Enthalpy of Mixing of Liquid Ni-Zr and Cu-Ni-Zr Alloys

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The partial ($\Delta\overline{H}_i$) and the integral (ΔH) enthalpies of mixing of liquid Ni-Zr and Cu-Ni-Zr alloys have been determined by high-temperature isoperibolic calorimetry at 1565 $\pm$ 5 K. The heat capacity (C_p) of liquid $Ni_{26}Zr_{74}$ has been measured by adiabatic calorimetry ($C_p = 53.5 \pm 2.2$ J mol^{-1} K^{-1} at 1261 $\pm$ 15 K). The integral enthalpy of mixing changes with composition from a small positive (Cu-Ni; ΔH ($x_{\text{Ni}} = 0.50$, $T = 1473$ to 1750 K) = 2.9 kJ mol^{-1}) to a moderate negative (Cu-Zr; $\Delta H(x_{\text{Zr}} = 0.46$, $T = 1485$ K) = -16.2 kJ mol^{-1}) and a high negative value (Ni-Zr; $\Delta H(x_{\text{Zr}} = 0.37$, $T = 1565$ K) = -45.8 kJ mol^{-1}). Regression analysis of new data, together with the literature data for liquid Ni-Zr alloys, results in the following relationships in kJ mol^{-1} (standard states: Cu (l), Ni (l), and Zr (l)):for Ni-Zr ($1281 \leq T \leq 2270$ K),

$$\Delta\overline{H}_{\text{Ni}} = x^2 \left(\begin{array}{c} (333 \pm 55) + (-1.39 \pm 0.20) \cdot \dfrac{10^5}{T} + (-3.89 \pm 0.40) \cdot \dfrac{10^7}{T^2} + (-4468 \pm 226)\, x \\ + (1.29 \pm 0.36) \cdot \dfrac{10^5 x}{T} + (11{,}451 \pm 1178)\, x^2 + (-11{,}431 \pm 1473)\, x^3 + (4053 \pm 826)\, x^4 \end{array} \right)$$

$$\Delta\overline{H}_{\text{Zr}} = (1 - x)^2 \left(\begin{array}{c} (-130.0 \pm 7.9) + (-7.45 \pm 0.32) \cdot \dfrac{10^4}{T} + (-3.89 \pm 0.40) \cdot \dfrac{10^7}{T^2} + (-928 \pm 108)\, x \\ + (1.29 \pm 0.36) \cdot \dfrac{10^5 x}{T} + (5310 \pm 658)\, x^2 + (-8189 \pm 1302)\, x^3 + (4053 \pm 826)\, x^4 \end{array} \right)$$

$$\Delta H = x(1 - x)\, \alpha_{\text{Ni-Zr}}$$

$$\alpha_{\text{Ni-Zr}} = (-130.0 \pm 7.9) + (-7.45 \pm 0.32) \cdot \frac{10^4}{T} + (-3.89 \pm 0.40) \cdot \frac{10^7}{T^2} + (-464 \pm 54)\, x + (6.43 \pm 1.82) \cdot \frac{10^4 x}{T} + (1769 \pm 219)\, x^2 + (-2047 \pm 326)\, x^3 + (811 \pm 171)\, x^4$$

for Cu-Ni-Zr ($T = 1565 \pm 5$ K),

$$\Delta H = x_{\text{Cu}}\, x_{\text{Ni}} \alpha_{\text{Cu-Ni}} + x_{\text{Cu}} x_{\text{Zr}}\, \alpha_{\text{Cu-Zr}} + x_{\text{Ni}}\, x_{\text{Zr}} \alpha_{\text{Ni-Zr}} + x_{\text{Cu}} x_{\text{Ni}} x_{\text{Zr}} \alpha_{\text{Cu-Ni-Zr}}$$

$$\alpha_{\text{Cu-Ni}} = (11.1 \pm 0.6) + (1.1 \pm 0.1)\, x_{\text{Ni}}$$

$$\alpha_{\text{Cu-Zr}} = (-42.9 \pm 5.2) + (-44.2 \pm 10.3)\, x_{\text{Cu}} + (30.2 \pm 10.6)\, x_{\text{Cu}}^5$$

$$\alpha_{\text{Cu-Ni-Zr}} = (-570.4 \pm 28.8) + (3010.9 \pm 184.9)\, x_{\text{Zr}} - (3349.8 \pm 268.6)\, x_{\text{Zr}}^2 + (-942.8 \pm 55.7)\, x_{\text{Ni}}^2$$

I. INTRODUCTION

SINCE the Al-Cu-Ni-Zr system is a basis for the production of bulk amorphous materials by rapid solidification techniques from the liquid state,[1,2] it is of great scientific interest to determine the partial and the integral thermodynamic functions of liquid and undercooled liquid alloys. Such data, as was pointed out previously,[3,4] are important in order to understand their extremely good glass-forming ability in multicomponent metallic systems as well as for processing improvements. In order to measure the thermodynamic properties of the Al-Cu-Ni-Zr quaternary, it is necessary to have reliable thermochemical data for its constituent binaries and ternaries first. In a series of articles, we have reported in detail the thermodynamic properties of liquid Al-Cu, Al-Ni, Cu-Ni,[5] Cu-Zr,[3] Al-Zr,[4] Al-Cu-Ni,[6] and Al-Cu-Zr[4] alloys. This article deals with the direct calorimetric measurements of the partial and the integral enthalpies of mixing of liquid Ni-Zr and Cu-Ni-Zr alloys and the heat capacity of liquid $Ni_{26}Zr_{74}$. In a subsequent article, we will present similar data for the liquid ternary Al-Ni-Zr and for the liquid quaternary Al-Cu-Ni-Zr alloys.

II. EXPERIMENTAL

The partial and the integral enthalpies of mixing of liquid Ni-Zr and Cu-Ni-Zr alloys were determined using a high-temperature isoperibolic calorimeter described previously.[7] The experiments were carried out under pure argon gas at atmospheric pressure. For the measurements, the thermocouples were made of Pt-6 pct Rh/Pt-30 pct Rh, and a thermopile

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Table I. Heat Content of the Reference Material ZrO_2 at 1565 ± 5 K

