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

Josef Tomiska*

Institute of Physical Chemistry, University of Vienna, Waehringerstr. 42, A-1090 Vienna, Austria

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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 ${}^{\mathrm{l}}k$.

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 $\mu_k^{E''}$) 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:

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

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 $G^E(T,x_k)$ is connected with the partial

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* Tel.: +43 1 4277 52464.
E-mail address: josef.tomiska@univie.ac.at.
URL: http://www.univie.ac.at/tomiska.

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

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

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

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):

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

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 $^{197}Au^{+}$ and $^{106}Pd^{+}$, therefore. Combining Eqs. (1)–(3) yield the difference of the corresponding partial molar Gibbs energies ($G_{Au}^{E} - G_{Pd}^{E}$) as:

$$G_{Au}^{E} - G_{Pd}^{E} = RT\left[\ln\left(\frac{J_{Au}}{J_{Pd}}\right) - \ln\left(\frac{x_{Au}}{x_{Pd}}\right)\right] - {}^{t}C_{0}^{G}(T) \tag{5a}$$

with

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

As the temperature dependent term ${}^{t}C_{0}^{G}(T)$ 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 ${}^{t}C_{0}^{G}(T)$ 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):

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

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 $Z^E(T,x)$ (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 ${}^{j,k}Z^{E}(x)$ 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 ${}^{t}Z^{E}(x)$ 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]:

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

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

$${}^{t}Z^{E} = x_{Au}x_{Co}x_{Pd}[{}^{t}C_{1}^{Z} + {}^{t}C_{2}^{Z}x_{Co} + {}^{t}C_{3}^{Z}x_{Pd} + \ldots], \tag{7b}$$

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

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

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

$${}^{j,k}Z^{E}(x) = x_{j}\sum_{n=1}^{{}^{j,k}N}{}^{j,k}C_{n}^{Z}x_{n}^{k}, \tag{7d}$$

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 ${}^{j,k}Z^{E}(x)$, 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:

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

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

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 ${}^{t}C_{n}^{G}$, and the ternary calibration constant ${}^{t}C_{0}^{G}(T)$ only:

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

Table 1
Values of the TAP-parameters ${}^{j,k}C_n^{\mathrm{Z}}$ of the binary boundary systems ($C_n^{\mathrm{G}} = C_n^{\mathrm{H}} - T\,C_n^{\mathrm{S}}$).

System *j*–*k*	*n*	${}^{j,k}C_n^{\mathrm{H}}$ (J/mol)	${}^{j,k}C_n^{\mathrm{S}}$ (J/(mol K))	Ref.
Au–Co	1	24,090	8.647	[8,10]
	2	74,360	44.64	
	3	−152,500	−104.9	
	4	76,260	52.96	
Co–Pd	1	−40,420	−14.06	[9]
	2	−21,830	−3.349	
Pd–Au	1	25,360	12.44	[3]
	2	−104,000	−47.13	
	3	17,010	5.510	

3. Experimental

The measuring device was a computer-aided Knudsen cell mass spectrometer as described elsewhere [1–3]. It consists of a single focusing 90° magnetic sector, 200 mm radius, instrument manufactured by Hitachi (Model RMU-6M) and modified in this laboratory. Instrument control and data acquisition are both by microcomputer. Detailed specifications and ratings of the experimental set-up are given elsewhere [1–3].

The samples were contained in an alumina inner effusion cell and lid, which were enclosed within an outer tungsten cell with a tantalum lid. The diameter of the effusion orifices in the inner lid were 0.75–1.2 mm. The heating was by electron bombardment, and temperatures were measured with a platinum, platinum–rhodium thermocouple. The thermocouple was calibrated by means of thermal arrests in the ion current signal obtained upon cooling through the melting temperature of the pure metal samples: Cu, Ni, Co, Fe, and Pd. The thermocouple calibration was reproducible to ±2 K. The high quality of this technique has been already illustrated previously by original recordings of the calibration procedure by means of Ni in [12], and Co in [13]. Ions were formed by means of a 16 eV electron beam having a current of 60 μA.

