

**USE OF K-DIMENSIONAL SPACE, « AFFIGRAPHY », TO PREDICT  
PHASE DIAGRAM STRUCTURE FOR N-COMPONENT, (N + K)-  
PHASE MULTISYSTEMS**

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## ABSTRACT

This paper discusses new algebraic methods to predict the qualitative structure of (P, T) and similar type phase diagrams. Chemical multisystems are considered that have  $n$  independent chemical components and  $n + k$  phases, with no solution. Graphical representations are developed by use of composition and reaction matrices, and based on equilibrium thermodynamics. The problem is expressed in terms of the optimum of the G function, written in a (linear) programming problem. Two types of duality between the representations are stressed, in the geometric and algebraic (or combinatorial) sense. The construction of phase composition space (chemography), reaction space and chemical potential saturation space is discussed in the general framework. A new type of space, in combinatorial and geometric duality with the chemography is introduced: the « *affigraphy* ». The thermodynamic meaning of affigraphy originates from adding to the condition that  $n$  phase assemblages are obtained at optimum or equilibrium, the condition that the  $k$  remaining phases cannot appear; this is expressed by the positivity of the  $k$  affinities of the dissociation of these phases. Affigraphy is organized by the affinity vectors of  $k$  independent chemical reactions around an hyperinvariant point in a  $k$ -dimensional space; the vectors are the column vectors of the chemical reaction matrix. As a « *fundamental theorem* », it is demonstrated that the intersection of the affigraphy space by a two-dimensional plane gives the structure of the feasible (P, T) diagrams. Several consequences of this result are outlined on simple examples. Aspects of the structure of  $n + 3$ ,  $n + 4$  and  $n + 5$  systems are discussed; a thermodynamic understanding and generalization of Zen's polyhedra is proposed. A rule for predicting all the possible stability successions on univariant lines for  $n + k$  systems is given. Other results on the prediction of stability sequences in multidimensional domains, on the structure of degenerate systems, as well as ways of generalization and new types of diagrams are proposed. The qualitative Schreinemakers' rules for two-dimensional diagrams are seen as consequences of the laws that rule the arrangements of vectors and hyperplanes in the affigraphy. New algorithms to construct phase diagrams are proposed, that may particularly be useful when only a partial set of data on the system is available.

*Key-words:* multisystems; phase diagrams; duality; chemography; affigraphy; chemical affinity; mathematical programming; Schreinemakers rules; Zen polyhedra; potential solutions; degenerate systems; metastability successions; closed net; pseudosections;  $n+4$ ;  $n+5$ ;  $n+k$

## INTRODUCTION

Numerous works have been dedicated to the understanding of the qualitative structure<sup>1</sup> of phase diagrams; elementary information on the graphical representation of chemical systems may be gained, without quantitative thermodynamic data, provided the composition of the phases is known. Gibbs phase rule (Gibbs, 1876, 1878) provides first information of this type; in the general case in a two parameter pressure-temperature diagram, and if  $n$  is the number of independent chemical components, the domains of the plane correspond to  $n$ -phase assemblages, the limits between these domains correspond to chemical reactions that associate  $n + 1$  phases and, at the invariant points,  $n + 2$  phases co-exist. Combinatorial analysis easily allows the counting of the possibilities to choose groups of  $n$ ,  $n + 1$  or  $n + 2$  phases among the  $n + k$  possible phases. In his work at the beginning of the century, Schreinemackers (1915-1925)<sup>2</sup> pursued this analysis and in particular showed how in (P,T) diagrams the lines corresponding to the chemical reactions are ordered around the invariant points, depending on the composition of the phases involved. This work has been exposed and discussed by Zen (1966a, 1966b, 1967) for its application to the mineralogical assemblages relevant to earth sciences. After studying  $n + 2$  systems and the organization of reactions around invariant points, Zen studied the more complex  $n + 3$  phase systems. Invariant points themselves are organized in the (P, T) plane depending on the composition of the phases. « *Polyhedra* » and « *closed nets* » were introduced as tools to understand this structure and to predict the finite set of the possible diagrams to which the real physical diagram of the particular system will belong. The observation of the co-existence or of

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<sup>1</sup> Expression « *qualitative structure* » or « *structure* » will often be preferred to « *topology* » frequently used in the same meaning; the combinatorial aspect seems more important than the properties of continuity, frontier and so on, allowing to speak of topology; this last word is generally not used in its proper mathematical meaning; from a mathematical point of view it would be more correct to speak of « *combinatorial geometry* » or « *matroidal structure* ».

<sup>2</sup> 29 papers have been published by Schreinemackers during the years 1915-1925, in the Proceedings of Koninklijke Akademie van Wetenschappen Te Amsterdam, under the general title: « *In-, Mono-, and Di-variant Equilibria* »; they will be designated here by Schreinemackers, 1915-1925; only the first and last paper of this series are reported in the list of references. A complete collection of the papers has been gathered by the Pennsylvania State University, University Park, Pennsylvania, June 1965, 322 p.

the incompatibility of phases in natural systems may allow one to choose the most likely diagram. Such an approach has been followed by Burt (1972) and explained on a general standpoint by Korzhinskii (1959). A few authors recently set forth rules that apply to the still more complex  $n + 4$  phase systems (Guo, 1980 a, b, c, 1981, 1984, Guo and Chen, 1982; Uzdansky, 1987). The utility of structural studies has been emphasized for a long time; it allows to put order in the observations, in the results of experimental studies and calculated predictions whose precision is always limited. It also allows to make qualitative predictions. In Ferry ed. (1982) a general introduction to the graphical representation of phases can be found. The structural properties of phase diagrams have been discussed in many other fields, especially in metallurgy (Prince, 1963).

## 1. OUTLINE

In the present work, similarly to the previous authors, we are still first interested by the *qualitative properties* of the diagrams. The approach presented is theoretical but the main results are rather simple. A general outline is now given, with little mathematics, to help introduce the reading. Chemical systems (or « multisystems ») are considered that contain  $n$  independent components, with which  $n + k$  different species may be built. Each of them will correspond to a physically distinct phase, as it is the case for the multiphase assemblages met in geology. So the species will be termed phases and there will be one component per phase. The case of solid (or liquid) solutions will not be treated on a general standpoint. The composition of the  $n + k$  phases in the  $n$ -component system can be described in an  $n \times (n + k)$  chemical composition matrix,  $C$ . Composition vector of any phase will be designated by the name of the phase. A list of symbols and vector and matrix notations is given at the end of the paper.

As generally understood, phase diagrams such as (P, T) diagrams, represent the univariant equilibria that may be obtained between different sets of generally  $n + 1$  phases belonging to a given chemical multisystem. In order to construct the univariant curves, the possible equilibria are usually considered one by one in the literature; for each of them equations of the type  $\Delta G(P, T) = 0$  are written, where the variation

in Gibbs free energy relates both sides of the chemical reaction. In a linear approximation, Clapeyron relations allow to compute the slopes of the univariant lines.

### 1.1. Basic choices

At variance with the last point of view, phase diagrams will be considered here as *geometrical two- or three- dimensional views onto a given multidimensional structure taken as a whole and described by a single mathematical problem*<sup>3</sup>. This problem reflects a thermodynamic problem as follows: let a closed system be defined by the  $n$  quantities of  $n$  independent components; the information is given that  $n + k$  phases may be constructed. Pressure  $P$  and temperature  $T$  are fixed. The problem is to know what will be the contents in the  $n + k$  phases at thermodynamic equilibrium, depending on both the overall system composition and the values of pressure and temperature. There are  $n + 2$  physico-chemical parameters ( $n$  composition parameters plus  $P$  and  $T$ ) on the system allowing to compute the  $n + k$  unknowns. As will be illustrated in the text, the problem will be set as a *mathematical programming problem*: minimize the Gibbs free energy of the whole system dependent on  $n + 2$  parameters. This minimization method is less often used than writing the different mass action laws for each of the relevant chemical reactions, but is equivalent (e.g. Smith and Missen, 1982). When changing the values of  $P$  and  $T$  and the system composition as parameters, the mineral associations will change. This will eventually define different domains in the  $P, T$  space and boundary univariant curves of the phase diagram.

In parallel to the last point of view, the important choice will be done to *disconnect the algebraic structure of the problem from the thermodynamics*, or to *disconnect the mathematical variance of the system from its physical one*. If the mathematical structure of the problem is considered independently of the physical parameters  $P$  and  $T$ ,  *$k$  independent parameters instead of two can be taken*; they are the lacking parameters to the  $n + k$  unknowns, when the  $n$  initial content constraints have been taken into account. Algebraically, there are

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<sup>3</sup> Although the word « *diagram* » is restricted to a two or three-dimensional space that can be graphically represented, it may sometimes be used by extension in the place of the word « *space* » for dimension greater than three.

indeed  $k$  independent chemical reactions whose  $\Delta G$ 's can be taken as  $k$  independent parameters to completely characterize the system, although the  $\Delta G$ 's eventually all depend on two parameters  $P$  and  $T$ .

Multidimensional mathematical spaces will be considered whose appropriate intersection or projection provide the searched two-dimensional representations or phase diagrams. The  $n$ -dimensional *chemography* depicts the phase relations in the system given by the columns of  $\mathbf{C}$  matrix. For  $n \leq 3$  concentrations may be represented in a plane; when  $n = 4$ , a tetrahedron may still be viewed in two dimension; for higher values of  $n$ , chemography is no longer directly representable in a single view. When considering now the chemical reactions, a *k-dimensional space may be defined* where the opposite of the  $\Delta G$ 's of the  $k$  independent reactions chosen are represented. In a first step, it will be considered that this choice is possible independently of the usual two parameters  $P$  and  $T$ .

In order to choose  $k$  specific reactions a convenient way is to select first a  $n$ -phase basis, i.e. a set of  $n$  independent phases in the algebraic sense allowing to write the composition of all the phases. The  $k$  remaining phases allow to define  $k$  chemical reactions corresponding to the dissociation of each of them in the  $n$ -phase basis; each of the  $k$  reactions is written with the corresponding phase on the left and a combination of the basic  $n$  phases on the right. When the basis is changed, the new writing of the reactions is computed by elementary matrix operations.

### 1.2. Absent phase vectors

The  $-\Delta G$ 's quantities are equivalently considered as the affinities of the dissociation of the  $k$  phases. They are analogous to the « *standard affinities* » defined in Prigogine and Defay (1946) for the reactions from which phases are constructed from a given set of basic phases. The affinity of dissociation of phase  $M$  is noted as  $A^{(M)} = -\Delta G^{(M)}$ ; extending the conventions used in the literature on multisystems, phase  $M$  is written between brackets because its dissociation or disappearance is considered. If the affinity is positive, the corresponding reaction leads to the absence of the phase. In the  $k$ -dimensional space, one unitary or basic vector may be defined for each affinity and called « *absent phase vector* »: the affinity is unity for this reaction and zero for the other

reactions of the  $k$  independent affinity set. The basic affinity vector may also be noted as  $\mathbf{A}^{(m)}$  in bold or  $\langle \mathbf{A}^{(m)} \rangle$  or similarly to the composition vectors, the absent phase vectors will be designated by the name of the phase between brackets, such as  $(M)$ ; the notation is the same as for the scalar affinity of the dissociation reaction of phase  $M$  but there is no ambiguity in general. The  $k$  unit affinity vectors of the chosen  $k$  reactions will define a basis of the  $-\Delta G$ 's or total affinity space. The co-ordinates of the system affinity vector are the values of the affinities for the  $k$  independent reactions chosen reported along the  $k$  basic unit affinity vectors, in vector  $\underline{a}$ . In order to identify it from the  $n$ -phase basis, the  $k$  basis may be called a *co-basis*. Thanks to matrix operations, unit affinity vectors may be defined for all the possible  $n + k$  phases in the  $k$ -dimensional co-basis and total affinity vector  $\mathbf{A}^{\text{tot}}$  may be defined by its  $n + k$  coordinates on the  $n + k$  unit affinity basis. When the phases present in the system are  $A, B, C, \dots$ , their mole numbers verify  $x_A > 0, x_B > 0, x_C > 0, \dots$  and  $A^{(A)} = 0, A^{(B)} = 0, A^{(C)} = 0, \dots$ . Then the absent phases  $M, N, P, \dots$  verify  $x_M = 0, x_N = 0, x_P = 0, \dots$ , and  $A^{(M)} > 0, A^{(N)} > 0, A^{(P)} > 0, \dots$ . This can also be expressed as  $A > 0, (A) = 0$  for the first group of  $n$  phases and  $M = 0, (M) > 0$  for the second group of  $k$  phases. The  $k$ -dimensional space of the  $\mathbf{A}^{(m)}$  will be called « *affigraphy* » (Guy and Pla, 1992). The independent chemical reactions may be described in an  $k \times (n + k)$  chemical reaction matrix  $\mathbf{R}$  where the coefficients of the  $n + k$  phases (columns) are written for each reaction (lines). If the composition matrix  $\mathbf{C}$  has been written with an  $n$ -phase basis, the reaction matrix may be written with the help of the other  $k$  phases as a co-basis. The  $k$  remaining phases may be constructed with the  $n$  phases in the basis; they thus define  $k$  chemical reactions. Generic element  $r_{if}$  of  $\mathbf{R}$  matrix ( $k$  rows;  $n + k$  columns) is the coefficient of phase  $i$  in reaction  $f$ . Matrix  $\mathbf{R}$  is written with the help of matrix  $\mathbf{C}$  in duality as explained in the appendices.

