

# Thermodynamic Modeling of Mg-Ca and Al-Ca Binary Systems

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Knowledge of the phase equilibria of Mg-alloy systems is crucial for improving existing alloys and developing new ones. Besides, processing of materials depends strongly on accurate thermodynamic data of the material system. By thermodynamic modeling a set of optimized model parameters of Mg-Ca and Al-Ca systems are obtained by considering the experimental phase equilibria and thermodynamic data available in the literature. From these set of optimized model parameters, the phase diagrams as well as thermodynamic properties can be calculated. The calculated diagrams of these two binaries agree well with the experimental data. As Mg-Ca and Al-Ca are two constituent binaries of Mg-Al-Ca ternary system, the results of the current research can be used to develop the ternary phase diagrams.

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## 1. INTRODCUTION

Research on Mg alloys is fueled nowadays by the need for low-density materials that suit aerospace and automobile industries. It has been found that the addition of low cost Ca to Mg-Al based alloys can improve the high temperature properties, such as creep resistance [1].

Since Mg-Al-Ca system can be calculated from the thermodynamic optimization of the three constituent binary systems, thermodynamic analysis must start with binaries. Although several optimizations are done for these systems, still additional work is necessary. For instance, in Mg-Ca system, to describe Gibbs energy of formation of Mg<sub>2</sub>Ca stoichiometric compound, Agarwal *et al.* [2] used four temperature dependent terms, which may not represent the true behavior of this compound. The higher number of parameters in binary systems not only difficult to interpret but may also result in higher uncertainty while developing ternary or higher order systems. Moreover in Al-Ca system the lattice stability of pure elements and number of parameters to describe liquid phase by Kevorkov *et al.* [3] and by Ozturk *et al.* [4] are different. These cause difficulty for developing thermodynamic description for higher order system based on the available models for the binaries. In the current work, Mg-Ca and Al-Ca systems are re-optimized using appropriate model. In thermodynamic optimization, all available phase equilibria and thermodynamic data are evaluated simultaneously to obtain a set of consistent model equations for the Gibbs free energy of all phases as a function of temperature

and composition. Winphad computer program developed by CompuTherm™ LLC, USA, is used for optimization and calculation of the binary phase diagrams.

## 2. LITERATURE REVIEW

### 2.1 Mg-Ca System

#### 2.1.1 Phase Diagram Data

Nayeb-Hashemi and Clark [5] critically evaluated this system. The stable phases in Mg-Ca systems are: the liquid, the (Mg)hcp solid solution, the (Ca)bcc, the (Ca)fcc, and the congruent intermetallic compound Mg<sub>2</sub>Ca. The solid solubility of Mg in (Ca)bcc and (Ca)fcc has not been determined and apparently negligible [5]. The solubility of Ca in Mg was measured by several researchers [7-10]. Among them Burke [10] and Vosskuhler [8] agree fairly well, whereas others reported larger solubility. Haughton [7] mentioned the difficulties in determining solubility limits and reported an experimental phase diagram for the system. The complete liquidus temperatures of the phase diagram were determined by Barr [11] and Paris [12]. In the experimental work of Barr [11], the purity of starting element was low and there was significant loss of Ca during alloying. Paris [12] got slightly different result than Barr [11] but he did not comment on the purity of the materials. But the last measurement by Klemm and Dinkelacker [13] agrees fairly well with that of Haughton [7]. Chase [14] determined the melting

points of starting Ca and Mg are 1115K and 923K respectively. Haughton [7] reported that the eutectic reaction occurs at  $(89.5 \pm 0.5)$  at.% Mg at 790K, this is consistent with Agarwal *et al.* [2].

