Monatshefte für Chemie 106, 73—84 (1975)

Enthalpies of Formation of Solid Cobalt—Tellurium Alloys

By

Kurt L. Komarek, Peter Matyas, and **Johann Mikler**

Institute of Inorganic Chemistry, University of Vienna, Austria

With 2 Figures

(Received October 5, 1974)

The enthalpies of formation of solid Co—Te alloys were determined at room temperature with an isoperibol solution calorimeter of the submarine type. Co—Te alloys and mechanical mixtures of the pure components were dissolved in separate experiments in a saturated hydrochloric acid (8.000*n*)—bromine mixture and the enthalpies of formation obtained by difference. For the NiAs-type β-phase $\Delta H_f^\circ(N_{\mathrm{Te}}) = (4.079\text{–}15.017\, N_{\mathrm{Te}})$ kcal · g-atom^{-1} and for the marcasite-type γ-phase $\Delta H_f^\circ(N_{\mathrm{Te}}) = (3.787\text{–}14.400\, N_{\mathrm{Te}})$ kcal · g-atom^{-1}. Combining these results with data from the literature integral thermodynamic properties of solid Co—Te alloys were calculated at room temperature and at 600 °C.

In a previous investigation of the thermodynamic properties of cobalt—tellurium alloys[1] it was suggested that the enthalpies of formation published in the literature[2] do not agree with the other data and should therefore be redetermined.

The cobalt—tellurium system is characterized by two compounds, hexagonal $Co_{1-x}Te$ with NiAs-structure and orthorhombic $CoTe_2$ of the marcasite type. $Co_{1-x}Te$ has a maximum range of homogeneity from 55 at% Te at 980 °C to 65 at% Te at 970 °C with a congruent melting point of 1,015 °C at 56.2 at% Te, and $CoTe_2$ is stable between 66.7 and 69.7 at% Te and decomposes peritectically at 764 °C into $Co_{1-x}Te$ and a Te-rich melt[3].

Since the investigation mentioned above[1] some additional thermodynamic information has become available. *Geiderikh, Gerassimov,* and *Matlasevich*[4] have determined the heat of formation of $CoTe_2$ by *emf* measurements. The same authors obtained by similar measurements on $Co_{1-x}Te$ partial molar[5] and molar[6] quantities. *Mills*[7] measured heat capacities of solid alloys in the $Co_{1-x}Te$ and $CoTe_2$ phase fields.

In the present investigation the enthalpies of formation of solid cobalt—tellurium alloys were measured by solution calorimetry. In separate experiments alloy specimens and mixtures of the pure components were dissolved in bromine-hydrochloric acid and the enthalpies of formation determined by difference.

Experimental

Materials

The materials used in this study were tellurium (in lumps) with a purity of 99.99% (ASARCO, USA) and 0.1 mm thin cobalt foil with a purity of 99.99% (Sherritt Gordon Mines, Ltd., Canada). The tellurium was further purified by melting in vacuo[8]. The two components, weighed to within ± 0.05 mg on a semi-microbalance (total weight $\approx$ 10 g), were placed into a quartz capsule which was evacuated to 10^{-3} torr, three times backfilled with Ti-gettered Ar and evacuated, and finally sealed under a vacuum of 10^{-4} torr. The ampoules were heated 24 h at 600 °C, the temperature was then raised to 950 °C over a period of 2 days, then quickly to 1,100 °C and kept for a day. The alloys in the $Co_{1-x}Te$ phase field were cooled within 12 h to 850 °C, and then quenched in ice water. The samples were powdered, passed through a sieve, again sealed in a quartz capsule under vacuum, heat treated for 14 days at 750 °C, quenched and immediately put into the calorimeter. The $CoTe_{2+x}$ samples were slowly cooled from 1,100 °C to 700 °C (30 °C per day), then cooled to 500 °C within 24 h, and quenched in ice water. The samples were powdered and put through a sieve, the specimen with 67 at% Te heat treated at 700 °C for 14 days, the one with 68 at% Te at 600° for 21 days, and the one with 69 at% Te at 500 °C for 48 days. After quenching the samples were again sealed and the heat treatment was repeated to insure equilibration of the alloys. The phase composition of all equilibrated samples was checked by X-ray analysis. Powder patterns were obtained with a Kristalloflex IV (Siemens, Karlsruhe) in Debye-Scherrer cameras (57 mm diameter) using the asymmetric film method and CoK_α radiation with a Fe filter. All samples were one-phase with the exception of the specimen with 65.5 at% Te ($CoTe_{1.90}$) which was deliberately placed in the two-phase region.

