

The excess enthalpies of liquid Ga–Pb–Te alloys

R. Blachnik^{*}, E. Klose, F. Römermann

Institute of Chemistry, University Osnabrück, Barbarastrasse 7, D-49069 Osnabrück, Germany

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Abstract

The excess enthalpies of liquid alloys in the ternary Ga–Pb–Te system were determined at 1173 K in a heat-flow calorimeter for the sections $\text{Ga}_y\text{Pb}_{1-y}\text{Te}$ with $y=0.2, 0.4, 0.5, 0.6$ and 0.8 and for the section $\text{Ga}_{0.5}\text{Pb}_{0.5}\text{Te}$ at 1073 K. The enthalpy surface in the ternary system is characterized by a line of minima from the composition Ga_2Te_3 to the composition PbTe in the limiting binaries. The excess enthalpies in the binary systems were fitted with the association or regular solution model using the program of H.-L. Lukas. For an analytical description of the ternary system, the association model was used with additional ternary interaction parameters. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Enthalpies of mixing; High-temperature calorimetry; Ga–Pb–Te system

1. Introduction

The knowledge of thermodynamic data of binary and ternary systems is necessary to calculate the data of multicomponent systems. For this reason, the excess enthalpies of liquid alloys in systems with tellurium were measured in earlier investigations [1–10]. The excess enthalpies in metal–tellurium systems are often nearly triangular shaped functions of concentration. The exothermic minima of these curves were close to the composition of a congruently melting compound in the system. Wagner [11] assumed associates in the melt to explain this behaviour. Based on this hypothesis, Sommer [12,13] presented a thermodynamic formalism, which allows to fit the experimental data in such systems. These optimized data sets can be used to calculate the phase diagrams of multi-

component systems of technical relevance. Within the systematic investigation of systems with tellurium, we have measured the excess enthalpies of liquid Ga–Pb–Te alloys.

2. Experimental

The measurements were performed with the aid of a high-temperature heat-flow calorimeter [14], using the isoperibolic procedure. The experimental arrangement and the procedure for the determination of H^E have been described elsewhere [1–4]. In this paper, only some relevant details are given. Ga (Ingal Stade, 99.999%) and Pb (Alfa, 99.999%) were used for the preparation of the binary alloys $\text{Ga}_y\text{Pb}_{1-y}$ by melting Ga and Pb in evacuated and sealed silica tubes.

The measurements started on the metal-rich side of the sections $\text{Ga}_y\text{Pb}_{1-y}\text{Te}$ with binary $\text{Ga}_y\text{Pb}_{1-y}$ alloys, which were brought into the calorimeter tube

^{*}Corresponding author. Fax: +49-541-969-2370; e-mail: blachnik@physik.uni-osnabrueck.de

and heated to the temperature of the measurement. Small amounts of pure Te (Alfa, 99.999%) were consecutively added from ambient temperature ($T=298$ K) after temperature equilibration. On the tellurium-rich part of the system, small amounts of $\text{Ga}_y\text{Pb}_{1-y}$ were successively added to liquid tellurium. The temperature of the measurements was 1173 K, and in addition 1073 K, for the section $\text{Ga}_{0.5}\text{Pb}_{0.5}\text{-Te}$. The enthalpy increments $H_{(T)}-H_{(298.15\text{ K})}$ of $\text{Ga}_y\text{Pb}_{1-y}$ and Te were needed to calculate H^E of the ternary alloys. They were determined in separate experiments by dropping $\text{Ga}_y\text{Pb}_{1-y}$ or Te from room temperature in liquid $\text{Ga}_y\text{Pb}_{1-y}$ and Te, respectively, to the temperature of the measurements. The calibration of the calorimeter was carried out after each measurement by dropping pieces of tin into a second tube, which ends in the liquid alloy. The enthalpy increments $H_{(T)}-H_{(298.15\text{ K})}$ of tin were taken from Barin [15]. The reproducibility of the heat effects was better than

$\pm 5\%$ on the metal-rich side. On the tellurium-rich side of the system, we observed a higher deviation of the measured values. As a consequences, we discarded these data. All experiments were carried out under dry argon gas at atmospheric pressure.