Bath Metal	Amount of Bath (n), mmol	Added Substance	Added Amount (Δn), mmol	Area (F), mV s mol^{-1}	Calibration Factor (W), kJ mol^{-1} mV^{-1} s	Heat Content of ZrO_2 ($\Delta H^{1565}{}_{298}$), kJ mol^{-1}
		Cu	2.187	2222	0.0229	—
Cu	76.033	Cu	2.647	2213	0.0229	—
		ZrO_2	1.122	3743	—	85.69
		Cu	1.770	1971	0.0258	—
Cu	74.755	Cu	1.978	2067	0.0246	—
		ZrO_2	1.029	3401	—	85.70
		Al	4.874	2025	0.0239	—
Al	84.211	ZrO_2	1.611	3612	—	86.34
		Al	4.696	2059	0.0235	—
		ZrO_2	1.115	3605	—	84.72
Al	75.482	Al	3.411	1671	0.0290	—
		ZrO_2	1.353	2771	—	80.39
		Al	4.259	1620	0.0299	—
		ZrO_2	1.795	2763	—	82.61
Al	71.400	ZrO_2	1.148	3066	—	82.51
		Al	3.956	1779	0.0272	—
		Al	3.337	1827	0.0265	—
		ZrO_2	1.091	3052	—	85.48
Al	76.789	Al	3.737	1731	0.0280	—
		ZrO_2	1.094	2943	—	83.30
		Al	3.430	1711	0.0283	—

$\Delta \hat{H}^{1565}_{298} = 84.1 \pm 2.0$ kJ mol^{-1}.

was made of W-5 pct Re/W-20 pct Re. The alloy samples were prepared from copper (99.999 pct purity), nickel (99.98+ pct purity), and zirconium (99.8+ pct purity). The Cu was from Alfa (Johnson Matthey GmbH, Germany), and the Al and Zr were from Goodfellow Cambridge Ltd., England. The heat effects were measured by successive dropping of solid samples (pure components) from 298 K through a charging tube into a zirconium oxide crucible containing the melt. The masses of the added samples of the pure components were so small that the composition change in the bath did not exceed 1 to 3 at. pct. This allows direct determination of the partial values of the enthalpies of mixing of all components, *i.e.*, Cu, Ni, and Zr, in the same experimental run. All samples in the charging magazine had a rod-shaped geometry with a diameter of 1 to 2 mm.

The partial enthalpies of mixing of liquid Ni-Zr alloys were measured using a method described previously.[8,9] The calibration factor of the initial bath alloy was determined by adding, at the beginning of each series of measurements, a few cylindrical ZrO_2 samples. These samples were from the same material as the reaction crucibles. The heat content of the ZrO_2 samples (ΔH^T_{298}) at the measuring temperature of 1565 ± 5 K, referred to 298 K, was determined in six independent measurements using pure copper and pure aluminum, respectively, as a bath and as a calibration material. The results are given in Table I.

The measurements in the ternary system were performed along two vertical sections of $x_{Ni}/x_{Zr} = 0.64/0.36$ and $x_{Ni}/x_{Zr} = 0.36/0.64$, with $0 \leq x_{Cu} \leq 1$, using the method described in Reference 9. Sometimes, the determination of the composition dependence of the calibration factor using a numerical solution of Eq. [7], given in Reference 9, is found to be unsuitable, because the sum of the areas under the time-temperature curves, which are due to the solution of each component, is equal to or near zero. Additional calibrations were, therefore, performed with ZrO_2 samples at the beginning, the middle, and the end of each series of measurements. The calibration factor increases linearly with the mole number of the liquid bath (Δn_Σ). A linear fit of these values determines $W(\Delta n_\Sigma)$. The composition dependencies of the partial ($\Delta \overline{H}_i$) and the integral (ΔH) enthalpies of mixing at constant measured temperature, in the range of 1565 ± 5 K, are calculated using the following relationships:

$$\Delta \overline{H}_{Cu} = -\Delta H^T_{289,Cu} + W(x)\, F_{Cu}(x) \quad [1]$$

$$\Delta \overline{H}_i = -\Delta H^T_{289,i} - \Delta H_{fus,i} + W(x)\, F_i(x),$$
$$i = \text{Ni and Zr} \quad [2]$$

$$\Delta H(x) = (1 - x)(1 - y)\, \Delta \overline{H}_{Ni}(x) + (1 - x)y\, \Delta \overline{H}_{Zr}(x) + x\, \Delta \overline{H}_{Cu}(x) \quad [3]$$

where F_i is the area under a temperature-time curve due to the dissolution of 1 mole of component i in the liquid bath, y is the mole fraction of Zr in the Ni-Zr alloy with $x = 0$, and $\Delta H_{fus,i}$ is the molar heat of fusion of a metal i (nickel or zirconium), where $x = x_{Cu}$. The values of the heat content of the components and the heat of fusion of Ni and Zr were taken from Reference 10. In Eq. [2], the differences between the unknown heat capacity in the undercooled liquid state and the known data in the crystalline state are not taken into account.

The heat capacity was measured using an adiabatic calorimeter. Details concerning the calorimeter setup and the measurement procedure have been described previously.[11]

Table II. Heat Capacity of Liquid $Ni_{26}Zr_{74}$

Sample 1			Sample 2		
Temperature, K	Heat Capacity, J mol^{-1} K^{-1}	Excess Heat Capacity, J mol^{-1} K^{-1}	Temperature, K	Heat Capacity, J mol^{-1} K^{-1}	Excess Heat Capacity, J mol^{-1} K^{-1}
1246	54.7	11.8	1262	52.3	9.4
1247	50.7	7.8	1266	54.1	11.2
1251	54.9	12.0	1268	56.4	13.5
1252	55.1	12.2	1270	52.9	10.0
1254	54.9	12.0	1276	55.4	12.5
1256	54.0	11.1	—	—	—
1259	48.4	5.5	—	—	—
1260	49.2	6.3	—	—	—
1261	54.5	11.6	—	—	—
1264	53.4	10.5	—	—	—
1265	55.5	12.6	—	—	—
1266	54.7	11.8	—	—	—
1269	54.9	12.0	—	—	—
1271	54.6	11.7	—	—	—
1273	52.4	9.5	—	—	—
1278	54.2	11.3	—	—	—

III. RESULTS AND DISCUSSION

A. *Liquid Ni-Zr Alloys*

The experimental data for the enthalpy of mixing of liquid Ni-Zr alloys[12–15] are rather limited, especially with respect to the temperature dependence of ΔH. Moreover, most of the calorimetric investigations are concentrated on Ni-rich alloys and were performed using alumina[12,13] or reaction crucibles with an inside surface lined with yttria.[15] These data seem to be too exothermic, because of the Zr side reaction with the alumina or the yttria. The most reliable data are by Rosner-Kuhn *et al.*,[14] which were determined by a levitation calorimeter both for Ni-rich alloys ($T = 1916$ K; $0 \leq x_{Zr} \leq 0.34$) and Zr-rich alloys ($T = 2270$ K; $0.46 \leq x_{Zr} \leq 1$). However, these results are not sufficient for an adequate analytical description of $\Delta H(x,T)$, especially if one takes into account a 10 pct composition error resulting from Ni evaporation during the measurements at 2270 K.[14] Some additional experimental investigations are required in order to firmly establish the partial and the integral enthalpy of mixing over a wide range of compositions and temperatures. Therefore, we have measured $\Delta \overline{H}_i$ and ΔH calorimetrically at 1565 K in the composition ranges of $0.08 \leq x_{Zr} \leq 0.15$ and $0.37 \leq x_{Zr} \leq 0.80$, using zirconia reaction crucibles. Additionally, the temperature dependence of the heat capacity of the lowest-melting eutectic composition ($Ni_{26}Zr_{74}$) was determined directly using an adiabatic calorimeter. The heat capacities of the pure liquid components used to calculate the excess heat capacity of liquid $Ni_{26}Zr_{74}$ were taken from Reference 16.