Calorimeter

The isoperibol solution calorimeter used in this investigation was of the submarine type and corresponds to the slightly modified version[9] of the model used by *Gross* et al.[10]. A drawing is shown in Fig. 1 *.

The inner calorimeter vessel (a), constructed from thin copper sheet (15 cm I.D., 24 cm high) and of about 3,200 ml capacity, is centered within the stronger brass calorimeter jacket (18.4 cm I.D., 25.5 cm high) (b) by small insulating spacers (i). The vessel (a) is closed by a thin copper lid (d) with a skirt of copper sheet (e) brazed to it which dips about 2 cm below the surface of the water to ensure that there is no significant temperature difference between the lid and the water in vessel (a). Also brazed into the lid are small tubes (f) through which pass the inner stirrers (g). These

---

* The authors are greatly indebted to the late Prof. *Ph. Gross* for his invaluable help and advice in constructing the calorimeter.

tubes also dip below the water level and help to reduce water evaporation. Two brass adapters brazed to the inside of the inner vessel provide attachment for the thermistor (t), and an inner bath heater (l), when used.

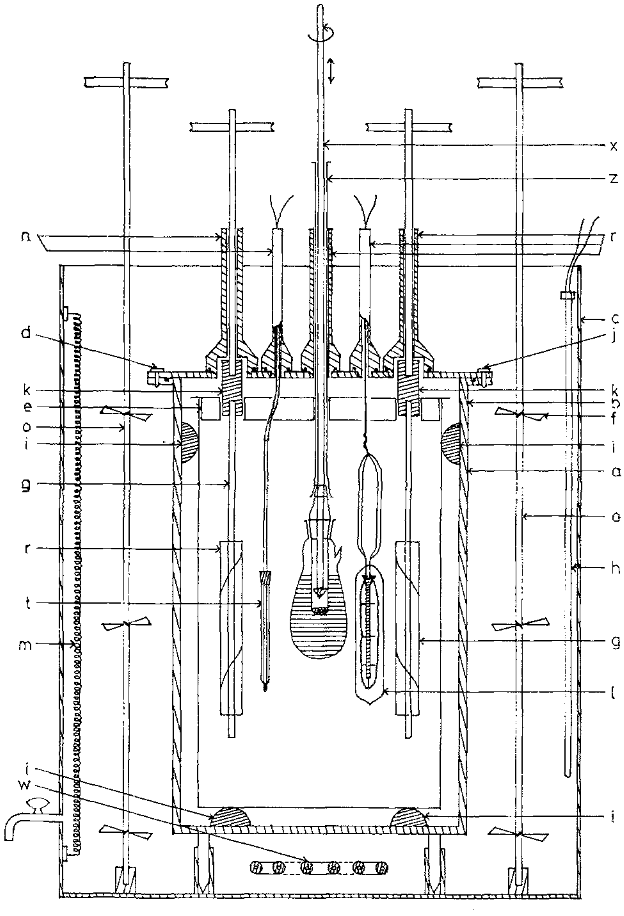

Fig. 1. Schematic drawing of the isoperibol solution calorimeter of the submarine type. a = inner calorimeter vessel; b = calorimeter jacket; c = outer thermostat vessel; d = copper lid; e = skirt of sheet copper; f = tubes for inner stirrers; g = inner stirrers; h = copper sheathed thermistor; i = insulating spacers; j = brass plate; k = "Tufnol" insulators; l = manganine heater for calibration; m = low-voltage heater; n = threaded copper tubes; o = outer stirrers; r = reaction vessel; t = thermistor for measuring the calorimeter temperature; w = 2.5 kW-heater; x = ground glass stirrer; z = hollow shaft for ground glass stirrer

The vessel (b) is closed by a strong brass plate (j) which is secured to the flange by eight bolts. A neoprene "O" ring between the plate and the flange provides a water-tight seal. Screwed into the top plate and sealed to it by "O" rings are five hollow tubes. Two of these, of stronger construction than the others, serve as bearings for the stirrer shafts, while the other three accommodate the various electrical leads and the stirrer shaft for the reaction vessel. To reduce heat conduction along the stirrer shafts, the shafts are split along their length by "Tufnol" insulators (k).