3. Binary systems

3.1. The Ga–Te system

Four intermediate compounds were observed in the system Ga–Te: GaTe and Ga_2Te_3 melt congruently at 1108 K and 1071 K. Ga_3Te_4 decomposes in a peritectic reaction at 1049 K and the high-temperature phase Ga_2Te_5 is formed in a eutectoid reaction at 680 K and decomposes peritectically at 757 K [4].

The thermodynamic properties of the melt have been studied by several authors. Table 1 contains a review of their data.

Table 1
Investigations on the Ga–Te, Pb–Te and Ga–Pb systems

Author	Investigation	Reference
<i>Ga–Te system</i>		
Oh and Lee	optimization	[16]
Irle et al.	optimization	[4]
Castanet and Bergman	enthalpies of mixing	[17]
Said and Castanet	enthalpies of mixing	[18]
Glazov et al.	enthalpies of mixing	[19]
Alfer et al.	enthalpies of mixing	[20]
Katayama et al.	activities of Ga	[21]
Srikanth and Jacob	activities of Ga	[22]
Predel et al.	activities of Te	[23]
Takeda et al.	c_p values	[24]
<i>Pb–Te system, optimizations</i>		
Clavaguera-Mora et al.		[26]
Kattner et al.		[27]
Leo Ngai et al.		[28]
Kuznetsov et al.		[29]
<i>Ga–Pb system</i>		
Mathon et al.	optimization	[30]
Ansara	optimization	[31]
Bros	enthalpies of mixing	[32]
Miame	enthalpies of mixing	[33]
Predel and Stein	enthalpies of mixing	[34]
Kononenko et al.	activities of Pb	[35]
Sommer et al.	activities of Pb	[36]
Kwong and Munir	activities of Pb	[37]
Desideri and Piacente	activities of Pb	[38]

Table 2

Coefficients of the association model of the binary Ga–Te, Pb–Te and Ga–Pb systems

System i,j	Ga–Te 2,3	Pb–Te 1,1	Ga–Pb 0,0
$\Delta H_{A,B}^0$ /[kJ mol ⁻¹]	-292.4	-57.8	—
$\Delta S_{A,B}^0$ /[J K ⁻¹ mol ⁻¹]	-173.7	-10.7	—
$C_{A,B}^H$ /[kJ mol ⁻¹]	—	—	13.1
$C_{A,B}^S$ /[J K ⁻¹ mol ⁻¹]	—	—	—
$C_{A,A,B}^H$ /[kJ mol ⁻¹]	184.5	13.4	—
$C_{A,A,B}^S$ /[J K ⁻¹ mol ⁻¹]	210.7	3.1	—
$C_{B,A,B}^H$ /[kJ mol ⁻¹]	124.8	-13.4	—
$C_{B,A,B}^S$ /[J K ⁻¹ mol ⁻¹]	126.2	-8.6	—

Thermodynamic data for liquid Ga–Te alloys have recently been optimized with the assumption of Ga₂Te₃ associates in the liquid [9]. The exothermic minimum of H^E is found at $x_{Te}=0.58$ at -39.5 kJ mol⁻¹ ($T=1173$ K). In the present work, the same file of data was used together with the new unary SGTE description for Te. The resulting coefficients are listed in Table 2.

3.2. The Pb–Te system

The compound PbTe melts congruently at 1197 K. Two eutectics are found in the system [25]. One is degenerated close to the melting point of Pb, the other is found at 684 K and $x_{Te}=0.89$. The excess enthalpies at 1219 K are exothermic with a minimum of -26.7 kJ mol⁻¹ at $x_{Te}=0.53$. The system was often studied in the past and optimized by several authors (Table 1). The analytical description of the liquid Pb–Te phase has been presented in a previous paper [10].

