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COMPARATIVE THERMODYNAMIC ANALYSIS OF THE BINARY SYSTEM Bi–Sb

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Abstract

Results of the comparative thermodynamic analysis of the binary system Bi–Sb obtained by DTA measurements and predicting are presented in this paper. Activities, activity coefficients, partial and integral molar quantities for Bi and Sb at temperatures 973, 1073 and 1173 K in the investigated binary system Bi–Sb determined by DTA measurements and thermodynamic predicting are given. An excellent agreement between the experimental and predicted results is reached. Also, a phase diagram of the investigated system Bi–Sb obtained by DTA shows good agreement with literature and it can be concluded that DTA could be satisfactorily used for quantitative thermodynamic analysis of any binary system containing equilibrium between solid and liquid solutions. It was also determined that conclusion about linear dependence of *gKs* constant for binary eutectic systems and systems with phase transformation is valid for binary system containing equilibrium between solid and liquid solutions too.

Keywords: Bi–Sb system, DTA, thermodynamic analysis

Introduction

There are just a few articles about binary system Bi–Sb, which contains equilibrium between solid and liquid solutions. Phase diagram was determined by M. Hansen and K. Anderko [1], with a liquidus accurately known to ±5° and somewhat less accurate solidus. These results are cited in the well known books, such as R. Hultgren *et al.* [2] and C. J. Smithells [3]. M. Kawakami [4] calorimetrically determined heats of formation by direct reaction of the liquid elements for alloys with composition $x_{Sb}=0.21–0.77$ at temperature 1073 K. O. Kubaschewski and W. Seith [5] found mixing heats of the components in solid state at temperature 298 K. Solid solutions in the binary system Bi–Sb was studied by Y. E. Geguzin and B. Y. Pines [6] and they determined specific heat for the alloy with $x_{Sb}=0.63$ in the temperature interval 623–823 K.

Results of the comparative thermodynamic analysis of the investigated binary system obtained by DTA measurements and predicting method proposed by

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Chou are presented in this paper as a contribution to complete thermodynamic description of this system.

Experimental

For thermodynamic analysis of the binary system Bi–Sb differential thermal analysis was used. Descriptions of this experimental technique has been reported in literature [7–9]. Metallic Bi and Sb used in experiments were of p.a. purity.

Results and discussion

a) Phase diagram determination

For phase diagram determination, pure metals Bi and Sb and six alloys with molar content of Bi: 0.836; 0.680; 0.533; 0.390; 0.250 and 0.124 were used. All samples had a constant volume of 0.1 cm^3. There are no data in literature about DTA using for determination of the phase diagram of binary systems containing equilibrium between solid and liquid solutions. For that reason, beginning of the peak was used for solidus line determination, and the end of the peak was used for liquidus line determination.

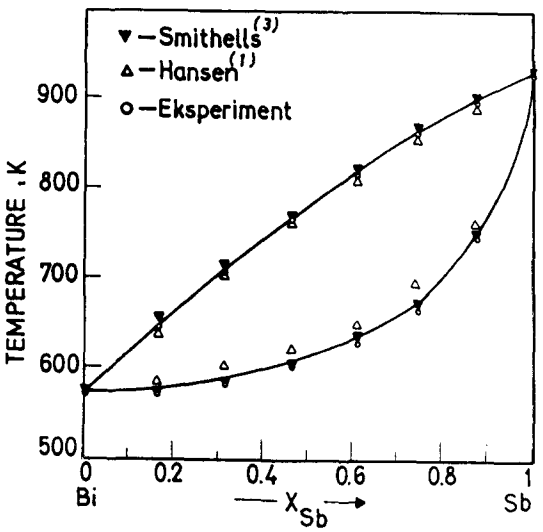

Fig. 1 Phase diagram of the binary system Bi–Sb

Phase diagram of the binary system Bi–Sb obtained by DTA is given in Fig. 1 and it may be seen that experimental data shows good agreement with literature [2, 3].

