

Thermodynamic evaluation of the Ni–Zn system

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Abstract

Optimization of thermodynamic and phase diagram data about the solid and liquid Ni–Zn alloys is performed. The temperature and concentration dependences of the Gibbs free excess energy is described by means of polynomials. The calculated phase boundaries are compared with the experimental boundaries.

1. Introduction

The phase diagram of the Ni–Zn system (Fig. 1) was studied experimentally and the results summarized by Hansen and Anderko [1]. Later we continued the construction of the Ni–Zn equilibrium diagram by investigating its nickel-rich part [2].

We have recently performed a thermodynamic evaluation of the equilibria between liquid and solid (f.c.c. structure) Ni–Zn solutions [3].

The aim of the present study was to evaluate the temperature and composition dependences of the Gibbs free excess energy (integral value) G^E , and partial values (\bar{G}_{Zn}^E and \bar{G}_{Ni}^E) on the basis of the available thermochemical data, including that obtained using thermodynamic coupling of the equilibrium phase boundaries.

The equilibrium concentrations at the horizontal lines were calculated considering, in pairs, two phase equilibria only at fixed temperatures, taken from the experimental phase diagram.

2. Analytical description of thermodynamic properties

In order to carry out a study properly, the temperature dependence of the phase stabilities G^0 for the pure constituents, conventionally referred to their stable phases at $T=298.15$ K and $P=101\,325$ Pa, should be determined. Following the usual conventions the reference phases used were nickel (f.c.c.; α phase) and zinc (h.c.p.).

Table 1 contains the coefficients for calculation of the free molar Gibbs energies (phase stability) for pure nickel (f.c.c.), nickel (liquid), nickel (b.c.c.) [4, 5] and

for zinc (liquid), zinc (f.c.c.), zinc (b.c.c.) and zinc (h.c.p.) [6]. The phase stability parameters of b.c.c. nickel and b.c.c. zinc are used for the thermodynamic description of all the intermediate compounds (β , β_1 , γ and δ) in the Ni–Zn system.

The analytical representation of the molar excess Gibbs free energy $G^{E,\phi}$ for phase ϕ was performed with the approaches proposed by Bale and Pelton [7], Lukas *et al.* [8] and Tomiska [9] using the Margules [10] polynomial:

$$G^{E,\phi} = X(1-X)(U^{\phi}_0 + U^{\phi}_1X + U^{\phi}_2X^2 + \dots) \quad (1)$$

where ϕ is the phase, X is the mole fraction of zinc in the alloy and U^{ϕ}_i are the coefficients which are linearly dependent on the temperature.

The partial molar free excess energy of Gibbs for the constituents (e.g. the excess chemical potentials \bar{G}_{Zn}^E and \bar{G}_{Ni}^E) have been calculated using the following equations obtained through eqn. (1):

$$\begin{aligned} \bar{G}_{Ni}^{E,\phi} &= G^{E,\phi} - X \frac{\partial G^{E,\phi}}{\partial X} \\ &= X^2(U^{\phi}_0 + U^{\phi}_1(2X-1) + U^{\phi}_2(3X^2-2X) + \dots) \end{aligned} \quad (2)$$

$$\begin{aligned} \bar{G}_{Zn}^{E,\phi} &= G^{E,\phi} + (1-X) \frac{\partial G^{E,\phi}}{\partial X} \\ &= (1-X)^2(U^{\phi}_0 + U^{\phi}_12X + U^{\phi}_23X^2 + \dots) \end{aligned} \quad (3)$$

where $X = X_{Zn}^{\phi}$.

When necessary, the data on the partial excess free energies of zinc in the literature, referred originally to liquid zinc, have been transferred to the reference h.c.p. zinc state. For this purpose, the following equation, which we obtained from Spencer's [6] relationships (Table 1) was used:

TABLE 1. Phase stabilities of nickel and zinc (standard (f.c.c. nickel and h.c.p. zinc states; $T=273$ K; $P=101$ kPa) where $G^0 = a + bT + cT \ln T + dT^2 + eT^7 + f/T$ J mol⁻¹

Phase	Zn (L)	Ni (L)	Zn (α)	Ni (α)	Zn (b.c.c.)	Ni (b.c.c.)	Zn (h.c.p.)
a	-3629.1	11235.527	-4178.2	-5179.159	-3572.2	3535.925	-6459.2
b	161.624	108.457	98.8181	117.853	98.0015	114.298	100.5115
c	-31.38	-22.096	-20.7359	-22.096	-20.7359	-22.096	-20.7359
d	0.0	-4.8407×10^{-3}	-6.2551×10^{-3}	-4.8407×10^{-3}	-6.2551×10^{-3}	-4.8407×10^{-3}	-6.2551×10^{-3}
e	0.0	-3.82318×10^{-21}	0.0	0.0	0.0	0.0	0.0
f	0.0	0.0	-41631	0.0	-41631	0.0	-41631