As an important result, *the  $n + k$  unit affinity vectors in  $k$ -dimensional affigraphy behave like the column vectors of matrix  $\mathbf{R}$* ; it is analogous to the case of chemography where present phase vectors are given by the columns of  $\mathbf{C}$  composition matrix. The physical unit used to measure the unitary affinity is the same as that used for the free energies and chemical potentials.

### 1.3. H<sub>2</sub>O system

The discussion of a simple example on a  $k = 2$  system will give a first understanding. In that case the dimension of affigraphy and of the (P, T) diagram are the same and the two diagrams coincide thanks to a change of co-ordinates. The H<sub>2</sub>O system is a one component - three phase (solid, liquid and vapor) system whose composition **C** matrix is

	l	v	s
l	1	1	1

where liquid l is chosen as the basis; the composition of v and s with respect to l is indicated in the second and third columns of the matrix. Well-known pressure - temperature diagram is represented in Fig. 1A. There is one invariant point. The three univariant lines radiating from it are named by the absent phases in the corresponding reactions, (v), (l) and (s) respectively. The two-dimensional domains limited by the lines may also be defined by the absent phases. In the domain where liquid is stable, the solid and the vapor are lacking; it is noted by (v, s) and is limited by the two lines (v) and (s) corresponding to the reactions  $s = l$  (v lacking) and  $v = l$  (s lacking) respectively. And so on for the other domains (s, l) and (v, l) for the vapor and the solid.

The affinities of the dissociation of the phases with respect to the liquid basic phase are  $A^{(v)} = g^v - g^l$ ,  $A^{(s)} = g^s - g^l$  corresponding to reactions  $v = l$  and  $s = l$  respectively. The basis is here reduced to one phase: the liquid l, and the co-basis is two-dimensional with two absent phases (v) and (s) as unit vectors. The quantities of solid, liquid and vapor in the system are  $x_s$ ,  $x_l$  and  $x_v$  respectively. The following relations hold in the liquid domain:

$$x_v = 0, A^{(v)} > 0$$

$$x_s = 0, A^{(s)} > 0$$

$$x_l > 0, A^{(l)} = 0$$

The interconnected directions of the three vectors depicting the univariant lines are given by the columns of the  $(k \times (n + k)) = (2 \times 3)$  reaction matrix; two independent reactions are written in lines, the three



phases are read in the columns; the coefficients are those in the two independent reactions:

	(l)	(s)	(v)
(s)	-1	1	0
(v)	-1	0	1

The notation of line and column indices is given between brackets. Contrary to the ordinary notation of reaction matrix, we have reported here the relations between the three vectors (l) (s) and (v) (or  $\mathbf{A}^{(l)}$ ,  $\mathbf{A}^{(s)}$  and  $\mathbf{A}^{(v)}$ ) in the basis (s), (v). Vector  $(-1, -1)^T$  indeed represents  $\mathbf{A}^{(l)}$  in the basis  $\mathbf{A}^{(s)} (1, 0)^T$ ,  $\mathbf{A}^{(v)} (0, 1)^T$  and the three vectors  $\mathbf{A}^{(v)}$ ,  $\mathbf{A}^{(l)}$  and  $\mathbf{A}^{(s)}$  do represent the diagram of water with the right definition of reactions and domains. *We are thus able to find back a known phase diagram by a specific use of the reaction matrix.*

#### 1.4. Chemical reactions in the k-dimensional frame; (P, T) diagrams

The same method will be followed and extended, for the case when k is arbitrary and greater than 2. Affigraphy may be viewed as a generalization of the two dimensional structure around the invariant point described for  $k = 2$ , defined by the  $n + k$  column vectors of the chemical reaction matrix representing each an absent phase. The situation for  $k = 2$  is particular because the reactions are defined by just one absent phase and so coincide with the absent phase vectors. In the general case, the chemical reactions will be varieties defined by collections of  $k - 1$  absent phase vectors ( $= n + 1$  present phases in a reaction). This is the definition of hyperplanes in the affigraphy i.e.  $k - 1$  dimensional varieties in a k-dimensional space, where a linear variety is the multidimensional generalization of a line, surface etc. The chemical reactions are read as the lines of the chemical reaction matrix and in k-dimensional space correspond to all the possible ways to gather  $k - 1$  unit affinity vectors among the  $n + k$ . We will call « *basic hyperplanes* » the hyperplanes constructed with the basic affinity vectors; they contain the origin (other hyperplanes may be envisaged not containing the phase absent vectors and in general position).

In the  $\text{H}_2\text{O}$  reaction matrix, the two independent reactions are  $s = l$  and  $v = l$ . They correspond to the absence of v and s respectively. However, the corresponding lines are named (s) and (v) and not (v) and (s). The horizontal index does not refer here to the whole line as usual for a reaction matrix but merely

refers to affinity vector co-ordinates. In composition matrix a line index also refers to vector co-ordinates and not to the whole line. With the new type of notation, the two matrices **C** and **R** are on an equal footing. In affigraphy, the definition of the equation of an hyperplane (corresponding to a chemical reaction) must be distinguished from the co-ordinates of a vector. In the case  $k = 2$ , the hyperplane (a line) in the equation of which the coefficient of  $(v)$  is zero is perpendicular to the other basic vector  $(s)$ <sup>4</sup>. So the line contains vector  $(v)$  which is perpendicular to  $(s)$ . *From a general point of view, hyperplane representing chemical reaction  $\{(A), (B), (C) \dots\}$  where the named phases are absent in the reaction, contains affinity vectors  $(A), (B), (C) \dots$*

One essential result of the paper is that *chemical reaction matrix may be read in columns*. For a given chemical system at equilibrium, a duality is observed between, on the first hand, the association of  $n$  phases in equilibrium (paragenesis) pointed in the chemography and defined by the domain limited by the corresponding vectors of the chemical composition matrix; and on the second hand, the  $k$  absent phases (remaining from the complete  $n + k$  set) that belong to the affigraphy domain limited by the corresponding absent phase vectors of the chemical reaction matrix. Conversely, a meaning may be given to the lines of the composition matrix: they give the equations of the limits between  $n$ -phase sets in the chemography as explained in App. 2.

If one now gets back to the ordinary two-dimensional  $(P, T)$  phase diagrams, the  $k$  affinities or  $-\Delta G$ 's of the basic reactions are not actually independent; only two of them are, since all the  $g$ 's depend on  $P$  and  $T$ . Geometrically, this corresponds to an intersection of affigraphy with a two dimensional plane. We are then driven to *the essential theorem that, in the linear approximation where the values of the  $g$ 's are linearized in  $P$  and  $T$ , the  $(P, T)$  diagrams result from the intersection of the affigraphy vectors by two dimensional planes*. This is a ready way to predict the structure of phase diagrams. The univariant lines correspond to the intersection of the two-dimensional plane with the affigraphy hyperplanes. The invariant points result from the intersection of  $k - 2$  vectors with the two-dimensional plane, or equivalently from the intersection of two hyperplanes. This method allows generalizations for the correlation between chemical reactions and absent phase vectors that could not be done while remaining in a two dimensional diagram where the analogy works only for  $k = 2$  (in that case the  $(P, T)$  diagram comes down to the affigraphy).

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<sup>4</sup>For simplicity we speak of perpendicularity between two vectors although no scalar product is defined. The underlying property is that some of the co-ordinates of the two vectors are zero and the others non zero, such that the sum of the products of corresponding co-ordinates is zero. In the same manner, we can speak of a vector perpendicular to an hyperplane. In Fig. 1, basic affinity vectors are not drawn perpendicular to one another.

### 1.5. Example of sulfur system ( $n = 1$ , $k = 3$ )

This may be enlightened on an example with  $k = 3$ ; let us take a simple  $n = 1$  system as for instance the sulfur system (four phases  $S_\alpha$ ,  $S_\beta$ ,  $S_{\text{liquid}}$  and  $S_{\text{vapor}}$ ) described by the composition matrix

	$S_\alpha$	$S_\beta$	$S_l$	$S_v$
$S_\alpha$	1	1	1	1

Here, the affigraphy is three dimensional and composed of four vectors representing each an absent phase organized according to the columns of the corresponding reaction matrix:

	$(S_\alpha)$	$(S_\beta)$	$(S_l)$	$(S_v)$
$(S_\beta)$	-1	1	0	0
$(S_l)$	-1	0	1	0
$(S_v)$	-1	0	0	1

where  $(S_\alpha)$  represents affinity vector  $A^{(S_\alpha)}$  and so on. The basis is defined by  $S_\alpha$  and the co-basis by the three other phases. According to the preceding theorem, the cutting by a two-dimensional plane gives the structure of a possible  $P$ ,  $T$  phase diagram, Fig. 1B. The diagram has the known structure of the sulfur diagram; the univariant lines are defined by two absent phase vectors, and the invariant points by one absent phase vector. The construction gives a method to define stability levels as will be discussed thoroughly below. More complicated examples than for  $n = 1$  will also be discussed in the rest of the paper (e.g. Fig. 31).

In brief, *the ordinary two dimensional phase diagram is immersed in a higher  $k$ -dimensional space, representing the absence of the phases as measured by their dissociation affinity*, in the sense we have given. In a way, this is possible thanks to a mathematical extension of the meaning of ordinary parameters such as  $P$ ,  $T$  and  $A$ .

### 1.6. Contents of the paper

In spite of, or because its simplicity, the preceding theorem leads to a great number of consequences. It may allow to predict the structural properties of phase diagrams currently demonstrated in the literature by

pieces of reasoning adapted to each property: it may for instance forecast the Schreinemakers laws on the arrangements of univariant lines around invariant points, give a proper theoretical understanding of Zen's polyhedra in the case  $k = 3$ , give a general rule to prognosticate all stability successions along univariant lines for arbitrary value of  $k$ . Similarly, Guo's, Usdansky's etc. rules on  $n + 4$  systems will find suitable explanation therein. The understanding and predicting of potential solutions will be readily achieved as well as the properties of degenerate systems; the present framework will provide insight on systems with solid solutions. Also, ways of rigorous generalization for phases with negative quantities of some of their components and corresponding reactions will be provided. The connection between several types of diagrams, namely composition diagrams, chemical potential saturation diagrams, chemical potential grids, reaction space, affigraphy and (P,T) diagrams will be enlightened with indication of new types of diagrams. An algebraic approach to affinity will be proposed. At last, schemes for new algorithms for constructing phase diagrams, with the possible account of a limited amount of data will be provided.

It is the objective of the paper to present the mathematical tool allowing to predict all the listed structural properties and discuss the general structure of phase diagrams. The proposed approach does not render the complicate problems more simple but at least provides a systematic way to handle them. A still more abstract approach based on matroid theory (Guy and Pla, 1986; Pla, 1989a) is developed closely parallel to the one presented here and will be published in a separate paper (Guy and Pla, in prep.); the questions related to the qualitative positioning of the chemical or algebraic items (phases, reactions etc.) with respect to one another in the diagrams, and to the subsequent counting and enumeration of the solutions of the problems of interest will be discussed therein.

The affigraphy approach has proven very fertile and it was not possible to examine in detail all its consequences, even on problems of common application, nor to re-examine with this idea all the literature on phase diagrams. We leave this for the future and for those readers interested with whom we shall be disposed to communicate. An however large number of applications has been discussed in the present paper, even briefly, based on the consideration of simple examples that are

model systems to natural systems. Some of them are discussed in detail from an algebraic point of view so as to make the reader understand the theory. The main part of the paper is made of sections 2, 3 and 4 (examples) and 6 (P, T diagrams). The other sections are mostly other applications and are independent in a first approximation. Four mathematical appendices are given at the end as a theoretical support to the main text. Some sections written in small print are of technical and more limited character and may be omitted at first reading. The points exposed in the present section are developed for some technical aspects in following sections. One may prefer to go directly to Sect. 3.4 or 4.

