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Thermodynamic assessment of the Al–Ca binary system using random solution and associate models

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Abstract

The thermodynamic properties of the binary Al–Ca system are investigated. The assessment is carried out by means of the computer program Thermo-Calc, using models for the Gibbs energy of individual phases. In the present study, both associate and random solution models are tested for the system to better reproduce the experimental data. The results from the two models are compared with each other and with experimental data in the literature. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Al–Ca; Thermodynamics; Modeling; Phase diagram; Associates; Intermetallics

1. Introduction

In many binary systems containing alkali earth elements, stoichiometric intermetallic compounds often form with melting temperatures much higher than those of the constitutive pure elements. Correspondingly, there is a deep valley in the enthalpy of mixing in the liquid phase. When the random solution model is used for the liquid phase with the Redlich–Kister polynomial [1], it is found that higher-order interaction parameters in the liquid are typically needed to reproduce the liquidus around the high-melting-temperature intermetallic compounds, and it often results in a less satisfactory liquidus at other compositions. The Al–Ca binary alloy is one of these systems with a very high melting temperature compound (Al₂Ca) compared to those of pure Al and Ca. A short-range ordering tendency in the liquid state in this system is likely. The recent experimental studies [2,3] on the liquid Al–Ca alloys provide strong evidences for the existence of molecular-like Al₂Ca species, called associates.

In the present work, the thermodynamic properties of the Al–Ca system are modeled, and the two models for the liquid phase are considered, i.e., the random solution model [4] with the free Al and Ca atoms only and the associate model [5–7] with both free atoms and the Al₂Ca associates. There are four intermetallic phases in the

system which are all treated as stoichiometric compounds. The results from the two models are compared with each other and with the available experimental data.

2. Experimental information

The experimental equilibrium phase diagram information for the Al–Ca binary system [8] was collected in several phase diagram compilations [9–11]. The phase diagram presented by Hansen and Anderko [12] with the two confirmed binary compounds, Al₂Ca and Al₄Ca, (after Refs. [13,14]) has been accepted as a complete phase diagram until now. Most recent studies [15,16], however, indicated that there exist two more compounds in the system, Al₁₄Ca₁₃ and Al₃Ca₈. Their crystal structures were investigated and well defined by X-ray analysis. The four binary compounds and their crystal structures are listed in Table 1. In this section, experimental thermodynamic and phase equilibrium data in the literature will be reviewed.

Table 1
The binary compounds in the Al–Ca system

Phase	Model	Crystal structure	Prototype and Ref.
Al ₄ Ca	(Al) ₄ (Ca) ₁	b.c.t. (D1 ₃)	Al ₄ Ba [14]
Al ₂ Ca	(Al) ₂ (Ca) ₁	f.c.c. (C15)	Cu ₂ Mg [13]
Al ₁₄ Ca ₁₃	(Al) ₁₄ (Ca) ₁₃	Monoclinic	– [15]
Al ₃ Ca ₈	(Al) ₃ (Ca) ₈	Triclinic	Ca ₈ In ₃ [15,16]

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2.1. Thermodynamic data

Kocherov et al. [17] utilized a conventional isothermal calorimeter with two different methods to measure the enthalpies of formation of Al–Ca alloys. In the first method, a self-sealing calorimetric bomb (also known as combustion method) was employed for the mixtures with compositions ranging from 20.0 to 46.0 at.% Ca. In the second method, the alloys and mixtures with compositions between 2.5 and 86.0 at.% Ca were dissolved in HCl. The results obtained for the compositions of 20.0 at.% Ca (Al₄Ca) and 32.7 at.% Ca (mainly Al₂Ca) are:

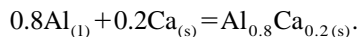
ΔH_f (Al_{0.8}Ca_{0.2}, s, 298 K) = -41.8 ± 6.3 kJ/mol of atoms (combustion).

ΔH_f (Al_{0.8}Ca_{0.2}, s, 298 K) = -43.9 ± 4.2 kJ/mol of atoms (dissolution).

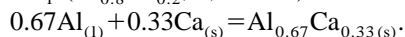
ΔH_f (Al_{0.673}Ca_{0.327}, s, 298 K) = -71.1 ± 6.3 kJ/mol of atoms (combustion).

ΔH_f (Al_{0.673}Ca_{0.327}, s, 298 K) = -73.2 ± 4.2 kJ/mol of atoms (dissolution).

In another more recent investigation by Notin et al. [18], the enthalpies of mixing of the Al-rich (<45 at.% Ca) intermediate phases were measured at 953 and 1038 K using calorimetry. Each calorimetric signal recorded corresponds to the enthalpy change during the addition of a solid Ca piece in each step to an Al melt in the crucible. From the measurements, Notin et al. [18] were able to determine the enthalpies of formations of Al₄Ca and Al₂Ca. The chemical reactions and their enthalpy values for the formation of these intermetallic compounds are:



ΔH_f (Al_{0.8}Ca_{0.2}, s, 953 K) = -27.2 kJ/mol of atoms



ΔH_f (Al_{0.67}Ca_{0.33}, s, 1038 K) = -40.6 kJ/mol of atoms where the uncertainties were not given.

The most recent studies [15,16] show the existence of the two new compounds, Al₁₄Ca₁₃ and Al₃Ca₈. The enthalpy of formation of the Al₃Ca₈ phase was measured at room temperature by Kevorkov et al. [19] as:

ΔH_f (Al₃Ca₈) = -13.7 ± 1.3 kJ/mol of atoms.