TABLE 2. Excess Gibbs energy coefficients for the liquid (L) and solid (α , f.c.c.) solutions, as well as for the intermediate phases β , β_1 and γ of the Ni–Zn system (standard f.c.c. nickel and h.c.p. zinc states; $T=273$ K; $P=101$ kPa), where $U^{(\nu)}(T) = \lambda^{(\nu)} + \psi^{(\nu)}T$ ($\nu=0, 1, 2, \dots$)

Phase	ν	$\lambda^{(\nu)}$	$\psi^{(\nu)}$	Temperature range (K)
Liquid (L)	0	-6566	-6.9390	$T \geq 1313$
	1	-40470	-7×10^{-5}	
	2	-230154	189.6404	
Liquid (L)	0	-683706	659.9862	$1148 \leq T \leq 1313$
	1	2841052	-2766.7229	
	2	-3056979	2883.1789	
Liquid (L)	0	-1171896	951.0873	$T < 1148$
	1	372888	-301.3346	
	2	753566	618.8473	
Solid solution (f.c.c.; α)	0	-55403	19.5671	
	1	-24611	9.6836	
	2	-103469	84.5500	
β_1 (tetragonal; AuCu type)	0	205253	-86.2718	
	1	-983614	422.8278	
	2	-68910	44.6328	
	3	1414505	-578.4583	
β (b.c.c.; CsCl type)	0	5914654	-4613.0700	
	1	-3.592786×10^7	28024.52	
	2	70713418	-55567.7883	
	3	-46049488	36452.4498	
γ (Cu_5Zn_8 type)	0	734057	-525.4261	
	1	-2052113	1354.7102	
	2	1158304	-686.1924	
	3	29520	-66.5447	
δ (CoZn_{13} type)	0	-75076	31.1665	
	1	-36451	26.7484	
	2	-64521	47.3468	

$$\Delta G^{0, L \rightarrow \text{h.c.p.}} = -2829.9 - 61.1125T + 10.6441T \times \ln T - 6.2551 \times 10^{-3}T^2 - \frac{41631}{T} \text{ J mol}^{-1} \quad (4)$$

3. Results and discussion

3.1. Solid solutions (f.c.c.; α phase)

An optimization of the thermochemical data on the Ni–Zn solid solutions was performed earlier [3] using

the above-mentioned approaches [7–10]. In this study we reassessed our thermodynamic description including some supplementary data about the α – β_1 equilibria at 693 K [11] and 905 K [12].

Another reason for the reassessment is that recently proposed expressions for calculation of the free molar Gibbs energy of the pure nickel phases, namely f.c.c. nickel, liquid nickel and b.c.c. nickel [4, 5], were used (see Table 1) instead of those of Mey [13] applied in our previous work [3].

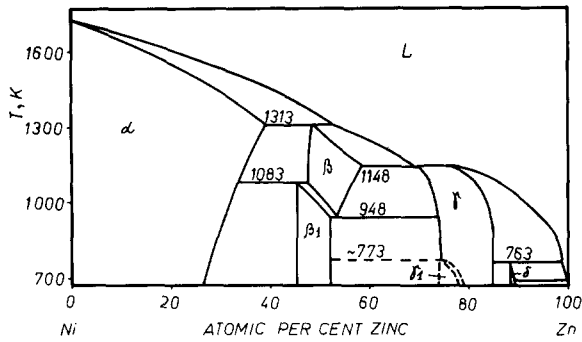


Fig. 1. The experimental Ni–Zn phase diagram [1, 2] used as the basis for the evaluation.

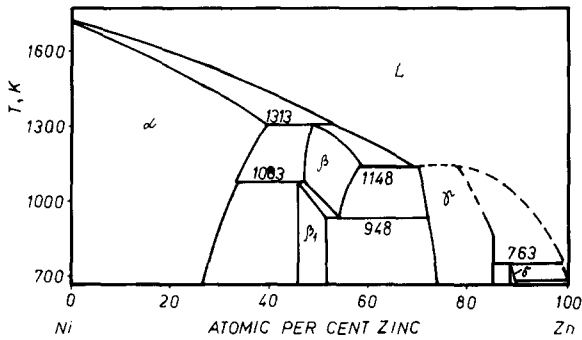


Fig. 2. The calculated equilibrium curves (—) and the γ –L phase boundaries (---) which could not be fitted by the present evaluation.