At the beginning of an experiment the effusion cell was heated to about 1200 K for a period of approximately 10 h in order to establish a thermal steady state within the apparatus. The temperature was then raised to the top of the range to be covered and was kept constant until instrument readings had become stable. Data were collected by repeated scanning the principal isotope peak for one component, with the temperature being automatically recorded with each scan, and then doing the same for the other component. During this procedure the temperature was found to be constant within ±1.5 K. The temperature was then lowered 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. The temperature range covered in these investigations was about 90–180 K. To prevent crystallization of the sample, the lower temperature limit was varied in relation to the composition of the sample.

Alloys preparation has been performed by arc melting of appropriate proportions of the elements. The preparations were re-melted several times, and then annealed in closed quartz tubes for several days to help ensure homogeneity. The metals were obtained from commercial sources (Au: 99.9998%, Bauer KG, Wien; Co: 99.998, Pd: 99.998%, Johnson Matthey, UK). Micrographic examination proved the homogeneity of the samples. The total loss of mass owing to vaporization during melting was typically less than 0.3%, and the sample compositions were hence assumed to be the same as the original mixtures. Measurements with the mass spectrometer on different samples from the same preparation gave identical results within experimental uncertainty.

Table 2
Constants d^0 and d^1 of Eq. (6), the relation between the ion current ratios ($J_{\mathrm{Au}}/J_{\mathrm{Pd}}$) and the inverse sample temperature of the investigated ternary Au–Co–Pd melts (x_{Co}, x_{Pd} mole fractions of Co and Pd, respectively).

No.	x_{Co}	x_{Pd}	d^0	d^1
1	0.097	0.805	−2.793	2048
2	0.097	0.805	−2.592	1530
3	0.098	0.098	0.573	3541
4	0.098	0.098	0.274	4322
5	0.147	0.147	0.659	2513
6	0.147	0.147	0.281	3004
7	0.149	0.703	−1.968	1605
8	0.149	0.703	−1.893	1371
9	0.196	0.196	0.587	1729
10	0.196	0.196	0.346	2336
11	0.199	0.602	−1.404	1566
12	0.199	0.602	−1.485	1668
13	0.246	0.246	0.228	1767
14	0.246	0.246	0.302	2001
15	0.247	0.506	−1.050	1717
16	0.247	0.506	−1.105	1868
17	0.297	0.297	−0.045	1593
18	0.297	0.297	−0.156	1944
19	0.299	0.401	−0.754	2071
20	0.299	0.401	−0.675	1945
21	0.349	0.349	−1.010	3312
22	0.349	0.349	−0.687	2317
23	0.349	0.301	−0.349	2197
24	0.349	0.301	−0.514	2616
25	0.396	0.207	−0.352	3182
26	0.396	0.207	−0.212	2966
27	0.398	0.399	−1.782	4096
28	0.398	0.399	−1.619	3401
29	0.447	0.107	0.258	3667
30	0.447	0.107	−0.005	4101
31	0.448	0.448	−3.187	5886
32	0.448	0.448	−3.077	5298

4. Results and discussion

The mass spectrometric investigations of this work were performed in 32 runs for 16 different alloy concentrations with constant ratios of the mole fractions: (a) $x_{\mathrm{Co}}/x_{\mathrm{Au}} = 1$, and (b) $x_{\mathrm{Pd}}/x_{\mathrm{Co}} = 1$ as presented in Table 2. In each run the ion current intensities J_{Au} and J_{Pd} (of ${}^{197}\mathrm{Au}^+$ and ${}^{106}\mathrm{Pd}^+$) were determined at about 10–20 temperatures 10 times, altogether at least 100 values each. This give a total amount of about 9000 measuring points for the determination of the molar excess quantities Z^{E} of ternary Au–Co–Pd melts over the whole range of composition.

