

## Thermodynamic Properties of Vanadium–Tellurium Alloys\*

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Tellurium vapor pressures of vanadium–tellurium alloys were determined in the range of the NiAs-derivative structures between 765 and 1365 K and between 54 and 66.7 at.% Te by an isopiestic method. The partial molar thermodynamic quantities of tellurium were derived; they indicate the appearance of a miscibility gap below about 825 K with a critical point around 64.7 at.% Te. The solidus line was estimated between 773 and 1273 K from the tellurium activities and the experimentally determined liquidus line; good agreement was found between the calculated values and those obtained from differential thermal analysis.

### Introduction

A number of X-ray studies of the vanadium–tellurium system (1–6) revealed—besides monoclinic  $V_5Te_4$ —a series of phases between about 52 and 66.7 at.% Te with crystal structures derived from the NiAs-type. Although no complete phase diagram has been established up to now (except for the tentative diagram of Elliott (7)), and many of the phase relationships are still unclear a general view of this particular part of the system can be derived from the results of Haraldsen and co-workers (2, 4). At 1273 K the undistorted NiAs-structure ( $\gamma_1$ ) was found only in a narrow composition range between about 52.5 and 54.5 at.% Te, followed by a monoclinic phase  $\gamma_2$  extending to about 62.3 at.% Te. In samples quenched from 1023 K the hexagonal  $\gamma_1$ -phase had disappeared and  $\gamma_2$  was found between about 55.6 and 63 at.% Te; at compositions close to 64 at.% Te a hexagonal

phase  $\gamma_3$  with the  $Cd(OH)_2$ -type structure was detected followed by another monoclinic phase  $\gamma_4$  up to about 65 at.% Te. However, no decision was possible whether these phases are separated by narrow two-phase fields or by second-order transitions. Røst *et al.* (4) discovered that the X-ray patterns of samples with the composition  $V_2Te_3$  were different if slowly cooled or quenched from 1023 K, resp., and suggested the existence of an additional monoclinic phase  $V_2Te_3$  at lower temperatures. Between somewhat less than 60 and 64.3 at.% Te slowly cooled samples were heterogeneous containing  $V_2Te_3$  and  $\gamma_4$ ; the tellurium-rich boundary of  $\gamma_4$  at room temperature was given as close to 66 at.% Te. Brunie and Chevreton (5) investigated the crystal structure of samples with 61.54 at.% Te and concluded that the  $V_2Te_3$  of (4) was rather a  $V_5Te_8$ -phase (isotypic with  $V_5Se_8$  and  $V_5S_8$ , space group  $F2/m - C_{2h}^3$ ) transforming into  $\gamma_2$  (space group  $I2/m - C_{2h}^3$ ) at elevated temperatures.

Up to date no thermodynamic measure-

\* Dedicated to Professor M. J. Sienko.

ments have been reported in the literature for vanadium-tellurium alloys. Therefore it was decided to extend the investigation of transition metal-chalcogen systems with NiAs-derivative structures (8-15) by a study of the thermodynamic properties of this particular system using a well-established isopiestic technique. Furthermore it was hoped to gain additional information on the phase relationships supplementing a separate investigation of the vanadium-tellurium phase diagram (16).

### Experimental Method

The experimental details of the isopiestic method employed have been described previously (8, 12). Since Grønvold *et al.* (2) had reported that samples with more than 45.5 at.% V had attacked quartz, little alumina crucibles (10 mm o.d., 15 mm high; Degussit AL 23, Degussa, FRG) were used as sample containers. They were put into the usual quartz crucibles which had been ground in such a way that each crucible served as a lid for the one below.

Starting materials for all experiments were vanadium foil (0.125 mm) with a purity better than 99.8% (Goodfellow Metals, England) and tellurium lumps with a purity of 99.999% (Alfa-Ventron, Mass.). The metallic impurities of the vanadium were specified as 300 ppm Si, 70 ppm Fe, 15 ppm Cr, 2 ppm Al, 1 ppm each Ag and Mn, and less than 1 ppm each Ca, Cu, and Mg. No data were furnished concerning the oxygen content.