### 2.1.2 Thermodynamic Data

Davison and Smith [15] suggested the heat of formation of  $Mg_2Ca$  as  $-39.50$  kJ/mol which was the average of calorimetric measurements of King and Kleepaa [16], and Gartner [17]. Also, Davison and Smith mentioned that the heat of formation determined by King and Kleepaa [16] was  $-40.50 \pm 1.25$ , which is, according to them, "the most precise and probably the most reliable." Chiotti *et al.* [18] determined the enthalpy of fusion of  $Mg_2Ca$ . The activity of Mg was measured by Sommer [19] and V.P. Mashovets and Puchkov [21] by vapor pressure measurement at 1010K and 1073K respectively. The activity of Ca in Mg-Ca liquid was also determined by Sommer [19] at 1010K. The enthalpy of mixing of liquid Mg and Ca was measured by both Sommer *et al.* [20] and Agarwal *et al.* [2] using high temperature calorimetry but at different temperatures namely; 1150K and 1023K respectively.

## 2.2 Al-Ca System

### 2.2.1 Phase Diagram Data

In Al-Ca system most experimental investigations mainly deal with Al-rich corner, which is technically interesting for aluminum alloys. As a result of this, only limited experimental work of Ca rich part was reported. Recently, Kevorkov and Schmid-Fetzer [23] reported two new intermetallic compounds; AlCa,  $Al_3Ca_8$  in addition to the established  $Al_4Ca$  and  $Al_2Ca$ . But they did not report the crystal structure of AlCa. After submission of their paper, the work of Huang and Corbett [25] came to their knowledge. In which Huang and Corbett reported the occurrence of  $Al_{14}Ca_{13}$  compound with monoclinic structure instead of AlCa. Therefore, from the most recent publications [4,23,24], it can be concluded that the stable phases in this system are: the liquid, (Al)fcc, ( $\beta$ Ca)bcc, ( $\alpha$ Ca)fcc and four intermetallic compounds;  $Al_4Ca$ ,  $Al_2Ca$ ,  $Al_{14}Ca_{13}$ ,  $Al_3Ca_8$ . Among them  $Al_4Ca$ ,  $Al_{14}Ca_{13}$  melt incongruently forming liquid and  $Al_2Ca$  at the peritectic transformation temperatures of 973K and 906K

respectively [4].  $Al_2Ca$ ,  $Al_3Ca_8$  melt congruently. The crystal structures of  $Al_{14}Ca_{13}$ ,  $Al_3Ca_8$  were investigated using X-ray analysis by Huang and Corbett [24]. According to Kevorkov and Schmid-Fetzer, the solubility regions of Ca in (Al) and Al in (Ca) are negligible [23]. Matsuyama [25] reported two eutectic reactions one in Ca rich side, other in Al rich side and determined most of the liquidus lines on the basis of thermoresistometric and thermal investigations. They determined the eutectic point of the Al-rich side with the composition of 5.24 at.% Ca at 889K. Later it was found by Kevorkov *et al.* [3] that there are two eutectic points on the Ca-rich side instead of one mentioned by Matsuyama [25]. These eutectic reactions occur at 66.2 at. % Ca, 829K and 79.5 at.% Ca, 833K [3].

### 2.2.2 Thermodynamic Data

For  $Al_{14}Ca_{13}$  intermetallic compound there is no experimental enthalpy of formation data reported in the literature up to date due to the sluggish formation kinetics of the phase and thus difficulty of preparing an  $Al_{14}Ca_{13}$  rich sample [4]. Kevorkov *et al.* [3] determined the partial enthalpy of mixing experimentally. They reported  $\Delta h_{Ca} = -89.9 \pm 1.6$  kJ/mol at 978K which is in good agreement with the data of Notin *et al.* [26]. Sommer *et al.* [27] used high temperature calorimetry for determining the enthalpy of mixing of liquid at temperatures ranging between 1125K and 1190K. Their experimental results are in good agreement with Notin *et al.* [26] as well. Ozturk *et al.* [4] compared the enthalpy of mixing data in the liquid phase at 1453K with experimental values. They reported a deep valley in the enthalpies with a trend shows that the minimum of the curve is shifted towards the Al side. This indicates strong interactions between the atoms in the liquid at composition around that of the  $Al_2Ca$  compound. Jacob *et al.* [28] determined activities in the liquid Al-Ca alloys using Knudsen effusion method at 1373K. Schürmann *et al.* [29] calculated the activities of Ca in the liquid alloys by using boiling point determination technique.

