking at Figure 68, it is evident that the experimental heat capacity curve is still increasing at even 400 K. It is quite possible that the glass transition is broadened to such an extent that the experimental heat capacity curve would be nearly reach the liquid heat capacity curve at high enough temperatures if decomposition did not occur first. Another possibility is that the poly(L-methionine) is more crystalline than originally thought, perhaps as much as 50% crystalline. This would then account for the difference in the experimental and calculated liquid heat capacities. One further possibility is that the poly(L-methionine) may be involved in cross-linking, this too causing the observed ΔC_p to be less than the expected ΔC_p. Considering the rather preliminary proposed structure of poly(L-methionine) suggested by Colonna-Cesari and Premilat,[29] and the side group of the poly(amino acid), crosslinking does not immediately seem likely. It is however, quite likely that the sample is more crystalline than first thought, and that the broadened glass transition is still in progress at the conclusion of the experimental determination of heat capacity.

Although the discussion the differences observed between the experimental solid and the calculated liquid heat capacities presented above does not provide

convincing proof that a broadened glass transition is occurring in poly(L-methionine) above 260 K, the results of the qualitative studies do. We are therefore confident that the positive deviations of the experimental solid heat capacities from the calculated solid heat capacities observed in poly(L-methionine) can be attributed to a broadened glass transition.

Now consider the case of poly(L-serine) shown in Figure 69. The difference between the calculated heat capacity for the solid and the calculated heat capacity for the liquid is 30.68 J/(mol K) at 390 K, and 41.31 J/(mol K). Taking the number of mobile beads for poly(L-serine) as three or four, this results in an expected ΔC_p of approximately 33 J/(mol K) or 44 J/(mol K) respectively at the glass transition. Thus the differences are reasonable, and the use of addition schemes to calculate a liquid heat capacity is further justified. For poly(L-serine), the difference between the experimental solid heat capacity and the calculated liquid heat capacity at 390 K is only 15.04 J/(mol K). The average difference for the temperature range 300 to 390 K is 31.94 J/(mol K). Again this suggests that the ΔC_p measured is approximately one-half of the ΔC_p expected. Again, it must be pointed out that the experimental heat capacity curve for the poly(L-serine) is still on the rise at the end of the experiment (390 K), and might in fact reach the liquid heat capacity curve if decomposition did not occur first. It is also quite likely, as mentioned in Chapter III, that the crystallinity of this sample may be as high as 50%. Furthermore, the possibility of crosslinking is quite probable for the poly(L-serine) with its mobile OH group at the end of the side chain. The differences observed in the experimental

solid heat capacities and the calculated liquid heat capacities can, for poly(L-serine) be easily accounted for. Based on these considerations and the results of one of the qualitative studies, we are confident that the poly(L-serine) is undergoing a broadened glass transition. This can account for the deviations of the experimental heat capacities from the calculated heat capacities at temperatures above 290 to 300 K.

VII. CALCULATION OF H, S, AND G FUNCTIONS

With the knowlege of heat capacities down to absolute zero temperature, it becomes possible to calculate the thermodynamic functions enthalpy, H, entropy, S, and Gibbs free energy, G, using the following equations:

$$H = H_0 + \int C_p dT \tag{26}$$

$$S = S_0 + \int \frac{C_p}{T} dT \tag{27}$$

$$G = H - TS \tag{28}$$

The *ATHAS* data bank has computer programs set up to calculate the functions H, S, and G with provided heat capacity data. In these programs, S_O, the entropy of a perfect crystal at absolute zero is taken as zero according to the third law of thermodyanmics. The function H is calculated as $H - H_O$. The Gibbs free energy

function, G, is then calculated according to Eq. (28).

Now that heat capacities have been measured for the majority of poly(amino acids) and a number of copolymers, it is possible to calculate the important thermodynamic function, enthalpy, entropy, and Gibbs free energy. As an example, we have calculated these functions for the first three simplest poly(amino acids) - polyglycine, poly(L-alanine), and poly(L-valine). The results of these calculations are graphed in Figures 70 - polyglycine, 71 - poly(L-alanine), and 72 - poly(L-valine).