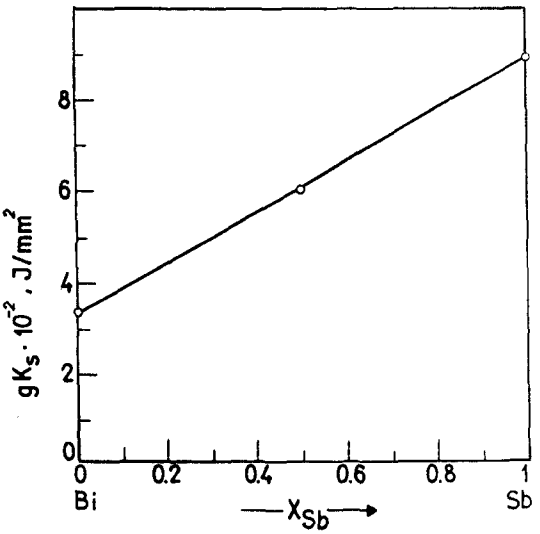

Fig. 2 Dependence of *gKs vs.* composition for Bi–Sb system

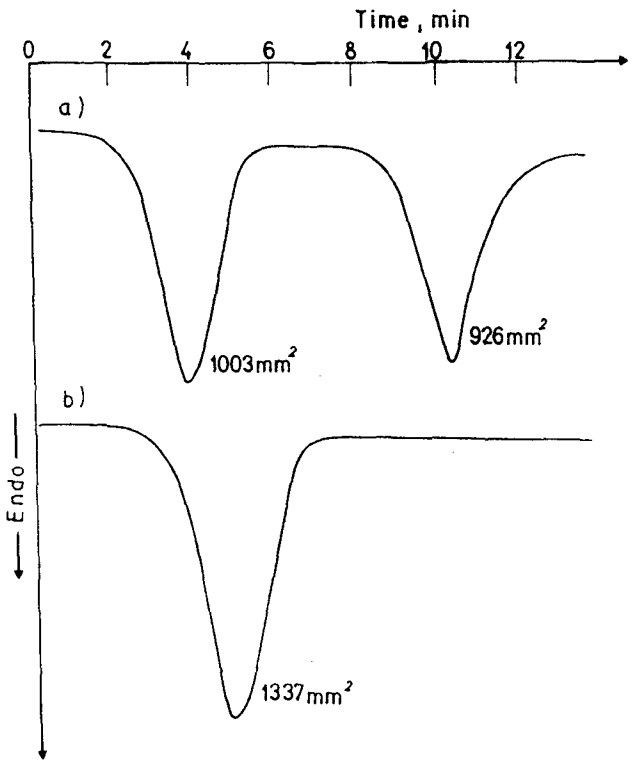

Fig. 3 DTA curves for first (a) and second (b) melting (sample $x_{Bi} = 0.836$)

b) Quantitative thermodynamic DTA analysis

According to basic equation of the quantitative DTA [8]:

$$m\Delta H_T^\circ = gKs\int \Delta T \, dT \tag{1}$$

where is: m – mass of the sample, ΔH_T° – reaction enthalpy, gKs – calibration constant and $\int \Delta T dT$ – peak area, it is necessary to determine the value of calibration constant, gKs. It is known from literature [11, 12] that there is a linear dependence of gKs from binary system composition. That was also confirmed in this case, and obtained values of gKs *vs.* composition are presented in Fig. 2. So, conclusion about linear dependence of gKs constant for binary eutectic systems [11] and systems with phase transformations [12] is valid for binary systems containing equilibrium between solid and liquid solutions too.

For the quantitative DTA analysis of the investigated binary system Bi–Sb, well known methodology with two meltings [6] was used for determination of the mixing enthalpies in liquid and solid state. During the first melting, metal