### 3. METHODOLOGY

The storage, retrieval and manipulation of thermodynamic data with the aid of the computer require accurate analytical representation of thermodynamic properties of different phases in the system under question. Values of the standard Gibbs energies,  $G^\circ$ , of each component are entered and stored in the database along with parameters which define the Gibbs energy of mixing according to Redlich-Kister polynomial model and Gibbs free energy of formation of stoichiometric compound. The phase diagram and thermodynamic data (activity and heat and entropy of mixing, partial Gibbs free energy) were critically assessed for all phases in the Mg-Ca and Al-Ca systems from room temperature to above the liquidus temperatures at the atmospheric pressure. All these data were optimized to obtain a set of model parameters for Gibbs energy of the liquid and all solid phases as function of composition and temperature. The model parameters are collected in a thermodynamic database. Binary phase diagrams and thermodynamic properties were calculated using this database and compared with the results from the literature.

### 4. THERMODYNAMIC MODELS

#### 4.1 Unary Phases

The Gibbs energy of the pure element,  $i$ , with a certain phase  $\phi$ , is described as a function of temperature by the following equations:

$$\begin{aligned} {}^0G_i^\phi(T) &= G_i^\phi(T) - H_i^{SER} \\ {}^0G_i^\phi(T) &= a + bT + cT \ln T + dT^2 + eT^3 \\ &+ fT^{-1} + gT^7 + hT^9 \end{aligned} \quad (1)$$

Where  $H_i^{SER}$  the molar enthalpy of the stable element reference (SER) is at 298.15K and 1bar, and  $T$  is the absolute temperature. The value of the coefficient  $a$  to  $h$  are taken from the SGTE compilation by Dinsdale [35].

#### 4.2 Disordered Solution Phases

The Gibbs energy of a disordered solution phase is described by the following equation:

$$G = x_i {}^0G_i^\phi + x_j {}^0G_j^\phi + RT [x_i \ln x_i + x_j \ln x_j] + {}^{ex}G^\phi \quad (2)$$

where  $\Phi$  denotes the phase in equation and  $x_i$ ,  $x_j$  denote the mole fraction of component  $i$  and  $j$  respectively. The first two terms on the right hand side of the above equation represent the Gibbs energy of the mechanical mixture of the components, the third term is the ideal Gibbs energy of mixing, and the fourth term is the excess Gibbs energy. The excess Gibbs energy is represented using the Redlich-Kister equation:

$${}^{ex}G^\phi = x_i x_j \sum_{n=0}^{n=m} {}^nL_{i,j}^\phi (x_i - x_j)^n \quad (3)$$

$$\text{with } {}^nL_{i,j}^\phi = a_n + b_n \times T \quad (n=0, \dots, m)$$

Where  $a_n$  and  $b_n$  are model parameters to be optimized in terms of experimental and thermodynamic data.

#### 4.3 Stoichiometric Phases

The Gibbs energy for stoichiometric compounds is described by the following equation:

$$\begin{aligned} G^\phi &= x_i {}^0G_i^{\phi_1} + x_j {}^0G_j^{\phi_2} + \Delta G_f \\ \Delta G_f &= a + b.T \end{aligned} \quad (4)$$

Where  $x_i$ ,  $x_j$  are the mole fraction of component  $i$  and  $j$  and  ${}^0G_i^{\phi_1}$ ,  ${}^0G_j^{\phi_2}$  represent the Gibbs energy of a component in its standard state. However the Gibbs energy of the compound phase may refer to a different crystal structures from those of the pure elements,  $\Phi_1$  and  $\Phi_2$ .  $\Delta G_f$  is the Gibbs energy of formation per mole of atoms of the stoichiometric compound; the parameters  $a$  and  $b$  are obtained by optimization in of the phase equilibria and thermodynamic data.