For the Al₁₄Ca₁₃ phase, there are no experimental enthalpy of formation data reported in the literature up to date. The reason for this is probably the sluggish formation kinetics of the phase and thus the difficulty of preparing an Al₁₄Ca₁₃-rich sample as reported by Kevorkov and Schmid-Fetzer [16], although they assumed the phase as AlCa instead of Al₁₄Ca₁₃.

The Gibbs energies and the entropies of formation of Al₂Ca and Al₄Ca were also determined by different techniques [20,21]. Notin et al. [20] used a solid electrolyte galvanic cell technique where they investigated the Ca|CaF₂(Al,Ca) cell between the temperature range of 750–900 K. The Gibbs energy and entropy values for the formation of Al₄Ca and Al₂Ca are:

ΔG_f (Al_{0.8}Ca_{0.2}, 800 K) = -17800 ± 140 J/mol of atoms.

ΔG_f (Al_{0.67}Ca_{0.33}, 800 K) = -28500 ± 300 J/mol of atoms.

ΔS_f (Al_{0.8}Ca_{0.2}, 800 K) = -1.1 ± 0.5 J/K/mol of atoms.

ΔS_f (Al_{0.67}Ca_{0.33}, 800 K) = -6.1 ± 1.1 J/K/mol of atoms

Veleckis [21] employed the hydrogen titration method using CaH₂(s) as the titration product. The Ca activities were first calculated and then integrated with the corresponding electromotive forces in Ca–Ca²⁺–(Al–Ca)-type galvanic cells yielding the Gibbs energy expressions for Al₄Ca and Al₂Ca between 673 and 903 K as:

ΔG_f (Al₄Ca) = $-(20.18 \pm 0.38) + (4.29 \pm 0.78) \times 10^{-3} T$ kJ/mol of atoms.

ΔG_f (Al₂Ca) = $-(31.28 \pm 0.46) + (5.67 \pm 0.93) \times 10^{-3} T$ kJ/mol of atoms.

Sommer et al. [22] determined the concentration dependencies of the enthalpies of mixing of liquid alloys using high-temperature calorimetry at temperatures ranging between 1125 and 1190 K. Measurements were performed in two concentration ranges, from 2.7 to 17.3 and 51.4 to 95.1 at.% Ca, respectively. Experimental results by Notin et al. [18], as described earlier for the Al-rich alloys in the liquid state, are in good agreement with those of Sommer et al. [22]. There is a deep valley in the enthalpy of mixing in the liquid phase. The distribution of the data points throughout the entire composition range is asymmetric. It is shifted towards the Al-rich side where the most stable intermetallic compound, Al₂Ca, is formed.

The activities in the liquid Al–Ca alloys were determined by Jacob et al. [23] using the Knudsen effusion method for the composition range <38 at.% Ca and >44 at.% Ca at 1373 K. By combining the results from the two ranges, the activities for the entire composition range in liquid phase were obtained at 1373 K. Schurmann et al. [24] utilized the boiling point determination technique to measure the vapor pressure of Ca over the calcium–aluminum melts between 1480 and 1635 K and evaluated the activities of Ca in the liquid alloys.

2.2. Phase equilibrium data

Hansen and Anderko [12] summarized the early experimental data on the Al–Ca system. Earlier studies [9,10] assumed that the phase Al₃Ca (25 at.% Ca) existed with a melting point at around 963 K. It was later shown by a comprehensive X-ray work [14] that the intermetallic phase with higher Al content is Al₄Ca but not Al₃Ca. It crystallizes in a b.c.t. structure with lattice parameters of $a = 4.36$ Å and $c = 11.09$ Å [14]. Al₄Ca melts incongruently at the peritectic reaction temperature (973 K) forming liquid (10 at.% Ca) and Al₂Ca (33 at.% Ca) [11]. The Al₂Ca phase has f.c.c. structure with a lattice parameter of $a = 8.038$ Å [13] and melts congruently at 1352 K. The recently discovered Al₃Ca₈ phase [15,16] in the system is triclinic in crystalline nature and melts congruently at around 850 K. It has the lattice parameters of $a = 9.484$ Å, $b = 9.592$ Å and $c = 9.671$ Å, and the unit cell with the

angles of $\alpha=99.02^\circ$, $\beta=101.13^\circ$ and $\gamma=119.55^\circ$ [15]. The $\text{Al}_{14}\text{Ca}_{13}$ phase has monoclinic structure with lattice parameters of $a=15.55 \text{ \AA}$, $b=9.87 \text{ \AA}$ and $c=9.73 \text{ \AA}$, and the unit cell with the angles of $\alpha=90^\circ$, $\beta=108.09^\circ$ and $\gamma=90^\circ$ [15]. It melts incongruently at the peritectic reaction temperature of about 906 K forming liquid (61.6 at.% Ca) and Al_2Ca phases [16].

Comprehensive thermal and thermoresistometric investigations [11] were the basis of the Al–Ca equilibrium diagram. Matsuyama [11] found two eutectic reactions and determined most of the liquidus lines, as well. The eutectic point is determined precisely on the Al-rich side with the composition of 5.24 at.% Ca at 889 K. The other eutectic point found was on the Ca-rich side and approximately with the composition of 65 at.% Ca at 818 K [11]. Lately, it has been shown that there are two eutectic points on the Ca-rich side instead of one reported by Matsuyama [11]. These eutectic reactions occur at around 829 K and 833 K with the compositions of 66.2 and 79.5 at.% Ca, respectively [16]. The solid solubility of Ca in Al was found to be less than 0.03 at.% at 873 K [25].

3. Thermodynamic models

There are two types of phases in the system, i.e., solution phases and intermetallic compounds. The solution phases are modeled using one sublattice. The intermetallic compounds are modeled with two sublattices. The detailed expressions for the Gibbs energy of the phases will be presented below in terms of 1 mol of the formula unit.