The vessel (b) is supported in the outer brass thermostat vessel (37.5 cm I.D., 45.3 cm high) (c) by three feet which locate in tubes in the base of the outer vessel. This vessel also carries three low-wattage heaters (m)—approximately 20 V variable supply required—and a copper sheathed thermistor (h) as sensing element for the electronic control unit. At the base of the vessel is a 2.5 kW heater for rapid heating of the outer bath. During an experiment the calorimeter vessel (a) was filled with water, the space between calorimeter (a) and jacket (b) was filled with air and the thermostat (c) filled with water so that the jacket was covered at least 8 cm high with water. The temperature of the water in the thermostat was controlled to within $\pm$ 0.0006 °C by using suitably arranged heaters and an electronic controller. The temperature of the water inside the calorimeter vessel was measured by a thermistor. The constants in the equation of the resistance of the thermistor, $R = A \exp (B/T)$, were obtained by calibration at the triple point of $Na_2SO_4 \cdot 10\,H_2O$ (32.38 °C) and at the melting point of diphenyl ether (26.86 °C) to $A = 5.236 \cdot 10^{-2}\,\Omega$ and $B = 3088.31$ K (R at 298.15 = 1650.11 Ω). The energy equivalent ε was determined by electrical calibration with a specially constructed heater before and after the reaction.

The energy input (6102 A DC Power Supply, Hewlett-Packard) was evaluated in the usual way by measuring the heater resistance, the voltage drop across it, and the time of current flow $E_{\mathrm{calth}} = U^2 \cdot t/R \cdot 4.184$. The heater consisted of a manganine wire ($\approx$ 67 Ω) sealed in a glass bulb under He atmosphere. Its resistance was determined by comparing the voltage drop across it with that of a 1 Ω-standard resistor (Cambridge Instr. Comp., Ltd.) connected in series. For the determination of the voltage across the heater a voltage divider, consisting of two precision resistors (Cambridge Instr. Co., Ltd.) with resistances of 100 kΩ and 1 kΩ, resp., were used. The potentiometer (Precision Vernier Potentiometer, Type 5590 A, H. Tinsley & Co., Ltd.) was operated with a galvanometer (Type 5656, H. Tinsley & Co., Ltd.) and the time of current flow was determined by a precision chronometer allowing exact readings of 0.01 min. The thermistor which was used to measure the temperature response of the calorimeter was a branch in a Wheatstone bridge consisting of two matched 2,000 Ω resistors (Cambridge Instr. Co., Ltd.) and a resistance box (Type 2541-5-LF.I., H. Tinsley & Co., Ltd.). The thermistor resistance could be determined to within $\pm$ 0.01 Ω using a null voltmeter (Type 419 A DC, Hewlett-Packard). The energy equivalent ε was expressed in terms of the ratio $\Delta R/R_m$ which is proportional to ΔT in the range of experimental values; ΔR is the resistance difference of the thermistor, corrected for the heat exchange, and R_m the value of R averaged over the main period. The correction for the heat exchange was performed numerically according to the method of *Regnault* and *Pfaundler* by using the values for R instead those for the temperature. The errors caused by this substitution are negligible according to the model calculations of *Gunn*[11]. For the cooling constant values between 2.9×10^{-3} and 3.0×10^{-3} were found. The results were recalculated at the standard temperature (298.15 K) employing the ε's determined before and after the reaction[12] with $\Delta\,\varepsilon$ a measure of $\Delta\,C_p$ of the reaction. Since the experimental conditions were chosen so that the final temperatures were close to 298.15 K, the corrections were very small and the relatively large uncertainty in $\Delta\,C_p$ had hardly any influence on the total error of the final results.

Experimental Procedure

In a series of preliminary tests the most suitable solvent for Co—Te alloys and for the pure components was found to be 8.0*n*-HCl saturated with bromine, with excess bromine as the second liquid phase. The excess bromine assured a fast reaction and a constant concentration of the resulting final solution. When preparing the solvent it was observed that saturation in the Br_2—HCl—H_2O system at room temperature is a very slow process which takes at least 24 h. Accordingly HCl and Br_2 (both p. a. Merck, Darmstadt) were equilibrated at 25 °C by shaking for several hours in a closed container, and the solution left standing for 24 h before use. In all experiments the solvent was two-phase at the start but completely clear and one-phase at the end. In separate experiments it was established that $TeBr_4$, probably formed in the reaction, strongly increases the solubility of Br_2 in the hydrochloric solution.

