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A new method for the derivation of the closed nets in the phase diagram space of multisystems. I. The absent phase substitution method

J. HU[1,2], H. YIN[2] AND Z. DUAN[1,3]
[1]The Key Laboratory of Mineral Resources, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China
[2]College of Material and Biological Engineering, Chengdu University of Technology, Chengdu 610059, China
[3]Department of Chemistry, 0340, University of California, San Diego, La Jolla, CA 92129, USA (duanzhenhao@yahoo.com)

ABSTRACT A new convenient combinatorial method is developed here to derive the invariant points in multisystem closed nets – the absent phase substitution (APS) method. It substantially simplifies the derivation of the closed nets in multisystems with many components and phases. For the multisystems whose total phase number (N_{PS}) ≤ twice the number of the absent phases (m) in an invariant assemblage, the method can yield regular closed nets with or without globally absent phases; for other multisystems, the method can yield the regular closed nets with globally absent phases. As examples, the APS method was used to predict: (1) the regular closed nets of unary to quinary $n + 4$-phase multisystems, unary 6-phase multisystem and ternary 8-phase multisystem; (2) the basic properties of the regular closed nets of the quaternary and quinary multisystems with $n + 4$ and $n + 5$ phases. Two multisystems were chosen to demonstrate how to select a realistic closed net from the numerous possible closed nets of a complex multisystem, and how to derive a realistic partially closed-net, closed-net-diagram and the related realistic straight-line-net-diagram. Comparisons of our APS method for the derivation of complicated closed nets with other methods indicate that this method is much simpler and more efficient.

Key words: closed net; invariant point; multisystem; phase diagram; the absent phase substitution method.

INTRODUCTION

The graphical representation (or geometrical analysis) of multi-phase equilibria initiated by Shreinemakers (1915–1925) can serve as a powerful theoretical tool in many scientific fields, such as physics, chemistry, chemical engineering, geology, etc. The method was developed mainly for determining topology in pressure–temperature phase diagrams of a given single invariant system (Zen, 1966a,b). In the past half century, attention has turned to systems consisting of two or more invariant assemblages (or invariant systems), which were called 'multisystems' by Korzhinsky (1957) and Korzhinskii (1959).

In a multisystem, the total number of the possible phases exceeds the phase number of an invariant assemblage (the maximum allowed by the Gibbs phase rule). On a phase diagram of a multisystem, the univariant curves intersect each other at the same invariant point to form a bundle, and different bundles constitute a complicated net through the connection of univariant curves. If every univariant curve in a net terminates at two invariant points (namely doubly terminating), the net is a completely closed net (Zen, 1966a, p. 403). A closed net has such essential features: there is at least one metastable invariant point in the net (Zharikov, 1961), and the stable part of any univariant curve lies between two adjacent stable invariant points and includes the two points (Guo, 1980a, 1981b). A real phase diagram of a multisystem always has some univariant curves terminating at only one stable invariant point, so it is never entirely closed, but partially or completely open.

Although closed nets are not real phase diagrams, they include all the potential topology of real phase diagrams. They serve as topological generating functions, from which all the potential forms of real phase diagrams can be derived (Guo, 1980c, 1985; Guo & Wang, 1988; Cheng & Guo, 1989; Stout & Guo, 1994).

In past decades, many contributions have been made to the related study of closed nets of multisystems, e.g. Day (1972, 1976, 1978), Braun & Stout (1975), Barron & Barron (1977), Burt (1978), Chesworth (1980), Guo (1979, 1980a,b,c, 1981a,b, 1984, 1985), Cai (1981, 1982), Cheng (1983, 1986), Cheng & Guo (1989), Korzhinskii (1959); Kujava *et al*. (1965), Kujava & Eugster (1966), Zen (1966a, 1967, 1974), Guo & Jin (1980), Mohr & Stout (1980), Wang (1980), Guo & Cai (1982), Guo & Wang (1982), Roseboom & Zen (1982), Vielzeuf & Boivin (1984), Stout (1985, 1990), Usdansky (1987, 1989), Guo & Cheng (1989), Tan (1990), Stout & Guo (1994), Hu (1998); Kletetschka & Stout (1999), Hu *et al*. (2000), Guy & Pla (2002), Zharikov (1961), Zen & Roseboom (1972), etc.

Zen (1966a) proposed the $n + 3$-phase closed net theory and derived closed-net-diagrams and straight-line-net-diagrams of unary and binary $n + 3$-phase multisystems using the so-called 'representation polyhedron' approach. Zen & Roseboom (1972) extended the same treatment to ternary $n + 3$-phase multisystems. By making a new divariant field to extend the system, Roseboom & Zen (1982) derived the representation polyhedra of the unary multisystems with five to seven phases. However, this technique cannot be applied to multi-component systems. In view of that, Roseboom & Zen (1982) proposed the approach of 'overlapping stability fields', and used it to derive closed-net-diagrams and representation polyhedra of the binary multisystems of five or six phases.

Guo (1980a) initiated a study of the closed nets of $n + 4$-phase multisystems (Roseboom & Zen, 1982). Guo (1980a) put forward a fundamental theorem on univariant curves, which was re-stated by Guo (1984): 'The stable portion, if any, of a univariant curve can only be a segment between two adjacent stable invariant points, in spite of the number of the invariant points with which this univariant curve is associated'. Here, all the univariant curves, either compositionally degenerate or not, are uniquely defined by the phase assemblages derived from the combinatorial rules. Based on this theorem, Guo (1980a) proposed a method to derive closed nets. According to this method, a closed net can be obtained by eliminating all supposed metastable invariant points on each univariant curve, leaving two stable invariant points on each curve. In addition, Guo & Wang (1982) put forward a combination principle for closed nets. It was proved by Cai (1982), and re-stated by Guo (1984) that any closed net of $n + k$ ($k > 3$)-phase multisystem must be a combination of two or more distinct $n + 3$ order submultisystem closed nets belonging to the given $n + k$-phase multisystem, if it is not one of submultisystem. This principle suggests a method for the construction of closed nets: all the $n + k(k > 3)$-phase closed nets can be derived from $n + 3$-phase closed nets in theory. This is the so-called combination method (Guo, 1980b, 1984). The methods above were successfully used to derive the closed nets, closed-net-diagrams, straight-line-net-diagrams, the basic forms (or concrete configurations) of unary, binary and ternary multisystems (Guo, 1980a,b,c, 1981a, 1984, 1985).

In general, none of the theories or methods in the literature is satisfactory for studying the closed nets of the complex multisystems of many components and phases. For example, the approach of overlapping stability fields can only apply to binary systems, but not to other multisystems (Guo & Cai, 1982; Guo, 1984). The representation polyhedron approach is also impractical for multisystems of many components and phases because of the great difficulty in the plotting, visualisation and theoretical analysis of the representation polyhedra. The methods of Guo (1980a), Guo & Wang (1982) also have some limitations: (i) There is no way to predict the metastable invariant points; (ii) For a complex multisystem, it is very subtle and complex to list and exclude the numerous univariant curves and invariant points; (iii) Although the closed nets of the $n + k(k > 3)$-phase multisystems can be derived with the combination method in theory, it will be very complicated to apply this method to the multisystems of much more than $n + 3$ phases.

Because of the various problems in the existing methods above, we developed a convenient combinatorial method for direct derivation of closed nets, the absent phase substitution (APS) method, which greatly simplifies the derivation of the closed nets with many components and phases. This report begins with a new general nomenclature for various kinds of multisystems, followed by a presentation of the main steps, with examples, validation, applicable range and advantages of the APS method, as well as application of the APS method to the derivation of some complicated closed nets and closed-net diagrams.

CLASSIFICATION OF MULTISYSTEMS

The Gibbs phase rule is expressed as

$$F = C - P + 2 - R, \qquad (1)$$

where C, P and R are the numbers of inert independent components, phases and the restrictions on the intensive variables, respectively. In most cases, '2' refers to temperature and pressure. In some cases, there are additional intensive variables influencing the thermodynamic properties of the system, such as the chemical potentials of perfectly mobile components in an open system, electric or magnetic field, and interfacial tension (potential) etc. For instance, the chemical potentials of mobile components such as H_2O, CO_2, Na_2O, K_2O, can be regarded as external thermodynamic conditions. Under these conditions, the phase rule should be extended as

$$F = C - P + Q - R(Q \geq 2). \qquad (2)$$

The so-called $n + k(k > 2)$-phase multisystems etc. (where n is the component number) usually refer to those where temperature and pressure are variables.

According to the Gibbs phase rule 1 or 2, the phase number of an invariant assemblage in an n-component system, N_{PI} is not always $n + 2$ (the subscripts 'P' and 'I' stand for 'Phase' and 'Invariant assemblage', respectively). For example, in the salt-water system at constant temperature and pressure ($R = 2$), the N_{PI} equals n; if only temperature or pressure is constant ($R = 1$), the N_{PI} will be $n + 1$. That is to say, the simplest multisystems are not always the $n + 3$-phase systems, and an $n + 3$-phase system is not always a multisystem. Apparently, the nomenclature of $n + k$-phase multisystems cannot summarize the numerous possible relations between the total phase number and the component number of a multisystem.

