

Communication

Partitioning of Calcium Between Liquid Silver and Liquid Iron

MARTIN BERG, JAEWOO LEE, and DU SICHEN

The partitioning of calcium between liquid silver and liquid iron at 1823 K and 1873 K (1550 °C and 1600 °C) was studied experimentally using a closed molybdenum container. The calcium potential in the container was controlled by the composition of the alloys in equilibrium. The results agreed well with previous experimental measurements and indicated that the effect of temperature was not very pronounced in the temperature range studied.

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One of the common methods for performing thermodynamic studies on metallurgical systems is to equilibrate a suitable reference system, for which the thermodynamic properties are well known, with the system of interest. Due to the very low solubility of calcium in liquid iron,^[1-4] iron-calcium alloys are not suitable as reference system for thermodynamic measurements on calcium containing phases at steelmaking temperatures. An alternative is the silver-calcium system. This, however, requires good knowledge of the thermodynamic properties of the silver-calcium system at the temperature of interest. Experimental measurements on the silver-calcium system over the whole composition range have been made at 1073 K to 1273 K (800 °C to 1000 °C), by Delcet and Egan^[5] and Fischbach^[6] using EMF technique and Knudsen effusion technique, respectively. Wakasugi and Sano^[7] as well as Tago *et al.*^[8] measured the activity coefficient of calcium in liquid silver at low calcium contents in the temperature range 1570 K to 1831 K (1297 °C to 1558 °C) using CaC₂- and CaO-saturated slags in equilibrium with liquid silver. Fujiwara *et al.*^[9] studied the partitioning of calcium between liquid silver and liquid iron at 1823 K (1550 °C). The aim of the present work is to provide additional experimental measurements on the

silver-calcium system at steelmaking temperatures and discuss the applicability of the existing experimental data and models.

Experimental measurements were made in order to study the partitioning of calcium between liquid silver and liquid iron at 1823 K and 1873 K (1550 °C and 1600 °C). A detailed description of the furnace setup can be found in a previously published work^[1] and only a brief description is given here. A vertical resistance furnace with Kanthal Super heating elements and an alumina reaction tube was used. To enable fast cooling of the samples after equilibration without withdrawing them from the furnace, the upper part of the reaction tube was interconnected to a water cooled aluminum chamber. By suspending the samples from a steel rod connected to a computer-controlled lifting system, they could be moved quickly from the hot zone of the furnace into the cooling chamber. The furnace was sealed using O-rings and radial seals. Two separate gas inlets, one at the bottom of the furnace and one in the upper aluminum chamber, allowed for both keeping a constant gas flow during the experiments as well as injecting a higher flow of gas directly at the sample during cooling. The furnace temperature was controlled by a type B thermocouple (70 pct Pt/30 pct Rh to 94 pct Pt/6 pct Rh). A second type B thermocouple, placed with its tip just below the sample, was used to measure the temperature of the sample.

The principle of the experiments was to equilibrate a liquid calcium-iron alloy with a liquid calcium-silver alloy in a closed container. By using a closed container, the calcium activity is controlled by the amount of calcium in the alloys. A molybdenum container with a conical closing was used to hold the samples during the experiments, see Figure 1 for a schematic illustration. A previous work has shown that this type of container can maintain moderate vapor pressures while allowing for release of overpressures during heating.^[10]

For each run, 15 g of iron powder (99.9 pct, supplied by Alfa Aesar) and 15 g of silver powder (99.99 pct, supplied by Alfa Aesar) were held at 773 K (500 °C) for 60 minutes in H₂ gas (99.995 pct, supplied by AGA) in order to reduce any surface oxides. The silver powder was mixed with calcium granules (99.5 pct, supplied by Alfa Aesar). The powders were placed in a calcium oxide crucible (99.9 pct, supplied by TEP Ceramics) as shown in Figure 1. The crucible was placed inside the molybdenum holder which was sealed by carefully pushing the conical molybdenum lid in place. Care was taken to ensure a tight and straight fit. The crucible arrangement was inserted into the hot zone of the furnace. After sealing the furnace, it was evacuated for 3 hours using a vacuum pump followed by refilling using argon gas (99.999 pct, supplied by AGA). An argon gas flow of 0.1 l/min was used during the experiments. The furnace was heated up at 2 K/min. After reaching the target temperature, the samples were equilibrated for 24 hours

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before being raised quickly into the water-cooled aluminum chamber. A gas flow rate of 1 l/min was used during cooling. The silver and iron alloys were separated and ground carefully in order to obtain clean pieces. Approximately 1 g of each alloy was analyzed using ICP-SFMS (Thermo Fischer Element XR). Samples were also examined in scanning electron microscope (Hitachi S-3700N with a Bruker EDS analyzer) to ensure that no significant amount of calcium containing inclusions was present.

