

## Thermodynamic Properties of Chromium—Tellurium Alloys

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Tellurium vapor pressures of chromium—tellurium alloys were determined in the range of NiAs-type structures between 800 and 1,300 K and between 55 and 62 at% Te by an isopiestic method. The partial molar quantities of tellurium were derived, and the results critically compared with data reported in the literature.

(*Keywords: Chalcogenides; Chromium—tellurium alloys; Tellurides; Thermodynamic properties; Transition metal tellurides*)

### *Thermodynamische Eigenschaften von Chrom—Tellur-Legierungen*

Die Tellurdampfdrücke von Chrom—Tellur-Legierungen wurden mit Hilfe einer isopiesticischen Methode im Bereich der Phasen mit NiAs-ähnlichen Strukturen zwischen 800 und 1300 K und zwischen 55 und 62 At% Te bestimmt. Die partiellen molaren Eigenschaften von Tellur wurden daraus abgeleitet, und die Resultate kritisch mit Literaturwerten verglichen.

### Introduction

In a series of investigations activities of selenium and tellurium, resp., were determined in the binary systems with the 3d-metals of the eighth group, i.e. iron, cobalt, and nickel<sup>1-6</sup>. Special attention was paid to the nonstoichiometric NiAs-type phases in these systems, and their thermodynamic properties were interpreted by a theoretical model. In the chromium—tellurium system a series of phases exist which exhibit crystal structures related to the NiAs-type<sup>7-12</sup>. Some thermodynamic measurements have been reported in literature: *Grønsvold* and *Westrum*<sup>13</sup> measured heat capacities of Cr<sub>5</sub>Te<sub>6</sub>, Cr<sub>3</sub>Te<sub>4</sub>, and Cr<sub>2</sub>Te<sub>3</sub> between 5 and 350 K, *Grønsvold*<sup>14</sup> measured heat capacities of Cr<sub>3</sub>Te<sub>4</sub> between 298 and 950 K, and *Goncharuk* and *Lukashenko*<sup>15, 16</sup> determined thermodynamic properties in the range between 52 and 100 at% Te by an emf-

method, however, without proper knowledge of the phase diagram<sup>12,17</sup>. It was the objective of the present study to determine the partial pressure of tellurium in alloys with chromium in the range of the NiAs-related structures by an isopiestic method to derive the partial thermodynamic properties of tellurium. Furthermore it was hoped to gain some additional information on the phase relationships in the chromium—tellurium system.

### Experimental Method

The starting materials for all experiments were chromium with a purity of 99.997% referred to metallic impurities containing 0.22-0.46% oxygen, 0.028-0.038% hydrogen and 0.0002% nitrogen (AVIQUIPO-Corp., U.S.A.) and tellurium with a purity of 99.999% (ASARCO, New York, U.S.A.). The experimental details of the isopiestic method employed have been described previously<sup>5,6</sup>. A preliminary isopiestic run equilibrating chromium powder with tellurium vapor showed that equilibrium had not been reached after more than six weeks. Therefore a master alloy with the approximate composition  $\text{Cr}_3\text{Te}_4$  was used in powder form as starting material in all experimental runs. Chromium was powdered and baked out in vacuum for two hours at 1,000 K and  $10^{-1}$  Pa to remove hydrogen. Stoichiometric amounts of this chromium powder and finely powdered tellurium (together about 60 g) were sealed in an evacuated quartz capsule, thoroughly mixed and heated at 670 K for five days. The temperature was then raised slowly within four days to 1,300 K and kept there for another five days. The alloy was then cooled to room temperature, the capsule was opened, and the chromium telluride was finely powdered, sealed again in a quartz capsule and homogenized at 670 K for four weeks. Between 150 and 250 mg of this  $\text{Cr}_3\text{Te}_4$  master alloy were weighed into each quartz crucible on a semi-microbalance to within  $\pm 0.05$  mg, and approx. 45 of these crucibles were used in each run. The temperature of the tellurium reservoir and of each sample was determined by raising and lowering a calibrated Pt/Pt-10% Rh thermocouple. The temperature gradient in the equilibration tube was checked several times during each experiment. After equilibration the tube was quenched, and the composition of the alloys was calculated from the weight gain or loss which was attributed to gain or loss of tellurium. Representative samples were checked for their composition by X-ray analysis.