3.1. Solution phases: liquid, f.c.c. and b.c.c.

The solution phases in the random solution model is treated as a substitutional solution, (Al, Ca), with the Gibbs energies expressed:

$$G_m^\Phi = x_{\text{Al}}^0 G_{\text{Al}}^\Phi + x_{\text{Ca}}^0 G_{\text{Ca}}^\Phi + RT(x_{\text{Al}} \ln x_{\text{Al}} + x_{\text{Ca}} \ln x_{\text{Ca}}) + {}^{xs}G_m^\Phi \quad (1)$$

where ${}^0G_i^\Phi$ is the molar Gibbs energy of the pure element in the liquid state with the structure Φ , from Dinsdale [26]. ${}^{xs}G_i^\Phi$ is the excess Gibbs energy, expressed in Redlich–Kister polynomials as follows:

$${}^{xs}G_m^\Phi = x_{\text{Al}}x_{\text{Ca}} \sum_{j=0}^n L_{\text{Al,Ca}}^\Phi (x_{\text{Al}} - x_{\text{Ca}})^j \quad (2)$$

where ${}^jL_{\text{Al,Ca}}^\Phi$ is the j th-order binary interaction parameter expressed as ${}^jA^\Phi + {}^jB^\Phi T$, and ‘A’ and ‘B’ are model parameters to be evaluated from experimental information.

On the other hand, in the associate model, the liquid phase is assumed to have three species (i.e., Al, Ca and

Al_2Ca) based on the enthalpy of mixing in the liquid. The Gibbs energy of the liquid is written as:

$$G_m^L = y_{\text{Al}}^0 G_{\text{Al}}^L + y_{\text{Ca}}^0 G_{\text{Ca}}^L + y_{\text{Al}_2\text{Ca}}^0 G_{\text{Al}_2\text{Ca}}^L + RT(y_{\text{Al}} \ln y_{\text{Al}} + y_{\text{Ca}} \ln y_{\text{Ca}} + y_{\text{Al}_2\text{Ca}} \ln y_{\text{Al}_2\text{Ca}}) + {}^{xs}G_m^L \quad (3)$$

where ‘y’ shows the mole fractions of each species in the liquid. ${}^{xs}G_i^L$ is again the excess Gibbs energy and expressed as follows:

$${}^{xs}G_m^L = y_{\text{Al}}y_{\text{Ca}} \sum_{j=0}^n L_{\text{Al,Ca}}^L (y_{\text{Al}} - y_{\text{Ca}})^j + y_{\text{Al}}y_{\text{Al}_2\text{Ca}} \sum_{j=0}^n L_{\text{Al,Al}_2\text{Ca}}^L (y_{\text{Al}} - y_{\text{Al}_2\text{Ca}})^j + y_{\text{Al}_2\text{Ca}}y_{\text{Ca}} \sum_{j=0}^n L_{\text{Al}_2\text{Ca,Ca}}^L (y_{\text{Ca}} - y_{\text{Al}_2\text{Ca}})^j \quad (4)$$

3.2. Intermetallic phases

There are four stable intermetallic compounds in the Al–Ca system (see Table 1). They are modeled as stoichiometric compounds, and their Gibbs energy functions are written as:

$$G_m^{\text{Al}_a\text{Ca}_b} = a {}^0G_{\text{Al}}^{\text{fcc}} + b {}^0G_{\text{Ca}}^{\text{fcc}} + A^{\text{Al}_a\text{Ca}_b} + B^{\text{Al}_a\text{Ca}_b} T \quad (5)$$

for Al_4Ca , Al_2Ca , $\text{Al}_{14}\text{Ca}_{13}$ and Al_3Ca_8 , respectively. ${}^0G_{\text{Al}}^{\text{fcc}}$ and ${}^0G_{\text{Ca}}^{\text{fcc}}$ are the molar Gibbs energies of the f.c.c. Ca and f.c.c. Al, respectively.

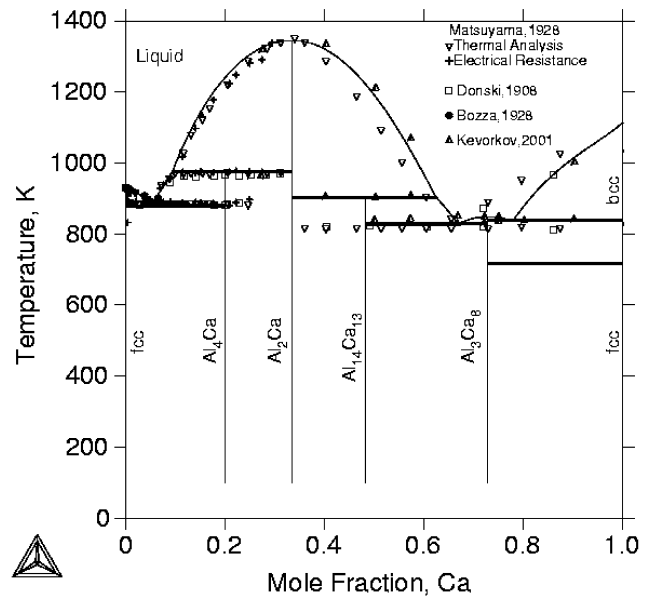


Fig. 1. Calculated phase diagram using random solution model, compared with experimental data by Donski [9], Bozza and Sonnino [10], Matsuyama [11] and Kevorkov and Schmid-Fetzer [16].

