# Types of Invariant Phase Assemblages of Four-Component System with Two Independent Intensive Variables

| 大夕データ | 言語: eng | 出版者: 公開日: 2017-10-03 | キーワード (Ja): キーワード (En): 作成者: 山崎, 正男, 板野, 昇平 メールアドレス: 所属: | MRL | https://doi.org/10.24517/00011290

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December 1975

### Types of Invariant Phase Assemblages of Four-Component System with Two Independent Intensive Variables

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Abstract Sixty-eight types of invariant assemblages of four-component system with two independent intensive variables are described being topologically classified into terahedral, five-vertex polyhedral, and six-vertex polyhedral groups, which contain respectively 31, 26, and 11 types. The topological features being unique to a particular type are expressed by a combination of symbols and by a perspective or stereoscopic drawing. Four types are not degenerated. All other types bear any of such topological relations that cause degeneration as polymorphism, an compositionally co-linear or co-planar relation. The arrangement of univariant lines arround the invariant point and the assemblages of phases in the divariant sectors are also described being illustrated diagramatically for all types of invariant assemblages.

#### 1 Introduction

Diagrams illustrating heterogeneous phase equilibria in the field of intensive variables such as pressure and temperature are widely used in the phase petrology. Many diagrams have been constructed for systems of petrological interest experimentally or empirically by many authors. Principle and method of construction of the diagram have also been discussed by certain authors from different view points, since Schreinemakers' theorem was published. Zen (1966) has discussed the method in detail from the geometric view point, and demonstrated topologically nineteen types of invariant assemblages of three-component system, constructing a series of diagrams illustrating the configuration of Schreinemakers bundles of the types.

For the study of mineral assemblages in natural rocks, it is desirable to clarify the basic relations in multi-component equilibria. For this reason we have examined the equilibrium relationship among phases of fixed compositions of the four-component system from the topological view point. As a result, we obtained sixty-eight possible types of invariant assemblages, which we intend to describe below.

#### 2 Invariant assemblages and symbolic expressions

Group symbol An invariant assemblage of a four-component system consists of six phases, and their compositions are chemographically depicted by a polyhedral solid. On the basis of the shape of polyhedron, the types of invariant assemblages are classified into the terahedral, five-vertex polyhedral, and six-vertex polyhedral groups which are respectively represented by the symbols [4], [5,n], and [6,n], where n indicates the number of faces of each polyhedron. As will be shown later, n is 6 or 5 in the five-vertex polyhedral group, and 8, 7, 6, or 5 in the last group. The polyhedra that have no concaved suface are taken into account in the above classification, and two points in the group [4] and a point in the group [5,n] are either within or on the surface of the polyhedron, and each group is divided into subgroups according to the situation of those points as well as to the number of faces of polyhedron. Each type of invariant assemblage is represented by a combination of symbols that indicates the topological situation being unique to that particular type, as will be explained below.

Plane figures The six phases as well as the six points representing the compositions of corresponding phases are denoted by A, B, C, D, E, and F throughout this paper. Symbols such as A=B and A=B=C indicate that the phases are in polymorphic relation and the corresponding points occupy the same position.

The tie line between A and B is expressed by  $\overline{AB}$ . When C is on  $\overline{AB}$ , i. e. A, C, B are compositionally co-linear, the situation is expressed by  $\overline{ACB}$ , and  $\overline{ACDB}$  indicates that phases A, C, D, and B are co-linear. Compositionally co-linear five and six phases do not appear in the invariant assemblages described in this paper.

A triangle, ABC, a quadrilateral, ABCD, and pentagon, ABCDE, are respectively expressed by  $\overline{ABC}$ ,  $\overline{ABCD}$ , and  $\overline{ABCDE}$ . Travelling along the sides of the polygons, one meets successively each vertex in the order or in the reverse order of the vertices shown in the symbols. Therefore,  $\overline{AC}$  and  $\overline{BD}$  are the diagonals of ABCD.

The situation that D is on <u>ABC</u> is expressed by <u>ABC(D)</u>. The symbols <u>ABC(D)(E)</u>, <u>ABCD(E)</u>, and <u>ABCDE</u> represent assemblages of compositionally co-planar five phases which are invariant ones in three-component systems. Compositionally co-planar six phases do not apper in the invariant assemblages described below.

Tetrahedral solids A tetrahedron, ABCD, is expressed by [ABCD]. A point, E, within [ABCD] is expressed by [ABCD[E]] and when the point is on the surface of the solid, it is expressed by [ABCDE]. The vertices of the terahedron for each type of invariant assemblage of the terahedral group are denoted always as A, B, C, and D, and two points within or on the surface of the solid are labeled E and F. The tetrahedral group can be topologically divided into three subgroups with respect to the positions of E and F, and the subgroups are expressed by the symbols [4](E)(F), [4] $\bar{E}$ (F), and [4] $\bar{E}$ F.

Five-vertex polyhedra Five-vertex polyhedra are derived from an original tetrahedron, (ABCD), by addition of a new vertex, E. The shape of the solid thus formed depends

on the position of E as illustrated in Fig. 1 a. When E is at such positions as  $E_1$  and  $E_3$ , the polyhedra obtained have six faces, and when E is at  $E_2$  on the extention of a face of the original terahedron, the solid formed is a pyramid with a quadrilateral base. When E is at  $E_4$ ,  $E_5$ , and  $E_6$ , the newly formed solids are also terahedral in shape and one of the vertices of the original tetrahedron is either within or on the surface of the new solids.