### Results

A total of six successful experiments with reservoir temperatures between 756 and 900 K and sample temperatures between 800 and 1,300 K were evaluated. The equilibration times ranged between 23 and 58 days. In some cases samples at higher temperatures ( $> 1,100$  K) had a greenish appearance suggesting that oxidation had occurred to some extent during the experiment. However, careful X-ray investigation of the bulk samples showed no lines of chromium oxide on the powder films which proved that oxidation was restricted to a very thin surface layer and had only a negligible influence on the composition. On the other hand, the oxygen content of the pure chromium had to be

considered in calculating the sample compositions. The values given here were all computed with an average oxygen content of 0.34%; the weight of the chromium was reduced by this amount and it was assumed that the oxygen did not interfere with the reaction between chromium and tellurium. As an alternative, one could reasonably

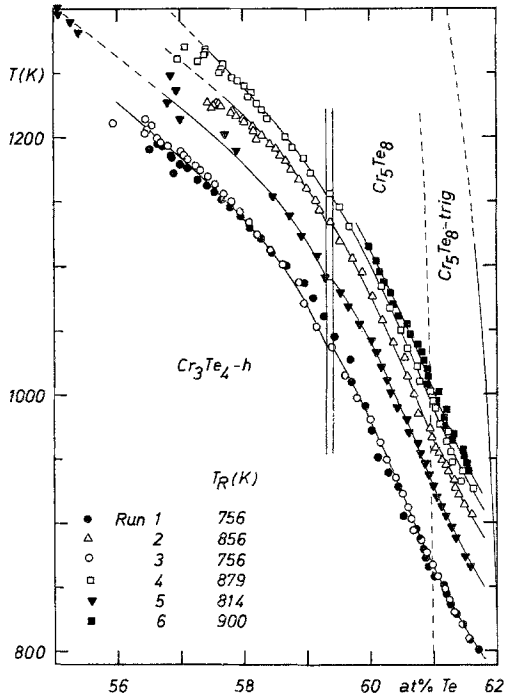


Fig. 1. Sample composition versus sample temperature

assume that all the oxygen is bound as  $\text{Cr}_2\text{O}_3$ , which would not further react with tellurium. With these considerations the given compositions would become richer in tellurium on the average by 0.18 at%.

The equilibrium curves (sample temperature vs. sample composition) are shown in Fig. 1\*. It is estimated that the uncertainty of the compositions is approx.  $\pm 0.25$  at% and that of the temperatures approx.  $\pm 1-2$  K. The reproducibility of the experimental results was

\* A Table in which the numerical data (results of the isopiestic experiments and the experimental conditions) are summarized may be obtained upon request.

confirmed by running two different experiments (run 1 and 3) with the same reservoir temperature. As can be seen from Fig. 1, the equilibrium curves are practically identical.