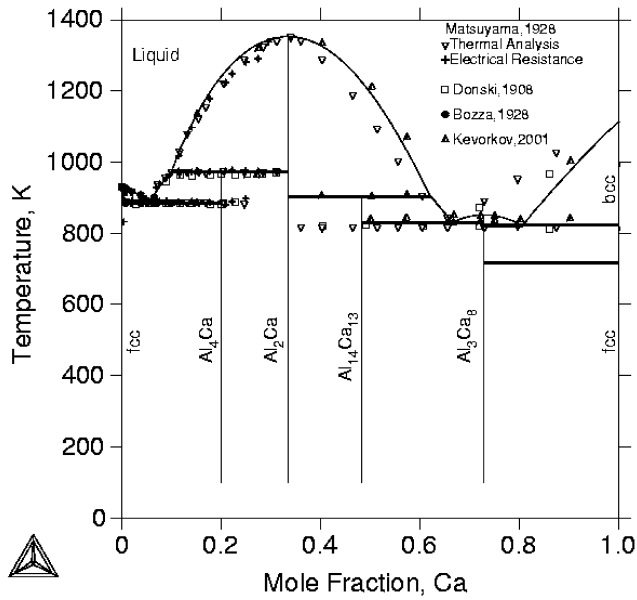


Fig. 2. Calculated phase diagram using associate model, compared with experimental data by Donski [9], Bozza and Sonnino [10], Matsuyama [11] and Kevorkov and Schmid-Fetzer [16].

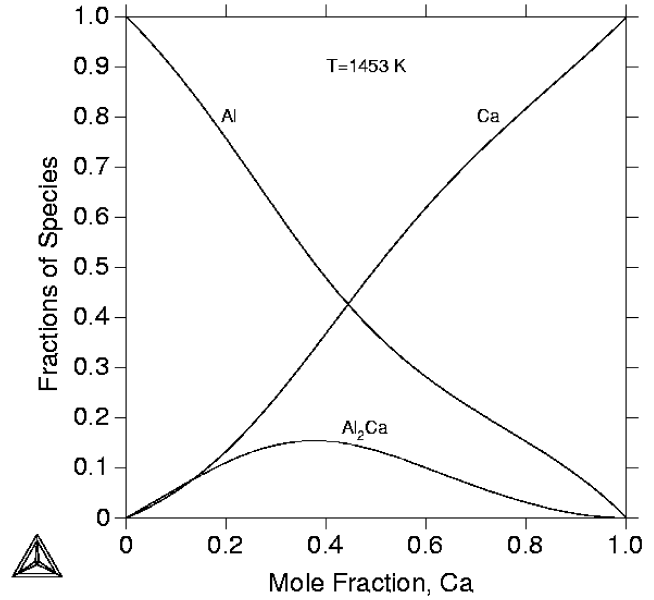


Fig. 3. Site fraction change of each of the species as a function of Ca concentration in the liquid phase, calculated using the associate model for the liquid phase.

4. Evaluation of thermodynamic parameters and computational results

The model parameters ('A' and 'B') were evaluated using the Parrot module [27] in Thermo-Calc [28]. This program is able to take various kinds of experimental data

in one operation. It works by minimizing an error sum with each of the selected data values given a certain weight. The weight is chosen and adjusted based upon the data uncertainties given in the original publications and upon the modeler's judgment when examining all data simultaneously. All thermodynamic calculations are carried out

Table 2
Experimental and calculated phase equilibria data

Invariant reactions	Reaction type	Experimental data			Calculated data (associate)		Calculated data (random solution)	
		T (K)	at.% Ca in liquid	Ref.	T (K)	at.% Ca in liquid	T (K)	at.% Ca in liquid
Liquid = Al + Al ₄ Ca	Eutectic	884	5.6	[9]	885.9	5.45	881.2	5.45
		886	6.4	[10]				
		889	5.2	[11]				
		886	–	[16]				
Liquid = Al ₁₄ Ca ₁₃ + Al ₃ Ca ₈	Eutectic	818	–	[11]	830.5	66.40	829.4	66.81
		820	–	[9]				
		829	66.2	[16]				
Liquid = Al ₃ Ca ₈ + βCa	Eutectic	818	–	[11]	822.5	80.53	837.3	77.79
		820	–	[9]				
		833	79.5	[16]				
Liquid = Al ₂ Ca	Congruent	1352	33.3	[11]	1354.0	33.33	1346.4	33.33
		1359	33.3	[16]				
Liquid = Al ₃ Ca ₈	Congruent	852	72.7	[16]	852.0	72.72	849.5	72.72
Liquid + Al ₂ Ca = Al ₄ Ca	Peritectic	973	10.0	[11]	974.0	9.89	976.1	9.32
		973	–					
Liquid + Al ₂ Ca = Al ₁₄ Ca ₁₃	Peritectic	906	61.6	[16]	905.5	61.97	905.7	62.29

using Thermo-Calc. A complete and self-consistent thermodynamic description for the Al–Ca binary system is thus obtained and listed in the Appendix for both the random solution model and the associate model. The reference state of the Gibbs energy of individual phases is the so-called standard element reference (SER), i.e., the enthalpies of the pure elements in their stable state at 298.15 K [26].

The optimization procedure starts with the liquid phase and its equilibria with the pure Al and Ca phases. The model parameters of the Al₂Ca phase were then evaluated because of the congruent melting of the phase and the

extensive liquidus associated with the Al₂Ca phase. The thermodynamic parameters of the other phases were optimized one after another. Many iterations were necessary to reproduce all experimental data. Finally, the model parameters of all phases were optimized simultaneously with all experimental data included.

