MASS-SPECTROMETRIC DETERMINATION OF THERMODYNAMIC PROPERTIES OF LIQUID Co-Cr ALLOYS

JITKA HAVRÁNKOVÁ, JAN VŘEŠŤÁL, JOSEF TOMISKA

Thermodynamic excess functions of Co-Cr alloys in the liquid phase have been investigated by Knudsen-cell mass spectrometry in the concentration range 0.272–0.605 atomic fraction (at. fr.) of Cr in the temperature range 1710–1860 K. The molar excess Gibbs energies, entropies, and enthalpies as well as the thermodynamic activities of components in the Co-Cr system were obtained using composition and temperature dependence of the ratio of intensities of ^{59}Co and ^{52}Cr ions. The results show that subregular solution model would fit the measured data well: (2-parameter thermodynamically adapted power (TAP) series: C_n^{H} in J/mol: $C_1^{\mathrm{H}} = -18400$, $C_2^{\mathrm{H}} = 13000$, C_n^{S} in J/(mol.K): $C_1^{\mathrm{S}} = -2.5$, $C_2^{\mathrm{S}} = 0.2$.)

STANOVENÍ TERMODYNAMICKÝCH VLASTNOSTÍ KAPALNÝCH SLITIN Co-Cr EFÚZNÍ METODOU S HMOTNOSTNÍM SPEKTROMETREM

Efúzní Knudsenovou metodou s hmotnostním spektrometrem byly studovány dodatkové termodynamické funkce v kapalné fázi soustavy Co-Cr v koncentračním rozsahu 0,272–0,605 at. zl. Cr a v teplotním rozsahu 1710–1860 K. Byly získány hodnoty molárních dodatkových Gibbsových energií, entropií, entalpií a termodynamických aktivit v soustavě Co-Cr analýzou teplotní a koncentrační závislosti naměřených poměrů intenzit proudů, odpovídajících iontům ^{59}Co a ^{52}Cr. Výsledky lze dobře aproximovat modelem subregulárního roztoku: (2parametrový termodynamicky adaptovaný polynom (TAP): C_n^{H} v J/mol: $C_1^{\mathrm{H}} = -18400$, $C_2^{\mathrm{H}} = 13000$, C_n^{S} v J/(mol.K): $C_1^{\mathrm{S}} = -2{,}5$, $C_2^{\mathrm{S}} = 0{,}2$.)

Key words: mass spectrometry, metals, thermodynamics, cobalt, chromium

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Mgr. J. Havránková, Prof. RNDr. J. Vřešťál, DrSc., Institute of Physical Chemistry, Masaryk University Brno, Kotlářská 2, CZ 611 37 Brno, Czech Republic. e-mail: {jih, vrestal}@chemi.muni.cz

Prof. Dr. J. Tomiska, Institute of Physical Chemistry, University of Vienna, Währingerstr. 42, A1090 Wien, Austria.

1. Introduction

The cobalt-chromium system, as a basis of many technologically important materials, is of considerable interest. Nevertheless, experimental thermodynamic investigations of liquid Co-Cr alloys are very scarce: The investigation of Argent et al. [1] yields the values of thermodynamic activities and Gibbs energies of mixing for 4 alloys of the composition from 0.2 to 0.8 at. fr. Cr at 1873 K, only. Therefore, this study can be considered the first investigation of the thermodynamic mixing behavior of liquid Co-Cr system by the use of the Knudsen-cell mass spectrometry.

2. Thermodynamic treatment

Determination of the molar excess functions in liquid Co-Cr alloys was performed by mass spectrometric measurements of the temperature dependence of ion-current intensities J_{Co} and J_{Cr} of the characteristic isotopes $^{59}\mathrm{Co}$ and $^{52}\mathrm{Cr}$ of the appropriate gaseous species. Thermodynamic evaluation is based upon the relation between the difference of molar excess chemical potentials $\mu_{\mathrm{j}}^{\mathrm{E}}$ (partial excess Gibbs energies $G_{\mathrm{j}}^{\mathrm{E}}$, j = Co, Cr) of cobalt and chromium in the liquid phase inside the Knudsen cell (closed crucible with a small knife-edge shaped orifice) and the *corresponding ion current intensities* J_{j} [2]:

$$\begin{aligned} RT\{\ln(J_{\mathrm{Cr}}(T,x_{\mathrm{Cr}})/J_{\mathrm{Co}}(T,x_{\mathrm{Cr}})) - \ln(x_{\mathrm{Cr}}/(1-x_{\mathrm{Cr}}))\} &= \\ = \mu_{\mathrm{Cr}}^{\mathrm{E}}(T,x_{\mathrm{Cr}}) - \mu_{\mathrm{Co}}^{\mathrm{E}}(T,x_{\mathrm{Cr}}) &+ C_0^{\mathrm{G}}(T) \end{aligned} \tag{1}$$