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

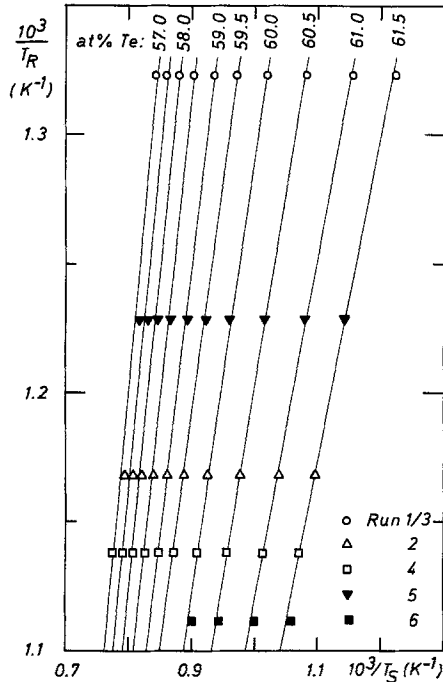


Fig. 2. Reciprocal reservoir temperature versus reciprocal sample temperature

by *Mills*<sup>18</sup> only  $\text{Te}_2$  is present in the gas phase in significant amounts under the conditions of our experiments although a more recent study by *Hoareau et al.*<sup>19</sup> suggests a somewhat higher amount of  $\text{Te}_3$ . Neglecting all other species besides  $\text{Te}_2$ , the activity of Te can be readily computed<sup>2</sup> according to

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

where  $p_{\text{Te}_2, T_S}$  is the partial pressure of tellurium above the sample at the sample temperature  $T_S$  and  $p_{\text{Te}_2, T_S}^\circ$  and  $p_{\text{Te}_2, T_R}^\circ$  are the vapor pressures of pure tellurium at the sample temperature  $T_S$  and the reservoir

temperature  $T_R$ , resp. The standard states chosen are  $\text{Cr}_{(s)}$  and  $\text{Te}_{(l)}$ . The vapor pressure of liquid tellurium was calculated from *Brooks'* equation<sup>20</sup>:

$$\log p = -5960.2/T + 9.7248, \quad (2)$$

with  $p$  in Pa and  $T$  in K. This equation is in excellent agreement with the more recent results of a number of different investigators (cf. Ref.<sup>18</sup>) including those of *Chernozubov et al.*<sup>21</sup>.

Table 1. *Partial molar properties of tellurium in chromium—tellurium alloys at 1,073 K: smoothed values at selected compositions; standard states:  $\text{Cr}_{(s)}$  and  $\text{Te}_{(l)}$ . (Values in parentheses are obtained by extrapolation)*

at% Te	Phase	$\ln a_{\text{Te}}$	$\Delta \bar{G}_{\text{Te}}$	$\Delta \bar{H}_{\text{Te}}$	$\Delta \bar{S}_{\text{Te}}$
			kJ g-atom <sup>-1</sup>	kJ g-atom <sup>-1</sup>	J K <sup>-1</sup> g-atom <sup>-1</sup>
55.0	(a)	(-5.20)	(-46.4)	(-105.0)	(-54.6)
56.0	(a)	(-4.78)	(-42.6)	(-99.5)	(-53.0)
57.0	(a)	-4.25	-37.9	-92.5	-50.9
58.0	(a)	-3.52	-31.4	-82.0	-47.2
59.0	(a)	-2.59	-23.1	-60.5	-34.9
59.3	(b)	-2.28	-20.3	-50.0	-27.7
59.4	(b)	-2.28	-20.3	-50.0	-27.7
60.0	(c)	-1.67	-14.9	-38.5	-22.0
61.0	(d)	-0.65	-5.8	-20.0	-13.2
61.7	(d)	-0.06	-0.5	-11.5	-10.3

(a)  $\text{Cr}_3\text{Te}_4$ -h; (b)  $\text{Cr}_3\text{Te}_4$ -h +  $\text{Cr}_5\text{Te}_8$ ; (c)  $\text{Cr}_5\text{Te}_8$ ; (d)  $\text{Cr}_5\text{Te}_8$ -trig.

The reciprocal sample temperatures, interpolated at fixed compositions from Fig. 1, are plotted in Fig. 2 versus the reciprocal reservoir temperatures for the composition range between 57.0 and 61.5 at% Te. As can be seen, data points of equal composition fall generally on straight lines. This does not only prove the consistency of the different sets of data but can also be used to calculate the partial molar enthalpies of tellurium,  $\Delta \bar{H}_{\text{Te}}$ , employing a form of the *Gibbs-Helmholtz* equation<sup>2</sup>. For the enthalpy of vaporization of tellurium used in this calculation a value of 114.1 kJ mol<sup>-1</sup> was taken<sup>20</sup>. The  $\Delta \bar{H}_{\text{Te}}$ -values were computed in intervals of 0.5 at%; they are presented in Fig. 3. 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 1,073 K (being an average temperature for all samples) by means of  $\Delta \bar{H}_{\text{Te}}$ -values from the smoothed curve in Fig. 3. The composition dependence of  $\ln a_{\text{Te}}$  at 1,073 K is shown in

Fig. 4. Table 1 contains values of the partial molar properties of tellurium at selected compositions.