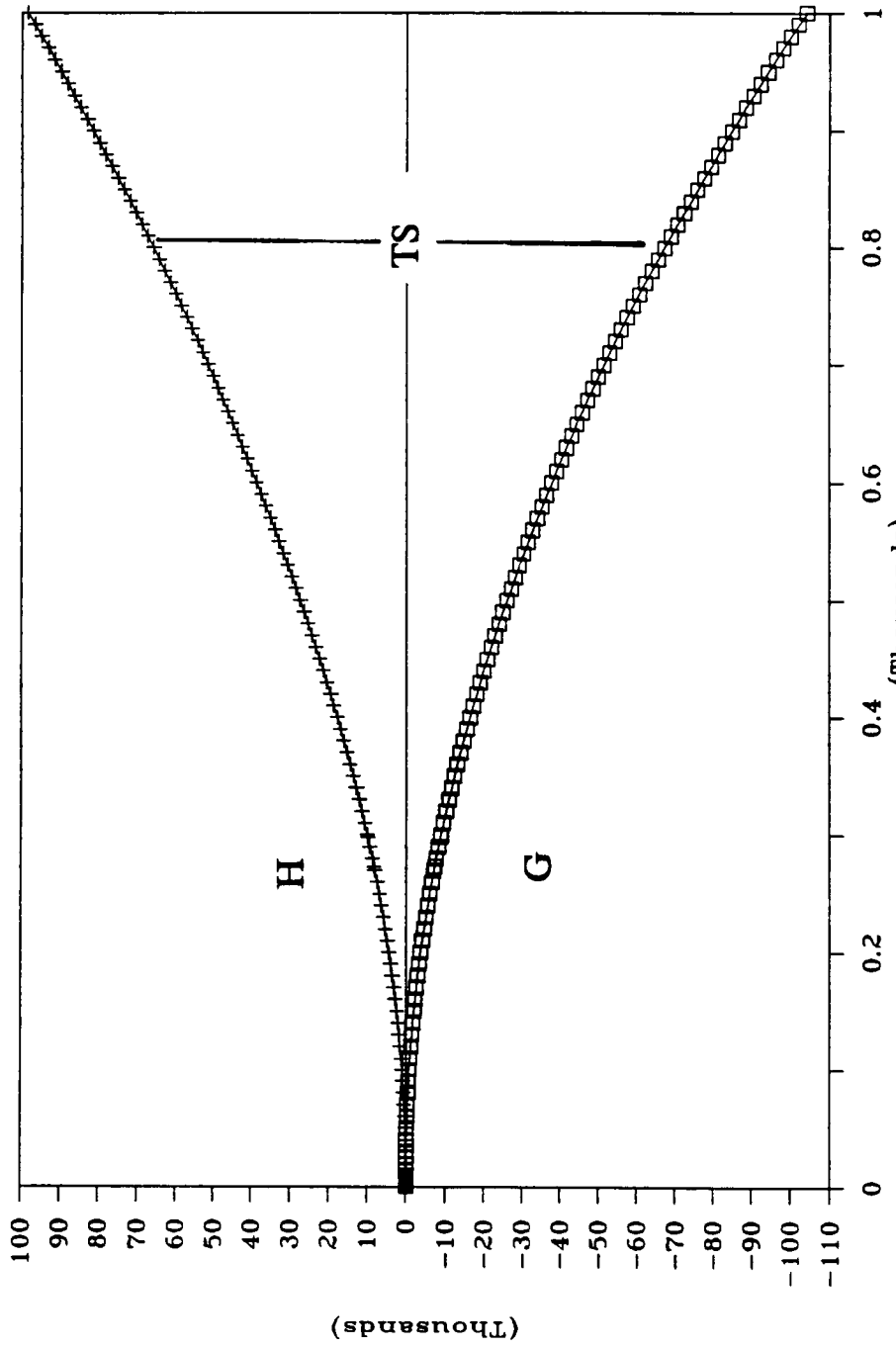


Figure 70 Enthalpies, Entropies, and Free Energies of Polyglycine. Top curve (◇): Enthalpies, H. Bottom curve (+): Free Energies, G.

