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Application of Graham Scan Algorithm in Binary Phase Diagram Calculation

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Graham scan, a computational geometric algorithm for finding a two-dimensional convex hull, is introduced to calculate binary phase diagrams. This algorithm is modified and applied to find the convex hull of discrete points in the space of Gibbs energy vs mol fraction. The modified Graham scan algorithm has a very low computational cost, which improves efficiency in binary phase diagram calculation.

Keywords binary system, computational studies, phase diagram, thermodynamic stability

1. Introduction

One decade ago, a strategy for phase diagram calculation was proposed by Chen et al.[1,2] to overcome the difficulty in finding the most stable phase equilibria. A continuing effort to solve the problem has led to the current phase diagram calculation software package Pandat.[3,4] A general strategy for multicomponent, multiphase phase diagram calculation in Pandat has been described in Ref 1. The general strategy certainly covers the binary systems. However, a special computational geometric algorithm for finding a convex hull, the Graham scan, is suitable for binary phase diagram calculations. This algorithm is not only very efficient for binary systems but is also an important algorithm for multicomponent phase diagram calculations. This study will first describe briefly the strategy for binary phase diagram calculations. It will then present the original Graham scan algorithm and apply it to find the convex hull of the discrete points in the space of Gibbs energy vs mol fraction at a constant temperature and pressure. The algorithm is modified to further improve the computational efficiency.

2. Brief Description of Binary Phase Diagram Calculation

The strategy to calculate a binary phase diagram at constant pressure has been described in detail.[2] With the assumption that the Gibbs energy function for each phase in a binary system is given, the critical calculation step is to find the stable phase equilibria at a constant temperature. Figure 1(a) shows a Gibbs energy (G) vs mol fraction (x) diagram for a hypothetical binary system with phases α, β, γ, and δ, where α and β are solution phases, and γ and δ are stoichiometric compounds. In Fig. 1(b), a lower envelope of the Gibbs energy curves is drawn using a thick, dark line, which represents the Gibbs energies for stable phase equilibria. Obtaining this envelope requires the information on the relative positions among the Gibbs energy curves. Because it is much easier to compare the relative positions of points than curves, each Gibbs energy curve for a solution phase is partitioned into n points along the compositional axis, as shown in Fig. 2(a) with $n = 11$. Figure 2(b) shows the lower part of the convex hull for these points. As long as the value of n is large enough, the lower part of the convex hull in Fig. 2(b) is a very good approximation of the envelope of the Gibbs energy curves in Fig. 1(b).

Chen et al.[2] did not explicitly state how to calculate the lower part of the convex hull. An algorithm designed directly from Eq 6 in Ref 2 compares all of the points to the tangent line formed between two points. If none of the points is below the tangent line, then the two points are in stable equilibrium. The computational cost of this algorithm is $O(n^2)$, where n is the number of divisions into which the compositional axis is partitioned and the O notation represents an upper bound on the computational cost within a constant factor.[5]

Because the points in stable equilibria form a lower convex hull, finding these points is equivalent to searching for a convex hull of this set of points. For a convex hull of a set of points in two-dimensional space, there are some faster algorithms than $O(n^2)$. The most elegant one is the Graham scan algorithm.[6–8]

3. Two-Dimensional Convex Hull Algorithm: The Graham Scan

When at Bell Laboratories, Graham[6] developed a fast algorithm for locating a two-dimensional convex hull. This algorithm is now called the Graham scan algorithm.[7–9] The Graham scan algorithm also marks the beginning of the computational geometry. Before his algorithm, the previous one used at Bell Laboratories had the computational cost