(R – gas constant, T – temperature in K, x_{Cr} – mole fraction of Cr in liquid phase), where $C_0^{\mathrm{G}}(T)$ is the temperature-dependent calibration constant containing isotope-specific and mass-spectrometric quantities. Standard states of both Co and Cr correspond to pure elements in the liquid state at pressure 10^5 Pa and at the solution temperature. An algebraic best fit of the experimental data was performed in two steps: First, the linear dependence of the natural logarithm of the partial pressures proportional to ion-current intensities of the components j (j = = Co, Cr) on T^{-1} may be assumed and it can be approximated by linear regression for each run. The gained best fit of parameters $(d_0(x_{\mathrm{Cr}}), d_1(x_{\mathrm{Cr}}))$ reduced voluminous experimental peak data

$$\ln(J_{\mathrm{Cr}}/J_{\mathrm{Co}}) = d_0(x_{\mathrm{Cr}}) + d_1(x_{\mathrm{Cr}})/T. \tag{2}$$

Second, the difference $(\mu_{\mathrm{Cr}}^{\mathrm{E}}(T,x_{\mathrm{Cr}}) - \mu_{\mathrm{Co}}^{\mathrm{E}}(T,x_{\mathrm{Cr}}))$ in Eq. 1 was approximated by means of the TAP (thermodynamically adapted power) series representation of the binary molar excess function Z^{E} $(Z = G, H, S)$

$$Z^{\mathrm{E}} = (1 - x_{\mathrm{Cr}}) \sum_{n=1}^{N} C_n^{\mathrm{Z}} x_{\mathrm{Cr}}^n, \tag{3}$$

where N is the number of the TAP-parameters C_n^{Z}. The Weierstrass approximation theorem guarantees that these approximations can be done with arbitrary high accuracy [3] when appropriate number of parameters C_n^{Z} is used.

The corresponding expressions for the molar excess chemical potentials $\mu_{\mathrm{j}}^{\mathrm{E}}$ (j = Cr, Co) are:

$$\mu_{\mathrm{Cr}}^{\mathrm{E}} = (1 - x_{\mathrm{Cr}})^2 \sum_{n=1}^{N} n C_n^{\mathrm{G}} x_{\mathrm{Cr}}^{n-1}, \tag{3a}$$

$$\mu_{\mathrm{Co}}^{\mathrm{E}} = \sum_{n=1}^{N} C_n^{\mathrm{G}} x_{\mathrm{Cr}}^{n} (1 - n + n x_{\mathrm{Cr}}). \tag{3b}$$

Substituting Eqs. 2 and 3 in Eq. 1 yields the final best fit formula

$$RT\{d_0 + d_1/T - \ln(x_{\mathrm{Cr}}/(1 - x_{\mathrm{Cr}}))\} = C_0^{\mathrm{G}}(T) + \sum_{n=1}^{N} C_n^{\mathrm{G}} x_{\mathrm{Cr}}^{n-1} \{n - (1+n) x_{\mathrm{Cr}}\}. \tag{4}$$

The TAP-parameters $C_n^{\mathrm{G}}(T)$ as well as $C_0^{\mathrm{G}}(T)$ calibration constant may be adjusted by means of suitable least square computer procedure in order to fit the experimental values $RT\{d_0 + d_1/T - \ln(x_{\mathrm{Cr}}/(1 - x_{\mathrm{Cr}}))\}$ of all investigated alloy samples as a function of x_{Cr} at constant temperature as close as possible. The temperature dependence of the TAP-parameters $C_n^{\mathrm{G}}(T)$ and calibration constant $C_0^{\mathrm{G}}(T)$ is in accordance with Eq. 1:

$$C_n^{\mathrm{G}}(T) = C_n^{\mathrm{H}} - T C_n^{\mathrm{S}} \quad (n = 0, 1, 2, \ldots, N). \tag{5}$$

The temperature independent parameters C_n^{H} and C_n^{S} can be used for calculations of molar enthalpy H^{E} and molar entropy of mixing S^{E}, respectively, by means of Eq. 3 ($Z = H, S$).

3. Experimental technique

The Knudsen-cell mass spectrometric apparatus has been described previously [4, 5]. The simple monopole instrument model MX-7304 with ion source 1560014-T01 (Elektron, Ukraine) and with the mass range 2–200 Dalton, modified at the Institute of Physics of Materials, Academy of Sciences of the Czech Republic, was employed.