Considering this fact, we propose a new general and systematic nomenclature for the various multisystems on the basis of the following expression (Hu, 1998; Yin *et al*., 2002):

$$N_{PS} - N_{PI} = m > 0, \quad (3)$$

where N_{PS} is the total number of the phases in an arbitrary multisystem (the subscript 'S' stands for 'System'). It should be noted that, in many multisystems, all invariant assemblages have one or more common phases in equilibrium with the other phases in every invariant assemblage. In order to facilitate the study of the phase relations of these systems, these common phases should be excluded from the system through a proper projection. Thus, they should not be included in the system after projection, and so contribute nothing to N_{PS} and N_{PI} (see Thompson, 1957; Albee, 1965; Harvie *et al.*, 1982, 1984). The same is below.

According to Eq. (3), if N_{PS}−N_{PI}=m, the multisystem can be defined as an m-level (or m-grade) multisystem. For convenience, the closed nets of an m-level multisystem are also called m-level closed nets. For the $n + k$-phase multisystems, $N_{PS}=n+k$, $N_{PI}=n+2$, $m=k-2$. Because of the simplicity, 1-level multisystems can be called simple, elementary or primary multisystems, while the other multisystems, such as 2-, 3-, and 4-level multisystem etc., can be simply called complex or high-level multisystems.

NEW METHOD FOR THE DERIVATION OF CLOSED NETS – *ABSENT PHASE SUBSTITUTION METHOD*

The absent phase substitution method

For an m-level, N_{PS}-phase multisystem, an invariant assemblage has $N_{PI}(=N_{PS} - m)$ coexisting phases and m absent phases. According to Shreinemakers' notation (Zen, 1966a), each invariant assemblage or point can be identified by enclosing its m absent phases within the brackets '[ ]', and each univariant assemblage or curve, by enclosing its $(m + 1)$ absent phases within the parentheses '( )'.

For the derivation of a closed net, all the invariant points in the net need to be determined first, and then all the univariant curves arranged between the known invariant points. The arrangement of univariant curves can be done by using the phase compositions and Schreinemakers' rules or so-called 'univariant scheme'(Zen, 1966b, p. 13), and many petrologists and geochemists are familiar with the technique for this step (Zen, 1966b; Barron & Barron, 1977; Linde & Andrew, 1982; Usdansky, 1983). Thus, this study is focused on the method for the determination of invariant points, not for the net topology.

Take a unary 4-phase (1-level) multisystem. It has four possible invariant points, [1], [2], [3] and [4], all of which are in the unique closed net. For convenience, '{1/2/3/4}' is used for the set of the four points and the closed net. To obtain an invariant assemblage label, one phase label is taken in the net label {1/2/3/4} and placed in '[ ]'. In this procedure, all the phase labels in {1/2/3/4} are legal candidates. That is, the four phase labels are optional for this purpose. So the '/' here means 'optional'.

According to the combination principle (Guo & Wang, 1982; Guo, 1984), to obtain the closed nets of a high-level multisystem, it is possible in principle to derive them from the combination of the closed nets of its 1-level subsystem. Take a unary 5-phase (2-level) multisystem as an example. For any of its 1-level closed nets, there is a phase absent in the whole net (Guo, 1980a), such as {1,2/3/4/5} and {2,1/3/4/5}. If these two nets are used as the combining elements, [1, 2] will be the common invariant point of the two nets, and should at first be omitted from the two nets (Guo & Wang, 1982). After eliminating [1, 2], two partially closed nets are obtained: {1,3/4/5} and {2,3/4/5}, which are two parts of a (completely) closed net. Apparently, 1 and 2 occupy the same position in the two partially closed net labels, so they are the optional phases (candidates) of the same position. In view of this fact, {1,3/4/5} and {2,3/4/5} can be incorporated into {1/2,3/4/5}. This is a closed net label of the unary 5-phase system. Through this label, one can easily write out all the invariant points in the corresponding closed net: [1, 3], [1, 4], [1, 5], [2, 3], [2, 4] and [2, 5].

In this way, other closed net labels of the unary 5-phase system can be derived, too, but it will be more complex to apply this method to high-level multisystems. Through the analysis of the essential features of closed nets and the closed net labels derived with the method above, a more convenient method is found that can do the same work. The procedures follow:

(i) Divide all the N_{PS} phases into m groups, any group having at least one phase. If a group has more than one phase, the adjacent absent phases are separated by '/' (slash) in an arbitrary sequence. However, different grouping ways mean different closed nets (or different sets of invariant assemblages or points).

(ii) Put the m groups of phases in the set symbol '{…}' in an arbitrary sequence and separate different groups with commas. The result is a closed net label. The positions that the m groups of absent phases occupy are called absent phase positions.

In a closed net label, if the phase number in group j (namely on the absent phase position j, where j = 1,2, m) is N_{Pj} the net can be defined as (N_{P1}-N_{P2}-…-N_{Pj}-…-N_{Pm}) type. Apparently, the types of closed nets vary with the change in the match of these N_{Pj}'s.

To get an invariant assemblage or point, it is necessary to choose one absent phase label in each group, and place them into '[ ]'. Since each group has more than one candidate phase, there are usually many possible options to derive an invariant assemblage. Finishing all the different options results in a set of invariant assemblages or points, which determines a closed net. Following the steps above, one can easily derive a closed net. This procedure in itself is an operation of repeated substitution of an absent phase label in the current invariant point label. Generally, for a given type of closed net, all the possible members can be obtained by starting with an arbitrary closed net and then repeating the substitution of the absent phases in a current known closed net. This approach is called the 'absent phase substitution' (APS) method.

It is necessary to note that any pair of absent phase labels in the same group (on the same position) cannot appear simultaneously in one invariant assemblage label, but they can appear at the same position in different invariant assemblage labels.

Examples

The key point of the APS method is essentially to find all the combinations of the N_{PS} phase labels in m groups (or on m positions) for an m-level multisystem. With the APS method, any (N_{P1}-N_{P2}-…-N_{Pj}-…-N_{Pm}) type of closed nets can be very easily derived. Taking a binary 7-phase (3-level) multisystem as an example. Following the method above, there should be three absent phase positions in the set symbol '{ }'. So we can divide the seven phases into three groups, and separate the different absent phases in any group with '/', e. g. group 1: 1/6; group 2: 2/3; group 3: 4/5/7.

Finally, let each group occupy a position in '{}', respectively. The resulting label of the closed net is '{1/6,2/3,4/5/7}', where the group positions and the absent phases of any group in the net label can be arranged in arbitrary sequence. However, if the three groups are group 1: 1/2, group 2: 3/6, group 3: 4/5/7, the resulting closed net will be {1/2,3/6,4/5/7}, which is different from {1/6,2/3,4/5/7}.

At this time, it is easy to derive all the invariant assemblages or points in a derived closed net. Taking {1/6,2/3,4/5/7} as an example, if one phase label is chosen from each group, and placed in '[ ]', an invariant assemblage or point such as '[1, 2, 4]' is obtained. The remaining invariant assemblages or points in the closed net can be obtained in the same way, see Table 1. In this example, phase 1 and 6 (in group 1) are at the same position, so they cannot appear in one invariant assemblage at the same time, but they can appear at the same position in the labels of different invariant assemblages. Similar conclusions apply to the phases in the other groups.

More examples of the APS method are listed in Table 2, and the results are completely equivalent to those of Guo (1980a, 1985), Roseboom & Zen (1982), but our method is much simpler.

Analysis of the results

For a (N_{P1}-N_{P2}-…-N_{Pj}-…-N_{Pm}) type of closed net, the number of invariant points, N_{IP} and the number of univariant curves, N_{UC} can be calculated as follows:

$$N_{IP} = N_{P1} \times N_{P2} \times \cdots \times N_{Pj} \times \cdots \times N_{Pm} \times \left(\sum_j N_{Pj} = N_{PS} \right), \tag{4}$$

$$N_{UC} = \frac{N_{IP} \times N_{UC}^0}{2}, \tag{5}$$

where N_{UC}^0 is the number of the univariant curves about an invariant point. Note that N_{PI} and N_{IP} have different definitions.