Although a separate investigation of the phase diagram is being performed<sup>12</sup> a few remarks on the phase relationships should be made at this point for a better understanding of Figs. 1, 3, and 4. As can be seen from Fig. 1 vapor pressures were measured in three different phases, the monoclinic  $\text{Cr}_3\text{Te}_4$ -h, which is a high temperature modification of

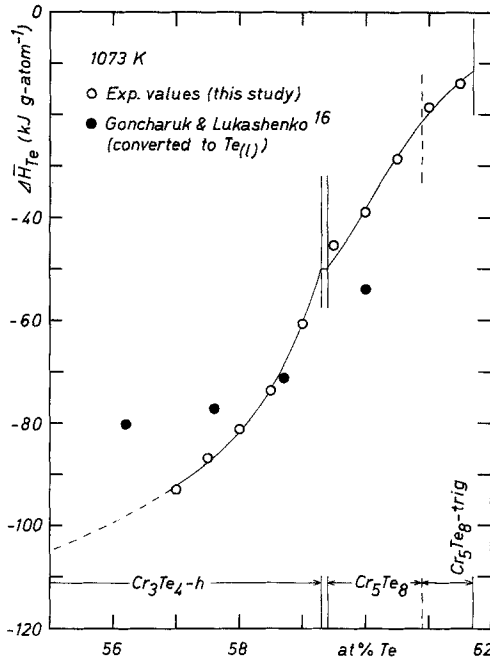


Fig. 3. Partial molar enthalpies of tellurium. Standard states:  $\text{Cr}_{(s)}$  and  $\text{Te}_{(l)}$

$\text{Cr}_3\text{Te}_4$ , the monoclinic  $\text{Cr}_5\text{Te}_8$ , and its trigonal modification  $\text{Cr}_5\text{Te}_8$ -trig. While the equilibrium curves show a kink—confirmed by X-ray diffraction—between 59.3 and 59.4 at% Te corresponding to the two-phase field between  $\text{Cr}_3\text{Te}_4$ -h and  $\text{Cr}_5\text{Te}_8$ , they do not allow a definite decision about the position of the transition from  $\text{Cr}_5\text{Te}_8$  to  $\text{Cr}_5\text{Te}_8$ -trig. However, it is probable that the wiggles in these curves between 61.0 and 61.5 at% Te are connected with this transition. The tellurium-rich phase boundary of  $\text{Cr}_5\text{Te}_8$ -trig was found to be at 62 at% Te up to 850 K<sup>17</sup>; the activity measurements seem to indicate that this boundary shifts to lower tellurium contents with increasing temperature since at 1,073 K  $\ln a_{\text{Te}}$  would reach a positive value at 62 at% Te (cf. Fig. 4). Therefore a value of 61.7 at% Te was adopted for this temperature.

## Discussion

The results of the present study can be compared with the data of *Goncharuk and Lukashenko*<sup>15,16</sup>. In the first paper<sup>15</sup> they determined partial molar *Gibbs* energies of chromium between 623 and 723 K at four different compositions (65.0, 69.8, 78.6, and 88.6 at% Te) by an emf