The five-vertex polyhedron with six triangular faces has one body diagonal. Let the body diagonal be  $\overline{AE}$  and remaining three vertices B, C, and D, as shown in Fig. 1 b,  $\overline{AE}$  passes through the triangle  $\overline{BCD}$  within the solid, and the polyhedron is expressed by the symbol [ABCDE]. The five-vertex polyhedron of pyramid shape is formed by intersection of the body diagonal and one of the edges of the six-face polyhedron

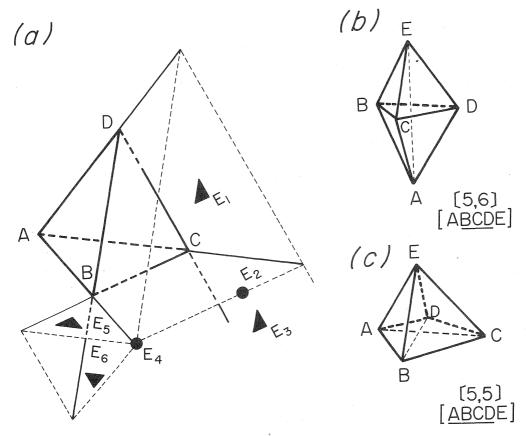


Fig. 1 (a) Relation between the position of vertex E added to the tetrahedron ABCD and the shape of solid thus formed. When E is at  $E_1$  and at  $E_2$  five-vertex polyhedra with six triangular faces [ABCDE] and [BADEC] are formed respectively. When E is at  $E_2$ , a pyramed with quadrilateral base, [ABED] is formed. In the cases of  $E_4$ ,  $E_5$ , and  $E_6$  the solids are tetrahedral in shape, [AECD], and the vertex B of the original tetrahedron is on AE when E is at  $E_4$ , on  $E_6$  when E is at  $E_5$ , and within the solid,  $E_6$  when E is  $E_6$ .

(b) Five-vertex polyhedron with six faces, [ABCDE]. Body diagonal  $\overline{AE}$  penetrates triangle BCD. Invariant assemblages of this polyhedral type are represented by [5,6].

(c) Pyramid with quadrilateral base, (ABCDE). The invariant assemblages of this type are expressed by (5,5).

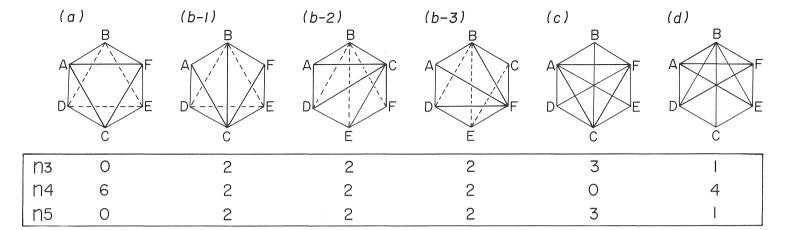
mentioned above. When the quadrilateral base and the apex are respectively denoted as  $\underline{ABCD}$  and  $\underline{E}$ , the solid is represented by symbol  $[\underline{ABCDE}]$ . In describing the invariant assemblage types of the five-vertex polyhedral type, the solid representing each type is always expressed as  $[\underline{ABCDE}]$  for the subgroups of six-face polyhedron and as  $[\underline{ABCDE}]$  for the five-face or pyramidal polyhedron subgroups. Then the subgroups of the five-vertex polyhedral group are indicated by the symbols [5,6] [F], [5,6], [5,5] [F], and [5,5]. All invariant assemblages of [5,5] subgroup are degenerated by the compositionally co-planar relation among four phases A, B, C, and D.

Six-vertex polyhedra In the six-vertex polyhedral group, all six phases of the invariant assemblage are represented by the vertices of the solid, and no polymorphic and compositionally co-linear relations are present among them. Compositionally co-planar four and five phases appear as the result of degeneration. As illustrated in Fig. 2, there are two types of six-vertex polyhedra that are not degenerated. The solids have eight triangular faces and three body diagonals, and are considered to be derived from a terahedron, [BCDE], by addition of two new vertices, A and F, as illustrated in (a') and (b') or Fig. 2. The two types are represented by the symbols [6,8]ABCDEF and [6,8]A[BCDE]F respectively. The former has three body diagonals,  $\overline{AE}$ ,  $\overline{BC}$ , and  $\overline{DF}$ , that are isolated to one another, and  $\overline{AF}$  forms an edge. In the latter type,  $\overline{AF}$  is a body diagonal that penetrates the original tetrahedron [BCDE], and two other body diagonals,  $\overline{AE}$  and  $\overline{DF}$ , meet  $\overline{AF}$  at A and F respectively.

The intersection of two body diagonals introduces a quadrilateral that lies within the solid. The polyhedron of the former type is thus transformed into a bipyramidal solid indicated by [6,8]ABCDEF, where A and F are allotted to the apices. The interesection of a body diagonal with one of the edges forms a quadrilateral face reducing the number of faces by one. The types with one or more quadrilateral faces are expressed by [6,n]ABCDEF.