### 5. RESULTS AND DISCUSSION

#### 5.1 Mg-Ca System

##### 5.1.1 Phase Diagram

The model-calculated phase diagram of Mg-Ca system is shown in relation to the experimental

results from the literature in Figure 1. It can be seen from this figure that there is a good agreement between the experimental and calculated results. On Ca rich region this calculated phase equilibria data agrees fairly well with the results from the literature. The values of optimized model parameters are shown in Table 1.

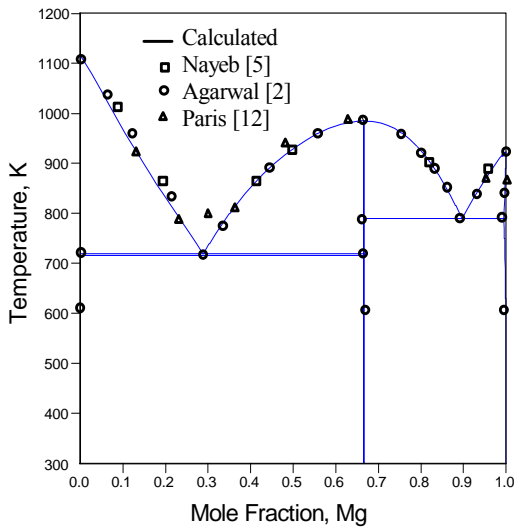


Figure 1: Optimized Mg-Ca with experimental data from the literature.

Table 1: Parameters for the liquid phase,  $Mg_2Ca$  stoichiometric phase of Mg-Ca system:

Phase	Terms	a(J/mole)	b(J/mole)
Liquid	$L_0$	-24018.6	1.94327
	$L_1$	-1785.73	4.47241
	$L_2$	14387.5	-22.9827
$Mg_2Ca$	$\Delta G_f$	-12704.4	1.80939

### 5.1.2 Thermodynamic properties

Thermodynamic data for the liquid and the  $Mg_2Ca$  intermetallic compound are available in the literature. In Figure 2 the model-calculated enthalpy of mixing shows good agreement, with experimental data measured by Sommer *et al.* [20]. Although Agarwal *et al.* [2] also measured the enthalpy of mixing at 1023K, their results were not considered because they contradict those of Sommer *et al.* [20]. However, Mishra *et al.* [33] mentioned that considering energy

parameters values at 1023K instead of 1150K could minimize this discrepancy.

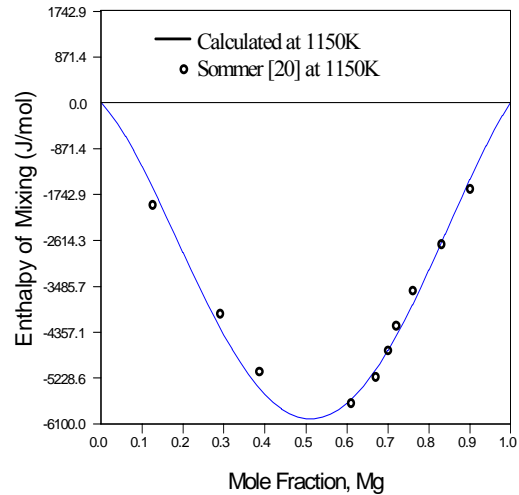


Figure 2: Enthalpy of mixing Mg-Ca liquid at 1150K.

The activity of Mg in Mg-Ca liquid at 1080K is shown in Figure 3. It can be seen from this figure that calculated Mg activity agrees with the experimental results of Sommer [19]. Also, the figure shows that Mg mixing in the Mg-Ca liquid demonstrates negative deviation from Raoult's ideal solution.