The results of the measurements are given in Tables II and III and are also shown in Figure 1, in combination with literature data,[12–15] as a function of $\Delta H/x(1 - x)$. It can be easily seen that the data of References 12, 13, and 15 (solid points) are more negative, due to side reactions of Zr with Al_2O_3 or Y_2O_3, than the results of Rosner-Kuhn *et al.*[14] or the new results (open points). The solid points are, therefore, omitted in the analytical description of $\Delta \overline{H}_i$ and ΔH of the liquid Ni-Zr alloys. The new experimental data measured at 1565 K are distributed parallel to the data at 1916 and 2270 K, and their values are about 20 kJ mol^{-1} more negative (Figure 1). Therefore, two or three terms are sufficient for an adequate description of the temperature dependence of ΔH. A simultaneous regression analysis of the partial and integral enthalpies of mixing at 1575 K, excess heat capacity at 1281 K, and literature integral enthalpy of mixing at 1916 and 2270 K results in the following relationships (in kJ mol^{-1}):

$$\Delta \overline{H}_{Ni} = x^2 \left(\begin{aligned} &(333 \pm 55) + (-1.39 \pm 0.20) \cdot \frac{10^5}{T} + (-3.89 \pm 0.40) \\ &\cdot \frac{10^7}{T^2} + (-4468 \pm 226)\, x + (1.29 \pm 0.36) \cdot \frac{10^5 x}{T} \\ &+ (11{,}451 \pm 1178)\, x^2 + (-11{,}431 \pm 1473)\, x^3 \\ &+ (4053 \pm 826)\, x^4 \end{aligned} \right) \quad [4]$$

$$\Delta \overline{H}_{Zr} = (1 - x)^2 \left(\begin{aligned} &(-130.0 \pm 7.9) + (-7.45 \pm 0.32) \cdot \frac{10^4}{T} + (-3.89 \pm 0.40) \\ &\cdot \frac{10^7}{T^2} + (-928 \pm 108)x + (1.29 \pm 0.36) \cdot \frac{10^5 x}{T} \\ &+ (5310 \pm 658)x^2 + (-8189 \pm 1302)x^3 \\ &+ (4053 \pm 826)x^4 \end{aligned} \right) \quad [5]$$

Table III. Enthalpies of Mixing of Liquid Ni-Zr Alloys

Added Element (i)	Added Amount (Δn_i), mmol	Mole Fraction (x_{Zr})	Area (F_I), mV s mol^{-1}	Partial Enthalpy ($\Delta \overline{H}_i$), kJ mol^{-1}	Integral Enthalpy (ΔH), kJ mol^{-1}
Starting amount (mmol): n_{Ni} = 74.544; n_{Zr} = 6.8513; T = 1565 K					
ZrO_2	1.1111	0.0842	2993	—	—
ZrO_2	0.9677	0.0842	3006	—	—
Ni	2.9341	0.0842	2068	−1.4	−16.6
Zr	1.0688	0.0827	−4491	−186.3	−17.3
Ni	2.7552	0.0869	2027	−0.7	−17.8
Zr	1.4974	0.0912	−4407	−189.5	−19.2
Ni	2.5728	0.0974	1916	−0.9	−20.8
Zr	1.5829	0.1035	−4365	−195.0	−21.6
Ni	3.0567	0.1096	1864	−0.1	−22.6
Zr	1.3209	0.1154	−4262	−194.6	−23.8
Ni	2.6325	0.1195	1825	−1.2	−24.3
Zr	1.1718	0.1238	−3788	−178.3	−24.5
Ni	3.2169	0.1272	1807	−3.1	−25.5
Zr	1.3242	0.1302	−3571	−167.4	−26.2
Ni	3.2680	0.1336	1808	−6.1	−26.6
Zr*	1.5193	0.1370	−4016	−198.7	−28.3
Ni*	3.1010	0.1408	1499	−3.9	−32.8
Starting amount (mmol): n_{Ni} = 11.804; n_{Zr} = 49.300; T = 1565 K					
ZrO_2	1.9039	0.8102	2798	—	—
ZrO_2	1.6280	0.8102	2772	—	—
Zr	2.2220	0.8102	1800	−4.8	−18.9
Ni	2.6819	0.7970	−570	−75.0	−20.7
Ni	2.9289	0.7639	−652	−78.5	−23.7
Zr	1.9151	0.7507	1732	−6.2	−23.7
Ni	2.9255	0.7392	−594	−77.6	−25.2
Ni	3.3123	0.7087	−519	−76.2	−26.9
Ni	3.3191	0.6788	−485	−76.2	−29.0
Zr	2.0039	0.6686	1517	−3.6	−27.8
Ni	3.7843	0.6579	−364	−72.6	−29.2
Ni	3.7945	0.6296	−424	−76.2	−32.4
Ni	3.7076	0.6038	−501	−81.0	−36.2
Zr	1.4218	0.5947	1090	−10.2	−36.9
Ni	3.8030	0.5863	−304	−72.9	−34.3
Ni	3.8797	0.5639	−399	−78.8	−38.6
Ni	4.1080	0.5424	−255	−72.4	−37.7
Zr	1.9326	0.5360	828	−14.5	−42.0
Ni	4.2546	0.5300	−305	−75.8	−40.5
Ni	4.4215	0.5100	−160	−68.1	−38.9
Ni	4.6362	0.4908	−141	−67.4	−40.8
Zr	1.9951	0.4854	751	−12.7	−41.4
Ni	4.4624	0.4811	−217	−72.4	−44.7
Ni	6.6212	0.4610	−23	−60.0	−40.9
Ni	6.3895	0.4393	−120	−66.5	−47.9
Zr	1.8778	0.4329	625	−19.4	−41.4
Ni	6.1833	0.4276	52	−55.1	−43.3
Ni	5.5563	0.4111	107	−51.7	−43.9
Ni	5.8051	0.3964	216	−45.5	−42.4
Zr	2.2308	0.3933	457	−33.4	−43.2
Ni	6.5394	0.3898	104	−52.4	−47.4
Ni	6.8973	0.3747	220	−46.5	−45.6
Zr	2.3557	0.3714	169	−51.4	−47.6