The new sets of polynomial parameters (Table 2) for the solid solutions (U^{α}_{ν}) and liquid solutions (U^L_{ν}) describe perfectly the liquidus–solidus lines between them (Figs. 1 and 2).

Table 3 contains calculated values of the excess partial molar Gibbs energies of nickel and zinc in the α phase, together with data from the literature [11, 14–16], all of them for $T=973$ K.

3.2. Liquid solutions (phase L; liquid)

3.2.1. Liquid solution–solid solution equilibria

The thermochemical data on Ni–Zn liquid solutions are very limited; in the literature we found only the study of Mozeva *et al.* [17], concerning weak concentrations of zinc. We used it [3] in order to obtain the set of polynomial coefficients describing the thermodynamic properties of the liquid phase above 1313 K (the peritectic temperature). These coefficients were reassessed in this work (Table 2) for the reasons already mentioned in Section 3.1.

Table 4 contains the experimental values \bar{G}^E_{Zn} calculated with the activity coefficients of zinc for $T=1748$ K given by Mozeva *et al.* [17] and the corresponding values obtained through eqn. (3) with the parameters from Table 2 (for $T>1313$ K). Satisfactory agreement between the two sets of results is observed.

TABLE 3. Experimental and calculated thermodynamic data on the solid Ni–Zn solutions (α phase) at 973 K (standard f.c.c. nickel and h.c.p. zinc states; $T=298$ K; $P=101$ kPa)

X_{Zn}	\bar{G}^E, α_{Zn} (J mol ⁻¹)	\bar{G}^E, α_{Ni} (J mol ⁻¹)	G^E, α (J mol ⁻¹)	Reference
0.1	–29720	–130	–3090	Vassilev [14]
0.1	–32480	–3610	–6600	Lyazgin <i>et al.</i> [15]
0.1	–30970	–110	–3200	Anantatmula and Masson [11]
0.1	–35120	–220	–3710	Vogelbein <i>et al.</i> [16]
0.1	–32430	–210	–3430	This work
0.2	–27840	–720	–6140	Vassilev [14]
0.2	–24950	–1910	–6520	Lyazgin <i>et al.</i> [15]
0.2	–27710	–700	–6100	Anantatmula and Masson [11]
0.2	–28260	–1170	–6590	Vogelbein <i>et al.</i> [16]
0.2	–28790	–850	–5960	This work
0.3	–26790	–1400	–9020	Vassilev [14]
0.3	–19340	–3780	–8450	Lyazgin <i>et al.</i> [15]
0.3	–20180	–3210	–8300	Anantatmula and Masson [11]
0.3	–22860	–3290	–9140	Vogelbein <i>et al.</i> [16]
0.3	–25090	–2100	–8990	This work

TABLE 4. Comparison between the experimental data [17] on the excess partial molar Gibbs energies of zinc in the liquid solutions and the present assessment, for $T=1748$ K (standard f.c.c. nickel and h.c.p. zinc states; $T=298$ K; $P=101$ kPa)

X_{Zn}	$\bar{G}^{E,L}_{Zn}(\text{exp})$ (J mol ⁻¹)	$\bar{G}^{E,L}_{Zn}$ (J mol ⁻¹)	X_{Zn}	$\bar{G}^{E,L}_{Zn}(\text{exp})$ (J mol ⁻¹)	$\bar{G}^{E,L}_{Zn}$ (J mol ⁻¹)
0.0191	–12010	–19370	0.0564	–18450	–19850
0.0227	–18040	–19460	0.0607	–19310	–19840
0.0227	–13940	–19460	0.0636	–20220	–19830
0.0258	–17160	–19530	0.0745	–16240	–19730
0.0382	–16600	–19740	0.0745	–16240	–19730
0.0395	–18250	–19760	0.0791	–16240	–19670
0.0395	–17740	–19760	0.08545	–17550	–19560
0.0473	–20220	–19830			

3.2.2. Liquid solutions: β phase equilibria

Because of the lack of thermochemical data about the liquid solutions for temperatures less than 1313 K, we were obliged to make use of the β –L equilibria curves only [1] in order to obtain the pertinent polynomial parameters shown in Table 2 (for the interval 1313–1148 K). The calculated and the experimental equilibria curves are plotted in Fig. 2 and Fig. 1 respectively. The reproduction of the liquidus line is very good and that of the solidus a little worse.