The powdered sample was put in a thin-walled (0.5 mm) cylindrical glass container with two male ground glass joints. The lower ground joint (34/35) fitted into the pear-shaped reaction vessel (120 ml) and the upper ground joint (29/32) was connected with a glass stirrer (Fig. 1). The ground joints were sealed with Apiezon wax and the part of the stirrer which was cylindrically ground was lubricated with an inert grease (Halocarbon Stopcock Grease, Halocarbon Products Corp., N.J., USA). 100.0 ml 8.000*n*-HCl (p. a. Merck) were filled into the reaction vessel through a thin glass tube attached on one side and then 12.00 ml Br_2 (p.a. Merck) added under cooling with a dry ice—acetone mixture. The glass tube was sealed and the solvent equilibrated as outlined above. The reaction was initiated by breaking the bottom of the thin-walled sample container with a sharp tap of the thorn attached to the bottom of the stirrer.

The calorimeter was tested in accordance with *Gunn* and *Cunningham*[13] by determining the heat of solution of Mg (0.2118 g) in 1.000*m*-HCl (100 ml). A fine hole was drilled into the shaft of the stirrer, to allow H_2 formed in the reaction to escape. The heat of solution at 298.15 K was found to be — 111.20 kcal · mole^{-1} *, in very good agreement with the results of other authors: — 111.30[13], — 111.27[14], and 111.322[15] kcal · mole^{-1}. The error in the determination of the energy equivalent was estimated to be 0.13%.

Experimental Results and Discussion

The reaction in the calorimeter on dissolving the pure components, referred to one gram-atom of Co, can be formally expressed by the following equation:

$$\begin{aligned}&\mathrm{Co(s)} + (1+y)\ \mathrm{Te(s)} + [b\,\mathrm{Br};\ h\,\mathrm{HCl};\ w\,\mathrm{H_2O}]\ \ (\mathrm{l};\ \text{2-phase}) =\\ &[\mathrm{CoBr_2};\ (1+y)\ \mathrm{TeBr_4};\ (b-6-4y)\mathrm{Br};\ h\,\mathrm{HCl}:\ w\,\mathrm{H_2O}]\ (\mathrm{l};\ \text{1-phase})\end{aligned} \tag{1}$$

---

* Throughout this paper 1 $\mathrm{cal_{th}}$ = 1 cal = 4.184 J.

Writing a similar equation for the alloy and subtracting it from the one above we get

$$\mathrm{Co(s)} + (1 + y)\ \mathrm{Te(s)} = \mathrm{CoTe}_{(1+y)}\mathrm{(s)};\ \Delta H_m\ (\mathrm{CoTe}_{(1+y)};\ \mathrm{s}) \qquad (2)$$

Dividing the equation by $2 + y$ we obtain $\Delta\ \mathrm{H}_f{}^\circ$ (N_{Te}; s), the result referred to one gram-atom of alloy. It is important that the resulting final solutions are one-phase so that the slow equilibration between bromine and the hydrochloric solution is eliminated as a source of error. The results of a typical calorimetric run are listed in Table 1*. The enthalpies of formation, obtained by the reaction sequence mentioned above, are given in Table 2, with the values listed both referred to one gram formula weight CoTe_{1+y} and to one gram-atom of alloy. At least two measurements were performed with each sample. For the component

Table 1. *Experimental Data for the Determination of the Enthalpy of Formation of a* Co—Te *Alloy by Solution Calorimetry*