The first experimental run (No. 1) where pure vanadium was equilibrated with tellurium vapor showed that the time required to reach thermodynamic equilibrium was extremely long (more than 5 weeks). Therefore master alloys with the approximate composition  $V_2Te_3$  were used in powder form as starting material in all following runs. The vanadium foil was cut into small strips, degreased by acetone, and dried.

Stoichiometric amounts of vanadium and finely powdered tellurium (total weight between 4 and 7 g) were filled into an alumina container inside a quartz tube which was sealed under vacuum (about  $10^{-1}$  Pa) after flushing several times with purified argon. The mixture was heated at 670 K for about 2 days, the temperature was then raised slowly within 4 days to 1300 K and kept there for another 2 days. After cooling slowly down to room temperature (within about 5 days), the alloy was comminuted to a very fine powder and stored in an evacuated desiccator over silica gel.

The alumina crucibles were cleaned with aqua regia, whereas all quartz parts were treated with an acid mixture (5% HF, 30%  $HNO_3$ , rest dist.  $H_2O$ ); they were rinsed with distilled water and dried. The assembled isopiestic apparatus including the alumina crucibles was degassed by heating at 1200 K and  $10^{-1}$  Pa for several hours.

Between 80 and 150 mg of the master alloy were weighed into each alumina crucible on a semimicrobalance to within  $\pm 0.05$  mg. Normally up to 18 samples were equilibrated in each run. The temperature of the tellurium reservoir and of each sample was determined by raising a Pt-Pt10%Rh thermocouple; the temperature gradient in the equilibration tube was checked several times during each experiment. After equilibration which lasted between 14 and 56 days depending on the reservoir temperature, the experiment was terminated by quenching the reaction tube in water. The composition of the samples was calculated from their weight gain or loss which was attributed to gain or loss of tellurium.

### Results

A total of nine successful experiments with reservoir temperatures between 719 and 953 K and sample temperatures between 765 and 1364 K were evaluated. The results and the experimental conditions are

listed in Table I. It is estimated that the uncertainty of the compositions is at most  $\pm 0.15$  at.% and that of the temperatures approx  $\pm 1$  to 2 K. The equilibrium curves (i.e., sample temperature vs sample composition), which are actually isobars, are shown in Fig. 1 together with some information on the phase diagram. The hatched stripes indicate the stability range of the individual phases according to Grønvold *et al.* (2) whereas the solidus line was derived from differential thermal analysis (DTA) measurements (16) and thermodynamic considerations (see below). Since no discontinuities could be detected in these equilibrium curves which would hint at the existence of two-phase fields between  $\gamma_2$  and  $\gamma_3$  as well as  $\gamma_3$  and  $\gamma_4$ , it must be concluded

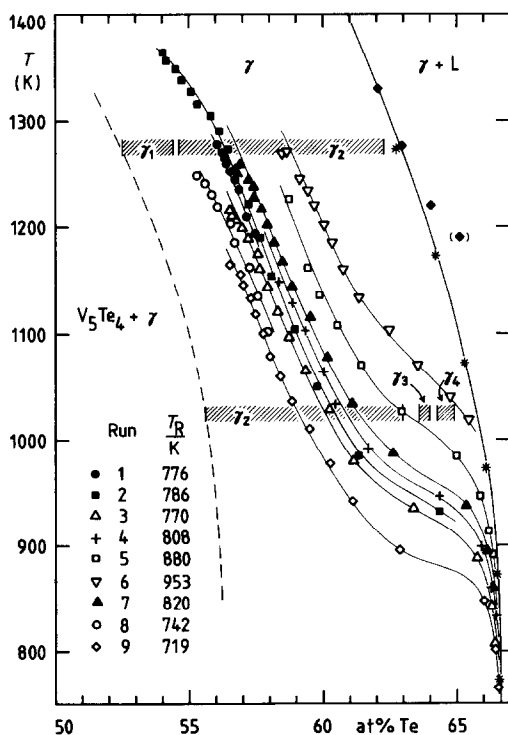


FIG. 1. Sample temperature versus sample composition; the hatched stripes indicate the extension of the different phases at the corresponding temperatures according to (2);  $\blacklozenge$  = phase boundary from DTA; \* = phase boundary from thermodynamics.

