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Thermodynamic excess quantities of ternary Au–Co–Pd melts by computer-aided Knudsen cell mass spectrometry

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ABSTRACT

Computer-aided Knudsen cell mass spectrometry is used for the thermodynamic investigations on ternary Au–Co–Pd melts over the entire range of composition. The "digital intensity-ratio" (DIR)-method has been applied for the determination of the thermodynamic excess quantities, and the ternary thermodynamically adapted power (TAP) series concept is used for algebraic representation of the thermodynamic mixing behavior. The corresponding TAP parameters as well as the values of the molar excess Gibbs energies G^{E}, of the molar heats of mixing H^{E}, of the molar excess entropies S^{E}, and of the thermodynamic activities at 1800 K are presented.

1. Introduction

The technical interest on Pd-alloys is connected with the fact that palladium is in many properties similar to platinum. Of course, Pt is still a bit nobler and shows a higher melting point than Pd, but Pd is considerably lighter and cheaper than platinum, and therefore palladium will often be used instead of platinum. Feature of the present study is the first experimental investigation of the molar excess quantities of ternary Au–Co–Pd melts over the entire range of composition by means of computer-aided Knudsen cell mass spectrometry [1–3]. This is possible, because the expectation has been verified that employing an earlier suggested overall best fit technique [4,5] reduces considerably both the experimental effort and the time spent on evaluation.

2. Measuring technique and data evaluation

Following the Knudsen cell mass spectrometry the vapor pressures will be determined from the effusion of vaporized sample material out of an isothermal vessel which is called "Knudsen cell" [1–3]. Usually the Knudsen cells are manufactured as (cylindrical) crucibles with a small knife-edge shaped orifice (0.5–1.5 mm diameter) in the lid. The Knudsen cell is employed as the "gas source", and the effusing molecular beam is directed into the ionization chamber of the connected high-temperature mass spectrometer (see [1,2]). Detection of the ionized vapor species by means of an electron multiplier yields the ion current intensities J_k of the investigated isotopes ^{1}k.

These ion current intensities J_k are proportional to the partial vapour pressures p_k of the appropriate alloy components:

$$p_k(T, x_k) = \frac{D_I J_k(T, x_k) T}{D_k(T)} \tag{1}$$

where T is the temperature in K, x_k is the mole fraction of component k, D_I is an instrumental geometric constant, and $D_k(T)$ is an isotope specific constant (for details see [1]). Using this proportionality the thermodynamic evaluation based upon the well known relation between the partial molar excess Gibbs energies G_k^{E} ("molar excess chemical potentials $\mu_k^{\mathrm{E}''}$) of the alloy components k (this work: k = Au, Co, Pd) in condensed phases and the partial pressure p_k of the corresponding gas phase:

$$G_k^{\mathrm{E}}(T, x_k) = RT\left[\ln\left(\frac{p_k(T, x_k)}{p_k^{\circ}}\right) - \ln x_k\right] \tag{2}$$

where R is the gas constant, and p_k^0 is the vapour pressure of pure component k.

All other thermodynamic excess properties are determined by means of the corresponding thermodynamic relations: e.g., the molar excess Gibbs energy $G^{\mathrm{E}}(T,x_k)$ is connected with the partial

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molar excess Gibbs energies G_k^{E} of Au and Pd by:

$$G_{\mathrm{Au}}^{\mathrm{E}} = G^{\mathrm{E}} - x_{\mathrm{Co}}\left[\frac{\partial G^{\mathrm{E}}}{\partial x_{\mathrm{Co}}}\right] - x_{\mathrm{Pd}}\left[\frac{\partial G^{\mathrm{E}}}{\partial x_{\mathrm{Pd}}}\right], \tag{3a}$$

$$G_{\mathrm{Pd}}^{\mathrm{E}} = G^{\mathrm{E}} - x_{\mathrm{Co}}\left[\frac{\partial G^{\mathrm{E}}}{\partial x_{\mathrm{Co}}}\right] + (1 - x_{\mathrm{Pd}})\left[\frac{\partial G^{\mathrm{E}}}{\partial x_{\mathrm{Pd}}}\right]. \tag{3b}$$

The molar heat of mixing H^{E}, and the molar excess entropy S^{E} are computed from the temperature dependence of the G^{E}-values (x denotes generally dependence on mole fractions x_k):

$$G^{\mathrm{E}}(T, x) = H^{\mathrm{E}}(x) - T\,S^{\mathrm{E}}(x). \tag{4}$$

The numerical value of the instrumental geometric constant D_{I} in Eq. (1) depends strongly on the actual position of the Knudsen cell with respect to the ion source, however [1,2]. With ternary Au–Co–Pd melts this problem can be overcome without any additional experimental effort by employing the digital intensity-ratio (DIR) technique. This technique is based upon the fact that the each difference of the partial molar excess Gibbs energies of two alloy components is independent from this D_I constant, as can be verified easily from Eqs. (1) and (2).

