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Mass-spectrometric determination of the thermodynamic mixing behavior of liquid ternary Fe–Ni–Cr alloys

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Abstract

Thermodynamic investigations on liquid ternary Fe–Ni–Cr alloys have been performed by means of the computer-aided Knudsen cell mass spectrometry. Ternary thermodynamically adapted power (TAP) series are used for the algebraic representation of the thermodynamic excess properties. At 1950 K, the molar excess Gibbs energy G^E is negative in the predominant part of Gibbs triangle (minimum value: -2980 J/mol at $x_{Ni}=0.55$, $x_{Cr}=0.45$), and positive only near the liquid binary Cr–Fe alloys (maximum value: 940 J/mol at $x_{Cr}=0.375$, $x_{Fe}=0.625$). The molar heat of mixing H^E is exothermic for nearly all Fe–Ni–Cr melts (minimum value: -4770 J/mol at $x_{Fe}=0.38$, $x_{Ni}=0.62$). Only the Cr-richest ternary melts near the Ni–Cr binary alloys are slight endothermic (maximum value: 80 J/mol at $x_{Ni}=0.125$, $x_{Cr}=0.87$). The molar excess entropy S^E is slight negative for ternary Fe–Ni–Cr melts near the two binary boundary systems Fe–Ni and Cr–Fe with a minimum S^E value of -1.27 J/mol K at $x_{Cr}=0.40$ and $x_{Fe}=0.60$, and slight positive at the side of binary Ni–Cr melts (maximum S^E value: 1.35 J/mol K at $x_{Ni}=0.50$, $x_{Cr}=0.50$).

The Fe-activities of liquid ternary Fe–Ni–Cr alloys as determined, in this work, show slight negative deviations from the ideal behavior in the range of composition below the section of constant mole fraction $x_{Cr}/x_{Ni}=1$, and slight positive deviations from Raoult's law above this section line. The Ni-activities of all ternary Fe–Ni–Cr melts show negative deviation from the ideal behavior. The Cr-activities show slight positive deviations from Raoult's law in the range of composition on the left-hand side of the section of constant mole fraction $x_{Ni}/x_{Fe}=1$, and slight negative deviations from the ideal behavior on the right-hand side of this section line. The results of this work can be used successfully for phase-diagram calculations. © 1998 Elsevier Science B.V.

Keywords: Activity; Mass spectrometry; Metals; Ternary alloys; Thermodynamics

1. Introduction

Ternary Fe–Ni–Cr alloys are of great technical and fundamental research interest as the basis for austenitic stainless steels. Nevertheless, in literature the only experimental data of the liquid phase have been the results of activity measurements at 1873 K by Belton and Fruehan [1], Gilby and St. Pierre [2], and Wagner et al. [3]. The authors had to carry out the very time-consuming mass-spectrometric investigations, and to determine experimentally the thermodynamic mixing behavior of the ternary system

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Fe–Ni–Cr. The aim of this work is to primarily investigate the molar excess functions, and the thermodynamic activities over the whole liquid phase. The thermodynamic evaluation has been performed by means of the digital intensity ratio (DIR) method [4].

2. Measuring technique and data evaluation

In the Knudsen cell mass spectrometry, the effusion of vaporized sample from an isothermal vessel, which is called the 'Knudsen cell', is applied for the determination of the molar mixing properties, and of the thermodynamic activities of alloy systems by means of the relation between the partial vapor pressures p_k, and the molar excess chemical potentials μ_k^{E} of the investigated components k,

$$\mu_k^{\mathrm{E}}(x_k, T) = RT[\ln[p_k(x_k, T)/(x_k p_k^0(T))]], \qquad (1)$$

where x_k is the mole fraction of component k, T the temperature in K, R the gas constant, and p_k^0 the vapor pressure of pure component k. Following this method, the Knudsen cell is employed as the 'gas source' of a high-temperature mass spectrometer, and the effusing vapor beam is directed into the ionization chamber of the mass spectrometer. This technique makes possible, in principle, the direct determination of the molar excess chemical potentials μ_k^{E}, because the ion-current intensities J_k^j of the characteristic isotopes j of the appropriate vapor species k are proportional to the partial pressures p_k,

$$p_k(x_k, T) = J_k^j(x_k, T)T/(D_k^j D_{\mathrm{I}}) \qquad (2)$$

(D_k^j is an isotope specific constant, and D_{I} the instrumental geometric constant sensitivity factor). Within the temperature ranges, in which the temperature dependence of the logarithms of the partial pressures of the components k may be assumed as inverse proportional to temperature, the measured ion-current intensities J_k can be fitted by $(d_k^0(x_k), d_k^1(x_k)$ are best-fit parameters):

