

THERMODYNAMICS OF LIQUID Fe–Si AND Fe–Ge ALLOYS

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Abstract

The enthalpies of mixing of liquid binary Fe–Ge (1765±5 K) and Fe–Si (1750±5 K) alloys were determined using a high-temperature isoperibolic calorimeter. The thermodynamic properties of Fe–Ge melts were also studied by electromotive force method in the temperature range of 1250–1580 K. The comparison of our measurement results with literature data has been performed. The extreme negative values of integral enthalpy of mixing and alternating-sign deviations from Raoult's law for germanium can be explained by the influence of binary clusters formation.

Keywords: calorimetry, electromotive force method, Fe–Ge, Fe–Si, liquid alloys, thermodynamics

Introduction

Enthalpies of mixing of liquid Fe–Si alloys were numerously studied by high-temperature calorimetry [1–11] and electromotive force (*emf*) method [12, 13]. The calorimetric data on binary Fe–Si system show satisfactory agreement, Fig. 1. Only data [3] are understated by absolute value at $x_{\text{Si}} \geq 0.625$ and data [2] are overstated at $x_{\text{Si}} = 0.5$. Chart has simulated an integral enthalpy of mixing ($\Delta_{\text{mix}}H$) [14] for all concentration ranges based on [1, 5] data generalization ($\Delta_{\text{mix}}H^{\text{mm}} = -38.3 \text{ kJ mol}^{-1}$ at $x = 0.45$). $\Delta_{\text{mix}}H$ data determined by *emf* [12] correlate well with calorimetry-measured values [1–11], thus *emf* data [13] are overstated by absolute value.

The heat of mixing of liquid Fe–Ge alloys was studied by Yesin [15] (calorimetry at 1880 K) in the whole concentration range. Later the calorimetric method was used by Castanet and Shlapak [16–18] (Fig. 2). Castanet determined the partial mixing enthalpy of iron at indefinite dilution at 1274 K ($\Delta_{\text{mix}}\bar{H}_{\text{Fe}}^{\infty} = -36.2 \text{ kJ mol}^{-1}$) [17]. Enthalpies of mixing in Fe–Ge system excepted calorimetry were also studied via Knudsen effusion technique [19, 20]. The thermodynamic activity of components in this system has been derived by *emf* [21], Knudsen effusion technique [19, 20] and distribution coefficient

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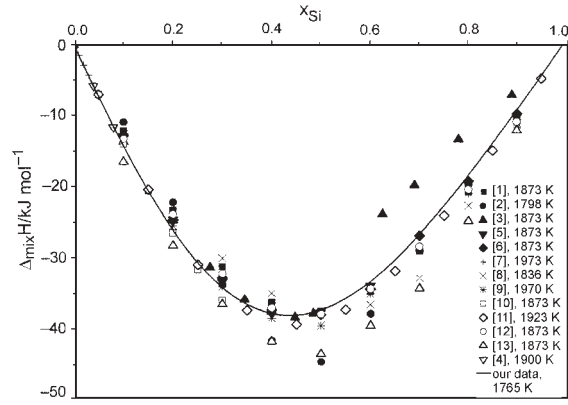