The thermodynamic mixing quantities of ternary Au–Co–Pd melts have been determined in this work by measurements on the temperature dependence of the ion–current intensities J_{Au} and J_{Pd} of the characteristic isotopes $^{197}\mathrm{Au}^{+}$ and $^{106}\mathrm{Pd}^{+}$, therefore. Combining Eqs. (1)–(3) yield the difference of the corresponding partial molar Gibbs energies ($G_{\mathrm{Au}}^{\mathrm{E}} - G_{\mathrm{Pd}}^{\mathrm{E}}$) as:

$$G_{\mathrm{Au}}^{\mathrm{E}} - G_{\mathrm{Pd}}^{\mathrm{E}} = RT\left[\ln\left(\frac{J_{\mathrm{Au}}}{J_{\mathrm{Pd}}}\right) - \ln\left(\frac{x_{\mathrm{Au}}}{x_{\mathrm{Pd}}}\right)\right] - {}^{t}C_0^{\mathrm{G}}(T) \tag{5a}$$

with

$${}^{t}C_0^{\mathrm{G}}(T) = RT\left[\ln\left(\frac{D_{\mathrm{Au}}p_{\mathrm{Au}}^{0}}{D_{\mathrm{Pd}}p_{\mathrm{Pd}}^{0}}\right)\right]. \tag{5b}$$

As the temperature dependent term ${}^{t}C_0^{\mathrm{G}}(T)$ contains all isotope specific factors, the DIR-method makes a thermodynamic evaluation of mass spectrometric measurements really possible without knowing the numerical values of the single factors. The ${}^{t}C_0^{\mathrm{G}}(T)$ term can be considered as an adjusting parameter which plays only the role of a ternary calibration constant.

Owing to the extensive mass spectrometric data (in this work: about 9000 measuring points) the concentration and temperature dependences of the molar excess properties are determined by means of separate best fits. Within the temperature ranges, in which the logarithms of the partial pressures of the components k may be assumed as inverse proportional to the temperature, the measured ion-current intensities J_{k}, and consequently also the ratios of them can be fitted linearly ($d^{0}(x)$ and $d^{1}(x)$ are best fit parameters):

$$\ln\left[\frac{J_{\mathrm{Au}}}{J_{\mathrm{Pd}}}\right] = d^{0}(x) + \frac{d^{1}(x)}{T}. \tag{6}$$

As pointed out in [4], the determination of the concentration dependence of the molar mixing effects is a non-trivial problem: Traditional evaluation techniques allow only the determination of the ternary molar excess properties $Z^{\mathrm{E}}(T,x)$ (Z = Gibbs energy G, heat of mixing H, entropy S) along concentration lines with constant ratio of the mole fractions of two components. These problems can be solved using the overall best fit technique as suggested in [4]. All the mass spectrometric data of all investigated alloy samples can be evaluated together by one algebraic overall best fit.

Following this new DIR (best fit) technique it is only necessary, to express all ternary excess quantities Z^{E} by means of suitable algebraic formulas employing the same set of parameters. The formulas must be truly representative of the experimental data, and in the limit case of a vanishing component k (k = Au, Co, Pd) the description of the ternary molar excess functions Z^{E} must reduce necessarily to the molar excess property ${}^{j,k}Z^{\mathrm{E}}(x)$ of the corresponding binary system j–k (j–k = Au–Co; Co–Pd; Pd–Au) [4,5].