M ($\mathrm{CoTe}_{1.30}$) = 224.8132 g · mole^{-1}	$\mathrm{CoTe}_{1+y}: y = 0.30;\ N(\mathrm{Te}) = 0.5652$	
M ($\mathrm{Co}_{0.4348}\mathrm{Te}_{0.5652}$) = 97.7448 g · g-at.$^{-1}$	mixture of the components	alloy
m (Te)/g	1.7736	
m (Co)/g	0.6300	
m ($\mathrm{CoTe}_{1.30}$)/g		2.4034
n (Co)/mole	0.01069	0.01069
m (8.000n-HCl)/g	112.675	112.675
m (Br_2, l)/g	37.428	37.428
$\varepsilon_i/\mathrm{cal_{th}}$	— 103,620	— 100,388
$\varepsilon_f/\mathrm{cal_{th}}$	— 103,781	— 100,641
R_B/Ω	1,650.00	1,650.00
R_C/Ω	1,624.80	1,630.60
$\Delta\ R_{(\mathrm{corr.})}/\Omega$	— 19.3450	— 18.2074
$10^2\ (\Delta\ R_{(\mathrm{corr.})}/R_m)$	— 1.1793	— 1.1090
$q\ (T_C)/\mathrm{cal_{th}}$	1,221.99	1,113.31
$q\ (T_B)/\mathrm{cal_{th}}$	1,223.89	1,116.11
q (298.15)/$\mathrm{cal_{th}}$	1,223.93	1,116.14
$\Delta\ H_m$ (298.15)/kcal · mole^{-1}	— 114.493	— 104.410
$\Delta\ H_N$ (298.15)/kcal · g-at.$^{-1}$	— 49.78	— 45.40

The meaning of the symbols not explained in the text is as follows: R = resistance of thermistor; B and C = points on the initial and final periods, resp.; $\Delta\ R_{(\mathrm{corr.})}$ = the corrected temperature rise expressed as change of the thermistor resistance; $q\ (T)$ = the experimental heat at temperature T; subscripts m and N (= N_{Te}) refer to the formulas CoTe_{1+y} and $\mathrm{Co}_{1-N}\mathrm{Te}_N$, resp.

---

* Similar tables for all the other compositions can be obtained by request from the authors.

Table 2. *Standard Enthalpies of Formation of* Co—Te-*Alloys and the Corresponding Enthalpies of Solution of the Mixtures of the Elements and the Alloys at Standard Temperature* (298.15 K)

y in $CoTe_{1+y}$	Compos., At% Te	Phase	$-\Delta H_N$, sol $\{(1-N)Co + N \cdot Te\}$ kcal · g-at⁻¹		$-\Delta H_N$, sol $(Co_{1-N}Te_N)$ kcal · g-at⁻¹		$-\Delta H_f°$ $(Co_{1-N}Te_N)$ kcal · g-at⁻¹	
			exp.	calc. Eq. (3)	exp.	calc. Eq. (4); (5)	exp.	calc. Eq. (6); (7)
0.00	50.00		50.21	50.346				
0.30	56.52	β	49.78	49.785	45.40; 45.31	45.377	4.38; 4.47	4.41
0.40	58.33	β	49.92	49.630	45.00; 44.85	44.950	4.92; 5.07	4.68
0.50	60.00	β		49.486	44.41; 44.45	44.555	5.08[a]; 5.04[a]	4.93
0.60	61.54	β		49.354	44.32; 44.08	44.192	5.03[a]; 5.27[a]	5.16
0.70	62.96	β	49.03	49.232	43.99; 43.91	43.856	5.04; 5.12	5.38
0.90	65.52	β + γ		49.011	43.26		5.75[a]	
1.00	66.67		49.13	48.913				
1.030	67.00	γ		48.884	43.08; 43.01	43.023	5.80[a]; 5.87[a]	5.86
1.125	68.00	γ		48.798	42.71; 42.77	42.793	6.09[a]; 6.03[a]	6.01
1.200	68.75		48.57	48.733				
1.226	69.00	γ		48.712	42.65; 42.53	42.563	6.06[a]; 6.18[a]	6.15

[a] The value for the heat of solution of the mixture of the elements used in calculating this value has been interpolated by means of Eq. (3).

mixtures exactly 0.6300 g Co and the appropriate amount of Te (1.9941 to 3.0009 g) were used, the number of moles in reaction (1) being $n = 0.01069$ g-atom^{-1} (based on the atomic weights of Co = 58.9332 and Te = 127.60). The enthalpies of solution of the component mixtures, ΔH_{sol} [Co; $(1 + y)$ Te; s], when plotted as a function of y, gave a straight line. Its equation, calculated by linear regression analysis and referred to the atom fraction of Te, is

$$\frac{\Delta H\,(N_{\text{Te}})}{\text{kcal}\cdot\text{g-atom}^{-1}} = -54.646 + 8.600\,N_{\text{Te}} \tag{3}$$

with the standard deviation, $\sigma_e = \pm\,0.35$ kcal · g-atom^{-1}. The enthalpies of solution, treated by linear regression analysis, follow for the β-phase the equation

