Thermodynamic calculation of calcium metal prepared by vacuum aluminothermic reduction method

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Abstract. In references for aluminothermic reduction of metal calcium thermodynamic calculation are choose metal temperature range for the liquid or gaseous state thermodynamics calculation, the results show that the temperature at which the reaction can occur is very high. In this article, by comparing the two calculation methods under normal pressure, the theoretical initial reaction temperature of the four reactions is very high under normal pressure. The lowest temperature is the reaction to generate 3CaO·Al₂O₃, but the reaction still needs to exceed 2421K. The results of the two calculation methods is very different. These are 222K, 78K, 151K, and 85K. At 10Pa, Theoretical initial reaction temperature of the four reactions are 859K, 877K, 928K, and 878K. If the calculation result of the high-temperature region is substituted for the calculation result of the whole temperature interval, the theoretical initial reaction temperature of the four reactions are respectively 1329K, 1344K, 1374K and 1374K at 10Pa. The difference value of each reaction is 470K, 472K, 446K, and 459K.

1. Introduction
At present, the main production methods of calcium metal include electrolysis[1-3] and thermal reduction[4-12]. Electrolysis is the main method of industrial production of metals in China. The principle of electrolysis is based on electrode potential different from impurity elements of calcium metal, selective discharge of the anode and selective deposition of the cathode. In the preparation of calcium metal by a thermal process, aluminothermic method, silicon thermal method, and carbon thermal method are the hot topics.

2. Thermodynamic calculation under normal pressure
The standard Gibbs free energy equation in the high-temperature section was used in most thermodynamic calculations in the references to replace the equation in the full temperature section with the standard Gibbs free energy equation. The theoretical initial reaction temperature calculated was relatively high. In this paper, the Gibbs free energy was calculated in different temperature ranges. The standard reaction thermal effect was calculated and compared with the first approximate thermodynamic calculation. Refer to reference 13 for the specific calculation formula. Since the approximate calculation is not accurate at high temperature and there is a certain deviation from the conclusion. It is necessary to accurately calculate the reactions in the preparation of calcium metal by vacuum aluminothermic reduction method.
The reactions in the preparation of calcium metal by vacuum aluminothermic reduction method are all multi-step reactions. At high temperature, calcium is constantly dissolved in excess aluminum during the reduction process. The dissolution of calcium in aluminum greatly reduces the activity of calcium. When the concentration of calcium in aluminum rises and reaches saturation, the calcium ceases to dissolve, releasing the metallic calcium. Aluminothermic reduction of calcium mainly occurs in the following five reactions:

\[
\begin{align*}
6\text{CaO}+2\text{Al} &= 3\text{Ca}+3\text{CaO} \cdot \text{Al}_2\text{O}_3 \quad (1) \\
4\text{CaO}+2\text{Al} &= 3\text{Ca}+\text{CaO} \cdot \text{Al}_2\text{O}_3 \quad (2) \\
7\text{CaO}+4\text{Al} &= 6\text{Ca}+\text{CaO} \cdot 2\text{Al}_2\text{O}_3 \quad (3) \\
33\text{CaO}+14\text{Al} &= 21\text{Ca}+12\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \quad (4) \\
19\text{CaO}+12\text{Al} &= 18\text{Ca}+\text{CaO} \cdot 6\text{Al}_2\text{O}_3 \quad (5)
\end{align*}
\]

2.1. Standard Gibbs free energy of conclusion calculation

Refer to reference 13 for the thermodynamic data of each substance in the conclusion calculation method, which is listed in table 1. Due to the lack of CaO·6Al2O3 thermodynamic data in reference 13, the reaction equation (5) is not calculated in this paper. According to the thermodynamic data in table 1, the Gibbs free energy of the reaction equations (1) to (4) at different temperature intervals are calculated, and the results are shown in table 2-5.