$$\ln[J_k(T, x_k)T/D_{\mathrm{I}}] = d_k^0(x_k) + d_k^1(x_k)/T \qquad (3)$$

With liquid ternary Fe–Ni–Cr alloys, the difficulties caused by problems concerning the accurate actual value of the instrumental geometric factor D_{I}, can be overcome without any additional effort by applying the well-tried DIR method which is based on determining the thermodynamic mixing effects from the differences of the molar excess chemical potentials of the two alloy components Fe and Cr, because these differences are independent from the D_{I} constant, as can be verified easily. For the presented mass-spectrometric investigations, it has been convenient to determine the ion-current intensities of $^{56}\mathrm{Fe}^+$ and $^{52}\mathrm{Cr}^+$. Substituting from Eqs. (2) and (3) in Eq. (1) and forming the difference $\mu_{\mathrm{Fe}}^{\mathrm{E}} - \mu_{\mathrm{Cr}}^{\mathrm{E}}$ yields (x denotes dependence on both, x_{Fe} and x_{Cr})

$$\mu_{\mathrm{Fe}}^{\mathrm{E}} - \mu_{\mathrm{Cr}}^{\mathrm{E}} = RT[d^0(x) + d^1(x)/T - \ln(x_{\mathrm{Fe}}/x_{\mathrm{Cr}})] - {}^{\mathrm{t}}C_0^{\mathrm{G}}(T) \qquad (4a)$$

with

$${}^{\mathrm{t}}C_0^{\mathrm{G}}(T) := RT\ln[(D_{\mathrm{Fe}}p_{\mathrm{Fe}}^0)/(D_{\mathrm{Cr}}p_{\mathrm{Cr}}^0)], \qquad (4b)$$

and

$$d^i(x) := d_{\mathrm{Fe}}^i(x_{\mathrm{Fe}}) - d_{\mathrm{Cr}}^i(x_{\mathrm{Cr}})\ (i = 0, 1) \qquad (4c)$$

${}^{\mathrm{t}}C_0^{\mathrm{G}}(T)$ denotes in Eq. (4a) the calibration constant for the two components Fe and Cr in the liquid ternary Fe–Ni–Cr system whose value is determined by the actual ratings of the experimental set-up.

Employing Eq. (4b) as a regression formula for algebraic best fit of the mass-spectrometric data requires a suitable algebraic representation for the left-hand side of Eq. (4a). Useful expressions, for this purpose, are derived from the representation of the thermodynamic excess functions Z^{E} (Z^{E}=heat of mixing H^{E}, excess entropy S^{E}, excess Gibbs energy G^{E}) of ternary systems by means of the thermodynamic adapted power (TAP) series concept [4]:

$$Z^{\mathrm{E}} = {}^{\mathrm{t}}Z^{\mathrm{E}} + {}^{\mathrm{BBS}}Z^{\mathrm{E}} \qquad (5a)$$

where ${}^{\mathrm{t}}Z^{\mathrm{E}}$ is called 'ternary interaction term', a homogeneous polynomial in all three mole fractions x_j (${}^{\mathrm{t}}C_n^{\mathrm{E}}$ adjustable ternary parameters; n=1, 2, ...):

$${}^{\mathrm{t}}Z^{\mathrm{E}} = x_{\mathrm{Cr}}x_{\mathrm{Ni}}x_{\mathrm{Fe}}[{}^{\mathrm{t}}C_1^{\mathrm{Z}} + ({}^{\mathrm{t}}C_2^{\mathrm{Z}}x_{\mathrm{Fe}} + {}^{\mathrm{t}}C_3^{\mathrm{Z}}x_{\mathrm{Ni}} + {}^{\mathrm{t}}C_4^{\mathrm{Z}}x_{\mathrm{Cr}}) + \ldots]. \qquad (5b)$$

In Eq. (5a) the term ${}^{\mathrm{BBS}}Z^{\mathrm{E}}$ denotes the contributions of the three binary boundary systems j–k (j, k=1, 2, 3; 1=Fe, 2=Ni, 3=Cr):

$${}^{\mathrm{BBS}}Z^{\mathrm{E}} = {}^{\mathrm{Fe,Ni}}Z^{\mathrm{E}} + {}^{\mathrm{Ni,Cr}}Z^{\mathrm{E}} + {}^{\mathrm{Cr,Fe}}Z^{\mathrm{E}}. \qquad (5c)$$