## 2. THE PRIMAL PROGRAMMING PROBLEM

*Mathematical programming* theory has already been applied for predicting the thermodynamic equilibrium in complex systems (e.g. Smith and Missen, 1982); the use of the mathematical programming concepts in the present paper is new because mostly geometric and qualitative. Mathematical programming and especially linear programming has been applied in earth sciences for different purposes (e.g. Gordon 1973, Greenwood, 1967) that will not be discussed here.

In the composition  $(n \times n + k)$  matrix  $\mathbf{C}$ , the rows refer to chemical components (number:  $n$ ) and the columns to the phases (number:  $n + k$ ): generic element  $c_i^j$  is the number of moles of chemical component  $i$  contained in one mole of phase  $j$ ; a set of  $n$  independent phases may equivalently be chosen instead of the  $n$  basic components. A priori, a chemical system is defined by the  $n + k$  mole numbers  $x_j$  of the possible phases in the system: they define the column vector  $\mathbf{x}$  ( $j = 1, \dots, n + k$ ); vectors and matrices will be written in bold. In the closed systems being considered, the total amount (in number of moles)  $\underline{c}_i$  of each of the  $n$  chemical components  $i$  is constant<sup>5</sup>. This defines column vector  $\underline{\mathbf{c}}$  ( $i =$

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<sup>5</sup> Thanks to matrix operations discussed in the text, the  $n + k$  dimensional vectors will be projected onto lower  $n$ - or  $k$ - dimensional subspaces. In order to avoid confusion with  $n + k$  dimensional vectors, vectors in lower  $n$ - or  $k$ - dimensional subspaces may be underlined. The values of the co-ordinates of  $\underline{\mathbf{c}}$  are dependent on the choice of the basis used to write composition matrix  $\mathbf{C}$ .

1,..., n)<sup>6</sup>. The whole range of the possible system compositions will be obtained by varying the  $\underline{c}_i$  and taking them as parameters. The values of the molar Gibbs free energies of the  $n + k$  phases will be noted as  $g^j$  (row vector  $\underline{g}$ ) in arbitrary units (joule for instance); we said that we ignored the thermodynamic data of the phases and, in the sequel, the  $g^j$  will also be taken as parameters.

Thermodynamically, the chemical equilibrium for specified  $P$  and  $T$  is obtained for the minimum of the Gibbs free energy of the whole system, with the constraints given by the conservation of chemical components and the positivity of the mole numbers. This reads:

$$\begin{aligned} \text{Min } G &= \text{Min } \underline{g}\underline{x} = \text{Min } \sum_{j=1}^{n+k} g^j x_j \\ \underline{C}\underline{x} &= \underline{c} \\ \text{(P)} \quad \underline{x} &\geq 0 \end{aligned}$$

The first line expresses the minimum condition, the second the conservation constraint and the third the condition of non-negativity of the phase contents. Problem (P) is called a linear programming problem because the constraints and the  $G$  function (cost or objective function) are linear forms on the variables (e.g. Pla, 1980, Jeter, 1986); the program is in its so-called standard form. The linearity of the objective function holds for systems where the phases have no solution, a situation common in a first approximation for many geological examples; if there is solution, this is no longer true since the molar free energies non-linearly depend on composition parameters (this frequent case is solved by specific algorithms, e.g. Smith and Missen, 1982); although it was mentioned that the case with solution would be avoided, some general information will be gained, even if the programming problem is non linear and without solving it completely. The important in our case is

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<sup>6</sup> The  $n + k$  or  $n$ - dimensionality of the composition for  $\underline{x}$  and  $\underline{c}$  spaces may be reduced by one by considering concentrations or mole fractions instead of mole numbers. In which case an additional condition is verified  $\sum_{j=1}^{n+k} x_j = 1$  or  $\sum_{i=1}^n c_i = 1$ ; this gives the equation of an hyperplane which, as already reminded, is a linear variety of dimension  $n - 1$  when  $n$  is the dimension of the space: mathematically, this operation is thus equivalent to cutting the composition vectors by an hyperplane and shifting from a linear (or vectorial) to an affine representation. In the following, both representations will be used and discussed separately if necessary.

that the Gibbs free energy function is convex and differentiable (see Dantzig, Johnson and White, 1958, White, Johnson and Dantzig, 1958).

Vector  $\mathbf{x}$  will be said a solution of (P) if it verifies  $\mathbf{Cx} = \underline{\mathbf{c}}$ . A solution  $\mathbf{x}$  will be said (primal) feasible if it verifies both constraints ( $\mathbf{Cx} = \underline{\mathbf{c}}$ ,  $\mathbf{x} \geq 0$ ). The so-called optimal solution  $\mathbf{x}^*$  also verifies the first condition. In a set of phases called a basis, the chemical composition of the system may be expressed by an independent combination in the algebraic sense of the « *basic* » phases. The basis will be said to be feasible if the coefficients  $x_j$  of the corresponding linear combination for the bulk system are positive. We can simply speak of a feasible basis. In matrix  $\mathbf{C}$ , the set of column indices of all the phases will be called  $M$ ; the set of the indices of the phases defining a basis will be called  $I$  and the set of the remaining indices will be called  $M-I$ . In general, the cardinal (i.e. the number of elements) of  $I$  is  $n$  and that of  $M-I$  is  $k$ . By extension, one may speak of an index in a basis when the phase is present in the corresponding association.

### 3. OPTIMUM CONDITIONS; THE AFFIGRAPHY

Detailed results of Mathematical Programming are exposed in Appendix 1. So-called « *simplex tableau* » that gathers all the information on the system (the objective function and the constraints) is presented. The following is mostly a consequence of the use of this tableau. Optimum solution is a basic solution that verifies two groups of conditions; the first conditions express the so-called primal feasibility and read

$$x_j \geq 0 \text{ for } j \text{ in the basis, } j \in I; n \text{ conditions}$$

and

$$x_j = 0 \text{ for } j \text{ outside the basis, } j \in M - I, k \text{ conditions}$$

The second group of conditions are the so-called dual feasibility conditions and may be expressed in our case by

-  $\Delta G^0 > 0$  for  $j$  outside the basis  $j \in M - I$ ,  $k$  conditions

and

-  $\Delta G^0 = 0$  for  $j$  in the basis  $j \in I$ ,  $n$  conditions

where the  $\Delta G^0$  is Gibbs free energy for the dissociation reaction of phase  $j$  as expressed in the  $n$ -phase basis  $I$ , as announced in Sect. 1. Each of these two groups of conditions are now examined.

### 3.1. First group of optimum condition; the structure of chemography

The first group of conditions implies that at equilibrium  $x$  belongs to a  $n$ -dimensional space, and is a conic convex linear combination of the phases defining the basis of this space; it is merely a convex combination when concentrations are considered that verify  $\Sigma x = 1^7$ . *Different possible  $n$ -phase representations are linearly dependent and equivalent thanks to matrix operations, and the system composition may be represented in one of them.* Such an  $n$ -dimensional space is called the *chemography*. The  $n$ -dimensional spaces corresponding to different possible equilibria all belong to the total  $(n + k)$ -dimensional composition space of the  $x$ 's. In the projection onto one of them chosen to represent all the compositions, (the chemography), they will overlap. This is not a problem as long as the equilibrium is defined by only  $n$  phases. In some particular cases where for instance the system is just at a reaction defined by  $n + 1$  phases, the preceding representation loses some information. Other spaces are then necessary to fully represent the proportions of the  $n + 1$  phases (Sect. 13). A domain of the chemography corresponds to the presence in the system of the phases limiting the domain for given  $P$  and  $T$  conditions.

A specific representation basis of phases may be chosen and termed  $I_0$ . By changes of bases, all the possible representations may be computed. Each column vector of  $C$  refers to a « *present phase* ».

It is useful to the general understanding of the paper to discuss the equations of the limits between the chemography domains. As an example, six phases are considered in an  $3 + 3$  system,  $A, B, C, D, E$

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<sup>7</sup> A conic convex combination of algebraic elements is a linear combination of these elements with all coefficients positive; it is simply convex when the sum of the positive coefficients amounts to 1; refer to Appendix 1.



and F in Fig. 2. The composition of the phases in the A, B, C basis is given by the matrix:

	A	B	C	D	E	F
A	1	0	0	0.4	0.4	0.2
B	0	1	0	0.2	0.4	0.4
C	0	0	1	0.4	0.2	0.4

In general, limits between chemography domains are hyperplanes gathering  $n - 1$  phases. The equations of such geometric varieties, here lines such as BC or BF for  $k = 3$  affine representation (Fig. 2), are given by the lines of matrix **C**. This is explained in detail in Appendix A2.1. The equation of line BC is given by  $A = 0$ , read in the first line of the matrix; phases B and C are absent in the equation. The phases D, E and F do not appear in the restriction of the line equation in the basis {A, B, C}. Other chemography boundaries are computed after basis changes in the matrix as illustrated in the appendix.

### 3.2. Second group of optimum conditions; definition of affigraphy

The second group of optimum conditions deals with  $k$  reactions whose  $\Delta G$ 's must be negative; the completion of these reactions would allow the synthesis of the  $k$  phases lacking at equilibrium. This is thermodynamically forbidden or, the presence of the phases is metastable. If an affinity is defined by  $A^{(j)} = -\Delta G^j$  for the dissociation of phase  $j$  in the basis, it must be positive; the conditions stated above are simply rewritten:

$$A^{(j)} \geq 0 \text{ for } j \text{ outside the basis, } j \in M - I, k \text{ conditions}$$

and

$$A^{(j)} = 0 \text{ for } j \text{ in the basis, } j \in M, n \text{ conditions}$$

The conditions express that total chemical affinity  $A^{\text{tot}}$  of the system belongs to a  $k$  dimensional space, and is a conic combination of the elementary dissociation affinities. Similarly to the composition space, *the different possible  $k$ - absent phase representations are linearly dependent*

and equivalent thanks to matrix operations and the system affinity may be represented in one of them. The k-dimensional diagram of affinities has been called the *affigraphy*; the physical meaning of this mathematical space will be submitted to restrictions discussed in the sequel. When an arbitrary basis  $l_0$  has been chosen as a representation basis in the chemography, a natural representation basis or co-basis for the affigraphy is  $M - l_0$ .

The k-dimensional spaces corresponding to different possible equilibria all belong to the  $(n + k)$ -dimensional total affinity space of the  $A$ 's. In the projection onto one of them chosen to represent all the affinities, (the affigraphy), they will overlap. This is not a problem as long as the equilibrium is defined by only k absent phases. In some particular cases where for instance the system is defined by  $k + 1$  absent phases because of composition or thermodynamic degeneracy (see below), the preceding representation loses some information. Other spaces are then necessary to fully represent the proportions of the  $k + 1$  absent phases (Sect. 13).

Within the algebraic frame, the thermodynamic chemical potentials of the phases and of the elements may be defined by row vectors  $\mu$  ( $n + k$  co-ordinates) and  $\underline{\mu}$  ( $n$  co-ordinates) respectively (see appendix A1); the potentials are related by  $\mu = \underline{\mu}C$  where  $C$  is composition matrix. The dissociation reaction of phase  $P_j$  in the basis  $l_0$  reads

$$P_j = \sum_{i=1}^n c_i^j P_i$$

where the summation is taken on the  $n$  phases  $P_i$  of the basis. At thermodynamic equilibrium the same relation holds between the potentials of the phases and

$$\mu^j = \sum_{i=1}^n c_i^j \mu^i$$

If the system is in basis  $l_0$  then each of the  $\mu$ 's of the phases in the basis is equal to the corresponding  $g$  and the potential of the absent phase is given by

$$\mu^j = \sum_{i=1}^n c_i^j g^i$$

With the help of chemical potentials, the k basic affinities may thus be interpreted in another way. The affinities of the basic dissociation reactions are defined by

$$A^j = -(\mu^j - g^j) = g^j - \mu^j$$

where the  $g^j$  are the molar Gibbs free energies, and the  $\mu^j$  the chemical potentials of the phases. In the affinity, the left hand side phase of the above reaction is defined by its free energy (the phase is present), and the right hand side by its chemical potential (the

presence of the phase is not specified). We can also consider a system in basis  $I$  and wonder whether phase  $j$  added to the system will be stable. This depends on the sign of the affinity  $A^j$  written as above. In the paper the word affinity mostly refers to phase dissociation reactions written *in a specified phase basis*.

At optimum, the affinities corresponding to the dissociation of the phases belonging to the basis are equal to zero; the corresponding phases are present, and the potentials are equal to the energies. Conversely, the affinities for the  $k$  absent phases are positive; the corresponding phases are actually absent; the potentials are lower than the energies. The equilibrium is thus not precepted by the nullity of all affinities. The relations between the affinities may be expressed more precisely with the help of the chemical reaction matrix  $R$ . The useful relation is here  $R \cdot A^T = \underline{a}^T$  connecting the  $n + k$  dimensional total affinity  $A$  to the projected affinity  $\underline{a}$  in the  $k$ -dimensional affigraphy;  $\underline{a}$  represents the affinities of  $k$  independent reactions for specified values of  $P$  and  $T$ . This is in mathematical correspondance to the closed system constraint in composition representation  $C \cdot x = \underline{c}$ .