For the temperature $T = 1800$ K in Fig. 1 it is shown that a satisfying overall best fit by means of the interactive evaluation module *cM3_KMS* as described recently [7] is achieved by using the simple homogeneous polynomial of third order as ternary interaction term (one adjustable parameter ${}^{t}C_1^{\mathrm{G}}$). Table 3 gives the values of the ternary interaction terms ${}^{t}C_n^{\mathrm{Z}}$ of ternary Au–Co–Pd melts according to Eqs. (7b) and (8a).

Following the DIR method there is a good check of the quality of the best fit results by determining the molar heats of mixing H^{E}, and the molar excess entropies S^{E} independently by means of Eq. (10):

$$R\,d^1(x) = {}^{t}C_0^{\mathrm{H}}(T) - x_{\mathrm{Co}}[{}^{t}C_1^{\mathrm{H}}(x_{\mathrm{Au}} - x_{\mathrm{Pd}}) + \ldots] - \frac{\partial^{\mathrm{BBS}} H^{\mathrm{E}}}{\partial x_{\mathrm{Cr}}}, \qquad (10a)$$

Table 3
Values of the ternary interaction terms ${}^{t}C_n^{\mathrm{Z}}$ of ternary Au–Co–Pd melts (${}^{t}C_n^{\mathrm{G}} = {}^{t}C_n^{\mathrm{H}} - T\,{}^{t}C_n^{\mathrm{S}}$).

n	${}^{t}C_n^{\mathrm{H}}$ (J/mol)	${}^{t}C_n^{\mathrm{S}}$ (J/(mol K))
1	28,860	7.570

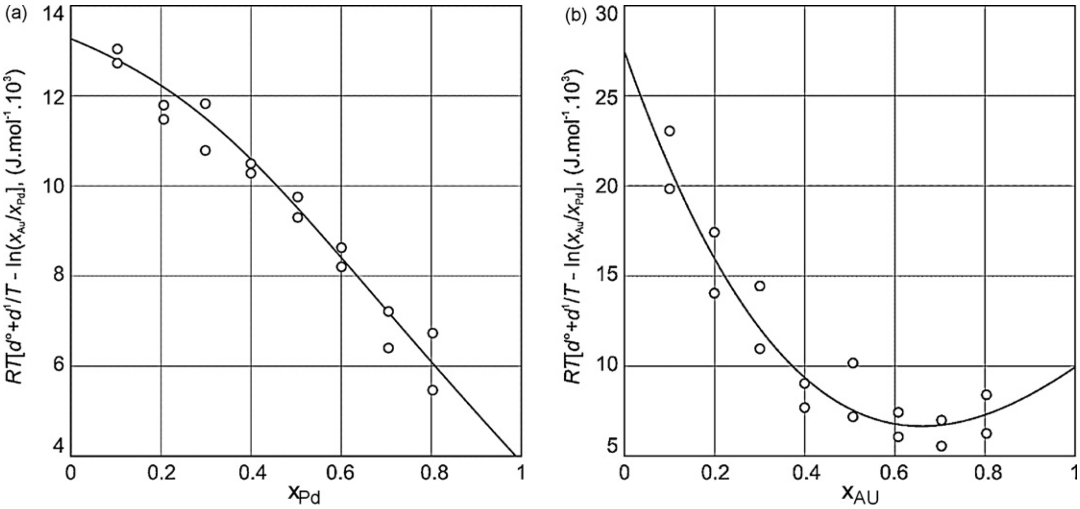

Fig. 1. $RT[d^0(x)+d^1(x)/T-\ln(x_{Au}/x_{Pd})]$ as function of the mole fraction x_{Au} ternary Au–Co–Pd melts at 1800 K (experimental points o; overall best fit curve based upon Eq. (9): —). (a) $x_{Co}/x_{Au}=1$, and (b) $x_{Pd}/x_{Co}=1$.