The samples were contained in an alumina inner effusion cell of 5 mm inner diameter and with alumina lid which were enclosed in an outer molybdenum cell with a molybdenum lid. The diameter of the effusion orifice in the inner alumina lid was 0.4 mm. The Knudsen cell was heated by a resistance furnace and temperature was measured with a Pt-PtRh10 thermocouple with accuracy ±0.1 K. Stability of temperature reading during the experiment was better than ±1 K. The thermocouple was calibrated by means of thermal arrest of Cu, Ni, Co, Fe pure metal samples [4, 5]. Ions were formed by of 15 eV electron beam having current of 50 μA. The temperature range covered was 1710–1860 K.

Measuring procedure started with heating of the effusion cell to about 1650 K for a period of approximately 1/2 hour to establish a thermal steady state within the apparatus and to prevent large weight losses of chromium by vaporization. The temperature was then raised to the top of the temperature range selected and was kept constant until instrument reading had become stable. Data were collected by mass spectrometer measuring ion current of the principal isotope peak 10-times for one component and 4-times for background and the same for the second component. The isotopes ^{52}Cr and ^{59}Co were chosen. The temperature was then lowered by about 10–20 K and the process was repeated after readings had once again become stable. The experiment was continued in this manner until the lower end of the temperature range was reached (usually 8 temperature readings). The alloy samples were prepared by arc melting of pure cobalt (Johnson Matthey, 99.999 wt. %) and of pure chromium (electrolytically deposited, imported by Lachema Brno a. s., 99.99 wt. %) in argon atmosphere in appropriate proportions. The metals were mechanically cleaned before melting. Chemical composition of samples was checked by electron microprobe analysis (Philips SEM 505) using a wavelength-dispersive analyzer (Microspec 2A), pure metals as standards and standard correc-

Table 1. Constants d_0 and d_1 of Eq. 2; the relation between the ion current ratios $\ln(J_{\mathrm{Cr}}/J_{\mathrm{Co}})$ and the inverse sample temperature of the investigated liquid Co-Cr alloys (x_{Cr} mole fraction of chromium)

No.	x_{Cr}	d_0	$d_1 \cdot 10^{-4}$
1	0.272	3.202	−455.4
2	0.294	3.283	−594.0
3	0.326	3.353	−191.4
4	0.348	3.489	−322.0
5	0.429	3.903	12.9
6	0.454	3.854	125.8
7	0.460	3.870	345.9
8	0.513	4.096	243.6
9	0.527	4.129	509.5
10	0.558	4.104	651.1
11	0.567	4.300	474.5
12	0.605	4.450	462.0

tions for atomic number, absorption and fluorescence of X-rays (ZAF-corrections). The chemical compositions of the investigated alloys are given in Table 1. No oxidation of the samples surface after experiments has been observed due to the low oxygen partial pressure in the apparatus caused by the using of titanium sublimation and discharge pumps in vacuum equipment. No significant reaction of metal samples with alumina crucible was observed.

4. Results and discussion

In 12 runs 12 different alloys with chromium content from 0.272 to 0.605 at. fr. (Table 1) have been mass spectrometrically investigated. The deviations of the experimental data from the computed regression lines (Eq. 2) were in no case higher than 5 %. The constants d_0 and d_1 are summarized in Table 1. The average value of accuracy of d_0 and d_1 was ± 0.3 and $\pm 0.03 \times 10^4$, respectively.

The experimental values of $RT\{d_0 + d_1/T - \ln(x_{\mathrm{Cr}}/(1 - x_{\mathrm{Cr}}))\}$ at the temperature $T = 1800$ K as a function of the mole fraction x_{Cr} are plotted in Fig. 1. As it can be seen, the satisfactory best fit according to Eq. 4 can be obtained by employing a 2-parameter ($N = 2$) TAP series for determination of G^{E}.

The concentration dependence of excess Gibbs energy values is plotted in Fig. 2 together with the concentration dependence of enthalpy of mixing H^{E}. The best

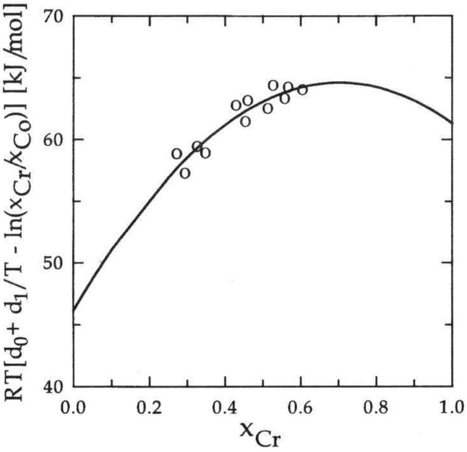

Fig. 1. $RT[d_0 + d_1/T - \ln(x_{\mathrm{Cr}}/x_{\mathrm{Co}})]$ as a function of the mole fraction x_{Cr} for liquid Co-Cr alloys at 1800 K. Experimental values: ○; curve based upon TAP parameters optimized for phase diagram computations (see Table 2) is identical with the original best-fit curve: —— .