The results from the chemical analyses are presented in Table I. The calcium contents in the silver-calcium and iron-calcium alloys were 6 to 23 pct by weight and 6 to 33 ppm by weight, respectively. The composition range of the iron-calcium alloys is similar to a previous work by the authors.^[1] SEM investigations showed no presence of calcium containing inclusions in the samples, indicating that the holding time was long enough to allow flotation of any inclusions formed.

In order to evaluate the dependency of the activity of calcium, relative to pure liquid calcium, as a function of calcium content in silver, calcium in iron was used as a reference, as shown by Eq. [1]

$$a_{\text{Ca(l)}} = X_{\text{Ca in Fe}} \times \gamma_{\text{Ca(l)in Fe}} = X_{\text{Ca in Ag}} \times \gamma_{\text{Ca(l)in Ag}} \quad [1]$$

For a silver-calcium alloy in equilibrium with an iron-calcium alloy the calcium activity, with respect to the same reference, is identical in both phases. Thus, by using the analyzed calcium content in the iron and data

on the activity coefficient of calcium in liquid iron published previously,^[1] the calcium activity could be calculated. For the following calculations of the activity of calcium, relative to pure liquid calcium, it was assumed that the activity coefficient of calcium in iron is constant in the composition range studied and has the value 1551. The calculated mole fractions of calcium in the samples and the activities of calcium are presented in Table II. Figure 2 presents the activity of calcium as a function of the mole fraction of calcium in the silver-calcium alloys, along with data from Fujiwara *et al.*^[9] It can be seen that the data from the present study agree well with the data from Fujiwara *et al.*^[9] and that the results indicate a clear negative deviation from ideality. It can also be noted that the data above a mole fraction of calcium of approximately 0.5 from Fujiwara *et al.*^[9] show a considerable scatter. It is worthwhile to mention that this scatter is probably due to experimental difficulties. Attempts to make experiments above a mole fraction of calcium of 0.5 in the present work were not successful. The data also suggest that the effect of temperature on the activity curve is not very pronounced in the temperature range studied.

In order to obtain information about the calcium activity in silver-calcium alloys at steelmaking temperatures, extrapolations based on experimental data at 1073 K to 1273 K (800 °C to 1000 °C) by Fischbach^[6] have been used. Experimental results from equilibration of silver-calcium and iron-calcium alloys are presented in Figure 3 along with an extrapolation based on the data from Fischbach^[6] as well as a calculation using the Thermo-Calc software^[11] and the SSOL6 database.^[12]

From Figure 3, it can be seen that even though the overall trend shown by the experimental data and the two calculated lines are similar, there are differences. At mole fractions of calcium lower than approximately 0.5, the experimental data, based on the assumption that the activity coefficient of calcium in iron is constant in the composition and temperature range studied, agree reasonably well with the Thermo-Calc calculation with respect to the overall trend. The extrapolated line based on data from Fischbach,^[6] on the other hand, lies significantly higher in this composition range. The scatter of the experimental data at higher calcium contents makes it difficult to evaluate the consistency between experimental data and extrapolation/calculation. It can however be noted that the experimental data in general show a lower calcium activity in comparison with the extrapolation and the calculation at higher

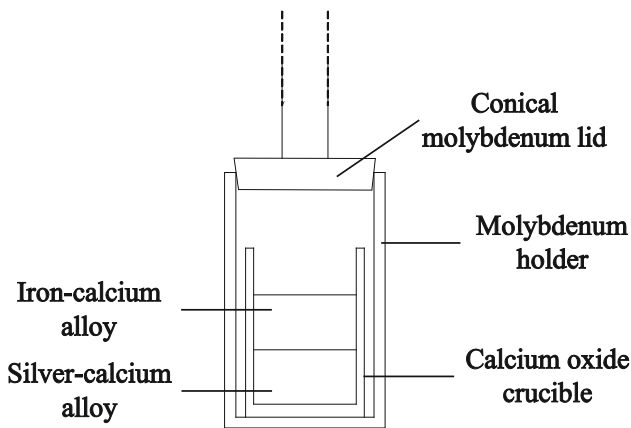


Fig. 1—Crucible arrangement.