Fig. 1 Integral enthalpies of mixing in liquid Fe-Si alloys

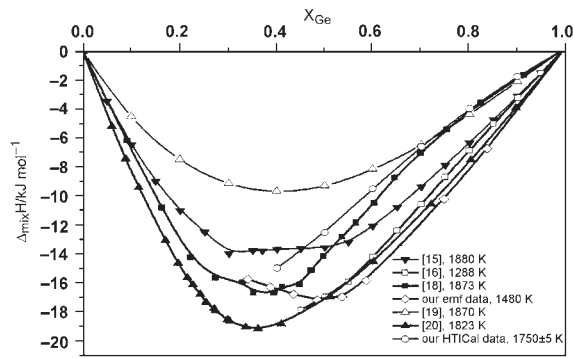


Fig. 2 Integral enthalpies of mixing in liquid Fe-Ge alloys

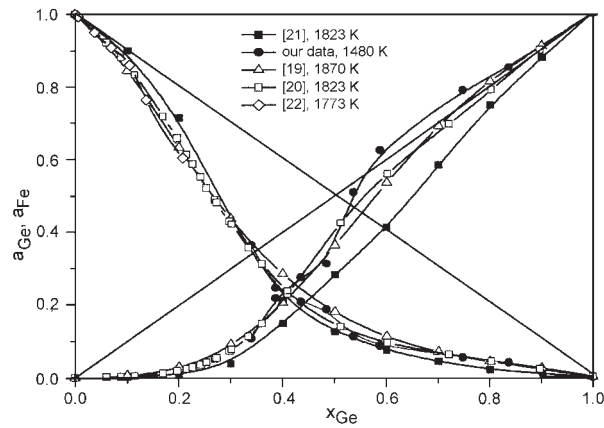


Fig. 3 Thermodynamic activities of components in liquid Fe-Ge alloys

method [22] (Fig. 3). As one can see in Fig. 3, the majority of the melts are characterized by negative deviations from ideal solutions. Integral excess Gibbs free energies of mixing ($\Delta_{\text{mix}}G^{\text{xs}}$) in Fe–Ge system [19–21, 23] are shown in Fig. 4.

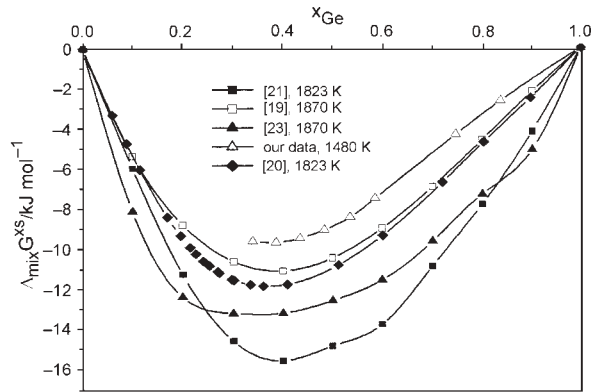


Fig. 4 Excess Gibbs free energies of mixing in liquid Fe–Ge alloys

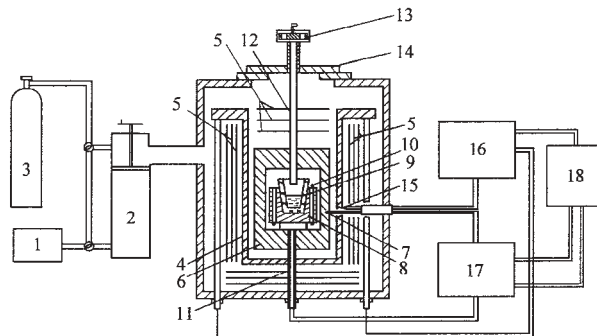


Fig. 5 A principal scheme of high-temperature isoperibolic calorimeter.

1 – high-pressure oil pump (2NVR-5DM model) equipped with Deluxe vacuum controller; 2 – vacuum diffusion-pump (N-05 model); 3 – the argon-filled gas balloon with mounted purification system; 4 – tungsten principal heater; 5 – molybdenum horizontal and vertical reflective shields; 6 – massive molybdenum block; 7 – thermocouple (W-Re 5/20 type) placed in isothermal zone of massive block; 8 – molybdenum cell for thermodynamical measurements; 9 – alumina crucible with the melt; 10 – battery of differential thermocouples; 11 – alumina two-channel pipe; 12 – alumina pipe for samples introduction into liquid bath; 13 – the revolving type mechanism for dropping of samples; 14 – water-cooled stainless-steel cover of furnace; 15 – thermocouple (W-Re 5/20 type) situated in the heater zone; 16 – the system (RIF-IV model) for automatic control and regulation of temperature; 17 – data acquisition system; 18 – personal IBM computer for data registration and treatment

The available thermodynamics data for Fe–Ge system (Figs 2–4) are in disagreement. Therefore in this work we have studied the thermodynamics of liquid Fe–Ge alloys using high-temperature isoperibolic calorimetry (HTICal) and *emf*.

The enthalpies of mixing liquid Fe–Si alloys have been studied sufficiently, therefore this system has been used as a reference for calorimeter testing, Fig. 5.

Experimental procedures

Both (HTICal and *emf*) measurements were carried out under purified argon at atmospheric pressure. The alloy samples for *emf* were prepared by standard arc-melting technique from silicon (purity, 99.99 mass%), germanium (purity, 99.999 mass%) and iron (purity, 99.95 mass%) reactives of Alpha. The same materials as well as tungsten (Alpha, purity, 99.96 mass%) have been applied for HTICal experiments. The salts KCl, NaCl and FeCl₂ (Riedel-de Haën Co.) were used for liquid electrolyte preparation.

The isoperibolic calorimeter (Fig. 5) differs from already presented model [24]: namely differential thermocouples battery (10) has been placed in a cell. At the beginning of HTICal experiment, samples of silicon or germanium were dropped into alundum crucible (9) containing the same molten element for the device calibration. The heat effects were measured by introduction of iron samples at a standard temperature (298 K) into a liquid bath (1765±5 or 1750±5 K). For the final calorimeter calibration, dropping of weighted tungsten samples were used.