The calculated phase diagram using a random solution model for the liquid phase is shown in Fig. 1. The interaction parameters up to second order, ${}^2L_{Al,Ca}^{liquid}$, were used for the liquid (see Appendix A). In the associate model, the Gibbs energy for the formation of Al₂Ca species in the liquid is calculated using two optimizing

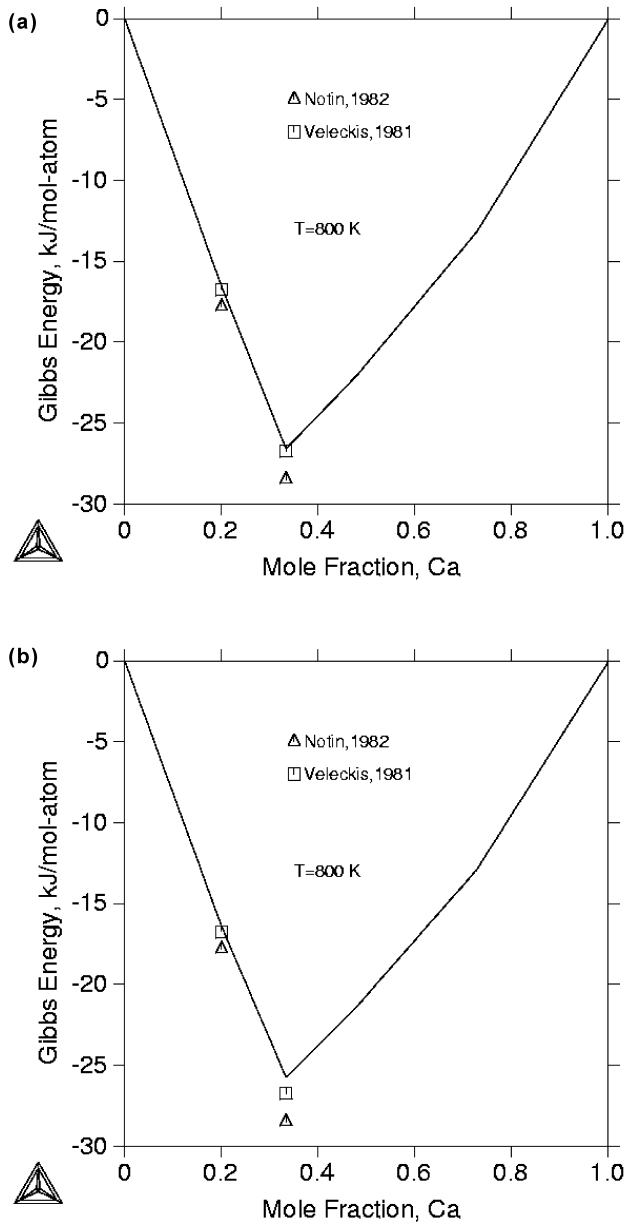


Fig. 4. Gibbs energy of formation at 800 K as a function of Ca concentration. (a) Random solution model, and (b) associate model, compared with the experimental data by Notin et al. [20] and Veleckis [21].

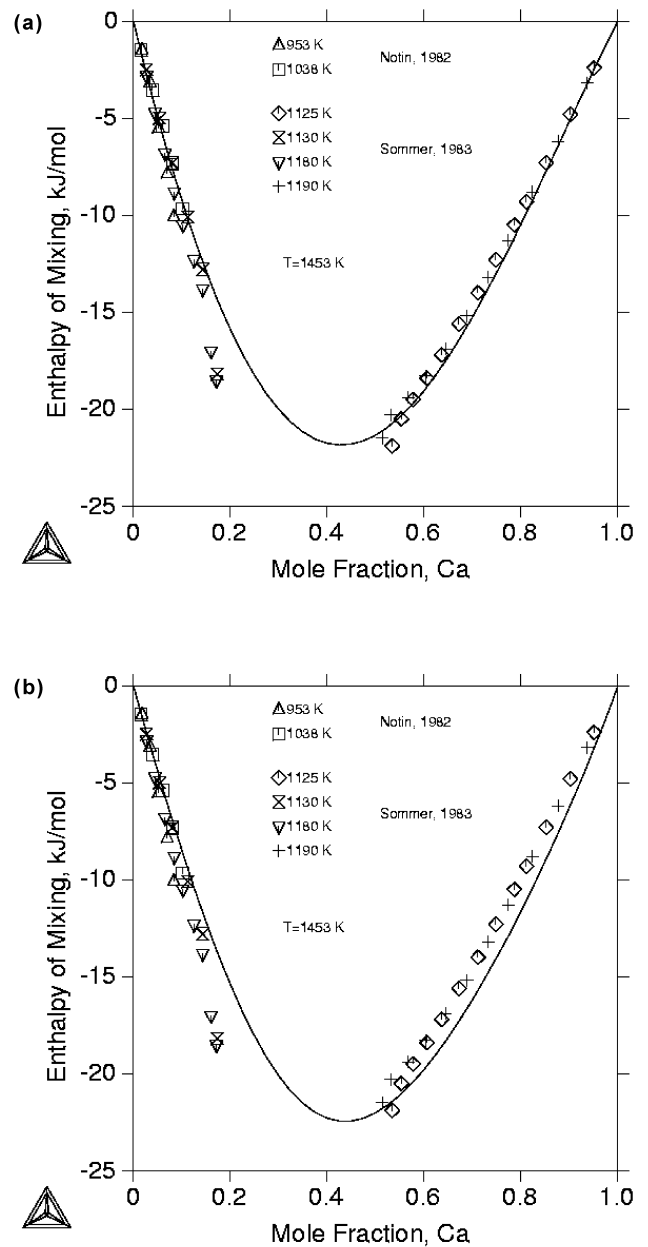


Fig. 5. Enthalpy of mixing as a function of Ca concentration in the liquid. (a) Random solution model, and (b) associate model, compared with the experimental data by Notin et al. [18] and Sommer et al. [22].

variables. In addition, the interactions among the free atoms and between these free atoms and the associates are considered using ${}^0L_{Al,Ca}^{liquid}$ and ${}^0L_{Al_2Ca,Ca}^{liquid}$ and ${}^0L_{Al_2Ca,Al}^{liquid}$, respectively (see Appendix A). The resulting phase diagram from the associate model is shown in Fig. 2. Both calculated and experimental temperatures, and Ca contents in a liquid phase at invariant equilibria are listed in Table 2.