Following the TAP concept the terms $^{j,k}Z^{\mathrm{E}}$ in Eq. (5c) are represented by

$$^{j,k}Z^{\mathrm{E}}(x) = x_j \sum_{n=1}^{N_j} j,kC_n x_k^n, \tag{6}$$

where N is the number of adjustable parameters $^{j,k}C_n$. The customary classification of binary alloys with respect to the complexity of their excess properties may be performed with more clarity: The TAP parameter $^{j,k}C_1$ and $^{j,k}C_2$ characterize the regular and subregular solution contributions. Interchange of the components (for old $x_k \rightarrow x_j$ and old $x_j \rightarrow x_k$: old $^{k,j}C_l \rightarrow$new $^{j,k}C_n$) may be performed by means of a simple formula:

$$^{j,k}C_n = \sum_{l=1}^{N} k,jC_1(-1)^{1-n}\binom{l-1}{n-1}, \quad (n = 1, 2, \ldots N). \tag{7}$$

The temperature dependence of the G^{E} values makes possible to determine the molar heat of mixing H^{E} and the molar excess entropy S^{E} in accordance with Eq. (3) by:

$$G^{\mathrm{E}}(T) = H^{\mathrm{E}} - T\,S^{\mathrm{E}}. \tag{8}$$

As the negative first derivative of the molar excess Gibbs energy G^{E} with respect to the mole fraction x_{Cr} is equal to the difference of chemical excess potentials of Fe and Cr$(\mu_{\mathrm{Fe}}^{\mathrm{E}} - \mu_{\mathrm{Cr}}^{\mathrm{E}})$, differentiation of Eq. (5a) in terms of G^{E} with respect to x_{Cr} yields:

$$\mu_{\mathrm{Fe}}^{\mathrm{E}} - \mu_{\mathrm{Cr}}^{\mathrm{E}} = -\partial G^{\mathrm{E}}/\partial x_{\mathrm{Cr}} = -[{}^{\mathrm{t}}C_1^{\mathrm{G}} x_{\mathrm{Ni}}(x_{\mathrm{Fe}} - x_{\mathrm{Cr}}) + \ldots] - \partial^{\mathrm{BBS}} G^{\mathrm{E}}/\partial x_{\mathrm{Cr}}. \tag{9}$$

The required regression formula is then obtained by substituting from Eq. (9) in Eq. (4c), and rearrangement:

$$-\,[{}^{\mathrm{t}}C_1^{\mathrm{G}} x_{\mathrm{Ni}}(x_{\mathrm{Fe}} - x_{\mathrm{Cr}}) + \ldots] - \partial^{\mathrm{BBS}} G^{\mathrm{E}}/\partial x_{\mathrm{Cr}} + {}^{\mathrm{t}}C_0^{\mathrm{G}}(T) = RT[d^0(x) + d^1(x)/T - \ln(x_{\mathrm{Fe}}/x_{\mathrm{Cr}})]. \tag{10a}$$

The corresponding TAP expression of $\partial^{\mathrm{BBS}}G^{\mathrm{E}}/\partial x_{\mathrm{Cr}}$ is obtained from Eqs. (5c) and (6):

$$\partial^{\mathrm{BBS}} G^{\mathrm{E}}/\partial x_{\mathrm{Cr}} = -\sum_{n=1}^{N_1} \mathrm{Fe,Ni}C_n x_{\mathrm{Ni}}^n + x_{\mathrm{Ni}} \sum_{n=1}^{N_2} \mathrm{Ni,Cr}C_n n x_{\mathrm{Cr}}^{n-1} + \sum_{n=1}^{N_3} \mathrm{Cr,Fe}C_n x_{\mathrm{Fe}}^{n-1}(x_{\mathrm{Fe}} - n x_{\mathrm{Cr}}). \tag{10b}$$

3. Experimental

Alloys preparation has been performed by induction melting in argon atmosphere in a centrifugal casting equipment. Zone melted iron (99.95%; 0.01% C), electrolytic chromium (99.99 wt.% Cr; Ni, Fe the rest), and nickel (Johnson and Matthey 99.99%, Si, Fe as impurities) were used as base materials. Finally, the samples were homogenized by casting in the cold cylindrical mold. Electron microanalysis confirmed the homogeneity and the composition of prepared samples.

The temperature range covered in these investigations was ca. 70–120 K. To prevent crystallization of the sample, the lower temperature limit was varied in relation to the composition of the sample. Data were collected by scanning the principal isotope peak ten times for one component and four times for background and the same for the other components. The temperature was then lowered to ca. 10–15 K, until the lowest end of the temperature was reached. Vacuum system consist of ion-discharge and ion-sublimation pumps and ensure the oil-free vacuum of the order 10^{-6} Pa. No oxidation of the sample surface was observed after the experiments. Check measurements of the sample composition after experiments by means of an electron microanalyser gave a good agreement for all ingots with the original sample compositions.