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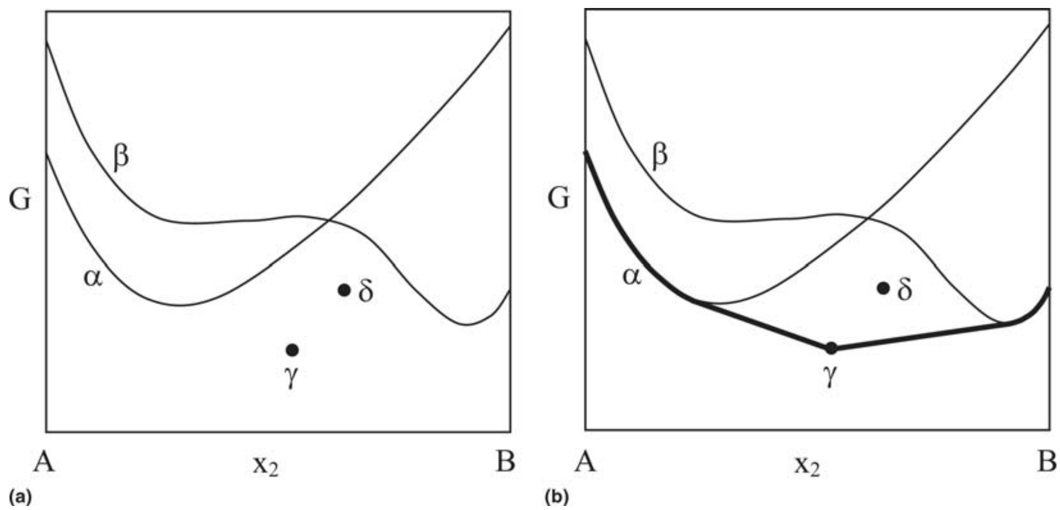

Fig. 1 (a) Gibbs energy vs molar fraction diagram at constant pressure and temperature. (b) The stable equilibrium states are expressed as the lower envelope (black curve) of the Gibbs energy curves of phases.

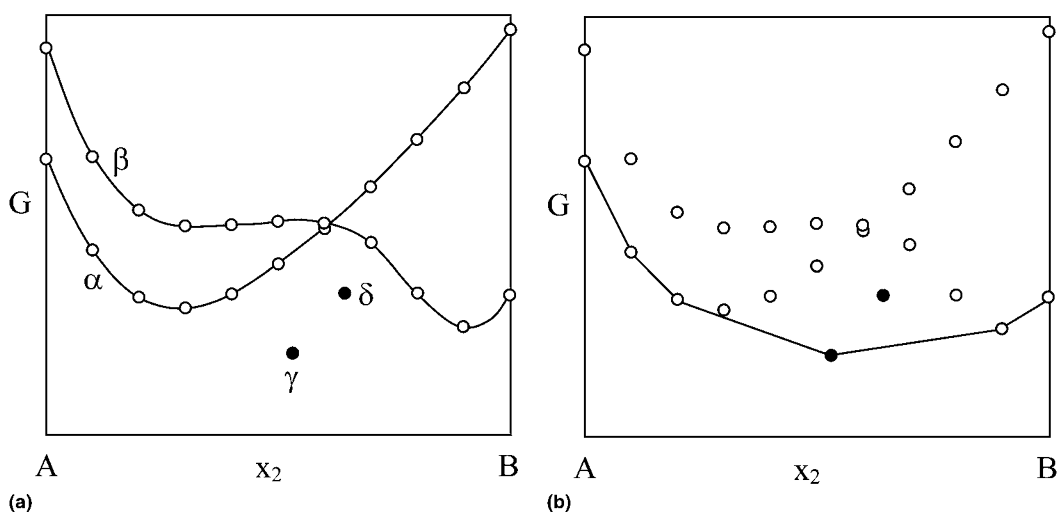

Fig. 2 (a) α and β are partitioned into a series of hypothetical stoichiometric phases. (b) The lower part of the convex hull for the stoichiometric points

of $O(n^2)$. When n increases, the cost increases on the order of n^2. However, the Graham scan algorithm costs only $O(n\log n)$.

Because only the lower part of the convex hull is of interest in calculating the stable phase equilibria, many points in Fig. 2(b) can be excluded before applying the convex hull algorithm. At any given composition, only the point with the lowest Gibbs energy could be the most stable. In other words, only the lowest point among the points with the same composition is considered in finding the convex hull. These points are shown in Fig. 3(a).

Following is an explanation of how the Graham scan algorithm finds the convex hull for the set of points in Fig. 3(a). The first step is to find an extreme point in this set. The point at the pure component A, point 1 in Fig. 3(b), is such an extreme point. The second step is to connect this extreme point with other points and construct line segments, as is shown in Fig. 3(b). These line segments are then sorted by the polar angles with respect to the selected extreme point 1. If there is a tie on the polar angle during sorting, then the closer the point is to the extreme point, the smaller the polar angle will be. If using only the numbers on the line segments to represent the line segments, the line segments in Fig. 3(b) are sorted in the order of 2, 3, 4, 7, 5, 6, 9, 12, 11, 13, 10, and 8. Points 6 and 9 have the same polar angle. Because point 6 is closer to point 1 than point 9, point 6 is put before point 9 in the sorted list. The third step is finding the hull. This step relies on the fact that every vertex on a convex hull represents a left turn in the counterclockwise traversal of the convex hull boundary and that the line segment with the smallest polar angle must be on the convex hull. The process was started at the first line segment $1 \rightarrow 2$, which is on the convex hull. Then examine the next point (point 3). Because the angle formed from $1 \rightarrow 2 \rightarrow 3$ is a left turn, 3 is kept in the vertex list. Next examine point 4.

