

this point of view. This theme, being essentially independent of the H_3 problem, will be treated in a later paper.

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Thermodynamics of Nonstoichiometric Nickel Tellurides.*

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

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Heat capacities of the nickel tellurides were measured at compositions $NiTe_{1.1}$ and $NiTe_{2.0}$ (near limits of homogeneity of the δ phase) and at one intermediate composition, $NiTe_{1.5}$, 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 $NiTe_2$ 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 $NiTe_{1.5}$ and hence is useful in interpolating to other intermediate compositions.

INTRODUCTION

THE interesting nature of the nickel/tellurium system was first indicated by Tengnér,¹ who asserted the existence of a continuous solid-solution range between the compounds $NiTe$ and $NiTe_2$. He suggested that in proceeding from $NiTe$, which has a hexagonal structure² of the NiAs type, to $NiTe_2$, which has a hexagonal structure¹ of the $Cd(OH)_2$ type, nickel atoms are removed from the $00\frac{1}{2}$ position but not from the 000 position so that in $NiTe_2$ 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 $\frac{2}{3}\frac{1}{3}\frac{1}{4}$ and $\frac{1}{3}\frac{2}{3}\frac{3}{4}$ and the basic structure and lattice constants undergo very little change. More recent work by Barstad and Grønvold³ has shown the $NiTe_{1.00}$ is a heterogeneous product and that the single phase region, the δ phase, extends from about $NiTe_{1.08}$ to $NiTe_{2.00}$ for samples heat treated at 450°C. This unusually wide range of homogeneity makes the δ phase of considerable interest.

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

Samples with compositions from $NiTe$ to $NiTe_2$ were studied by Klemm and Fratini⁴ by x-ray diffraction, magnetic susceptibility measurements and pycnometry. A short series of magnetic measurements was later made⁵ 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 temperature⁶; measurements of magnetic susceptibility and magnetization intensity from about 80°K to the melting point⁷; x-ray and density determinations near 25°C and magnetic susceptibility measurements from 90 to 723°K⁸; and x-ray diffraction analysis of the temperature dependence of the lattice constants to 800°.⁸

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

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¹ S. Tengnér, *Z. anorg. u. allgem. Chem.* **239**, 126 (1938).

² I. Oftedal, *Z. physik. Chem.* **128**, 135 (1927).

³ J. Barstad and F. Grønvold, *Acta. Chem. Scand.* (to be published).

⁴ W. Klemm and N. Fratini, *Z. anorg. u. allgem. Chem.* **251**, 222 (1943).

⁵ F. M. Gal'perin and T. M. Perekalina, *Doklady Akad. Nauk SSSR* **69**, 19 (1949).

⁶ V. P. Zhuze and A. R. Regel, *Zhur. Tekh. Fiz.* **25**, 978 (1955).

⁷ E. Uchida and H. Kondoh, *J. Phys. Soc. Japan* **11**, 21 (1956).

⁸ A. Schneider and K. H. Imhagen, *Naturwiss.* **44**, 324 (1957).

are nonstoichiometric compounds) are summarized by Klemm,⁹ Ehrlich,¹⁰ and Haraldsen.¹¹ 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. Elcock¹² has discussed the problem of the transitions in nonstoichiometric compounds with particular reference to magnetic properties of transition element chalcogenides, and Lotgering¹³ 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 formation¹⁴ and five measurements of the mean heat capacity over wide temperature ranges¹⁵ of a nickel telluride with composition NiTe and a mention⁶ 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 NiTe_{1.1}, NiTe_{1.5}, and NiTe_{2.0} were heated in evacuated and sealed silica tubes. All three samples were fused for two hours at 1000°C. They were then cooled, fragmented, 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 NiTe_{2.0} 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 tellurides exceeds 0.01%.