3.3. The Ga–Pb system

This system contains a miscibility gap in the liquid. The data of the monotectic point are $x_{Pb}=0.945$ and $T=586$ K. The critical and eutectic temperatures are, respectively, 879 and 302.8 K [30]. The thermodynamic properties of Ga–Pb melts were reported for different temperatures. These are presented in Table 1. In this work, thermodynamic functions of the melt were optimized with the assumption of a regular behaviour using the data available in the literature. The excess enthalpies are weakly endothermic with

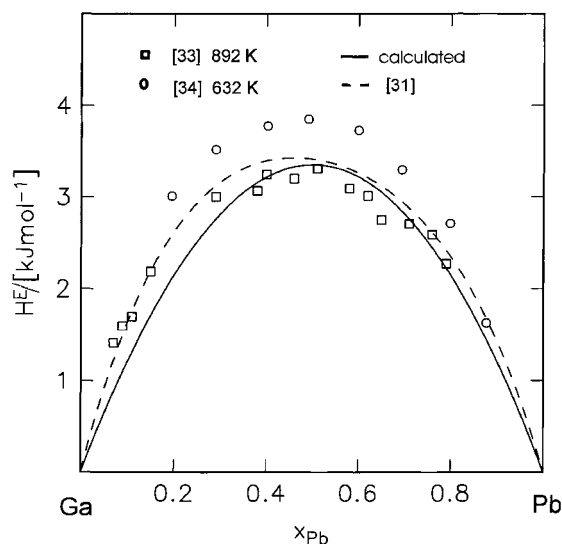


Fig. 1. Calculated and experimental excess enthalpies of liquid Ga–Pb alloys.

a maximum of ca. 3.0 kJ mol⁻¹ at $x_{Pb}=0.5$. The experimental and calculated data for H^E are given in Fig. 1.

4. The ternary Ga–Pb–Te system

The ternary phase diagram was only investigated close to the Pb–Te region [39] and contains no ternary compound. The PbTe–GaTe section of the system was reported by Abilov et al. [40] and the PbTe–Ga₂Te₃ section was investigated by Baranetz et al. [41]. Rogacheva et al. [42] found broad ranges of solid solutions in the system.

5. Analytical description

5.1. Binary systems

The tellurium systems contain the associates Ga₂Te₃ and PbTe in the melts. The thermodynamic functions of the limiting binaries were calculated according to the association model of Sommer [12,13]. The determination of the coefficients of the model (Table 2) and the calculation of the thermodynamic functions were performed with the optimiza-

tion software BINGSS and BINFKT, developed by Lukas et al. [43–45].

5.2. Ternary system

For an analytical description of the ternary Ga–Pb–Te system, the association model was also used. Additional parameters representing interactions between associates and pure components, respectively those between associates [46], were needed to obtain the best fit. From the coefficients of the limiting binaries and taking into account ternary interactions, the excess enthalpies were determined as follows:

$$\begin{aligned}
 H_{\text{GaPbTe}}^E = & \frac{n_{\text{Ga}}n_{\text{Pb}}}{n} C_{\text{Ga,Pb}}^H + n_{\text{Ga}_2\text{Te}_3} \Delta H_{\text{Ga}_2\text{Te}_3}^0 \\
 & + \frac{n_{\text{Ga}}n_{\text{Ga}_2\text{Te}_3}}{n} C_{\text{Ga,Ga}_2\text{Te}_3}^H \\
 & + \frac{n_{\text{Te}}n_{\text{Ga}_2\text{Te}_3}}{n} C_{\text{Te,Ga}_2\text{Te}_3}^H \\
 & + n_{\text{PbTe}} \Delta H_{\text{PbTe}}^0 + \frac{n_{\text{Pb}}n_{\text{PbTe}}}{n} C_{\text{Pb,PbTe}}^H \\
 & + \frac{n_{\text{Te}}n_{\text{PbTe}}}{n} C_{\text{Te,PbTe}}^H \\
 & + \frac{n_{\text{Pb}}n_{\text{Ga}_2\text{Te}_3}}{n} C_{\text{Pb,Ga}_2\text{Te}_3}^H \\
 & + \frac{n_{\text{Ga}}n_{\text{PbTe}}}{n} C_{\text{Ga,PbTe}}^H \\
 & + \frac{n_{\text{Ga}_2\text{Te}_3}n_{\text{PbTe}}}{n} C_{\text{Ga}_2\text{Te}_3,\text{PbTe}}^H \quad (1)
 \end{aligned}$$

The coefficients of the last three terms were fitted by a numerical optimization procedure using the least squares method [47] and are given in Table 3.

