The interesting nature of the nickel/tellurium system was first indicated by Tengné, who asserted the existence of a continuous solid-solution range between the compounds NiTe and NiTe₂. He suggested that in proceeding from NiTe, which has a hexagonal structure of the NiAs type, to NiTe₂, which has a hexagonal structure of the Cd(OH)₂ type, nickel atoms are removed from the 00l position but not from the 000 position so that in NiTe₂ alternate full and depleted planes of nickel atoms are present in the structure parallel to (001). The tellurium atoms are not appreciably displaced from the positions 2 1 1 and 3 1 1 and the basic structure and lattice constants undergo very little change. More recent work by Barstad and Grønvold has shown the NiTe₁.₀₀ to be a heterogeneous product and that the single phase region, the δ phase, extends from about NiTe₁.₀₈ to NiTe₂.₀₀ for samples heat treated at 450°C. This unusually wide range of homogeneity makes the δ phase of considerable interest. Heat capacities of the nickel tellurides were measured at compositions NiTe₁.₁₀ and NiTe₂.₀₀ (near limits of homogeneity of the δ phase) and at one intermediate composition, NiTe₁.₅₀, from 5 to 350°K. Heat capacity values and entropy and enthalpy increments are tabulated. No evidence of order-disorder transitions, or thermal anomalies, or of contributions to the thermal properties from the anisotropy or phonon scattering by the holes in the structure on approaching the composition NiTe₂ was observed. Although simple additivity of the heat capacities of the constituent elements failed to represent that of the solution compositions adequately, a Kopp-Neumann treatment in terms of the limiting compositions of the δ phase gives good agreement with the experimental heat capacity and entropy of NiTe₁.₁₀ and hence is useful in interpolating to other intermediate compositions.

It is also relatively free from magnetic complications, making it particularly suitable for a thermodynamic study.

Samples with compositions from NiTe to NiTe₂ were studied by Klemm and Fratini by x-ray diffraction, magnetic susceptibility measurements and pycnometry. A short series of magnetic measurements was later made on a nickel telluride with composition NiTe. Recently, the nickel tellurides have been studied over a wide range of compositions by several techniques: measurements of electrical and thermal conductivity and thermal emf at room temperature; measurements of magnetic susceptibility and magnetization intensity from about 80°K to the melting point; x-ray and density determinations near 25°C and magnetic susceptibility measurements from 90 to 723°C²; and x-ray diffraction analysis of the temperature dependence of the lattice constants to 800°⁰.

The relationships of the nickel tellurides to other chalcogenides of the transition elements (many of which

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This point of view. This theme, being essentially independent of the H₃ problem, will be treated in a later paper.

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Thermodynamics of Nonstoichiometric Nickel Tellurides.¹

I. Heat Capacity and Thermodynamic Functions of the δ Phase from 5 to 350°K

E. F. Westrum, Jr., C. Chou, and R. E. Machol, Department of Chemistry, University of Michigan, Ann Arbor, Michigan

AND

F. Grønvold, Chemical Institute A, University of Oslo, Blindern, Norway

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INTRODUCTION

THE interesting nature of the nickel/tellurium system was first indicated by Tengné, who asserted the existence of a continuous solid-solution range between the compounds NiTe and NiTe₂. He suggested that in proceeding from NiTe, which has a hexagonal structure of the NiAs type, to NiTe₂, which has a hexagonal structure of the Cd(OH)₂ type, nickel atoms are removed from the 00l position but not from the 000 position so that in NiTe₂ alternate full and depleted planes of nickel atoms are present in the structure parallel to (001). The tellurium atoms are not appreciably displaced from the positions 2 1 1 and 3 1 1 and the basic structure and lattice constants undergo very little change. More recent work by Barstad and Grønvold has shown the NiTe₁.₀₀ to be a heterogeneous product and that the single phase region, the δ phase, extends from about NiTe₁.₀₈ to NiTe₂.₀₀ for samples heat treated at 450°C. This unusually wide range of homogeneity makes the δ phase of considerable interest.