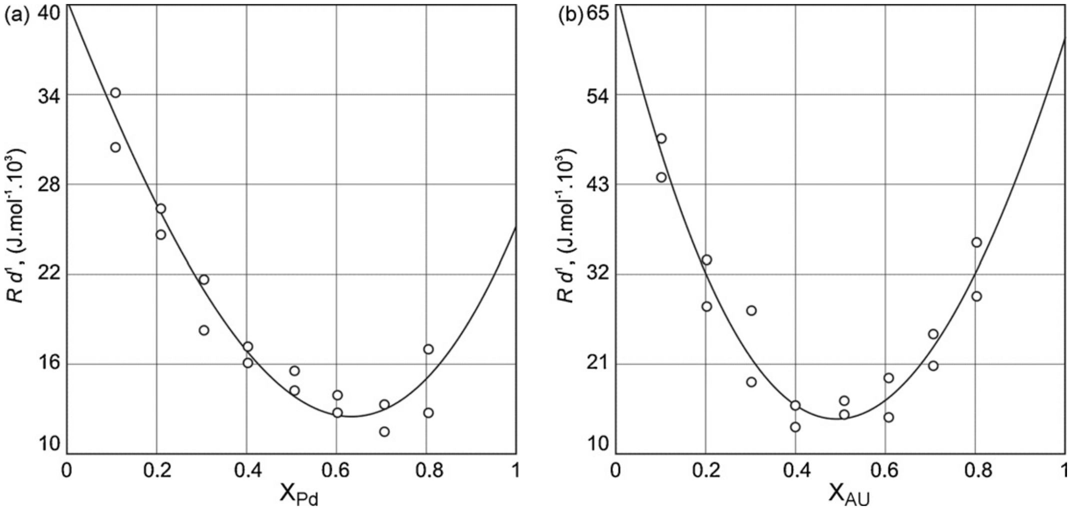

Fig. 2. $Rd^1(x)$ as function of the mole fraction x_{Au} ternary Au–Co–Pd melts at 1800 K (experimental points o; overall best fit curve based upon Eq. (10a): —). (a) $x_{Co}/x_{Au}=1$, and (b) $x_{Pd}/x_{Co}=1$.

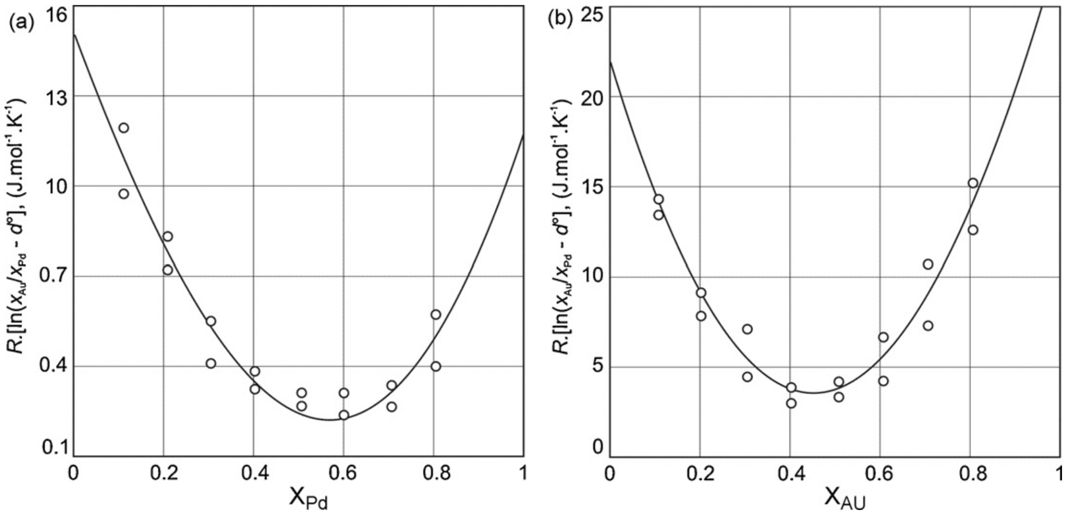

Fig. 3. $R[\ln(x_{Au}/x_{Cr})-d^0(x)]$ as function of the mole fraction x_{Au} ternary Au–Co–Pd melts at 1800 K (experimental points o; overall best fit curve based upon Eq. (10a): —). (a) $x_{Co}/x_{Au}=1$, and (b) $x_{Pd}/x_{Co}=1$.