In Fig. 3, affigraphy corresponding to composition matrix of Sect. 3.1. is given. The equations of the hyperplanes corresponding to the different chemical reactions in the system are computed in App. A2.2. In this appendix, the relations between affigraphy vectors and hyperplanes is discussed. The different chemical reactions in the system are given by the lines of reaction matrix, written for the different choices of possible co-bases. All the corresponding hyperplanes intersect along the  $n + k$  column vectors of matrix  $R$ . Other representations of the affigraphy may be proposed. In Fig. 4A an affine representation of the affigraphy corresponding to Fig. 3 is given; in Fig. 4B and 4C, a convex polyhedron is constructed on the vectors of the affigraphy and in Fig. 4D another affine representation of the affigraphy is represented. The constructions are explained in the captions. Chemical reactions correspond to hyperplanes (dimension  $k - 1$ ) constructed in all the possible manners with the column vectors of  $R$  matrix; all the hyperplanes ( $C_{n+k}^{k-1}$  in number) intersect along the same  $n + k$  affinity vectors that are the column vectors of  $R$  matrix. The total number of chemical reactions is  $C_{n+k}^{n+1}$  because each chemical reaction associates  $n + 1$  phases among the  $n + k$  possible phases; in the affigraphy each hyperplane representing a chemical reaction contains  $k - 1$  vectors; the total number of such hyperplanes is the same as the previous number because

$C_{n+k}^{n+1} = C_{n+k}^{n+k-(n+1)} = C_{n+k}^{k-1}$ . The equations of all the hyperplanes describing all the possible chemical reaction in the system are obtained by use of the pivoting procedure described in Appendix 1 to have all the different possible bases of affinity space.

Affigraphy is in *combinatorial duality* with chemography. In other words, groups of  $k$  phases are considered that remain (or are supplementary) when sets of  $n$  chemography phases have already been chosen in the whole  $n + k$  set. The words primal and dual may be used in this combinatorial sense. In the same manner as affigraphy is defined from chemography, chemography may conversely be defined from affigraphy; this can be expressed in condensed form by  $\alpha = \chi^*$  where  $\chi$  designates chemography and  $\alpha$  affigraphy and the operation «  $*$  » means the combinatorial duality; conversely  $\chi^{**} = \alpha^* = \chi$ . Because of this duality any attribute of the chemography has an equivalent in the affigraphy, and conversely any property that is true for the affigraphy needs not be demonstrated for the chemography, provided the translation is done from one type of space to the other. The restatement of properties in one space from the other will not be done systematically. As an example: « *co-reactions* » will be written between reactions or, other said, « *reactions* » may associate  $k + 1$  absent phases of the affigraphy; they join  $n - 1$  present phases and correspond to the hyperplanes of the chemography. The equations of the « *reactions* » of the chemography thus give the boundaries of the different domains corresponding to the different bases and are obtained by reading the lines of matrix  $C$ . This result also expresses the duality between two types of chemical reactions, those produced by the variation of the free energies  $g$ 's of the phases, that is to say by the variation of the physical parameters  $P$  and  $T$ ; and those produced by the variation of the chemical composition of the whole system; this variation may be expressed by the contents  $c_j$  that are the dual quantities to the  $g^j$ , behind which are  $P$  and  $T$ . Some generalizations of the dual relations between chemography and affigraphy are proposed in Section 10.

### 3.3. General geometric approach to chemography and affigraphy

Another understanding of affigraphy and chemography may be gained by considering again  $(n + k)$ -dimensional composition and affinity

spaces. Different linear varieties of interest in composition  $\mathbf{x}$  space have the following nomenclature:

- linear variety  $\mathbf{C}\mathbf{x} = \mathbf{C}\mathbf{x}_0 = \underline{\mathbf{c}}$  is called  $V$ ; it is the intersection of  $n$  hyperplanes in a  $n + k$  dimensional space; its dimension is thus  $k$  if the hyperplanes are in a general position; it is parallel to  $\mathbf{C}\mathbf{x} = 0$ , named  $V_0$ , which defines the kernel or null space (e.g. Fisher, 1989) of the linear application ( $k$  is called the nullity). Lines of  $\mathbf{R}$  matrix generate the kernel  $V_0$  because  $\mathbf{C}\mathbf{R}^T = 0$  (Appendix A1).  $\mathbf{x}_0$  is the initial composition of the system.
- the  $n$ -dimensional image by  $\mathbf{C}$  of the  $n + k$  dimensional phase space, and containing the origin  $0$ , is called  $W_0$ ; it is orthogonal to  $V$ ; it is the space of the columns of  $\mathbf{C}$ ; it allows to shift from  $\mathbf{x}$  to its projection  $\underline{\mathbf{c}}$ . In the projection, unit vectors of the  $n + k$  dimensional composition  $\mathbf{x}$  space project along the  $n + k$  vectors of matrix  $\mathbf{C}$ .  $W$  is parallel to  $W_0$  and contains  $\mathbf{x}_0$ .

Similarly to those related to matrix  $\mathbf{C}$ , varieties may be defined as related to  $\mathbf{R}$  matrix acting on affinity  $\mathbf{A}^{\text{tot}}$ . The equivalent in affinity space of  $\underline{\mathbf{c}}$ , projection of initial composition, is  $\underline{\mathbf{a}}$ ; if  $P$  and  $T$  are known the  $g$ 's are known and so the affinities of  $k$  independent reactions; this defines vector  $\underline{\mathbf{a}}$ . In the generalized framework, one may conceive a  $\underline{\mathbf{a}}$  point independently of the physical parameters  $P$  and  $T$ .

- linear variety  $\mathbf{R}\mathbf{A}^T = \mathbf{R}\mathbf{A}_0^T = \underline{\mathbf{a}}$  is called  $V'$ ; it is parallel to  $V'_0$ :  $\mathbf{R}\mathbf{A}^T = 0$ , which is the kernel of  $\mathbf{R}$ ; it is the space of the lines of  $\mathbf{C}$ .  $\mathbf{A}_0$  is the total  $n + k$  dimensional initial affinity of the system.
- the  $k$ -dimensional image by  $\mathbf{R}$  of the  $n + k$  dimensional affinity space, and containing the origin, is called  $W'_0$ ; it is the space of the columns of  $\mathbf{R}$ ; in the projection unit vectors of the  $n + k$  dimensional  $\mathbf{A}$  space project along the  $n + k$  vectors of matrix  $\mathbf{R}$ .  $W'$  is parallel to  $W'_0$  and contains  $\mathbf{A}_0$ .

On both  $\mathbf{x}$  and  $\mathbf{A}$  sides, conventional relations  $\text{Im } \mathbf{C}^T = (\text{Ker } \mathbf{C})^\perp$  hold and connect spaces  $V$  and  $W_0$ , and  $W'_0$  and  $V'$  respectively (« Im » means image, « Ker » kernel and symbol «  $^\perp$  » means the orthogonal).

The combined representation of the system at optimum has a geometrical interpretation. On one hand, the mineralogical composition of the system, that one would at first define in an  $n + k$  dimensional space, may be represented in the  $n$ -dimensional space  $W$  of chemical components, the "chemography"; one shifts from  $\mathbf{x}$  to  $\underline{\mathbf{c}}$ . For  $\underline{\mathbf{c}}$  fixed,  $\mathbf{x}$

belongs to the  $k$ -dimensional variety  $V$  defined by conservation constraint  $Cx = \underline{c}$ . The projection  $\underline{c}$  of  $x$  onto the  $n$ -dimensional variety  $W_0$  perpendicular to that variety is independent of  $x$ . Initial composition  $x_0$  also projects on the same point. *It is natural to project  $x$  on that variety, because at equilibrium the system belongs to an  $n$  dimensional basis and also because the projected position is independent of the bases, i.e. of  $P$  and  $T$ .*

On the other hand, after  $n$  conservation constraints are considered,  $k$  pieces of information are lacking for the resolution of the problem to know the  $n + k$  components of  $x$ .  $K$  independent potentials are imposed through the choice of  $P$  and  $T$ ; in other words the affinities  $\underline{a}$  of  $k$  independent reactions give the lacking constraints. All chemical affinities fulfill the condition imposed by the choice of physical parameters  $RA^T = R.A_0^T = \underline{a}$ , where  $R$  is the chemical reaction matrix. It is  $n$  dimensional, and define space  $V'$ . In a similar way to what is done for the chemography, *it is natural to project the total affinity vector onto the linear variety  $W'_0$  perpendicular to  $V'$  because the projection of  $A^{\text{tot}}$  onto  $W'_0$  is constant, independent of the composition of the system; this gives another justification of affigraphy.* One then shifts from  $A$  to projected  $\underline{a}$ . The projection of the initial affinity vector  $A_0$  is also the same.

### 3.4. First examples

The graphical illustration of the above geometrical concepts may be done only for systems with  $n + k \leq 3$ ; in Fig. 5A the complete  $x$  space is illustrated for  $n = 1$ ,  $k = 2$ ; varieties  $V$  and  $W_0$  are represented. In Fig. 5B the chemography of this system is obtained by projecting the unitary vectors of the space  $x$  (Fig. 5A) onto variety  $W_0$ . In Fig. 5C an affinity space is given and portrays the three affinities of the phases. Spaces  $V'$  and  $W'_0$  are represented. In Fig. 5D the affigraphy is represented after projecting the basic vectors of the total affinity space (Fig. 5C) onto variety  $W'_0$ . The origin in the affigraphy is  $\Omega$ .

In Appendix A2.3, the systematic exploring of all the chemography bases, by the determination of the intensive properties (affigraphy regions) for each possible basis, is done by the method described in Appendix A1.5 for a  $(3 + 3)$  system; the corresponding associated chemography and affigraphy are represented in Fig. 6, 7 and 8;

explanations are given in the captions and the appendix. Fig. 7A through J gives all the corresponding regions of chemography and affigraphy. Fig. 8A is a new representation; for each chemography domain, several bases are possible; these correspond to several affigraphy domains that are represented as insert in the chemography itself. Fig. 8B is the dual representation where, for each affigraphy domain, the possible chemography bases are represented; in this case where  $k = 2$ , this representation is equivalent to an usual two-dimensional thermodynamic diagram such as (P,T) diagram.

### 3.5. Complementarity relations

At optimum the following condition are verified

$$\mathbf{A} \cdot \mathbf{x} = (\mathbf{g} - \underline{\mu}) \cdot \mathbf{x} = \mathbf{g} \cdot \mathbf{x} - \underline{\mu} \cdot \mathbf{C} \mathbf{x} = \mathbf{g} \cdot \mathbf{x} - \underline{\mu} \cdot \underline{\mathbf{c}} = 0$$

because at equilibrium

$$\underline{\mu} = \underline{\mu} \mathbf{C} \text{ and } \underline{\mu} \cdot \underline{\mathbf{c}} = \mathbf{g} \cdot \mathbf{x} = G$$

Condition  $\mathbf{A} \cdot \mathbf{x} = 0$  is called the complementarity condition<sup>8</sup>: it expresses that the components of  $\mathbf{x}$  which are non zero correspond to the components of  $\mathbf{A}$  that are equal to zero, and conversely for the other components.

### 3.6. The hyperinvariant point

The origin of the  $k$ -dimensional affigraphy space is  $\Omega$ . The missing phase vectors are organized around  $\Omega$  as predicted by the columns of  $\mathbf{R}$  matrix. In the  $k$ -dimensional hyperspace,  $\Omega$  represents an hyperinvariant point where all the phases are present together. It is a generalization of the invariant point of the  $k = 2$  dimensional space. Zharikov (1961) and Laffitte (1961) postulated the existence of a  $k$ -dimensional space where all the phases could be present together, as a generalization of the 2-dimensional (P,T) space. According to phase rule, the variance or degree of freedom of the system is given by  $v = n + p - \phi$ , where  $n$  is the

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<sup>8</sup> A writing such as  $\mathbf{A} \cdot \mathbf{x}$  and others of the same type is a condensed form to write  $\sum_{j=1}^{n+k} A_j^i x_j$  although no scalar product is defined.

number of independent chemical components,  $p$  of physical parameters and  $\phi$  of co-existing phases. In order  $n + k$  phases co-exist, there must be  $k$  physical parameters instead of the usual  $P$  and  $T$ ; this was a first justification for considering at most a  $k$ -dimensional space; the authors gave no more thermodynamic basis to such a space that was never used in the literature.