TABLE I  
EXPERIMENTAL ISOPIESTIC RESULTS IN THE  
VANADIUM-TELLURIUM SYSTEM:  
STANDARD STATE:  $\text{Te}_{(l)}$

No.	at.% Te	$T_S$ (K)	$\ln a_{\text{Te}}$ ( $T_S$ )	$\Delta \bar{H}_{\text{Te}}$ (kJ g-atom <sup>-1</sup> )	$\ln a_{\text{Te}}$ (1073 K)
Run 1 $T_R = 776$ K 39 days					
1	56.06	1277	-3.47	-61.7	-4.57
2	56.24	1270	-3.44	-61.2	-4.50
3	56.36	1264	-3.41	-60.9	-4.45
4	56.43	1258	-3.39	-60.7	-4.39
5	56.52	1252	-3.36	-60.4	-4.33
6	56.74	1244	-3.33	-59.8	-4.25
7	56.88	1235	-3.29	-59.4	-4.16
8	57.13	1210	-3.17	-58.6	-3.92
9	57.46	1194	-3.10	-57.4	-3.75
Run 2 $T_R = 786$ K 56 days					
1	54.08	1364	-3.70	(-65.8)	-5.27
2	54.15	1356	-3.67	(-65.5)	-5.20
3	54.52	1348	-3.64	(-64.8)	-5.12
4	54.76	1338	-3.60	(-64.4)	-5.03
5	55.10	1327	-3.56	(-63.8)	-4.93
6	55.32	1315	-3.51	(-63.3)	-4.82
7	55.83	1304	-3.47	(-62.2)	-4.70
8	56.14	1290	-3.41	-61.5	-4.57
9	56.49	1272	-3.34	-60.5	-4.40
10	56.80	1249	-3.24	-59.6	-4.18
11	57.22	1222	-3.11	-58.3	-3.91
12	57.69	1190	-2.96	-56.6	-3.59
13	58.09	1154	-2.78	-55.0	-3.22
14	58.96	1104	-2.51	-51.2	-2.68
15	59.79	1051	-2.20	-47.3	-2.09
16	61.35	985	-1.76	-43.4	-1.33
17	64.37	932	-1.37	-48.8	-0.54
Run 3 $T_R = 770$ K 37 days					
1	56.51	1216	-3.27	-60.5	-4.07
2	56.60	1211	-3.25	-60.2	-4.01
3	56.80	1206	-3.22	-59.6	-3.96
4	56.99	1199	-3.19	-59.1	-3.88
5	57.21	1189	-3.14	-58.3	-3.78
6	57.59	1175	-3.07	-57.0	-3.63
7	57.65	1161	-3.00	-56.7	-3.48
8	57.92	1144	-2.91	-55.7	-3.30
9	58.31	1121	-2.79	-54.1	-3.05
10	58.74	1097	-2.66	-52.3	-2.78
11	59.36	1066	-2.47	-49.4	-2.44
12	60.22	1029	-2.24	-45.9	-2.02
13	61.16	980	-1.91	-43.7	-1.44
14	63.39	935	-1.57	-44.1	-0.84
15	65.77	888	-1.18	-64.6	+0.32
16	66.31	843	-0.77	(-70.3)	+1.38
17	66.43	808	-0.42	(-71.4)	+2.21