Cryostat and Calorimeter

The Mark I cryostat and technique employed for low-temperature adiabatic calorimetry are described elsewhere.¹⁶ The copper calorimeter (laboratory designation W-7) was similar to calorimeter W-5¹⁵; 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 NiTe_{1.1}, 168.080 g NiTe_{1.5}, and 120.065 g NiTe_{2.0}. The smaller amount of NiTe_{2.0} 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 Ni_xTe_(1-x);

⁹ W. Klemm, *Naturwiss.* **37**, 150 (1950); **37**, 172 (1950).

¹⁰ P. Ehrlich, *Z. anorg. Chem.* **260**, 19 (1949).

¹¹ H. Haraldsen, *Z. angew. Chem.* (to be published).

¹² E. W. Elcock, *Proc. Roy. Soc. (London)* **A227**, 102 (1954).

¹³ F. K. Lotgering, *Z. physik. Chem. N.F.* **4**, 238 (1955); *Philips Research Repts.* **11**, 190 (1956).

¹⁴ C. Fabre, *Compt. rend.* **105**, 277 (1887).

¹⁵ W. A. Tilden, *Trans. Roy. Soc.* **A203**, 139 (1904).

¹⁶ E. F. Westrum, Jr., and A. F. Beale, Jr., *J. Am. Chem. Soc.* (to be published).

TABLE I. Heat Capacity of nickel tellurides (in cal/mole deg).

$T, ^\circ\text{K}$	C_p	$T, ^\circ\text{K}$	C_p	$T, ^\circ\text{K}$	C_p	$T, ^\circ\text{K}$	C_p
NiTe _{1.1} (formula weight Ni _{0.4765} Te _{0.5235} = 94.79g)							
Series I		16.44	0.1829	79.97	3.916	206.52	5.771
5.44	0.0065	18.23	0.2493	87.07	4.175	216.13	5.817
6.44	0.0099	20.20	0.3369	94.38	4.391	225.83	5.860
7.56	0.0154	22.43	0.4482	87.69	4.196	235.58	5.903
8.65	0.0240	24.95	0.5910	95.21	4.414	245.31	5.941
		27.44	0.7470	103.23	4.613	255.16	5.982
		30.08	0.9234	111.74	4.796	265.11	6.026
Series II		33.18	1.143	120.27	4.957	275.09	6.081
5.41	0.0064	36.60	1.393	123.47	5.006	285.08	6.132
6.38	0.0093	40.37	1.670	129.99	5.110	295.18	6.174
7.33	0.0140	44.61	1.974	138.62	5.229	298.82	6.181
8.34	0.0209	49.47	2.308	147.64	5.334	308.92	6.217
9.36	0.0302	55.05	2.674	157.35	5.435	318.95	6.248
10.34	0.0427	51.25	2.433	167.52	5.523	328.91	6.274
11.34	0.0576	56.11	2.740	177.63	5.598	338.80	6.294
12.44	0.0765	61.85	3.079	187.57	5.665	347.16	6.321
13.63	0.1018	67.67	3.381	197.10	5.721		
14.93	0.1356	73.54	3.647				