Symbolic expressions of invariant assemblage types Among sixty-eight invariant assemblage types, Nos. 1, 32, 58, and 59 are not degenerated. All other types bear one or more factors of topological relation that cause the degeneration of system. The topological situation that is unique to each type is indicated by a combination of symbols. For example, No. 19 is represented by  $(4)\overline{E}\overline{F}-\overline{CFD},BCD(E)/BFD(E)/$ . The unique features of this type are that one point is on one of the faces of the tetrahedron, and that other point is on one of the sides of the same face. Therefore, the system contains compositionally co-planar five phases. The symbols  $\overline{CFD}$  and  $\overline{BCD(E)}$  sufficiently indicate these unique features. However, there are two alternative cases with respect to the position of E on  $\overline{BCD}$ , and it is needed to chose one of them in order to describe the topological relations of the univariant assemblages. The symbol  $\overline{BFD(E)}$  indicates that E is chosen to be not on  $\overline{CFD}$  but on  $\overline{BFD}$ , and since it is not essential to the topology of the type, the symbol is shown being enclosed by slashes.

Order of descrption The sixty-eight types of invariant assemblages are arranged in



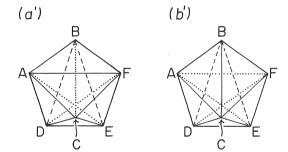


Fig. 2 (a) and (b 1–3) Projections of two types of six-vertex polyhedron with eight triangular faces. Among twelve edges, six correspond to the sides of hexagonal outline and remaining six are projected as diagonals of the hexagon. (b 1–3) are projections of the same solid in different directions. Among all possible ways of drawing six diagonals, (a) and (b 1–3) are only the cases of projections of solids, in which the edges on the hidden side are drawn with broken lines. (c) and (d) can not be projections of solid since three diagonals intersect one another at the center of the hexagon.  $n_3$ ,  $n_4$ , and  $n_5$  are total number of vertices at which meet three, four, dnd five edges respectively. A vertex at which meet less than five edges emits one or two body diagonals, since five tie lines must meet at each vertex.

(a') and (b') are perspectives of the solids of types (a) and (b) respectively illustrating the derivations of the solid from an original tetrahedron, [BCDE], by adding vertices A and F. In (a'), three body diagonals (dotted lines) are isolated one another and each vertex emits one diagonal. The invariant assemblage of this type is expressed by (6,8) ABCDEF. In (b'), the tie line  $\overline{AF}$  is a body diagonal that penetrates the original tetrahedron [BCDE], and meets two other body diagonals  $\overline{AE}$  and  $\overline{DF}$  at A and F respectively. The invariant assemblage of this type is expressed as (6.8) A[BCDE]F.

the following order:

(4)(E)(F)	Nos. 1-6.	No. 1 is not degenerated.
$(4)\overline{E}(F)$	Nos. 7-13	
$(4)\overline{\mathrm{EF}}$	Nos. 14-31	
(5,6)(F)	Nos. 32-39.	No. 32 is not degenerated.
$(5,6)\overline{\mathbf{F}}$	Nos. 40-46	
(5,5)(F)	Nos.47-49	
$(5,5)\overline{\mathbf{F}}$	Nos.50-57	
(6,8)	Nos. 58-63.	Nos. 58, 59 are not degenerated.
(6,7)	Nos. 64, 65	
(6,6)	Nos. 66, 67	
(6.5)	Nos. 68	

Polymorphic three phases are only in No. 31, and polymorphic two phases are in Nos. 6, 13, 16, 22, 23, 25, 28, 29, 46, and 57. No. 30 contains two pairs of polymorphic two phases.

#### 3 Univariant assemblages

When a phase, for example F, is removed from the invariant assemblage, remaining five phases constitute an assemblage on a univariant line which will be labeled (F). The reactions that take place on the univariant lines are classified into seven types, each of which corresponds to a particular topological relation among the phases. The possible topological relations are either tetragonal, (ABCD(E)) and (ABCDE), or five-vertex polyhedral, (ABCDE) and (ABCDE).

Type 1 The reaction corresponding to the configuration (ABCD(E)) is

(F) 
$$E=A+B+C+D$$

where the stoichiometric coefficients of phases, though not specified, are all positive.

Type 2 The reaction corresponds to (ABCDE) and is

(F) 
$$A + E = B + C + D$$

Type 3 The configuration is  $(ABCD\overline{E})$ , where E is on  $\underline{BCD}$ , i.e.  $\underline{BCD(E)}$ . The system bears compositionally co-planar relation among four phases, and is degenerated. The reaction is

(F) 
$$E=B+C+D$$

The phase A does not participate in the reaction and the stoichiometric coefficient of A is zero.

Type 4 The topological relation is (ABCDE) and the reaction is

$$(F)$$
  $A+C=B+D$ 

Phase E does not take part in the reaction.

Type 5 The topological relation is  $(ABCD\overline{E})$ , where E is on CD, and the system is degenerated by the co-linear relation,  $\overline{CED}$ , and the reaction is

$$(F)$$
  $E=C+D$ 

The phases A and B do not participate in the reaction.

Type 6 The tetrahedron  $(ABCD\overline{E})$  bears a polymorphic relation D=E and the reaction is

$$(F)$$
  $D=E$ 

A, B, and C do not participate in the reaction.

Type 7 When all five phases are compositionally co-planar, they constitute an invariant assemblage of three-component system and no reaction actually takes place among them. In this paper the reaction is expressed as

The combination of univariant reaction types is shown for each types of invariant assemblage by symbolic sign  $(n_1n_2, n_3n_4n_5, n_6n_7)$  where  $n_1$  indicates the total number of reactions of type i. The symbol facilitates understanding of the topological situation of each invariant assemblage. Thus  $n_1 + n_2$  is 6 for the types that are not degenerated, and  $n_7$  is not zero for the types, Nos. 14, 15, 16, 19, 20, 22, 24, 25, 26, 28, 29, 30, 31, 52, 53, 54, 55, 57, and 67, each of which can be derived by addition of a vertex from one of the nineteen types of invariant assemblage of three–component system described by Zen (1966).