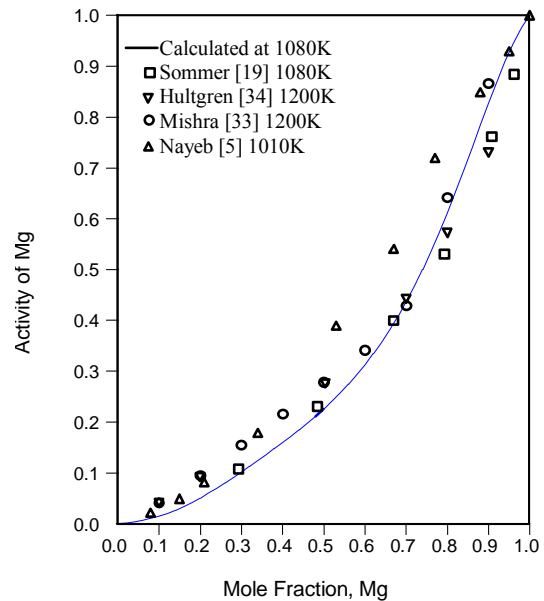


Figure 3: Activity of Mg in Mg-Ca liquid.

It can be seen from Figure 4 that the calculated activity of Ca agrees with the results obtained by

Sommer [19], however it deviates from the results of Hultgren *et al.* [34] and Mishra *et al.* [33], this is probably due to the fact that they obtained their results at different temperature.

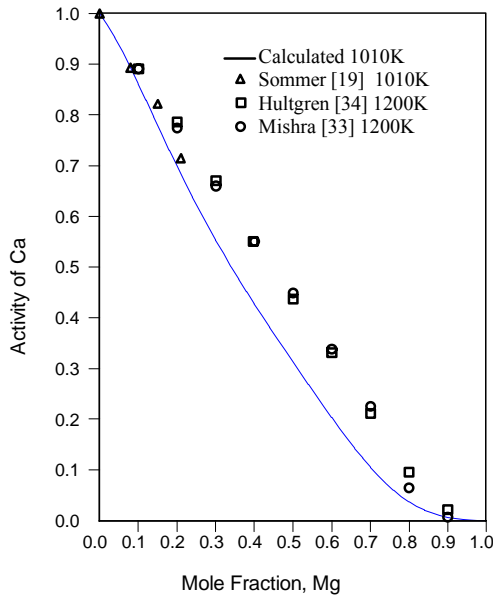


Figure 4: Activity of Ca in Mg-Ca liquid.

The calculated heat and entropy of formation of  $Mg_2Ca$  stoichiometric compound at 298K is -38.113 kJ/mol and 101.5911 kJ/mol.K respectively. Davison and Smith [15] and King and Kleepaa [16] proposed the enthalpy of formation at 298K as -39.50 kJ/mol and  $-40.50 \pm 1.25$  kJ/mol respectively which are very close to the values resulted from the current model.

The partial Gibbs free energy of Mg and Ca in Mg-Ca liquid at 1100K are calculated and compared with the experimental data from the literature Figures 5 and 6, respectively.

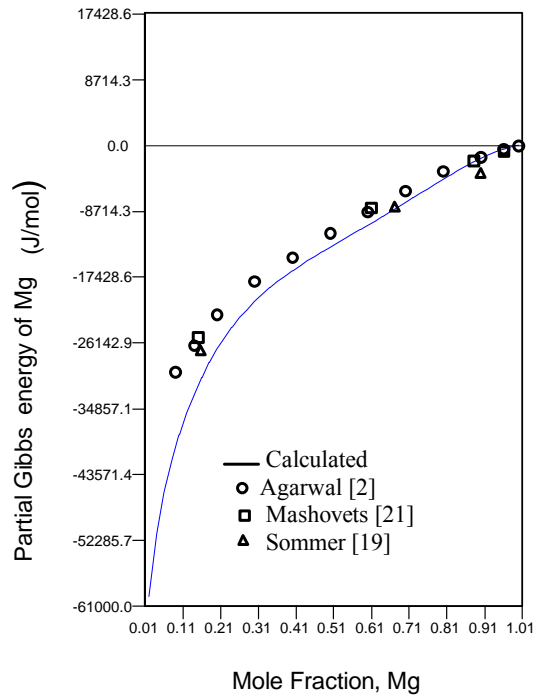


Figure 5: Partial Gibbs energy of Mg in Mg-Ca liquid.