In a closed net label, there may be a set of positions occupied by the same number of absent phases, e.g. the first and second positions in {1/6,2/3,4/5/7}. These positions are in fact equivalent. If there are q different sets of equivalent positions in the label of an arbitrary closed net, the number of all the possible closed nets, N_{Net} can be predicted in the following way:

$$N_{Net} = \frac{\mathbf{C}_{N_{PS}}^{N_{P1}} \mathbf{C}_{N_{PS}-N_{P1}}^{N_{P2}} \mathbf{C}_{N_{PS}-N_{P1}-N_{P2}}^{N_{P3}} \cdots \mathbf{C}_{N_{Pm}}^{N_{Pm}}}{\mathbf{P}_{N_{Set1}}^{N_{Set1}} \mathbf{P}_{N_{Set2}}^{N_{Set2}} \cdots \mathbf{P}_{N_{Setq}}^{N_{Setq}}}, \tag{6}$$

where N_{setk} is the number of the k^{th} set of equivalent positions, $\mathbf{C}_j^i$ and $\mathbf{P}_j^i$ are the numbers of the combinations and permutations of taking i elements from the set of j elements, respectively. For instance, {1/6,2/3,4/5/7} and {1/2,3/6,4/5/7} are both (2-2-3) type of closed nets. Both of them have $2 \times 2 \times 3 (= 12)$ invariant points, and $(12 \times 4)/2 (= 24)$ univariant curves. In one of the two net labels, there is only one set of equivalent positions, so the number of this type of closed nets is $(\mathbf{C}_7^2 \mathbf{C}_5^2 \mathbf{C}_3^3)/\mathbf{P}_2^2 = 105$.

If there is only one absent phase in a group, that phase is globally absent, or absent in the whole net. In this case, the net is called *non-typical* (Guo, 1980a, 1984) or *degraded* closed net here. This kind of nets can serve as the basic elements in the construction of complex closed nets, so they are very important, too. If no group has only one absent phase, the closed net is *typical* (Guo, 1980a, 1984), or *non-degraded* here. Such

Table 1. The derivation of the invariant assemblages or points in the binary 7-phase closed net {1/6,2/3,4/5/7}.

Option number	The chosen absent phases			The derived invariant assemblage or point
	From group 1	From group 2	From group 3	
	1/6	2/3	4/5/7	
1	1	2	4	[1, 2, 4]
2	1	2	5	[1, 2, 5]
3	1	2	7	[1, 2, 7]
4	1	3	4	[1, 3, 4]
5	1	3	5	[1, 3, 5]
6	1	3	7	[1, 3, 7]
7	6	2	4	[2, 4, 6]
8	6	2	5	[2, 5, 6]
9	6	2	7	[2, 6, 7]
10	6	3	4	[3, 4, 6]
11	6	3	5	[6, 3, 5]
12	6	3	7	[3, 6, 7]

Table 2. The closed nets of unary, binary and ternary $n + 4$-phase systems and unary $n + 5$-phase system.

Multisystem	N_{IP}	N_{Net}	Closed nets
Unary 5-phase multisystem	$2 \times 3 = 6$	$C_5^2C_3^3 = 10$	{1/2, 3/4/5} {1/3, 2/4/5} {1/4, 2/3/5} {1/5, 2/3/4} {2/3, 1/4/5} {2/4, 1/3/5} {2/5, 1/3/4} {3/4, 1/2/5} {3/5, 1/2/4} {4/5, 1/2/3}
Binary 6-phase multisystem	$2 \times 4 = 8$	$C_6^2C_4^4 = 15$	{1/2, 3/4/5/6} {1/3, 2/4/5/6} {1/4, 2/3/5/6} {1/5, 2/3/4/6} {1/6, 2/3/4/5} {2/3, 1/4/5/6} {2/4, 1/3/5/6} {2/5, 1/3/4/6} {2/6, 1/3/4/5} {3/4, 1/2/5/6} {3/5, 1/2/4/6} {3/6, 1/2/4/5} {4/5, 1/2/3/6} {4/6, 1/2/3/5} {5/6, 1/2/3/4}
Binary 6-phase multisystem	$3 \times 3 = 9$	$C_6^3C_3^3/P_2^2 = 10$	{1/2/3, 4/5/6} {1/2/4, 3/5/6} {1/2/5, 3/4/6} {1/2/6, 3/4/5} {1/3/4, 2/5/6} {1/3/5, 2/4/6} {1/3/6, 2/4/5} {1/4/5, 2/3/6} {1/4/6, 2/3/5} {1/5/6, 2/3/4}
Ternary 7-phase multisystem	$2 \times 5 = 10$	$C_7^2C_5^5 = 21$	{1/2, 3/4/5/6/7} {1/3, 2/4/5/6/7} {1/4, 2/3/5/6/7} {1/5, 2/3/4/6/7} {1/6, 2/3/4/5/7} {1/7, 2/3/4/5/6} {2/3, 1/4/5/6/7} {2/4, 1/3/4/6/7} {2/5, 1/3/4/6/7} {2/6, 1/3/4/5/7} {2/7, 1/3/4/5/6} {3/4, 1/2/5/6/7} {3/5, 1/2/4/6/7} {3/6, 1/2/4/5/7} {3/7, 1/2/4/5/6} {4/5, 1/2/3/6/7} {4/7, 1/2/3/5/6} {5/6, 1/2/3/4/7} {5/7, 1/2/3/4/6} {6/7, 1/2/3/4/5} {6/7, 1/2/3/4/5}
Ternary 7-phase multisystem	$3 \times 4 = 12$	$C_7^3C_4^4 = 35$	{1/2/3, 4/5/6/7} {1/2/4, 3/5/6/7} {1/2/5, 3/4/6/7} {1/2/6, 3/4/5/7} {1/2/7, 3/4/5/6} {1/3/4, 2/5/6/7} {1/3/5, 2/4/6/7} {1/3/6, 2/4/5/7} {1/3/7, 2/4/5/6} {1/4/5, 2/3/6/7} {1/4/6, 2/3/5/7} {1/4/7, 2/3/5/6} {1/5/6, 2/3/4/7} {1/5/7, 2/3/4/6} {1/6/7, 2/3/4/5} {2/3/4, 1/5/6/7} {2/3/5, 1/4/6/7} {2/3/6, 1/4/5/7} {2/3/7, 1/4/5/6} {2/4/5, 1/3/6/7} {2/4/6, 1/3/5/7} {2/4/7, 1/3/5/6} {2/5/6, 1/3/4/7} {2/5/7, 1/3/5/6} {2/6/7, 1/3/4/5} {3/4/5, 1/2/6/7} {3/4/6, 1/2/5/7} {3/4/7, 1/2/5/6} {3/5/6, 1/2/4/7} {3/5/7, 1/2/4/6} {3/6/7, 1/2/4/5} {4/5/6, 1/2/3/7} {4/5/7, 1/2/3/6} {4/6/7, 1/2/3/5} {5/6/7, 1/2/3/4}
Unary 6-phase multisystem	$2 \times 2 \times 2 = 8$	$C_6^2C_4^2C_2^2/P_3^3 = 15$	{1/2, 3/4, 5/6} {1/2, 3/5, 4/6} {1/2, 3/6, 4/5} {1/3, 2/4, 5/6} {1/3, 2/5, 4/6} {1/3, 2/6, 4/5} {1/4, 2/3, 5/6} {1/4, 2/5, 3/6} {1/4, 2/6, 3/5} {1/5, 2/3, 4/6} {1/5, 2/4, 3/6} {1/5, 2/6, 3/4} {1/6, 2/3, 4/5} {1/6, 2/4, 3/5} {1/6, 2/5, 3/4}

N_{IP}, the total number of invariant points in a closed net; N_{Net}, the total number of possible closed nets.

nets have higher level and more complicated phase relations.

Comparison with previously reported methods

In order to demonstrate the capability and the efficiency of our method, it is compared with the most representative methods reported previously (Guo, 1980a; Roseboom & Zen, 1982) using some specific examples.

For instance, the derivation of the representation polyhedra and closed nets of binary 6-phase multisystem by Roseboom & Zen (1982) is much more complex than ours. Similar derivation of ternary 7-phase multisystems will be more difficult. If the method of Guo (1980a) is used to derive the closed nets in Table 2, some metastable invariant points and univariant curves must be known and excluded in advance (see Table 3). Since Guo (1980a) did not give an approach to this problem, the successful choice of the metastable invariant points and univariant curves usually has to rely on a formidable number of trials and errors. Additionally, if a (N_{P1}-N_{P2}-…-N_{Pj}-…-N_{Pm}) type of closed net ($N_{P1} \le N_{P2} \le \cdots \le N_{Pj} \cdots \le N_{Pm-1}$) is derived with the combination method (Guo, 1980b; Guo & Wang, 1982), it will need $N_{P1} \times N_{P2} \times \cdots \times N_{Pj} \cdots \times N_{Pm-1}$ combining elements and $N_{P1} \times N_{P2} \times \cdots \times N_{Pj} \cdots \times N_{Pm-1} - 1$ steps. This can be determined by analysing the closed net and its 1-level combining elements. For the combination method, for example, it will take $i \times j$ combining elements and $i \times j - 1$ steps to derive the $(i - j - k)$ type of closed net $(i \le j \le k)$. Comparatively speaking, our APS method is much simpler and more intuitive than those of Guo (1980a, 1985) and Guo & Wang (1982).

Validation of the method

Suppose net A is an *arbitrary* net of an *m*-level multisystem of N_{PS} phases derived (and labelled) with the APS method, [i, j, k, …, o, p] is an *arbitrary* invariant

Table 3. The derivation of the invariant assemblages or points in some closed nets.