This symbolic expression facilitates the determination of the type of any invariant mineral assemblage whose equations of univariant reactions are known. It must be added, however, that certain symbols are shared by two or three types as shown bellow:

Nos.	6, 13	(20,000,40)
	10,12	(10, 203, 00)
	16, 22	(00, 200, 31)
	18,49	(00, 420, 00)
	21, 39	(01, 203, 00)
	25, 28	(00, 002, 22)
	26, 55	(00, 014, 01)
	33, 47	(22, 020, 00)
	34, 36	(13, 200, 00)
	35, 48	(11,220 00)
	41, 50	(02, 220, 00)
	42, 44	(03, 003, 00)
	43, 51	(01, 023, 00)
	45, 46	(02, 000, 40)
	58, 59	(06, 020, 00)
	60, 61	(04, 020, 00)
	62, 65, 66	(02, 040, 00)
	63, 68	(00,060,00)

#### 4 Univariant lines and divariant assemblages

For each type of invariant assemblages a diagram illustrating the arrangement of univariant lines around the invariant point, Schreinemakers bundle, and the assemblage of phases in each divariant sector between two neighbouring univariant lines are constructed.

The univariant lines are drawn according to the method explained by Zen (1966) in detail. Phases on both sides of the equation of the univariant reaction are specified on both sides of the univariant line. The labels of the reactions of type 7 are not shown in the diagram. The line labeled (A) is drawn upwards from the invariant point arbitrary for all types except the cases where (A) is of type 7. Choise is also made arbitrary between two configurations in the relation of mirror image.

The divariant assemblage consists of four phases which are chemographically depicted by a tetrahedron, and is illustrated in the diagram by showing the tie lines that form the edges of each tetrahedron.

#### Acknowledgments

We sincerely thank Mr. Kenji Nakamura of Kanazawa University for his help in preparing the figures. Our thanks are also due to Prof. Takashi Fujii of Tsukuba University who kindly gave us much information.

#### Reference

Zen, E-an (1966) Construction of pressure-temperature diagrams for multicomponent systems after the method of Schreinemakers —— A geometric approach; U.S.G.S. Bull. 1225, 1-56.

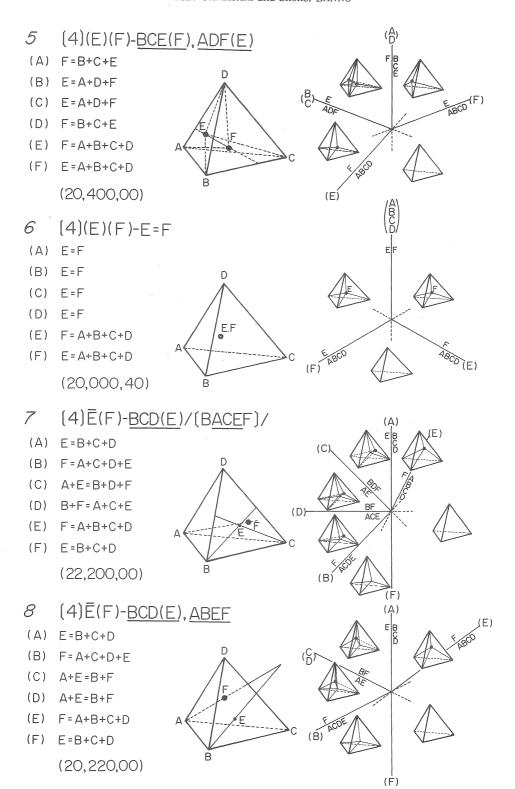
Fig. 3 Type number and symbol, perspectives illustrating compositional relation of phases, equations of univariant reactions, symbol of combination of reaction types, figure illustrating univariant lines and divariant assemblages in field of two intensive variables are shown for each invariant assemblage type.

In perspectives for invariant assemblages points within and on the surface of solid are shown with large and small solid circles respectively. Polymorphic phases are shown by double circles

In the figures for divariant assemblages, only those within the solid are shown by small circles.

### (A)(4)(E)(F)/(ACDEF),(DABFE)/(A) F=B+C+D+E(B) A+F=C+D+E (C) D+E=A+B+F(C) (D) E=A+B+C+F(E) F = A + B + C + D(F) E = A + B + C + D(42,000,00) (4)(E)(F)-<u>ABF(E)</u>/(A<u>CDE</u>F)/ (A) F=B+C+D+E (A)(B) (B) A+F=C+D+E(C) E=A+B+F (D) E= A+B+ F (E) F = A + B + C + D(F) E = A+B+C+D В (31,200,00)(É) (4)(E)(F)-AEF 3 FCOE (A) F = B + C + D + E(B) E = A + F(C) E=A+F ABCD (F) (D) E = A + F(E) F = A + B + C + D(F) E = A + B + C + DВ (E) (30,003,00) (4)(E)(F)-ABFE 4 (A) F=B+C+D+E(B) E=A+C+D+F(C) A+F=B+E (D) A+F=B+E(B) (E) F = A + B + C + D(F) E = A + B + C + D(40,020,00)

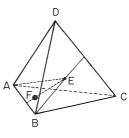
(E)

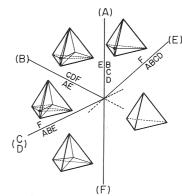


# 9 $(4)\bar{E}(F)-\underline{BCD(E)},\underline{ABE(F)}$

- (A) E=B+C+D
- (B) A+E=C+D+F
- (C) F = A + B + E
- (D) F = A + B + E
- (E) F = A + B + C + D
- (F) E=B+C+D

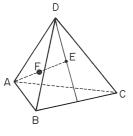
(11,400,00)