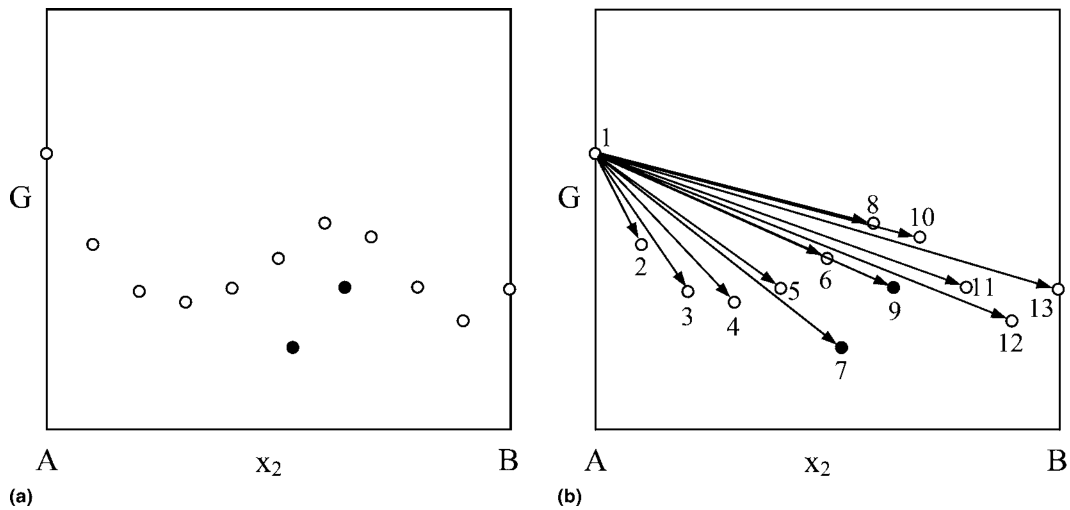

Fig. 3 Graham scan algorithm. (a) The points are considered for the lower part of the convex hull. (b) The lower part of the convex hull for the stoichiometric points

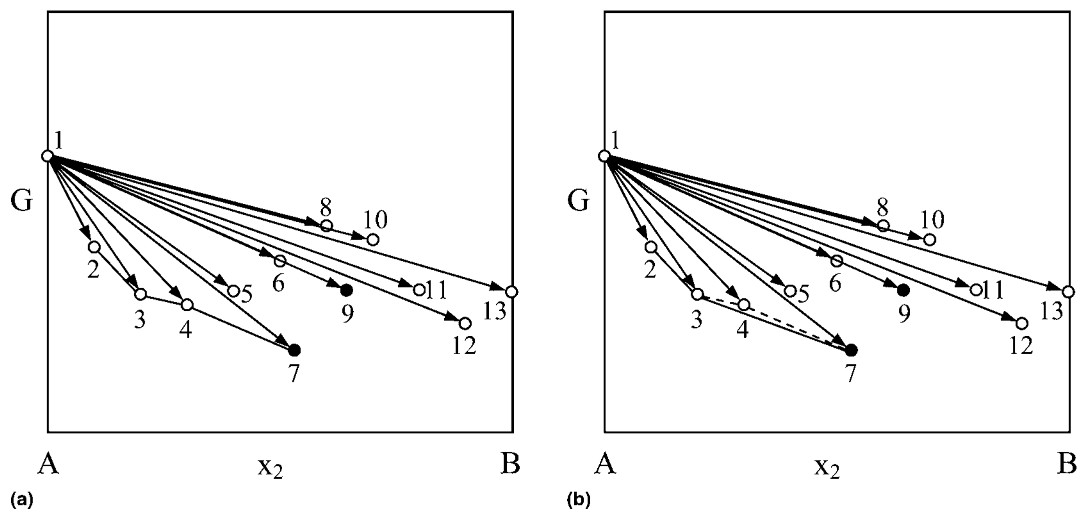

Fig. 4 Finding the lower hull in the Graham scan algorithm. (a) Angle $3 \rightarrow 4 \rightarrow 7$ is a non-left turn. (b) Point 4 is dropped, and the angle $2 \rightarrow 3 \rightarrow 7$ is a left turn.