Generally speaking, at  $\Omega$ , the phases may be seen as all present, but the amounts of some of them may be zero; or the phases may be considered as all absent, but their dissociation affinities are zero, so they are at saturation, and they could appear. So there is an indetermination in the thermodynamic sense, but also in the sentences that can be used. The actually observed phases depend on the history of the system. At an invariant point for  $k = 2$  the same paradox holds: all the phases are present, but the invariant point is also the intersection of the univariant lines defined by the absence of the phases. When the system is actually in  $\Omega$ , this represents an improbable case of what we can call thermodynamic degeneracy (t.d.). In terms of Gibbs free energy, the situation of « thermodynamic degeneracy » where more than  $n + 2$  phases co-exist may be understood on a  $(G, X)$  diagram. For instance consider a system  $n = 2$ ,  $k = 4$ . The Gibbs free energy of the phases could be represented along a vertical axis, and the composition along the horizontal axis. In case of t.d. the  $g$ 's of the six phases would be collinear and so any association of two to six phases is stable. The situation of t.d. is discussed more fully below in Section 6.3. for the consequences in phase diagrams.



#### 4. EXAMPLES OF ASSOCIATED CHEMOGRAPHIES AND AFFIGRAPHIES

Examples of associated chemographies and affigraphies for different  $n$  and  $k$  values are given in figures 10 through 19. For each example, corresponding **C** and **R** matrices are recorded in the captions. In the upper part of each figure, the usual affine representation is used for the chemography; phases are represented as points that belong to the hyperplane  $\sum_i x_i = 1$ . Below the chemography, a vectorial representation

is used for the affigraphy; the absent phases are represented by vectors. Each affinity vector has a positive part represented by a solid line, and a negative part represented by a dotted line; in some drawings the negative part may be lacking. A third, affine, representation of the affigraphy may be added; it is obtained by intersecting the affinity vectors by the arbitrarily chosen hyperplane  $\sum_i (P_i) = 1$ , where  $(P_i)$ , or  $A^{(P_i)}$ , is the

dissociation affinity of phase  $P_i$ . This operation allows one to gain one dimension, as in the chemography. Due to the structure of **R** matrix, the affinity vectors do not all cut the  $\sum(P_i) = 1$  hyperplane along their positive part<sup>9</sup>. As a convention, and when the representation is possible, a black point will be chosen when the representation hyperplane cuts the positive part of the affinity vector, and a white point when the negative part is cut. The hyperplane  $\sum(P_i) = 1$  has no particular physical meaning and other affine representations of the affigraphy are possible, contrary to the case of chemography for which the hyperplane  $\sum_i x_i = 1$  has a

specific interpretation. For the same reason the vectors may be normalized to one in matrix **C**, but this has no basic meaning in matrix **R**<sup>10</sup>.

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<sup>9</sup> See also Sections 6 and 9.

<sup>10</sup> One could decide however that the affinity of the total disequilibrium of the system amounts to one, and that the different affinities of the independent reactions are proportions of this unit such that  $\sum_i A^{(i)} = 1$ .

Values of  $n$  have been taken from 1 to 4, and values of  $k$  from 2 to 4: this leads to 12 possibilities that can all be represented. When the dimensionality is equal to 4, only the affine representations may be used. The case  $k = 1$  has no interest. The cases  $n = 3$ ,  $k = 2, 3$  have already been illustrated previously and are not given again in this group of figures. When affine representation is utilized for both diagrams, some types of symmetry may be observed between chemography and affigraphy. For instance, the case  $n = 3$ ,  $k = 2$  may be obtained from the case  $n = 2$ ,  $k = 3$  by exchanging the corresponding chemography and affigraphy. However, as has been said, the representation points may have a different algebraic meaning in the chemography and in the affigraphy; in the first case, only positive parts of vectors are usually possible (points are all black), and in the second, positive and negative parts are possible (points are black or white); so the whole set of  $n$  and  $k$  values has been kept unless some appropriate generalization are defined (see Sect. 10). On each figure the regions of the chemography and of the affigraphy are in thermodynamic correspondence as explained in the preceding section. For example, in Fig. 17 ( $n = 4$ ,  $k = 2$ ), if the system is in the basis BCDF of the chemography, then it must in the same time be in the convex cone (A)(E) of the affigraphy (the position of the global system is represented by a star). Classes of topological arrangements of the points in the chemography correspond to classes of arrangements of vectors in the affigraphy. The correlation between the classes needs matroid theory and will not be discussed here on a general standpoint. In Fig. 20 to 22, examples are given of associated chemographies and affigraphies for different topological arrangements of the chemography for a  $3 + 3$  system. A discussion of chemography classes for  $3 + 3$  systems may be found in Day (1972), Zen and Roseboom (1972). Stout (1990) discusses quaternary system chemographies.

## 5. STABILITY SEQUENCES

Sequences of phase assemblages may be observed in increasing or decreasing stability order in the two dimensional (P, T) diagram regions;

they have been predicted for unary, or unary and binary, systems by several authors (Kujawa and Eugster, 1966<sup>11</sup>, Zen, 1967, etc.), following Ostwald's work (1902, quoted in Zen op. cit.) for unary systems. This discussion may be done in the affigraphy space before any two-dimensional diagram is considered. The rules obtained on the stability sequences in the affigraphy will be transported in the two-dimensional (P, T) diagrams.

Domains may be defined in the affigraphy as limited by sets of  $k$  affinity or absent phase vectors; each corresponds to an  $n$ -phase basis of the chemography. These domains are referred to as cobases. The phases of the chemography bases are listed by simple complementation to the list of the phases of the affigraphy co-bases. A field correlated to a stable basis of the chemography is limited by the  $k$  positive parts of the affigraphy vectors. But other fields may be considered where 1, 2, ...,  $k$  negative parts of the vectors are taken. We will note **(-A)** the negative part of vector **(A)**. When the negative part of one or several vectors is considered in the affigraphy, one or several phases do not appear in the system. They should be present however from a thermodynamic point of view, perhaps not together, since their affinity of precipitation is positive; so they define metastable associations. For instance, in the generalized co-basis (A, -B, -C, D...) phases B and C do not participate to a possible domain in the chemography whereas they should <sup>12</sup>; the corresponding basis (M, N, P...) complementary to the set (A, B, C, D..) thus has two degrees of metastability. We will call «*degree of metastability*» or «*stability level*» of a basis of the chemography, the *number of negative vectors in the corresponding co-basis of the affigraphy*. This definition correlates with that given in the literature (number of more stable phase assemblages) and allows generalizations. The stability level of one basis

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<sup>11</sup> In their paper, these authors give interesting terminology on categories of phase sets that will not be repeated here and to which the reader should refer.

<sup>12</sup> In the following the co-basis {(A), (-B), (-C), ...} will be written (A, -B, -C, ...) or simply (A-B-C...), or even A-B-C... when there is no ambiguity; and the same rule holds for the bases where comas and parentheses may be omitted in the cases where they would be utilized. When  $n \neq k$ , bases and cobases may be distinguished by their number of elements. Similarly, collections of phases or absent phases, and collections of vectors in the chemography or affigraphy, may be identified and the vectors may not be written in bold font.

will be indicated by an index associated to the list of the phases; for instance  $(M, N, P, \dots)^0$  will be a stable basis (zero negative vector in the corresponding co-basis), and  $(M, N, P, \dots)^1$  will be a singly metastable basis (one negative vector in the corresponding cobasis) and so on. The ordering of the stability levels allows one to define a basis stability « *sequence* ». The corresponding bases are classed by increasing Gibbs free energy (less and less stable or more and more metastable).

More generally, the stability level of any variety of the phase space will be defined by the number of negative vectors of the supplementary set of the dual affigraphy space; we will call « *stability signature* » of a variety, the complete set of corresponding co-vectors with the indication of their positive or negative sign<sup>13</sup>. By extension of the vocabulary, the stability level of a linear variety or portion of variety (point, line, plane, p-dimensional variety... hyperplane) in the affigraphy itself or in (P, T) diagram may be alluded to as the number of negative part vectors involved in the definition of this variety; although by symmetry the stability of a variety in affigraphy should be defined by a property of the corresponding supplementary set *in chemography*. In a first approach, no negative quantity of a phase is possible in a basis; no negative sign appears for the individual phases of the basis; only a collective index is indicated for its stability level, whereas phases in the cobases may have negative signs because of possible negative part vectors; generalized bases with negative proportions of the phases (or equivalently negative phases) are discussed in Section 10.

For a given domain of the affigraphy, and for each possible class of chemical composition in the chemography, several bases may be accessible at different stability levels. The procedure to find these levels can first be illustrated on examples. A unary system with three phases (n

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<sup>13</sup> The word « *stability sequence* » is also used in literature in a spatial meaning different from the present energetic one; in affigraphy words it is the list of the oriented (positive or negative) affinity vectors along the different portions of an univariant line (Sect. 8); in order to avoid confusion with the « *stability sequences* » at a given point (in the sense of the present section), « *stability successions* » would be more appropriate in this geometrical sense. As a generalization, we will call multidimensional « *stability pattern* », the correlated set of the stability signatures for the different spatial domains limited by a set of k hyperplanes (Sect. 8).

$= 1, k = 2$ ) is considered, Fig. 23. The domain of the affigraphy delimited by the positive part of (C) and the negative part of (A), as a sub-region of the (B, C) field, is selected; the accessible cobases are (BC) (-AC) and (-A-B), so that a point in the chosen region may belong to the convex cones (B)(C), (-A) (C) and (-A) (-B). The corresponding bases are A, B, and C respectively; according to the above rule, their stability levels are respectively 0, 1 and 2, written as  $A^0$ ,  $B^1$  and  $C^2$ . The stability sequence is thus A, then B then C, or  $A < B < C$  because in that case  $g^A < g^B < g^C$ . Another sequence of phases is displayed in the figure for domain (A, -B). In Fig. 24, an example is presented for a  $n = 1, k = 3$  system. The different reaction planes, defined in the affigraphy by pairs of vectors, also intersect along other vectors than the basic affinity vectors. The new vectors correspond to the so-called indifferent crossing (i.c.) points on the thermodynamic diagrams (see Section 6.4 below for notation of i.c. vectors and points); for such indifferent crossing vectors, different co-bases are accessible, and so different bases, related in general to different incompatible chemical compositions, unless in case of particular degenerate situations (in the cases where  $n = 1$ , the system is always degenerate). The i.c. vectors allow the definition of subregions of the affigraphy. In the figure, a three-dimensional domain of the affigraphy is considered as bounded by two basic vectors (-A), (C) and one i.c. vector (-A-D, BC)<sub>ic</sub> respectively; its intersection by the two-dimensional plane connecting the extremities of (B), (C) and (D) vectors is shown; the accessible co-bases are (BCD), (-ABC), (-AC-D) and (-A-B-D) corresponding to the sequence  $A^0 < D^1 < B^2 < C^3$  of bases. Metastable phase D is associated to cobase -ABC; the degree of metastability is just one and A is surely the stable phase; when C is considered, as associated to cobase -A-B-D, it may be concluded that the three phases A, B and D are more stable than C, but the sequence of these phases is unknown.

The general procedure to find the sequence of bases in increasing or decreasing stability order for a given region of the affigraphy is defined as follows. 1) the different subregions of the affigraphy are listed, as limited in all the possible manners by positive and negative vectors and indifferent crossing vectors. 2) For a given subregion of the affigraphy,

the list of the accessible co-bases (with all possibilities of positive and negative vectors) is written; to it corresponds a list of bases. To each of the bases an index is affected that corresponds to the number of negative parts of the affinity vectors in the corresponding cobasis. 3) In the chemography the different subregions are defined in a way similar to that done in 1) for the affigraphy. 4) For each subregion of the chemography the list of the accessible bases is established. 5) This list is compared to the bases obtained for the chosen region of the affigraphy in step 2). 6) For each region of the chemography the sequence of bases is determined according to the indices determined in 2); this ends the procedure. The different steps may be automated. In the general case, more than one base with the same degree of stability may be possible for a given region of the chemography; this is the reason why the stability level as defined above does not allow a total ordering of the bases. The sub-order of the bases having the same stability index is dependent on the value of the thermodynamic functions of the phases, and may not be determined by the sole affigraphy approach. In Section 10 below, stability sequences are generalized to affigraphy co-bases when phases with negative compositions are allowed in chemography space.

