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Thermodynamic Properties of Cobalt–Tellurium Alloys*†

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Activities of tellurium in cobalt–tellurium alloys were determined by an isopiestic method between 530° and 1030°C and between 50 and 70 at.% Te. Partial molar quantities were calculated for the β-CoTe (NiAs) and the γ-$CoTe_2$ (marcasite) phase. Activities of tellurium in β-CoTe show the same characteristic concentration dependence previously observed in NiTe (NiAs) with an inflection point at 58 at.% Te. The partial molar enthalpy $\Delta\bar{H}_{Te}$ has an approximately constant value of about −12 kcal/g-atom between 55 and 62 at.% Te. Integral thermodynamic quantities were calculated by Gibbs–Duhem integrations. The phase boundaries of the β-CoTe and the γ-$CoTe_2$ phases were determined. $CoTe_2$ has a maximum range of homogeneity of 66.7 to 69.6 at.% Te. No other compounds were found in the system. The solid solubility of tellurium in cobalt at 850°C is <0.1 at.% Te.

Based on a statistical model of random distribution of cobalt atoms over the 00 1/2 layers, activities and partial molar entropies were calculated and compared with experimental data. Excellent agreement could be obtained in the composition range of constant $\Delta\bar{H}_{Te}$ by assuming interaction between nearest neighbor vacancies. The interaction energy was calculated to be 1020 cal/g-atom in δ-NiTe and 1090 cal/g-atom in β-CoTe.

In a previous paper (*1*) thermodynamic properties of nickel–tellurium alloys have been reported. The present publication is concerned with a similar investigation of cobalt–tellurium alloys. The cobalt–tellurium system is characterized by two compounds, congruent melting CoTe and incongruent melting $CoTe_2$ (*2*). CoTe is a typical nonstoichiometric compound, although its range of homogeneity is apparently more limited than that of the homologous NiTe phase. Oftedal (*3*) reported for CoTe a hexagonal structure of the NiAs-(B8)-type and Tengnér (*4*) observed that with increasing tellurium content the NiAs-structure of CoTe changed continuously by subtraction of cobalt atoms into the hexagonal $Cd(OH)_2$-(C6)-structure of $CoTe_2$ thus forming a continuous range of solid solution between the two limiting compositions CoTe and $CoTe_2$. Tengnér also found that the C6-structure transforms at lower temperatures to the orthorhombic marcasite-(C18)-structure. Haraldsen, Grønvold, and Hurlen (*5*) made magnetic, pycnometric, and X-ray measurements on Co–Te alloys, annealed at 600° and 335°C, and reported two compounds. They found that the range of homogeneity of the β(NiAs) phase is $CoTe_{1.20}$–$CoTe_{1.80}$ (54.5 to 63.4 at.% Te) at 600°C and $CoTe_{1.30}$–$CoTe_{1.70}$ (56.5 to 63 at.% Te) at 335°C and that characteristic reflections of the $Cd(OH)_2$ structure appear at about $CoTe_{1.50}$ (60 at.% Te).

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* The authors were formerly with New York University where this work was performed.

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Between $CoTe_{2.00}$ and $CoTe_{2.09}$ (66.67 to 67.64 at. % Te) the γ-phase with marcasite structure is stable at least up to 770°C with no indication of a continuous series of solid solutions between CoTe and $CoTe_2$ even at high temperatures. Ariya, Kolbina, and Apurina (*6*) showed the solubility range of the β-phase to be $CoTe_{1.20}$–$CoTe_{1.89}$ (54.5 to 65.4 at. % Te) at 900°C and the tellurium-rich limit at room temperature to be $CoTe_{1.44}$ (59.1 at. % Te). From the variation of the enthalpy of formation of cobalt tellurides with composition, they concluded the existence of the phases Co_5Te_6 (54.5 at. % Te) and Co_3Te_4 (57.1 at. % Te). Dudkin and Dyul'dina (*7*) studied the Co–Te phase diagram between 30 and 100 at. % Te above 300°C by thermal, metallographic, and X-ray analysis. According to their results the β(NiAs) phase melts congruently at ~1010°C and extends from $CoTe_{1.19}$ to $CoTe_{1.64}$ (54.3 to 62.1 at. % Te) at 600°C. The γ(marcasite) phase is formed by a peritectic reaction at 749°C and has a narrow range of homogeneity from $CoTe_{2.01}$ to $CoTe_{2.11}$ (66.8 to 67.8 at. % Te). Above the peritectic reaction tellurium shows retrograde solubility in the β phase. Chevreton (*8*) studied the composition Co_3Te_4 (57.1 at. % Te) by X-ray analysis and found the 00.1 reflection forbidden in the NiAs-structure, indicative of alternate full cation layers and cation layers containing vacancies perpendicular to the *c*-axis as in the $Cd(OH)_2$-structure. The cation vacancies in the vacancy layers are, however, randomly distributed and not ordered as in Ti_3Te_4, V_3Te_4, and Cr_3Te_4. Cambi, Elli, and Giudici (*9*) investigated the decomposition of $CoTe_2$ thermogravimetrically and by X-ray analysis. From their results they concluded that the γ(marcasite) phase has a range of homogeneity of $CoTe_{1.50}$–$CoTe_2$ (60 to 66.6 at. % Te) at about 600°C and the β(NiAs) phase of $CoTe_{0.78}$–$CoTe_{1.12}$ (43.8 to 52.8 at. % Te) at about 800°C.