NiTe _{1.5} (formula weight Ni _{0.4} Te _{0.6} = 100.04g)							
Series I		Series II		42.83	1.915	171.91	5.514
6.33	0.0108	6.18	0.0104	47.10	2.197	181.61	5.586
7.29	0.0167	7.12	0.0153	51.87	2.494	191.29	5.652
8.34	0.0240	8.14	0.0233	57.19	2.803	200.90	5.708
9.28	0.0382	9.11	0.0355	63.15	3.125	206.43	5.735
10.24	0.0556	10.07	0.0504	69.84	3.440	216.26	5.785
11.20	0.0702	11.13	0.0690	76.60	3.723	226.08	5.828
12.27	0.0923	12.43	0.0963	73.70	3.603	235.89	5.871
13.44	0.1231	13.82	0.1343	78.72	3.807	245.75	5.912
14.72	0.1654	15.41	0.1892	85.34	4.053	255.65	5.949
16.22	0.2205	17.18	0.2605	92.54	4.272	265.60	5.986
17.97	0.2968	19.03	0.3479	100.77	4.488	275.68	6.021
19.95	0.3967	21.08	0.4564	109.14	4.676	285.61	6.055
22.06	0.5143	23.32	0.5880	117.37	4.836	295.57	6.084
24.30	0.6480	25.71	0.7394	126.07	4.990	305.64	6.114
26.75	0.8084	28.36	0.9164	134.78	5.121	315.65	6.139
29.50	0.9943	31.53	1.135	143.56	5.235	325.63	6.160
		35.12	1.386	152.66	5.337	335.65	6.188
		38.88	1.649	162.16	5.432	345.72	6.217
NiTe _{2.0} (formula weight Ni _{0.3333} Te _{0.6667} = 104.64g)							
Series I		Series III		39.95	1.792	190.65	5.589
5.86	0.0120	5.90	0.0123	44.06	2.054	200.27	5.648
6.79	0.0169	6.76	0.0164	48.63	2.336	209.80	5.700
7.56	0.0230	7.40	0.0216	53.72	2.623	219.36	5.749
8.53	0.0357	8.26	0.0313	59.32	2.918	212.33	5.711
9.48	0.0515	9.23	0.0475	65.36	3.212	221.75	5.756
		10.26	0.0648	71.74	3.481	231.53	5.808
Series II		11.38	0.0887	78.15	3.732	241.59	5.853
5.75	0.0113	12.66	0.1206	84.81	3.972	251.78	5.893
6.86	0.0172	14.11	0.1671	92.01	4.196	262.05	5.928
7.91	0.0270	15.76	0.2313	99.89	4.391	272.32	5.967
8.98	0.0434	17.68	0.3179	108.39	4.583	282.57	6.001
9.94	0.0601	19.89	0.4337	109.78	4.614	292.75	6.035
10.94	0.0800	22.17	0.5710	118.18	4.775	302.97	6.062
12.08	0.1055	24.51	0.7212	126.70	4.925	301.49	6.062
13.36	0.1421	24.37	0.7119	135.20	5.054	311.64	6.087
14.82	0.1929	26.99	0.8904	143.73	5.169	321.43	6.114
16.40	0.2581	29.82	1.091	152.58	5.267	330.87	6.140
18.15	0.3414	32.83	1.302	161.71	5.363	340.47	6.158
20.05	0.4461	36.19	1.538	171.18	5.444	348.23	6.177
22.14	0.5693			180.91	5.519		