As formulas which are based upon the assumption of ternary regular solution disagree often strongly with the experimental results [6], profitable expressions require therefore an essentially ternary interaction term ${}^{t}Z^{\mathrm{E}}(x)$ describing possible ternary mixing effects [4,5]. With the concomitant advantage that no reasoning is necessary any more on best weighting factors of the three binary contributions. All together the simplest form of ternary molar excess quantities is [5,7]:

$$Z^{\mathrm{E}} = {}^{t}Z^{\mathrm{E}} + {}^{\mathrm{BBS}}Z^{\mathrm{E}}, \tag{7a}$$

where ${}^{t}Z^{\mathrm{E}}(x)$ is a polynomial in all three mole fractions x_k (${}^{t}C_n^{\mathrm{Z}}n$ adjustable ternary parameters; n = 1,2,. . .):

$${}^{t}Z^{\mathrm{E}} = x_{\mathrm{Au}}x_{\mathrm{Co}}x_{\mathrm{Pd}}[{}^{t}C_1^{Z} + {}^{t}C_2^{Z}x_{\mathrm{Co}} + {}^{t}C_3^{Z}x_{\mathrm{Pd}} + \ldots], \tag{7b}$$

and ${}^{\mathrm{BBS}}Z^{\mathrm{E}}$ is the simple sum of molar excess properties ${}^{j,k}Z^{\mathrm{E}}(x)$ of all three binary boundary systems j–k:

$${}^{\mathrm{BBS}}Z^{\mathrm{E}} = {}^{\mathrm{Au,Co}}Z^{\mathrm{E}} + {}^{\mathrm{Co,Pd}}Z^{\mathrm{E}} + {}^{\mathrm{Pd,Au}}Z^{\mathrm{E}}. \tag{7c}$$

The simplest representation of the molar excess quantities ${}^{j,k}Z^{\mathrm{E}}(x)$ of the binary boundary systems j–k is the binary “thermodynamic adapted power series” (TAP-series) [5,7]:

$${}^{j,k}Z^{\mathrm{E}}(x) = x_j \sum_{n=1}^{{}^{j,k}N} {}^{j,k}C_n^{Z}x_n^{k}, \tag{7d}$$

where ${}^{j,k}N$ is the number of adjustable binary 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 sub-regular solution contributions as pointed out in [5]. Interchange of the components, as well as conversion of the various literature proposals for polynomial representing of ${}^{j,k}Z^{\mathrm{E}}(x)$, especially of the frequently used, but distinctly more complicated Redlich–Kister polynomial into the TAP-series and vice versa can be performed easily by means of the algorithm developed, e.g. in [7]. As carried out in [5,7] the TAP series concept reduces considerably the computational effort.

In accordance with Eq. (4), the TAP parameters of the molar excess Gibbs energy G^{E}, of the molar heat of mixing H^{E}, and of the molar excess entropy S^{E} are connected by:

$${}^{t}C^{\mathrm{G}} = {}^{t}C^{\mathrm{H}} - T{}^{t}C^{\mathrm{S}}, \tag{8a}$$

$${}^{j,k}C_n^{\mathrm{G}} = {}^{j,k}C_n^{\mathrm{H}} - T{}^{j,k}C_n^{\mathrm{S}}. \tag{8b}$$

Substituting in Eq. (5a) from Eqs. (6) and (7) yields the required best fit formula. For ternary Au–Co–Pd melts all three binary boundary systems are well-established in literature: The Au–Co melts [8] as well as the Co–Pd [9] and Pd–Au [3] liquid alloys have been determined mass-spectrometrically, and the resultant molar excess Gibbs energies of all three binary boundary systems have been used successfully for the calculations of the binary phase diagrams (Au–Co: will be published; Co–Pd [10]; Pd–Au [11]). Using the TAP-parameters as summarized in Table 1 the regression problem is, therefore, reduced to the adjusting of the ternary interaction parameters ${}^{t}C_n^{\mathrm{G}}$, and the ternary calibration constant ${}^{t}C_0^{\mathrm{G}}(T)$ only:

$$RT\left[d^{0}(x) + \frac{d^{1}(x)}{T} - \ln\left(\frac{x_{\mathrm{Au}}}{x_{\mathrm{Pd}}}\right)\right] = {}^{t}C_0^{\mathrm{G}}(T) - x_{\mathrm{Co}}[{}^{t}C_1^{\mathrm{G}}(x_{\mathrm{Au}} - x_{\mathrm{Pd}}) + \ldots] - \frac{\partial{}^{\mathrm{BBS}}G^{\mathrm{E}}}{\partial x_{\mathrm{Cr}}}. \tag{9}$$