The heat of solution of CoTe in bromine water was measured by Fabre (*10*). Ariya *et al.* (*6*) determined the heats of formation of Co–Te alloys between 54.5 and 66.6 at. % Te at 25°C, and found a maximum at 57 at. % Te and a linear change with composition between 58.3 and 66.6 at. % Te. Moody and Thomas (*11*) calculated the enthalpy of formation of CoTe from lattice energies which they derived from Kapustinskii's empirical equations. Eror and Wagner (*12*) found pronounced negative deviations from Raoult's law in the composition range between CoTe and $CoTe_2$ by the dew-point method. However, they found that the vapor pressures were too low to get meaningful quantitative activities. Gibart and Vacherand (*13*) grew single crystals of the β-phase and obtained mostly crystals of the composition $CoTe_{1.49}$ (59.8 at. % Te). From the tellurium vapor pressure, estimated heat capacities, and heats of formation (*6*) they calculated integral molar free energies.

Although the phase boundaries in the Co–Te system seem to be reasonably well established, thermodynamic information is quite incomplete. One objective of this investigation was the determination of the thermodynamic activities of tellurium, especially in the β and γ phases, by an isopiestic method. Cobalt specimens were equilibrated in a temperature gradient with tellurium vapor from a reservoir kept at the temperature minimum. Phase boundaries at various temperatures were verified from discontinuities in the specimen composition–temperature plots.

Experimental Procedure

The materials were 99.999 % tellurium (American Smelting and Refining Corp.), 1-mil thick cobalt sheet of 99.99 % purity (Mackay Co., New York), and 3-mil thick cobalt sheet of 99.9 % purity (Sherritt Gordon Mines Ltd., Canada) with the following impurities: 0.1 % Ni, 0.014 % C, 0.018 % Fe, 0.004 % S, and 0.005 % Cu.

Annular specimens were punched from the sheet, cleaned, weighed on an analytical balance to an accuracy of ±0.1 mg, loaded into graphite crucibles, and reweighed. The crucibles had press fit lids with two 0.3-mm grooves cut into them to allow equilibration with the tellurium vapor phase. All graphite parts were machined from high-density rods (G grade, Basic Carbon Corp.) and were baked out before use at 1100°C in vacuum (<0.1 μ Hg) for 24 hours. The crucibles were placed in a quartz equilibration tube with a centrally located quartz thermocouple well. All quartz parts were cleaned by successive rinsing in hot cleaning solution, nitric acid, and distilled water. They were then dried, evacuated for 24 hours, heated to 900°C and back filled with argon before cooling. The tellurium reservoir, cast in a quartz crucible, was at the bottom of the equilibration tube; at the top the tube was attached to a standard 55/50 taper quartz joint for evacuation. The assembly was evacuated to 0.01 μ Hg and sealed. Then the positions of the samples relative to the thermocouple well were carefully measured. The reaction tube was positioned in a preheated resistance furnace with two separately controlled zones so that temperature gradients up to 500°C could be imposed on the tube. A 380°C temperature gradient was necessary to obtain samples across both the CoTe and $CoTe_2$ phase fields. The temperature of the reservoir and of the samples was measured by raising and lowering a calibrated Pt/Pt-10% Rh thermocouple in the central thermocouple well. Equilibration times varied from 10 days to 2 months. The runs were terminated by quenching the quartz tube in cold water. The crucibles were again weighed after equilibration, and the tellurium content was equated to the weight gain of the sample. Chemical analysis showed that the loss of tellurium from the samples during quenching was negligible. A more detailed description of the experimental procedure is given in the previous paper (*1*).

Attributing the tellurium content of the sample entirely to the weight change of the crucible is only valid if we have no appreciable vaporization of cobalt and no reaction between graphite and tellurium and/or cobalt. Therefore, various experiments were conducted to test the validity of this