¹ W. Klemm and N. Fratini, Z. anorg. u. allgem. Chem. 251, 222 (1943).
⁵ A. Schneider and R. H. Imhagen, Naturwiss. 44, 324 (1957).
are nonstoichiometric compounds) are summarized by Klemm, Ehrlich, and Haraldsen. The widespread occurrence of phases showing NiAs–Cd(OH)₂-like structures have made studies of their thermodynamic properties highly desirable. In addition to the primary effects of vacancies, the variety of transitions possible in compounds of this type adds to the complexity of the analysis. Elcock has discussed the problem of the transitions in nonstoichiometric compounds with particular reference to magnetic properties of transition element chalcogenides, and Lotgering has discussed it with specific reference to iron sulfides. Configurational order-disorder transitions also seem possible; for example, ordering of the holes may appear either within the alternate planes partially filled with metal atoms or by transfer of atoms from filled to partially filled planes.

The study of the thermodynamics of the nickel/tellurium system is designed to determine whether such transitions are present, and to elucidate the thermodynamic properties, including zero-point entropies, as functions of composition of the phases. The only previous thermodynamic studies have been one determination of the heat of formation and five measurements of the mean heat capacity over wide temperature ranges of a nickel telluride with composition NiTe and a mention of the heat capacity of NiTe₂. The present paper reports the results of heat capacity measurements from 5 to 350 K on three compositions covering the range of homogeneity of the δ phase.

**EXPERIMENTAL**

**Preparation and Purity of Samples**

Metallic nickel was prepared from the British Drug Houses, Ltd., nickel oxide—low in cobalt and iron, by reduction with dry, purified hydrogen gas for four hours at 1000°C. Spectrographic analysis showed only traces of Cu and Mg and no Co or Fe. The CP tellurium was purified by repeated vacuum distillation in silica vessels. Spectrographic analysis showed no impurities, except possibly traces of Si and Mg. Accurately weighed quantities of the elements corresponding to the compositions NiTe₁.₄, NiTe₁.₅, and NiTe₂ were heated in evacuated and sealed silica tubes. All three samples were fused for two hours at 1000°C. They were then cooled, fragmented, and annealed in vacuo at 500°C for 30 days, and cooled to room temperature over a period of two days. An additional heating for two weeks at temperatures gradually decreasing from 500 to 300°C was needed for NiTe₂ to take up a slight amount of unreacted tellurium. Thereafter the samples were kept in vacuo or under dry helium except for transfer to the calorimeter, which was done either in a dry box or at a relative humidity below 20%. It is estimated that neither the total impurity nor the uncertainty in the composition of the nickel tellurium exceeds 0.01%.

**Cryostat and Calorimeter**

The Mark I cryostat and technique employed for low-temperature adiabatic calorimetry are described elsewhere. The copper calorimeter (laboratory designation W-7) was similar to calorimeter W-5; it was gold-plated inside and out, had only four vanes, and had a capacity of 40.33 cc. The specific heat of the calorimeter was separately determined (using the same thermometer and heater, and exactly the same amount of indium-tin solder for sealing and Apiezon-T grease for thermal contact with the thermometer and heater); it represented from 20% to 40% of the total heat capacity observed. The platinum resistance thermometer (laboratory designation A-3) has been calibrated by the National Bureau of Standards, and the temperatures are believed to correspond with the thermodynamic scale within 0.03° from 10° to 90°K, and within 0.04° from 90° to 350°K. Precision is considerably better, so that the individual measured temperature increments are probably accurate to a millidegree after corrections for quasi-adiabatic drift.

**Procedure**

The calorimeter was loaded with sample, evacuated, filled with helium at 2 cm Hg pressure at 300°K (to provide thermal contact between calorimeter and sample), sealed, placed in the cryostat, and cooled over a period of several days to approximately 4°K. The weights of sample used were 173.963 g of NiTe₁.₄, 168.080 g NiTe₁.₅, and 120.065 g NiTe₂. The smaller amount of NiTe₁.₅ was caused by the lower bulk density of the foliated, tabular crystals of NiTe₂, occasioned by the eminent basal cleavage of its lamellar crystalline structure. Care was taken not to compress this material into the calorimeter, to avoid changes of heat capacity which might result from cold working.

**Computation and Results**

The actual heat capacity determinations are listed in Table I in chronological order, so that the individual temperature increments can be inferred from the adjacent mean temperatures. These values are expressed in terms of the defined thermochemical calorie, equal to 4.1840 absolute joules. The ice point is taken to be 273.15°K and the atomic weights of nickel and tellurium as 58.69 and 127.61, respectively. The data are expressed in terms of one mole of mixture ("mole"), equivalent to the gram formula weight of Ni₄Te₁₋₂;
direction for the finite temperature increments employed has been added to each observed value of \( i.e., 94.79 \text{ g of NiTe}_{1.5} \).