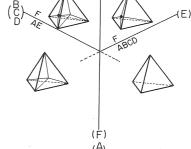




## /O (4) $\bar{E}$ (F)-BCD(E), $\bar{A}$ FE

- (A) E=B+C+D
- (B) F=A+E
- (C) F = A + E
- (D) F = A + E
- (E) F = A + B + C + D
- (F) E=B+C+D (10,203,00)



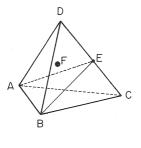


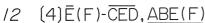
(E)

(A)

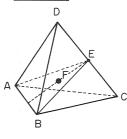
## // $(4)\bar{E}(F)-\bar{CED}/(ABDE(F))/$

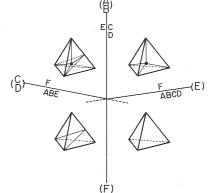
- (A) E=C+D
- (B) E=C+D
- (C) F = A + B + D + E
- (D) C+F=A+B+E
- (E) F=A+B+C+D
- (F) E=C+D (21,003,00)

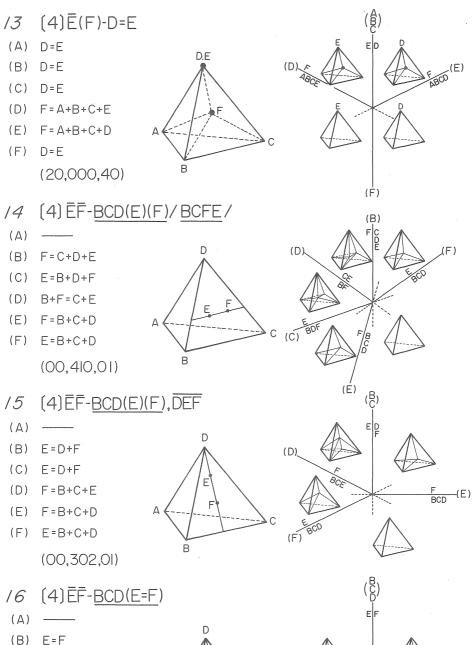




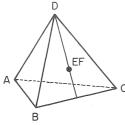
- (A) E=C+D
- (B) E=C+D
- (C) F=A+B+E
- (D) F=A+B+E
- (E) F=A+B+C+D
- (F) E=C+D (IO,203,00)

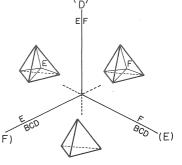


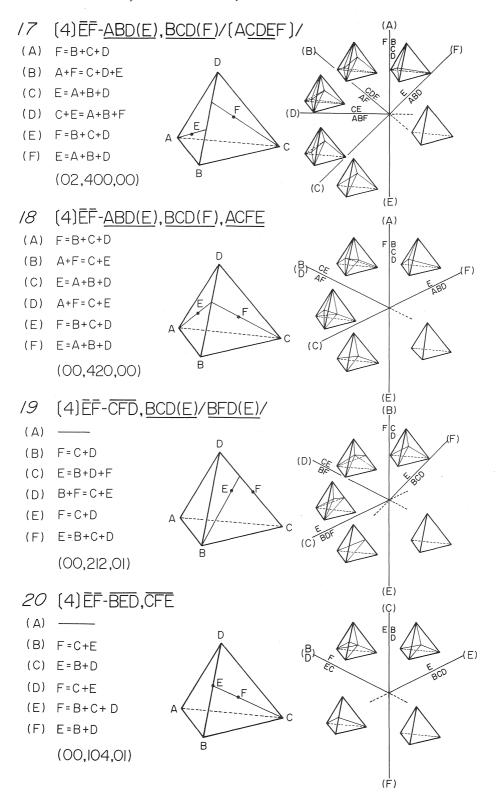




- (C) E=F
- (D) E=F
- (E) F=B+C+D
- (F) E=B+C+D (00,200,31)