TABLE I—Continued

No.	at.% Te	$T_S$ (K)	$\ln a_{Te}$ ( $T_S$ )	$\Delta \bar{H}_{Te}$ (kJ g-atom <sup>-1</sup> )	$\ln a_{Te}$ (1073 K)
Run 4 $T_R = 808$ K 29 days					
1	58.35	1149	-2.52	-54.0	-2.92
2	58.87	1129	-2.41	-51.7	-2.70
3	59.36	1103	-2.27	-49.4	-2.42
4	60.03	1065	-2.05	-46.5	-2.01
5	60.48	1034	-1.86	-45.2	-1.67
6	61.70	992	-1.58	-42.9	-1.18
7	64.33	947	-1.25	-48.5	-0.52
8	65.91	899	-0.86	-66.3	+0.58
9	66.29	861	-0.52	(-70.1)	+1.41
10	66.47	834	-0.26	(-71.6)	+2.04
Run 5 $T_R = 880$ K 17 days					
1	58.73	1227	-2.21	-52.3	-2.94
2	59.43	1162	-1.89	-48.9	-2.31
3	59.88	1137	-1.76	-47.0	-2.06
4	60.56	1108	-1.60	-45.0	-1.76
5	61.42	1071	-1.39	-43.3	-1.38
6	62.94	1027	-1.12	-43.2	-0.90
7	65.00	985	-0.83	-55.4	-0.28
8	65.89	947	-0.55	-66.1	+0.43
9	66.21	913	-0.28	(-69.4)	+1.08
10	66.35	892	-0.10	(-70.6)	+1.50
Run 6 $T_R = 953$ K 14 days					
1	58.66	1270	-1.80	-52.7	-2.71
2	58.50	1269	-1.79	-53.3	-2.72
3	59.16	1245	-1.69	-50.3	-2.47
4	59.44	1234	-1.64	-48.9	-2.35
5	59.69	1220	-1.58	-47.7	-2.22
6	60.05	1202	-1.49	-46.4	-2.05
7	60.33	1185	-1.41	-45.6	-1.89
8	60.74	1161	-1.29	-44.6	-1.67
9	61.33	1133	-1.14	-43.4	-1.40
10	62.50	1103	-0.98	-42.8	-1.11
11	63.52	1070	-0.79	-44.4	-0.77
12	64.73	1041	-0.61	-52.1	-0.43
13	65.43	1019	-0.47	-60.7	-0.11
Run 7 $T_R = 820$ K 27 days					
1	56.91	1259	-2.92	-59.3	-3.90
2	56.75	1254	-2.90	-59.8	-3.86
3	56.81	1250	-2.88	-59.6	-3.82
4	57.25	1245	-2.86	-58.2	-3.76
5	57.44	1238	-2.83	-57.5	-3.68
6	57.42	1228	-2.78	-57.6	-3.60
7	57.71	1217	-2.73	-56.5	-3.48
8	57.93	1203	-2.66	-55.6	-3.34
9	58.19	1186	-2.58	-54.6	-3.17
10	58.52	1168	-2.49	-53.2	-2.98
11	58.87	1144	-2.37	-51.7	-2.73

TABLE I—Continued

No.	at.% Te	$T_S$ (K)	$\ln a_{Te}$ ( $T_S$ )	$\Delta \bar{H}_{Te}$ (kJ g-atom <sup>-1</sup> )	$\ln a_{Te}$ (1073 K)
12	59.54	1116	-2.22	-48.4	-2.43
13	60.20	1078	-2.00	-46.0	-2.03
14	61.10	1036	-1.74	-43.8	-1.57
15	62.62	988	-1.42	-42.9	-1.01
16	65.38	938	-1.05	-59.9	-0.09
17	66.15	895	-0.70	(-68.8)	+0.83
18	66.35	861	-0.40	(-70.6)	+1.55
Run 8 $T_R = 742$ K 28 days					
1	55.29	1248	-3.75	(-63.4)	-4.75
2	55.60	1241	-3.72	(-62.7)	-4.67
3	55.84	1230	-3.67	(-62.2)	-4.56
4	56.06	1219	-3.62	(-61.7)	-4.45
5	56.55	1203	-3.54	-60.3	-4.27
6	56.70	1185	-3.46	-60.0	-4.09
7	57.26	1126	-3.34	-58.2	-3.84
8	57.59	1135	-3.20	-57.0	-3.55
9	57.93	1102	-3.02	-55.6	-3.19
Run 9 $T_R = 719$ K 29 days					
1	56.57	1165	-3.65	-60.3	-4.19
2	56.94	1156	-3.61	-59.2	-4.08
3	57.08	1146	-3.56	-58.8	-3.98
4	57.32	1133	-3.49	-57.9	-3.83
5	57.51	1118	-3.41	-57.1	-3.66
6	57.79	1100	-3.31	-56.2	-3.46
7	58.06	1079	-3.18	-55.2	-3.22
8	58.43	1060	-3.07	-53.6	-3.00
9	58.87	1037	-2.93	-51.7	-2.73
10	59.55	1011	-2.76	-48.4	-2.42
11	60.30	978	-2.53	-45.7	-2.03
12	61.12	942	-2.26	-43.7	-1.58
13	62.89	896	-1.89	-43.1	-0.93
14	66.01	848	-1.45	(-67.3)	+0.55
15	66.46	802	-0.99	(-71.5)	+1.72
16	66.58	765	-0.57	(-72.4)	+2.69