Table I. Experimental Conditions and Analysis Results

Sample ID	T [K (°C)]	Pct Ca in Ag	Pct Ca in Fe
1	1823 (1550)	11.5	0.00085
2	1823 (1550)	17.7	0.00108
3	1823 (1550)	23.4	0.00331
4	1873 (1600)	5.93	0.00060
5	1873 (1600)	11.6	0.00059
6	1873 (1600)	14.9	0.00115
7	1873 (1600)	15.2	0.00109
8	1873 (1600)	16.6	0.00177

Table II. Calculated Mole Fractions of Calcium in Silver and Iron and Calcium Activity

Sample ID	$X_{Ca \text{ in Ag}}$	$X_{Ca \text{ in Fe}} \times 10^5$	$a_{Ca(l)}$
1	0.259	1.18	0.0183
2	0.367	1.50	0.0233
3	0.451	4.61	0.0715
4	0.145	0.836	0.0130
5	0.261	0.822	0.0128
6	0.320	1.60	0.0249
7	0.325	1.52	0.0236
8	0.345	2.47	0.0383

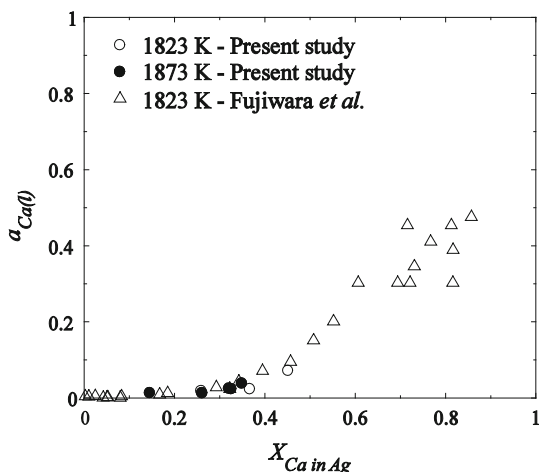


Fig. 2—Activity of calcium, relative to pure liquid calcium, as a function of mole fraction of calcium in silver including data from Fujiwara *et al.*^[9]

calcium contents. It should also be remembered that the experimental data are presented based on the assumption that the activity coefficient of calcium in iron is constant in the composition range studied.

As an illustration of the effect of the data chosen to calculate the calcium activity of silver-calcium alloys at 1823 K (1550 °C), the activity coefficient of calcium in liquid silver, relative to pure liquid calcium, at low calcium contents was calculated using an extrapolation based on the data from Fischbach^[6] and the calculation using Thermo-Calc. At a mole fraction of calcium of 0.01, the activity coefficients differ by a factor of almost 200, with Thermo-Calc giving the lower value. Furthermore, the value reported by Wakasugi and Sano^[7] and Tago *et al.*^[8] at 1823 K (1550 °C) is approximately 10 times higher compared to the value calculated using Thermo-Calc. This comparison reveals evidently that there are uncertainties in the available data for the activity of calcium in liquid silver in the temperature range discussed. Even though there are thermodynamic data available over the whole composition range at lower temperatures, it seems to have limited applicability at steelmaking temperatures.

Fischbach^[6] suggested that the relation between the activity coefficient of calcium in silver, relative to pure liquid calcium, and the mole fraction of calcium could be described using a third-order power series in the form

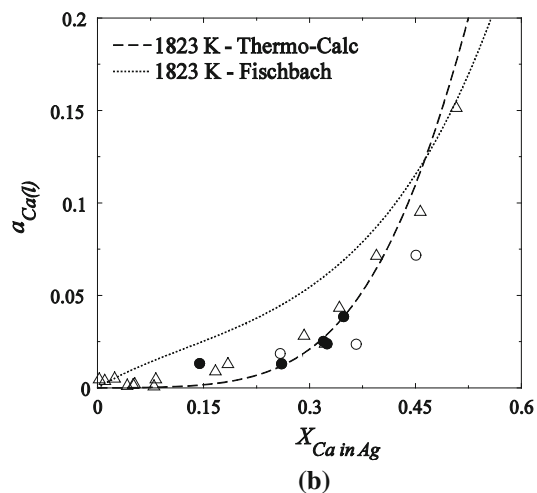
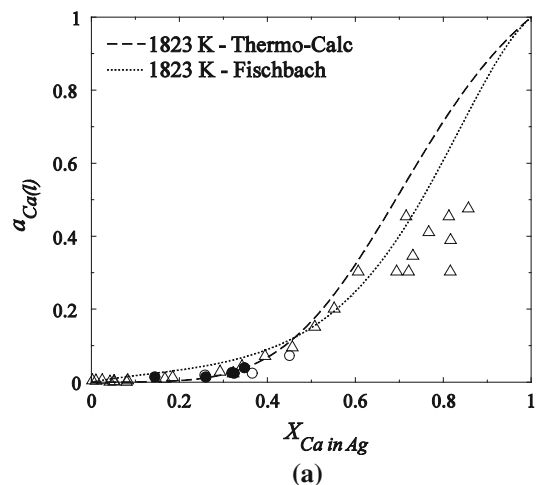