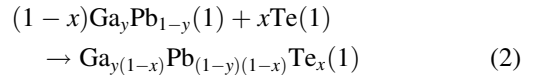
6. Results and discussion

The heat effect ΔQ of mixing was determined for five sections with constant concentration ratio of two components ($y_{\text{Ga}}/y_{\text{Pb}}=0.2, 0.4, 0.5, 0.6$ and 0.8) at

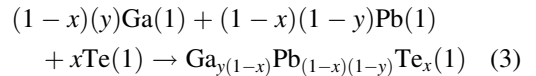
Table 3
Ternary interaction parameters of the association model of the Ga–Pb–Te system

Ga–Pb–Te	kJ mol^{-1}
$C_{\text{Ga,PbTe}}^H$	205.8
$C_{\text{Pb,Ga}_2\text{Te}_3}^H$	31.9
$C_{\text{Ga}_2\text{Te}_3,\text{PbTe}}^H$	28.7

1173 K and for one section with $y_{\text{Ga}}/y_{\text{Pb}}=0.5$ at 1073 K. The experimental enthalpies H_{exp}^E of the reaction



and the ternary excess enthalpies H^E of the reaction



are presented in Table 4 and in Fig. 2 (for one section).

A projection of the isoenthalpic lines onto the Gibbs triangle is given in Fig. 3. It shows that the exothermic values decrease smoothly from the maximum in the binary Ga–Te system at Ga_2Te_3 to the corners of the ternary system.

Ternary interaction parameters were at first not used in the calculation of ternary data from H^E data of the constituent binaries. However, the enthalpy curves of the ternary mixtures could not be reproduced (Fig. 2, dashed line). The Ga–Pb–Te system contains binary associates which are in equilibrium with constituent non-associated atoms. Therefore, ternary interactions had to be considered. The best fit was obtained, if one assumes the following ternary interactions

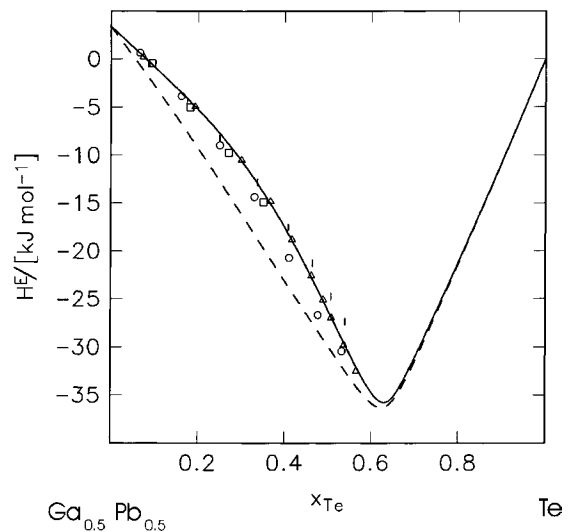


Fig. 2. $\text{Ga}_{0.5}\text{Pb}_{0.5}$ –Te section ($T=1173$ K); symbols represent different series of measurements.

Table 4

Heat effects ΔQ , experimental excess enthalpies according to the reaction $(1-x)\text{Ga}_y\text{Pb}_{1-y}(1)+x\text{Te}(1)\rightarrow\text{Ga}_{y(1-x)}\text{Pb}_{(1-y)(1-x)}\text{Te}_x(1)$ and ternary excess enthalpies according to the reaction $(1-x)(y)\text{Ga}(1)+(1-x)(1-y)\text{Pb}(1)+x\text{Te}(1)\rightarrow\text{Ga}_{y(1-x)}\text{Pb}_{(1-x)(1-y)}\text{Te}_x(1)$ in the Ga–Pb–Te system at 1173 K of the sections $\text{Ga}_y\text{Pb}_{1-y}\text{–Te}$ and at 1073 K of the section $\text{Ga}_{0.5}\text{Pb}_{0.5}\text{–Te}$