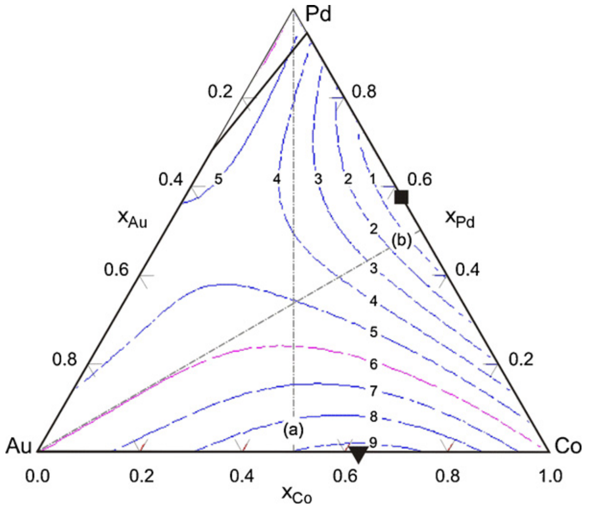

Fig. 4. Molar excess Gibbs energy G^E of ternary Au–Co–Pd melts at 1800 K in J/mol (the liquid phase field after [14] is surrounded by thick lines; investigated lines with constant ratio of the mole fraction ((a) $x_{Co}/x_{Au} = 1$, and (b) $x_{Pd}/x_{Co} = 1$) - · - ·; minimum value (□); maximum value (▼); contour lines: (1) −5000; (2) −4000; (3) −3000; (4) −2000; (5) −1000; (6) 0; (7) 1000; (8) 2000; (9) 3000.

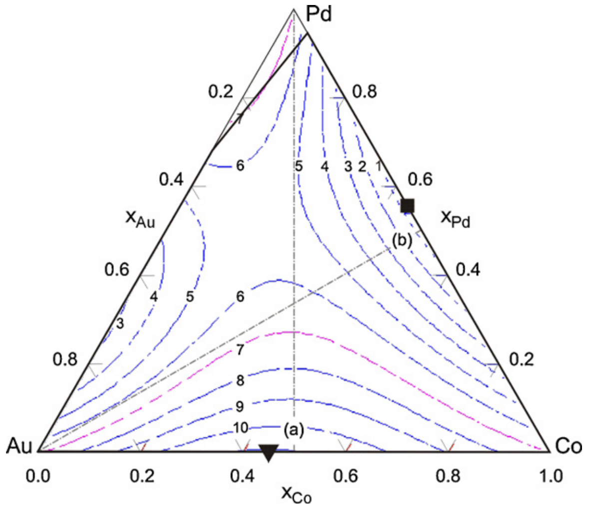

Fig. 5. Molar heat of mixing H^E of ternary Au–Co–Pd melts at 1800 K in J/mol (the liquid phase field after [14] is surrounded by thick lines; investigated lines with constant ratio of the mole fraction (a) $x_{Co}/x_{Au} = 1$, and (b) $x_{Pd}/x_{Co} = 1$) - · - ·; minimum value (□); maximum value (▼); contour lines: (1) −12,000; (2) −10,000; (3) −8000; (4) −6000; (5) −4000; (6) −2000; (7) 0; (8) 2000; (9) 4000; (10) 6000.

$$R\left[\ln\left(\frac{x_{Au}}{x_{Pd}}\right) - d^0(x)\right] = {}^tC_0^S - x_{Co}[{}^tC_1^S(x_{Au} - x_{Pd}) + \ldots] - \frac{\partial^{BBS}S^E}{\partial x_{Cr}}, \tag{10b}$$

In Eq. (10) ${}^tC_0^H(T)$ and ${}^tC_0^S(T)$ are the corresponding ternary H^E- and S^E-calibration constants for the two components Au and Pd. The results of these best fits are presented in Figs. 2 and 3. The small scattering of the experimental data indicates satisfactory accuracy of the best fit data of this investigation. Employing the DIR method, regressions by Eqs. (10a) and (10b) yield necessarily algebraic description of H^E and S^E data as obtained from the temperature dependence of the molar excess Gibbs energy G^E by means of Eq. (9). The uncertainties of the data are about 5–7%.