i.e., 94.79 g of NiTe_{1.1}, 100.04 g NiTe_{1.5}, and 104.64 g NiTe_{2.0}. An analytically determined "curvature" correction for the finite temperature increments employed has been added to each observed value of $\Delta H/\Delta T$.

Because of the low pressure in the calorimeter, the values thus corrected to dH/dT are equal to C_p^0 or C_{int}^0 within the limits of the experimental error.

The heat capacity *versus* temperature curve (Fig. 1)

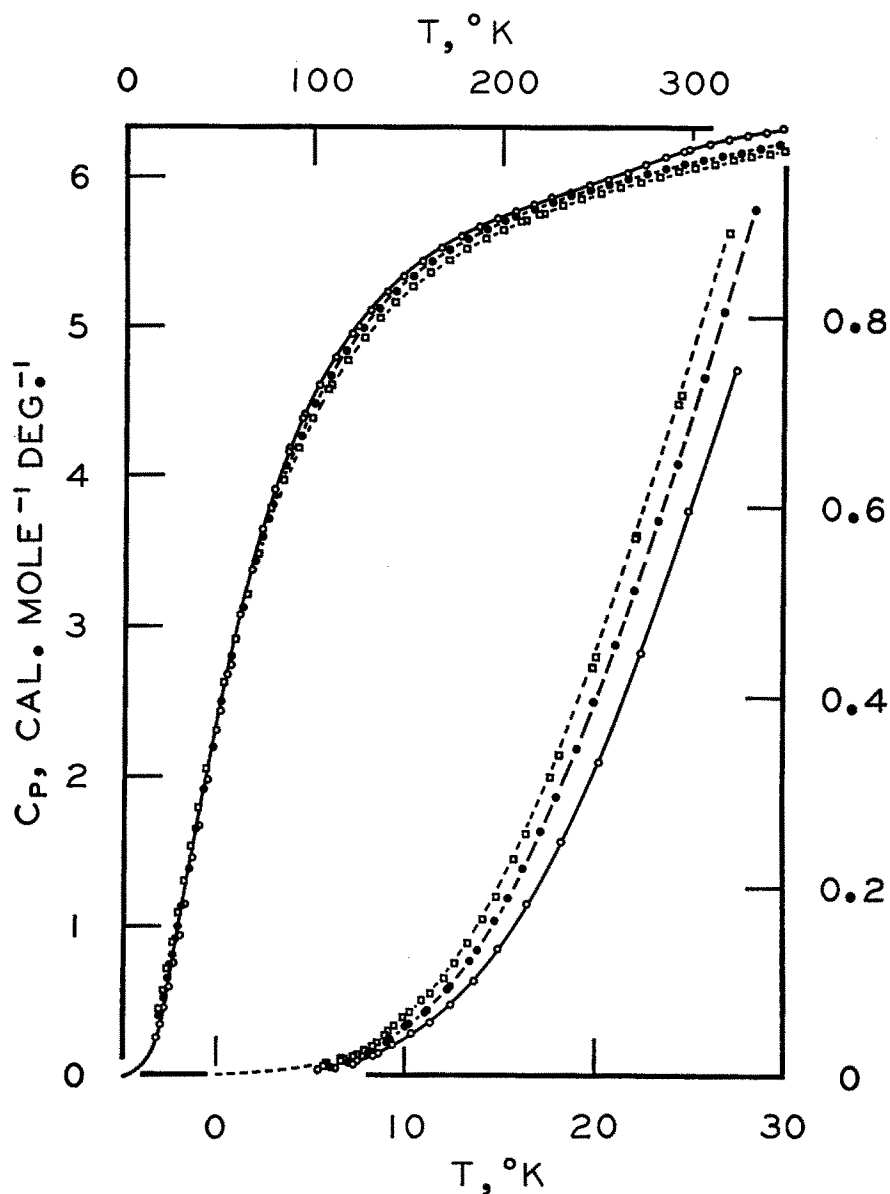


FIG. 1. The experimental "molal" heat capacities of the δ -phase nickel tellurides. \circ represents $\text{Ni}_{0.4762}\text{Te}_{0.5238}$; \bullet , $\text{Ni}_{0.4}\text{Te}_{0.6}$; and \square , $\text{Ni}_{0.3333}\text{Te}_{0.6667}$.

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 $0.001 \text{ cal mole}^{-1} \text{ deg}^{-1}$; the deviations were not normally distributed and in a few cases were close to $0.01 \text{ cal mole}^{-1} \text{ deg}^{-1}$. 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 , $S^0 - S_0^0$, and $(H^0 - H_0^0)/T$ 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 $\pm 0.01 \text{ cal mole}^{-1} \text{ deg}^{-1}$, 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 $\text{NiTe}_{1.1}$ which occurs near 270°K . This amounts to about 0.01 cal

TABLE II. Thermodynamic properties of nickel tellurides (in cal/mole deg).