Because of the low pressure in the calorimeter, the values thus corrected to \( dH/dT \) are equal to \( C_p^{\circ} \) or \( C_{sat}^{\circ} \) within the limits of the experimental error.

The heat capacity versus temperature curve (Fig. 1)
FIG. 1. The experimental "molal" heat capacities of the \( \delta \)-phase nickel tellurides. O represents \( \text{Ni}_6 \), \( \text{Te}_0 \), \( \delta \); •, \( \text{Ni}_0 \), \( \text{Te}_0 \), \( \delta \); and □, \( \text{Ni}_0 \), \( \text{Te}_0 \), \( \delta \).

has the usual sigmoid shape and no singularities or inflections other than the major inflection predicted by Debye theory, with one exception (noted below). Above 30 K, most of the points deviated from the curve by less than 0.001 cal mole\(^{-1}\) deg\(^{-1}\); the deviations were not normally distributed and in a few cases were close to 0.01 cal mole\(^{-1}\) deg\(^{-1}\). Experience indicates that these deviations are not reproducible and presumably not significant. Below 30 K the measurements become progressively less accurate, due to the smaller absolute heat capacity, the smaller temperature intervals, and the decreased sensitivity of the thermometer.

Values of \( C_p^0 \), \( S_0^0 - S_0^\delta \), and \( (H^0 - H_0^\delta)/T \) at selected temperatures are shown in Table II. The enthalpy and entropy increments were computed by numerical integration, using graphically interpolated values of heat capacity. The values of entropy are considered to be accurate to \( \pm 0.01 \) cal mole\(^{-1}\) deg\(^{-1}\), even at the higher temperatures, and the enthalpy values are considered accurate to \( \pm 0.1\% \), except at the lowest temperatures. Some of the tabular data are given to an additional digit because, while it is not significant on an absolute basis, it is significant on a relative basis, as when the entropies or enthalpies at different temperatures or compositions are compared.

**DISCUSSION**

Over the temperature range thus far investigated, there is no evidence of transitions or other anomalous behavior, except for a small, nearly constant, upward displacement in the heat capacity of NiTe\(_{1.1}\) which occurs near 270 K. This amounts to about 0.01 cal
mole$^{-1}$ deg$^{-1}$ and hence is barely visible in Fig. 1. The heat capacity differences between the three compositions are so small and so regular that there is no reason to suspect anomalies at intermediate compositions.

The entropy increments between 298.15° and 0°K are 9.567, 9.597, and 9.614 cal mole$^{-1}$ deg$^{-1}$ for the NiTe$_{1.1}$, NiTe$_{1.5}$, and NiTe$_{2.0}$, respectively. The closeness of these values to one another is somewhat coincidental; for at constant temperature, the heat capacities increase with increasing tellurium content below about 60°K, and with decreasing tellurium content above this temperature.

**Applicability of the Kopp-Neumann Rule**

In the statistical treatment of solid solutions, the conventional simplifying assumption$^{17}$ that the partition function can be factored into vibrational and configurational contributions is frequently made. This resolution, of course, implies the independence of vibrational specific heat and configuration.

Fig. 2. Increment of the heat capacity of formation of NiTe
(A) from the elements, (B) from terminal δ-phase compositions.

Au—Ni system and of Coffer et al. on the Mg—Cd system in evidencing appreciable deviations from the rule. However in this system the structure types of the Ni, Te, and δ phases are different. Thus, there is even less reason for expecting good agreement with the Kopp-Neumann rule than in the Au—Ni and the Mg—Cd systems.

The increment in the heat capacity due to the formation of the solid solution was evaluated for NiTe1.5, for example, by the following expression:

\[ \Delta C_p = C_{p,Ni0.4Te0.6} - (0.4667C_{p,Ni0.4762Te0.5238} + 0.5333C_{p,Ni0.3333Te0.6667}) \]

The heat capacity of tellurium is taken from a smooth curve plotted through the combined data of Anderson and of Slansky and Coulter. The heat capacity of nickel is taken from Busey and Giauque corrected by subtraction of the electronic contribution taken from the measurements of Rayne and Kemp and assumed to be proportional to the absolute temperature. Other corrections (cf. Stoner) are negligible. From the \( C_p \) values of the three compositions calculated by this procedure and presented in Fig. 2(A), appreciable deviations from additivity are evident, especially near 30°K. Since the condition of the same structure type has not been met, this disagreement is hardly to be classed as a violation of the Kopp-Neumann rule; however, it would suggest caution in the application of the rule in the estimation of heat capacities of alloys. In many respects the deviations have a semiquantitative counterpart in the Au—Ni and the Mg—Cd systems.