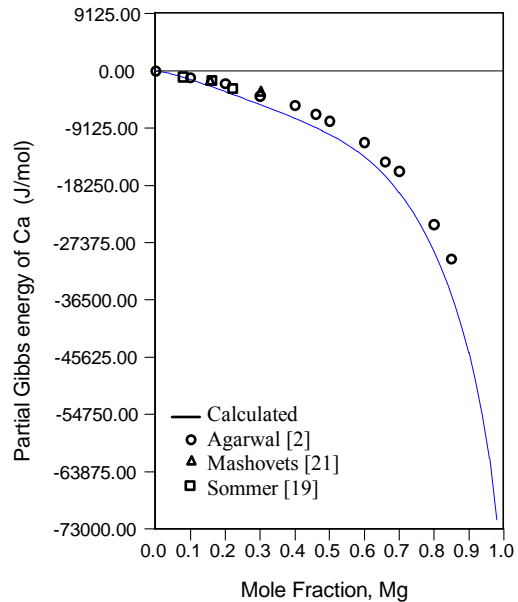


Figure 6: Partial Gibbs energy of Ca in Mg-Ca liquid.

Furthermore, Agarwal *et al.* [2] reported experimental results for the partial enthalpy of mixing of Ca in Mg-Ca liquid at 1032K. Their results are compared with the calculated values from the present model and shown in Figure 7.

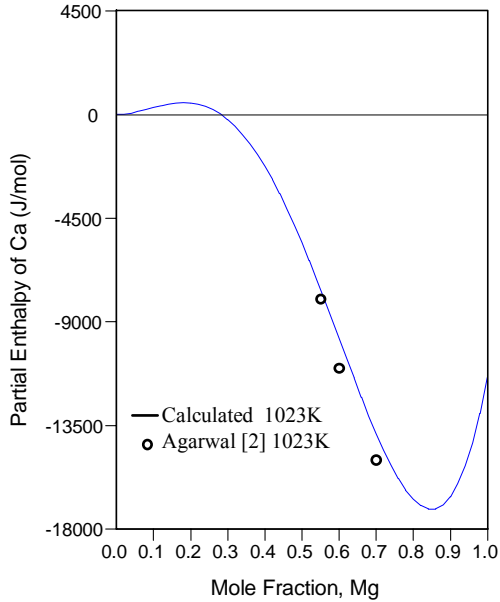


Figure 7: Partial enthalpy of Ca in Mg-Ca liquid.

## 5.2 Al-Ca System

### 5.2.1 Phase Diagram:

The optimized phase diagram of Al-Ca system in relation to experimental data from the literature is shown in Figure 8. Agreement between the model-calculated phase diagram and the measured liquidus and other critical points of Kevorkov and Schmid-Fetzer [3,23] can be seen in this figure. However, the results of Matsuyama [25] are not consistent with the current analysis of the Al-rich side. This is due to the fact that in their analysis, they considered only  $Al_4Ca$  and  $Al_2Ca$  as intermediate compounds in this system.

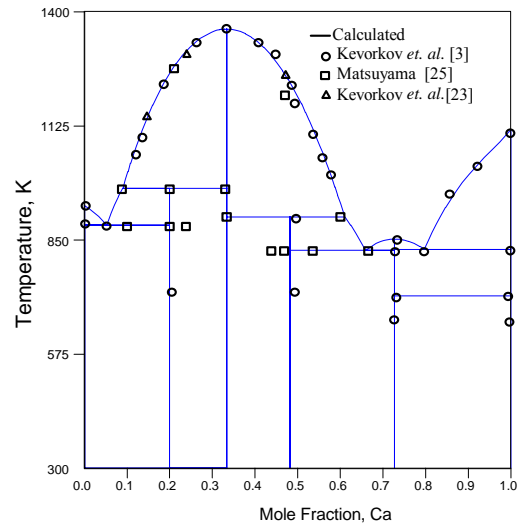


Figure 8: Calculated Al-Ca phase diagram with experimental data from the literature