The mass spectrometric investigations of this study yield the molar excess Gibbs energy G^E, the molar heat of mixing H^E, and the molar excess entropy S^E of ternary Au–Co–Pd melts as displayed by means of contour lines in the Gibbs triangles of Figs. 4–6. The stable liquid phase field after [14] is surrounded by thick lines, and the two investigated lines with constant ratio of the mole fraction are marked by means of dot–dash lines.

Table 4 gives the G^E-, H^E-, and S^E-values as well as the resultant thermodynamic activities of the three constituents of ternary Au–Co–Pd melts with constant ratio of the mole fraction: (a) $x_{Co}/x_{Au} = 1$, and (b) $x_{Pd}/x_{Co} = 1$ at 1800 K. The molar excess properties of arbitrary ternary Au–Co–Pd melts can be computed by means of Eq. (11), and using the parameter values as given in Tables 1 and 3:

$$Z^E = x_{Au}x_{Co}x_{Pd}\,{}^tC_1^Z + x_{Au}\sum_{n=1}^{4}{}^{Au,Co}C_n^Z x_{Co}^n + x_{Co}\sum_{n=1}^{2}{}^{Co,Pd}C_n^Z x_{Pd}^n + x_{Pd}\sum_{n=1}^{3}{}^{Pd,Au}C_n^Z x_{Au}^n. \tag{11}$$

As displayed in Fig. 4 our mass spectrometric measurements at 1800 K result in a negative molar excess Gibbs energy G^E of ternary Au–Co–Pd melts over the predominant range of composition. The minimum G^E value of −5910 J/mol ($x_{Au} = 0$, $x_{Pd} = 0.575$) is identical with the minimum G^E value of the binary Co–Pd melts. Only the Au–Co-based ternary melts with less than 24% Pd show positive G^E values with a maximum G^E value of 3350 J/mol ($x_{Co} = 0.625$, $x_{Pd} = 0$) which is coinciding with the maximum G^E value of the binary Au–Co melts.

Fig. 5 shows that this investigation yields molar heat of mixing H^E of ternary Au–Co–Pd melts at 1800 K which is exothermic within the predominant part of Gibbs triangle. The minimum H^E value of −13,000 J/mol ($x_{Au} = 0$, $x_{Pd} = 0$) is coinciding with the H^E minimum of the binary Au–Co melts. Only some Au–Pd-based ternary melts with a Co content less than 3% shows endothermic H^E values. The Au–Co-based ternary melts with less than 27% Pd show clear endothermic behavior, with a maximum H^E value of 8320 J/mol ($x_{Co} = 0.45$, $x_{Pd} = 0$) which is identical with the maximum H^E value of the binary Au–Co melts.

As shown in Fig. 6 at 1800 K the molar excess entropy S^E as obtained in this investigation is positive within for Au–Co-based ternary melts with less than 30% Pd with a maximum S^E value of 3.15 J/mol K ($x_{Co} = 0.375$, $x_{Pd} = 0$) which is coinciding with the