It is a left turn for the angle formed from $2 \rightarrow 3 \rightarrow 4$. This point is kept in the vertex list. However, the next point 7 forms a non-left turn for the angle $3 \rightarrow 4 \rightarrow 7$ (Fig. 4a). Point 4 is dropped from the convex hull vertex list, and the angle $2 \rightarrow 3 \rightarrow 7$ forms a left turn, as seen in Fig. 4(b). Repeat this procedure until the right-most extreme point (point 13) is reached. Because point 13 is the right-most point, it must be one of the vertex points on the convex hull. The final lower convex hull vertex list is $1 \rightarrow 2 \rightarrow 3 \rightarrow 7 \rightarrow 12 \rightarrow 13$ (see Fig. 2b for the convex hull vertices). The upper convex hull is not of interest in the stable phase equilibrium calculation. Therefore, it is unnecessary to calculate the full convex hull.

The most expensive step in the above Graham scan algorithm is the sorting step, which costs $O(n\log n)$, where n is the total number of points considered. Then, the overall computational cost of Graham scan algorithm is $O(n\log n)$.

4. The Modified Graham Scan Algorithm

The Graham scan algorithm is designed for finding a general convex hull. The convex hull of the Gibbs energy curve of stable phase equilibria is a special type of hull. First, the points are already sorted along the compositional axis. Second, only the lower part of the hull is required. This specialty leads to the modification of the Graham scan.

In Fig. 5(a) points are already sorted in the order of 1 through 13 by the composition. Start from the line segment $1 \rightarrow 2$ and keep adding points one by one from points 3 through 6. Each of these added points forms a left turn with two previous points. However, the next point (point 7) forms a non-left turn with points 6 and 5. Point 6 is dropped. Examine the segment $4 \rightarrow 5 \rightarrow 7$. It is still a non-left turn, and point 5 is dropped. For the same reason, point 4 is

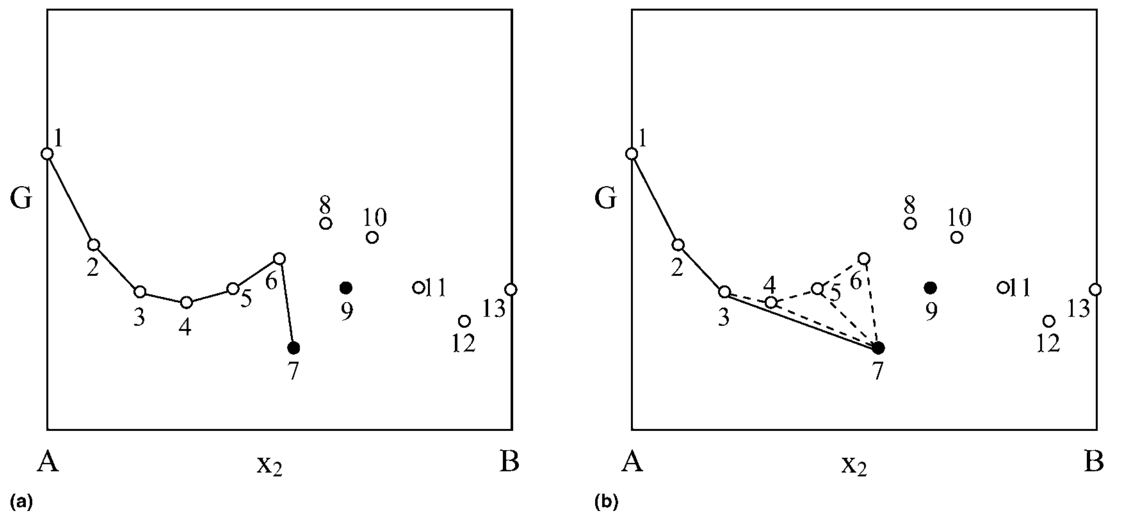

Fig. 5 Modified Graham scan algorithm. (a) Angle 5 → 6 → 7 is a non-left turn. (b) Drop points 6, 5, and 4 until the angle 2 → 3 → 7 forms a left turn

dropped. Finally, segment 2 → 3 → 7 forms a left turn, as shown in Fig. 5(b). This procedure continues until the last point (point 13) is reached. The final lower convex hull vertex list is 1 → 2 → 3 → 7 → 12 → 13, which is the same as that resulting from the original Graham scan algorithm, although the procedures for obtaining these lists are different.