The Knudsen cell mass spectrometer employed, in this work, has been described elsewhere [5]. The simple monopole instrument model MX 7304 (Electron, Ukraine) having the mass range 2–200 amu was modified in the Institute of Physics of Materials ASCR. The Knudsen cell part of the combination with mass spectrometer consists of the alumina effusion cell containing the sample, which was closed by alumina lid having an orifice in diameter 1.2 mm. The alumina effusion cell is enclosed in an outer molybdenum cell with a tantalum lid, which is heated by a resistance furnace. The temperature of the sample in the effusion cell is measured with a Pt/PtRh10 thermocouple, calibrated by means of the melting points of several pure metals. Ions were formed by means of a 15 eV electron beam having a current of 50 μA. Detailed specifications and ratings of the experimental set-up are given in Ref. [5].

4. Results and discussion

The mass-spectrometric investigations, of this work, were performed in eight runs for four different alloy concentrations as presented in Table 1. The constants d^0 and d^1 summarized in Table 1 were computed according to Eq. (4c) from the corresponding $d^i_{\rm Cr}(x_{\rm Cr})$ and $d^i_{\rm Fe}(x_{\rm Fe})$ values of Eq. (3) (i=0, 1). These investigations, together with the mass-spectrometric measurements along the section with constant ratio of the mole fractions $x_{\rm Cr}/x_{\rm Ni}$ =1/5 recently reported (Table 1 in Ref. [6]) gave a total of 16 runs for eight different alloy concentrations for the first determination of the molar excess quantities $Z^{\rm E}$ of ternary Fe–Ni–Cr melts over the whole field of the liquid phase. The deviations of the experimental data from the computed regression lines (Eq. (3)) were never higher than 5%.

Table 1
Constants d^0 and d^1 of the regression formula (10a) computed by means of Eq. (4c) from the best-fit data (Eq. (3)) of the measured ion currents $J_{\rm Fe}$ and $J_{\rm Cr}$ as a function of the sample temperature T of the investigated ternary Fe–Ni–Cr melts ($x_{\rm Ni}$, $x_{\rm Cr}$ mole fractions of nickel and chromium, respectively)

Nr.	$x_{\rm Ni}$	$x_{\rm Cr}$	d^0	d^1
1	0.135	0.063	0.081	1681
2	0.135	0.063	−0.049	1853
3	0.277	0.122	−0.574	1239
4	0.277	0.122	−0.422	1050
5	0.409	0.187	−1.095	830
6	0.409	0.187	−0.996	749
7	0.535	0.255	−2.020	893
8	0.535	0.255	−1.891	752
9 [a]	0.302	0.057	0.400	950
10 [a]	0.302	0.057	0.546	789
11 [a]	0.440	0.080	0.145	474
12 [a]	0.440	0.080	0.119	435
13 [a]	0.558	0.111	−0.386	226
14 [a]	0.558	0.111	−0.361	109
15 [a]	0.685	0.138	−1.179	155
16 [a]	0.685	0.138	−1.068	16.5

[a] Experimental data from [6].

Table 2
Values of the TAP parameters ${}^{j,k}C_n$ of the binary boundary systems in the liquid phase ($C^{\rm G}_n = C^{\rm H}_n - C^{\rm S}_n T$). The conversion of the TAP parameter ${}^{j,k}C_n$ to the coefficients of any other polynomial representation may be performed by means of a simple modular procedure as developed in Ref. [10]

System j–k	Ref.	n	${}^{j,k}C^{\rm H}_n$/(J/mol)	${}^{j,k}C^{\rm S}_n$/(J/mol K)
Fe–Ni	[7]	1	−10500	−1.85
		2	−12000	−2.35
		3	−6000	−5.05
Ni–Cr	[8]	1	−3975	5.387
		2	5400	0
Cr–Fe	[9]	1	−4300	−3.00
		2	−3500	−3.80

The thermodynamic data of the liquid phase of the three binary systems are well established in literature: The Fe–Ni melts have been determined mass spectrometrically, and the TAP parameters of both the liquid Ni–Cr alloys as well as the Cr–Fe melts have been assessed by means of phase-boundary calculations based upon experimental data of the bcc and fcc phases. The resultant molar excess Gibbs energies of all three binary boundary systems have been used successfully for the calculations of the binary phase diagrams [7–9]. Using the TAP parameters as summarized in Table 2, the regression problem is, therefore, reduced to the adjusting of the ternary interaction only parameters in Eq. (10a). For the mean temperature T=1950 K in Fig. 1, it is shown that a satisfying overall best fit is achieved by using the simple homogeneous polynomial of third order as ternary interaction term (one adjustable parameter).