* Solid-liquid phase region.

$$\Delta H = x\,(1 - x)\,\alpha_{Ni-Zr}$$

$$\alpha_{Ni-Zr} = (-130.0 \pm 7.9) + (-7.45 \pm 0.32) \cdot \frac{10^4}{T} + (-3.89 \pm 0.40) \cdot \frac{10^7}{T^2} + (-464 \pm 54)\,x + (6.43 \pm 1.82) \cdot \frac{10^4 x}{T} + (1769 \pm 219)\,x^2 + (-2047 \pm 326)\,x^3 + (811 \pm 171)\,x^4 \quad [6]$$

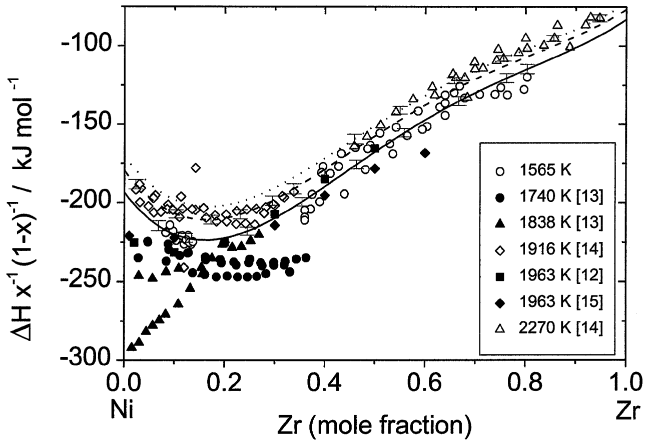

Fig. 1—Integral enthalpy of mixing of liquid Ni-Zr alloys divided by $x(1 - x)$ as a function of composition and temperature: points are experimental data; solid, dashed, and dotted lines result from Eq. [6] at 1565, 1916, and 2270 K, respectively; and vertical bars show confidence bands at tolerance 0.05. Standard states: Ni (l) and Zr (l).

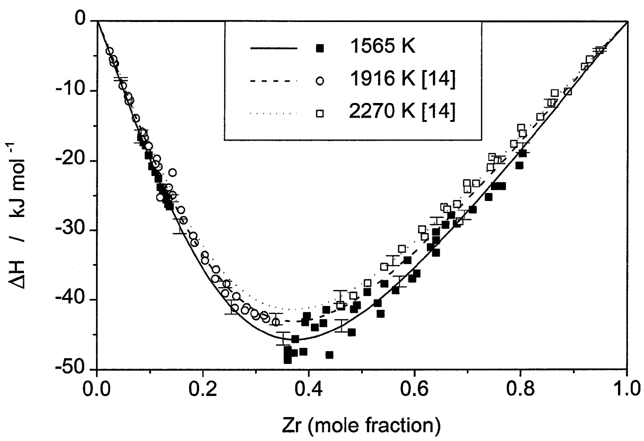

Fig. 2—The integral enthalpies of mixing of liquid Ni-Zr alloys: points are experimental data; lines result from Eq. [6] at 1565, 1916, and 2270 K; and vertical bars show confidence bands at tolerance 0.05. Standard states: Ni (l) and Zr (l).

where x is the mole fraction of Zr ($0 \leq x \leq 1$) and T is the temperature in Kelvin ($1565 \leq T \leq 2270$ K). It should be emphasized that, here and for Eqs. [7], [9] through [14], and [16] through [18], only those coefficients having standard errors less than one-half of their magnitudes were taken to be significant. The solid, dashed, and dotted lines in Figures 1 and 2 represent the values from Eq. [6] at 1565, 1916, and 2270 K, respectively.

The limiting partial enthalpies of mixing of Zr in undercooled liquid Ni and of Ni in undercooled liquid Zr, at 1565 and 2270 K, are −195 and −172 and −84 and −74 kJ mol^{-1}, respectively. The minimum of ΔH within the studied range of temperatures shows up near the composition of 37±3 at. pct Zr, with −45.7 and −41.4 kJ mol^{-1} at 1565 and 2270 K, respectively.

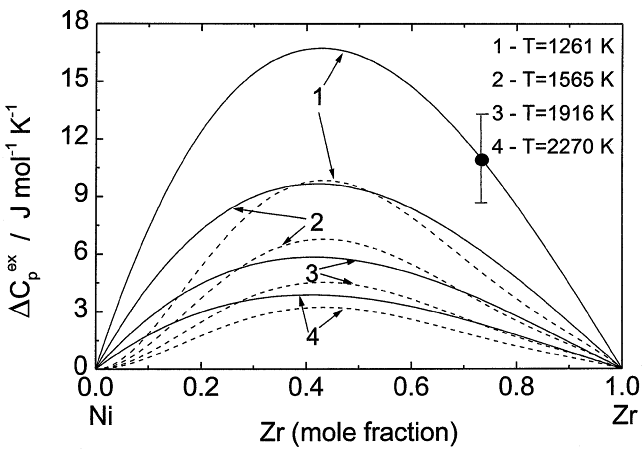

Fig. 3—Excess heat capacity of liquid and undercooled liquid Ni-Zr alloys: solid lines are new results according to Eq. [7]; dashed lines are results using Eq. [13] from Ref. 14, and the solid point is the mean value of the data given in Table II.

Finally, from Eq. [6], it follows that the excess heat capacity of the liquid Ni-Zr alloys ($\Delta C_p^{ex}(x,T) = d\Delta H(x, T)/dT$) is given by

$$\Delta C_p^{ex}(x, T) = x\,(1 - x)\,\frac{10^7}{T^2}\left((7.45 \pm 0.32) + \frac{7778 \pm 800}{T} + (-6.43 \pm 1.82)\,x\right)\quad (\text{j mol}^{-1}\ \text{K}^{-1}) \qquad [7]$$

The curves in Figure 3 are calculated from Eq. [7] (solid lines), in comparison to the results calculated using Eq. [13] from Reference 14 (dashed lines). The directly determined ΔC_p^{ex} of liquid $Ni_{26}Zr_{74}$ at 1261 ± 15 K agrees, within the experimental error, with the calculated one. The maxima of ΔC_p^{ex} show up in the same composition range as the minima of the integral enthalpy of mixing. The values of the maxima are about 30 pct higher than the respective ones given by Rosner-Kuhn *et al.*,[14] due to the consideration of the additional experimental results given in Tables II and III.

B. *Liquid Cu-Ni-Zr Alloys*

The results obtained for the partial and the integral enthalpies of mixing of the liquid ternary alloys of the vertical composition sections, with $x_{Ni}/x_{Zr} = 0.64/0.36$ and $x_{Ni}/x_{Zr} = 0.36/0.64$, are summarized in Tables IV and V, respectively. Figure 4 shows the composition dependencies of the experimentally determined partial enthalpies of mixing in combination with the same ones of the constituent binary alloys, *i.e.*, Cu-Zr,[3] Ni-Cu,[6] and Ni-Zr.