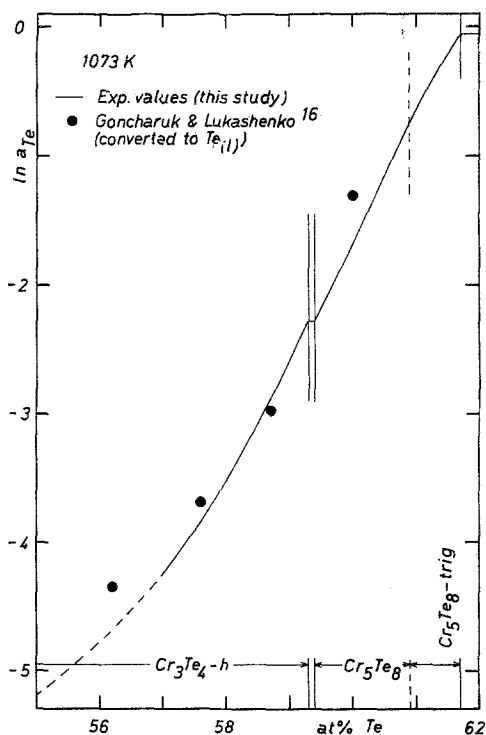


Fig. 4. Activities of tellurium at 1073 K. Standard states:  $Cr_{(s)}$  and  $Te_{(l)}$

method. For the evaluation of the measurements they assumed the existence of a two-phase field ( $Cr_2Te_3 + Te$ ) in the given temperature range and derived integral thermodynamic data for the phase  $Cr_2Te_3$  which corresponds to  $Cr_5Te_8-trig$  in the present investigation. However, phase diagram studies by *Klepp and Ipser*<sup>17</sup> and by *Klepp et al.*<sup>12</sup> have shown that two previously undetected phases exist in the composition range from 62 at% Te to pure solid tellurium: monoclinic  $CrTe_3$  between 74 and 75 at% Te decomposing peritectically at 753 K, and a phase  $Cr_{\sim 1.3}Te_3$  with a related structure decomposing peritectoidally at 731 K. This means that two of the above compositions<sup>15</sup> are in the two-

phase field ( $\text{Cr}_5\text{Te}_8\text{-trig} + \text{Cr}_{\sim 1.3}\text{Te}_3$ ) and two in the range ( $\text{CrTe}_3 + \text{Te}$ ). In fact, careful inspection of the Fig. in Ref.<sup>15</sup> showing emf-values as a function of temperature for the four different compositions reveals two sets of data; instead of one common straight line two separate ones can be drawn corresponding to the two different two-phase regions. From these lines the partial molar *Gibbs* energies of chromium can be estimated: At 668 K, the temperature selected by *Goncharuk* and *Lukashenko*, one obtains  $\Delta \overline{G}_{\text{Cr}} \approx -90 \text{ kJ g-atom}^{-1}$  ( $\ln a_{\text{Cr}} = -16.2$ ) for ( $\text{CrTe}_3 + \text{Te}$ ) and  $\Delta \overline{G}_{\text{Cr}} \approx -88 \text{ kJ g-atom}^{-1}$  ( $\ln a_{\text{Cr}} = -15.8$ ) for ( $\text{Cr}_5\text{Te}_8\text{-trig} + \text{Cr}_{\sim 1.3}\text{Te}_3$ ). The small change of the activity across the two phases indicates a rather small thermodynamic stability compared with the phase mixture  $\text{Cr}_5\text{Te}_8\text{-trig} + \text{Te}$  which may also explain why  $\text{CrTe}_3$  and  $\text{Cr}_{\sim 1.3}\text{Te}_3$  were not discovered earlier. With these data and assuming a negligible solubility of chromium in solid tellurium one can derive  $\Delta G \approx -23 \text{ kJ g-atom}^{-1}$  for  $\text{CrTe}_3$  at 74.5 at% Te and 668 K. For the same temperature one can estimate  $\Delta G$ -values for  $\text{Cr}_{\sim 1.3}\text{Te}_3$  at 70 at% Te and  $\text{Cr}_5\text{Te}_8\text{-trig}$  at 62 at% Te by combining the data derived from the emf-measurements of *Goncharuk* and *Lukashenko*<sup>15</sup> with the present data. One gets  $\Delta G$ -values of  $-27 \text{ kJ g-atom}^{-1}$  and  $-34 \text{ kJ g-atom}^{-1}$ , respectively. All these values are referred to  $\text{Cr}_{(s)}$  and  $\text{Te}_{(s)}$  as standard states.