System	N_{IP}	N_{UC}	N_{IP}	N_{UC}	$N_{IP}^* - N_{IP}$	$N_{UC}^* - N_{UC}$
Unary 5-phase system	$C_5^2 = 10$	$C_5^3 = 10$	$2 \times 3 = 6$	$6 \times 3/2 = 9$	4	1
Unary 6-phase system	$C_6^3 = 20$	$C_6^4 = 15$	$2 \times 2 \times 2 = 8$	$8 \times 3/2 = 12$	12	3
Binary 6-phase system	$C_6^2 = 15$	$C_6^3 = 20$	[a] $2 \times 4 = 8$	$8 \times 4/2 = 16$	7	4
			[b] $3 \times 3 = 9$	$9 \times 4/2 = 18$	6	2
Ternary 7-phase system	$C_7^2 = 21$	$C_7^3 = 35$	[c] $2 \times 5 = 10$	$10 \times 5/2 = 25$	11	10
			[d] $3 \times 4 = 12$	$12 \times 5/2 = 30$	9	5

N_{IP}^*, N_{UC}^*: The numbers of all the possible invariant points and univariant curves of the multisystem calculated from the combinatorial rule; $N_{IP}^* - N_{IP}, N_{UC}^* - N_{UC}$: The numbers of the supposed metasable invariant points and univariant curves of the multisystem to be determined and excluded, respectively.

[a] For 8-point closed net.
[b] For 9-point closed net.
[c] For 10-point closed net.
[d] For 12-point closed net.

point in net A, and (i, j, k, …, o, p, q) is an *arbitrary* univariant curve originating from that point, where 'q' can be any of the other $N_{PS} - m(=N_{PI})$ phase labels of the system. According to the APS method, 'q' must be on a specified position in the label of net A. Without loss of the generality, we can suppose 'q' and 'p' are on the same position in the label of net A. Then [i, j, k, …, o, q] must be another invariant point in net A. According to the combinatorial rules, there are totally $m + 1$ possible points on the curve (i, j, k, …, o, p, q). The labels of these points can be determined by selecting m labels from the $m + 1$ absent phase labels of the curve. These point labels can be divided into two groups: the first group consists of [i, j, k, …, o, p] and [i, j, k, …, o, q], where only one of 'p' and 'q' is included, and 'p' and 'q' are located at the same absent phase position. So these two points belong to net A. The second group consists of the other $m - 1$ point labels, where both 'p' and 'q' are included, and 'p' and 'q' are located at different absent phase positions. So the points in this group do not belong to net A, that is, they are the metastable invariant points that are excluded from net A by the APS method.

The result above means that, in an arbitrary net derived with the APS method, an arbitrary univariant curve originating from an arbitrary invariant point terminates at another invariant point in the net, no other point can stably exist on the curve. In brief, every univariant curve in the net is doubly terminating, which is in agreement with the fundamental theorem on univariant curves of Guo (1980a, 1981b). According to the definition of a closed net in the introduction or Zen (1966a, p. 403), the net must be completely closed. In other words, any net label derived with the APS method defines a closed net.

The reliability of APS method is also supported by the combination principle (Guo & Wang, 1982; Guo, 1984), because all the closed nets derived with the APS method can be derived from the combination of 1-level closed nets, as stated earlier. In addition, the general method of Guy & Pla (2002) may be a useful reference for finding the direct thermodynamic and mathematic foundation of the new method.

It needs to be stressed that the compositional degeneracy in a multisystem does not limit the validity of the APS method. In a compositionally degenerate multisystem, two or more univariant curves with different labels may represent the same degenerate reaction (whose phase number is less than the usual reaction). In these differently labelled univariant curves, each curve has two stable invariant points (end points) on it, and each of these points is shared by other univariant curves. As a result, there may be more than two stable invariant points existing on a degenerate curve. In this study, the univariant curves representing the degenerate reaction are treated as distinct ones, although they have the same participating phases. So the fundamental theorem on univariant curves of Guo (1980a, 1981b) is still correct, and the APS method is valid for both of the compositionally degenerate and non-degenerate multisystems.

Applicable range and advantages of the APS method

In a closed net label of an m-level multisystem, there are m positions for putting the absent phases. If the closed net is non-degraded (namely typical), there are at least two absent phases on any of the m positions, so the total number of the absent phases on the m positions cannot be less than $2m$. This means that if one wants to obtain non-degraded closed nets with the APS method, it must satisfy

$$N_{PS} \geqslant 2m. \quad (7)$$

For example, in the closed net label of unary 6-phase (3-level) multisystem, there are three absent phase positions. Putting the six phases on the three positions only yields one type of non-degraded closed net: (2-2-2) type, such as {1/2,3/4,5/6},{1/3,2/4,5/6},{1/6,2/3,4/5}, etc. Of course, when $N_{PS} \geqslant 2m$, the APS method can also produce degraded closed nets, such as the (1-1-4) and (1-2-3) types of closed nets of unary 6-phase multisystem.

On the other hand, if $N_{PS} < 2m$ there is at least one position at which there is only one absent phase. In these cases, the APS method can only offer the degraded closed nets. For example, in the closed net label of unary 8-phase (5-level) multisystem, there are five absent positions (Here, $8 < 2 \times 5$). Putting the eight phases on the five positions will lead to at least two positions with only one phase on each of them, e.g. {1/2,3/4,5/6,7,8}.

If Eq. (3) is substituted into Eq. (7) to eliminate N_{PS} it will result in an equivalent equation of Eq. (7):

$$N_{PI} \geqslant m. \quad (8)$$

So the upper level limit of the multisystem whose non-degraded closed nets can be derived with the APS method is

$$m = m_{max} = N_{PI}. \quad (9)$$

If Eq. (9) is substituted into Eq. (3) for m, then it can produce

$$N_{PS} = 2N_{PI} = 2m_{max}. \quad (10)$$

Eq. (10) means that if $N_{PS} \leqslant 2N_{PI}$ the APS method can give both degraded and non-degraded closed nets; otherwise, the APS method can only give degraded closed nets.

For any closed net derived with the APS method, the absent phase labels in any group can be put in an arbitrary sequence, that is, their positions are exchangeable. Of course, the positions of two arbitrary singly existing phase labels in the net label are exchangeable, if any. Besides, the positions with the same number of phase labels are equivalent to each other in the net label, so the set of phase labels on arbitrary two equivalent positions can be exchanged as a whole.

For the closed nets that cannot be derived with the APS method, each of them can be expressed as a combination of appropriate combining elements (namely 1-level or higher-level closed nets derived with the APS method). In these nets, however, two exchangeable phase labels in one combining element may be no longer exchangeable in another combining element, that is, their positions are not exchangeable in the whole closed net. This phenomenon remarkably reduces the pair number of exchangeable phase labels, and thus the phase labels that are exchangeable in the whole closed net are notably less than those in the elements, usually few or non-existent. Likewise, the equivalent positions in the whole net label are usually nonexistent or notably less than those in the relevant elements.

The exchangeability of the phase labels and the equivalence of the positions in the closed net labels reflect the regularity of the connection relationship between the invariant points. They are closely associated with the symmetry of the closed nets and their representation polyhedra. For this reason, the closed nets derived with the APS method are defined as regular closed nets, and those that cannot be derived with the APS method are irregular closed nets. For example, all the $n + 3$-phase and $n + 4$-phase closed nets are regular, see Table 2 or Guo (1980a), while the irregular closed nets can only exist in 3-level or higher-level multisystems, e.g. all the unary 7-phase closed nets and one type of unary 6-phase closed nets are irregular. Zen (1966a), Zen & Roseboom (1972), Roseboom & Zen (1982) and Guo (1980b, 1981a, 1984, 1985) gave some representation polyhedra of regular closed nets of unary to ternary multisystems. Roseboom & Zen (1982) and Guo (1984, 1985) gave some representation polyhedra of the unary irregular closed nets with six and seven phases.

In this study, the APS method is not only a method for the derivation of closed nets, but also a standard for the classification of closed nets. In the next paper of this series, we will show that the irregular closed nets of various multisystems can be obtained and notated through the combination of appropriate regular closed nets.

According to Eqs (9) and (10), with the increase in N_{PI} (and/or the components of the system), the ranges of the levels and total phase numbers of the multisystems that have non-degraded regular closed nets increase rapidly, as shown in Table 4.

APPLICATION

Because of the great difficulty in theory, few reports about closed nets of multisystems with more than three components can be found in the literature, e.g. Zen (1974), Barron & Barron (1977). Unlike other methods, applying the APS method to a multi-component, $n + k(k > 3)$-phase multisystem it does not lead to an apparent increase in complexity. In this study, the APS method is used to derive the closed nets of some more complicated multisystems.