that they are very narrow or that the corresponding phase transformations are of second order.

In an isopiestic experiment the total pressure in the closed system is determined by the vapor pressure of the pure volatile component which is kept at the lowest temperature. According to the critical compilation by Mills (17) only  $Te_2$  is present in the gas phase in significant amounts under the given experimental conditions. The surprisingly high concentration of  $Te_5$  in tellurium

vapor reported by Hoareau *et al.* (18) has not been confirmed by Neubert (19) in his mass-spectrometric study of gaseous tellurium. Neglecting therefore all other species but  $\text{Te}_2$  and taking pure liquid Te as the reference state, the activity of Te can readily be computed (9) according to

$$a_{\text{Te}, T_S} = \left( \frac{p_{\text{Te}_2, T_S}}{p_{\text{Te}_2, T_S}^0} \right)^{1/2} = \left( \frac{p_{\text{Te}_2, T_R}^0}{p_{\text{Te}_2, T_S}^0} \right)^{1/2}, \quad (1)$$

where  $p_{\text{Te}_2, T_S}$  is the partial pressure of tellurium above the sample at the sample temperature  $T_S$  and  $p_{\text{Te}_2, T_S}^0$  and  $p_{\text{Te}_2, T_R}^0$  are the vapor pressures of pure tellurium at the sample temperature  $T_S$  and the reservoir temperature  $T_R$ , respectively. The vapor pressure of liquid tellurium was calculated from Brooks' equation (20):

$$\ln p = - \frac{13,723.9}{T} + 22.3922, \quad (2)$$

(with  $p$  in Pa and  $T$  in K) which is in excellent agreement with the more recent results of a number of different investigators (cf. Ref. (17)) including those of Chernozubov *et al.* (21).

Partial molar enthalpies of mixing were

computed according to the method used by Ettenberg *et al.* (8) in the nickel-tellurium system. It is based on a form of the Clausius-Clapeyron equation originally derived by Birchenall and Cheng (22):

$$\frac{1}{T_R} = \frac{\Delta H}{\Delta H_v^0} \frac{1}{T_S} + C, \quad (3)$$

where  $C$  is an integration constant,  $\Delta H_v^0$  the enthalpy of vaporization of 2 g-atoms of pure liquid tellurium, and  $\Delta H$  the enthalpy change corresponding to the transfer of tellurium from a sample to the vapor phase; as shown in Ref. (8) it is related to  $\bar{\Delta H}_{\text{Te}}$  according to the equation

$$\Delta H = \Delta H_v^0 - 2\bar{\Delta H}_{\text{Te}}. \quad (4)$$

In Fig. 2 reciprocal sample temperatures, interpolated at fixed compositions from Fig. 1, are plotted versus the reciprocal reservoir temperatures. As can be seen, data points of equal composition fall generally on straight lines which is additionally a good test for the internal consistency of the different experimental runs. From the corresponding slopes  $\bar{\Delta H}_{\text{Te}}$ -values were calcu-