The partial functions for Ni, Cu, and Zr change gradually with the ratio x_{Ni}/x_{Zr}. From Figure 4(b), it follows that an anomalous variation of the partial enthalpy of mixing of zirconium in liquid Cu-rich alloys, which was discussed earlier in Reference 3, will also show up for the ternary alloys.

Figure 5 shows the composition dependencies of the integral enthalpy of mixing of the liquid Cu-Ni-Zr alloys. The points represent the values calculated from the three partial functions. The dashed lines are values calculated on the

Table IV. Enthalpies of Mixing of Liquid $Ni_{64}Zr_{36}$-Cu Alloys

Added Element (i)	Added Amount (Δn_i), mmol	Mole Fraction (x_{Cu})	Area (F_i), mV s mol^{-1}	Partial Enthalpy ($\Delta\bar{H}_i$), kJ mol^{-1}	Integral Enthalpy (ΔH), kJ mol^{-1}
Run 1: starting amount (mmol): n_{Cu} = 76.033; T = 1568 K					
ZrO_2	1.1220	1	3743	—	—
Cu	2.1873	1	2176	0	0
Cu	2.6467	1	2214	0	0
Ni	3.1107	0.9815	2883	7.7	−0.2
Zr	1.9042	0.9523	−162	−65.9	−1.1
Zr	1.7200	0.9324	−680	−78.7	−2.1
Ni	2.9932	0.9079	2464	1.3	−3.2
Cu	1.9009	0.8937	1999	−0.5	−3.8
Zr	1.2431	0.8889	−917	−85.2	−4.4
Ni	2.3356	0.8722	2029	−8.3	−5.6
Ni	2.5009	0.8506	2059	−6.9	−6.5
Zr	1.424	0.8337	−901	−85.6	−7.2
Cu	2.4642	0.8298	1865	−1.9	−8.0
Ni	3.6337	0.8176	1951	−8.6	−8.0
Zr	1.9952	0.7959	−1052	−90.1	−9.4
Zr	2.3383	0.7802	−940	−87.4	−9.9
Ni	4.0716	0.7581	1613	−16.2	−11.2
Cu	2.5051	0.7471	1812	−1.1	−11.3
ZrO_2	1.0282	0.7471	3091	—	—
Zr	2.2703	0.7427	−816	−84.4	−11.5
Ni	3.7291	0.7244	1525	−17.9	−12.5
Ni	4.3901	0.7010	1496	−18.3	−13.3
Zr	2.5729	0.6819	−918	−87.9	−14.5
Cu	2.4516	0.6781	1782	−0.5	−14.3
Ni	4.4600	0.6700	1513	−17.3	−14.2
Zr	2.9774	0.6519	−904	−87.8	−15.8
Zr	3.4938	0.6370	−781	−84.4	−16.1
Ni	6.0988	0.6163	1272	−23.4	−17.8
Cu	2.0787	0.6062	1740	−0.4	−17.9
Zr	3.4422	0.6021	−772	−84.4	−17.7
Ni	5.9744	0.5843	1275	−22.9	−19.2
Ni	5.4514	0.5639	1355	−20.4	−19.5
Zr	3.1112	0.5494	−803	−85.7	−20.6
Cu	3.6428	0.5491	1693	−0.9	−20.4
ZrO_2	0.0982	0.5491	2812	—	—
Run 2: starting amount (mmol): n_{Ni} = 43.049; n_{Zr} = 24.595; T = 1568 K					
ZrO_2	1.0015	0	3404	—	—
Ni	3.3918	0	928	−37.4	−47.2
Zr	2.0412	0	−101	−64.5	−47.1
Cu	1.5342	0.0102	1927	−3.6	−47.4
Cu	1.3721	0.0294	2022	−1.1	−47.5
Ni	3.1346	0.0374	951	−36.7	−47.4
Zr	1.9141	0.0363	−395	−71.7	−47.7
Cu	2.1338	0.0482	2127	1.8	−47.4
Cu	2.0535	0.0719	2016	−0.6	−47.2
Cu	2.3808	0.0957	1871	−3.8	−46.8
Ni	3.4055	0.1061	989	−35.2	−46.0
Zr	2.0686	0.1029	−696	−79.6	−46.3
Cu	2.5838	0.1139	1997	−0.2	−45.8
Cu	2.812	0.1385	1884	−2.4	−44.9
Cu	3.0952	0.1639	1902	−1.1	−43.3
Ni	3.8143	0.1736	977	−34.4	−42.6
Zr	2.1026	0.1688	−827	−83.7	−43.3
ZrO_2	1.1394	0.1688	3091	—	—
Cu	2.3226	0.1759	1877	−1.3	−42.5
Cu	3.0685	0.1958	1952	1.4	−40.6
Cu	3.6381	0.2193	1959	2.6	−38.5
Ni	3.6286	0.2281	1204	−27.1	−36.4
Zr	2.1048	0.2227	−917	−87.1	−38.5