Starting amount $n_{\text{Ga}_y\text{Pb}_{1-y}}(\text{mol})$	Added amount $n_{\text{Te}}(\text{mol})$	Mole fraction x_{Te}	Heat effect $\Delta Q/\text{J}$	Experimental excess enthalpy $H_{\text{exp}}^E/(\text{J mol}^{-1})$	Ternary excess enthalpy $H^E/(\text{J mol}^{-1})$
1	2	3	4	5	6
<i>Ga_{0.2}Pb_{0.8}–Te</i>					
0.010575	0.000971	0.084	–0.3	–3753	–1602
	0.001002	0.157	3.0	–6757	–4777
	0.001706	0.258	–10.5	–11992	–10249
	0.001878	0.344	–38.7	–18154	–16614
	0.002705	0.439	–59.9	–25093	–23774
0.007656	0.000701	0.084	2.0	–3485	–1333
	0.001015	0.183	–1.2	–8040	–6121
	0.001229	0.278	–7.3	–12939	–11243
	0.001693	0.377	–23.4	–19169	–17706
0.008847	0.000744	0.078	3.6	–3067	–900
	0.001170	0.178	–2.4	–7777	–5845
	0.001151	0.257	–4.5	–11690	–9946
	0.001368	0.334	–15.5	–16222	–14657
	0.001199	0.389	–23.5	–20175	–18740
	0.002250	0.471	–74.3	–27870	–26627
0.006470	0.000997	0.134	4.5	–5322	–3298
	0.000937	0.230	–2.8	–10004	–8195
	0.002190	0.389	–30.1	–19947	–18513
	0.001184	0.451	–15.7	–23735	–22445
	0.000908	0.490	–26.5	–27299	–26101
	0.000980	0.527	–22.4	–30164	–29052
	0.000872	0.555	–0.4	–31041	–29995
	0.001176	0.588	33.1	–29930	–28963
	0.001411	0.616	48.3	–28023	–27120
<i>Ga_{0.4}Pb_{0.6}–Te</i>					
0.011185	0.000660	0.056	3.0	–2228	850
	0.001453	0.160	–5.9	–7297	–4558
	0.001940	0.267	–11.5	–12788	–10399
	0.002154	0.358	–37.7	–18887	–16795
	0.002421	0.437	–29.9	–23518	–21682
	0.001940	0.487	–33.7	–26932	–25261
	0.001532	0.521	–29.7	–29361	–27799
0.008104	0.000824	0.092	3.3	–3720	–761
	0.001065	0.189	1.4	–7914	–5271
	0.001536	0.297	–10.1	–13644	–11352
	0.002233	0.411	–36.5	–21280	–19360
	0.002405	0.499	–66.0	–28795	–27161
0.008993	0.000754	0.077	1.9	–3235	–227
	0.001317	0.187	0.7	–8.065	–5416
	0.001560	0.288	–1.9	–12700	–10378
	0.001922	0.382	–29.9	–18940	–16925

Table 4 (Continued)