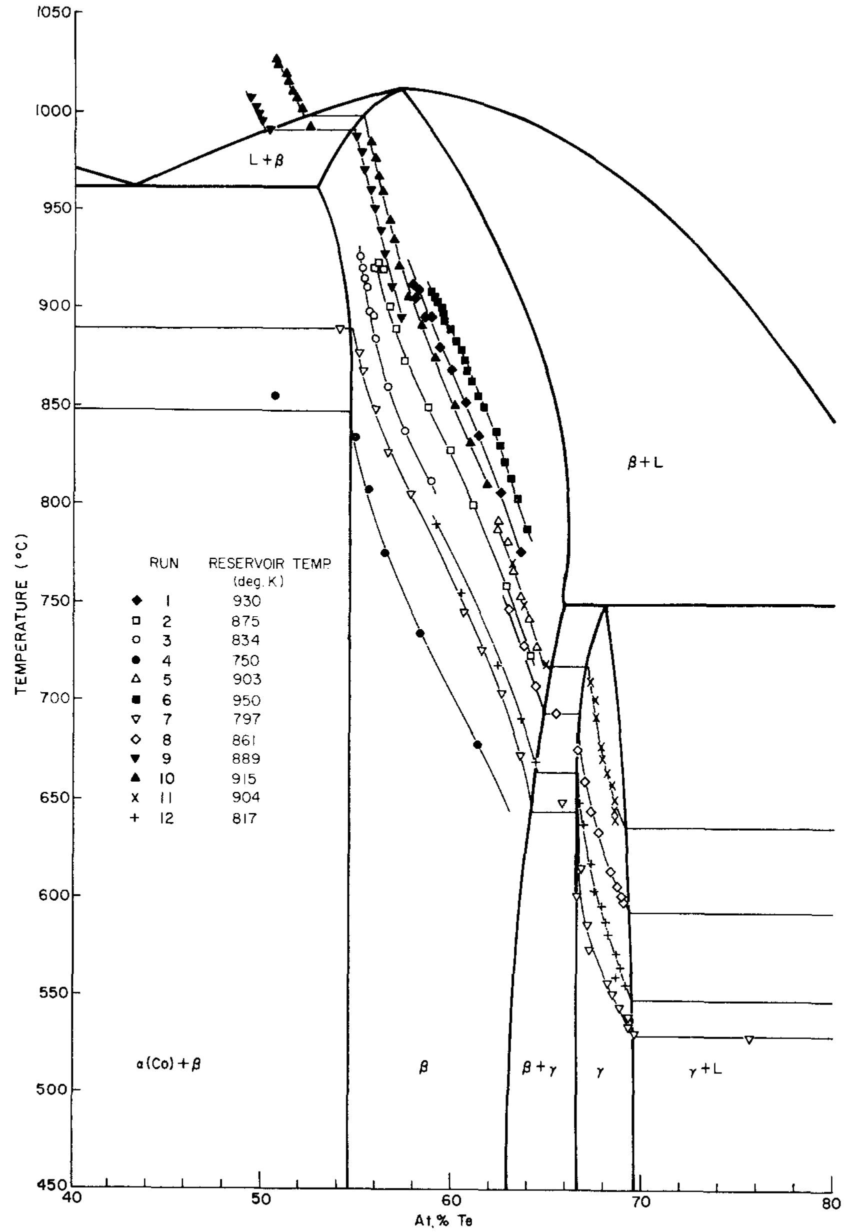

FIG. 1. Specimen composition versus specimen temperature and partial Co–Te phase diagram.

procedure. Several graphite crucibles containing cobalt samples were sealed in an evacuated quartz tube and heated at approximately 920°C for 2 weeks. Neither the graphite crucibles nor the cobalt samples showed any significant weight change. An empty graphite crucible was included in one of the runs, and, again, no weight change was observed. To further ascertain the suitability of graphite crucibles, sample #8 in Run 1 was contained in a special covered quartz crucible. As can be seen from Fig. 1, sample #8 falls on a smooth curve with the samples in graphite crucibles. No appreciable error is therefore introduced by equating the entire crucible weight change to the tellurium gain.

The error associated with weighing is ±0.1 at.% Te. The determination of the sample position involves the measurement of the bottom of the thermocouple well and the crucible position. In addition, the finite thickness of the sample is also included in this measurement. Inclusion of the measurement error inherent in the temperature profiling of the tube leads to a total estimated error in sample position of ±2 mm. This is equivalent to an additional ±0.1 at.% Te error in composition. Therefore, the total estimated error is ±0.2 at.% Te.

For X-ray analysis, samples were powdered, passed through a 350-mesh screen and placed in 0.3-mm glass capillaries. The capillaries were loaded into a Debye–Scherrer X-ray camera and irradiated with Ni-filtered Cu*Kα* radiation for 4 hours.

Experimental Results

After a number of runs with 3-mil-thick cobalt samples it was obvious that samples in the $CoTe_2$ phase field were not attaining equilibrium. The activity curves did not appear similar nor did they yield good enthalpy data, and the curves did not exhibit the characteristic large increase in activity at the stoichiometric composition. On the other hand, activity curves for the CoTe phase were of similar shape, and excellent enthalpy data were obtained. Calculations indicated that the amount of tellurium delivered to the samples through the vapor phase was far in excess of requirements. Therefore, the most likely explanation for this behavior is a marked difference in the diffusivities of the two compounds. Since the CoTe phase exists over a wide composition range through a cobalt vacancy defect mechanism, this high diffusivity is not unexpected.

One-mil-thick cobalt sheets and very long equilibration times were employed in Runs 7, 8, 11, and 12 to attain equilibrium in the $CoTe_2$ phase. This procedure was most successful. The activity curves were of similar appearance, and good enthalpy data were obtained. The results for the 1-mil samples which lie in the CoTe phase field were in good agreement with the earlier data on 3-mil specimens. Apparently, the nonequilibrium of the 3-mil thick $CoTe_2$ samples did not have any effect upon samples in the CoTe phase field of the same run, and these CoTe data were therefore included in the results.

The experimental specimen composition–temperature data of the equilibrated samples are plotted in Fig. 1. Also included in the figure is the phase diagram in the range of our experiments (*2*). Phase boundaries obtained from the breaks of our experimental specimen temperature–composition curves have been incorporated in Fig. 1.

If the vapor phase in equilibrium with an alloy contains more than one molecular species of the component i of the alloy, the activity, a_i, will be related to the partial pressures of the molecular species $i_1, i_2, i_3, \ldots, i_n$ (the subscript indicating the number of atoms in a molecule) as follows:

$$a_i = p_i/p_i^\circ = (p_{i_2}/p_{i_2}^\circ)^{1/2} = (p_{i_3}/p_{i_3}^\circ)^{1/3} = \ldots = (p_{i_n}/p_{i_n}^\circ)^{1/n}. \quad (1)$$

The total pressure for an isopeistic experiment will still be fixed by the reservoir temperature but the molecular composition of the vapor phase will now be a function of temperature. The activity can, however, be calculated if the total vapor pressure and the dissociation constants linking the various molecular species are known as functions of temperature. If only one molecular species is present, and dissociation or association can be neglected, the activity is defined by the appropriate term in Eq. (1) and can be calculated from the total vapor pressure. Equations (2) and (3) of the previous publication (*1*) have been incorrectly written and should be replaced by the definitions given above together with Eq. (1).