3.2.3. Liquid solutions: γ phase equilibria

No thermodynamic data about the liquid solutions with high zinc contents have been found; thus the

TABLE 5. Experimental or calculated thermodynamic data on the β_1 phase (standard f.c.c. nickel and h.c.p. zinc states; $T=273$ K; $P=101$ kPa)

$T=693$ K				
X_{Zn}	\bar{G}^E, β_1_{Zn} (J mol ⁻¹) (1)	\bar{G}^E, β_1_{Ni} (J mol ⁻¹) (3)	\bar{G}^E, β_1_{Zn} (J mol ⁻¹) (4)	\bar{G}^E, β_1_{Ni} (J mol ⁻¹) (4)
0.4550	-35990	-5870	-37020	-6010
0.4575	-36990	-5030	-35910	-6940
0.4675	-38260	-3940	-31440	-10790
0.4900	-28920	-12510	-21240	-20160
0.5000	-21600	-19680	-16700	-24610
0.5100	-13770	-27960	-12180	-29220
0.515	-10030	-31900	-9940	-31580
0.519	-7220	-34900	-8150	-33490
0.520	-	-	-7710	-33970

 $T=905$ K

X_{Zn}	\bar{G}^E, β_1_{Zn} (J mol ⁻¹) (2)	\bar{G}^E, β_1_{Ni} (J mol ⁻¹) (3)	\bar{G}^E, β_1_{Zn} (J mol ⁻¹) (5)	\bar{G}^E, β_1_{Ni} (J mol ⁻¹) (6)	\bar{G}^E, β_1_{Zn} (J mol ⁻¹) (4)	\bar{G}^E, β_1_{Ni} (J mol ⁻¹) (4)
0.455	-29570	-5630	-26410	-4490	-30200	-5830
0.460	-29450	-5800	-25560	-5240	-28260	-7470
0.470	-27460	-7520	-23540	-7260	-24320	-10890
0.480	-23690	-10930	-21170	-9400	-20360	-14470
0.490	-18790	-16340	-17930	-12460	-16390	-18220
0.495	-16140	-18920	-	-	-14400	-20150
0.500	-13440	-21590	-11470	-18810	-12420	-22110
0.505	-10840	-24210	-	-	-10440	-24110
0.510	-8390	-26740	-5130	-25260	-8470	-26140
0.520	-4320	-31060	-2060	-28510	-4570	-30290

(1) smoothed experimental data of Anantatmula and Masson [11]; (2) smoothed experimental data of Liang *et al.* [12]; (3) values of the excess partial molar Gibbs energies of nickel, calculated using the Gibbs–Duhem equation; (4) values calculated using the polynomial coefficients from Table 2 and eqns. (2) and (3); (5), (6) original data of Lau *et al.* [19].

TABLE 6. Experimental and calculated thermodynamic data on the β phase (standard f.c.c. nickel and h.c.p. zinc states; $T=298$ K, $P=101$ kPa)

$T=1100$ K					
X_{Zn}	\bar{G}^E, β_{Zn} (J mol ⁻¹) (1)	\bar{G}^E, β_{Ni} (J mol ⁻¹) (1)	\bar{G}^E, β_{Zn} (J mol ⁻¹) (2)	\bar{G}^E, β_{Zn} (J mol ⁻¹) (3)	\bar{G}^E, β_{Ni} (J mol ⁻¹) (3)
0.48	-12830	-8320	-13010	-16670	-12020
0.49	-10750	-10290	-10290	-13690	-14820
0.50	-8090	-12920	-7670	-11220	-17250
0.51	-5450	-15600	-4390	-9240	-19260
0.52	-3490	-17670	-3380	-7750	-20840
0.54	-960	-20490	-	-6160	-22620
0.56	+260	-22230	-	-6280	-22460

(1) data of Lau *et al.* [19]; (2) data of Liang *et al.* [21]; (3) values of the excess partial molar Gibbs energies of zinc and nickel, calculated with the polynomial coefficients from Table 2.

pertinent parameters (for $T < 1148$ K (Table 2)) were assessed from the L– γ equilibria curves [1]. However, unlike all other parameters in Table 2, they do not describe satisfactorily the corresponding γ –L phase

boundaries (Fig. 2). This might indicate that the γ –L phase boundaries need to be determined more accurately.