Following the DIR method a check of the accuracy of the regression results can be performed by using Eq. (11)

$$(H^{\rm E}_{\rm Fe} - H^{\rm E}_{\rm Cr}) + {}^{\rm t}C^{\rm H}_0(T) = Rd_1(x) \qquad (11)$$

for determining the heats of mixing $H^{\rm E}$ independently. In Eq. (11), ${}^{\rm t}C^{\rm H}_0(T)$ is the corresponding ternary $H^{\rm E}$-calibration constant for the two components Fe and Cr. The results of this best fit are presented in Fig. 2. Satisfactory accuracy of the best-fit data of this inves-

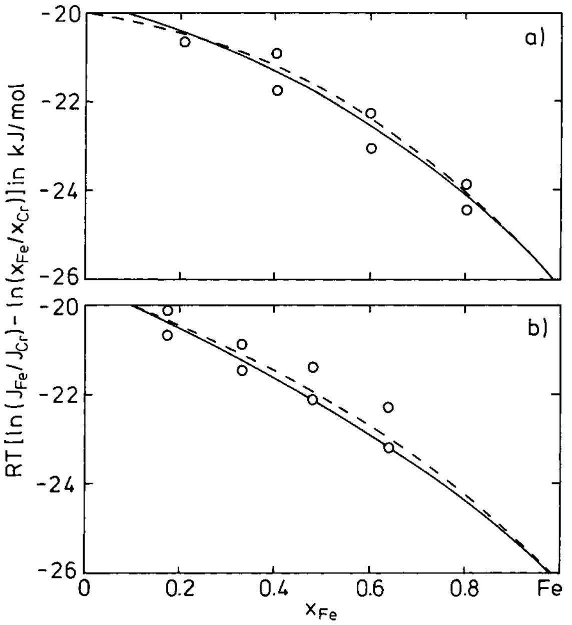

Fig. 1. $RT[d^0+d^1/T-\ln(x_{Fe}/x_{Cr})]$ as a function of the mole fraction x_{Fe} of liquid ternary Fe–Ni–Cr alloys at 1950 K (Overall best-fit curve based upon Eq. (10b) - - -; Experimental points ○; Curve based upon ternary interaction term $^{t}C_1$ optimized for phase-diagram computations ———). (a) x_{Cr}/x_{Ni}=0.46; (b) x_{Cr}/x_{Ni}=0.19 [6].

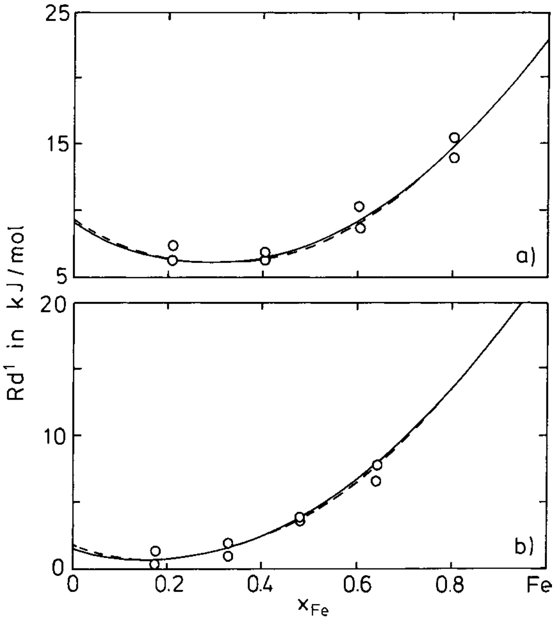

Fig. 2. (Rd^1) as a function of the mole fraction x_{Fe} of liquid ternary Fe–Ni–Cr alloys at 1950 K (Overall best-fit curve based upon Eq. (11) - - -; Experimental points ○; Curve based upon ternary interaction term $^{t}C_1$ optimized for phase-diagram computations ———). (a) x_{Cr}/x_{Ni}=0.46; (b) x_{Cr}/x_{Ni}=0.19 [6].