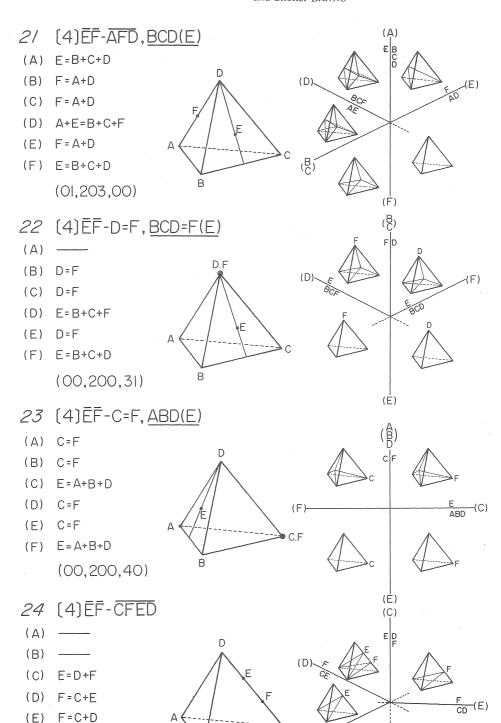


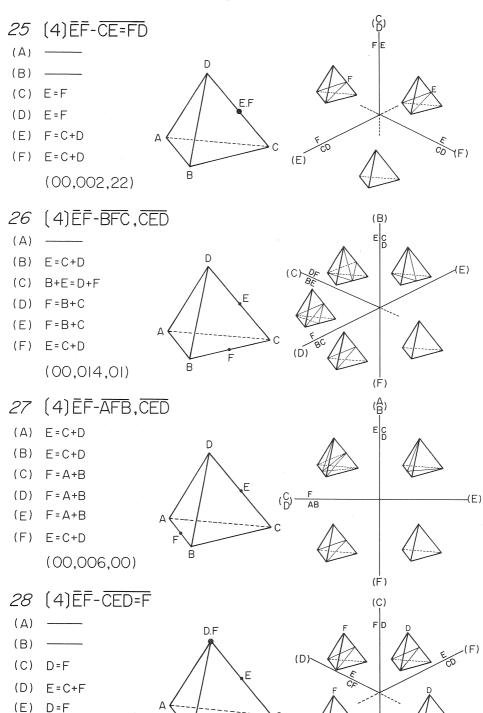




(F) E=C+D

(00,004,02)

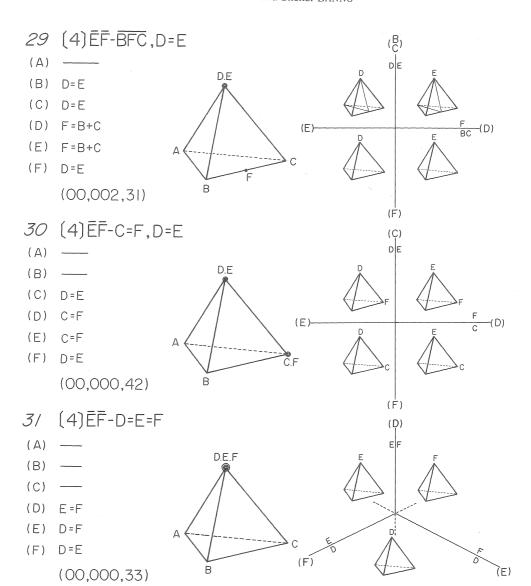




(Ė)

(F) E=C+D

(00,002,22)



## (5,6)(F)/(BCDE(F)),(BAEDF)/32 (A) F=B+C+D+E(B) F = A + C + D + E(C) B+F=A+D+E (D) A+E=B+C+F(E) A+F=B+C+D (F) A+E=B+C+D(33,000,00)(B) 33 (5,6)(F)-<u>ABEF</u>/(BCDE(F))/ (A) FCDE (A) F=B+C+D+E(B) F = A + C + D + E(C) A+E=B+F (D) A+E=B+FВ (E) A+F=B+C+D (F) A+E=B+C+D (22,020,00) (B) 34 (5,6)(F)-BCD(F)/(BAEDF)/ (A) F=B+C+D(B) F = A + C + D + E(C) B+F=A+D+E (D) A+E=B+C+F (E) F=B+C+D(C) (F) A+E=B+C+D (13,200,00)35 (5,6)(F)-ABEF,BCD(F) (A) F=B+C+D (B) F = A + C + D + E(C) A+E=B+F (D) A+E=B+F (E) F=B+C+D

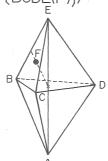
(F)

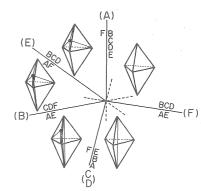
A+E=B+C+D (11,220,00)

# 36 (5,6)(F)-<u>ABE(F</u>)/(BCDE(F))/

- (A) F=B+C+D+E
- (B) A+E=C+D+F
- (C) F=A+B+E
- (D) F=A+B+E
- (E) A+F=B+C+D
- (F) A+E=B+C+D

(13,200,00)

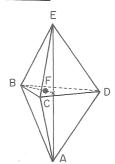


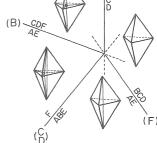


# 37 (5,6)(F)-<u>ABE(F),BCD(F)</u>

- (A) F=B+C+D
- (B) A+E=C+D+F
- (C) F = A + B + E
- (D) F=A+B+E
- (E) F=B+C+D
- (F) A+E=B+C+D

(03,300,00)

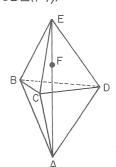


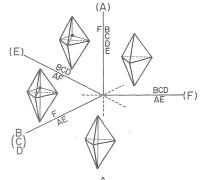


## 38 (5,6)(F)-AFE/(BCDE(F))/

- (A) F=B+C+D+E
- (B) F = A + E
- (C) F=A+E
- (D) F= A+E
- (E) A+F=B+C+D
- (F) A+E=B+C+D

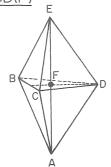
(12,003,00)

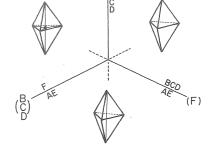




## 39 (5,6)(F)-AFE,BCD(F)

- (A) F=B+C+D
- (B) F=A+E
- (C) F=A+E
- (D) F=A+E
- (E) F=B+C+D
- (F) A+E=B+C+D
  - (01,203,00)





## 40 (5,6) F-CDE(F)/(BACEF)/ (A) F=C+D+E (B) F=C+D+E(C) A+E=B+D+F(C) (D) B+F=A+C+E (E) A+F=B+C+D(F) A+E=B+C+D(04,200,00)(B) (5,6)F-CDE(F),ABEF (A) (A) F=C+D+E(E) (B) F=C+D+E(C) A+E=B+F (D) A+E=B+F (E) A+F=B+C+D (F) A+E=B+C+D (02,220,00)(B) 42 (5,6)F-CFD/(BADEF)/ (A) F = C + DFC (B) F = C + D(D) (C) B+F=A+D+E (D) A+E=B+C+F (E) F=C+D(F) A+E=B+C+D (C) (03,003,00)43 (5,6)F-CFD, ABEF (₽) (A) F=C+DFC (B) F=C+D(C) A+E=B+FBCD (F) (D) A+E=B+F (E) F=C+D(F) A+E=B+C+D