Derivation of the complete systems of closed nets of complex multisystems

(1) Quaternary 8-phase ($n + 4$) multisystem. In this example, $N_{PS} = 8$, $m = 2$, $N_{PS} > 2m$. In terms of the APS method, there are two groups of absent phases in every closed net label. The eight phases should be divided into two groups, where the phase number in each group should not be fewer than two. There are no more than three ways to group the absent phases: (i) two phases are placed in one group, and the other six phases in the other; (ii) three phases in one group, and the other five phases in the other; (iii) there are four phases in each group. The regular closed nets obtained in these ways belong to three types: (2-6) type, (3-5) type and (4-4) type, where the (2-6) type has $C_8^2(= 28)$ nets; the (3-5) type, $C_8^3(= 56)$ nets; and the (4-4) type, $C_8^4/2(= 35)$ nets, see Table 5. If the three types of closed nets in Table 5 are derived with the combination method, it will need two, three and four combining elements and 1, 2 and 3 steps for one closed net, respectively. It will be much more difficult to derive the nets in Table 5 with the method of Guo (1980a). If the derivation of the above nets is done with the representation polyhedron approach of Zen (1966a); Zen & Roseboom (1972), the task will be very arduous.

(2) Quinary 9-phase ($n + 4$) multisystem. In this case, $N_{PS} = 9, m = 2, N_{PS} > 2m$. The nine phases should be divided into two groups, so the non-degraded regular closed nets belong to three types: (2-7) type, (3-6) type and (4-5) type. Here, only the complete system of the (2-7) type of closed nets is listed (Table 6).

(3) Ternary 8-phase ($n + 5$) multisystem. This system has three absent phase positions in its closed net labels. If only one position is occupied by single phase, the possible regular closed nets must belong to the (1-2-5) type and (1-3-4) type. Table 7 shows the regular closed nets where phase 1 is absent.

Table 4. The multisystems for which the absent phase substitution method can give non-degraded regular closed nets.

The N_{PI} of multisystems	3	4	5	6	7	8	9	10	11	…
The m range of multisystems	≤3	≤4	≤5	≤6	≤7	≤8	≤9	≤10	≤11	…
The N_{PS} range of multisystems	≤6	≤8	≤10	≤12	≤14	≤16	≤18	≤20	≤22	…

Table 5. The regular closed nets of quaternary 8-phase system.

The (2-6) type of regular closed nets $N_{IP} = 2 \times 6 = 12$ $N_{Net} = C_8^2 C_6^6 = 28$	{1/2, 3/4/5/6/7/8} {1/3, 2/4/5/6/7/8} {1/4, 2/3/5/6/7/8} {1/5, 2/3/4/6/7/8} {1/6, 2/3/4/5/7/8} {1/7, 2/3/4/5/6/8} {1/8, 2/3/4/5/6/7} {2/3, 1/4/5/6/7/8} {2/4, 1/3/5/6/7/8} {2/5, 1/3/4/6/7/8} {2/6, 1/3/4/5/7/8} {2/7, 1/3/4/5/6/8} {2/8, 1/3/4/5/6/7} {3/4, 1/2/5/6/7/8} {3/5, 1/2/4/6/7/8} {3/6, 1/2/4/5/7/8} {3/7, 1/2/4/5/6/8} {3/8, 1/2/4/5/6/7} {4/5, 1/2/3/6/7/8} {4/6, 1/2/3/5/7/8} {4/7, 1/2/3/5/6/8} {4/8, 1/2/3/5/6/7} {5/6, 1/2/3/4/7/8} {5/7, 1/2/3/4/6/8} {5/8, 1/2/3/4/6/7} {6/7, 1/2/3/4/5/8} {6/8, 1/2/3/4/5/7} {7/8, 1/2/3/4/5/6}
The (3-5) type of regular closed nets $N_{IP} = 3 \times 5 = 15$ $N_{Net} = C_8^3 C_5^3 = 56$	{1/2/3, 4/5/6/7/8} {1/2/4, 3/5/6/7/8} {1/2/5, 3/4/6/7/8} {1/2/6, 3/4/5/7/8} {1/2/7, 3/4/5/6/8} {1/2/8, 3/4/5/6/7} {1/3/4, 2/5/6/7/8} {1/3/5, 2/4/6/7/8} {1/3/6, 2/4/5/7/8} {1/3/7, 2/4/5/6/8} {1/3/8, 2/4/5/6/7} {1/4/5, 2/3/6/7/8} {1/4/6, 2/3/5/7/8} {1/4/7, 2/3/5/6/8} {1/4/8, 2/3/5/6/7} {1/5/6, 2/3/4/7/8} {1/5/7, 2/3/4/6/8} {1/5/8, 2/3/4/6/7} {1/6/7, 2/3/4/5/8} {1/6/8, 2/3/4/5/7} {1/7/8, 2/3/4/5/6} {2/3/4, 1/5/6/7/8} {2/3/5, 1/4/6/7/8} {2/3/6, 1/4/6/7/8} {2/3/7, 1/4/5/6/8} {2/3/8, 1/4/5/6/7} {2/4/5, 1/3/6/7/8} {2/4/6, 1/3/5/7/8} {2/4/7, 1/3/5/6/8} {2/4/8, 1/3/5/6/7} {2/5/6, 1/3/4/7/8} {2/5/7, 1/3/4/6/8} {2/5/8, 1/3/4/6/7} {2/6/7, 1/3/4/5/8} {2/6/8, 1/3/4/5/7} {2/7/8, 1/3/4/5/6} {3/4/5, 1/2/6/7/8} {3/4/6, 1/2/5/7/8} {3/4/7, 1/2/5/6/8} {3/4/8, 1/2/5/6/7} {3/5/6, 1/2/4/7/8} {3/5/7, 1/2/4/6/8} {3/5/8, 1/2/4/6/7} {3/6/7, 1/2/4/5/8} {3/6/8, 1/2/4/5/7} {3/7/8, 1/2/4/5/6} {4/5/6, 1/2/3/7/8} {4/5/7, 1/2/3/6/8} {4/5/8, 1/2/3/6/7} {4/6/7, 1/2/3/5/8} {4/6/8, 1/2/3/5/7} {4/7/8, 1/2/3/5/6} {5/6/7, 1/2/3/4/8} {5/6/8, 1/2/3/4/7} {5/7/8, 1/2/3/4/6} {6/7/8, 1/2/3/4/5}
The (4-4) type of regular closed nets $N_{IP} = 4 \times 4 = 16$ $N_{Net} = C_8^4 C_4^4 / P_2^2 = 35$	{1/2/3/4, 5/6/7/8} {1/2/3/5, 4/6/7/8} {1/2/3/6, 4/5/7/8} {1/2/3/7, 4/5/6/8} {1/2/3/8,4/5/6/7} {1/2/4/5, 3/6/7/8} {1/2/4/6, 3/5/7/8} {1/2/4/7, 3/5/6/8} {1/2/4/8, 3/5/6/7} {1/2/5/6, 3/4/7/8} {1/2/5/7, 3/4/6/8} {1/2/5/8, 3/4/6/7} {1/2/6/7, 3/4/5/8} {1/2/6/8, 3/4/5/7} {1/2/7/8, 3/4/5/6} {1/3/4/5, 2/6/7/8} {1/3/4/6, 2/5/7/8} {1/3/4/7, 2/5/6/8} {1/3/4/8, 2/5/6/7} {1/3/5/6, 2/4/7/8} {1/3/5/7, 2/4/6/8} {1/3/5/8, 2/4/6/7} {1/3/6/7, 2/4/5/8} {1/3/6/8, 2/4/5/7} {1/3/7/8, 2/4/5/6} {1/4/5/6, 2/3/7/8} {1/4/5/7, 2/3/6/8} {1/4/5/8, 2/3/6/7} {1/4/6/7, 2/3/5/8} {1/4/6/8, 2/3/5/7} {1/4/7/8, 2/3/5/6} {1/5/6/7, 2/3/4/8} {1/5/6/8, 2/3/4/7} {1/5/7/8, 2/3/4/6} {1/6/7/8, 2/3/4/5}

Table 6. The (2-7) type of closed nets of quinary 9-phase multisystem ($N_{IP} = 2 \times 7 = 14$, $N_{Net} = C_9^2 C_7^7 = 36$).