Since under our experimental conditions the tellurium vapor exists principally as the dimer, Te_2 (*1*), the activity of tellurium is expressed by

$$a_{Te} = (p_{Te_2}/p_{Te_2}^\circ)^{1/2}. \quad (2)$$

At equilibrium the vapor pressure of tellurium over each sample of a run is equal to that of the pure tellurium reservoir at the temperature minimum. The activity is therefore equal to

$$a_{Te} = \left(\frac{p_{Te_2}^\circ \text{ Reservoir Temp.}}{p_{Te_2}^\circ \text{ Specimen Temp.}}\right)^{1/2}. \quad (3)$$

The standard states chosen are liquid tellurium and solid cobalt. The vapor pressure of liquid tellurium was calculated from

$$\log P(\text{atm}) = -5.9602 \times 10^3/T + 4.7129$$

(*14*). This equation is in excellent agreement with the most recent results of Brebrick (*15*) who measured tellurium vapor pressures from 370° to 615°C and of Baker (*16*) whose investigation was carried out between 708° and 1507°C. From Fig. 1, sample temperatures T_s were interpolated at fixed compositions and their reciprocal values were plotted as a function of the reciprocal reservoir temperatures, T_R. From the slopes A of these straight lines (Table I) partial molar enthalpies $\Delta\bar{H}_{\mathrm{Te}}$ were calculated using a form of the Clausius–Clapeyron equation

$$\frac{1}{T_R} = A\frac{1}{T_s} + C = \frac{\Delta H}{\Delta H_v^\circ}\frac{1}{T_s} + \frac{R}{\Delta H_v^\circ}(C_1 - C_2). \quad (4)$$

C_1 and C_2 are integration constants, $\Delta H_v^\circ = 27.3$ kcal/g-mole of Te_2 (*14*) is the enthalpy of vaporization of pure tellurium, and $\Delta H = \Delta H_v^\circ - 2\Delta\bar{H}_{\mathrm{Te}}$ is the enthalpy change corresponding to the transfer of tellurium from an equilibrated alloy sample to the vapor phase. The $\Delta\bar{H}_{\mathrm{Te}}$ values are also listed in Table I. From the known vapor pressure of tellurium and the measured specimen and reservoir temperatures, the activities of tellurium were calculated using Eq. (3). The values were corrected for 600° and 875°C with the partial molar enthalpies of Table I by means of the Gibbs–Helmholtz equation and are plotted in Fig. 2. Average activities, partial molar free energies, and entropies were computed for one-phase alloys and are shown in Table I. By Gibbs–Duhem integrations the activity of cobalt and the partial molar enthalpy of cobalt were obtained and the integral thermodynamic properties calculated. They are plotted in Fig. 3.

X-ray analysis of equilibrated specimens confirmed the existence of the known phases but did not reveal new compounds. X-ray films of $CoTe_2$ were quite spotty in appearance, presumably due to a preferred orientation of the powder. Only sample #10 of Run 8 appeared to be in the CoTe–$CoTe_2$ two-phase region.

Discussion

Our data are in essential agreement with the phase diagram presented by Elliott (*2*) which is based mainly on a thermal, metallographic, and X-ray analysis of various alloys by Dudkin and Dyul'dina (*7*). Only the previously reported compounds CoTe and $CoTe_2$ were observed with a clearly marked two-phase field between them as shown in Figs. 1 and 2. The last three samples of Run 4 and the last five samples of Run 7 did not pick up any tellurium. Therefore, at least above 850°C no other compound exists between CoTe and pure cobalt. The solubility of Te in pure Co is therefore below the accuracy of our measurements (0.1 at.%). The CoTe phase does not exist at the stoichiometric composition in the temperature range 830° to 990°C. The values for the Co-rich CoTe phase boundary observed in this study are 54.5 ± 0.5 at.% Te at 845°C and 54.9 ± 0.3 at.% Te at 890°C. These data are in good agreement with

TABLE I

PARTIAL MOLAR THERMODYNAMIC QUANTITIES OF SOLID Co–Te ALLOYS

Comp. (At.% Te)	A	$-\Delta\bar{H}_{\mathrm{Te}}$ (kcal/g-atom)	$-\Delta\bar{S}_{\mathrm{Te}}$ (e.u.)	$-\Delta\bar{S}_{\mathrm{Te}}$ (e.u.) (calc.)	$-\Delta\bar{G}_{\mathrm{Te}}$ (875°C) (kcal/g-atom)	$-\log a_{\mathrm{Te}}$ (875°C)	$-\Delta\bar{G}_{\mathrm{Te}}$ (600°C) (kcal/g-atom)	$-\log a_{\mathrm{Te}}$ (600°C)
55.0	1.803	11.0	4.2	4.2	6.15	1.17	7.31	1.83
56.0	1.861	11.8	5.7	5.7	5.31	1.01	6.83	1.71
57.0	1.883	12.1	6.6	6.6	4.52	0.86	6.35	1.59
58.0	1.897	12.3	7.3	7.3	3.94	0.75	5.95	1.49
59.0	1.897	12.3	7.7	7.7	3.47	0.66	5.59	1.40
60.0	1.883	12.1	7.9	7.9	2.99	0.57	5.23	1.31
61.0	1.853	11.7	8.1	7.9	2.47	0.47	4.67	1.17
62.0	1.817	11.2	8.1	7.7	1.94	0.37	4.15	1.04
63.0	1.766	10.5	8.0	7.4	1.37	0.26	3.56	0.89
64.0	1.730	10.0	8.1	—	0.74	0.14	—	—
67.0	1.080	1.1	−0.2	—	—	—	1.28	0.32
67.5	1.095	1.3	0.5	—	—	—	0.88	0.22
68.0	1.110	1.5	1.0	—	—	—	0.60	0.15
68.5	1.117	1.6	1.4	—	—	—	0.36	0.09
69.0	1.168	2.3	2.4	—	—	—	0.16	0.04