(B)

(01,023,00)

# 44 (5,6)F-DFE

- (A) F=D+E
- (B) F=D+E
- (C) F=D+E
- (D) A+E=B+C+F
- (E) A+F=B+C+D
- (F) A+E=B+C+D (O3,OO3,OO)

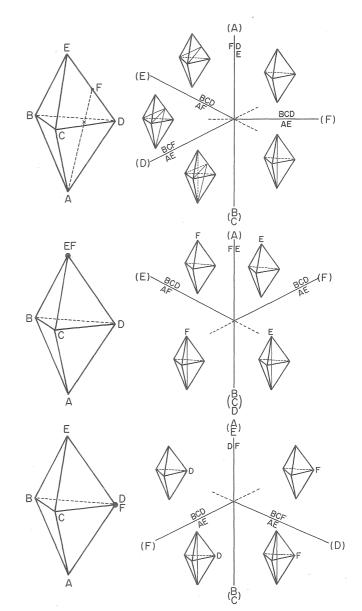
## 45 (5,6)F-E=F

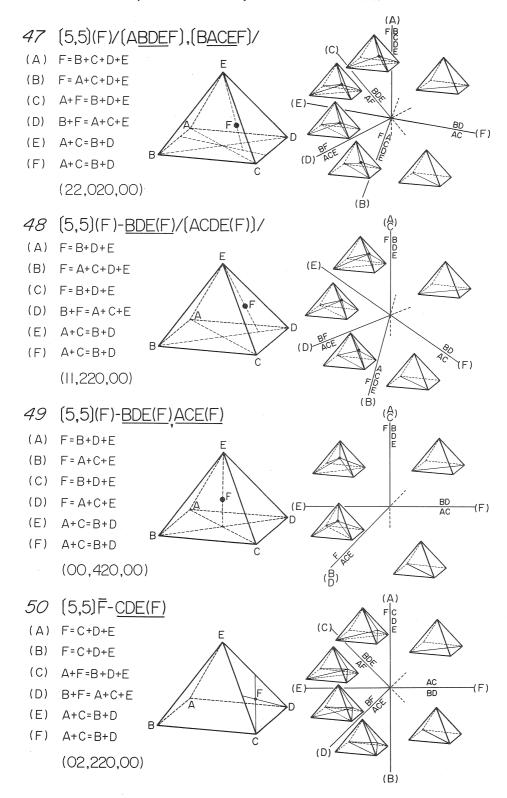
- (A) E=F
- (B) E=F
- (C) E=F
- (D) E=F
- (E) A+F=B+C+D
- (F) A+E=B+C+D (O2,000,40)

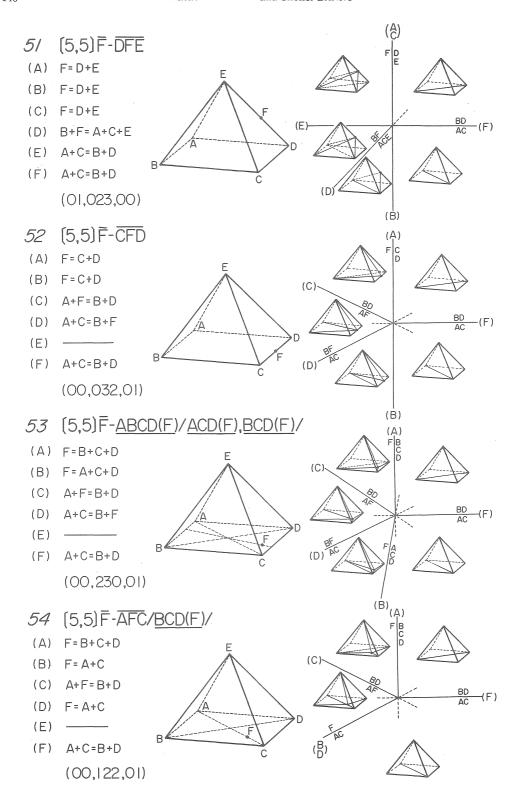
# 46 (5,6)F-D=F

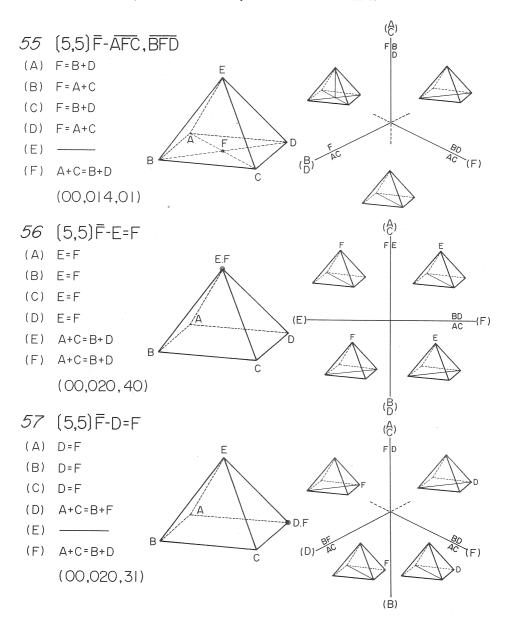
- (A) D=F
- (B) D=F
- (C) D=F
- (D) A+E=B+C+F
- (E) D=F
- (F) A+E=B+C+D