{1/2, 3/4/5/6/7/8/9}	{2/4, 1/3/5/6/7/8/9}	{3/7, 1/2/4/5/6/8/9}	{5/7, 1/2/3/4/6/8/9}
{1/3, 2/4/5/6/7/8/9}	{2/5, 1/3/4/6/7/8/9}	{3/8, 1/2/4/5/6/7/9}	{5/8, 1/2/3/4/6/7/9}
{1/4, 2/3/5/6/7/8/9}	{2/6, 1/3/4/5/7/8/9}	{3/9, 1/2/4/5/6/7/8}	{5/9, 1/2/3/4/6/7/8}
{1/5, 2/3/4/6/7/8/9}	{2/7, 1/3/4/5/6/8/9}	{4/5, 1/2/3/6/7/8/9}	{6/7, 1/2/3/4/5/8/9}
{1/6, 2/3/4/5/7/8/9}	{2/8, 1/3/4/5/6/7/9}	{4/6, 1/2/3/5/7/8/9}	{6/8, 1/2/3/4/5/7/9}
{1/7, 2/3/4/5/6/8/9}	{2/9, 1/3/4/5/6/7/8}	{4/7, 1/2/3/5/6/8/9}	{6/9, 1/2/3/4/5/7/8}
{1/8, 2/3/4/5/6/7/9}	{3/4, 1/2/5/6/7/8/9}	{4/8, 1/2/3/5/6/7/9}	{7/8, 1/2/3/4/5/6/9}
{1/9, 2/3/4/5/6/7/8}	{3/5, 1/2/4/6/7/8/9}	{4/9, 1/2/3/5/6/7/8}	{7/9, 1/2/3/4/5/6/8}
{2/3, 1/4/5/6/7/8/9}	{3/6, 1/2/4/5/7/8/9}	{5/6, 1/2/3/4/7/8/9}	{8/9, 1/2/3/4/5/6/7}

Table 7. The (1-2-5) and (1-3-4) types of closed nets of the ternary system of eight phases in which phase 1 is absent.

The (1-2-5) type of closed nets $N_{IP} = 1 \times 2 \times 5 = 10$ $N_{Net} = C_1^1 C_7^2\ C_5^5 = 21$	{1, 2/3, 4/5/6/7/8} {1, 2/4, 3/5/6/7/8} {1, 2/5, 3/4/6/7/8} {1, 2/6, 3/4/5/7/8} {1, 2/7, 3/4/5/6/8} {1, 2/8, 3/4/5/6/7} {1, 3/4, 2/5/6/7/8} {1, 3/5, 2/4/6/7/8} {1, 3/6, 2/4/5/7/8} {1, 3/7, 2/4/5/6/8} {1, 3/8, 2/4/5/6/7} {1, 4/5, 2/3/6/7/8} {1, 4/6, 2/3/5/7/8} {1, 4/7, 2/3/5/6/8} {1, 4/8, 2/3/5/6/7} {1, 5/6, 2/3/4/7/8} {1, 5/7, 2/3/4/6/8} {1, 5/8, 2/3/4/6/7} {1, 6/7, 2/3/4/5/8} {1, 6/8, 2/3/4/5/7} {1, 7/8, 2/3/4/5/6}
The (1-3-4) type of closed nets $N_{IP} = 1 \times 3 \times 4 = 12$ $N_{Net} = C_1^1 C_7^3\ C_4^4 = 35$	{1, 2/3/4, 5/6/7/8} {1, 2/3/5, 4/6/7/8} {1, 2/3/6, 4/5/7/8} {1, 2/3/7, 4/5/6/8} {1, 2/3/8, 4/5/6/7} {1, 2/4/5, 3/6/7/8} {1, 2/4/6, 3/5/7/8} {1, 2/4/7, 3/5/6/8} {1, 2/4/8, 3/5/6/7} {1, 2/5/6, 3/4/7/8} {1, 2/5/7, 3/4/6/8} {1, 2/5/8, 3/4/6/7} {1, 2/6/7, 3/4/5/8} {1, 2/6/8, 3/4/5/7} {1, 2/7/8, 3/4/5/6} {1, 3/4/5, 2/6/7/8} {1, 3/4/6, 2/5/7/8} {1, 3/4/7, 2/5/6/8} {1, 3/4/8, 2/5/6/7} {1, 3/5/6, 2/4/7/8} {1, 3/5/7, 2/4/6/8} {1, 3/5/8, 2/4/6/7} {1, 3/6/7, 2/4/5/8} {1, 3/6/8, 2/4/5/7} {1, 3/7/8, 2/4/5/6} {1, 4/5/6, 2/3/7/8} {1, 4/5/7, 2/3/6/8} {1, 4/5/8, 2/3/6/7} {1, 4/6/7, 2/3/5/8} {1, 4/6/8, 2/3/5/7} {1, 4/7/8, 2/3/5/6} {1, 5/6/7, 2/3/4/8} {1, 5/6/8, 2/3/4/7} {1, 5/7/8, 2/3/4/6} {1, 6/7/8, 2/3/4/5}

Prediction of some basic properties of the closed nets of the complex multisystems and their complete systems

For a complex multisystem, such as unary to quinary systems of $n + 4$ or $n + 5$ phases, all its closed nets and their related important information can be easily derived with the APS method. For example, the numbers of the invariant points and univariant curves can be directly calculated by Eqs (4) and (5). The total numbers of various regular closed nets can also be calculated with the permutation and combination approach, see Tables 8 and 9.

Selection of the realistic closed nets from numerous closed nets of a given complex multisystem and the derivation of the related partially closed nets

For a complex multisystem, there are numerous possible closed nets, which represent all the possible phase diagram topology of the system. With the constraints

Table 8. Some basic properties of the regular closed nets of unary to quinary system of $n + 4$ phases.

System	Type of closed nets	Total number of closed nets, N_{Net}	Number of the curves in a closed net, N_{UC}	Example
Unary system of five phases	(2-3)	$C_5^2 C_3^3 = 10$	$(2 \times 3) \times 3/2 = 9$	{1/2, 3/4/5}
Binary system of six phases	(2-4)	$C_6^2 C_4^4 = 15$	$(2 \times 4) \times 4/2 = 16$	{1/2, 3/4/5/6}
	(3-3)	$C_6^3 C_3^3 / P_2^2 = 10$	$(2 \times 4) \times 4/2 = 16$	{1/2, 3/4/5/6}
Ternary system of seven phases	(2-5)	$C_7^2 C_5^5 = 21$	$(2 \times 5) \times 5/2 = 25$	{1/2, 3/4/5/6/7}
	(3-4)	$C_7^3 C_4^4 = 35$	$(3 \times 4) \times 5/2 = 30$	{1/2/3, 4/5/6/7}
Quaternary system of eight phases	(2-6)	$C_8^2 C_6^6 = 28$	$(2 \times 6) \times 6/2 = 36$	{1/2, 3/4/5/6/7/8}
	(3-5)	$C_8^3 C_5^5 = 56$	$(3 \times 5) \times 6/2 = 45$	{1/2/3, 4/5/6/7/8}
	(4-4)	$C_8^4 C_4^4 / P_2^2 = 35$	$(4 \times 4) \times 6/2 = 48$	{1/2/3/4, 5/6/7/8}
Quinary system of nine phases	(2-7)	$C_9^2 C_7^7 = 36$	$(2 \times 7) \times 7/2 = 49$	{1/2, 3/4/5/6/7/8/9}
	(3-6)	$C_9^3 C_6^6 = 84$	$(3 \times 6) \times 7/2 = 63$	{1/2/3, 4/5/6/7/8/9}
	(4-5)	$C_9^4\ C_5^5 = 126$	$(4 \times 5) \times 7/2 = 70$	{1/2/3/4, 5/6/7/8/9}

Table 9. Some basic properties of the regular closed nets of unary to quinary system of $n + 5$ phases.

System	Type of closed nets	Total number of closed nets, N_{Net}	Number of the curves in a closed net, N_{UC}	Example
Unary system of six phases	(2-2-2)	$C_6^2C_4^2C_2^2/P_3^3 = 15$	$(2 \times 2 \times 2) \times 3/2 = 12$	{1/2, 3/4, 5/6}
Binary system of seven phases	(2-2-3)	$C_7^2C_5^2C_3^3/P_2^2 = 105$	$(2 \times 2 \times 3) \times 4/2 = 24$	{1/2, 3/4, 5/6/7}
Ternary system of	(2-2-4)	$C_8^2C_6^2C_4^4/P_2^2 = 210$	$(2 \times 2 \times 4) \times 5/2 = 40$	{1/2, 3/4, 5/6/7/8}
eight phases	(2-3-3)	$C_8^2C_6^3C_3^3/P_2^2 = 280$	$(2 \times 3 \times 3) \times 5/2 = 45$	{1/2, 3/4/5, 6/7/8}
Quaternary system of	(2-2-5)	$C_9^2C_7^2C_5^5/P_2^2 = 378$	$(2 \times 2 \times 5) \times 6/2 = 60$	{1/2, 3/4, 5/6/7/8/9}
nine phases	(3-3-3)	$C_9^3C_6^3C_3^3/P_3^3 = 280$	$(3 \times 3 \times 3) \times 6/2 = 81$	{1/2/3, 4/5/6, 7/8/9}
	(2-3-4)	$C_9^2C_7^3C_4^4 = 1260$	$(2 \times 3 \times 4) \times 6/2 = 72$	{1/2, 3/4/5, 6/7/8/9}
Quinary system of	(2-2-6)	$C_{10}^2C_8^2C_6^6\ /P_2^2 = 630$	$(2 \times 2 \times 6) \times 7/2 = 84$	{1/2, 3/4, 5/6/7/8/9/10}
10 phases	(2-3-5)	$C_{10}^2C_8^3C_5^5 = 2520$	$(2 \times 3 \times 5) \times 7/2 = 105$	{1/2, 3/4/5, 6/7/8/9/10}
	(2-4-4)	$C_{10}^2\ C_8^4C_4^4/P_2^2 = 1575$	$(2 \times 4 \times 4) \times 7/2 = 112$	{1/2, 3/4/5/6, 7/8/9/10}
	(3-3-4)	$C_{10}^3C_7^3C_4^4/P_2^2 = 2100$	$(3 \times 3 \times 4) \times 7/2 = 126$	{1/2/3, 4/5/6, 7/8/9/10}

imposed by the conditions concerned, however, only a very limited number of closed nets are suitable for depicting the phase relations of the given multisystem. Therefore, it is important to find out how to select the proper or realistic closed nets according to specific conditions.