As another example, in Fig. 25, a  $2 + 2$  system is studied. The chemography is represented in Fig. 25A; for each domain of the chemography, the list of the possible bases is indicated below the composition bar. For instance, for the compositions of the system between phases B and C, the four bases BC, AC, BD, AD are possible. For the region limited by (D) and (A) of the affigraphy, the list of the cobases is given, and the list of the corresponding bases with their stability index is then identified for each domain of the chemography below the composition bar (Fig. 25B). For instance cobase  $(-B,D)$  corresponds to base  $(AC)^1$  which may be obtained for chemography regions between A and B, and between B and C respectively. One notices that, in the domain between B and C, AD is the less stable basis and BC the most, and that two bases BD and AC have the same stability level equal to 1; in order to go further in the discussion, it is necessary to represent the  $g$  functions of the possible assemblages as is done above

the chemographic bar. One thus sees that for the composition of the system on B side the sequence is BD then AC, and for the composition on the C side, it is AC then BD; the limit between these two domains is dependent of the value of the  $g$  functions. When the basis AC is considered as associated to  $(-BD)$ , one knows that B must appear, but whether it is with A or C or D is unknown. B is associated to A in the AB domain (basis  $AB^0$ ) and to C in the BC domain (basis  $BC^0$ ). When  $AD^2$  is considered as associated to  $(-B-C)$  it may be concluded that B and C must be more stable but perhaps not together (actually the more stable bases are AC and AB and not BC). The synthesis of the stability sequences for the different composition domains and for the different affigraphy regions is given in Fig. 25C. This is a new representation where the ordinary (stable) composition bars in the different intensive (affigraphy) fields are augmented by new portions corresponding to phase associations of higher metastability. For a given composition region, one may readily know the different phase associations of different stability level that may be obtained in a given region of the phase diagram.

In Fig. 26, a more complicated  $3 + 2$  system is studied (cf. Fig. 3 to 5). In Fig. 26A, 7 regions of the chemography are defined with the corresponding list of accessible bases. The affigraphy is represented in Fig. 26B and a region is chosen and marked by a star (region I). The list of the cobases, corresponding bases, and list of bases with their stability index for all of the 7 regions of the chemography is given in Table 1. One sees that in the regions with more than three bases, i.e. in regions 4, 5 and 6 (four bases) and 7 (5 bases) respectively, two and three bases have an intermediate stability level equal to 1 (the highest and lowest stability levels are always represented by one basis). The ordering of the intermediate bases in these cases is dependent on the values of the  $g$  functions of the phases and variable with them; in Fig. 26C, an example is given of  $g$  values and the corresponding ordering of the bases in regions 4 through 7 is as follows: zone 4:  $ABC^0 < BCE^{1a} < CDE^{1b} < ADC^2$ ; zone 5:  $ABC^0 < ABE^{1a} < ADE^{1b} < ACD^2$ ; zone 6:  $ABC^0 < BCE^{1a} < BDE^{1b} < ABD^2$ ; zone 7:  $ABC^0 < BCE^{1a} < ADE^{1b} < BDE^{1c} < ACD^2$  where the sequence a, b, c ranks the bases whose stability level is one for all.

The synthesis of the stability sequences for the different composition domains and for the different affigraphy regions is given in Fig. 27. Such computations are allowed by the affigraphy approach and can be done automatically for  $k > 2$  spaces.

Metastability is relative to the whole system defined by its overall Gibbs free energy  $G$ . One can imagine partial metastability with respect to just one, or to a limited set of variables defined as a limited number of affinity vectors or combination of basic affinity vectors (e.g. with respect to  $T$  in a chemical potential saturation diagram or grid in the sense given in Sect. 13); the limits of the metastable fields may be projected onto one thermodynamic diagram; they will not coincide in general with the limits of stable associations of the basic diagram.

As a whole, the results of the present section are a generalization of Ostwald step rule stated for unary systems. The sequence of assemblages is dependent on the composition of the system.

## 6. THE (P,T) DIAGRAMS

### 6.1. The fundamental theorem

The affinity diagram or « *affigraphy* » presented in the preceding sections may be constructed for all kinds of phases, either of constant composition or with solid or liquid solution. In the following, we will restrict to the case with no solution; then, the Gibbs molar free energies of the phases may be expressed by relations that are independent of the quantities  $x_i$  of the phases in the system (that correspond to proportions of end-members in the case of solutions). The hypothesis will also be taken that, within some approximation, these relations are expressed by linear relations of the type:

$$g^j = v^j P + s^j T + u^j \quad (j = 1, \dots, n + k)$$

as a function of pressure and temperature; the coefficients  $v^j$ , molar volume,  $s^j$ , molar entropy, and  $u^j$  internal energy, are taken as constant; in the present approach, these constants are taken as parameters. The preceding relation is valid at least in a certain domain of pressure and temperature. At critical points, two surfaces  $g(P,T)$  merge into a single



one whose curvature may be important. This case will not be examined here. In the chosen « *representation basis* »  $I = I_0$ , the  $k$  components of the total affinity of the system along the basic affinities are  $A^0 = g^j - \mu^j = g^j - g^j(C^j)^{-1}C$  (this writing in general form, cf. App. A1, is equivalent to that in Sect. 3.2.; we usually take  $C^j = U_n$ ); due to the linear approximation on the  $g^j$ , these are linear combination of  $P$  and  $T$  that can be written in condensed form as

$$\begin{aligned} A^{(1)} &= A^{(1)}(P, T) \\ A^{(2)} &= A^{(2)}(P, T) \\ &\dots\dots\dots \\ A^{(k)} &= A^{(k)}(P, T) \end{aligned}$$

where the relations are linear. By eliminating  $P$  and  $T$  between these  $k$  relations,  $k - 2$  linear relations are obtained between the  $A^j$ ; these represent  $k - 2$  hyperplanes that define a two-dimensional plane (Fig. 28). If one merely wants to know the qualitative structure of the  $(P, T)$  diagrams, the following *fundamental theorem* is then arrived at:

*The qualitative structure of the  $(P, T)$  diagrams may be obtained by cutting by two-dimensional linear varieties, the  $n + k$  vectors and associated hyperplanes of the  $k$ -dimensional affigraphy space, constructed by the column vectors of the chemical reaction matrix.*

In the natural examples, the varieties are not linear;  $(P, T)$  is a two-dimensional surface, and there is a non Euclidean deformation of the affinity coordinates. In our approach, the values of the coefficients in  $g^j(P, T)$  are unknown, but one can imagine the different possible structures by cutting in the different possible manners. The potential solutions will be all the qualitatively possible ways to cut the affigraphy by two-dimensional planes; among these, one will fit the thermodynamic data of the system (Sect. 14). Other types of diagrams may also be obtained by the same operation (Sect. 13). In Appendix 3, the coordinates in the affigraphy frame of the origin of  $(P, T)$  plane, of the vectors  $P = 0$  and  $T = 0$  are computed, and, conversely, values for  $P$  and  $T$  are affected to  $\Omega$ . As already told, a reciprocal way to interpret our

approach is to say that (P, T) plane is plunged into a higher dimensional space and that, by doing this, one is able to predict and understand its structure.

## 6.2. Notations of points and lines in the (P, T) diagrams

In this section, some comprehensive remarks and examples are given on the properties and notations of invariant points and univariant lines in the diagrams, as resulting from the intersection operation defined in the last section. Expansion and new illustrations follow in the rest of the text (Sect. 6.3, 8.6., 9.4., 13). On a general standpoint, the dimension  $d''$  of the intersection of a  $d$ -dimensional variety with a  $d'$ -dimensional variety is found by considering that the first variety is defined by  $k - d$  hyperplane equations and the second variety by  $k - d'$  equations. The total number of equations is  $2k - d - d' = k - d''$ ; so  $d'' = d + d' - k$ ; this is a maximum. Among the  $2k - d - d'$  equations, some of them may be proportional if the position of the two varieties with respect to each other is not general, and the number of independent equations is bracketed by  $2k - d - d'$  and  $\sup(k - d, k - d')$ . The dimensionality of the intersection is bracketed by  $d + d' - k$  and  $\inf(d, d')$ <sup>14</sup>. For dimensions greater than 3, unusual features appear; for example, in a four-dimensional space, two two-dimensional planes usually intersect in one point (dimension 0;  $2 + 2 - 4 = 0$ ). In the intersection operation of affigraphy by two-dimensional (P, T) planes, hyperplanes of the affigraphy defined by  $k - 1$  vectors correspond to the chemical reactions or univariant lines of the (P, T) diagram; groups of  $k - 2$  vectors correspond to the invariant points (Fig. 28). Each vector of the affigraphy has a positive part and a negative part. In the collection of the  $k - 1$  vectors of the hyperplane, the number of negative parts may be zero, one ...  $k - 1$ ; so the total number of stability levels for univariant lines is  $k$  (the word stability is used in its thermodynamic sense as demonstrated in Sect. 5). A type of line may be chosen for each of these combinations: solid line for zero negative part of the vectors, dotted line for one negative part and so on. Similarly, the

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<sup>14</sup>  $\sup(a, b, c...)$  designates the greatest number among  $a, b, c...$ ;  $\inf(a, b, c...)$  designates the smallest number.

invariant points possess  $k - 1$  stability levels (0 to  $k - 2$  negative parts), and the divariant fields  $k + 1$ . The stability character of fields, lines or points lies on the affigraphy, not in the intersection operation.

In the (P, T) diagram, the notation of the points, lines and domains may be the same as the corresponding varieties of the affigraphy, although there is a reduction in dimensionality in the intersection operation. In general there is no ambiguity. The vectors of the affigraphy are usually referred to by bold letters, contrary to the points in the intersected (P, T) plane. The absent phases are indicated between brackets: the number of phases gives the dimensionality and so the nature of the variety, the values of  $n$  and  $k$  being known. In the notation, it can also be indicated if the positive or the negative part of the vector is concerned; as was told symbol  $-A$  may be used for the negative part of  $A$ .

In the case  $k = 2$ , the (P, T) diagram is simply equivalent to the affigraphy with a change in the origin, orientation and scale of the coordinate axes (Fig. 29A). In the case  $k = 3$ , the possible invariant points, related to vector ( $A$ ), are ( $A$ ) and ( $-A$ ) corresponding to the notation  $A$  and  $A'$  of Zen in his papers (op. cit.), see Fig. 30 below. As another example, in the case  $k = 5$  (Fig. 29B) the invariant points correspond to three vectors; for the three vectors ( $A$ ), ( $B$ ) and ( $C$ ), there are four possible types of invariant points ( $A, B, C$ ) ( $-A, B, C$ ) ( $-A, -B, C$ ), ( $-A, -B, -C$ ). Different line portions are also indicated in the figure: ( $ABCD$ ), ( $ABC-D$ ), ( $AB-C-D$ ), ( $A-B-C-D$ ) and ( $-A-B-C-D$ ). This extended notation of the varieties by taking into account the negative parts of the absent phase vectors is new and directly results from the affigraphy approach.

When crossing an invariant point along one univariant line, one vector is suppressed among the  $k - 2$  vectors that define this point and replaced by the remaining vector in the  $k - 1$  set defining the line. When crossing one invariant point, the sign of one vector among the  $k - 1$  defining the adjacent line portions changes.

In ordinary case (see exceptions in Sect. 10) the coefficients of the chemical reaction matrix are not all with the same sign, positive or negative; the affinity vectors cannot all be cut in their positive part by a two-dimensional plane, whatever its position. Thus, in the two dimensional section, it is not possible in general that all positive nor all negative parts of the vectors are implicated. So a (P, T) diagram cannot possess all points with the same stability level. Each invariant point is obtained once either stably or metastably and each assemblage occurs but once with a given stability level; this is related to the fact that linear varieties are considered, in similar assumption to the « *straight line hypothesis* » of several authors; the univariant lines are not expected to form closed loops (e.g. Mohr and Stout, 1980, Zharikov, 1961). Residual nets can be considered as defined by sections of the affigraphy different from that chosen for the actual (P, T) diagram; they contain the complementary sets of intersecting points and lines; their number increases with k. The number of invariant points in a diagram is  $C_{n+k}^n + 2$  whereas all the possible points with all stability levels amounts to (k - 1) times the last figure. The maximum number of stable invariant points is a priori  $C_{n+k}^n + 2 - 1$ ; in the case k = 3 it is  $n + k - 1 = n + 2$ . The actual number must be less, depending on the hypotheses made.

The general method to obtain (P,T) diagrams by intersecting the affigraphy by two dimensional planes is illustrated in Fig. 30A through G (n = 1, k = 3), and 31 (n = 3, k = 3). Some characteristic numbers of the phase diagrams depending on the value of k are reported in Table 2.