The partial enthalpy of iron mixing has been computed by the following equation:

$$\Delta_{\text{mix}} \bar{H}_{\text{Fe}} = -\Delta_{\text{mix}} H_{298\text{Fe}}^{\text{T}} - \frac{k}{n_{\text{Fe}}} \int_0^{\tau_{\infty}} \Delta T dt - \Delta_{\text{m}} H_{\text{Fe}} \quad (1)$$

where $\Delta_{\text{mix}} H_{298\text{Fe}}^{\text{T}}$ is the standard enthalpy for iron [25]; k – thermal coefficient of calorimeter; n_{Fe} – quantity of dropped iron sample, mol; τ_{∞} – time of temperature relaxation; t – time, ΔT – difference between temperature of melt at the moment t and equilibrium melt temperature, $\Delta_{\text{m}} H_{\text{Fe}}$ – iron enthalpy of melting.

The alpha function α_{Fe} ($\alpha_{\text{Fe}} = \Delta_{\text{mix}} \bar{H}_{\text{Fe}} / (1-x_{\text{Fe}})^2$, where x_{Fe} is molar fraction of Fe) was calculated. The integral enthalpy of mixing has been computed via α_{Fe} -function in accordance with Darken's method:

$$\Delta_{\text{mix}} H = (1-x_{\text{Fe}}) \int_0^{x_{\text{Fe}}} \alpha_{\text{Fe}} dx_{\text{Fe}} \quad (2)$$

The estimated intervals for computed data were calculated from σ' , which is least square regression deviation of smoothing α_{Fe} -function.

The electromotive force of concentration galvanic cells $(-)\text{Fe}_{\text{Solid}}|\text{FeCl}_2$ in KCl+NaCl (azeotropic solution)| $(\text{Fe-Ge})_{\text{Liquid}}(+)$ were determined in our *emf* study in the temperature range from 1250 up to 1580 K. The *emf* values were proceeded by temperature least squares regression for equation: $E=A+BT$, where E – *emf*, A and B are linear regression coefficients. It is known, that $\Delta_{\text{mix}} \bar{G}_i = -ZFE = RT \ln a_i$, alterna-

tively $\Delta_{\text{mix}} \bar{G}_i = \Delta_{\text{mix}} \bar{H}_i - T \Delta_{\text{mix}} \bar{S}_i$, where a_i – i -component activity, Z – ion charge, F – Faraday constant, $\Delta_{\text{mix}} \bar{S}_i$ – i -component partial entropy of mixing.

Thus following equations can be obtained for overcooled liquid iron:

$$\Delta_{\text{mix}} \bar{H}_{\text{Fe}} = -ZFA - \Delta_{\text{m}} H_{\text{Fe}} - \Delta_{\gamma \rightarrow \alpha} H_{\text{Fe}} \quad (3)$$

$$\Delta_{\text{mix}} \bar{S}_{\text{Fe}} = -ZFA - \Delta_{\text{m}} S_{\text{Fe}} - \Delta_{\gamma \rightarrow \alpha} S_{\text{Fe}} \quad (4)$$

where $\Delta_{\text{m}} S_{\text{Fe}}$ – iron entropy of melting $\Delta_{\gamma \rightarrow \alpha} H_{\text{Fe}}$ and $\Delta_{\gamma \rightarrow \alpha} S_{\text{Fe}}$ – enthalpy and entropy of phase transition between γ and α iron.

Integral excess thermodynamic functions of mixing have been obtained from partial ones by the integration of Gibbs–Duhem equation:

$$\Delta_{\text{mix}} \Phi = \int_0^{x_{\text{Fe}}} \Delta_{\text{mix}} \bar{\Phi}_{\text{Fe}} d \frac{x_{\text{Fe}}}{x_{\text{Ge}}} \quad (5)$$

where $\Delta_{\text{mix}} \Phi$ is excess thermodynamic function of mixing i.e. $\Delta_{\text{mix}} G^{\text{xs}}$, $\Delta_{\text{mix}} H$ and $\Delta_{\text{mix}} S^{\text{xs}}$.