To demonstrate the technique for the selection, we take the FeO–Fe_2O_3–SiO_2 system as an example. This system has seven phases: quartz (SiO_2, Qtz), ferrosilite ($FeSiO_3$, Fs), laihunite ($Fe_2Fe(SiO_4)_2$, Lai), fayalite (Fe_2SiO_4, Fa), hematite (Fe_2O_3, Hem), magnetite (Fe_3O_4, Mag) and wüstite (FeO, Wus). For this 2-level system, there are two types of non-degraded regular closed nets, (2-5) type and (3-4) type. The former has $\mathbf{C}_7^2(= 21)$ possible closed nets, and the latter has $\mathbf{C}_7^3(= 35)$ nets, totalling 56 nets, which depict all the possible phase relations in the system. Which of the 56 closed nets are the most realistic by the consideration of normal geological conditions?

It is well known that the molar volume change of a solid-phase reaction, $\Delta_r V_{m,s}$ usually varies little with the change of pressure or temperature, so the variation of $\Delta_r V_{m,s}$ will be negligible if the variations of pressure and temperature are not very great. Under such an approximation, the estimated equilibrium pressure of the reaction Lai = Mag + 2Qtz at 25 °C is *very negative*. That is, the reaction is impossible at 25 °C. This means that Lai + Mag + Qtz is a metastable univariant assemblage, so Lai, Mag and Qtz cannot simultaneously appear in any stable univariant or divariant assemblage. Therefore, at least one of them should be absent in any invariant assemblage in a physically possible net. This requirement can be satisfied by using laihunite, magnetite and quartz to constitute an independent group in the net label and using the other phases to form another group. Under this constraint, {Lai/Mag/Qtz, Hem/Wus/Fa/Fs} is the unique realistic net. The invariant points in the net are: [Lai, Hem]; [Lai, Wus]; [Lai, Fa]; [Lai, Fs]; [Mag, Hem]; [Mag, Wus]; [Mag, Fa]; [Mag, Fs]; [Qtz, Hem]; [Qtz, Wus]; [Qtz, Fa]; [Qtz, Fs]. Although this net excludes the metastable Lai + Mag + Qtz assemblage, it incorporates some other metastable assemblages, e.g. Hem + Wus, Hem + Fa, and Hem + Fs, see Table 10. The reason for this fact is as follows.

According to the arguments of Guo & Wang (1988), although the equilibrium between hematite and wüstite and the divariant assemblages including both of them are possible at extremely high pressures, they are impossible under normal geological conditions, so at least one of hematite and wüstite is absent in each invariant assemblage. The same is true for hematite and fayalite, and hematite and ferrosilite (Guo & Wang, 1988).

If the metastability of Hem + Wus, Hem + Fa, and Hem + Fs is used to constrain the (2-5) type of closed nets of the system, it will yield three possible nets: {Hem/Wus, Lai/Mag/Qtz/Fa/Fs}, {Hem/Fa, Lai/Mag/Qtz/Wus/Fs} and {Hem/Fs, Lai/Mag/Qtz/Fa/Wus}, respectively. In the first net, the invariant points are: [Hem, Lai]; [Hem, Mag]; [Hem, Qtz]; [Hem, Fa]; [Hem, Fs]; [Wus, Lai]; [Wus, Mag]; [Wus, Qtz]; [Wus, Fa]; [Wus, Fs]. It is obvious that all the assemblages including both hematite and wüstite are ruled out, and thus Guo & Wang (1988) regarded this net as the most realistic closed net of the system. In fact, the other two nets are also realistic. Of course, all three nets contain the metastable assemblage Lai + Mag + Qtz, and two of the three metastable assemblages Hem + Wus, Hem + Fa, and Hem + Fs, as can be seen in Table 10.

Guo & Wang (1988) suggested that the metastable assemblages in the selected possible closed nets be excluded from the final physically realistic phase diagram in a later step. This will leave a difficulty to the theoretical analysis and to the computation and plotting of the physically realistic net diagram. So it is better to exclude all four metastable assemblages (Hem + Wus, Hem + Fa, Hem + Fs and Lai + Mag + Qtz) from each closed net before the construction of the related straight-line-net. In this way, the same partially closed net {Hem, Lai/Mag/Qtz} can be obtained, although the initial possible closed nets are different from each other. In {Hem, Lai/Mag/Qtz}, there are only three invariant points: [Hem, Lai], [Hem, Mag] and [Hem, Qtz], where [Hem, Lai] and [Hem, Mag] degenerate into the same point. This is in agreement with the straight-line-net-diagram of Guo

Table 10. The metastable assemblages in the possible closed nets of the ternary 7-phase system Qtz–Fs–Lai–Fa–Hem–Mag–Wus.

Closed net	Invariant assemblage	Metastable assemblage to be excluded	The most realistic partially closed net
{Lai/Mag/Qtz, Hem/Wus/Fa/Fs}	[Lai, Wus], [Mag, Wus], [Qtz, Wus]	Hem + Fa, Hem + Fs	{Hem, Lai/Mag/Qtz}
	[Lai, Fa], [Mag, Fa], [Qtz, Fa]	Hem + Wus, Hem + Fs	
	[Lai, Fs], [Mag, Fs], [Qtz, Fs]	Hem + Wus, Hem + Fa	
{Hem/Wus, Lai/ Mag/Qtz/Fa/Fs}	[Wus, Lai], [Wus, Mag], [Wus, Qtz]	Hem + Fa, Hem + Fs	{Hem, Lai/Mag/Qtz}
	[Wus, Fa]	Hem + Fs	
	[Wus, Fs]	Hem + Fa	
	[Hem, Fa], [Hem, Fs]	Lai + Mag + Qtz	
{Hem/Fa, Lai/ Mag/Qtz/Wus/Fs}	[Fa, Lai], [Fa, Mag], [Fa, Qtz]	Hem + Wus, Hem + Fs	{Hem, Lai/Mag/Qtz}
	[Fa, Wus]	Hem + Fs	
	[Fa, Fs]	Hem + Wus	
	[Hem, Wus], [Hem, Fs]	Lai + Mag + Qtz	
{Hem/Fs, Lai/ Mag/Qtz/Wus/Fa}	[Fs, Lai], [Fs, Mag], [Fs, Qtz]	Hem + Wus, Hem + Fa	{Hem, Lai/Mag/Qtz}
	[Fs, Wus]	Hem + Fa	
	[Fs, Fa]	Hem + Wus	
	[Hem, Wus], [Hem, Fa]	Lai + Mag + Qtz	
{Hem, Wus/Fa/Fs/ Lai/Mag/Qtz}	[Hem, Wus], [Hem, Fa], [Hem, Fs]	Lai + Mag + Qtz	{Hem, Lai/Mag/Qtz}

& Wang (1988), but the procedures are much simpler.

There is a simple way to exclude all the assemblages Hem + Wus, Hem + Fa and Hem + Fs in a closed net, which can be realized by treating hematite as an absent phase. As a result, {Hem, Wus/Fa/Fs/Lai/Mag/Qtz} become the unique realistic closed net. It is a degraded closed net of the ternary 7-phase multisystem. It is not only the simplest, but also the most realistic because of the least number of metastable assemblages. It still contains the metastable univariant assemblage Lai + Mag + Qtz, leading to the unstability of the three invariant assemblages including it, as is shown in Table 10.

Derivation of closed-net-diagrams and straight-line-net-diagrams

The invariant points in a regular closed net can be generated by the APS method. In order to obtain a closed-net-diagram, it is necessary to arrange all invariant points and univariant curves in a proper way, which can be realized with the Shreinemakers' rules (Zen, 1966b) or so-called 'univariant scheme' about an invariant point (Zen, 1966a, p. 13). A univariant scheme means an arrangement of a bundle of univariant curves on the two sides of a given univariant curve. It is derived from Shreinemakers' rules, so it is equivalent to Shreinemakers' rules in arranging univariant curves, see (Zen, 1966a). Here we use univariant schemes to construct the bundles in the closed net.

As mentioned in the Introduction, there is at least one metastable invariant point in a closed net. If all the metastable invariant points are eliminated, it will yield a partially closed (or partially open) net, which is physically real or possible. If all the remaining univariant curves are supposed to be straight-lines, the partially closed net will become a straight-line net.