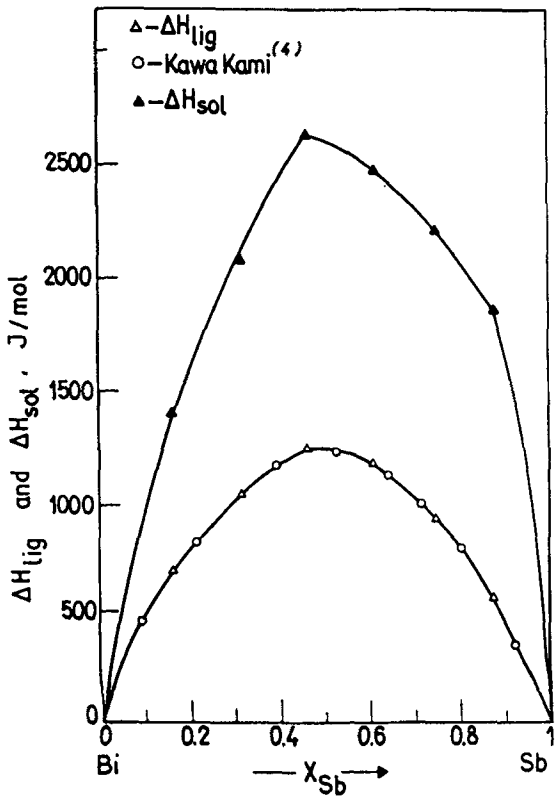

Fig. 4 Dependences of ΔH_{liq} and ΔH_{sol} *vs.* composition for Bi–Sb system

(Bi) with lower melting temperature is melted, then metal with higher melting temperature (Sb) and they mix. Enthalpy needed for this melting is given as

$$\Delta H_{\mathrm{I}} = x_{\mathrm{Bi}} L_{\mathrm{Bi}} + x_{\mathrm{Sb}} L_{\mathrm{Sb}} + \Delta H_{\mathrm{liq}} \tag{2}$$

where is: x_i – molar content of the component i, L_i – melting enthalpy of the component i and ΔH_{liq} – mixing enthalpy in liquid state.

During the second melting, allow got by the first melting is melted, and the enthalpy needed for this case is given as

$$\Delta H_{\mathrm{II}} = x_{\mathrm{Bi}} L_{\mathrm{Bi}} + x_{\mathrm{Sb}} L_{\mathrm{Sb}} + \Delta H_{\mathrm{liq}} - \Delta H_{\mathrm{sol}} \tag{3}$$

where is ΔH_{sol} – mixing enthalpy in solid state.

Difference between ΔH_{I} and ΔH_{II} presents ΔH_{sol},

$$\Delta H_{\mathrm{sol}} = \Delta H_{\mathrm{I}} - \Delta H_{\mathrm{II}} \tag{4}$$

DTA experiments for the investigated samples of given composition in the binary system Bi–Sb were done according to this methodology. Example of the DTA curve for alloy with composition $x_{\mathrm{Bi}} = 0.836$ is given in Fig. 3.

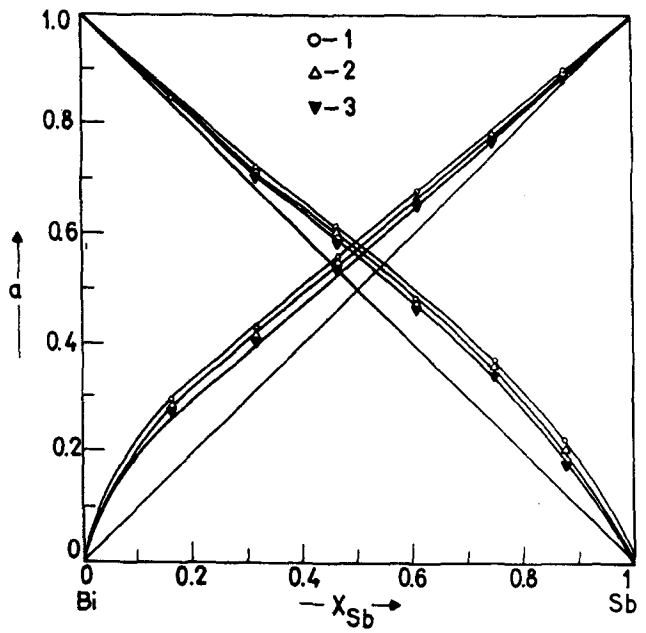

Fig. 5 Dependences of a_{Bi} and a_{Sb} *vs.* composition at 973 (1), 1073 (2) and 1173 K (3) obtained by DTA