Results and discussion

The results of Fe–Si and Fe–Ge system calorimetric study can be presented in the form of α_{Fe} -function concentration dependencies:

$$\alpha_{\text{Fe}} = -99.44 - 120.92x_{\text{Fe}} - 531.44x_{\text{Fe}}^2 + 764.25x_{\text{Fe}}^3 \quad (6)$$

(Fe–Si, 1765 K)

$$\alpha_{\text{Fe}} = -1931 - 25.96x_{\text{Fe}} - 293.42x_{\text{Fe}}^2 \quad (7)$$

(Fe–Ge, 1750 K)

In accordance with Eqs (2), (6) and (7), the integral enthalpies of mixing in Fe–Si and Fe–Ge system are:

$$\Delta_{\text{mix}} H_{(\text{Fe–Si})} = x_{\text{Fe}} (1 - x_{\text{Fe}}) (-99.44 - 60.46x_{\text{Fe}} - 177.15x_{\text{Fe}}^2 + 191.06x_{\text{Fe}}^3) \quad (8)$$

$$\Delta_{\text{mix}} H_{(\text{Fe–Ge})} = x_{\text{Fe}} (1 - x_{\text{Fe}}) (-1931 - 12.98x_{\text{Fe}} - 97.81x_{\text{Fe}}^2) \quad (9)$$

The partial and integral enthalpies of mixing with the estimated intervals are listed in Table 1.

As it can be seen in Fig. 1, $\Delta_{\text{mix}} H$ data determined here for liquid Fe–Si alloys are in good agreement with literature data. Our $\Delta_{\text{mix}} H$ data for Fe–Ge system is closer to that of [18] within the measurement deviations (Fig. 2). The obtained results reveal that the liquid alloys of both studied systems form with significant exothermal effects. It confirms the statement about strong interaction between atoms of different types in the melts. In the Fe–Si system such interaction is stronger than in Fe–Ge system, as it is demonstrated

Table 1 Partial and integral enthalpies of mixing in liquid Fe-Si and Fe-Ge alloys, kJ mol⁻¹

x_{Fe}	Fe-Si at 1765 K			Fe-Ge at 1750 K		
	$-\Delta_{\text{mix}} \bar{H}_{\text{Fe}} \pm 2\sigma$	$-\Delta_{\text{mix}} \bar{H}_{\text{Si}} \pm 2\sigma$	$-\Delta_{\text{mix}} H \pm 2\sigma$	$-\Delta_{\text{mix}} \bar{H}_{\text{Fe}} \pm 2\sigma$	$-\Delta_{\text{mix}} \bar{H}_{\text{Ge}} \pm 2\sigma$	$-\Delta_{\text{mix}} H \pm 2\sigma$
0.0	99.0±11	0	0	19.3±7.2	0	0
0.1	94.0±4.3	0.26±0.05	9.6±0.5	20.1±3.1	0.08±0.04	1.9±0.3
0.2	88.8±3.5	1.2±0.2	18.7±0.9	23.2±2.7	0.6±0.2	4.1±0.7
0.3	77.8±2.2	4.3±0.4	27.0±1.0	26.2±2.2	1.6±0.4	6.7±1.0
0.4	66.2±1.9	11.8±0.8	33.5±1.2	27.6±1.5	2.3±0.7	9.6±1.0
0.5	49.3±1.3	25.7±1.3	37.5±1.3	26.4±1.6	1.3±1.6	12.6±1.3
0.6	31.7±1.8	47.4±1.4	38.0±1.8	22.5±2.0	-3.7±4.6	15.0±1.6

Note: Here and in other table all data has been standardized to liquid silicon, germanium and undercooled liquid iron, estimated intervals are given for a probability of 0.95

Table 2 Thermodynamic properties of iron in liquid Fe-Ge alloys at 1480 K

x_{Fe}	$-\Delta_{\text{mix}}\bar{G}_{\text{Fe}}$	$-\Delta_{\text{mix}}\bar{G}_{\text{Fe}}^{\text{xs}}$	$-\Delta_{\text{mix}}\bar{H}_{\text{Fe}}$	$\Delta_{\text{mix}}\bar{S}_{\text{Fe}}$	$-\Delta_{\text{mix}}\bar{S}_{\text{Fe}}^{\text{xs}}$	a_{Fe}
	kJ mol ⁻¹			J mol ⁻¹ K ⁻¹		
0.164	39.52±0.24	17.29	40.5±1.3	-0.7±0.9	15.7	0.040±0.001
0.253	35.83±0.17	18.94	38.4±1.5	-1.8±1.1	13.2	0.054±0.001
0.414	30.01±0.06	19.15	33.9±1.0	-2.7±0.7	10.0	0.0873±0.0004
0.464	26.81±0.09	17.35	24.7±1.9	0.2±1.3	5.0	0.113±0.001
0.516	20.58±0.09	12.45	13.6±2.9	4.7±1.9	0.8	0.118±0.001
0.565	19.27±0.19	12.24	12.7±5.0	4.4±3.4	0.3	0.209±0.003
0.614	17.25±0.17	11.25	11.7±3.0	3.8±2.0	0.3	0.246±0.003
0.661	12.42±0.06	7.33	12.1±1.4	0.2±0.9	3.2	0.364±0.002