Fig. 3—Activity of calcium, relative to pure liquid calcium, as a function of mole fraction of calcium in silver including data from Fujiwara *et al.*^[9] as well as an extrapolation based on data from Fischbach^[6] and a calculation using Thermo-Calc in the composition range (a) $0 \leq X_{Ca \text{ in Ag}} \leq 1$, (b) $0 \leq X_{Ca \text{ in Ag}} \leq 0.6$. Note that the symbols used are the same as in Fig. 2.

$$\log(\gamma_{Ca(l) \text{ in Ag}}) = A \times (1 - X_{Ca \text{ in Ag}})^2 + B \times (1 - X_{Ca \text{ in Ag}})^3, \quad [2]$$

where A and B are temperature dependent parameters. Based on the results from the present study and data from Fujiwara *et al.*^[9] and Wakasugi and Sano^[7] a

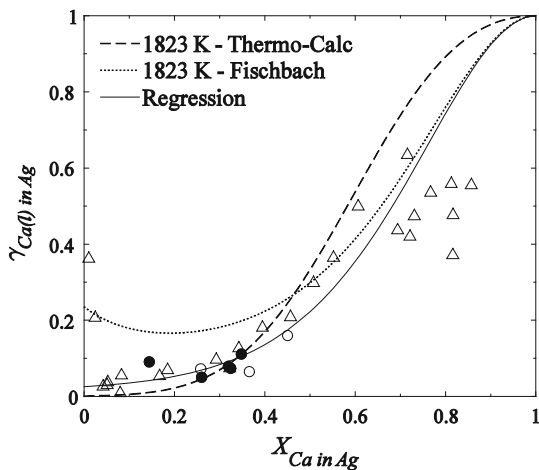


Fig. 4—Comparison between the calculated values of the activity coefficient of calcium, relative to pure liquid calcium, as a function of mole fraction of calcium in silver along with experimental data based on equilibration of silver-calcium and iron-calcium alloys. Note that the symbols used are the same as in Fig. 2.

regression analysis was made. Data in the temperature range 1823 K to 1873 K (1550 °C to 1600 °C) and the composition range $0.048 \leq X_{Ca \text{ in Ag}} \leq 0.46$ were used for the regression analysis. It should be mentioned that only the data in the composition range of the present study were used from the experiments based on equilibration of silver-calcium and iron-calcium alloys due to the uncertainties of this method at very high and very low calcium contents. The regression analysis leads to the equation

$$\log(\gamma_{Ca(l) \text{ in Ag}}) = -3.63 \times (1 - X_{Ca \text{ in Ag}})^2 + 2.04 \times (1 - X_{Ca \text{ in Ag}})^3 \quad [3]$$

under the conditions stated above. A comparison between the presented equation and the extrapolation based on data from Fischbach^[6] and the calculation using Thermo-Calc is shown in Figure 4 along with experimental data.

Note that Eq. [3] should only be used in the composition and temperature ranges mentioned above.

Calculation using this equation outside these ranges should be conducted with precaution. A thorough assessment of the silver-calcium system considering all available experimental data would be preferred to make the system truly useful as a reference system for thermodynamic measurements at steelmaking temperatures.

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REFERENCES

1. M. Berg, J. Lee, and Du. Sichen: *Metall. Mater. Trans. B*, 2017, vol. 48B, pp. 1715–20.
2. D.L. Sponseller, R.A. Flinn, and T. Metall: *Soc. AIME*, 1964, vol. 230, pp. 876–88.
3. M. Köhler, H.J. Engell and D. Janke, *Steel. Res.*, 1985, pp. 419–23.
4. B. Song and Q. Han: *Metall. Mater. Trans. B*, 1998, vol. 29B, pp. 415–20.
5. J. Delcet and J.J. Egan: *J. Less-Common Met.*, 1978, vol. 59, pp. 229–36.
6. H. Fischbach: *J. Less-Common Met.*, 1985, vol. 108, pp. 151–62.
7. T. Wakasugi and N. Sano: *Metall. Mater. Trans. B*, 1989, vol. 20B, pp. 431–33.
8. Y. Tago, Y. Endo, K. Morita, F. Tsukihashi, and N. Sano: *ISIJ Int.*, 1995, vol. 35, pp. 127–31.
9. H. Fujiwara, M. Tano, K. Yamamoto, and E. Ichise: *ISIJ Int.*, 1995, vol. 35, pp. 1063–71.
10. J. Gran and Du. Sichen: *Metall. Mater. Trans. B*, 2011, vol. 42B, pp. 921–24.
11. J.O. Andersson, T. Helander, L.H. Höglund, P.F. Shi, and B. Sundman: *Calphad.*, 2002, vol. 26, pp. 273–312.
12. SSOL6 - SGTE Alloy Solutions Database v6.0 as supplied by Thermo-Calc Software AB; 2016.