$$\frac{\Delta H\,(N_{\text{Te}})}{\text{kcal}\cdot\text{g-atom}^{-1}} = -58.725 + 23.617\,N_{\text{Te}} \tag{4}$$

with $\sigma_e = \pm\,0.12$ kcal · g-atom^{-1} and for the γ-phase the equation

$$\frac{\Delta H\,(N_{\text{Te}})}{\text{kcal}\cdot\text{g-atom}^{-1}} = -58.433 + 23.000\,N_{\text{Te}} \tag{5}$$

with $\sigma_e = \pm\,0.05$ kcal · g-atom^{-1}. The limit of error of the enthalpies of solution is between ± 0.1 and ± 0.4%. The enthalpies of formation of the β-phase are obtained by subtracting Eq. (4) from Eq. (3)

$$\frac{\Delta H_f{}^{\circ}\,(N_{\text{Te}})}{\text{kcal}\cdot\text{g-atom}^{-1}} = 4.079 - 15.017\,N_{\text{Te}} \tag{6}$$

with $\sigma_e = \pm\,0.37$ kcal · g-atom^{-1} and those of the γ-phase by subtracting Eq. (5) from Eq. (3)

$$\frac{\Delta H^{\circ}{}_f\,(N_{\text{Te}})}{\text{kcal}\cdot\text{g-atom}^{-1}} = 3.787 - 14.400\,N_{\text{Te}} \tag{7}$$

with $\sigma_e = \pm\,0.35$ kcal · g-atom^{-1}. The error of the enthalpies of formation is assumed to be ± 0.75 kcal · g-atom^{-1} which is twice the standard deviation of the data from the above linear expression. Within twice the limit of error the concentration dependence of $\Delta H_f{}^{\circ}$ in the β-phase can graphically be also expressed by a nonlinear function, i.e. a slight deviation from linearity cannot be ruled out. The enthalpies of formation at 298.15 K are plotted in Fig. 2 and the curves represented by Eq. (6) and Eq. (7) are shown as solid lines. As can be seen both in the β- and in the γ-phase $\Delta H_f{}^{\circ}$ tends to become more negative with increasing Te-concentration with an extrapolated maximum value of about −6.25 kcal · g-atom^{-1} at 69.7 at% Te. For comparison the

ΔH_f° data of *Matlasevich, Geiderikh,* and *Gerassimov*[6] and of *Ariya* et al.[2] are also shown in Fig. 2. *Matlasevich* et al. computed partial molar enthalpies of Co from *emf* measurements and obtained ΔH_f° at 700 K by Gibbs-Duhem-integration. Their data were corrected for 298.15 K with the C_p-data of *Mills*[7]. The agreement with our results can be considered as satisfactory. The calorimetric data of *Ariya* et al.[2], determined by solution calorimetry in hydrochloric acid saturated with bromine, disagree with both sets of results and are significantly more negative. The reason for this dicrepancy is entirely unclear[4]. The extreme value at 57 at% Te which was interpreted as being due to Co_3Te_4-compound formation[2] is completely absent in our curve. The partial molar enthalpy of tellurium in the β-phase can be obtained from Eq. (6) making use of the well-known relationship

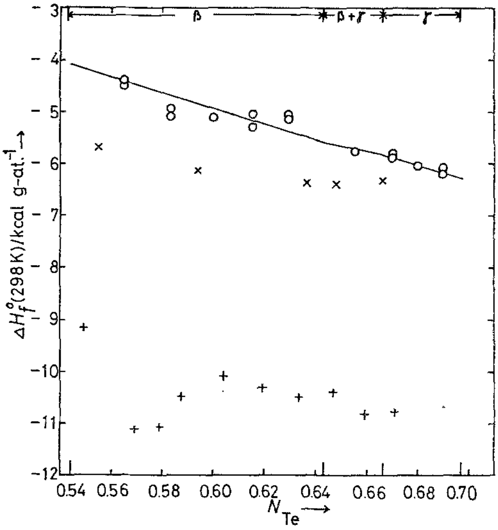

Fig. 2. Enthalpies of formation of solid Co—Te alloys. + = *Ariya* et al.[2]; × = *Matlasevich* et al.[6]; ○ = present investigation

$$\frac{\Delta \bar{H}_{Te}}{\text{kcal}\cdot\text{g-atom}^{-1}} = \Delta H_f^\circ + (1 - N_{Te})\frac{\partial \Delta H_f^\circ}{\partial N_{Te}} = -10.938 \qquad (8)$$