During the optimization, interactions between the Al and Al_2Ca and between the Ca and Al_2Ca were tested and found less important than the interactions between the Al and Ca in the liquid. The amount of each species in the liquid is calculated and shown in Fig. 3. It is found that

about 15% of the species in the liquid is Al_2Ca at compositions around 35 at.% Ca. All the other phases, i.e., the intermetallics, are treated as stoichiometric compounds. Each compound is described by the two model parameters and their values are listed in Appendix A.

In Fig. 4, Gibbs energies for the formation of the two compounds, i.e., Al_2Ca and Al_4Ca , are calculated and compared with the experimental results [20,21]. The comparison of the enthalpy of mixing data in the liquid phase [18,22] at 1453 K with our calculations (using both random solution and associate models) is illustrated in Fig. 5. There is a very deep valley in the enthalpies and a trend that the minimum of the curve in the Fig. is shifted

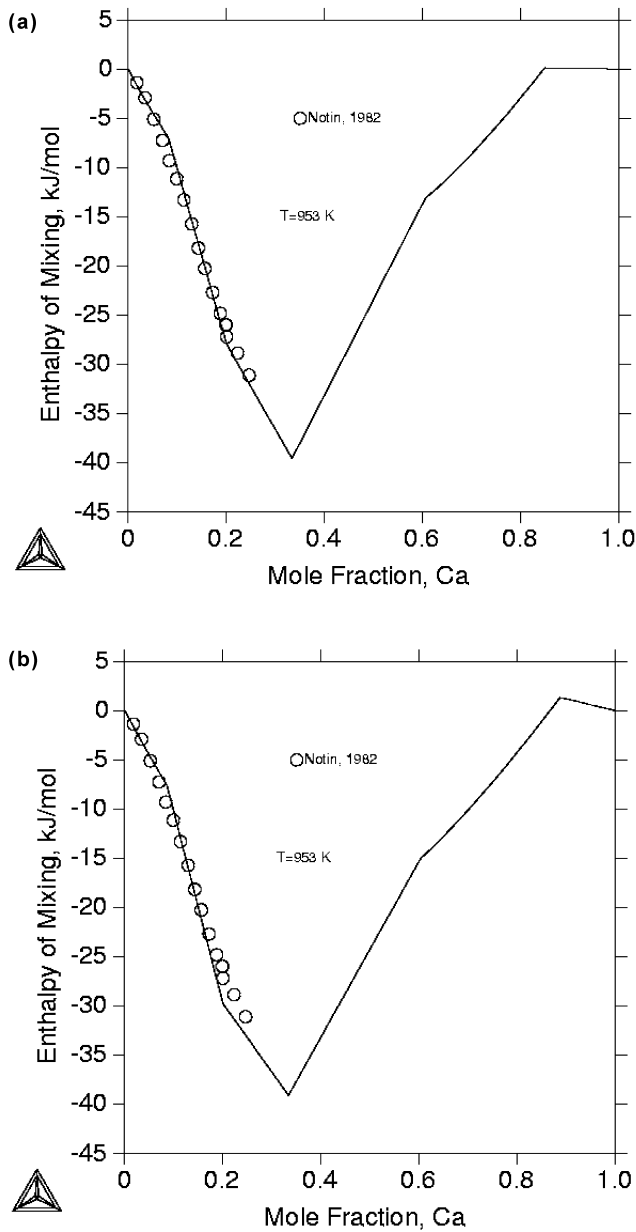


Fig. 6. Enthalpy of mixing at 953 K as a function of Ca concentration. (a) Random solution model, and (b) associate model, compared with the experimental data by Notin et al. [18].