T, °K	NiTe _{1.1} (formula weight Ni _{0.4762} Te _{0.6238} = 94.79g)			NiTe _{1.5} (formula weight Ni _{0.4} Te _{0.6} = 100.04g)			NiTe _{2.0} (formula weight Ni _{0.3333} Te _{0.6667} = 104.64g)		
	C _p ⁰	S ⁰ - S ₀ ⁰	(H ⁰ - H ₀ ⁰)/T	C _p ⁰	S ⁰ - S ₀ ⁰	(H ⁰ - H ₀ ⁰)/T	C _p ⁰	S ⁰ - S ₀ ⁰	(H ⁰ - H ₀ ⁰)/T
10	0.038	0.013	0.010	0.049	0.016	0.012	0.061	0.020	0.015
15	0.138	0.044	0.033	0.175	0.056	0.043	0.200	0.068	0.051
20	0.327	0.108	0.081	0.400	0.135	0.102	0.442	0.156	0.116
25	0.594	0.208	0.156	0.692	0.255	0.190	0.754	0.287	0.212
30	0.918	0.345	0.256	1.029	0.411	0.301	1.103	0.455	0.331
35	1.276	0.513	0.376	1.380	0.596	0.430	1.455	0.652	0.466
40	1.643	0.707	0.511	1.726	0.803	0.571	1.795	0.869	0.612
45	2.001	0.921	0.657	2.060	1.025	0.718	2.114	1.099	0.761
50	2.347	1.150	0.809	2.379	1.259	0.868	2.415	1.337	0.912
60	2.974	1.635	1.118	2.961	1.745	1.170	2.953	1.826	1.208
70	3.490	2.134	1.422	3.447	2.240	1.461	3.412	2.317	1.491
80	3.917	2.628	1.708	3.858	2.727	1.736	3.799	2.799	1.756
90	4.266	3.111	1.973	4.198	3.202	1.991	4.133	3.266	2.002
100	4.540	3.575	2.217	4.469	3.659	2.226	4.400	3.716	2.229
110	4.764	4.018	2.438	4.694	4.096	2.440	4.617	4.146	2.436
120	4.950	4.441	2.640	4.885	4.512	2.636	4.809	4.556	2.626
130	5.110	4.843	2.824	5.052	4.910	2.816	4.978	4.947	2.801
140	5.246	5.227	2.992	5.191	5.290	2.980	5.120	5.322	2.961
150	5.360	5.593	3.146	5.309	5.652	3.132	5.243	5.679	3.109
160	5.459	5.942	3.288	5.411	5.998	3.271	5.347	6.021	3.246
170	5.543	6.276	3.418	5.498	6.329	3.400	5.436	6.348	3.372
180	5.615	6.595	3.538	5.575	6.645	3.518	5.514	6.660	3.489
190	5.680	6.900	3.649	5.643	6.949	3.628	5.584	6.960	3.597
200	5.737	7.193	3.752	5.703	7.240	3.731	5.646	7.248	3.698
210	5.788	7.474	3.848	5.755	7.519	3.826	5.701	7.525	3.792
220	5.834	7.744	3.937	5.802	7.788	3.915	5.752	7.791	3.880
230	5.878	8.005	4.020	5.846	8.047	3.998	5.801	8.048	3.963
240	5.919	8.256	4.099	5.888	8.297	4.076	5.846	8.296	4.040
250	5.960	8.498	4.172	5.928	8.538	4.149	5.886	8.535	4.113
260	6.002	8.733	4.242	5.966	8.771	4.218	5.924	8.767	4.182
270	6.052	8.960	4.308	6.002	8.997	4.283	5.959	8.991	4.247
280	6.106	9.181	4.371	6.036	9.216	4.345	5.992	9.208	4.309
290	6.153	9.396	4.432	6.067	9.428	4.404	6.024	9.420	4.368
300	6.191	9.606	4.490	6.096	9.634	4.460	6.054	9.624	4.423
350	6.327	10.571	4.743	6.223	10.584	4.703	6.183	10.567	4.666
273.15	6.069	9.030	4.328	6.013	9.066	4.303	5.970	9.060	4.267
298.15	6.184	9.567	4.479	6.091	9.597	4.450	6.049	9.586	4.413

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 assumption¹⁷ that the parti-

tion 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. On this basis, a substitutional solid solution differs from its constituents only configurationally and would be expected to have a heat capacity equal to the sum of those of the constituents. Alternatively, the Kopp-Neumann rule may be stated in the following form: ΔC_p , the increment in heat capacity accompanying formation of the solid solution, is zero. In spite of its lack of a substantial theoretical basis or experimental verification, this rule has been used widely in the treatment of alloys in the absence of reliable data on these substances. The results of this research concur with those of DeSorbo on the

¹⁷ See, for example, R. H. Fowler and E. A. Guggenheim,

Statistical Thermodynamics (Cambridge University Press, New York, 1939), p. 568.