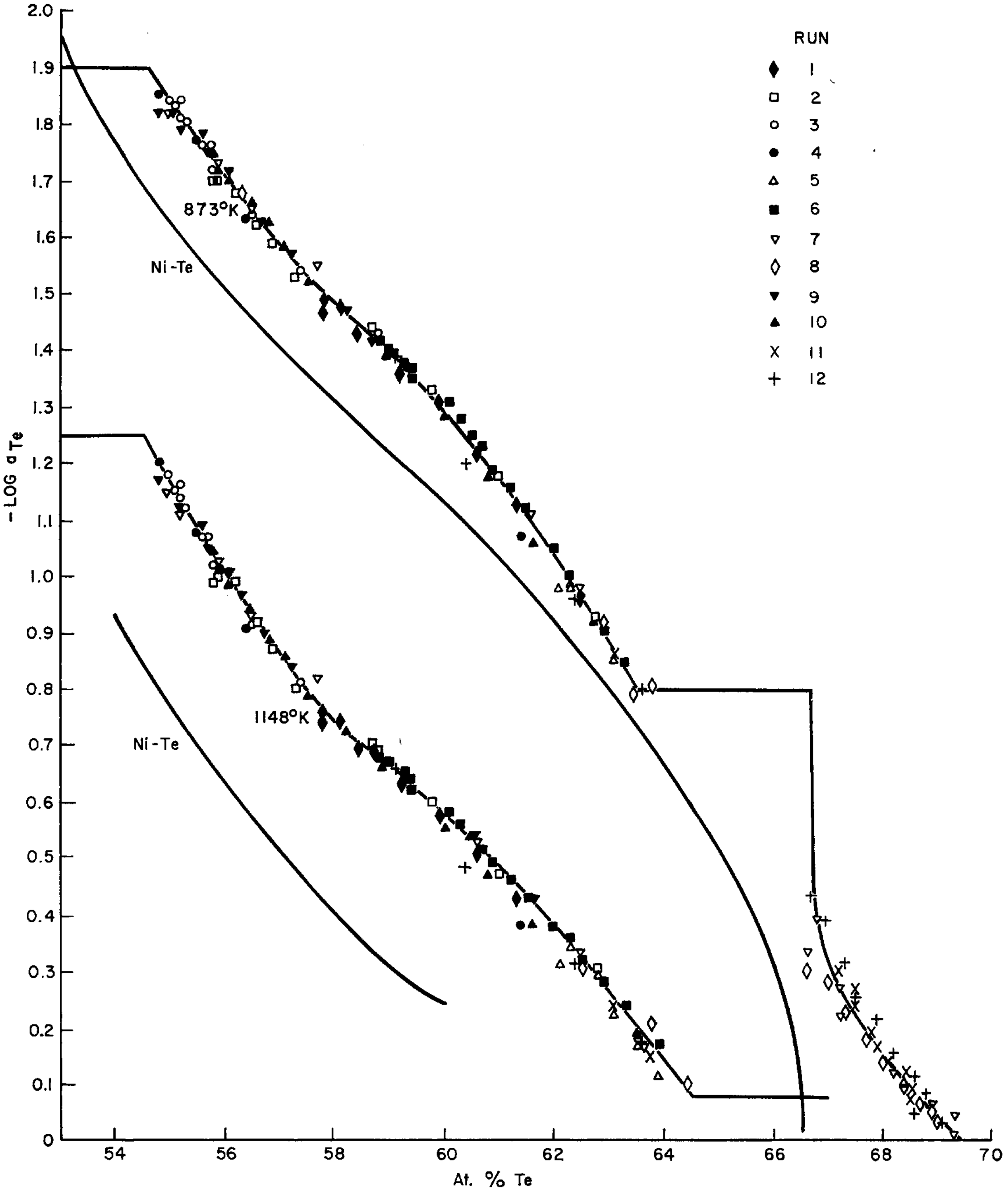

FIG. 2. Tellurium activities in the Co–Te system at 600 and 875°C.

the value of Ariya *et al.* (*6*) at 900°C (54.5 at. % Te), the value of Haraldsen *et al.* (*5*) at 600°C (54.5 at. % Te), and the value of Dudkin *et al.* (*7*) at 600°C (54.3 at. % Te). For the Te-rich boundary of this phase the values observed in this study are 64.0 ± 0.5 at. % Te at 660°C, 64.6 ± 0.4 at. % Te at 694°C, and 65.1 ± 0.3 at. % Te at 718°C. This is again in good agreement with the arithmetic mean of the value of 64.3% at. % Te reported by Haraldsen *et al.* (*5*) at 600°C and the value of 62.1 at. % Te of Dudkin *et al.* (*7*), also at 600°C.

The major area of disagreement is the compound $CoTe_2$. The homogeneity ranges reported by Dudkin *et al.* (*7*) and Haraldsen *et al.* (*5*) are 66.8 to 67.8