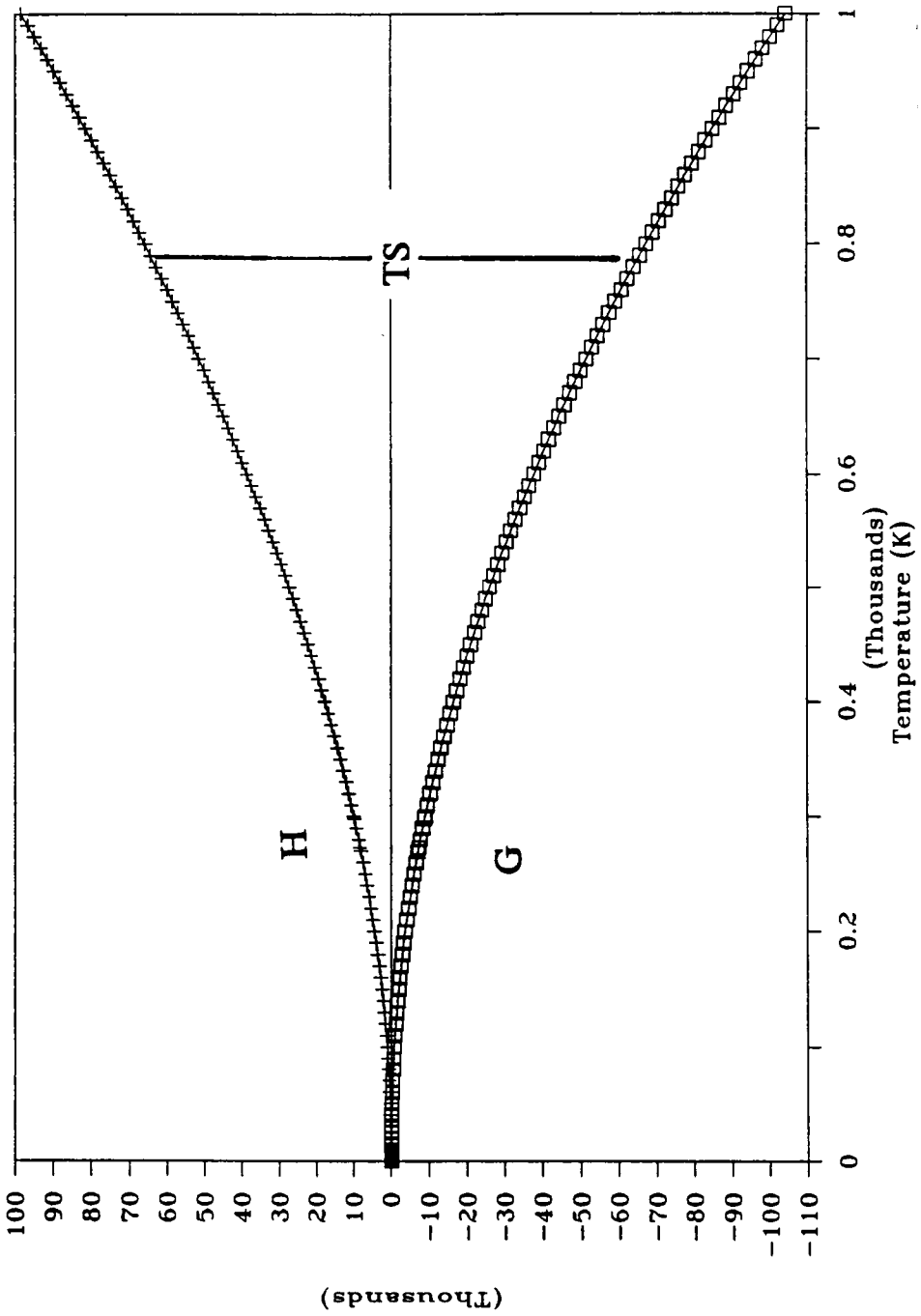


Figure 71 Enthalpies, Entropies, and Free Energies of Poly(L-alanine). Top curve (◇): Enthalpies, H. Bottom curve (+): Free Energies, G.