For a comparison with previous results[1] the enthalpy of formation given by Eq. (6) was corrected for a temperature of 873 K using extrapolated heat capacities for the β- and γ-phase[7] and critically compiled enthalpy values for pure cobalt and tellurium[16]. From the result,

ΔH_f° (873 K) $= 3.829 - 19.517\, N_{Te}$ (in kcal · g-atom^{-1}), the partial molar enthalpy $\Delta \overline{H}_{Te} = -15.7 \pm 1.5$ kcal · g-atom^{-1} was derived as outlined in Eq. (8). This value agrees within the limits of error with $\Delta \overline{H}_{Te} = -12.3 \pm 2.0$ kcal · g-atom^{-1}, obtained from isopiestic measurements[1]. Integral thermodynamic properties for Co—Te alloys at 600 °C with liquid Te as the standard state were recalculated from the present enthalpies of formation, compiled enthalpy and entropy data[7, 16], and previous free energies of formation[1]. The results, presented in Table 3, replace similar data[1], based on the ΔH^M-values of *Ariya* et al.[2]. Table 3 also lists the integral thermodynamic properties at 25 °C with solid Te as the standard state. From the entropy of formation and the standard entropies of Co and Te[16] the standard entropies of the β- and γ-phase are S°_{298} ($N_{Te} = 0.59$) $= 10.21$ e. u. and S°_{298} ($N_{Te} = 0.67$) $= 9.32$ e.u., resp. These values can be compared with the estimated values of *Mills*[17], $S^\circ_{298} = 9.09 \pm 1.0$ e.u. for the β-phase and $S^\circ_{298} = 8.83 \pm 1.0$ e. u. for the γ-phase. Assuming a statistical distribution of transition metal atoms and transition metal vacancies in the (00½) layers of the hexagonal NiAs-lattice of the β-phase and allowing for

Table 3. *Integral Thermodynamic Quantities of* Co—Te-*Alloys*

Comp. (at% Te)	Phases	$T = 873$ K Std. state: $Co_{(s)}$; $Te_{(l)}$			T = 273.15K Std. state: $Co_{(s)}$; $Te_{(s)}$		
		$-\Delta G^M$ kcal · g-at^{-1}	$-\Delta H^M$ kcal · g-at^{-1}	$-\Delta S^M$ e. u.	$-\Delta G^M$ kcal · g-at^{-1}	$-\Delta H^M$ kcal · g-at^{-1}	$-\Delta S^M$ e. u.
10	α — Co + β	0.76	1.26	0.57	0.79	0.76	— 0.12
20	α — Co + β	1.52	2.51	1.14	1.59	1.52	— 0.23
30	α — Co + β	2.28	3.77	1.70	2.38	2.28	— 0.34
40	α — Co + β	3.04	5.02	2.27	3.18	3.04	— 0.46
50	α — Co + β	3.80	6.28	2.84	3.97	3.80	— 0.57
55	β	4.18	6.90	3.12	4.37	4.18	— 0.63
57	β	4.37	7.29	3.35	4.63	4.48	— 0.50
59	β	4.47	7.68	3.68	4.87	4.78	— 0.29
61	β	4.47	8.07	4.13	5.01	5.08	+ 0.03
63	β	4.42	8.46	4.63	5.26	5.38	+ 0.41
65	β + γ	4.40	8.85	5.10	5.41	5.62	+ 0.70
67	γ	4.26	9.23	5.70	5.58	5.86	+ 0.98
69	γ	4.11	9.61	6.44	5.67	6.15	+ 1.60
70	γ + Te (l)	3.99	9.30	6.08	—	—	—
	γ + Te (s)	—	—	—	5.49	5.95	+ 1.55
80	γ + Te (l)	2.67	6.20	4.04	—	—	—
	γ + Te (s)	—	—	—	3.66	3.97	+ 1.03
90	γ + Te (l)	1.36	3.10	1.99	—	—	—
	γ + Te (s)	—	—	—	1.83	1.98	+ 0.52

a certain interaction between the vacancies, equations for various thermodynamic properties were derived[1, 18]. For the enthalpy of mixing of formation[18] we get