Table IV. Continued

Added Element (i)	Added Amount (Δn_i), mmol	Mole Fraction (x_{Cu})	Area (F_i), mV s mol^{-1}	Partial Enthalpy ($\Delta \overline{H}_i$), kJ mol^{-1}	Integral Enthalpy (ΔH), kJ mol^{-1}
Cu	3.6507	0.2321	2136	8.1	36.3
Cu	3.4288	0.2534	2143	9.5	−34.2
Cu	4.0598	0.2746	1958	5.4	−33.6
Ni	3.3152	0.2824	1101	−28.3	−33.2
Zr	1.8724	0.2770	−805	−85.2	−32.7
Cu	4.0283	0.2854	1913	4.7	−32.9
Cu	4.4343	0.3062	1932	6.5	−31.1
Cu	4.236	0.3264	1909	7.1	−29.9
Ni	3.3203	0.3324	1130	−25.7	−29.2
Zr	1.9733	0.3267	−828	−87.1	−29.6
Cu	4.2675	0.3336	1921	7.9	−29.4
Cu	4.1589	0.3508	1909	8.7	−28.6
ZrO_2	1.1167	0.3509	2713	—	—
Run 3: starting amount (mmol): n_{Ni} = 20.47; n_{Zr} = 11.71; n_{Cu} = 39.45; T = 1568 K					
ZrO_2	1.1930	0.5553	3418	—	—
Cu	1.4823	0.5552	1963	−2.6	−22.5
Cu	2.6467	0.5675	1941	−3.2	−23.1
Ni	3.494	0.5625	1642	−19.9	−22.9
Zr	1.993	0.5431	−1209	−91.8	−24.1
Zr	2.4709	0.5284	−1196	−91.7	−24.9
Ni	4.1141	0.5083	1524	−21.9	−24.9
Cu	2.0079	0.5017	1867	−3.8	−25.4
Zr	2.346	0.5009	−1131	−90.5	−25.1
Ni	3.9983	0.4842	1375	−25.1	−26.0
Ni	3.8688	0.4647	1442	−22.8	−25.6
Zr	2.2638	0.4505	−1260	−95.1	−26.5
Cu	2.2691	0.4515	1978	1.2	−27.1
Ni	4.8296	0.4474	1366	−24.1	−26.5
Zr	2.8492	0.4318	−1340	−97.9	−27.8
Zr	3.0432	0.4206	−1241	−95.8	−27.9
Ni	5.184	0.4060	1219	−26.4	−29.3
Cu	1.7703	0.4015	2016	5.4	−28.6
ZrO_2	1.2027	0.4015	2982	—	—
Zr	2.7242	0.4014	−1260	−97.1	−29.5
Ni	4.6235	0.3899	1126	−28.3	−30.8
Ni	4.7956	0.3760	1192	−25.8	−30.4
Zr	2.927	0.3652	−1116	−94.7	−31.8
Cu	2.3887	0.3668	1800	1.8	−31.2
Ni	5.247	0.3655	1159	−26.2	−30.9
Zr	3.0333	0.3551	−942	−90.1	−31.4
Zr	3.4192	0.3474	−868	−88.2	−31.4
Ni	5.9744	0.3369	1100	−26.4	−31.5
Cu	2.1196	0.3349	1693	1.3	−32.4
Zr	3.6692	0.3355	−831	−87.5	−31.8
Ni	6.4719	0.3253	996	−29.1	−32.4
Ni	5.1329	0.3143	993	−28.6	−31.9
Zr	2.9401	0.3071	−804	−87.9	−32.1
Cu	2.9504	0.3102	1854	8.6	−31.8
ZrO_2	1.3163	0.3103	2644	—	—

basis of smoothed functions of the partial enthalpy of copper using the following relation:

$$\Delta H_{y/(1-y)=\text{const}} = (1 - x)\left(\Delta H_{x=0} + \int_{x=0}^{x} \frac{\Delta \overline{H}_{Cu}(x)}{(1 - x)^2} dx\right) \quad [8]$$

where $x = x_{Cu}$. Both methods of calculation result in very close values. This confirms that the partial and the integral

Table V. Enthalpies of Mixing of Liquid $Ni_{36}Zr_{64}$-Cu Alloys

Added Element (i)	Added Amount (Δn_i), mmol	Mole Fraction (x_{Cu})	Area (F_i), mV s mol^{-1}	Partial Enthalpy ($\Delta \overline{H}_i$), kJ mol^{-1}	Integral Enthalpy (ΔH), kJ mol^{-1}
Run 4: starting amount (mmol): n_{Cu} = 74.755; T = 1566 K					
ZrO_2	1.0291	1	3432	—	—
Cu	1.7703	1	1971	0	0
Cu	1.9780	1	2067	0	0
Zr	1.8121	0.9887	590	−47.3	−1.1
Ni	2.3169	0.9637	2245	−3.4	−2.0
Zr	2.1706	0.9378	−27	−62.7	−3.3
Cu	1.7561	0.9264	1907	−1.4	−4.5
Zr	2.7878	0.9127	−93	−64.4	−4.5
Zr	3.1901	0.8828	−78	−64.1	−5.9
Ni	3.5145	0.8514	1678	−14.6	−7.7
Cu	1.5059	0.8368	1866	0.4	−7.4
Zr	2.6858	0.8269	−49	−63.4	−8.7
Zr	2.6924	0.8050	4	−61.9	−9.6
Zr	2.4523	0.7850	10	−61.7	−10.6
Ni	4.5111	0.7599	1289	−22.8	−11.4
ZrO_2	1.1313	0.7599	2899	—	—
Cu	1.5830	0.7458	1693	−1.2	−12.4
Zr	3.1594	0.7373	170	−56.9	−12.5
Zr	2.8415	0.7182	232	−55.1	−13.3
Zr	2.6727	0.7015	364	−50.9	−13.5
Ni	4.9847	0.6798	783	−36.1	−14.2
Cu	1.8159	0.6684	1605	−0.9	−14.8
Zr	3.0870	0.6628	637	−42.1	−14.0
Zr	3.7569	0.6457	594	−43.2	−15.4
Zr	3.6001	0.6281	674	−40.4	−15.9
Ni	5.8399	0.6071	403	−47.0	−16.9
Cu	2.0330	0.5973	1528	−0.7	−16.9
Zr	3.6001	0.5929	814	−35.2	−17.2
Zr	3.4894	0.5790	789	−35.7	−18.4
Ni	4.2181	0.5645	246	−51.8	−18.7
Zr	3.9202	0.5500	822	−33.9	−20.3
Zr	4.0517	0.5366	988	−27.9	−19.7
Ni	4.4276	0.5229	89	−57.1	−21.0
Cu	2.8214	0.5200	1300	−5.4	−21.2
ZrO_2	0.8846	0.5200	2402	—	—
Run 5: starting amount (mmol): n_{Ni} = 29.278; n_{Zr} = 32.970; T = 1568 K					
Zr	2.3526	0	1999	−3.0	−31.5
Ni	2.707	0	−794	−81.8	−32.4
Zr	2.4523	0	1902	−5.8	−33.2
Cu	1.7545	0.0122	1235	−12.7	−32.3
Cu	3.6743	0.0483	1275	−9.9	−31.4
Cu	3.4886	0.0927	1296	−8.2	−30.3
Cu	3.5547	0.1325	1141	−12.8	−29.9
Zr	2.7571	0.1492	1661	−7.8	−29.8
Ni	2.6218	0.1445	−678	−80.5	−29.9
Zr	2.3372	0.1405	1630	−8.8	−30.6
Cu	3.6019	0.1552	1191	−11.2	−29.2
Cu	3.4524	0.1865	1226	−9.9	−28.3
Cu	3.5342	0.2153	1252	−8.9	−27.4
Cu	3.8521	0.2436	1196	−10.3	−27.1
Zr	1.7182	0.2557	1757	−3.3	−24.6
Ni	2.4753	0.2507	−363	−70.8	−25.7
Zr	2.2703	0.2453	1682	−6.1	−26.2
Cu	4.7459	0.2583	1165	−11.0	−26.9
Cu	4.878	0.2885	1005	−15.3	−27.7
Cu	4.7679	0.3165	1121	−9.9	−25.7
Zr	2.3416	0.3267	1469	−8.3	−24.5
Ni	2.494	0.3206	−581	−79.4	−26.7
Zr	2.4786	0.3145	1347	−13.6	−27.4
Cu	5.1896	0.3245	1187	−6.9	−24.6
Cu	4.5759	0.3481	1006	−11.4	−25.9