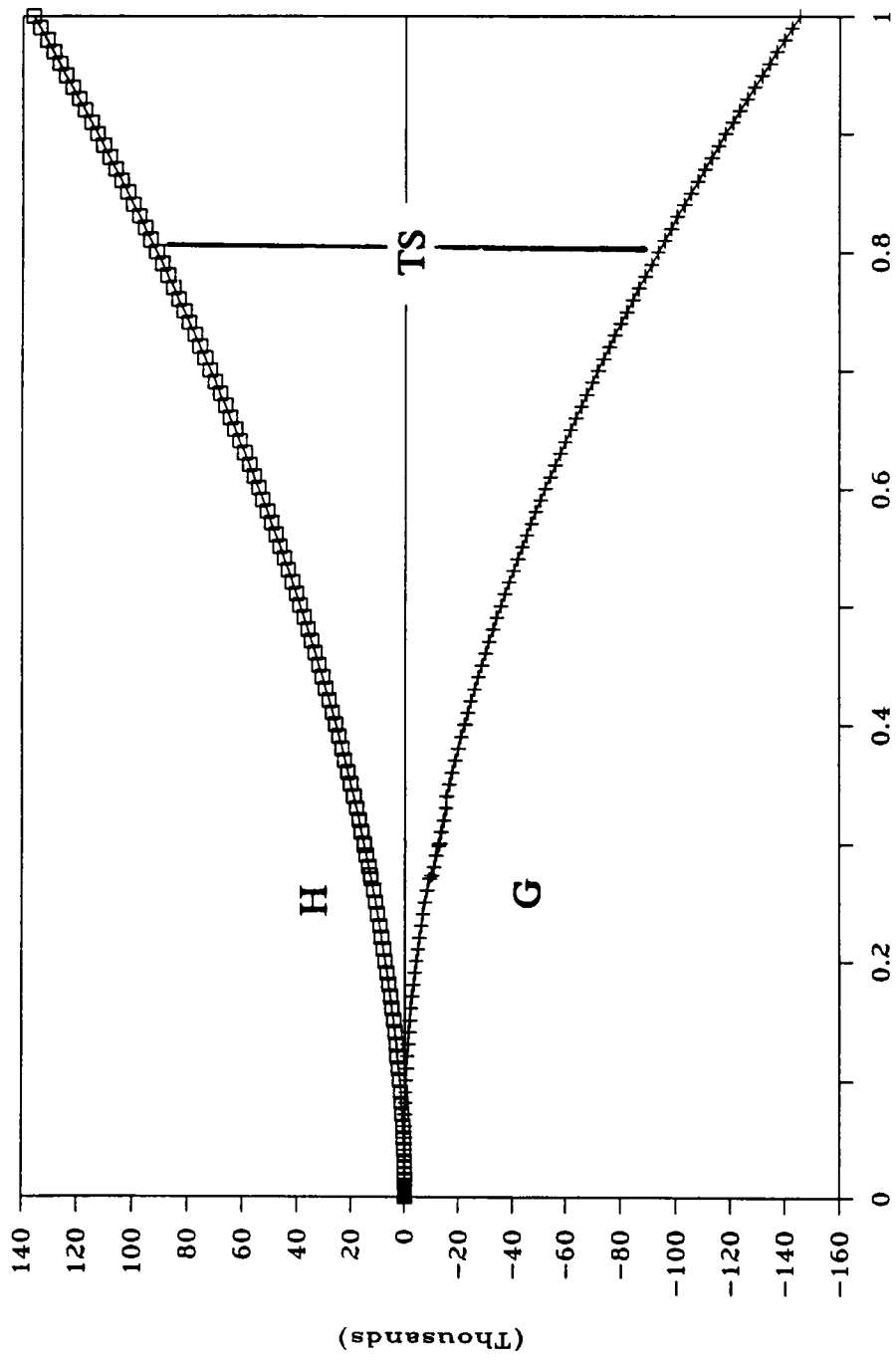


Figure 72 Enthalpies, Entropies, and Free Energies of Poly(L-valine). Top curve (◇): Enthalpies, H. Bottom curve (+): Free Energies, G.