Table 1 Thermodynamic quantities for binary system Bi–Sb obtained by DTA

a) 973 K

X_{Bi}	γ_{Bi}	a_{Bi}	γ_{Sb}	a_{Sb}	G_{Bi}^{XS}	G_{Sb}^{XS}	ΔG^{XS}	G_{Bi}^{M}	G_{Sb}^{M}	ΔG^{M}
1.000	1.000	1.000	–	–	–	–	–	–	–	–
0.836	1.016	0.850	1.781	0.291	132	4670	874	–1314	–9975	–2731
0.680	1.056	0.718	1.333	0.426	438	2327	1041	–2675	–6903	–4026
0.533	1.146	0.611	1.194	0.558	1105	1435	1259	–3989	–4719	–4330
0.390	1.240	0.483	1.102	0.672	1738	783	1155	–5887	–3211	–4254
0.255	1.447	0.368	1.042	0.777	2988	335	1011	–8076	–2043	–3580
0.124	1.783	0.222	1.025	0.897	4679	200	758	–12175	–876	–2283
0.000	–	–	1.000	1.000	–	–	–	–	–	–

b) 1073 K

X_{Bi}	γ_{Bi}	a_{Bi}	γ_{Sb}	a_{Sb}	G_{Bi}^{XS}	G_{Sb}^{XS}	ΔG^{XS}	G_{Bi}^{M}	G_{Sb}^{M}	ΔG^{M}
1.000	1.000	1.000	–	–	–	–	–	–	–	–
0.836	1.010	0.845	1.730	0.283	91	4889	876	–1502	–11261	–3099
0.680	1.043	0.710	1.293	0.413	379	2290	890	–3055	–7889	–4599
0.533	1.124	0.599	1.173	0.548	1046	1421	1221	–4572	–5366	–4943
0.390	1.209	0.471	1.094	0.668	1693	804	1150	–6717	–3599	–4814
0.255	1.413	0.360	1.036	0.772	3087	314	1020	–9114	–2308	–4041
0.124	1.679	0.209	1.001	0.876	4621	5	580	–13965	–1181	–2773
0.000	–	–	1.000	1.000	–	–	–	–	–	–

c) 1173 K

X_{Bi}	γ_{Bi}	a_{Bi}	γ_{Sb}	a_{Sb}	G_{Bi}^{XS}	G_{Sb}^{XS}	ΔG^{XS}	G_{Bi}^{M}	G_{Sb}^{M}	ΔG^{M}
1.000	1.000	–	–	–	–	–	–	–	–	–
0.836	1.003	0.839	1.675	0.274	30	5029	848	–1712	–12626	–3494
0.680	1.036	0.705	1.271	0.406	345	2337	981	–3400	–8791	–5129
0.533	1.092	0.582	1.138	0.532	863	1265	1051	–5279	–6155	–5688
0.390	1.188	0.463	1.075	0.656	1683	703	1085	–7510	–4112	–5436
0.255	1.331	0.339	1.024	0.763	2788	229	881	–10550	–2638	–4653
0.124	1.406	0.175	1.001	0.876	3320	6	419	–16998	–1291	–3247
0.000	–	–	1.000	1.000	–	–	–	–	–	–

By using of Eqs (2), (3) and (4), as well as the *gKs* dependence shown in Fig. 2, dependences ΔH_{liq} and ΔH_{sol} *vs.* molar content were determined and presented in Fig. 4. Results of M. Kawakami [2] are also shown in this figure, and good agreement can be noticed.

Activity determination for both components in binary system Bi–Sb was done based on the values of the enthalpy and entropy of mixing in liquid state. In this case, values of the mixing enthalpies were determined experimentally, while mixing entropy values were calculated based on equation for ideal solutions:

$$\Delta S_{id}^{m} = -R(x_{Bi}\ln x_{Bi} + x_{Sb}\ln x_{Sb}) \tag{5}$$

where R is universal gas constant.

Values for Planck potencial for corresponding compositions of the investigated system and temperatures, can be obtained from equation [13]:

$$P_{i,x,T} = \Delta S_{i,x,T}^{m} - (\Delta H_{i,x,T}^{m} / T). \tag{6}$$

Based on determined values for Planck potencial at temperatures 973, 1073 and 1173 K and by tangent construction on the dependence curve of Planck potencial *vs.* molar content, activities for components Bi and Sb at these temperatures were obtained. Calculated values for components Bi and Sb in the binary system Bi–Sb at temperatures 973, 1073 and 1173 K are given in Fig. 5.