Starting amount $n_{\text{Ga}_{1-y}\text{Pb}_y}/(\text{mol})$	Added amount $n_{\text{Te}}/(\text{mol})$	Mole fraction x_{Te}	Heat effect $\Delta Q/\text{J}$	Experimental excess enthalpy $H_{\text{exp}}^E/(\text{J mol}^{-1})$	Ternary excess enthalpy $H^E/(\text{J mol}^{-1})$
1	2	3	4	5	6
	0.002526	0.473	-52.9	-25797	-24080
	0.001755	0.522	-44.1	-29866	-28309
0.011779	0.000807	0.064	4.5	-2488	563
	0.001592	0.169	-0.4	-7215	-4506
	0.001737	0.260	-13.8	-12133	-9721
	0.001967	0.341	-27.7	-17228	-15080
0.009114	0.001101	0.108	11.9	-3612	-703
	0.000966	0.185	3.9	-6778	-4120
	0.001648	0.290	-8.5	-12266	-9950
	0.001810	0.377	-25.1	-17945	-15915
	0.001152	0.423	-21.3	-21220	-19339
	0.001455	0.472	-30.0	-24910	-23187
	0.001085	0.503	-33.1	-27868	-26248
	0.001105	0.531	-35.6	-30636	-29107
	0.000868	0.551	-28.0	-32601	-31138
<i>Ga_{0.5}Pb_{0.5}-Te, T=1073 K</i>					
0.013427	0.000984	0.068	1.5	-2793	389
	0.001125	0.136	-0.5	-5697	-2746
	0.001639	0.218	-64.7	-12969	-10300
	0.002205	0.307	-262.5	-29868	-27502
0.009711	0.000852	0.081	-0.2	-3438	-299
	0.001010	0.161	-5.3	-7301	-4436
	0.001220	0.241	-28.6	-12885	-10293
	0.001601	0.325	-141.2	-25982	-23678
	0.002065	0.410	-168.4	-38279	-36264
	0.001915	0.471	-139.2	-31133	-29328
<i>Ga_{0.5}Pb_{0.5}-Te</i>					
0.013541	0.000960	0.066	5.6	-2547	641
	0.001635	0.161	1.0	-6718	-3858
	0.001930	0.250	-14.6	-11546	-8987
	0.002153	0.330	-32.6	-16649	-14362
	0.002733	0.410	-64.1	-22739	-20724
	0.002927	0.477	-84.8	-28458	-26671
	0.003061	0.532	-54.5	-32022	-30424
0.010209	0.001055	0.094	6.8	-3553	-458
	0.001195	0.181	-4.4	-7820	-5022
	0.001524	0.270	-6.4	-12255	-9762
	0.001748	0.351	-20.5	-17122	-14906
0.010269	0.000819	0.074	3.5	-2962	201
	0.001643	0.193	7.3	-7725	-4970
	0.001940	0.300	-5.2	-12922	-10532
	0.001560	0.367	-17.0	-16987	-14826
	0.001395	0.417	-29.3	-20813	-18823
	0.001465	0.462	-34.3	-24416	-22579

Table 4 (Continued)

Starting amount $n_{\text{Ga}_y\text{Pb}_{1-y}}/(\text{mol})$	Added amount $n_{\text{Te}}/(\text{mol})$	Mole fraction x_{Te}	Heat effect $\Delta Q/\text{J}$	Experimental excess enthalpy $H_{\text{exp}}^E/(\text{J mol}^{-1})$	Ternary excess enthalpy $H^E/(\text{J mol}^{-1})$
1	2	3	4	5	6
	0.001012	0.489	–28.6	–26843	–25098
	0.000783	0.508	–23.7	–28633	–26953
	0.001291	0.537	–40.3	–31363	–29781
	0.001479	0.566	–42.3	–33961	–32478
0.009389	0.000911	0.088	3.5	–3582	–468
	0.001067	0.174	2.4	–7198	–4377
	0.001130	0.249	–3.4	–10829	–8263
	0.001656	0.337	–5.1	–15113	–12847
	0.001701	0.408	–20.4	–19536	–17513
	0.001668	0.464	–20.9	–23098	–21259
	0.001505	0.507	–31.8	–26443	–24757
	0.001386	0.540	–26.3	–28949	–27378
<i>Ga_{0.6}Pb_{0.4}–Te</i>					
0.013628	0.001051	0.072	9.3	–2544	609
	0.001218	0.143	5.3	–5414	503
	0.001893	0.234	0.6	–9524	–6923
	0.002538	0.330	–43.6	–16018	–13742
	0.001877	0.386	–27.6	–19631	–17547
	0.002250	0.443	–54.9	–24150	–22258
0.012549	0.001770	0.124	1.6	–5369	–2425
	0.001005	0.181	–8.4	–8472	–5721
	0.001828	0.268	–22.8	–13625	–11167
	0.001779	0.337	–34.1	–18313	–16086
	0.001219	0.377	–28.6	–21309	–19216
	0.001270	0.414	–28.0	–23979	–22011
	0.001497	0.452	4.9	–25094	–23254
0.010424	0.000875	0.077	8.2	–2709	391
	0.001479	0.184	1.1	–7442	–4701
	0.001394	0.264	–6.0	–11492	–9021
	0.001361	0.329	–14.5	–15301	–13047
	0.001264	0.379	–21.3	–18754	–16670
	0.001713	0.437	–44.6	–23534	–21642
	0.001242	0.472	–33.0	–26515	–24742
	0.001666	0.513	–39.6	–29748	–28113
	0.001082	0.537	–10.6	–30923	–29366
	0.000963	0.556	6.2	–31210	–29718
	0.001630	0.585	32.3	–30775	–29380
<i>Ga_{0.8}Pb_{0.2}–Te</i>					
0.018696	0.000812	0.042	16.8	–984	1529
	0.001213	0.098	13.9	–2854	–488
	0.001355	10.153	10.5	–4926	–2705
	0.001576	0.210	3.3	–7414	–5341
	0.001844	0.267	–5.7	–10308	–8385
	0.002168	0.324	–21.2	–13741	–11969
	0.001902	0.268	–31.4	–16773	–15115
	0.002274	0.413	–85.8	–21438	–19898