Taking a binary system of six phases as illustration. The six phases (from No. 1 to 6) are: forsterite, Fo, 1; enstatite, En, 2; quartz, Qtz, 3; anthophyllite, Ath, 4; talc, Tlc, 5; and water, W, 6. Here MgO is a mobile component whose activity serves as an intensive variable of the system, and thus it is no longer regarded as a component. In this way, the system is simplified into a compositionally degenerate binary system (SiO_2-H_2O), and the phase labels 1–6 are set according to the sequence of relative positions of the six phases on the binary chemography (from end-member SiO_2 to H_2O).

To get a realistic closed net, let's focus on the following degenerate reactions:

$$\mathrm{Fo} = \mathrm{MgO} + \mathrm{En} \quad (\mathrm{Mg_2SiO_4} = \mathrm{MgO} + \mathrm{MgSiO_3}), \tag{11}$$

$$\mathrm{En} = \mathrm{MgO} + \mathrm{Qtz} \quad (\mathrm{MgSiO_3} = \mathrm{MgO} + \mathrm{SiO_2}), \tag{12}$$

$$\mathrm{Fo} = 2\mathrm{MgO} + \mathrm{Qtz} \quad (\mathrm{Mg_2SiO_4} = 2\mathrm{MgO} + \mathrm{SiO_2}). \tag{13}$$

It is known that, with the decrease of the activity of MgO at given temperature and pressure, reaction (11) occurs first, and then reaction (12). Here, reaction (13) is realized through reactions (11) and (12), which can be expressed as: (13) = (11) + (12). As a result, no direct reaction equilibrium occurs between forsterite and quartz, that is to say, the assemblage Fo + Qtz is metastable. So Fo + Qtz should be excluded from further consideration. Under this constraint, there is only one realistic closed net: {Fo/Qtz,En/Ath/Tlc/W}, or {1/3,2/4/5/6}. The net-diagram of {1/3,2/4/5/6} is

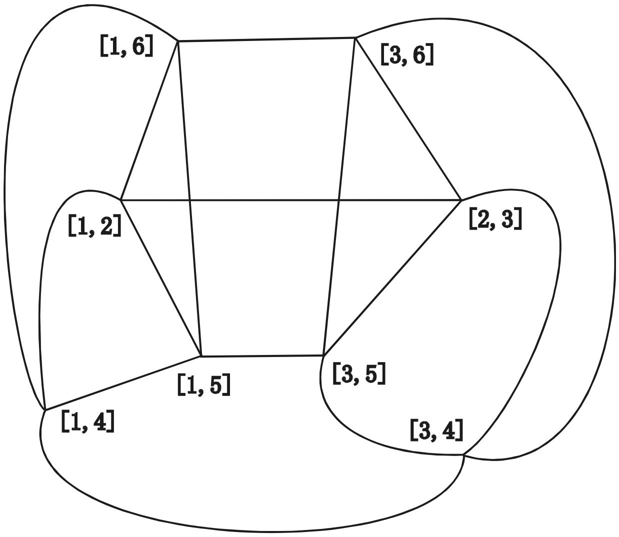

Fig. 1. The binary 6-phase closed-net-diagram {1/3,2/4/5/6}.

shown in Fig. 1, which is constructed with univariant schemes. It is equivalent to Fig. 9(h) of Guo (1984) derived from the combination of two degraded closed nets of binary 5-phase system.

In Fig. 1, because of the absence of the fluid phase W, the univariant curves intersecting at points [1, 6] and [3, 6] are all solid-phase reaction curves, so they should be very close to straight lines. This means that the curve linking [1, 6] and [1, 4] and the curve linking [3, 6] and [3, 4] should not bend down, so the invariant points [1, 4] and [3, 4] cannot be stable at the bottom of

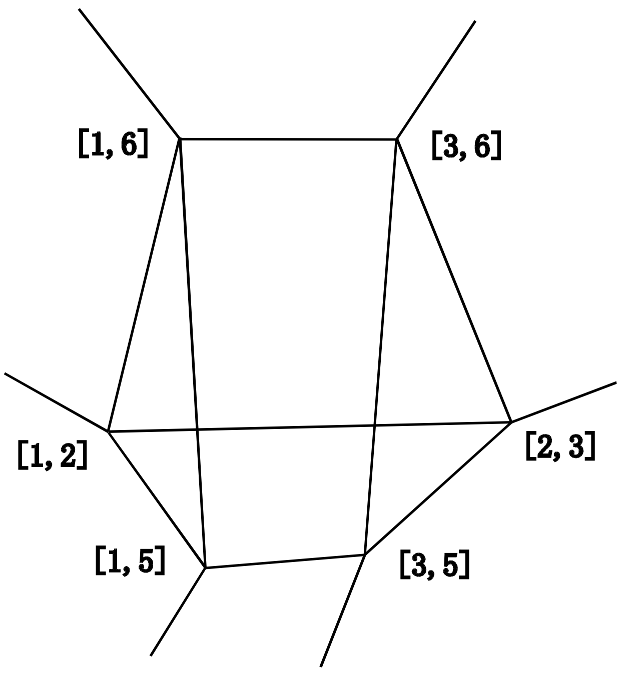

Fig. 2. A straight-line-net-diagram of binary 6-phase multisystem derived from Fig. 1.

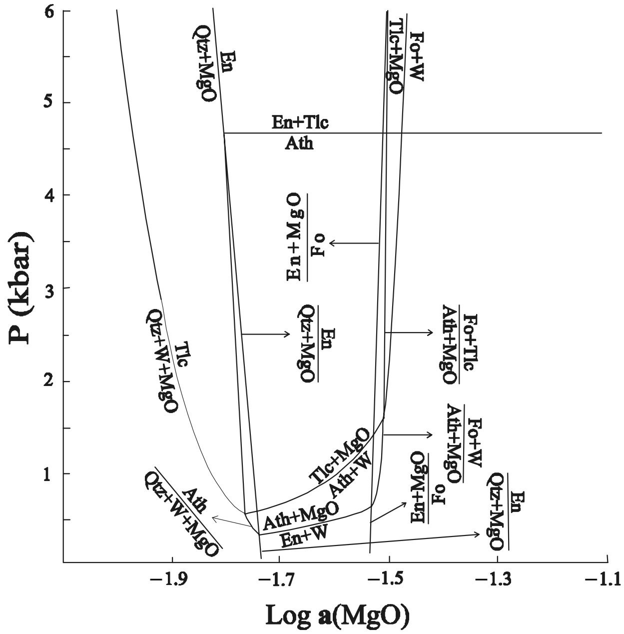

Fig. 3. The P-log a(MgO) diagram of the Fo–En–Qtz–Ath–Tlc–W system at 650 °C. The thermodynamic data were taken from Berman (1988), the HSMRK equation of state developed by Kerrick & Jacobs (1981) was used in the calculation, and the discrimination of stabilities of the invariant points and univariant curves were made with the *sign function matrix* (SFM) method of Hu *et al.* (2000). In the diagram, two or more univariant curves are incorporated into one because of the degeneracy of the corresponding reactions.

the net. Accordingly, the univariant curve between [1, 4] and [3, 4] is metastable, too. After excluding these two metastable invariant points and the curve between them, the closed net becomes a partially closed net, see Fig. 2.

However, it is still possible that some of the remaining invariant points in the net are metastable or nonexistent. This problem can be solved by calculation. We calculated the P-log$a$(MgO) diagrams of the system at 1000 and 650 °C (Hu, 1998; Yin *et al.*, 2002). The former degenerates into a binary 5-phase diagram where water remains metastable in the whole diagram, and the latter is given in Fig. 3.

It is found that the invariant point [3, 6] disappeared from Fig. 3, because the related curves cannot intersect at a point. It is easy to see that the topological configurations of Figs 2 and 3 are completely consistent with each other.

CONCLUSIONS

According to the definition of closed nets, we developed a new combinatorial method, the APS method, for the direct derivation of closed nets. Using this method, a few very simple operations are sufficient for the derivation of the closed nets of a given multisystem. Although the increase in the number of phases or components will greatly increase the complexity of phase relations, the simplicity of the APS method almost remains the same. This is a great advantage over the previously reported methods. In its application, we found that there are two very different types of closed nets, the regular and irregular closed nets. For the multisystems whose total phase number (N_{PS}) is not smaller than twice the absent phase number (m) of an invariant assemblage, the method can give both degraded and non-degraded regular closed nets; for the multisystems whose $N_{PS} < 2m$, the method can give degraded regular closed nets. These degraded regular closed nets can serve as the basic elements that are necessary in deriving the irregular closed nets with the improved combination method in our next study.

As working examples, the APS method is applied to the derivation of the degraded or non-degraded regular closed nets of the unary to quinary systems with $n + 4$ and $n + 5$-phases. At the same time, the general properties of closed nets of $n + 4$ and $n + 5$ phase multisystems are also predicted. In addition, for a complex multisystems, it is also illustrated how to select the realistic closed nets from the numerous closed nets under specific conditions, and how to get the partially closed nets, closed-net-diagrams and straight-line-net-diagrams of interest.

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