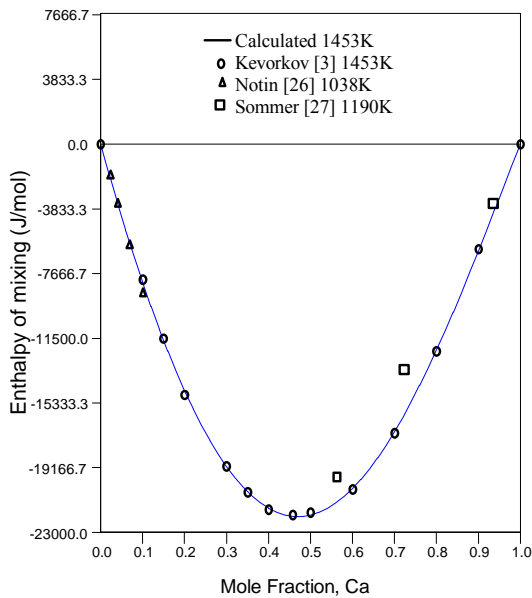
The calculated thermodynamic parameters are in Table 2. The lattice stability of pure component was considered by Kevorkov *et al.* [3] but this work and Ozturk *et al.* [4] did not consider it.

Table 2: The Model parameters for the liquid and the stoichiometric compounds in Al-Ca system.

Phase	Terms	a (J/mole)	b(J/mole)
Liquid	$L_0$	-87894.6	29.8567
	$L_1$	-12077.6	4.80628
	$L_2$	11427.8	-2.45047
	$L_3$	-1058.76	-.95372
$Al_4Ca$	$\Delta G_f$	-17272	2.23899
$Al_2Ca$	$\Delta G_f$	-29281.7	5.38176
$Al_{14}Ca_{13}$	$\Delta G_f$	-26058.5	5.63473
$Al_3Ca_8$	$\Delta G_f$	-15627.3	2.30139

### 5.2.2 Thermodynamic Properties

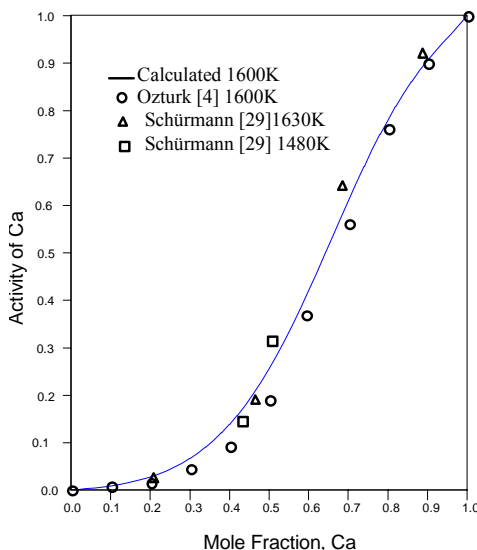
The calculated enthalpy of mixing of Al-Ca liquid in relation to the experimental results from the literature is presented in Figure 9.



**Figure 9:** Enthalpy of mixing of Al-Ca liquid at 1453 K

Figure 9, shows that there is an excellent agreement between this study and Kevorkov *et al.* [3] and Notin *et al.* [26], where, a reasonable agreement with Sommer *et al.* [27] was obtained. Nevertheless, an attempt to get close fit to enthalpy of mixing measured by Sommer *et al.* [27] would result in shift of liquidus line of  $Al_2Ca$  to higher temperature on Ca rich side.

The calculated activity of Ca agrees well with the results obtained by Ozturk *et al.* [4] and Schürmann *et al.* [29] as shown in Figure 10.



**Figure 10:** Activity of Ca in Al-Ca liquid.

The calculated thermodynamic properties for the four intermetallic compounds are compared with other data from the literature in Tables 3 to 6.

The thermodynamic properties of  $Al_2Ca$  are listed with data from the literature in Table-3. It can be seen that the enthalpy, entropy and Gibbs energy of formation of  $Al_2Ca$  obtained in this study agree with the results from the literature.