by $\Delta_{\text{mix}} \overline{H}_{\text{Fe}}^{\infty}$ values, which are equal to -99 and -19 kJ mol^{-1} and integral enthalpy of mixing (-38 and -15 kJ mol^{-1} at $x_{\text{Fe}}=0.6$) for Fe–Si and Fe–Ge systems, respectively.

Large negative values of $\Delta_{\text{mix}} H$ in liquid Fe–Si alloys testify that the interaction between atoms of different kinds essentially dominates. It is result of a microheterogeneity in the melts and statistical interatomic bonding with FeSi clusters formation [26]. Moreover, in liquid alloys of Fe–Ge system binary intermetallic clusters with total composition about Fe_5Ge_3 exist [27], which is a main reason for $\Delta_{\text{mix}} G^{\text{xs}}$ extremum shift to field of iron-enriched composition.

The iron thermodynamic properties in liquid Fe–Ge alloys computed from *emf* experimental data are shown in Table 2.

The smoothed thermodynamic functions of mixing are presented by following equations ($\Delta_{\text{mix}} H$ and $\Delta_{\text{mix}} G^{\text{xs}}$ in kJ mol^{-1} , $\Delta_{\text{mix}} S^{\text{xs}}$ in $\text{J mol}^{-1} \text{K}^{-1}$):

$$\Delta_{\text{mix}} H = x_{\text{Fe}}(1-x_{\text{Fe}})(-32.56 - 118.85x_{\text{Fe}} + 94.52x_{\text{Fe}}^2) \quad (10)$$

$$\Delta_{\text{mix}} G^{\text{xs}} = x_{\text{Fe}}(1-x_{\text{Fe}})(-11.02 - 48.38x_{\text{Fe}}) \quad (11)$$

$$\Delta_{\text{mix}} S^{\text{xs}} = x_{\text{Fe}}(1-x_{\text{Fe}})(-43.16 + 299.18x_{\text{Fe}} - 1366.07x_{\text{Fe}}^2 + 2424.8x_{\text{Fe}}^3 - 1449.25x_{\text{Fe}}^4) \quad (12)$$

The determined thermodynamic activity of components, integral enthalpy and excesses Gibbs free energy of mixing have been compared with literature data in Figs 2–4. The Fig. 3 illustrates, that the experimental thermodynamic activity of iron corresponds satisfactorily to results of [19–21], while germanium thermodynamic activity corresponds only to [19, 20]. In accordance with our results and [19], values of germanium activity coefficient at high concentrations of Ge are more than one. The existence of intermetallic clusters (related to Fe_5Ge_3 composition) in the binary melt [27] can explain this fact adequately. The experimental integral enthalpies of mixing (*emf* at 1480 K) show good agreement with literature calorimetric data [16] for $x_{\text{Ge}} > 0.5$ and [18] for $x_{\text{Ge}} < 0.5$ (Fig. 2). Difference between our experimental *emf* and HTICal data on $\Delta_{\text{mix}} H$ is caused by different temperatures of these studies. Comparison of our experimental $\Delta_{\text{mix}} G^{\text{xs}}$ data for Fe–Ge with literature shows, that integral excess Gibbs free energy of mixing possess more negative values at temperature increasing from 1480 up to 1873 K (Fig. 4).

Conclusions

The isoperibolic calorimetry and *emf* measurements are the most accurate and reproducible tools available for study of thermodynamics of mixing at high-temperature. The calorimetric studies of liquid Fe–Ge (1765 K) and Fe–Si (1750 K) alloys demonstrate the great negative $\Delta_{\text{mix}} H$ values for both systems. This associated with significant contribution of intermetallic clusters Fe_5Ge_3 and FeSi into liquid state thermodynamics. The negative deviations from Raoult's law are observed in Fe–Ge melts for $x_{\text{Ge}} < 0.56$ (*emf*, 1480 K). Whereas, compositions enriched by germanium are characterised by the posi-

tive deviations from ideal solution for germanium (Fig. 3). A good agreement between experimental data (HTICal and *emf*) and literature values are reached.

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