| Table 1. Thermodynamic data of substances in the conclusion calculation method. |
| --- |
| Pure Substance | A1 | A2 | A3 | A4 | A5 | \(\Delta H_{f,298}^\circ\) | \(S_{298}^\circ\) | Temperature |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Al(s) | 31.376 | -16.393 | -3.607 | 20.753 | 0 | 0 | 28.321 | 298-933 |
| Al(l) | 31.748 | 0 | 0 | 0 | 0 | 28839 | 71.489 | 298-933 |
| Al(g) | 20.799 | 0 | 0 | 0 | 0 | 377840 | 211.089 | 2767-3200 |
| Ca(s)\(\alpha\) | 24.125 | -3.356 | 0.331 | 20.414 | 0 | 0 | 41.422 | 298-720 |
| Ca(s)\(\beta\) | -0.377 | 41.279 | 0 | 0 | 0 | 36014 | 90.798 | 1112-1757 |
| Ca(l) | 29.288 | 0 | 0 | 0 | 0 | 36014 | 90.798 | 1112-1757 |
| Ca(g) | 20.832 | 0 | 0 | 0 | 0 | 208541 | 191.638 | 1757-2800 |
| CaO(s) | 49.622 | 4.519 | -6.945 | 0 | 0 | -634924 | 39.748 | 298-2888 |
| CaO(l) | 62.76 | 0 | 0 | 0 | 0 | -409722 | 187.813 | 2888-3500 |
| 3CaO·Al2O3(s) | 250.873 | 31.338 | -49.371 | 0 | 0 | -3584851 | 205.434 | 298-1808 |
| CaO·Al2O3(s) | 153.093 | 22.301 | -35.48 | 0 | 0 | -2322957 | 114.014 | 298-1878 |
| CaO·2Al2O3(s) | 258.236 | 40.083 | -64.015 | 0 | 0 | -3994046 | 177.82 | 298-2023 |
| 12CaO·7Al2O3(s) | 1263.401 | 274.052 | -231.375 | 0 | 0 | -19374012 | 1044.745 | 298-1800 |

| Table 2. The numerical values of the reaction equation (1) in the conclusion calculation method. |
| --- |
| \(\Delta A1\) | \(\Delta A2\) | \(\Delta A3\) | \(\Delta A4\) | \(\Delta A5\) | \(\Delta A6\) | \(\Delta A6'\) | Temperature/K |
| --- | --- | --- | --- | --- | --- | --- | --- |
| -37.236 | 26.942 | 0.506 | 19.736 | 0 | 0 | 28.321 | 298-720 |
| -110.742 | 160.847 | -0.487 | -41.506 | 0 | 0 | 71.489 | 298-933 |
| -111.486 | 128.061 | -7.701 | 0.000 | 0 | 0 | 81.798 | 1112-1757 |
| -22.491 | 4.224 | -7.701 | 0.000 | 0 | 0 | 90.798 | 1112-1757 |
| -47.859 | 4.224 | -7.701 | 0.000 | 0 | 0 | 187.813 | 2888-3500 |
Table 3. The numerical values of the reaction equation (2) in the conclusion calculation method.

| $\Delta A_1$ | $\Delta A_2$ | $\Delta A_3$ | $\Delta A_4$ | $A_6$ | $A_6'$ | Temperature/K |
|-------------|-------------|-------------|-------------|------|-------|---------------|
| -35.772     | 26.943      | 0.507       | 19.736      | 223678.772 | -253.595 | 298-720      |
| -109.278    | 160.848     | -0.486      | -41.506     | 252118.869 | -734.040 | 720-933      |
| 4CaO+2Al=3Ca+CaO·Al$_2$O$_3$ |
| -110.022    | 128.062     | -7.700      | 0.000       | 233812.850 | -728.957 | 933-1112     |
| -21.027     | 4.225       | -7.700      | 0.000       | 236879.059 | -176.476 | 1112-1757    |
| -46.395     | 4.225       | -7.700      | 0.000       | 742360.917 | -653.703 | 1757-1878    |

Table 4. The numerical values of the reaction equation (3) in the conclusion calculation method.

| $\Delta A_1$ | $\Delta A_2$ | $\Delta A_3$ | $\Delta A_4$ | $A_6$ | $A_6'$ | Temperature/K |
|-------------|-------------|-------------|-------------|------|-------|---------------|
| -69.872     | 53.886      | 1.014       | 39.472      | 464433.288 | -485.532 | 298-720      |
| -216.884    | 321.696     | -0.972      | -83.012     | 521314.098 | -1446.420 | 720-933      |
| 7CaO+4Al=6Ca+CaO·2Al$_2$O$_3$ |
| -218.372    | 256.124     | -15.400     | 0.000       | 484700.504 | -1436.253 | 933-1112     |
| -40.382     | 8.450       | -15.400     | 0.000       | 490833.894 | -331.293  | 1112-1757    |
| -91.118     | 8.450       | -15.400     | 0.000       | 1501797.890 | -1285.747 | 1757-2023    |

Table 5. The numerical values of the reaction equation (4) in the conclusion calculation method.

| $\Delta A_1$ | $\Delta A_2$ | $\Delta A_3$ | $\Delta A_4$ | $A_6$ | $A_6'$ | Temperature/K |
|-------------|-------------|-------------|-------------|------|-------|---------------|
| -306.764    | 283.951     | 55.259      | 138.152     | 1653822.302 | -2201.217 | 298-720      |
| -821.306    | 1221.286    | 48.308      | -290.542    | 1852961.507 | -5564.373  | 720-933      |
| 33CaO+14Al=21Ca+12CaO·7Al$_2$O$_3$ |
| -826.514    | 991.784     | -2.190      | 0.000       | 1724852.284 | -5528.799  | 933-1112     |
| -203.549    | 124.925     | -2.190      | 0.000       | 1746270.436 | -1661.402  | 1112-1757    |
| -381.125    | 124.925     | -2.190      | 0.000       | 5284713.083 | -5001.993  | 1757-2073    |

2.2. Standard Gibbs free energy of the first approximate thermodynamic calculation

Refer to reference 13 for the thermodynamic data of each substance in the first approximate thermodynamic calculation, which is listed in table 6. According to the thermodynamic data in table 6, the Gibbs free energy of the reaction equations (1) to (4) at different temperature intervals are calculated, and the results are shown in table 7-10.