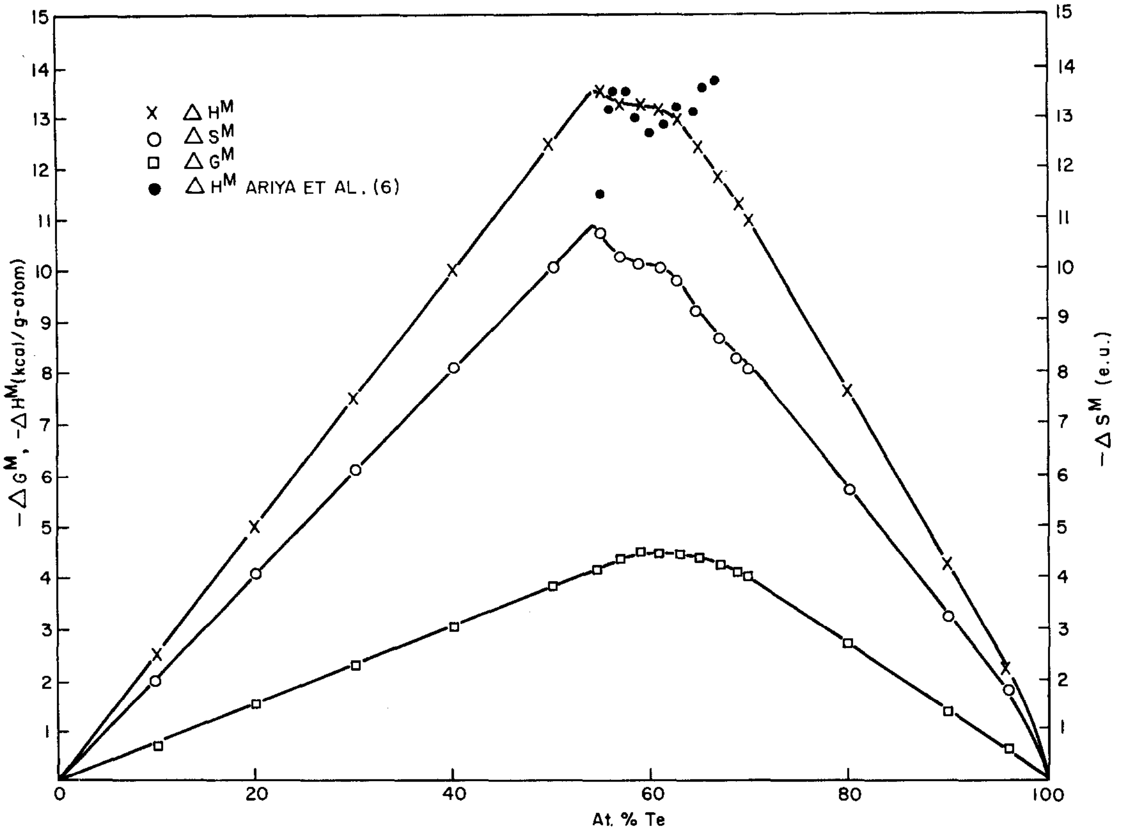

FIG. 3. Integral thermodynamic quantities of Co–Te alloys at 600°C.

at. % Te and 66.7 to 67.4 at. % Te, respectively. The maximum $CoTe_2$ solubility range determined in this study of 66.7 to 69.6 at. % Te is much wider.* It has to be emphasized that this composition range was attained after equilibration of thin 1-mil samples for over a month. Because of the low diffusivity in $CoTe_2$, it is unlikely that these results could be duplicated in bulk samples except with extremely long equilibration times. The results of this investigation indicate that the 1-mil samples were in thermodynamic equilibrium and, therefore, the boundaries shown in Fig. 1 are to be preferred to those found by previous investigators. $CoTe_2$ is stable at the stoichiometric composition and can accommodate a certain amount of excess tellurium atoms in the lattice, but no excess cobalt atoms. The homogeneity ranges of the β- and γ-phases suggested by Cambi *et al.* (*9*) are obviously in error.

As a consequence of the shift in phase boundaries the peritectic composition at 749°C of $CoTe_2$ is about 68 at. % Te. The retrograde solubility of tellurium in CoTe above the peritectic temperature is most probably not as pronounced as observed by Dudkin *et al.* (*7*), since the peritectic line ends at about 66 at. % Te.

The breaks in the specimen temperature–composition curves of Runs 9 and 10 at the $L/(L+\beta)$ boundary in Fig. 1 are about 10°C lower than the published liquidus (*2*). Since the congruent melting point of CoTe was not determined with very high accuracy by Dudkin *et al.* (*7*), the liquidus curve in this region should be shifted to lower temperatures.

All the sample temperature–composition curves in Fig. 1 are of similar shape with an inflection point in the CoTe phase field. From the isothermal activity–composition plot in Fig. 2 the composition of the inflection point can be estimated as about 58 at. % Te with an increasing slope of the activity curve above and below this composition. Such a behavior is characteristic of a partially disordered compound (*1*).

The activity curve of the $CoTe_2$ compound at 873°K in Fig. 2 has an almost vertical slope as it approaches the stoichiometric composition, indica-

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* Brostigen and Kjekshus (*18*) have made X-ray measurements on Cotez and a range of homogeneity from 66.5 ± 0.2 to 69.7 ± 0.2 at. % Te at 450°C which is in excellent agreement with the data reported in this paper.

tive of a highly ordered compound. The small scatter in the data points of Fig. 2 is most probably due to slight fluctuations of the sample composition about the equilibrium. Since the plot of reciprocal sample temperature vs reciprocal reservoir temperature is very sensitive to systematic deviations from equilibrium, the points would not fall on straight lines unless the deviations of the data points in Fig. 2 are about value which a mean constitutes true thermodynamic equilibrium.

The partial molar enthalpy of tellurium of the CoTe phase (Table I) is practically constant over the entire composition range with a tendency to decrease to less negative values at higher tellurium contents. The fairly constant $\Delta\bar{H}_{\mathrm{Te}}$ values are in general agreement with the observation of Ariya *et al.* (*6*)