Table V. Continued

Added Element (i)	Added Amount (Δn_i), mmol	Mole Fraction (x_{Cu})	Area (F_i), mV s mol^{-1}	Partial Enthalpy ($\Delta\overline{H}_i$), kJ mol^{-1}	Integral Enthalpy (ΔH), kJ mol^{-1}
Cu	5.7939	0.3713	1178	−1.9	−22.3
Zr	2.1958	0.3811	1207	−10.6	−22.8
Ni	2.7053	0.3749	−317	−71.8	−23.8
Zr	2.4764	0.3686	1014	−20.4	−27.5
Cu	4.8356	0.3752	1101	−4.5	−23.2
Cu	5.7797	0.3955	1090	−1.3	−21.9
Cu	4.7364	0.4144	816	−9.8	−25.7
Zr	2.2901	0.4199	919	−14.9	−21.4
Ni	3.2947	0.4132	−253	−71.0	−22.8

functions are determined correctly, and that their composition variations are consistent with the Gibbs–Duhem equation.

A least-squares regression analysis of the partial enthalpies of mixing of the ternary Cu-Ni-Zr alloys results the following relationships (in kJ mol^{-1}; $x = x_{Cu}$). Vertical section Cu-$Ni_{0.64}Zr_{0.36}$:

$$\Delta\overline{H}_{Cu} = (1-x)^2((-6.4 \pm 2.1) + (89.6 \pm 21.9)x + (-130.3 \pm 47.7)x^2)$$

$$\Delta\overline{H}_{Ni} = (11.1 \pm 0.6)x + (1-x)^2((-39.2 \pm 1.1) \qquad [9]$$

$$+ (-285.4 \pm 11.2)x^2 + (-2416.2 \pm 173.0)x^9) \qquad [10]$$

$$\Delta\overline{H}_{Zr} = (-51.4 \pm 2.9)x + (1-x)((-61.7 \pm 2.1) + (187.6 \pm 19.1)x + (119.0 \pm 36.5)x^2 + (-451.7 \pm 58.4)x^7) \qquad [11]$$

Vertical section Cu-$Ni_{0.36}Zr_{0.64}$:

$$\Delta\overline{H}_{Cu} = (1-x)^2(-15.1 \pm 1.2) \qquad [12]$$

$$\Delta\overline{H}_{Ni} = (11.1 \pm 0.6)x + (1-x)^2((-81.6 \pm 4.8) + (-137.8 \pm 55.5)x + (-429.6 \pm 123.8)x^2 + (-2044.9 \pm 800.1)x^9) \qquad [13]$$

$$\Delta\overline{H}_{Zr} = (-51.4 \pm 2.9)x + (1-x)((-4.9 \pm 1.9) + (92.5 \pm 17.7)x + (-163.6 \pm 32.9)x^2(-299.1 \pm 53.0)x^7) \qquad [14]$$

The experimental data of the integral enthalpy of mixing of the ternary alloys, together with the values of the constituent binaries,[3,5] were treated by means of a least-squares procedure, according to

$$\Delta H = x_{Cu}x_{Ni}\alpha_{Cu\text{-}Ni} + x_{Cu}x_{Zr}\alpha_{Cu\text{-}Zr} + x_{Ni}x_{Zr}\alpha_{Ni\text{-}Zr} + x_{Cu}x_{Ni}x_{Zr}\alpha_{Cu\text{-}Ni\text{-}Zr} \qquad [15]$$

where $\alpha_{Ni\text{-}Zr}$ was given previously by Eq. [6]. For the other α functions, the following relationships were found (T = 1565 K, in kJ mol^{-1}):

$$\alpha_{Cu\text{-}Ni} = (11.1 \pm 0.6) + (1.1 \pm 0.1)x_{Ni}$$

$$\alpha_{Cu\text{-}Zr} = (-42.9 \pm 5.2) + (-44.2 \pm 10.3)x_{Cu} \qquad [16]$$

$$+ (30.2 \pm 10.6)x_{Cu}^5 \qquad [17]$$

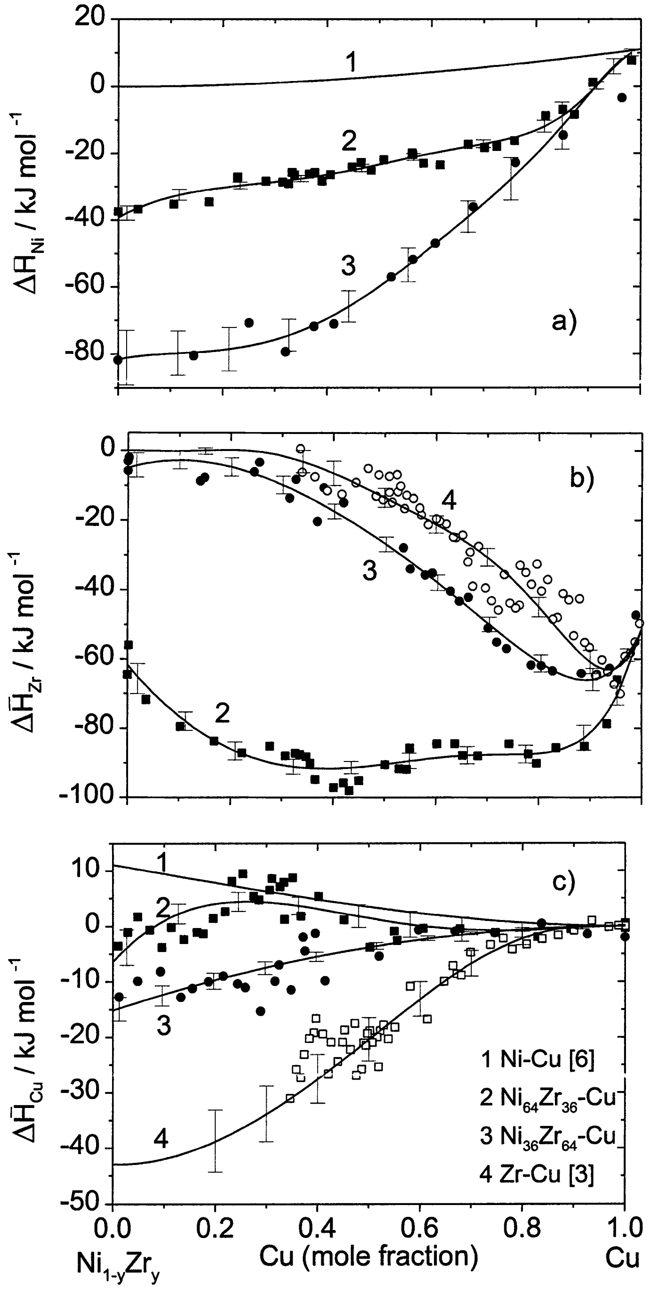

Fig. 4—(a) through (c) Partial enthalpy of mixing of (a) nickel, (b) zirconium, and (c) copper of ternary liquid and undercooled liquid Cu-Ni-Zr alloys at 1565 ± 5 K: vertical bars show confidence bands at tolerance 0.05. Standard states: Cu (l), Ni(l), and Zr (l).