Table 6. Thermodynamic data of substances in the first approximate thermodynamic calculation.

| Pure substance | $\Delta H_{f, 298}^\theta$ | $S_{298}^\theta$ | $T^\nu$ | $\Delta H^\nu$ | $T^M$ | $\Delta H^M$ | $T^B$ | $\Delta H^B$ | Temperature Range |
|---------------|-----------------|----------------|-------|---------------|------|-------------|------|-------------|------------------|
| Al            | 0               | 28.321         | 933   | 10711         | 2767 | 290775      | 298-3200       |
| Ca            | 0               | 41.422         | 720   | 920           | 1112 | 8535        | 1757           | 153636       |
| CaO           | -634294         | 39.748         |       |               |      |             |                 | 298-2800      |
| 3CaO·Al$_2$O$_3$ | -3584851       | 205.434        |       |               |      |             |                 | 298-1808      |
| CaO·Al$_2$O$_3$ | -2322957       | 114.014        |       |               |      |             |                 | 298-1878      |
| CaO·2Al$_2$O$_3$ | -3994046       | 177.820        |       |               |      |             |                 | 298-2023      |
| 12CaO·7Al$_2$O$_3$ | -19374012      | 1044.745       |       |               |      |             |                 | 298-1800      |
### Table 7. The first approximate thermodynamic calculation result of the reaction equation (1).

| Reaction equation | Temperature Range/K | ΔG°/J·mol⁻¹ |
|-------------------|---------------------|-------------|
| 6CaO(s)+2Al(s)=3Ca(s)(α)+3CaO·Al₂O₃(s) | 298–720 | 220913-34.57T |
| 6CaO(s)+2Al(s)=3Ca(s)(β)+3CaO·Al₂O₃(s) | 720–933 | 223673-38.404T |
| 6CaO(s)+2Al(l)=3Ca(s)+3CaO·Al₂O₃(s) | 933–1112 | 202251-15.444T |
| 6CaO(s)+2Al(l)=3Ca(g)+3CaO·Al₂O₃(s) | 1112–1757 | 227856-38.469T |
| 6CaO(s)+2Al(l)=3Ca(s)+3CaO·Al₂O₃(s) | 1757–1808 | 688764-300.795T |

### Table 8. The first approximate thermodynamic calculation result of the reaction equation (2).

| Reaction equation | Temperature Range/K | ΔG°/J·mol⁻¹ |
|-------------------|---------------------|-------------|
| 4CaO(s)+2Al(s)=3Ca(s)(α)+CaO·Al₂O₃(s) | 298–720 | 214219-22.646T |
| 4CaO(s)+2Al(s)=3Ca(s)(β)+CaO·Al₂O₃(s) | 720–933 | 216979-26.480T |
| 4CaO(s)+2Al(l)=3Ca(s)+CaO·Al₂O₃(s) | 933–1112 | 195557-3.520T |
| 4CaO(s)+2Al(l)=3Ca(g)+CaO·Al₂O₃(s) | 1112–1757 | 221162-26.545T |
| 4CaO(s)+2Al(l)=3Ca(l)+CaO·Al₂O₃(s) | 1757–1878 | 682070-288.871T |

### Table 9. The first approximate thermodynamic calculation result of the reaction equation (3).

| Reaction equation | Temperature Range/K | ΔG°/J·mol⁻¹ |
|-------------------|---------------------|-------------|
| 7CaO(s)+4Al(s)=6Ca(s)(α)+CaO·2Al₂O₃(s) | 298–720 | 446012-34.832T |
| 7CaO(s)+4Al(s)=6Ca(s)(β)+CaO·2Al₂O₃(s) | 720–933 | 451532-42.500T |
| 7CaO(s)+4Al(l)=6Ca(s)+CaO·2Al₂O₃(s) | 933–1112 | 408688-3.420T |
| 7CaO(s)+4Al(l)=6Ca(l)+CaO·2Al₂O₃(s) | 1112–1757 | 459898-42.630T |
| 7CaO(s)+4Al(l)=6Ca(g)+CaO·2Al₂O₃(s) | 1757–2023 | 1381714-567.282T |