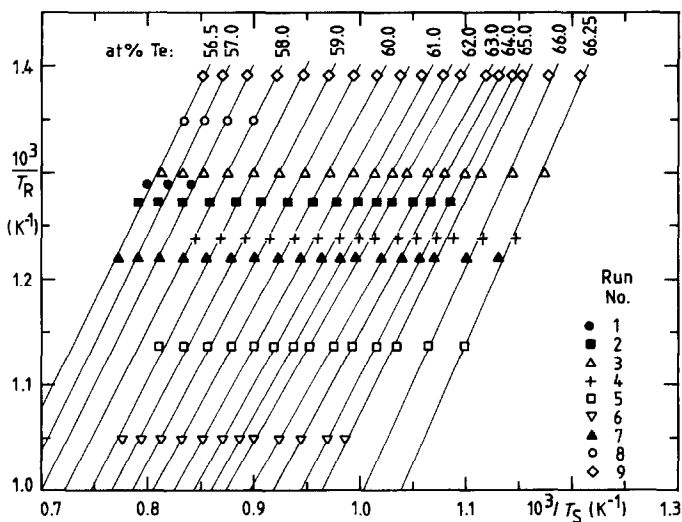


FIG. 2. Reciprocal reservoir temperature versus reciprocal sample temperature.

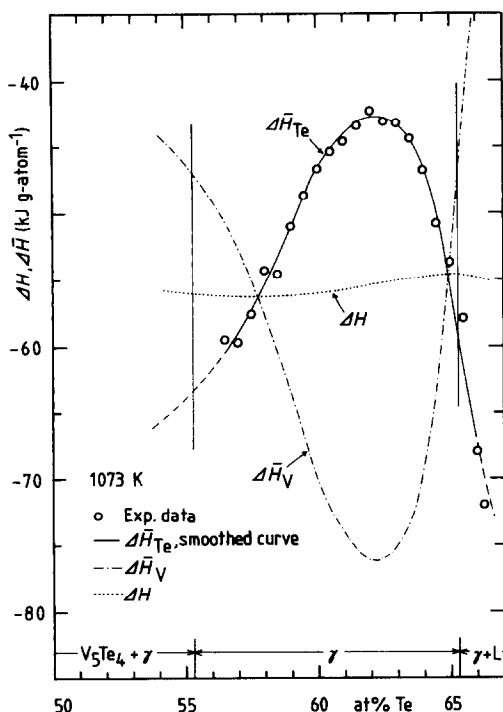


FIG. 3. Partial molar and integral enthalpies with experimental data points for tellurium; standard states:  $\text{V}_{(s)}$  and  $\text{Te}_{(l)}$ ; the extension of  $\gamma$  at 1073 K is indicated (where  $\gamma$  stands for the whole group of phases with NiAs-derivative structures).

lated according to Eqs. (3) and (4), using a value of  $\Delta H_{\text{V}}^0 = 114.1 \text{ kJ mole}^{-1}$  (20). They were computed in intervals of 0.5 at.% between 56.5 and 66 at.% Te with an additional value at 66.25 at.% Te (for the sake of clarity every other composition is left out between 62 and 65 at.% Te in Fig. 2). The experimental enthalpy values are presented in Fig. 3; the smoothed curve for  $\Delta \bar{H}_{\text{Te}}$  is shown as a dashed line below 56.5 at.% Te (because it had to be extrapolated) and above 66 at.% Te (where the uncertainty increases considerably because of the steepness of the equilibrium curves in Fig. 1); the corresponding values in Table I are set in parentheses.

Activities of tellurium were calculated for each sample at the corresponding sample temperature  $T_s$  with Eq. (1). They were

converted to a common temperature of 1073 K (being an average temperature for all samples) by means of  $\Delta \bar{H}_{\text{Te}}$ -values from the smoothed curve in Fig. 3 which are also listed together with the activities in Table I. The composition dependence of  $\ln a_{\text{Te}}$  at 1073 K is shown in Fig. 4. In addition, Table II contains values of the partial molar properties within the stability range of the NiAs-derivative structures at selected compositions.