$$\Delta H^M = 8E_i \frac{(N_{\mathrm{Te}} - 0.5)^2}{N_{\mathrm{Te}}} + (\mathrm{const.} + E_v)N_{\mathrm{Te}} - E_v \qquad (9)$$

where E_i is the interaction energy between cobalt vacancies and E_v the energy of formation of a cobalt vacancy. With $E_i = 1090$ cal · g-atom^{-1}[1] and with two $\Delta H_f°$ ($= \Delta H^M$) values at 56.0 and 64.0 at% Te obtained from Eq. (6) the Eq. (9) was solved. The enthalpies of formation thus calculated are expressed by the equation

$$\frac{\Delta H_f°(N_{\mathrm{Te}})}{\mathrm{kcal} \cdot \mathrm{g\text{-}atom}^{-1}} = 8.720 \frac{(N_{\mathrm{Te}} - 0.5)^2}{N_{\mathrm{Te}}} - 17.650\, N_{\mathrm{Te}} + 5.500 \qquad (10)$$

The line calculated from Eq. (10) deviates so little from the straight line that it is not shown in Fig. 2. A considerably higher interaction energy E_i would be required to make the curve fit the apparent experimental curvature. Since the deviations from linearity predicted by the statistical model for the NiAs-phase in the Co—Te system are within the experimental limits of error, the proof of the validity of the model will continue to rest primarily with the activity measurements[1].

Acknowledgment

The financial support of this investigation by the "Fonds zur Förderung der wissenschaftlichen Forschung" under grant number 1322 is gratefully acknowledged.

References

[1] *R. Geffken, K. L. Komarek*, and *E. Miller*, J. Solid State Chem. **4**, 153 (1972).

[2] *S. M. Ariya, E. M. Kolbina*, and *M. S. Apurina*, J. Neorg. Khim. **2**, 23 (1957).

[3] *K. O. Klepp* and *K. L. Komarek*, Mh. Chem. **104**, 105 (1973).

[4] *V. A. Geiderikh, Ya. I. Gerassimov*, and *O. B. Matlasevich*, Chem. Bond. in Crystals, 292. Minsk: Nauka i Tekhnika. 1969.

[5] *O. B. Matlasevich, V. A. Geiderikh*, and *Ya. I. Gerassimov*, Rev. Chim. minér. **9**, 191 (1972).

[6] *O. B. Matlasevich, V. A. Geiderikh*, and *Ya. I. Gerassimov*, J. Fiz. Khim. **47**, 277 (1973).

[7] *K. C. Mills*, Paper presented at the Third International Conference on Chemical Thermodynamics, 3–7 Sept. 1973, Baden/Vienna; to be published in Trans. Farad. Soc.

[8] *K. O. Klepp* and *K. L. Komarek*, Mh. Chem. **103**, 934 (1972).

[9] *P. Gross, C. Hayman*, and *S. Mwroko*, Trans. Farad. Soc. **65**, 2456 (1969).

[10] *P. Gross*, *C. Hayman*, and *D. L. Levi*, Trans. Farad. Soc. **50**, 477 (1954).

[11] *S. R. Gunn*, J. Chem. Thermodyn. **3**, 19 (1971).

[12] *J. Mikler*, Mh. Chem. **104**, 376 (1973).

[13] *S. R. Gunn* and *B. B. Cunningham*, J. Amer. Chem. Soc. **79**, 1563 (1957).

[14] *E. F. Westrum, Jr.*, and *L. Eyring*, J. Amer. Chem. Soc. **74**, 2045 (1952).

[15] *C. H. Shomate* and *F. H. Huffman*, J. Amer. Chem. Soc. **65**, 1625 (1943).

[16] *R. Hultgren*, *P. D. Desai*, *D. T. Hawkins*, *M. Gleiser*, *K. K. Kelley*, and *D. D. Wagman*, Selected Values of the Thermodynamic Properties of the Elements, Metals Park, Ohio: ASM. 1973.

[17] *K. C. Mills*, Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides. London: Butterworths. 1974.

[18] *H. Jelinek* and *K. L. Komarek*, Mh. Chem. **105**, 917 (1974).

Correspondence and reprints:
Prof. Dr. K. L. Komarek
Institut für Anorganische Chemie
Universität Wien
Währinger Straße 42
A-1090 Wien
Österreich