### Table 10. The first approximate thermodynamic calculation result of the reaction equation (4).

| Reaction equation | Temperature Range/K | ΔG°/J·mol⁻¹ |
|-------------------|---------------------|-------------|
| 33CaO(s)+14Al(s)=21Ca(s)(α)+12CaO·7Al₂O₃(s) | 298–720 | 1560840-206.429T |
| 33CaO(s)+14Al(s)=21Ca(s)(β)+12CaO·7Al₂O₃(s) | 720–933 | 1580160-233.267T |
| 33CaO(s)+14Al(l)=21Ca(s)+12CaO·7Al₂O₃(s) | 933–1112 | 1430206-72.547T |
| 33CaO(s)+14Al(l)=21Ca(l)+12CaO·7Al₂O₃(s) | 1112–1757 | 1609441-233.722T |
| 33CaO(s)+14Al(l)=21Ca(g)+12CaO·7Al₂O₃(s) | 1757–2073 | 4835797-2070.004T |

### 2.3. Comparison of the two calculation methods

By comparing the two calculation methods under normal pressure, drawing with as ordinate and T as abscissa, as shown in Fig. 1. It can be seen from the figure that the Gibbs free energy difference between the two calculation methods is relatively small in the low-temperature interval, while there is a great difference in the high-temperature interval, especially in the metal melting or gasification stage.

The theoretical initial reaction temperature of the two calculation methods was obtained by extending the Gibbs free energy curve in the high-temperature section to intersect the X-axis, as shown in table 1. As can be seen from the table, 11, the reaction temperature required for the above four reactions is very high under normal pressure. The lowest temperature is the reaction to generate 3CaO·Al₂O₃, but the reaction still needs to exceed 2421K. The difference between the results of the two calculation methods is quite large. For the sake of accuracy, the subsequent calculation is carried out by the conclusion calculation method.
Table. 11 The theoretical initial reaction temperature of the two calculation methods under normal pressure.

| Reaction equation          | Theoretical initial temperature/K | The conclusion formula calculation | First approximate thermodynamic calculation | Difference value |
|---------------------------|-----------------------------------|-----------------------------------|---------------------------------------------|------------------|
| 6CaO+2Al=3Ca+3CaO·Al₂O₃   | 2512                              | 2290                              | 222                                         |
| 4CaO+2Al=3Ca+CaO·Al₂O₃    | 2439                              | 2361                              | 78                                          |
| 7CaO+4Al=6Ca+CaO·2Al₂O₃   | 2587                              | 2436                              | 151                                         |
| 33CaO+14Al=21Ca+12CaO·7Al₂O₃ | 2421                              | 2336                              | 85                                          |

3. Thermodynamics calculation in vacuum

Under normal pressure, the temperature required for aluminum thermal reaction is very high, which is difficult to achieve. Therefore, the reaction needs to be carried out under vacuum conditions. The thermodynamics of the four reactions under vacuum conditions is calculated as follows. The Gibbs free energy of the four reactions can be obtained by the following formula under vacuum condition.

\[ \Delta G = \Delta G^\theta + RT \ln \left( \frac{p_{Ca}}{p^\theta} \right) \]  

(1)

Where, \( p_{Ca} \) is the vapor pressure producing Ca, \( p^\theta \) is the standard pressure (101325Pa), and \( R \) is 8.314.

At 10Pa, Gibbs free energy of the four reactions was plotted according to formula (6), as shown in Fig. 2. Can be seen from the figure in the reaction equation (1) to (4), Theoretical initial reaction temperature of the four reactions are respectively 859K, 877K, 928K and 878K. Calculated results are much lower than in the past. If the calculation result of the high-temperature region is substituted for the calculation result of the whole temperature interval, the theoretical initial reaction temperature of the four reactions are respectively 1329K, 1344K, 1374K, and 1374K. The difference value of the four reactions is 470K, 467K, 446K, and 459K.
4. Conclusion

Thermodynamic calculation of calcium metal prepared by vacuum aluminothermic reduction method can be concluded as follows:

1. The theoretical initial reaction temperature of the four reactions is very high under normal pressure. The lowest temperature is the reaction to generate 3CaO·Al₂O₃, but the reaction still needs to exceed 2421K.

2. The results of the two calculation methods is very different. These are 222K, 78K, 151K, and 85K.

3. At 10Pa, Theoretical initial reaction temperature of the four reactions are 859K, 872K, 928K, and 878K.

4. If the calculation result of the high-temperature region is substituted for the calculation result of the whole temperature interval, the theoretical initial reaction temperature of the four reactions are respectively 1329K, 1344K, 1374K and 1374K at 10Pa. The difference value of each reaction is 470K, 472K, 446K, and 459K.

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