### 6.3. Thermodynamic degeneracy

« *Thermodynamic degeneracy* » is arrived at when the position of the two-dimensional (P, T) plane is not arbitrary in the affigraphy; the physical probability of this situation will not be discussed. A justification was discussed in Sect.3.7. As another justification, when a new phase is added to a multi-system such that  $\Delta k = +1$  with  $\Delta n = 0$  then the dimension of the affigraphy is raised by one  $k' = k + 1$ . The old diagram is in a situation of thermodynamic degeneracy with respect to the new one since it is restricted to an hyperplane of the new affigraphy ( $k' - 1 = k$ ). Thermodynamic degeneracies allow to complete the understanding of the structure of the phase diagrams. Three types of degeneracies may be defined:

1) (P, T) plane may contain the invariant hyperpoint  $\Omega$ ; if so,  $\Omega$  is the only invariant point of the diagram. If the orientation of (P, T) plane is arbitrary with respect to the affigraphy vectors, all the univariant lines are visible on the (P, T) plane. When crossing  $\Omega$  along each of these lines, there is a change in the stability level of the line, from the level it had at one extremity in ordinary univariant lines, to the level at the other extremity; in this case there are no intermediate portions on the line and so no intermediate stability levels, contrary to the usual case. This situation is illustrated in Fig. 30E on the 1 + 3 system already studied (the general discussion on stability levels on univariant lines is done in Sect. 8.1.).

2) (P, T) may be parallel to varieties having dimensions from 1 (vector) to k - 1 (hyperplane); in that case, the invariant points that join together the vectors of the parallel variety do not appear, because (P, T) plane do not intersect them. In Fig. 30B, (P, T) plane is parallel to affigraphy vector (C), and the corresponding invariant point (C) disappears from the four points of the system; in Fig. 30C, (P, T) is parallel

to two vectors and two invariant points are suppressed. If  $(P, T)$  is parallel to a variety of dimension  $k - p$ , defined by  $k - p$  affigraphy vectors, the number of invariant points left is  $C_{n+k-p}^{k-2} = C_{n+p}^{k-2}$  because each invariant point regularly associates  $k - 2$  vectors. The missing points are rejected at infinite and some corresponding portions of univariant lines are lacking.

3)  $(P, T)$  may contain one or two vectors, or be contained in a variety of dimension 3 to  $k - 1$ . In that case, some of the intersecting points of the arbitrary  $(P, T)$  plane with the variety will merge.

4) The foregoing degeneracies may be associated.  $(P, T)$  plane may in the same time contain  $\Omega$ , and be parallel to a variety or, equivalently in that case, be contained in it. In Fig. 30F,  $(P, T)$  plane contains both  $\Omega$  and 1 vector, and in Fig. 30G,  $(P, T)$  contains  $\Omega$  and two vectors.

5) Other cases may be imagined depending on the dimensionality of the affigraphy. In the case  $k = 4$ , the  $(P, T)$  plane may cut the intersection of two planes belonging to the same hyperplane. This will be illustrated below as well as similar situations for  $k = 5$ .

6) For memory, one can imagine that thermodynamic degeneracy combines with chemographic composition degeneracy (Sect. 11). This will not be treated here.

In summary, cases of thermodynamic degeneracy show new types of invariant points, lower in number, and with new types of stability changes across the points, some steps being abolished. Also, in the case of thermodynamic degeneracy, the invariant points may gather more than  $n + 2$  phases. Such points usually correspond to  $k - 2$  vectors, or  $n + 2$  present phases. Two invariant points may have  $k - 2 - q$  vectors in common; if the  $(P, T)$  plane belongs to the hypervolume of  $k - 2 - q$  dimension, the two invariant points will merge in a single point with  $n + 2 + q$  present phases. New types of notations and rules must be defined for the stability levels of the points and the lines in these cases. No general statement will be given; a useful guide for that purpose is to consider the number of affigraphy vectors and the number of negative parts involved. The paradox on the presence and number of phases at such points is of the same nature as for the hyperinvariant point (cf. Sect. 3.5 above). The complexity of the notations for such points results from the fact that a same point may correspond to different types of pairs of neighboring line portions depending on the degenerate orientation of the two dimensional plane. Depending on the dimensionality of the space, the possibilities of types increase and a hierarchy of points with increasing degeneracy may be defined. An ordinary univariant line contains  $k - 1$  points; these points may merge two by two until one single point remains ( $\Omega$ ). So one can coalesce from 2 to  $k - 1$  points and there are  $k - 2$  possible thermodynamically degenerate point types on a line. The indifferent crossing points (see next section) are invariant points of particular type that may also disappear depending on the position of the intersecting  $(P, T)$  plane.

#### 6.4. Indifferent crossings

The question of the indifferent crossings (e.g. Zen, 1966b, 1967) can be discussed at the affigraphy level, prior to the construction of  $(P, T)$  diagrams. Invariant points in the  $(P, T)$  diagram correspond to affigraphy linear varieties of dimension  $k - 2$ , resulting from the intersection of pairs of hyperplanes; for ordinary invariant points,

two univariant curves (two hyperplanes) that intersect are always compatible from the composition point of view. For indifferent crossing points, univariant curves (hyperplanes) may intersect that do not correspond to the same composition of the system, that is to say that share less than  $n$  phases in common. Each hyperplane correspond to  $k - 1$  absent phases so that for both hyperplanes  $2k - 2$  phases at most may be absent, or other said  $n + k - (2k - 2) = n - k + 2$  phases may be present. This number may be lower than  $n$  for  $k > 2$ ; depending on the values of  $n$  and  $k$ , the chemical systems corresponding to the two intersecting hyperplanes may have zero common phase. The compositional dimension of the variety corresponding to indifferent crossing is  $n - k + 2$ , or other said only for degenerate compositions the indifferent crossing point will be compatible for both reactions. Various cases may be considered depending on the stability level of the hyperplanes that intersect. In the  $(P, T)$  diagram univariant curves of different stability level may thus intersect along indifferent crossing points of several types.

This situation is illustrated in Fig. 20 where the affigraphy planes may intersect along other vectors than the basic affinity vectors. For instance planes (A)(F) and (D)(C) intersect along line  $\Delta$ ; in the two-dimensional plane connecting the four points (A), (C), (D), (F) in the figure, line  $\Delta$  corresponds to the intersection of the diagonals of a face of the polyhedron constructed on the affigraphy vectors. The absence of the four phases A, C, D and F corresponds to the presence of only two phases B and E. Thus only for a composition of the system along the chemographic BE two-dimensional joint will the indifferent crossing point be compositionally compatible (here  $n - k + 2 = 2$ ). Another way to say is: reaction (A, F) corresponds to compositions taken in the quadrilateral CDEB of the chemography (Fig. 20) and the same for reaction (D, C) in the quadrilateral AFEB. Only along the common edge EB of both quadrilaterals are the compositions compatible.

The number of invariant points on a given univariant line is  $C_{k-1}^{k-2} = k - 1$ . Each invariant point corresponds to the meeting of  $n + 2$  reaction hyperplanes or other said of  $n + 1$  hyperplanes in addition to that corresponding to the line considered. So the total number of all the hyperplanes involved in the invariant points of a given univariant line is  $(k - 1)(n + 1)$  without counting the hyperplane defining the univariant line itself. The total number of hyperplanes corresponding to all chemical reactions is  $C_{n+k}^{n+1}$ . So the total number of indifferent crossing points along a given univariant line is  $n_{IC} = C_{n+k}^{n+1} - 1 - (k - 1)(n + 1)$ . The notation of the indifferent crossing points may be done according to the names and positive or negative part of the  $2k - 2$  affigraphy vectors involved, separated into two sets for the two hyperplanes. In a two-dimensional diagram, each of the two intersecting univariant lines may have  $k$  stability levels, so there are  $(k)^2$  possible types of indifferent crossing points. So far as stability is concerned, each of the phases in the  $(2k - 2)$  phase set must be considered independently for the sign, and there are  $2k - 1$  stability levels at most (if the same phase appears in the definition of both i.c. hyperplanes it will have the same sign because it corresponds to the same situation in the affigraphy frame). The number of stability levels is greater than  $k - 1$  in the ordinary case because the number of present phases is lower and so more absent phase vectors can appear in the place of the present phase ones. For  $n = 3$ ,  $k = 3$ , the total number of hyperplanes is  $15 - 1 = 14$  and the number of hyperplanes involved in the invariant points is 8 so the number of indifferent crossing points is 6 (the 4 affigraphy vectors left are taken two by two). That is verified on Fig. 20, 24 and 31. In these examples for  $k = 3$  each indifferent crossing point has four phase labels; their dimension is one however (points) resulting from the intersection of two

varieties of dimension  $k - 1$ ; in the label of i.c. point  $(-A-B, CD)_{ic}$ , Fig. 24, a coma separates the two intersecting hyperplanes and an index  $ic$  is written in order to avoid confusion. The two hyperplane portions may have different stability levels as described by the sign of the vectors; for this figure  $n = 1$ ,  $k = 3$  and we verify that  $n_{ic} = 1$  and  $2k - 2 = 4$  (number of vectors for an i.c. point). For  $n = 1$ ,  $k = 4$   $n_{ic} = 3$  verified in Fig. 37.

Another way to look at the problem is to consider pseudosections (e.g. Hensen, 1971). If different pseudo-sections are considered that correspond to the diagrams computed for specific chemical compositions, the indifferent crossings will correspond to the intersection of these diagrams. Some degenerate compositions may be at the border of the different composition domains and for them the indifferent crossing may correspond to the same composition.

This system degeneracy corresponding to a specific composition of the system (for which an indifferent crossing point may be obtained) must be distinguished from the structural degeneracy (phase composition degeneracy, Sect. 11 below, or thermodynamic degeneracy, Sect. 6.4 above). In the case of thermodynamic degeneracy other univariant lines are possible that correspond to varieties of dimension lower than  $k - 1$  that connect  $k - 2, \dots, 2, 1$  affigraphy vectors. When intersecting with the other possible lines, these lines may in turn give rise to indifferent crossing of special character that will not be numbered nor studied in detail here; this is merely an application of affigraphy and combinatorial analysis.

By generalization, if phases are accepted that have negative components or phase assemblages with negative phase amounts (see Sect. 10 below), then all univariant reactions are accessible to all compositions (a chemical system may be described by any phase basis provided some phase amounts are negative). The indifferent crossings will then correspond to pairs of composition systems that do not have the same « chemographic stability level »; this must be understood in its mathematical generalized composition sense, defined by the number of positive basic phases in the assemblage.

### 6.5. Pseudosections

As has been said, pseudosections are restricted (P, T) diagrams computed for a specific chemical composition of the system (e.g. Hensen, 1971)<sup>15</sup>. Let us discuss briefly the method to obtain them. For a given composition  $C^*$  of the system, one must first list all chemography bases that contain  $C^*$ , i.e. for which  $C^*$  may be expressed by a *positive* linear combination of the phases in the base. Let  $I_1$  be this list. Then, the list of chemical reactions accessible to composition  $C^*$  must be determined: in list  $I_1$ , all pairs of bases that share  $n - 1$  phases in common define  $n + 1$  phase accessible reactions. They compose list  $I_2$ . The pseudosection is then the diagram representing reactions of list  $I_2$ .

If composition  $C^*$  is degenerate, that is to say, belongs to a linear variety defined by  $n - p$  phases ( $n - 1, n - 2, \dots, 1$  phase) instead of belonging to a  $n$  phase basis, then, one must exclude from list  $I_1$  the bases that contain the  $n - p$  phases of the subspace; because a system composition described by phases in those bases could not be degenerate in the  $n - p$  subspace (a basis containing an hyperplane, cannot overlap it). For instance for  $n = 3$  (Fig. 2), if system composition belongs to line AB, the bases ABC, ABD, ABE and so on containing phases A and B must be excluded; because a composition described by a positive combination of phases A, B, C or A,

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<sup>15</sup> Hensen is probably among the first people to have used pseudosections although the term « *pseudosection* » as such is not employed in the 1971 paper.

B, D or A, B, E and so on does not strictly lie on line AB. This still diminishes the number of possible chemical reactions with which the final diagram (pseudosection) is constructed. On the whole, in a pseudosection, the number  $k$  may diminish and so the number of invariant points, univariant lines and stability levels. At worst, if the composition of a system strictly lies at a chemographic external phase, this phase is always stable and the (P, T) pseudosection has no point, nor line.

If bases with negative proportions of some of the phases are accepted, all bases are kept in above list  $I_1$  and the chemical reactions are written in a generalized sense (Sect. 10).