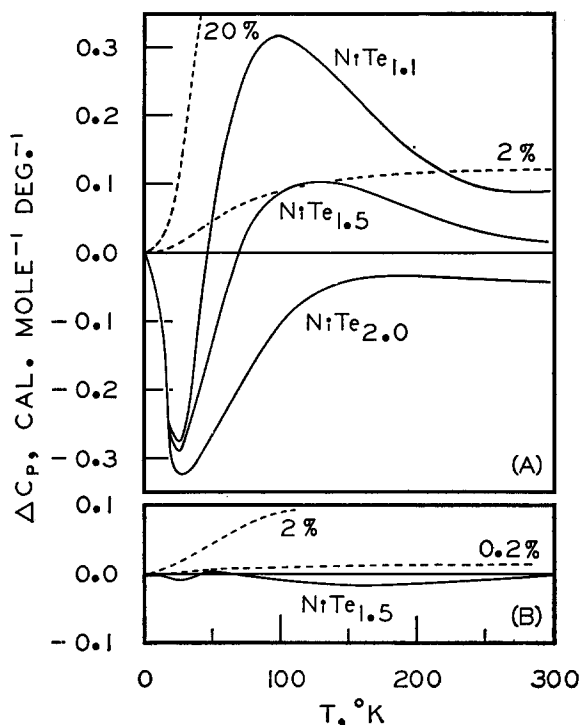


FIG. 2. Increment of the heat capacity of formation of NiTe_x . (A) from the elements, (B) from terminal δ -phase compositions.

Au–Ni system¹⁸ and of Coffey *et al.* on the Mg–Cd system¹⁹ 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 $\text{NiTe}_{1.5}$, for example, by the following expression:

$$\Delta C_p = C_{p, \text{Ni}_{0.4}\text{Te}_{0.6}} - (0.4C_{p, \text{Ni}} + 0.6C_{p, \text{Te}}).$$

The heat capacity of tellurium is taken from a smooth curve plotted through the combined data of Anderson²⁰ and of Slansky and Coulter.²¹ The heat capacity of nickel is taken from Busey and Giauque²² corrected by subtraction of the electronic contribution taken from the measurements of Rayne and Kemp²³ and assumed to be proportional to the absolute temperature. Other corrections (cf. Stoner²⁴) are negligible. From the C_p values of the three compositions calculated by this

¹⁸ W. DeSorbo, *Acta Met.* **3**, 227 (1955).

¹⁹ Coffey, Craig, Krier, and Wallace, *J. Am. Chem. Soc.* **76**, 241 (1954).

²⁰ C. T. Anderson, *J. Am. Chem. Soc.* **59**, 1036 (1937).

²¹ C. M. Slansky and L. V. Coulter, *J. Am. Chem. Soc.* **61**, 564 (1939).

²² R. H. Busey and W. F. Giauque, *J. Am. Chem. Soc.* **74**, 3157 (1952).

²³ J. A. Rayne and W. R. G. Kemp, *Phil. Mag.* (8) **1**, 918 (1956).

²⁴ E. C. Stoner, *Phil. Mag.* **22**, 81 (1936).

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 $\text{NiTe}_{1.5}$ from compositions $\text{NiTe}_{1.1}$ and $\text{NiTe}_{2.0}$, all within the solid solution region, are evaluated by the expression,

$$\Delta C_p' = C_{p, \text{Ni}_{0.4}\text{Te}_{0.6}} - (0.4667C_{p, \text{Ni}_{0.4762}\text{Te}_{0.5238}} + 0.5333C_{p, \text{Ni}_{0.3333}\text{Te}_{0.6667}})$$

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 $\text{NiTe}_{1.1}$ has been eliminated for this comparison. Percentage deviation curves based on the experimental heat capacity of $\text{NiTe}_{1.5}$ have been provided in Fig. 2 for convenience.