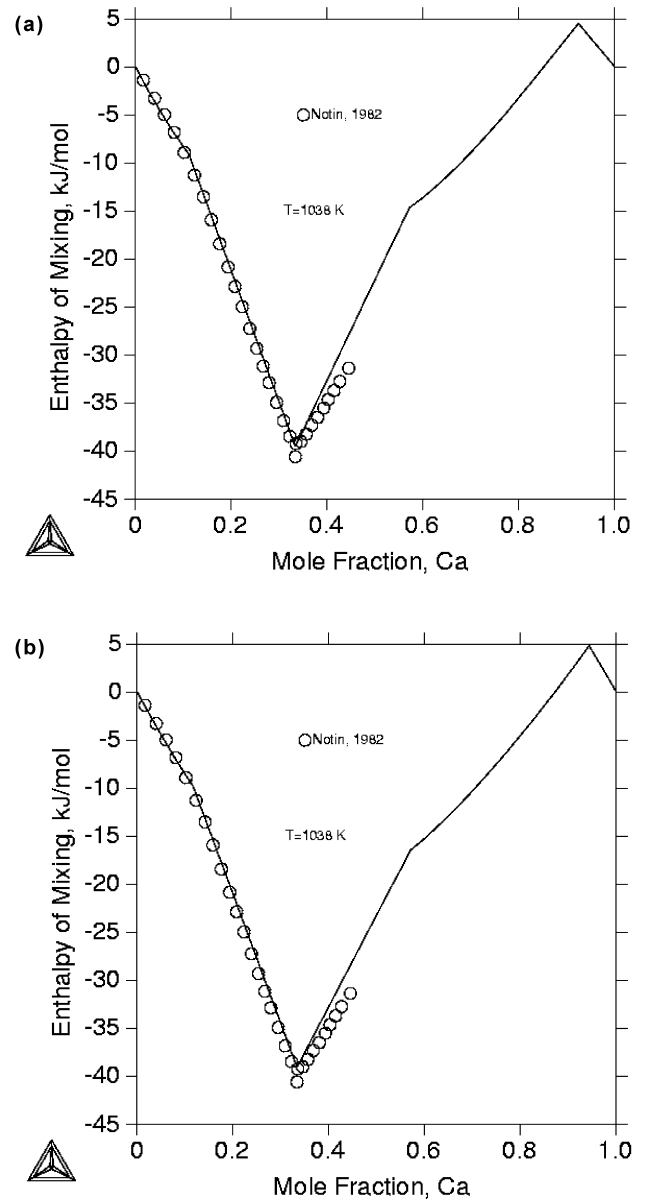


Fig. 7. Enthalpy of mixing at 1038 K as a function of Ca concentration. (a) Random solution model, and (b) associate model, compared with the experimental data by Notin et al. [18].

towards the Al side. This shows stronger interactions between the atoms in the liquid at compositions around that of the Al_2Ca phase. Enthalpy of mixing data [18] at lower temperatures (1038 and 953 K), where liquid and solid two-phase regions exist at some compositions, are also compared with our calculations in Fig. 6 and Fig. 7. Each change of slope in the figures shows the formation of a new phase as the composition changes. The experimentally measured Al activities in liquid [23,24] are compared in Fig. 8 with the calculations performed at 1600 K. The

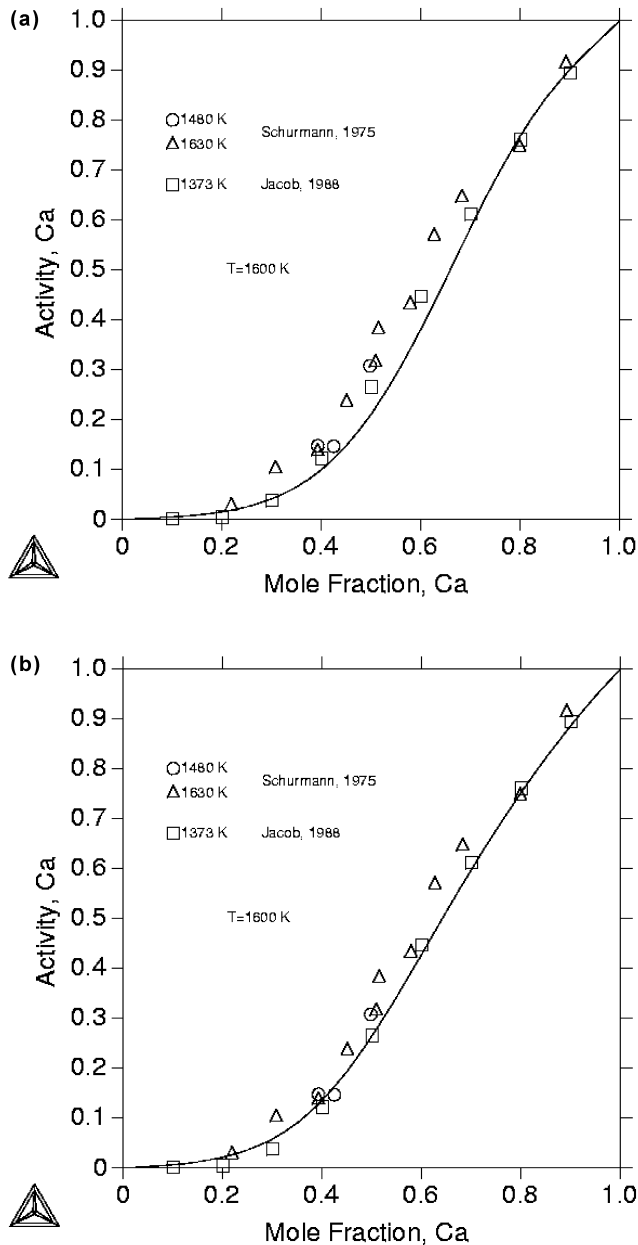


Fig. 8. Activities of Ca in the liquid as a function of Ca concentration. (a) Random solution model, and (b) associate model, compared with the experimental data by Schurmann et al. [24] and Jacob et al. [23]. The reference state of Ca is liquid.