Table 4 (Continued)

Starting amount $n_{\text{Ga}_y\text{Pb}_{1-y}}/(\text{mol})$	Added amount $n_{\text{Te}}/(\text{mol})$	Mole fraction x_{Te}	Heat effect $\Delta Q/\text{J}$	Experimental excess enthalpy $H_{\text{exp}}^E/(\text{J mol}^{-1})$	Ternary excess enthalpy $H^E/(\text{J mol}^{-1})$
1	2	3	4	5	6
	0.002275	0.452	-49.5	-24415	-22987
0.012578	0.001051	0.077	12.6	-2496	-77
	0.001413	0.164	14.8	-5442	-3250
	0.001737	0.250	3.8	-9246	-7281
	0.002248	0.339	-16.4	-14253	-12519
	0.001835	0.397	-23.9	-18043	-16462
	0.001127	0.428	-36.8	-21064	-19564
	0.001969	0.475	-47.5	-24962	-23585
	0.001111	0.498	-31.7	-27087	-25771
0.013372	0.000784	0.055	11.1	-1673	804
	0.001026	0.119	4.3	-4271	-1961
	0.001652	0.206	-0.3	-8220	-6138
	0.000842	0.243	-1.1	-10000	-8017
	0.001458	0.301	-14.8	-13389	-11557
	0.001691	0.358	-28.3	-17262	-15579
	0.001850	0.410	-41.5	-21303	-19757
	0.001277	0.442	-34.6	-23975	-22511
	0.001065	0.465	-31.7	-26102	-24700
	0.001335	0.492	-36.8	-28424	-27094
	0.001687	0.523	-45.6	-31011	-29760
	0.001811	0.552	-47.8	-33423	-32248

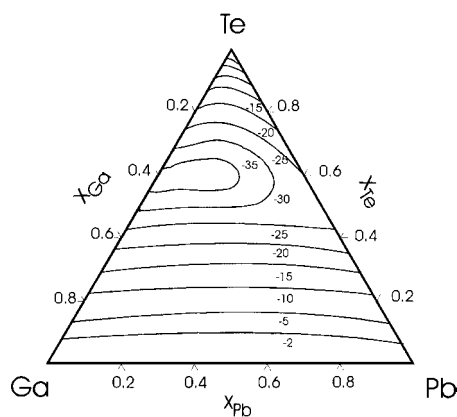


Fig. 3. Projection of the isoenthalpic lines on the Gibbs triangle in the Ga-Pb-Te system at $T=1173$ K in kJ mol^{-1} .

$\text{Ga}_2\text{Te}_3 \leftrightarrow \text{Pb}$, $\text{PbTe} \leftrightarrow \text{Ga}$ and $\text{Ga}_2\text{Te}_3 \leftrightarrow \text{PbTe}$ (Fig. 2, solid line). The observed excess enthalpies decrease slightly with increasing temperature. The effect is due to the dissociation of associates with increasing temperatures.

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