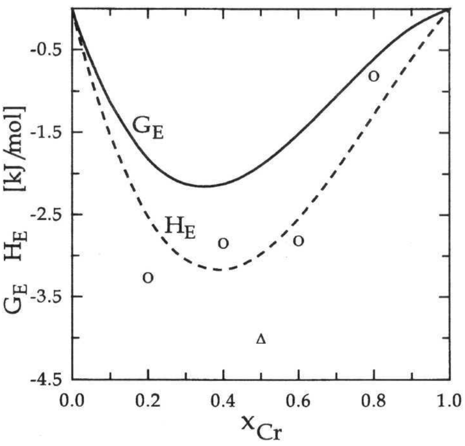

Fig. 2. Molar excess Gibbs energy G^{E} and molar enthalpy of mixing H^{E} of liquid Co--Cr alloys at 1800 K (liquid – Cr and liquid – Co reference state). G^{E}, this work:—— ; G^{E} from [1]: ○; H^{E}, this work: – – –; H^{E} using Miedema's model as estimated by [6]: Δ.

fit parameters $C_n^{\mathrm{G}}(T)$ obtained experimentally may be employed successfully for the binary phase diagram computations. Nevertheless, slight modifications of these best-fit parameters have been proved effective in obtaining even better agreement between calculated boundaries and the experimentally determined phase equilibria. Numerical values of C_n^{Z} (Z = G, H, S) optimized for phase diagram computations and the original best-fit parameters determined according to Eqs. 4 and 5 are presented in Table 2. A comparison shows that the values of the parameters C_n^{Z} are changed only slightly. Experimental values of [1] for G^{E} values and estimated value of H^{E} of [6] are shown for comparison in Fig. 2. It is evident that the G^{E}--values based upon our TAP parameters are less negative than the values from [1] though both investigations have been made with a Knudsen-cell mass spectrometry. The reason for this could be in the use of different experimental procedures.

Argent et al. [1] determined the activity of Co and Cr by vapour pressures measurement in three independent runs for one composition, one in alloy and two in pure components (standard state Co and Cr). However, this procedure could bring up the problems with small changes in the experimental sensitivity between different experiments [7]. These changes could probably be caused by small shifts in the position of the Knudsen cell which lead to large changes in the intensity of the ion current. In order to avoid this undesired effect, in our work we measure the ratio of the intensities of the ion currents produced by the alloy in a single experiment (Eq. 1, 2) without breaking the vacuum to make a sample change.

Table 2. Values of the TAP-parameters C_n^{Z} (Z = H, S) of liquid Co-Cr alloys ($C_n^{\mathrm{G}}(T) = C_n^{\mathrm{H}} - TC_n^{\mathrm{S}}$)

n	C_n^{H} [J.mol^{-1}]	C_n^{S} [J.mol^{-1}.K^{-1}]
1	−18400	−2.5
2	13000	0.2
1*)	−18360	−2.49
2*)	13010	0.21

*) Original best fit parameters

In Table 3 the experimental values of the molar excess Gibbs energy G^{E}, molar enthalpy of mixing H^{E}, the values of molar excess entropy S^{E}, and the thermodynamic activities a_{j} of the components j (j = Co, Cr) in Co-Cr alloys in the liquid phase obtained in this work at 1800 K are listed.

Liquid Co-Cr alloys are characterized by negative values of molar excess Gibbs energies G^{E} at 1800 K (Fig. 2, Table 3), negative values of molar excess entropies S^{E} (Table 3) and exothermic molar enthalpy of mixing H^{E} (Fig. 2, Table 3). (The