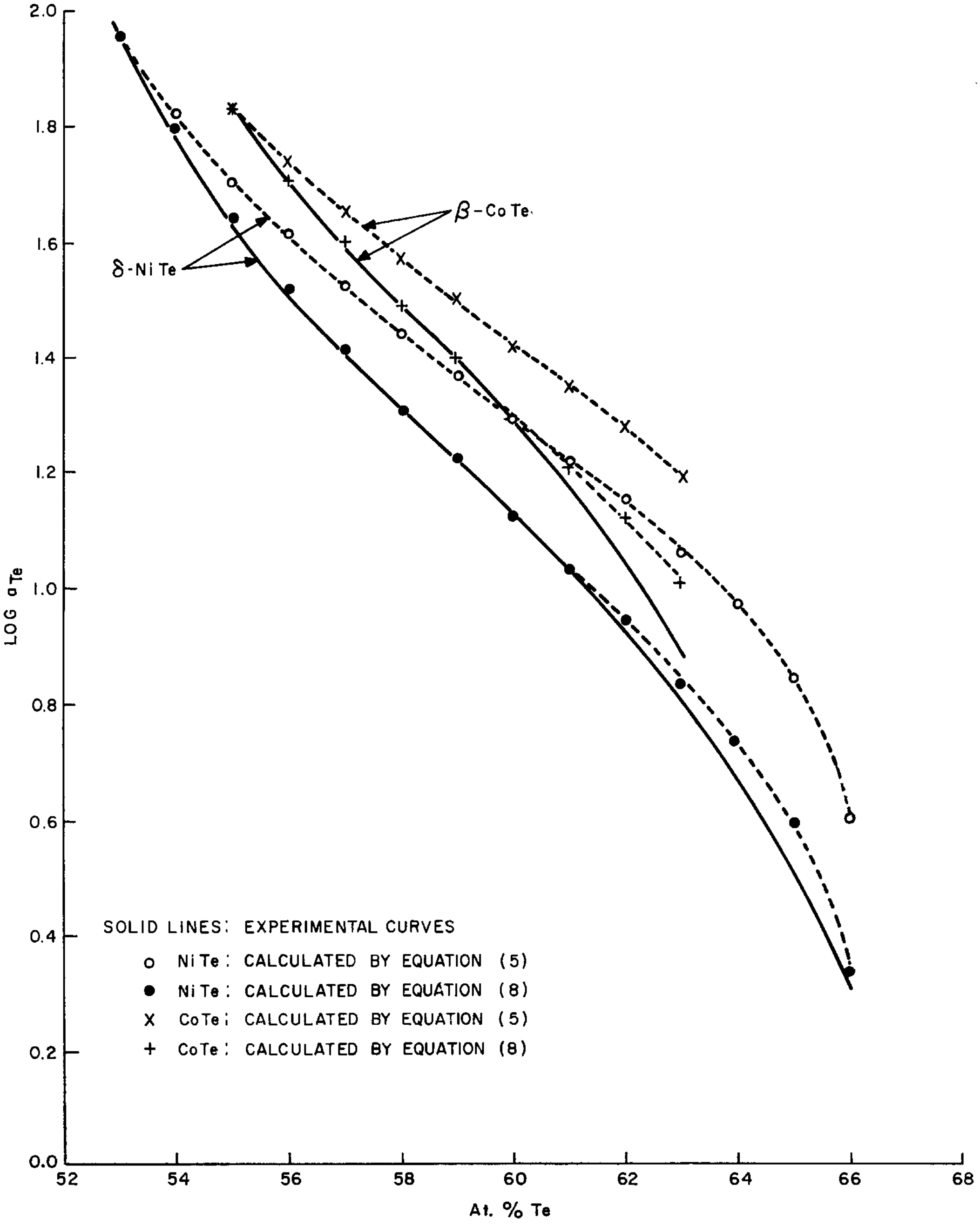

FIG. 4. Experimental and calculated activities of tellurium in δ-NiTe and β-CoTe at 600°C.

that at least over part of the range of homogeneity the enthalpies of formation of the CoTe phase vary linearly with composition. The variation of the partial molar enthalpies with composition in Table I clearly indicates the existence of a two-phase region between CoTe and $CoTe_2$. The integral molar free energies at 600°C in Fig. 3 were obtained by Gibbs–Duhem integration of the tellurium activities in Fig. 2. The most stable composition in the Co–Te system is that of the CoTe phase at about 60 at. % Te. However, the integral molar free energy of $CoTe_2$, is only slightly less negative.

Since no partial molar enthalpies of tellurium were obtained in the two-phase region between CoTe and Co, a Gibbs–Duhem integration based on our data alone could not be carried out. The enthalpies of formation of solid Co–Te alloys by Ariya *et al.* (*6*) were therefore recalculated for liquid tellurium as the standard state and on a kcal/g-atom basis and plotted in Fig. 3. The value of the intercept of the tangent to the curve for Co-rich alloys with the tellurium ordinate was found by drawing a line from 0 at. % Te to the ΔH values of Ariya at 54 at. % Te. The partial molar enthalpy was estimated as $\Delta\bar{H}_{Te} = -25$ kcal/g-atom and the Gibbs–Duhem integration performed. The integral molar enthalpies and the integral molar entropies plotted in Fig. 3 are unusually high compared with the integral molar free energies even if the enthalpy and entropy of fusion of tellurium are taken into account. As a consequence the ΔG^M value of the CoTe phase with the congruent melting point of about 1010°C at 57 at. % Te would be about zero at the melting point. Most probably the $\Delta\bar{H}_{Te}$ value for Co-rich alloys of −25 kcal/g-atom and therefore the enthalpies of formation of the Co–Te alloys are of smaller absolute magnitude than the values obtained by Ariya *et al.* (*6*) and should be redetermined. Gibart and Vacherand (*13*) estimated for $Co_{0.78}Te$ (56 at. % Te) at 600°C an integral free energy of formation of −17.5 kcal, most probably for one gram formula weight. This value will therefore equal −9.8 kcal/g-atom and has to be compared with our value of −4.2 kcal/g-atom at 600°C. Since the estimate by (*13*) is based on the enthalpies of formation of (*6*), the discrepancy is additional evidence that these values are too negative. It should be pointed out that our partial molar enthalpies $\Delta\bar{H}_{Te}$ are compatible with less negative ΔH^M values if for alloys in the CoTe phase field the ΔH^M values increase linearly with increasing tellurium concentration towards a maximum value at about 60 at. % Te.

In a previous paper (*1*) a statistical model was employed for the δ-NiTe (NiAs) phase assuming random distribution of transition metal atoms in the 00 1/2 layers of the hexagonal lattice. According to the model the following equations for the activities of cobalt and tellurium were derived:

$$\ln \lambda_{Co} = \ln\left(\frac{1 - 6\Delta N^*_{Te}}{8\Delta N^*_{Te}}\right) - \ln K - \frac{E_v}{kt} \tag{5}$$

$$\ln \lambda_{Te} = \ln\left\{\frac{(N_{Te} - 0.5)}{[N_{Te}(0.666 - N_{Te})]^{1/2}}\right\} + \text{const.} \tag{6}$$

K is the term for nonconfigurational contributions, E_v is the energy of formation of a vacancy in the 00 1/2 layer and $\Delta N_{Te} = N_{Te} - 0.5$. By matching the calculated and the experimental activities of tellurium in the Ni–Te system, good agreement could be obtained between the curves. Since β-CoTe also crystallizes in the NiAs-structure and the activity curves for δ-NiTe and β-CoTe are very similar in shape as can be seen in Fig. 2, the same model was employed.