Table 3
Values of the ternary interaction terms $^{t}C_n$ of Fe–Ni–Cr alloys in the liquid phase ($^{t}C_n^{G} = {}^{t}C_n^{H} - {}^{t}C_n^{S}\,T$)

n	$^{t}C_n^{H}$/(J/mol)	$^{t}C_n^{S}$/(J/mol K)
1 [a]	43700	20.18
1 [b]	44900	21.42
0	−15290	−19.83

[a] Ternary interaction terms optimized for phase-diagram computations.
[b] Original overall best-fit parameters.

tigation is indicated by the small scattering of the experimental H^E data. Regression by Eq. (11) yields necessarily identical H^E data as obtained from the temperature dependence of the molar excess Gibbs energy G^E by means of Eq. (8).

The ternary interaction terms as obtained by means of the overall best fit, in this work, may be employed successfully for the ternary-phase equilibria computations. Nevertheless, slight modifications of these best-fit parameters have been proved as being effectful to obtain even better agreement between the computed phase boundaries, and the experimentally determined phase equilibria [11]. The numerical values of the ternary interaction terms optimized for phase-diagram computations, the original overall best-fit parameters, and the numerical values of the ternary calibration constants are presented in Table 3. A comparison shows that the values of the parameters $^{t}C_1^{H}$ and $^{t}C_1^{S}$ have been diminished only by 2.5 and 6%, respectively. The resultant modified curves are also plotted in Figs. 1 and 2. As can be seen from both Figs. 1 and 2, the modifications are within the scattering range of the measurements. It is satisfied and reasonable, therefore, to substitute the parameter values of the original overall best fit by means of the modified ternary interaction term as presented in Table 3.

The present mass-spectrometric investigations on Fe–Ni–Cr melts yield at 1950 K the molar heat of mixing H^E, the molar excess entropy S^E, and the molar excess Gibbs energy G^E, as displayed by means of contour lines in the Gibbs triangles of Figs. 3–5. The resultant thermodynamic activity of the components

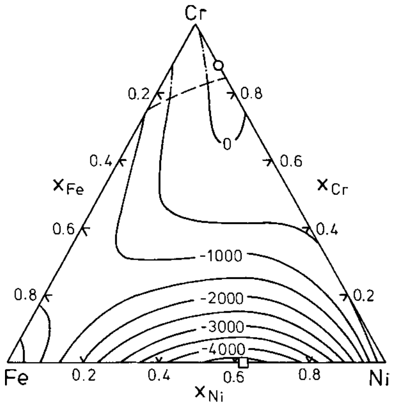

Fig. 3. Molar heat of mixing H^E of liquid ternary Fe–Ni–Cr alloys at 1950 K in J/mol (minimum value □; maximum value ○; liquid phase field boundary - - -; extrapolation - -).

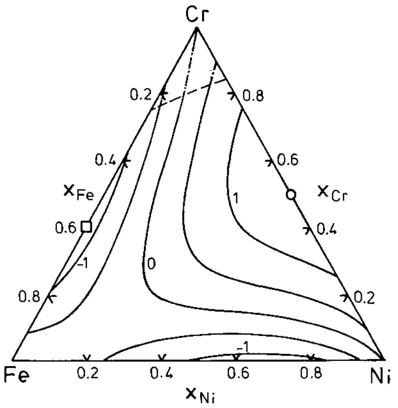

Fig. 4. Molar excess entropy S^E of liquid ternary Fe–Ni–Cr alloys at 1950 K in J/mol (minimum value □; maximum value ○; liquid phase field boundary - - -; extrapolation - -).

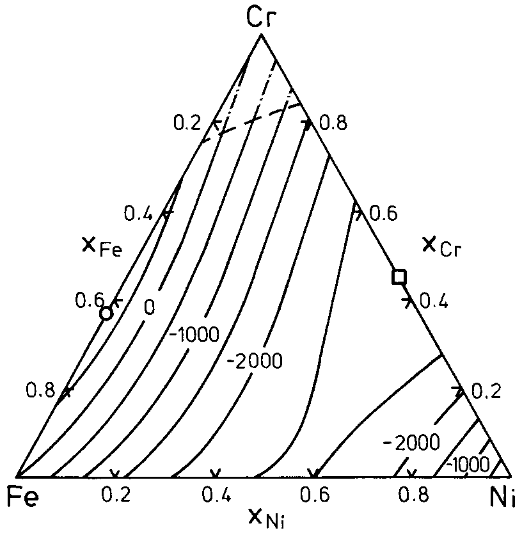

Fig. 5. Molar excess Gibbs energy G^E of liquid ternary Fe–Ni–Cr alloys at 1950 K in J/mol (minimum value □; maximum value ○; liquid phase field boundary - - -; extrapolation - -).