**Table 3:** Thermodynamic properties of  $Al_2Ca$  with experimental data from the literature.

Method [Ref]	T(K)	$\Delta_f H$ kJ/mol	$\Delta_f S$ J/mol.K	$\Delta_f G$ kJ/mol
HT [32]	673-903	-31.28±.46	-5.67±.93	
PC [26]	1038	-33.4±. 6		
emf[30]	800	-34.3±3.5	-6.1±1.1	-28.3±.3
DC[3]	298	-29.4±. 9		
A [3]	800	-29.7	-5.02	-25.7
Cal*	298	-29.28	-5.38	-27.7

HT: Hydrogen Titration, PC: Precipitation Calorimetry, DC: Dissolution Calorimetry A: Assessed, Cal\*: Calculated from this work.

The thermodynamic properties of  $Al_4Ca$  are listed with data from the literature in Table 4. The values obtained in this work agree with the results from the literature. Further, the calculated Gibbs energy of formation of this compound is similar to the assessed value of Kevorkov *et al.* [3].

**Table 4:** Thermodynamic properties of  $Al_4Ca$  with experimental data from the literature.

Method [Ref]	T(K)	$\Delta_f H$ kJ/mol	$\Delta_f S$ J/mol.K	$\Delta_f G$ kJ/mol
HT[32]	673-903	-20.18 ±0.38	-4.29 ±0.78	
PC[26]	1038	-18.7 ±0.3		
emf[30]	800	-19.4 ±3.3	-1.1±0.5	-17.8±0.14
A [3]	800	-21	-5.492	-16.6
Cal*	298	-17.272	-2.238	-16.60

HT: Hydrogen Titration, PC: Precipitation Calorimetry, A: Assessed, Cal\*: Calculated from this work.

The existence of two intermetallic compounds  $Al_3Ca_8$  and  $Al_{14}Ca_{13}$  is indicated in most recent studies [23,24]. Table 5 lists the thermodynamic properties of  $Al_3Ca_8$  in comparison with data from the literature. It can be seen that the enthalpy and Gibbs energy of formation of this compound agree with the results from the literature.

**Table 5:** Thermodynamic properties of  $Al_3Ca_8$  with experimental data from the literature.

Method [Ref]	T(K)	$\Delta_f H$ kJ/mol	$\Delta_f S$ J/mol.K	$\Delta_f G$ kJ/mol
DC[3]	298	-13.7±1.3		
A [3]	800	-14	-0.47	-13.6
Cal*	298	-15.63	-2.30	-14.94

DC: Dissolution Calorimetry, A: Assessed, Cal\*: Calculated from this work.

The thermodynamic properties for  $Al_{14}Ca_{13}$  are not available in the literature yet. Hence the calculated thermodynamic properties for this compound are compared with AlCa in Table 6. This is because until recently, it was believed that AlCa occurs instead of  $Al_{14}Ca_{13}$ . Nevertheless, it was noticed that the thermodynamic properties of these two compounds are very close.

**Table 6:** Thermodynamic properties of  $Al_{14}Ca_{13}$

Method [Ref]	T(K)	$\Delta_f H$ kJ/mol	$\Delta_f S$ J/mol.K	$\Delta_f G$ kJ/mol
Cal* $Al_{14}Ca_{13}$	298	-26.058	-5.63473	-24.378
A[3] AlCa	800	-22.8	-2.148	-21.1

Cal\*: Calculated from this work, A: Assessed.

## 6. CONCLUSION

Thermodynamic models were constructed for Mg-Ca and Al-Ca systems using phase equilibrium and thermodynamic data. Calculated binary phase diagrams from the thermodynamic parameters reproduced the experimental measured values very closely. An optimized self-consistent thermodynamic database has been developed. This database can now be employed to calculate other integral and partial thermodynamic properties such as entropy, Gibbs free energy and partial enthalpy. Mg-Ca and Al-Ca systems are also two binary constituents of the promising Mg-Al-Ca system. Few studies have been conducted on the thermodynamics and phase relationship of this ternary system, which can be obtained through thermodynamic modeling of Mg-Ca and Al-Ca systems along with the previously optimized Mg-Al system.

## 7. ACKNOWLEDGMENT

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