For β-CoTe, the calculated and experimental points at 600°C were matched at 55 at. % Te, and both the experimental and calculated activities are shown in Fig. 4 together with the same values for δ-NiTe matched at 53 at. % Te. The shape of the calculated activity curve is qualitatively the same as that of the experimental curve for both phases and for both theoretical and experimental curves the point of inflection occurs at the same composition; however, there is an increasing deviation with increasing tellurium content, with the experimental curves having the steeper slopes.

According to Anderson (*17*), in nonstoichiometric compounds, interactions between defects may have a significant influence on thermodynamic properties. Such interactions will give rise to an additional vacancy interaction term,

$$\exp(-4E_i M_v^2/M_s kt),$$

which has to be included in the grand partition function (GPF) in Eq. 7 of the previous publication (*1*). E_i is the interaction energy between cobalt vacancies, M_s is the total number of lattice sites, and M_v is the number of unoccupied sites in the 00 1/2 layers. This introduces additional terms into the equations for the activity of cobalt and tellurium.

$$\ln \lambda_{Co} = \ln\left(\frac{1 - 6\Delta N^*_{Te}}{8\Delta N^*_{Te}}\right) - \frac{16E_i}{kT}\left(\frac{\Delta N^*_{Te}}{1 + 2\Delta N^*_{Te}}\right) - \ln K - \frac{E_v}{kT}, \tag{7}$$

$$\ln \lambda_{\mathrm{Te}} = \ln\left(\frac{(N_{\mathrm{Te}}-0.5)}{[N_{\mathrm{Te}}(0.666-N_{\mathrm{Te}})]^{1/2}}\right) - \frac{4E_i}{kT}\left(\frac{1-2N_{\mathrm{Te}}}{2N_{\mathrm{Te}}^{2}}\right) + \text{const.} \qquad (8)$$

These terms and equations supersede the related expressions in the previous paper (*1*) which are incorrect. Tellurium activities were calculated again by matching the calculated and experimental points as before. Perfect agreement could be obtained for δ-NiTe between 53 and 61 at.% Te with $E_i = 1020$ cal/g-atom and for β-CoTe between 55 and 60 at.% Te with $E_i = 1090$ cal/g-atom as can be seen from Fig. 4. Even at higher tellurium concentrations the fit between the experimental values and those calculated by Eq. (8) is much better with interaction than without interaction.

Based on the same model, the partial molar entropies of tellurium can be calculated from

$$\Delta \bar{S}_{\mathrm{Te}} = (\Delta \bar{H}_{\mathrm{Te}}/T) - R \ln \lambda_{\mathrm{Te}}. \qquad (9)$$

The $\Delta \bar{S}_{\mathrm{Te}}$ values listed in Table I have been obtained by using the experimentally determined $\Delta \bar{H}_{\mathrm{Te}}$ values and the activities of tellurium calculated by Eq. (8). The data indicate perfect agreement between experimental and calculated partial molar entropies between 55 and 60 at.% Te.

In conclusion one can say that in both NiAs-phases, β-CoTe and δ-NiTe, the defect mechanism is the same and the activity–composition relationships are very similar. Activities and partial molar entropies in the composition range of constant partial molar entropies can be perfectly explained by assuming random mixing of transition metal atoms and vacancies in the defected layers of the hexagonal lattice with some interaction between nearest neighbor vacancies.

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References

1. M. Ettenberg, K. L. Komarek, and E. Miller, *J. Solid State Chem.* **1**, 583 (1970).
2. R. P. Elliott, "Constitution of Binary Alloys, First Supplement," McGraw–Hill, New York, 1965.
3. I. Oftedal, *Z. Phys. Chem.* **128**, 135 (1927).
4. S. Tengnér, *Z. Anorg. Allg. Chem.* **239**, 126 (1938).
5. H. Haraldsen, F. Grønvold, and T. Hurlen, *Z. Anorg. Allg. Chem.* **283**, 143 (1956).
6. S. M. Ariya, E. M. Kolbina, and M. S. Apurina, *Zh. Neorg. Khim.* **2**, 23 (1957).
7. L. Dudkin and K. A. Dyul'dina, *Russ. J. Inorg. Chem.* **4**, 1056 (1959).
8. M. Chevreton, Ph.D. thesis, Lyon, 1964.
9. L. Cambi, M. Elli, and E. Giudici, *Chim. Ind.* (*Milan*) **51**, 795 (1969).
10. C. Fabre, *C.R. Acad. Sci. Paris* **105**, 277 (1887).
11. G. Moody and J. Thomas, *J. Chem. Soc., A*, 1417 (1964).
12. N. G. Eror and J. B. Wagner, *Acta Met.* **11**, 1339 (1963).
13. P. Gibart and C. Vacherand, *J. Crystal Growth* **5**, 111 (1969).
14. L. S. Brooks, *J. Amer. Chem. Soc.* **74**, 227 (1952).
15. R. F. Brebrick, *J. Phys. Chem.* **72**, 1032 (1968).
16. E. H. Baker, *J. Chem. Soc., A* 1558 (1967).
17. J. S. Anderson, *Proc. Roy. Soc. Ser. A* **185**, 69 (1946).
18. G. Brostigen and A. K. Jekshus, *Acta Chem. Scand.* **24**, 1925 (1970).