are presented in Fig. 6 by means of contour lines in the Gibbs triangle, too. As can be seen from Fig. 3, the investigations of this work yielded at 1950 K a molar heat of mixing H^E exothermic for nearly all Fe–Ni–Cr melts. Only the Cr-richest ternary melts near the Ni–Cr binary alloys are slight endothermic with a maximum H^E value of 80 J/mol (x_{Ni}=0.125, x_{Cr}=0.87), in the binary Ni–Cr melts. The minimum H^E value is −4770 J/mol (x_{Fe}=0.38, x_{Ni}=0.62), coinciding with the minimum H^E value of the binary Fe–Ni alloys. Fig. 4 shows that the molar excess entropy S^E is slight negative for ternary Fe–Ni–Cr melts near the two binary boundary systems, Fe–Ni and Cr–Fe, with a minimum S^E value of −1.27 J/mol K at x_{Cr}=0.40 and x_{Fe}=0.60, in the binary Cr–Fe alloys. The Ni–Cr based ternary Fe–Ni–Cr melts show slight positive S^E values. The maximum S^E value is identical with that of the binary Ni–Cr melts (1.35 J/mol K at x_{Ni}=0.50, x_{Cr}=0.50). The uncertainties of the data are ca. 5%.

As displayed in Fig. 5, the mass-spectrometric measurements on Fe–Ni–Cr melts of this work yielded at 1950 K molar excess Gibbs energy G^E negative in the predominant part of Gibbs triangle. Positive G^E values have been determined only near the liquid binary Cr–Fe alloys with a maximum G^E value of 940 J/mol at x_{Cr}=0.375, x_{Fe}=0.625, coinciding with the maximum G^E value of the binary Cr–Fe melts. The minimum G^E value of −2980 J/mol at x_{Ni}=0.55, x_{Cr}=0.45 is identical with the minimum G^E value of the binary Ni–Cr melts with an uncertainty of ca. 5%.

The Fe-activities of liquid ternary Fe–Ni–Cr alloys as determined in this work show slight negative deviations from the ideal behavior in the range of composition below the section of constant mole fraction x_{Cr}/x_{Ni}=1, and slight positive deviations from Raoult's law above this section line (Fig. 6(a)). The Ni-activities of all ternary Fe–Ni–Cr melts show negative deviation from the ideal behavior (Fig. 6(b)). As can be seen from Fig. 6(c), the Cr-activities show slight positive deviations from Raoult's law in the