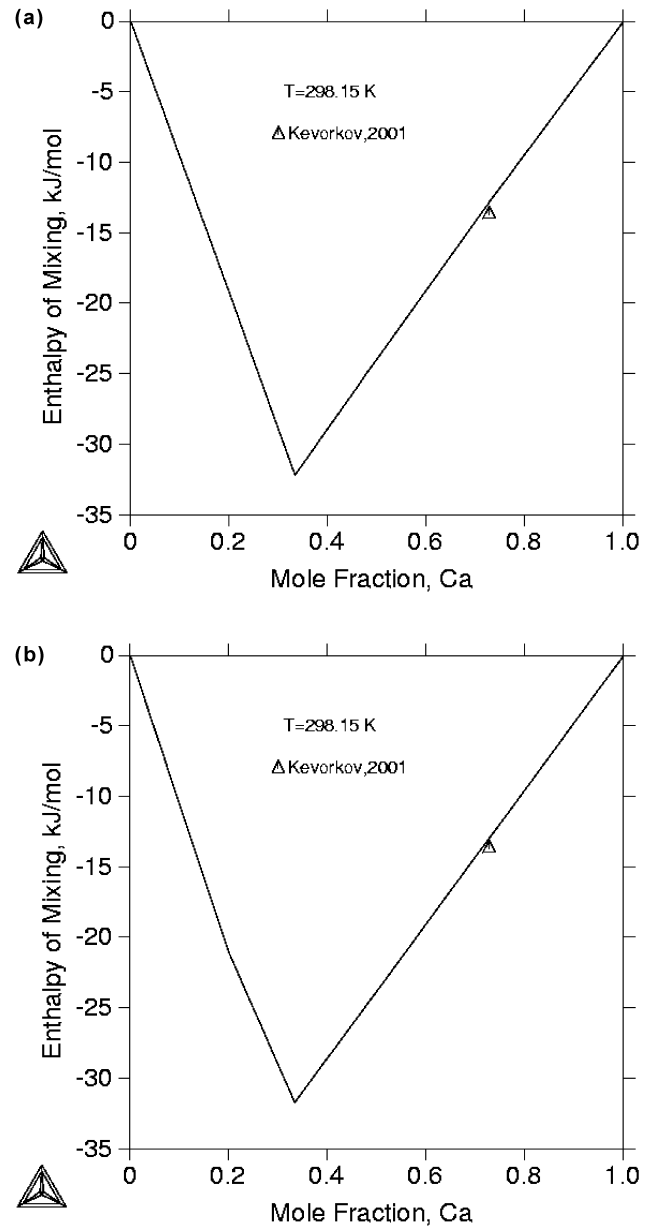


Fig. 9. Enthalpy of formation at 298.15 K as a function of Ca concentration. (a) Random solution model, and (b) associate model, compared with the experimental data by Kevorkov et al. [19].

calculated enthalpy of mixing at 298.15 K is also shown in Fig. 9 using both models.

5. Summary

A self-consistent thermodynamic description for the Al–Ca system is obtained with critically reviewed thermochemical and phase diagram data. Four binary phases are considered and their individual Gibbs energies are evaluated. Based on the experimental observation, the associate

model was tested for the liquid phase, in addition to the random solution model for the liquid phase. Both models yield satisfactory agreement with the experimental data.

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Appendix A. Thermodynamic descriptions for the Al–Ca system (all in S.I. units)

	Phase	Sublattice model	Evaluated description
Random solution model	Liquid	(Al,Ca)	${}^0L_{\text{Al,Ca}} = -85332 + 25.066T$ ${}^1L_{\text{Al,Ca}} = -28447 + 15.332T$ ${}^2L_{\text{Al,Ca}} = 8451 + 1.278T$
	Al ₄ Ca	(Al) ₄ (Ca) ₁	$G_{\text{Al,Ca}}^{\text{Al}_4\text{Ca}} = 4{}^0G_{\text{Al}}^{\text{fcc}} + {}^0G_{\text{Ca}}^{\text{fcc}} - 96238 + 16.809T$
	Al ₂ Ca	(Al) ₂ (Ca) ₁	$G_{\text{Al,Ca}}^{\text{Al}_2\text{Ca}} = 2{}^0G_{\text{Al}}^{\text{fcc}} + {}^0G_{\text{Ca}}^{\text{fcc}} - 96554 + 20.848T$
	Al ₁₄ Ca ₁₃	(Al) ₁₄ (Ca) ₁₃	$G_{\text{Al,Ca}}^{\text{Al}_{14}\text{Ca}_{13}} = 14{}^0G_{\text{Al}}^{\text{fcc}} + 13{}^0G_{\text{Ca}}^{\text{fcc}} - 670753 + 94.203T$
	Al ₃ Ca ₈	(Al) ₃ (Ca) ₈	$G_{\text{Al,Ca}}^{\text{Al}_3\text{Ca}_8} = 3{}^0G_{\text{Al}}^{\text{fcc}} + 8{}^0G_{\text{Ca}}^{\text{fcc}} - 141129 - 5.983T$
Associate model			${}^0L_{\text{Al,Ca}} = -68842 + 25.372T$ ${}^0L_{\text{Al}_2\text{Ca,Al}} = -30351 + 2.939T$
	Liquid	(Al,Ca,Al ₂ Ca)	${}^0L_{\text{Al}_2\text{Ca,Ca}} = -52132 + 0.848T$ $G_{\text{Al,Ca}}^{\text{Al}_2\text{Ca}} = 2{}^0G_{\text{Al}}^{\text{liquid}} + {}^0G_{\text{Ca}}^{\text{liquid}} - 77214 + 46.424T$
	Al ₄ Ca	(Al) ₄ (Ca) ₁	$G_{\text{Al,Ca}}^{\text{Al}_4\text{Ca}} = 4{}^0G_{\text{Al}}^{\text{fcc}} + {}^0G_{\text{Ca}}^{\text{fcc}} - 105347 + 29.090T$
	Al ₂ Ca	(Al) ₂ (Ca) ₁	$G_{\text{Al,Ca}}^{\text{Al}_2\text{Ca}} = 2{}^0G_{\text{Al}}^{\text{fcc}} + {}^0G_{\text{Ca}}^{\text{fcc}} - 95172 + 22.312T$
	Al ₁₄ Ca ₁₃	(Al) ₁₄ (Ca) ₁₃	$G_{\text{Al,Ca}}^{\text{Al}_{14}\text{Ca}_{13}} = 14{}^0G_{\text{Al}}^{\text{fcc}} + 13{}^0G_{\text{Ca}}^{\text{fcc}} - 666156 + 112.227T$
	Al ₃ Ca ₈	(Al) ₃ (Ca) ₈	$G_{\text{Al,Ca}}^{\text{Al}_3\text{Ca}_8} = 3{}^0G_{\text{Al}}^{\text{fcc}} + 8{}^0G_{\text{Ca}}^{\text{fcc}} - 142722 - 0.194T$

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