3.3. β_1 phase (f.c.t.; type AuCu [18])

The thermodynamic activities of zinc in the intermediate β_1 phase have been investigated by several workers [11, 12, 19, 20]. In order to obtain the activity coefficients γ_{Ni} of the nickel from the results of Anantatmula and Masson [11] ($T=693$ K) and those of Liang *et al.* [12], we integrated graphically the Gibbs–Duhem relation in the form

$$\ln \gamma_{Ni} = \int_0^X \frac{\ln \gamma_{Zn}}{(1-X)^2} dX - \frac{X}{1-X} \ln \gamma_{Zn} \quad (5)$$

where X is the mole fraction of zinc in the alloy. The results of the integration, together with the original data and the excess quantities obtained with the polynomial parameters (U^β , (Table 2)) and eqns. (2) and (3), are shown in Table 5. The original values of Lau *et al.* [19] are also given in Table 5 but are converted to the standard h.c.p. zinc and f.c.c. nickel states). The

phase boundaries between the β_1 phase and the adjacent α , β and γ regions are very well described (Figs. 1 and 2) with the pertinent sets of parameters represented in Table 2. The differences between the compositions of the experimental and calculated equilibrium curves are less than 2 at. %.

3.4. β phase (b.c.c.; type CsCl [18])

This is a high temperature phase, stable in the range 948–1313 K. Budurov and Wassilew [20] investigated the β and β_1 phase regions together; so their results are not convenient for our purpose here. The other experimental data available [19, 21] are for $T=1100$ K only.

The thermochemical properties of this compound were estimated from the interphase equilibria with the solid f.c.c. solutions and the β_1 phase. The corresponding set of polynomial parameters describe the phase boundaries between the β and the other adjacent phases moderately well (Figs. 1 and 2).

A comparison between the excess quantities estimated in this study and the experimental values [19, 21], converted to the standard h.c.p. zinc and f.c.c. model states is given in Table 6.

TABLE 7. Experimental or calculated thermodynamic data on the γ phase (standard f.c.c. nickel and h.c.p. zinc states; $T=298$ K; $P=101$ kPa)

$T=693$ K					
X_{Zn}	\bar{G}^E, γ_{Zn} (J mol ⁻¹) (1)	\bar{G}^E, γ_{Zn} (J mol ⁻¹) (2)	\bar{G}^E, γ_{Ni} (J mol ⁻¹) (3)	\bar{G}^E, γ_{Zn} (J mol ⁻¹) (4)	\bar{G}^E, γ_{Ni} (J mol ⁻¹) (4)
0.743	–	–9760	–30370	–11950	–30200
0.79	–9220	–9170	–39790	–6330	–48590
0.802	–8700	–8270	–43310	–5200	–53000
0.826	–5420	–5550	–55290	–3300	–61270
0.832	–4780	–4680	–59510	–2910	–63200
0.838	–4670	–3730	–64310	–2540	–65070
0.844	–3110	–2700	–69720	–2190	–66880
0.850	–810	–1605	–75920	–1880	–68620
$T=983$ K					
X_{Zn}	\bar{G}^E, γ_{Zn} (J mol ⁻¹) (5)	\bar{G}^E, γ_{Zn} (J mol ⁻¹) (4)	\bar{G}^E, γ_{Ni} (J mol ⁻¹) (4)		
0.7399	–6600 ± 5200	–7590	–26640		
0.7823	–5820 ± 3900	–4270	–37170		
0.8143	–5300 ± 3800	–2740	–43800		
0.8465	–2540 ± 2500	–1160	–50650		

(1) experimental data of Anantamula and Masson [11]; (2) smoothed experimental data of Anantamula and Masson; (3) values of excess partial molar Gibbs energies of nickel, calculated using the Gibbs–Duhem equation; (4) values calculated using the polynomial coefficients from Table 2; (5) experimental data of Budurov and Wassilew [20].

3.5. γ phase (γ -brass; type Cu_5Zn_8 [18])

According to the phase diagram [1] and some kinetic studies [22], one should be able to distinguish between the γ and γ_1 phases. However, the phase boundary between them is not well known [1] (Fig. 1), nor have the thermodynamic properties of the γ_1 phase been investigated. This is why we considered both compounds as one phase region (γ phase).