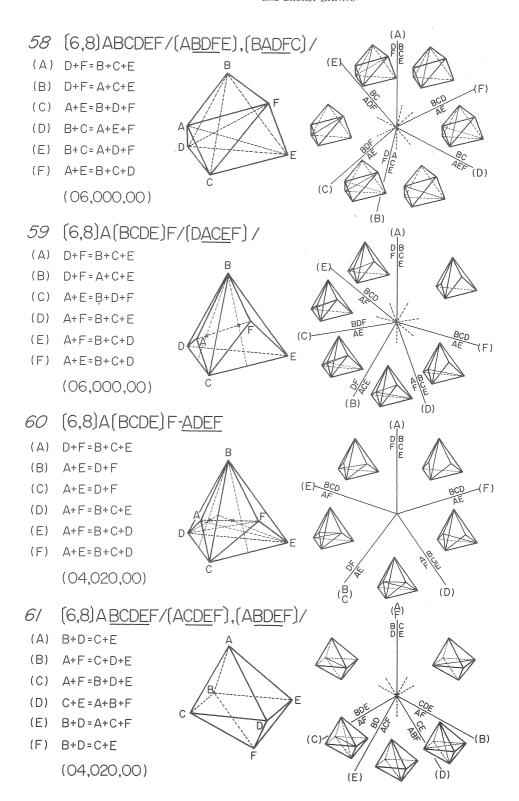
(02,000,40)

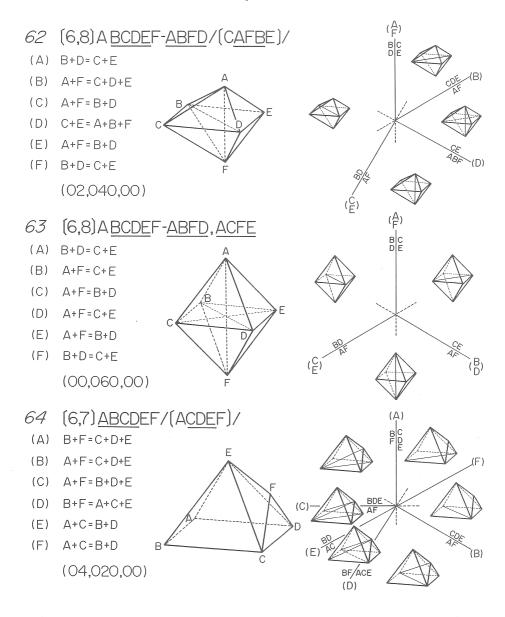


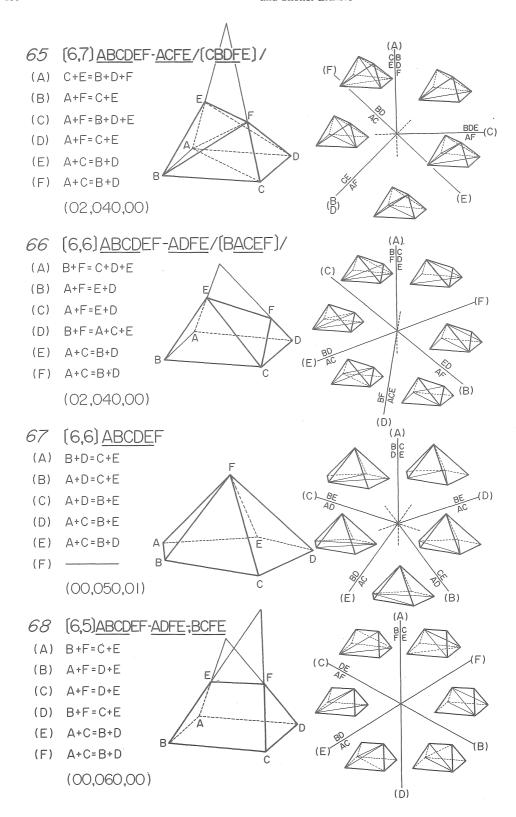












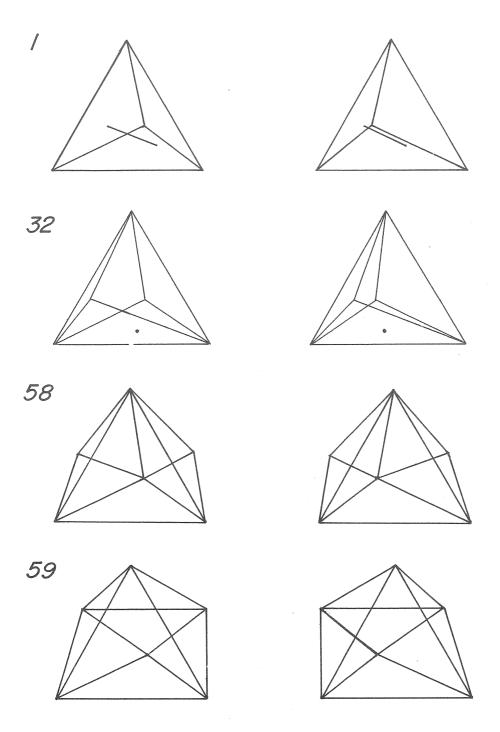


Fig. 4 Stereoscopic figures illustrating compositional relations of phases of invariant assemblage types Nos. 1, 32, 58, and 59, which are not degenerated.