The uncertainties in the partial molar properties were estimated by applying the laws of error propagation (23). Provided there are no systematic errors, the values of  $\ln a_{\text{Te}}$  at the sample temperatures should be accurate within  $\pm 0.03$  if temperatures are

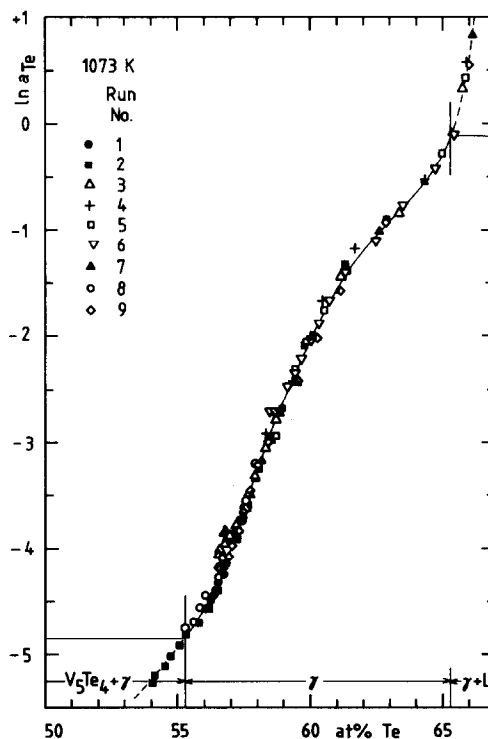


FIG. 4. Activities of tellurium at 1073 K; standard state:  $\text{Te}_{(l)}$ ; the extension of  $\gamma$  at 1073 K is indicated (where  $\gamma$  stands for the whole group of phases with NiAs-derivative structures). The values in the two-phase fields are hypothetical ones and are indicated by the dashed line.

TABLE II  
PARTIAL MOLAR PROPERTIES OF TELLURIUM  
(SMOOTHED VALUES) IN VANADIUM-TELLURIUM  
ALLOYS AT 1073 K; STANDARD STATE:  $\text{Te}_{(l)}$

at.% Te	$\ln a_{\text{Te}}$	$\Delta\bar{H}_{\text{Te}}$ (kJ g-atom <sup>-1</sup> )	$\Delta\bar{S}_{\text{Te}}$ (J g-atom <sup>-1</sup> K <sup>-1</sup> )
55.3 <sup>a</sup>	-4.85	(-63.3) <sup>b</sup>	(-18.7)
56.0	-4.59	(-61.8)	(-19.4)
57.0	-4.02	-59.0	-21.6
58.0	-3.27	-55.3	-24.3
59.0	-2.60	-51.0	-25.9
60.0	-2.06	-46.5	-26.2
61.0	-1.57	-44.0	-28.0
62.0	-1.21	-42.8	-29.8
63.0	-0.93	-43.3	-32.6
64.0	-0.66	-46.6	-37.9
65.0	-0.30	-55.4	-49.1
65.3 <sup>a</sup>	-0.12	-59.2	-54.2

<sup>a</sup> Limit of the stability range of the NiAs-derivative structures at 1073 K.

<sup>b</sup> Values in parentheses obtained by extrapolation.

accurate within  $\pm 2$  K; in a similar way the uncertainty in the partial molar enthalpies was estimated to be generally less than  $\pm 5$  kJ. With these values it turns out that the error in  $\ln a_{\text{Te}}$  at 1073 K may reach a maximum of about  $\pm 0.15$  for those compositions where the activities were determined at the low or high temperature limit of the experimental method. Thus the activity data between about 58 and 63 at.% Te which were obtained at temperatures close to 1073 K are expected to be the most accurate ones.