Because the points are already sorted, the sorting step in the original Graham scan could be eliminated. This step is the only expensive step, with a cost of $O(n\log n)$, and any other step costs no more than $O(n)$. Thus, the overall cost in this modified version of the Graham scan has a computational cost of only $O(n)$.

5. Calculation of Binary Phase Diagram

As long as there is the efficient modified Graham scan algorithm for finding the lower part of the convex hull of a set of discrete Gibbs energy points, it may follow the procedures described by Chen et al.[2] for calculating binary temperature composition phase diagrams. At each temperature, the accurate phase equilibrium boundaries are solved numerically with the local equilibrium condition (i.e., equal chemical potential conditions) and the initial values from the results of the convex hull. Boundaries at a series of temperatures form a full binary temperature-composition phase diagram.

As an example, the calculated binary phase diagram of Fe-Cr is shown in Fig. 6. The body-centered cubic (bcc) phase in this system exhibits a miscibility gap. This presents no difficulty for the modified Graham scan algorithm in finding the most stable phase equilibria.

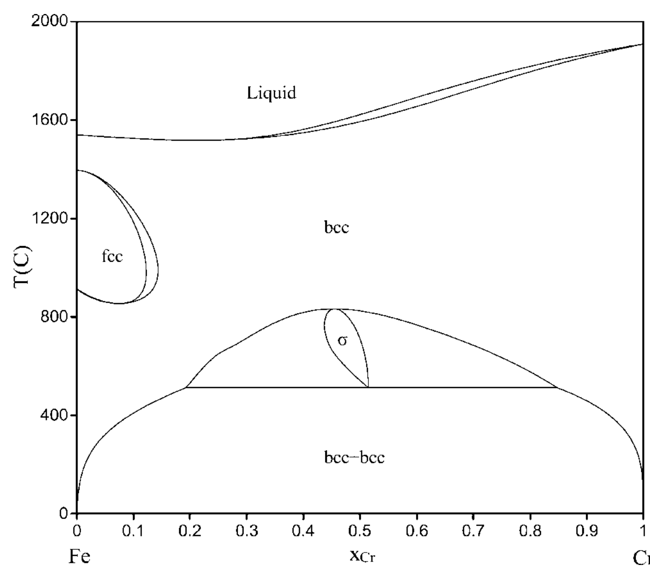

Fig. 6 Calculated binary phase diagram of Fe-Cr

6. Discussion

Tests have shown that it is enough to take n, the number of partitions of the compositional axis, to be 100 for finding stable phase equilibria. The authors did not pay attention to the computational cost of partitioning the Gibbs energies of a solution phase. If the cost of calculating the Gibbs energy of each point is high, the overall computational efficiency should be reevaluated.

Although the modified Graham scan finds the lower convex hull for the discrete Gibbs energy points, it does not find the full convex hull. To find the upper part of the hull, another scan with the right-turn criterion is required. The total computational cost is still $O(n)$.

In principle, convex hull algorithms can be applied in three-dimensional space[9] to a ternary isothermal section at constant pressure. However, three-dimensional convex hull algorithms are more complicated than two-dimensional ones. Convex hull algorithms in high dimensional space are also available,[9] but few are well-programmed. It is possible but difficult to apply those convex hull algorithms directly to multicomponent phase diagram calculation. The computational cost of finding the convex hull also increases with the number of dimensions.[9]

7. Summary

At constant pressure and temperature, Gibbs energies of stable phase equilibria form a lower part of a convex hull. Partitioning the continuous Gibbs energy curves of solution phases into discrete hypothetical stoichiometric phases enables us to use efficient convex hull algorithms on discrete points to find the convex hull of Gibbs energy points, including both the hypothetical stoichiometric phases and the stoichiometric phases from the system.

The Graham scan algorithm[6] was invented to find the convex hull for any set of two-dimensional points. This algorithm has a computational cost of $O(n\log n)$. Its most computationally expensive step is sorting the polar angles of the points relative to the chosen extreme point. Each of the other steps costs no more than $O(n)$. In searching for the convex hull of the discrete Gibbs energy points, the Graham scan is modified to take advantage of the special arrangement of the Gibbs energy points. Because Gibbs energy points are already stored in order of composition, the sorting step in the Graham scan could be eliminated, and the computational cost in searching for the lower part of the convex hull of Gibbs energy points is improved to be only $O(n)$.

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