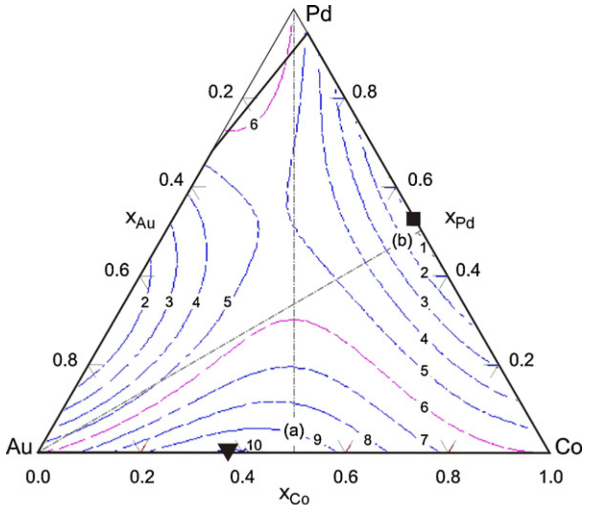

Fig. 6. Molar excess entropy S^E of ternary Au–Co–Pd melts at 1800 K in J/(mol K) (the liquid phase field after [14] is surrounded by thick lines; investigated lines with constant ratio of the mole fraction (a) $x_{Co}/x_{Au} = 1$, and (b) $x_{Pd}/x_{Co} = 1$) - · - ·; minimum value (□); maximum value (▼); contour lines: (1) −3.75; (2) −3.0; (3) −2.25; (4) −1.5; (5) −0.75; (6) 0; (7) 0.75; (8) 1.50; (9) 2.25; (10) 3.0.

Table 4
Molar excess Gibbs energy G^E, molar heat of mixing H^E, and molar excess entropy S^E as well as the thermodynamic activities a_k of ternary Au–Co–Pd melts with constant ratios of the mole fractions (a) $x_{Co}/x_{Au} = 1$, and (b) $x_{Pd}/x_{Co} = 1$ at 1800 K.

x_{Co}	x_{Pd}	G^E (J/mol)	H^E (J/mol)	S^E (J/(mol K))	a_{Au}	a_{Co}	a_{Pd}
(a) $x_{Co}/x_{Au} = 1$							
0.50	0.0	3060	8170	2.84	0.54	0.70	0
0.45	0.1	1690	4670	1.66	0.51	0.59	0.05
0.40	0.2	455	1750	0.72	0.47	0.49	0.11
0.35	0.3	−594	−561	0.02	0.44	0.38	0.18
0.30	0.4	−1430	−2250	−0.46	0.39	0.28	0.27
0.25	0.5	−2010	−3320	−0.72	0.34	0.19	0.38
0.20	0.6	−2310	−3760	−0.81	0.27	0.12	0.49
0.15	0.7	−2290	−3610	−0.73	0.21	0.07	0.62
0.10	0.8	−1930	−2890	−0.54	0.14	0.03	0.76
0.05	0.9	−1170	−1660	−0.27	0.07	0.01	0.89
0	1	0	0	0	0	0	1

x_{Pd}	x_{Au}	G^E (J/mol)	H^E (J/mol)	S^E (J/(mol K))	a_{Co}	a_{Pd}	a_{Au}
(b) $x_{Pd}/x_{Co} = 1$							
0.50	0.0	−5750	−12,800	−3.93	0.39	0.30	0
0.45	0.1	−3630	−7,400	−2.09	0.37	0.27	0.23
0.40	0.2	−2130	−3,780	−0.91	0.36	0.24	0.33
0.35	0.3	−1140	−1,640	−0.28	0.35	0.22	0.40
0.30	0.4	−529	−643	−0.06	0.33	0.20	0.46
0.25	0.5	−196	−472	−0.15	0.31	0.17	0.53
0.20	0.6	−48	−793	−0.41	0.27	0.14	0.61
0.15	0.7	−6	−1,270	−0.70	0.22	0.10	0.70
0.10	0.8	−10	−1,550	−0.85	0.16	0.06	0.80
0.05	0.9	−16	−1,260	−0.69	0.08	0.03	0.90
0	1	0	0	0	0	0	1

maximum S^E value of the binary Au–Co melts. Some Au–Pd-based ternary melts with a Co content less than 6% shows also positive S^E values. The molar excess entropy S^E of all other ternary Au–Co–Pd melts are negative at 1800 K. The minimum S^E value of −3.95 J/(mol K) ($x_{Co} = 0.473$, $x_{Au} = 0$) is identical with the minimum S^E value of the binary Co–Pd alloys.

5. Conclusions

The mass spectrometric investigations of this work yielded the thermodynamic excess quantities of ternary Au–Co–Pd melts within the whole Gibbs triangle. The representation of the molar excess quantities by means of the TAP series concept require only one ternary correction term, but this term is essential. Data conversion into other algebraic representations of molar excess properties can be performed easily by employing the conversion module *cMOD* as described in [7].

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