CHAPTER V

CONCLUSIONS

In Chapter I the goals of this research were discussed. These goals were defined based on a need for further understanding of the nature of biological macromolecules. At the heart of this understanding was the laying of a foundation for advanced thermal analysis of biological materials starting with the poly(amino acids) and ultimately extending the work to the proteins. In this thesis the first necessary steps are described for building this foundation by establishing a data bank of heat capacities consisting of sixteen poly(amino acids) which were based on the twenty common amino acids. For these sixteen poly(amino acids) reliable heat capacities have been measured in the temperature range 220 to 390 K. For thirteen of these sixteen poly(amino acids) heat capacities had never before been measured. In the process of laying this foundation, we were able to demonstrate that the number of small studies conducted earlier on the heat capacities of the three simplest poly(amino acids) – polyglycine,[8-10] poly(L-alanine),[11-15] and poly(L-valine)[16] – were plagued by gross experimental systematic errors, the most likely source of which was water content. Examination of the measured heat capacities led to some interesting information regarding the effects of water content, a notorious problem in studies of biological macromolecules. Not unexpectantly, water vaporization peaks were observed with peak temperatures slightly lower or higher than that of ordinary water.

Most importantly, we were able to demonstrate that for thermodynamic measurements, the water associated with the poly(amino acids) and copolymers can be removed and accounted for. Thus reliable thermodynamic measurements are possible.

The next step in the laying of this foundation was the extension of the analysis to copolymers of the poly(amino acids). For four copolymers, reliable heat capacities are now available in the temperature range 220 to 390 K. In addition, we were able to verify the copolymer rule of heat capacity additivity previously established for synthetic polymers. This important verification now leads the way for future extension to proteins.

In addition to these experimental studies, this thesis went one step further and attempted to provide a complete understanding of the heat capacity, a macroscopic property, in terms of its microscopic origin, the vibrational motion. It was demonstrated that the heat capacities of biological polymers can be linked to the vibrational spectrum in the same manner as has been accomplished for other solid, linear polymers. As a result, based on the vibrational spectra, heat capacities were calculated for all sixteen poly(amino acids) and four copolymers in the temperature range 0 to 1000 K. Agreement with experiment was observed in the temperature range of the experiment (220 to 390 K) for all but two of the poly(amino acids). These two poly(amino acids), poly(L-methionine) and poly(L-serine), demonstrated agreement between experiment and calculation for only limited low temperature ranges.

Poly(L-methionine) and poly(L-serine), the two poly(amino acids) for which only limited agreement was observed between experimental and calculated heat capacities present interesting additional information. Coupling a series of experimental methods including differential scanning calorimetry, X-ray powder diffraction, and a number of qualitative observations of physical changes upon changes in temperature with calculated liquid heat capacity curves for the two poly(amino acids), we are able to confidently attribute the lack of agreement to the presence of a broadened glass transition. In the process of these studies, we gave further evidence to the validity of addition schemes for liquid heat capacities.

As a result of the work described in this thesis, the foundation for the advanced thermal analysis of biological macromolecules has been layed. The path to future studies leading ultimately to a better understanding of the nature of peptides and proteins has been paved. As noted in the Chapter I, before any significant strides can be made in understanding the nature of proteins and interactions, very important strides must be made in understanding the simplest parts of proteins, the amino acids. This thesis took these first strides. There are a number of future studies which are of immediate interest in continuing the buildup of this foundation of knowledge. First since many of the poly(amino acids) are semi-crystalline, crystallinity estimates obtained by X-ray powder diffraction for all the samples would be of interest. For the less crystalline poly(amino acids), there are the possibilities of glass transitions existing either above or below the temperature range of the current work. While the heat capacity of the liquid state is not

accessible, it is possible to get good estimates via two routes. We have already shown that the empirical addition schemes provide one reasonable route. Liquid heat capacities for all poly(amino acids) and copolymers could be calculated based on these addition schemes. Another possible route involves the study of concentrated solutions to evaluate the partial molar heat capacities, extrapolated to the pure state. Only for the three simplest poly(amino acids) were we able to determine Θ_3-temperatures. For the remaining poly(amino acids), the values used for Θ_3 in the calculation of heat capacities were based on the values for the first three. Low temperature heat capacity studies would provide the necessary information to determine more correct Θ_3-temperatures for the remaining poly(amino acids) as well as the copolymers. These studies should be carried out in the future. Finally, the copolymer analysis provides for a natural extension to proteins. It is not unreasonable to assume that the heat capacities of proteins can be determined based on their component parts, as was done for the copolymers.

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