If, however, the increment in the heat capacity due to the formation of the solid solution of composition NiTe1.5 from compositions NiTe1.1 and NiTe2.0, all within the solid solution region, are evaluated by the expression,

\[ \Delta C_p' = C_{p,Ni0.4Te0.4} - (0.4667C_{p,Ni0.4762Te0.5238} + 0.5333C_{p,Ni0.3333Te0.6667}) \]

a valid test of the Kopp-Neumann rule may be made over this range of composition. The increments are shown in Fig. 2(B), and are seen to be in excellent agreement with the Kopp-Neumann rule. This is probably a consequence of the continuous change in structure across the solution range, as well as the small fractional variation in composition. The anomalous rise in heat capacity near 300°K in the NiTe1.1 has been eliminated for this comparison. Percentage deviation curves based on the experimental heat capacity of NiTe1.5 have been provided in Fig. 2 for convenience.

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23 J. A. Rayne and W. R. G. Kemp, Phil. Mag. (8) 1, 918 (1956).
The excellence of the agreement with this application of the Kopp-Neumann rule suggests that within at least the \( \delta \) phase in this system interpolation of the heat capacities, and even more reliably, interpolation of the thermodynamic functions may be made with confidence to intermediate compositions. For example, the entropy increment \( (S^{0.98.15°} - S^{0°K}) \) for NiTe\(_{1.5}\) interpolated from the terminal \( \delta \) phase compositions is 9.576 eu compared with the experimental value of 9.597 eu.

The plots of \( C_p/T \) versus \( T^2 \) in Fig. 3 indicate that the heat capacities have reached a \( T^3 \) dependence at the lowest temperatures and that there is no significant electronic contribution linear in \( T \). The third power dependence is especially interesting in NiTe\(_{2.0}\) which has a lamellar structure, a platy crystalline habit, and prominent basal cleavage. Phonon scattering by vacancies in the NiTe\(_{2.0}\) lattice may at some low temperature make appreciable contribution to the trend of \( C_p \). The temperature dependence of the heat capacity of lamellar lattices has been the subject of considerable discussion and the most recent investigation\(^2\) of the heat capacity of cadmium iodide (which differs only slightly from the cadmium hydroxide structure characteristic of NiTe\(_{2.0}\)) indicated a heat capacity proportional only to \( T^{.4} \) at the lowest temperatures reached in those experiments.

Debye characteristic temperatures are presented as a function of temperature for the three experimental compositions in Fig. 4. The \( C_v \) values have been obtained from the measured \( C_p \) values by application of the approximate Nernst-Lindemann relation:\(^3\) \( C_p - C_v = 0.0214C_p(T/T_m) \), in which \( T_m \) is the melting point of the sample (taken as approximately 900°C). No correction has been made for the presumably small electronic contribution to the heat capacity of the solid solutions. The calculated \( \theta \) values decrease slightly at the lowest temperatures, then increase to a maximum near 100°K. They then decrease first gradually and at higher temperatures precipitously and actually become negative when the observed heat capacity exceeds \( 3R \) (violation of the Dulong and Petit rule), a phenomenon not uncommon in alloys.\(^4\) The increase in heat capacity beyond the Dulong and Petit limit in the vicinity of 270°K is presumably due to electronic contributions. The electrical conductivity\(^5\) near 300°K, about 10\(^4\) ohm\(^{-1}\) cm\(^{-1}\), is intermediate between that of typical semiconductors and that of typical conductors. This fact and the general metallic natures of these substances have been noted\(^7\) to give "an alloyic character" to these compositions; yet the heat of formation of the stoichiometric compound NiTe from the elements\(^2\) is rather higher (\(-9\) kcal mole\(^{-1}\)) than that of typical alloys.

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\(^3\) W. Nernst and F. Lindemann, Z. Electrochem. 17, 817 (1911).