## Discussion

The most striking feature of the thermodynamic results in this system is the rather unusual and unexpected composition dependence of  $\Delta\bar{H}_{\text{Te}}$  (cf. Fig. 3). Actually, its shape implies a dent in the curve of the integral enthalpy in this composition range. Unfortunately, it is not possible to calculate accurate integral properties by a Gibbs-Duhem integration without any knowledge of the thermodynamics of the vanadium-rich

section of the system (including the  $\text{V}_5\text{Te}_4$ -phase). To obtain at least estimated values for the integral enthalpy in the range of the NiAs-derivative structures, it was attempted to calculate as a starting point one value for the enthalpy of formation using Miedema's empirical model (24, 25). Yet an additional problem arose from the fact that the necessary parameters for chalcogens are not included in the corresponding tables. Thus values for hypothetical metallic tellurium had to be estimated by extrapolation of the numbers in Table I of Ref. (25) for the preceding elements in the fifth row of the periodic system, i.e., In, Sn, and Sb. Employing Eq. (18) of Ref. (25) and using value of  $V_m^{2/3} \cong 6.7 \text{ cm}^2$ ,  $\Phi^* \cong 4.65 \text{ V}$ , and  $n_{\text{ws}}^{1/3} \cong 1.30 \text{ (g cm}^{-3}\text{)}^{1/3}$  for tellurium as well as the tabulated numbers for vanadium,  $\Delta H \cong -45 \text{ kJ g-atom}^{-1}$  was obtained for an alloy with 60 at.% Te; this corresponds to  $\Delta H \cong -56 \text{ kJ g-atom}^{-1}$  referred to  $\text{V}_{(s)}$  and  $\text{Te}_{(l)}$  as standard states. It is obvious that this can only be a very rough estimate; however, it allows to perform a Gibbs-Duhem integration yielding the composition dependence of  $\Delta\bar{H}_{\text{v}}$  and  $\Delta H$ , which are included in Fig. 3.

As indicated by the shape of the  $\Delta\bar{H}_{\text{Te}}$ -curve a weak dent exists in the curve for the integral enthalpy. The most probable explanation for it seems to be that it is connected with the appearance of a two-phase field at lower temperatures as reported by Haraldsen and co-workers (2, 4). In fact, if one computes values of  $\ln a_{\text{Te}}$  for decreasing temperatures below 1073 K the inflection point in the vicinity of 64 at.% Te (cf. Fig. 4) becomes more and more pronounced yielding finally a horizontal tangent at about 825 K. Since the exact phase relationships in this range are still unknown one could assume the appearance of a miscibility gap which would then have its critical point around 825 K and 64.7 at.% Te. Considering the increasing uncertainty in the  $\Delta\bar{H}_{\text{Te}}$ -values on approaching the tellu-

rium-rich end of the  $\gamma$ -phase (where  $\gamma$  stands for the whole group of phases with NiAs-related structures) this is in reasonable agreement with the results of Røst *et al.* (4) who located the two-phase field between about 60.0 and 64.3 at.% Te in slowly cooled samples.

In Fig. 4 it can be seen that  $\ln a_{\text{Te}}$  would become positive around 65.5 at.% Te which would be equivalent to an activity larger than one. This is taken as an indication that the tellurium-rich phase boundary is close to this composition at 1073 K. In order to compare the thermodynamic data with the results of preliminary DTA-measurements (16) it was attempted to calculate the solidus line in steps of 100 K between 773 and 1273 K. For this purpose the activity of tellurium at the corresponding composition of the liquidus (98.0, 95.0, 91.5, 88.5, 85.0, and 81.0 at.% Te at 773, 873, 973, 1073, 1173, and 1273 K, resp.) was approximated at each temperature by assuming Raoult's law to be valid for the liquid alloys. Since the activity has to be constant within a two-phase field the composition of the solidus could easily be found by comparison with the curve of  $\ln a_{\text{Te}}$  in the solid phase. The results are incorporated in Fig. 1 which demonstrates that there is generally good agreement with the results of the DTA-measurements.

In a number of previous publications (8-13, 15) a theoretical model was applied to describe the composition dependence of the partial molar thermodynamic properties of transition metal chalcogenides with the defected hexagonal NiAs-structure. The model assumes statistical distribution of the vacancies either in every or in every other transition metal layer. However, like in the chromium-tellurium system (14), it was not possible to evaluate the results of the present investigation in terms of this model since practically all experimental data points are in phases with monoclinically distorted crystal structures. This distortion

is probably caused by some degree of vacancy ordering, and this is clearly contradicting the basic assumptions of the model.

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