The second paper of *Goncharuk* and *Lukashenko*<sup>16</sup> deals with emf measurements on six alloys between 52 and 60 at% Te and between 753 and 923 K. They derived partial molar properties of chromium for 850 K, by *Gibbs-Duhem* integration of partial molar properties of tellurium, and consequently the integral thermodynamic data. For comparison with our tellurium activities values of  $\ln a_{\text{Te}}$  were converted to 1,073 K with the partial molar enthalpies of tellurium from Ref.<sup>16</sup>, and adjusted to  $\text{Te}_{(l)}$  as standard state; they are shown in Fig. 4 and are in very reasonable agreement with our data. Similarly,  $\Delta H_{\text{Te}}$ -values, again after conversion to  $\text{Te}_{(l)}$  as standard state, are compared with our data in Fig. 3. Although the order of magnitude is the same, the agreement is rather poor.

Since *Gibbs-Duhem* integration was not possible because of the limited composition range of our data integral thermodynamic properties were calculated by combining the directly measured partial molar quantities from the present study and those from Ref.<sup>16</sup>. However, the values showed rather large scattering with respect to their composition dependence. This as well as the discrepancies in the partial molar quantities of tellurium (cf. Figs. 3 and 4) may have several reasons, one of them the different experimental temperatures. The phase  $\text{Cr}_3\text{Te}_4\text{-h}$  transforms to its low-temperature modification with a maximum



temperature of 906 K at 57.14 at% Te<sup>12</sup>. At least one of the data points of *Goncharuk* and *Lukashenko*<sup>16</sup> (i.e. 57.6 at% Te) lies in the homogeneity range of the low-temperature phase whereas the isopiestic measurements were performed well above the transformation temperature. Another reason may be the assumption of the tellurium-rich phase boundary of the NiAs-typ phases at 60.5 at% Te in Ref. <sup>16</sup>. As discussed above it has been shown<sup>12,17</sup> that at 850 K the phase boundary is located at 62 at% Te and that it is slightly shifting to lower tellurium contents with increasing temperature. Finally the data of the present study become less reliable below 58 at% Te because of the increasing scatter of the experimental data points.

For the composition Cr<sub>3</sub>Te<sub>4</sub> (57.14 at% Te) a value of  $\Delta S_{1073} = -12.6 \text{ J K}^{-1} \text{ g-atom}^{-1}$  can be estimated by extrapolating the entropy data of *Grönvold*<sup>14</sup> to 1,073 K and by combining it with standard entropy data for chromium and tellurium from *Barin* et al.<sup>22</sup>. Using partial molar *Gibbs* energies from Ref. <sup>16</sup> and from this study  $\Delta G_{1073} = -36.2 \text{ kJ g-atom}^{-1}$  can be computed, resulting in  $\Delta H_{1073} = -49.7 \text{ kJ g-atom}^{-1}$  with all values at 1,073 K referred to Cr<sub>(s)</sub> and Te<sub>(l)</sub> as standard states. This can be converted to 298 K using tabulated thermodynamic functions from Refs. <sup>14</sup> and <sup>22</sup> to give a value  $\Delta H_{298} \approx -37 \text{ kJ g-atom}^{-1}$  now referred to Te<sub>(s)</sub>.

In a number of previous publications *Komarek* and co-workers<sup>1-6</sup> applied a theoretical model to describe the thermodynamic properties of transition metal chalcogenides with the defected hexagonal NiAs-structure. The model assumes random distribution of the vacancies in every or every other transition metal layer. However, it was not possible to evaluate the results of the present investigation in terms of this model since most of the experimental data points are in the monoclinic phases Cr<sub>3</sub>Te<sub>4</sub>-h and Cr<sub>5</sub>Te<sub>8</sub> probably with some degree of order for which the model cannot be strictly valid.

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