$$\alpha_{Cu\text{-}Ni\text{-}Zr} = (-570.4 \pm 28.8) + (3010.9 \pm 184.9)x_{Zr} - (3349.8 \pm 268.6)x_{Zr}^2 + (-942.8 \pm 55.7)x_{Ni}^2 \qquad [18]$$

With a view to a direct use of the thermodynamic properties, the given Eqs. [4] through [7] and [9] through [18] adequately describe the experimental results (Figures 2, 4, and 5). The parameters of these analytical representations provide no physical significance.

The strong compound-forming tendency of the investigated alloys causes a chemical short-range order in the liquid state, which depends on composition and temperature. The

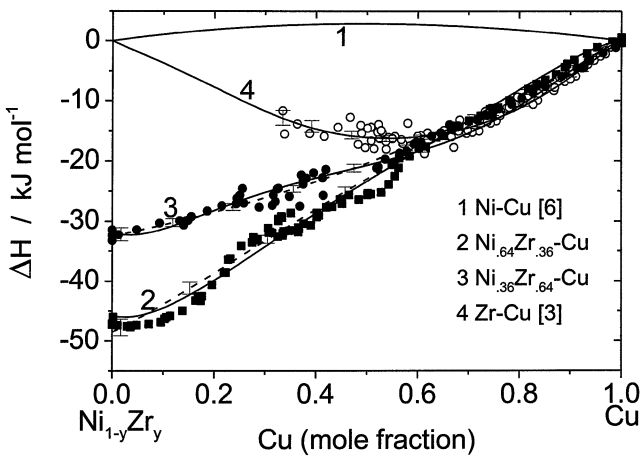

Fig. 5—Integral enthalpy of mixing of liquid and undercooled liquid Cu-Ni-Zr alloys at 1565 ± 5 K: points are measured values; solid lines result from Eq. [15]; dashed lines result from Eq. [8]; and vertical bars show confidence bands at tolerance 0.05. Standard states: Cu (l), Ni (l), and Zr (l).

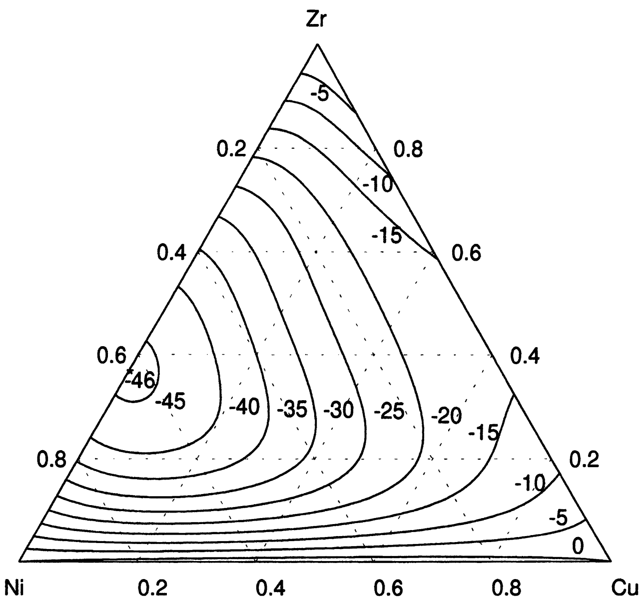

Fig. 6—Projection of the isoenthalpic lines on the Gibbs triangle of liquid and undercooled liquid Cu-Ni-Zr alloys at 1565 ± 5 K (kJ mol^{-1}).

association model describes the relation between the chemical short-range order and the thermodynamic properties, as has been shown for liquid Ni-Zr[17] and Cu-Ni-Zr.[18] The thermodynamic functions of the liquid ternary alloys are calculated on the basis of the model parameters of the three base binary systems.

A projection of the isoenthalpic lines on the Gibbs triangle of liquid and undercooled liquid Cu-Ni-Zr alloys, according to Eq. [15], is shown in Figure 6. The value of ΔH changes, with composition, from a small positive (Cu-Ni; $\Delta H(x_{\mathrm{Ni}} = 0.50) = 2.9$ kJ mol^{-1}) to a moderate negative (Cu-Zr; $\Delta H(x_{\mathrm{Zr}} = 0.46) = -16.2$ kJ mol^{-1}) and a high negative value (Ni-Zr; $\Delta H(x_{\mathrm{Zr}} = 0.37) = -45.8$ kJ mol^{-1}). The contribution of the fourth term of Eq. [15], which partly describes the ternary interactions, is shown separately in Figure 7. Obviously, the strongest attractive ternary interactions in this system show up at about $Ni_{60}Cu_{25}Zr_{15}$.

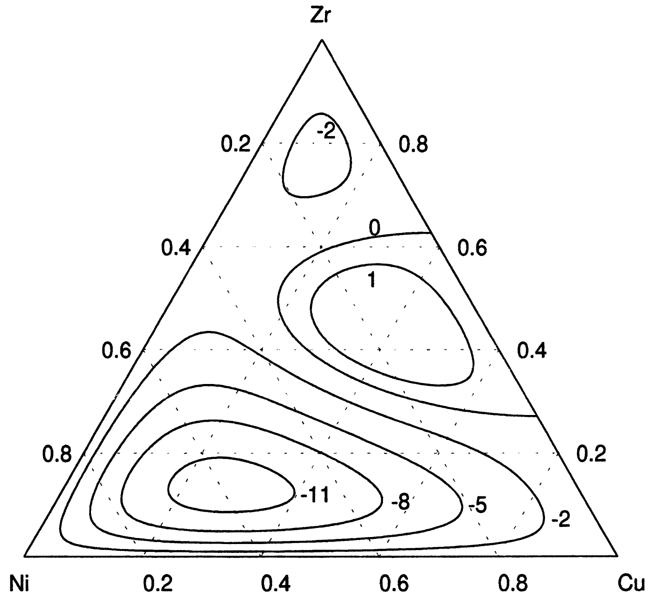

Fig. 7—Contribution of the fourth term of Eq. [15], which partly describes the ternary interactions of the integral enthalpy of mixing of liquid and undercooled liquid Cu-Ni-Zr alloys at 1565 ± 5 K (in kJ mol^{-1}).

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