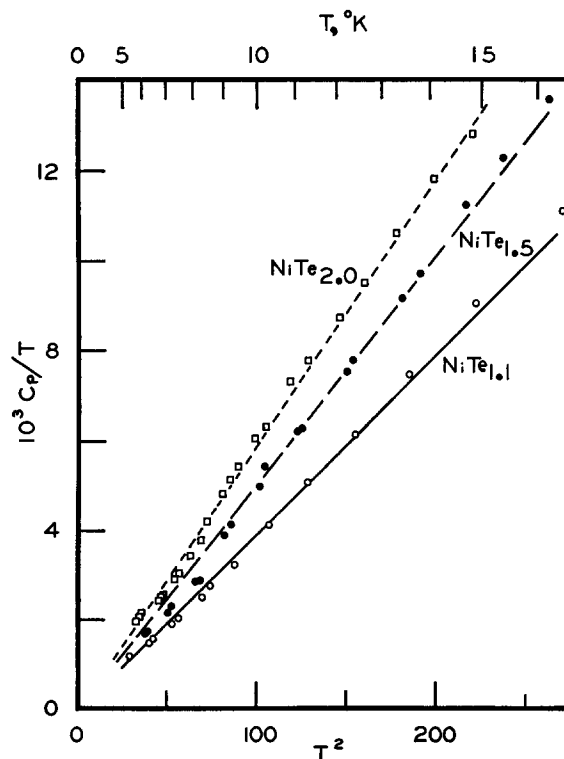


FIG. 3. C_p/T versus T^2 for NiTe_x .

The excellence of the agreement with this application of the Kopp-Neumann rule suggests that within at least the δ 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 ($S_{298.15}^0 - S_{0}^0$) for $\text{NiTe}_{1.5}$ interpolated from the terminal δ 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 $\text{NiTe}_{2.0}$ which has a lamellar structure, a platy crystalline habit, and prominent basal cleavage. Phonon scattering by vacancies in the NiTe_x 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 investigation²⁵ of the heat capacity of cadmium iodide (which differs only slightly from the cadmium hydroxide structure characteristic of $\text{NiTe}_{2.0}$) indicated a heat capacity proportional only to $T^{1.4}$ 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 relation²⁶: $C_p - C_v = 0.0214C_p^2(T/T_m)$, 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 θ 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

²⁵ Dworkin, Sasmore, and Van Artsdalen, J. Am. Chem. Soc. 77, 1304 (1955).

²⁶ W. Nernst and F. Lindemann, Z. Electrochem. 17, 817 (1911).

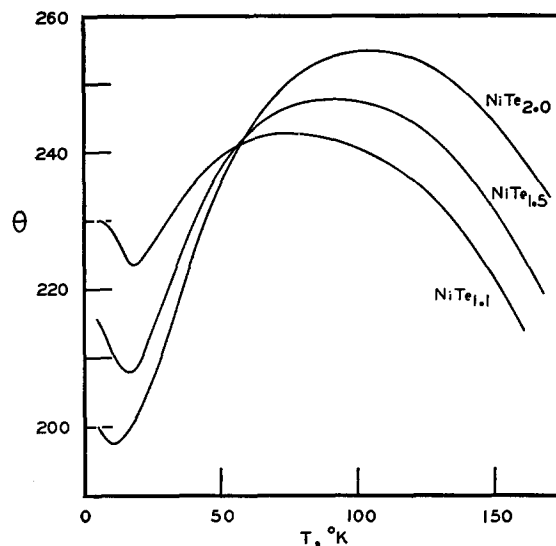


FIG. 4. Debye characteristic temperatures for NiTe_x .

not uncommon in alloys.¹⁸ 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 conductivity⁶ 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 noted⁷ to give "an alloyic character" to these compositions; yet the heat of formation of the stoichiometric compound NiTe from the elements²⁷ is rather higher (-9 kcal mole⁻¹) than that of typical alloys.

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²⁷ "Selected values of chemical thermodynamic properties," Natl. Bur. Standards Circular No. 500, Washington, 1952.