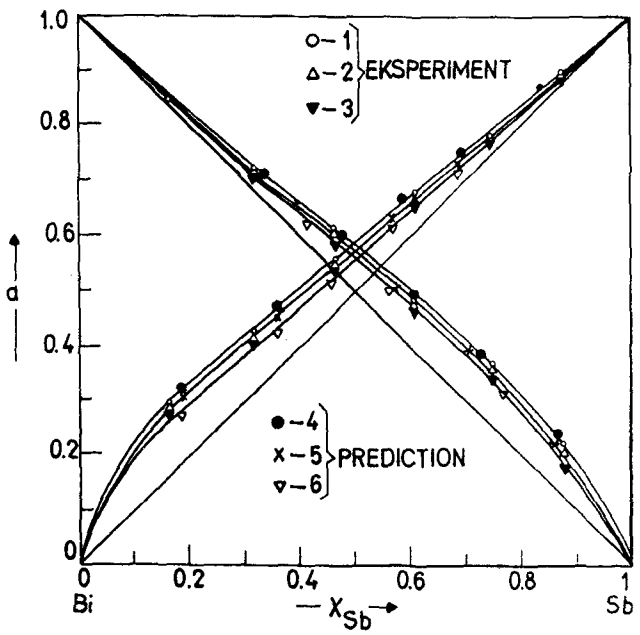

Fig. 6 Comparative analysis of the dependences of a_{Bi} and a_{Sb} *vs.* composition at 973 (1 and 4), 1073 (2 and 5) and 1173 K (3 and 6) obtained experimentally (DTA) and calculated (predicting, Chou)

Table 2 Thermodynamic quantities for binary system Bi–Sb obtained by Chou predicting method

a) 973 K

X_{Bi}	γ_{Bi}	a_{Bi}	γ_{Sb}	a_{Sb}	G_{Bi}^{XS}	G_{Sb}^{XS}	ΔG^{XS}	G_{Bi}^{M}	G_{Sb}^{M}	ΔG^{M}
0.90	1.019	0.917	2.480	0.248	151	7347	871	–701	–11279	–1759
0.80	1.031	0.825	1.635	0.327	249	3977	995	–1556	–9042	–3053
0.70	1.064	0.745	1.327	0.398	504	2287	1039	–2381	–7453	–3903
0.60	1.093	0.656	1.260	0.504	722	1870	1181	–3410	–5543	–4263
0.50	1.148	0.574	1.168	0.584	1116	1256	1186	–4491	–4351	–4421
0.40	1.215	0.486	1.127	0.676	1575	965	1209	–5837	–3168	–4236
0.30	1.337	0.401	1.064	0.745	2647	504	1057	–7392	–2381	–3884
0.20	1.605	0.321	1.036	0.829	3827	288	996	–9193	–1517	–3052
0.10	1.940	0.194	1.021	0.919	5361	169	688	–13266	–683	–1941

b) 1073 K

X_{Bi}	γ_{Bi}	a_{Bi}	γ_{Sb}	a_{Sb}	G_{Bi}^{XS}	G_{Sb}^{XS}	ΔG^{XS}	G_{Bi}^{M}	G_{Sb}^{M}	ΔG^{M}
0.90	1.017	0.915	2.180	0.218	147	6952	827	–792	–13589	–2072
0.80	1.026	0.821	1.585	0.317	231	4109	1007	–1759	–10249	–3457
0.70	1.051	0.736	1.313	0.394	447	2432	1042	–2734	–8309	–4406
0.60	1.080	0.648	1.237	0.495	687	1901	1173	–3870	–6273	–4831
0.50	1.130	0.565	1.150	0.575	1090	1247	1168	–5093	–4937	–5015
0.40	1.197	0.479	1.093	0.656	1608	796	1121	–6566	–3761	–4883
0.30	1.310	0.393	1.054	0.738	2409	472	1053	–8332	–2710	–4397
0.20	1.510	0.302	1.026	0.821	3676	231	920	–10681	–1759	–3543
0.10	1.630	0.163	1.007	0.906	4359	59	489	–16183	–881	–2411