In order to obtain the nickel partial thermochemical properties in this compound, at 693 K, we integrated eqn. (5) through the γ phase region (0.743–0.85 mol Zn). In Table 7, the excess molar Gibbs energies of zinc and of nickel found in this way are compared with those assessed with the corresponding set of polynomial coefficients (Table 2). This table also contains the experimental data of Budurov and Wassilew [20] for $T=983$ K. The phase boundaries between the β_1 and β phases and the γ phase, calculated with the relevant

TABLE 8. Experimental and calculated enthalpies of formation for the δ phase (standard f.c.c. nickel and h.c.p. zinc states; $T=298$ K; $P=101$ kPa)

X_{Zn}	$\Delta H^F, \delta$ (J mol ⁻¹) (1)	$\Delta H^F, \delta$ (J mol ⁻¹) (2)	$\Delta H^F, \delta$ (J mol ⁻¹) (3)
0.884	–6000	–	–16210
0.884	–	–17890	–16210

(1) data of Ahmad and Pratt [23] for $T=355$ K; (2) data of Cunat *et al.* [24] for $T=650$ K; (3) temperature-independent value calculated (eqn. (6)) with the polynomial coefficients from Table 2, from equilibrium data in the range 693–763 K.

TABLE 9. Experimental [1] and calculated equilibrium values at the horizontal lines of the phase diagram Ni–Zn

Equilibrium	T (K)	Experimental concentrations (mole fraction of Zn)	Calculated concentrations (mole fraction of Zn)
Peritectic	1313	$X^\alpha=0.395$ $X^L=0.525$ $X^\beta=0.485$	$X^\alpha=0.395/X^L=0.525$ $X^\alpha=0.395/X^\beta=0.489$ $X^\beta=0.488/X^L=0.524$
$\alpha+L \leftrightarrow \beta$			
Peritectoid	1083	$X^\alpha=0.335$ $X^{\beta_1}=0.455$ $X^\beta=0.475$	$X^\alpha=0.314/X^{\beta_1}=0.454$ $X^\alpha=0.315/X^\beta=0.460$ $X^\beta=0.474/X^{\beta_1}=0.453$
$\alpha+\beta \leftrightarrow \beta_1$			
Eutectoid	948	$X^{\beta_1}=0.520$ $X^\beta=0.535$ $X^\gamma=0.740$	$X^{\beta_1}=0.512/X^\beta=0.549$ $X^{\beta_1}=0.510/X^\gamma=0.720$ $X^\beta=0.511/X^\gamma=0.720$
$\beta \leftrightarrow \beta_1 + \gamma$			
Eutectic	1148	$X^\beta=0.585$ $X^\gamma=0.700$ $X^L=0.690$	$X^\beta=0.585/X^L=0.690$ $X^\beta=0.585/X^\gamma=0.700$ $X^\gamma=0.700/X^L=0.690$
$\beta + \gamma \leftrightarrow L$			
Peritectic	763	$X^\gamma=0.850$ $X^\delta=0.884$ $X^L=0.990?$	$X^\gamma=0.850/X^\delta=0.884$
$\gamma+L \leftrightarrow \delta$			

polynomial parameters (Table 2), coincide rather well with the experimental values (Figs. 1 and 2.)

3.6. δ phase (type CoZn_{13} [18])

This is a low temperature, almost stoichiometric phase. The enthalpies ΔH^F of formation are available in the literature [23, 24] for $T=355$ K [23] and $623 < T < 673$ K [24]. They are compared (Table 8) with the results obtained with the polynomial coefficients from Table 2. The latter values were assessed from the γ – δ equilibria at 693 and 763 K.

To estimate the partial enthalpies $\Delta \bar{H}_i$, we used the temperature dependence of the thermodynamic activity a_i , assuming that $\Delta \bar{H}_i$ of the constituents (i and j are zinc and nickel respectively) are temperature independent:

$$\ln a_i = \frac{\Delta \bar{H}_i}{RT} + \text{constant} \quad (6)$$

The value that we found ($-16\,210 \text{ J mol}^{-1}$) is nearer to that of Cunat *et al.* [24] ($-17\,890 \text{ J mol}^{-1}$), probably because they worked in a temperature range (623–673 K) approaching the range where we have done our estimations (691–763 K).

4. Conclusion

Using the experimental equilibrium diagram and some thermochemical data available in the literature we evaluated the thermodynamic properties of the solid and liquid Ni–Zn phases. Sets of parameters for polynomial expressions describing the molar excess Gibbs free energy for the liquid and solid solutions, as well as for the intermediate compounds, were obtained and the corresponding equilibrium curves were calculated and compared with the experimental curves. An idea of the accuracy of the assessment could be obtained by comparing the experimental and the calculated equi-

librium values at the horizontal lines of the phase diagram Ni–Zn (Table 9).

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