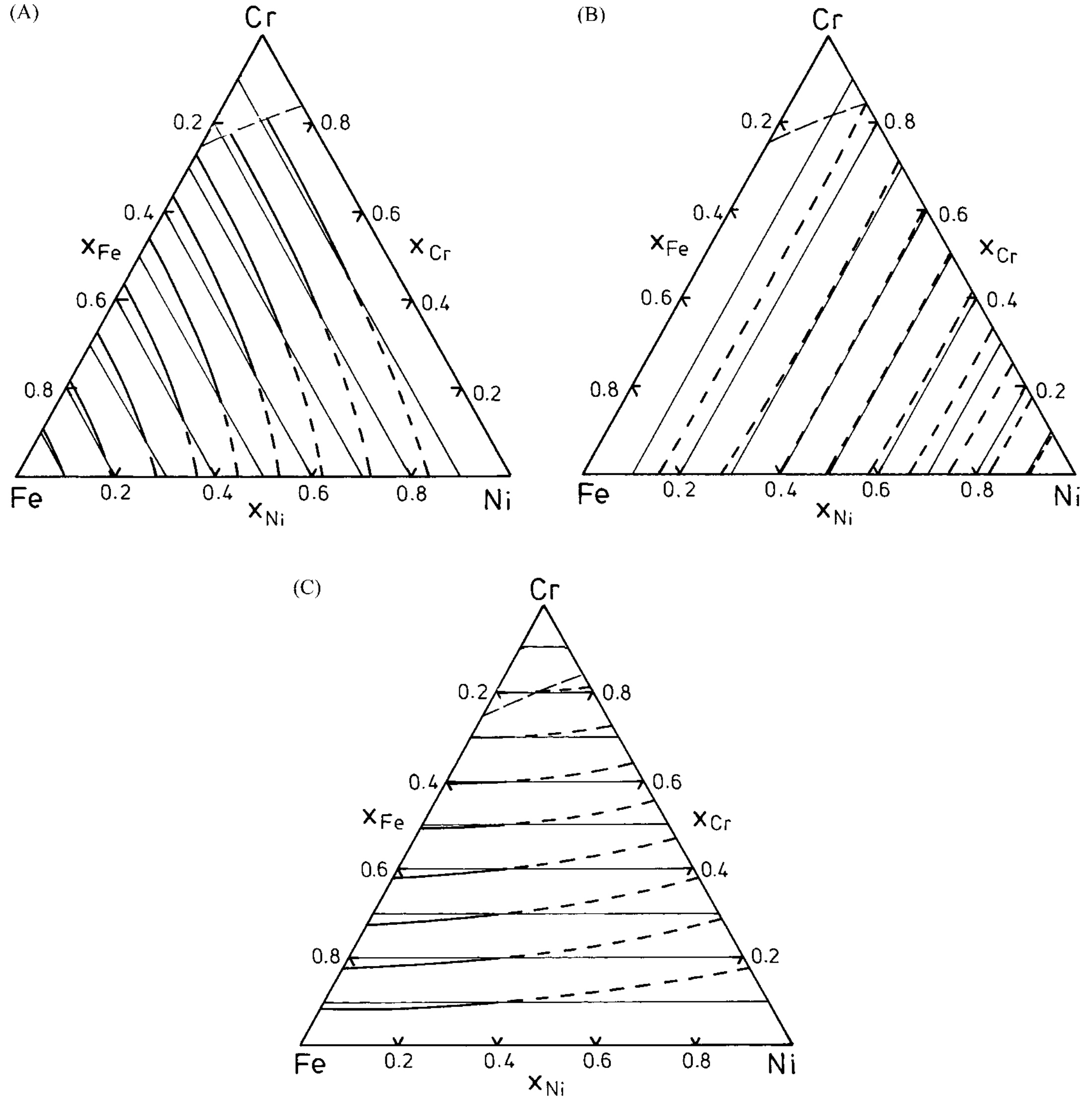

Fig. 6. Thermodynamic activity a_k in steps of 0.1 (a) k=Fe; (b) k=Ni; (c) k=Cr of liquid ternary Fe–Ni–Cr alloys at 1950 K in J/mol. (Raoult's law ———; Positive deviation from Raoult's law ———; negative deviations - - -).

range of composition on the left-hand side of the section of constant mole fraction $x_{Ni}/x_{Fe}=1$, and slight negative deviations from the ideal behavior on the right-hand side of this line.

5. Discussion.

The mass-spectrometric investigations, of this work, confirmed fully the preliminary results presented in Ref. [6]. However, it cannot be assumed generally that investigations along one ternary section of constant mole fraction are sufficient to determine accurate ternary molar excess functions over the whole Gibbs triangle phase field.

Three thermodynamic studies of molten ternary Fe–Ni–Cr alloys at 1873 K are reported in literature: The mass-spectrometric investigations performed by Belton and Fruehan [1], Gilby and St. Pierre [2], and Wagner et al. [3]. The latter authors studied activities in some dilute solutions of Cr and Fe in Ni, only. The plots of their results are not precise enough to allow reasonable conversion into a shape which could be compared with the results of this work. Gilby and St. Pierre [2] determined the activities of the three components in a series of Fe–Ni–Cr melts at 1873 K. In a separate set of experiments, the equilibrium vapors established over Fe–Cr–Ni alloys, containing up to $x_{\mathrm{Cr}}=0.50$ at 1873 K, were determined by collecting the effusate from thoria Knudsen cells. From these data the activities of Fe and Ni in ternary alloys have been calculated. With respect to the presentation of the results by Gilby and St. Pierre [2] a direct comparison with the results of this investigation is very difficult. The authors reported in Fe-rich alloys, the interactions between the three components are negligible; however, in Ni-rich alloys, the three principal interactions have significant positive values. A comparison with Fig. 6(a), Fig. 6(b) and Fig. 6(c) shows that the conclusions of these authors do not agree well with the results of this work. Belton and Fruehan [1] determined some activity coefficients data by means of Gibbs–Duhem integration of their mass-spectrometric measurements. Taking the binary data of Table 2 and re-evaluating their experimental data would yield activities indicating deviation tendencies from the ideal behavior similar to the results of this work.

The mass-spectrometric investigations, of this work, yielded the first experimental data for the thermodynamic mixing behavior of the liquid Fe–Ni–Cr alloys over the whole range of ternary compositions. The results of this work can be used successfully for phase-diagram calculations. As carried out elsewhere [7,11], the computations of phase equilibria based upon the thermodynamic data of this investigations yield phase boundaries in better agreement with experimental phase-equilibria data than in case of previous assessments.

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