c) 1173 K

X_{Bi}	γ_{Bi}	a_{Bi}	γ_{Sb}	a_{Sb}	G_{Bi}^{XS}	G_{Sb}^{XS}	ΔG^{XS}	G_{Bi}^{M}	G_{Sb}^{M}	ΔG^{M}
0.90	1.014	0.913	1.970	0.197	140	6612	787	–888	–15843	–2383
0.80	1.019	0.815	1.530	0.306	181	4147	974	–1995	–11548	–3906
0.70	1.033	0.723	1.297	0.389	315	2534	981	–3163	–9208	–4976
0.60	1.068	0.641	1.177	0.471	645	1593	1024	–4337	–7342	–5539
0.50	1.112	0.556	1.120	0.560	1035	1105	1070	–5724	–5655	–5689
0.40	1.177	0.471	1.075	0.645	1593	705	1060	–7342	–4276	–5502
0.30	1.290	0.387	1.039	0.727	2483	369	1003	–9258	–3109	–4954
0.20	1.380	0.276	1.019	0.815	3141	181	773	–12555	–1995	–4107
0.10	1.410	0.141	1.001	0.901	3351	11	345	–19105	–1017	–2826

According to known values of Bi and Sb activities, other thermodynamic quantities were determined: activity coefficients, partial and integral molar quantities for Bi and Sb at temperatures 973, 1073 and 1173 K. These results are presented in Table 1.

c) Thermodynamic predicting according to Chou

For binary systems containing equilibrium between solid and liquid solutions a thermodynamic predicting method proposed by Chou [10] could be used.

According to the basic equation in that method [10]:

$$d\ln a_1^l = -\Phi_1^l \, d\sigma/\sigma_o + \ln x_1^l \, d(1-\sigma/\sigma_o) \tag{7}$$

where is: a_1^l – activity of the component 1 in liquid solution, and:

$$\Phi_1^l = (x_2^l(x_1^s\Delta S_{m1}^\circ + x_2^s\Delta S_{m2}^\circ)/R - \left(x_2^s\sum\nolimits_{id}^{l} - x_2^l\sum\nolimits_{id}^{s}\right) -$$

$$- x_2^l(x_1^s\Delta H_{m1}^\circ + x_2^s\Delta H_{m2}^\circ)/R\Theta)/(x_2^s - x_2^l) \tag{8}$$

where is: $x_1^{l,s}$ – molar content of the component 1 in liquid and solid solution respectively, R – universal gas constant, ΔS_{mi}° – standard entropy of melting for component i, ΔH_{mi}° – standard enthalpy of melting for component i and $\Theta = 3000$ (according to Richardson assumption [10]) and:

$$\sum\nolimits_{id}^{l} = x_1^l \ln x_1^l + x_2^l \ln x_2^l \tag{9}$$

$$\sum\nolimits_{id}^{s} = x_1^s \ln x_1^s + x_2^s \ln x_2^s \tag{10}$$

Equations for calculation of activity of the component 2 in liquid solution could be derived analogically.

Data needed for calculation according to Chou predicting method are taken from Hultgren *et al.* [2].

Results of activities, activity coefficients and other thermodynamic quantities for Bi and Sb at temperatures 973, 1073 and 1173 K are given in Table 2.

Results obtained by Chou predicting method shows good agreement with experimental results (Fig. 6) which illustrates good consistence of the used predicting method.

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Zusammenfassung — Vorliegend werden die Resultate einer vergleichenden thermodynamischen Analyse des binären Systemes Bi–Sb dargelegt, die aufgrund von DTA-Messungen und Voraussagen erhalten wurde. Anhand von DTA-Messungen und thermodynamischen Voraussagen werden für Bi und Sb bei den Temperaturen 973, 1073 und 1173 K im untersuchten binären Bi–Sb-System Aktivitäten, Aktivitätskoeffizienten, partielle und integrale molare Größen angegeben. Es wurde eine ausgezeichnete Übereinstimmung zwischen experimentellen und vorausgesagten Ergebnissen erzielt. Auch das mittels DTA erstellte Phasendiagramm des untersuchten Bi–Sb-Systemes zeigt eine gute Übereinstimmung mit den Literaturangaben und man kann darauf schließen, daß DTA zufriedenstellend zur quantitativen thermodynamischen Analyse aller binären Systeme mit Gleichgewicht zwischen fester und flüssiger Lösung eingesetzt werden kann. Weiterhin wurde festgestellt, daß der Schluß auf die lineare Abhängigkeit der Konstante gKs von binären eutektischen Systeme und Systemen mit Phasenumwandlung auch für binäre Systeme mit Gleichgewicht zwischen fester und flüssiger Lösung gilt.