Table 3. Molar enthalpy of mixing H^E, molar excess entropies S^E, molar excess Gibbs energies G^E, and thermodynamic activities a_{Co} and a_{Cr} of liquid Co-Cr alloys at 1800 K (liquid – Cr and liquid – Co reference state)

x_{Cr}	G^E [J.mol^{-1}]	H^E [J.mol^{-1}]	S^E [J.mol^{-1}.K^{-1}]	a_{Co}	a_{Cr}
0.0	0	0	0.00	1.00	0.00
0.1	−1130	−1530	−0.22	0.89	0.054
0.2	−1820	−2520	−0.39	0.76	0.14
0.3	−2120	−3030	−0.51	0.62	0.24
0.4	−2120	−3160	−0.58	0.50	0.37
0.5	−1890	−2960	−0.60	0.40	0.49
0.6	−1510	−2530	−0.57	0.30	0.61
0.7	−1060	−1940	−0.49	0.22	0.72
0.8	−600	−1270	−0.37	0.15	0.81
0.9	−230	−600	−0.21	0.082	0.91
1.0	0	0	0.00	0.00	1.00

minimum G^E-value is -2120 J.mol^{-1} at 0.35 at. fr. Cr, minimum H^E-value is -3160 J.mol^{-1} at 0.40 at. fr. Cr and the minimum S^E-value is -0.60 J.mol^{-1}K^{-1} at 0.50 at. fr. Cr). In the liquid phase concentration dependence of the thermodynamic activities of both components, cobalt and chromium, show negative deviations from ideality (Fig. 3., Table 3). Data of [1] are shown for comparison in Fig. 3.

Data determined in the present work for G^E (Fig. 2) resemble those of [1]. Also the course of activities a_{Cr} and a_{Co} are similar to that in [1] (Fig. 3). Our data for H^E (Fig. 2) of equiatomic Co-Cr alloy agree well with the value calculated by Miedema's model [6] ($H^E = -4 + 1$ kJ.mol^{-1}).

In the Algebraic Intensity Ratio (AIR) method, we have a good check of quality of the experimental results by determining the enthalpies of mixing H^E by means of Eq. 6:

$$(H^E_{Cr} - H^E_{Co}) + C^H_0 = R\{\delta(d_0 + d_1/T)/d(1/T)\} = Rd_1. \qquad (6)$$

Fig. 4 gives the experimentally determined $R\{\delta(d_0 + d_1/T)/\delta(1/T)\}$ values vs. the mole fraction x_{Cr} as well as the "best-fit" curve according to Eq. 6. The small scatter of the experimental data in Fig. 4 indicates a good accuracy of the best-fit data.

5. Conclusion

Knudsen-cell mass spectrometric method used in this work yields the first complete thermodynamic description of liquid phase of the Co-Cr system in the temperature range 1710–1860 K. Our experimental results for G^E, a_{Co}, and a_{Cr}

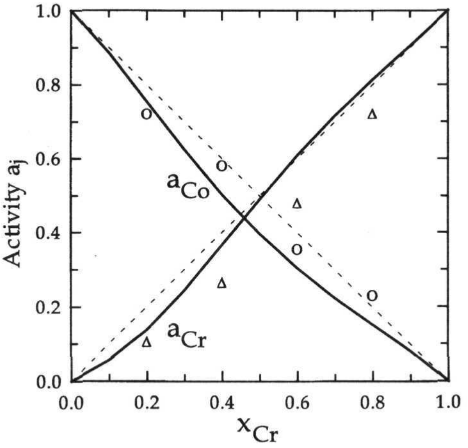

Fig. 3. Activity of components a_{Co} and a_{Cr} of liquid Co-Cr alloys at 1800 K. This work: ——; a_{Co} from [1]: o; a_{Cr} from [1]: △.

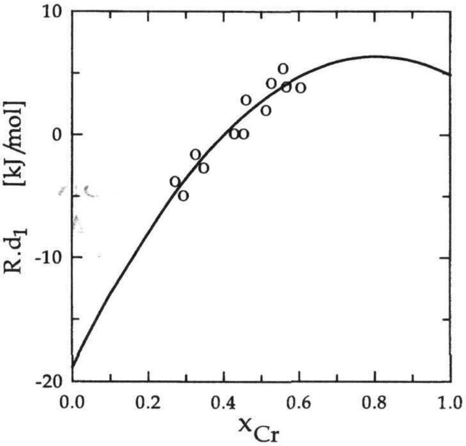

Fig. 4. Rd_1 as a function of the mole fraction x_{Cr} for liquid Co-Cr alloys at 1800 K. Experimental values: o; curve based upon TAP parameters as optimized for phase diagram computations (see Table 2) is identical with the original best fit curve: ——.

at 1800 K agree reasonably well with the results of Argent [1] at 1873 K and our experimental results for H^E agree well with theoretical guess by Miedema's model calculation of enthalpy of mixing for equimolar Co-Cr liquid alloy [6]. The determined values of constants form reliable basis for phase diagram calculation.

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