## 7. A DISCUSSION OF ZEN POLYHEDRA ( $k = 3$ ); GENERALIZATION

In the case  $k = 3$ , the structure of the possible (P,T) phase diagrams may be predicted with the help of the « *representation polyhedra* » proposed and constructed by Zen (1966b and subsequent papers) for their application to geological examples. The construction of these polyhedra is founded on empirical rules. These are based on the knowledge of the diagram structure for a given chemography (i.e. the Schreinemakers rules, Sect. 9); the justification is given by their power of prediction. Briefly stated, for each  $(n + 3)$ -phase system, a polyhedron can be constructed whose apices represent the invariant points. Each corresponds to an absent phase, and the edges connecting the apices represent the invariant reactions. The total polyhedron may be projected onto a sphere, and after cutting and opening the sphere, the projection may be applied to a plane. In this manner one obtains what Zen calls « *closed-net* » that contain all the information of the polyhedron (other kinds of nets, open or partially open nets, are defined by similar operations described in Zen). Because of all the possible intersections of the lines on the sphere, the closed net contains all the invariant points twice, both stable and metastable, which is not the case for the real phase diagrams. In the projection of the polyhedron, the different edges radiating from each apex must not coincide; this could happen depending on the plane of projection. In order to avoid this problem, Zen proposes that the edges of the polyhedron are not straight but curved lines. The (P, T) diagrams are parts of the closed nets, but which part is not known a priori. It should be stressed that, according to Zen himself (1966b; see further discussion in Zen and Roseboom, 1972) the polyhedron has no thermodynamic significance, and the three



dimensional space or volume within which it is constructed has no meaning; only its surface is utilized. On the whole, it is merely a tool which proves to be useful.

Without discussing in detail the use of polyhedra and closed nets in the literature, it can be shown that the affigraphy approach gives a thermodynamic significance to the polyhedra; it allows a revision of their practice and a generalization of their definition. In the case  $k = 3$ , the affigraphy indeed allows to define a polyhedron where each apex is the extremity of an affinity vector. In the approach based on the affigraphy, the (P,T) diagrams are obtained by an intersection of affigraphy by a plane, whereas it is a projection in the case of Zen 's polyhedra (or a part of the projection for the open nets supposed to be candidates to physical (P, T) diagrams). These two operations are equivalent. The projection of a point is a point and the projection of a edge is a line. In the intersection of the three-dimensional affigraphy, the intersection of a vector gives a point and the intersection of a plane gives a line. The difference is that in the affigraphy approach, a center is added to the polyhedron. The thermodynamic significance of this operation has been shown and, when an intersection operation is considered, the condition that the edges are curved is not necessary. The lengths of the vectors of the affigraphy may be normalized to one: the important is the direction of the vector, not the length. So the extremities may be on a sphere and a convex polyhedron may be drawn. The affigraphy may be synthesized in different ways: the apices may or may not be connected, the center (invariant hyperpoint) may or may not be represented and connected to the apices. Many examples have been given in the preceding figures (8B, 8C, 11D, 14D, 18D, 20D, 21D, 22D) and they are in exact correspondence with the polyhedra proposed by Zen, and Zen and Roseboom (op. cit.), e.g. tetrahedron for a 1 + 3 system, Fig. 11, pentagonal pyramid, for a 3 + 3 system Fig. 21D and so on.

In the affigraphy frame, the closed net corresponds to the projection of the entire affigraphy, whereas the open net or partially open net correspond to the intersection by two-dimensional planes of specific orientations, and the residual net to another complementary intersection. A thermodynamic significance for the nets is thus given. The intersection

by two-dimensional planes is in accordance with the physical straight line hypothesis (e.g. Mohr and Stout, 1980) where the univariant lines do not form loops, contrary to the case of closed net. In that case, the invariant points occur once either stable or metastable. In the intersection operation, some of the affigraphy vectors are cut along their positive part, some others along their negative part. So for a given orientation of the (P, T) plane, two nets may be defined that are symmetric with respect to the affigraphy center  $\Omega$ , and the stable and metastable points substitute to each other (the so-called inversion of topologies in potential diagrams results from the same consideration). A polyhedron with the metastable apices may also be drawn; this is new with respect to Zen and more in conformity with his representing of invariant points by pairs both stable and metastable.

In the case  $k > 3$ , the affigraphy can no longer be displayed as a polyhedron in  $R^3$ . Several ways can be found however to portray graphically the affigraphy and the information on the chemical system it conveys; but the unity of representation is lost because more than one projection may then be useful. A convex hyperpolyhedron can be defined in the  $k$ -dimensional space, and constructed on the  $n + k$  affinity vectors, in the same way a polyhedron was defined in  $R^3$  (other multidimensional figures may also be constructed by geometrical transformation of the basic hyperpolyhedron). The hyperpolyhedron can be projected as a hyperclosed-net onto lower dimensional spaces such as the two-dimensional plane or space  $R^3$ . The net gives the connections and hierarchy (similar to the mathematical « *treillis* ») between the different invariant points and univariant lines of the diagrams. For instance, the hyperpolyhedron of a 1 + 5 system is a simplex<sup>16</sup> in a ( $k = 5$ )-dimensional space, and is projected in Fig. 32. The univariant lines are groups of 4 phases and invariant points groups of 3 phases; the quadrilateral (A,B,D,E) gathers the four invariant points (A,B,E) (A,B,D) (B,D,E) and (A,D,E); point (A,B,E) also belongs to line (A,B,C,E).

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<sup>16</sup> A simplex is the convex envelope of  $k + 1$  independent points in a  $k$ -dimensional space.

The systematic discussion of the possible types of affigraphy and corresponding polyhedra or hyperpolyhedra, depending on the arrangements of the phase in the chemography, and more generally the link between symmetry properties of the affigraphy and chemography will be given elsewhere. This has been proposed for unary, binary and ternary systems by Zen (1966b, 1967) and Zen and Roseboom (1972).

## 8. REMARKS ON $N + 4$ , $N + 5$ AND $N + K$ SYSTEMS

The particular cases  $k = 4, 5$  are now examined. Meanwhile, some general results are derived that come in addition to those given in Sect. 6.2. and followings.

### 8.1. $n + 4$ systems: univariant lines and stability successions

The affigraphy approach and the Fundamental Theorem exposed in Sect. 6 above allow to discuss some properties of  $n + 4$  systems. The affigraphy is four dimensional. Univariant lines in the  $(P, T)$  diagram correspond to the intersection of the two dimensional  $(P, T)$  plane with the different three-dimensional hyperplanes defined by sets of three vectors taken in the  $n + 4$  affinity vector set. The invariant points on a given univariant line are the intersection of the  $(P, T)$  plane with the different two-dimensional planes defined by pairs of vectors inside the three vector set defining the univariant line. One can then propose to represent graphically this disposition on an affigraphy restricted to the three dimensional subspace of one univariant line; three vectors defining such subspace are represented in Fig. 33A. The intersection with the  $(P, T)$  plane is a one-dimensional line; the two dimensional  $(P, T)$  space itself cannot be represented since it is not a priori contained in the three-dimensional subspace. Only its intersection with the subspace -the univariant line- is visible. The univariant line may cut the three planes on three invariant points; according to the location of the intersection points, three stability levels may obtain according to the number of negative parts (zero, one or two) of the two basic affinity vectors of the intersected sector. The stability of the portions of the univariant line are defined according to the part, positive or negative, of the basic vectors of the

three dimensional sector they are crossing. One important result of this method is then that all the possible successions of invariant points and univariant line portions with different stability levels may be found by cutting three planes by a straight line. As told in Sect. 5 and in order to avoid mixing up, the word « *succession* » is preferred to the word « *sequence* » in the spatial meaning. Examples of this operation are given in Fig. 33A and 33B; the synthesis of the results is given in Fig. 34. There are eight possible successions.

These successions may also be obtained provided one single is known, and by use of the symmetries of the problem; the three basic vectors may change their sign one at a time, or by groups of two (symmetries with respect to the three planes defining the hyperplane) or all together (symmetry with respect to the hyperinvariant point). The starting succession of invariant points along one univariant line corresponds to line  $\Delta_1$  in Fig. 33B and is described by the following succession of invariant points

1) AB BC -AC

The parentheses around the labels are omitted for simplification. By inverting the signs of the phases (exchanging A in -A and reciprocally -A to A), we obtain

2) -AB BC AC

This is  $\Delta_1$  reversed. Then successively, B is changed to -B and C to -C on the starting succession:

3) A-B -BC -AC

4) AB B-C -A-C

Then, by successive pairs of permutations ( $A \rightarrow -A, B \rightarrow -B$ ), ( $A \rightarrow -A, C \rightarrow -C$ ) and ( $B \rightarrow -B, C \rightarrow -C$ ) one gets

5) -A-B -BC AC

6) -AB B-C A-C

7)      A-B   -B-C   -A-C

Lastly, the three permutations ( $A \rightarrow -A$ ,  $B \rightarrow -B$ ,  $C \rightarrow -C$ ) together lead to

8)      -A-B   -B-C   A-C

The eight successions of Fig. 34 are obtained. Successions 4 and 5 correspond to  $\Delta_2$ , and successions 7 and 8 correspond to  $\Delta_3$ . The stability levels of the line portions are determined by the points that border it; for instance, portion of line 4 between AB and B-C is noted AB-C with one negative vector (stability level 1); and the next portion between B-C and -A-C is -AB-C (stability level 2). At each crossing of an invariant point along an univariant line, the vector of the line portion not included in the definition of the point changes its sign. For instance by crossing point B-C the sign of A is changed and the two portions in contact with point B-C are AB-C and -AB-C respectively. Only one finite portion of stable univariant line may thus be obtained in the different univariant successions, it is comprised between the two stable invariant points when these are present (successions 1 and 2); a semi-infinite stable portion is obtained in successions 4 and 5. These rules will be stated on a general standpoint in Sect. 8.6. This approach may also allow to define closed loops for a monodimensional path rotating around  $\Omega$ : in Fig. 35 two examples of univariant loops are given as may be constructed by the method exposed for Fig. 33 (cf. also Guo, 1980a, 1984).

## 8.2. Affine representation of $n + 4$ systems

A three-dimensional affine representation of the affigraphy may be used for the  $n + 4$  systems. The  $n + 4$  affinity vectors may be cut by a three-dimensional hyperplane and then be graphically represented; the resulting  $n + 4$  points will be black or white depending on whether the positive or negative part of the vector is cut. In the affine representation, two-dimensional planes of the normal affigraphy correspond to lines connecting pairs of such points. These lines may cut a two-dimensional plane and thus define the structure of a (P, T) diagram. The rules for the stability levels of the invariant points that result from the intersection of

pairs of affinity vectors with the two-dimensional (P, T) plane, are easily derived. For this purpose, comparison is made with the method of the previous section, in such a way that there is agreement with the results of the three dimensional representations of Fig. 33A and B. The convexity properties in vectorial and affine representation are in correspondence: the consideration of a point located with respect to a set of vectors or of points gives similar rules for the stability levels as in previous sections. The resulting rules are summarized in Fig. 36. In Fig. 37 an example of a (P, T) diagram for a unary 1 + 4 system is shown by application of this method. Successive intersection of the affigraphy has been done by a three-dimensional hyperplane then by a two-dimensional plane; thanks to this new geometric procedure, different types of  $n + 4$  diagrams are obtained that are similar to those given by Usdansky (1987), Ceolin and others (1991). The different possible structures of the diagrams are gained according to the different ways to choose first the three-dimensional hyperplane and second the two-dimensional plane. All the possible structures will not be discussed here on a general standpoint.

Another representation of four dimensional systems is possible by use of three two-dimensional plane projections in correspondence with one another like in descriptive geometry (Baracs, 1987).

### *8.3. Discussion of other works on $n + 4$ systems*

In a series of papers, Guo (1980 a, b and c, 1981, 1984) and Guo and Cai (1982) discuss several properties of the  $n + 4$  diagrams. Kujawa, Dunning and Eugster (1965), Kujawa and Eugster (1966) examine the case of unary 1 + 4 systems, Roseboom and Zen (1982) also discuss binary 2 + 4 systems. These contributions will not be commented upon here in detail. One of the important conclusions common to these papers and to others dealing with the same matter is that for  $k = 4$ , it is no longer possible to depict all phase relations within a single closed net (and corresponding polyhedron) as in the case of  $n + 3$  systems. This result is clearly understandable in the affigraphy approach. For  $k = 3$  the structure that depicts the phase relations has its meaning in a three-dimensional space. For  $k = 4$  the corresponding structure has its meaning in a four-dimensional space that is no longer representable

without loss of information in a three-dimensional space, nor a fortiori in a two-dimensional space. Several intersections or projections in lower dimensional spaces are needed (e.g. four 1D, or 3 2D, or 2 3D representations). One may for instance imagine to cut the four-dimensional affigraphy by two three-dimensional spheres contained in two perpendicular three-dimensional hyperplanes; by projecting the obtained structures onto two-dimensional planes as is done with three-dimensional polyhedra, one thus obtains pairs of associated closed-nets. Guo (1980b) also uses « *complete systems of closed nets* » or polyhedra with two-phase vertices that can be understood in the affigraphy frame; in the second example, polyhedra indeed correspond to an affine representation of the affigraphy where vectors  $A^{(j)}$  -  $A^{(j)}$  give rise to points by intersection with a three-dimensional hyperplane. This is another way with respect to that exposed in Sect. 7 to obtain an affine representation of the affigraphy by cutting lines defined by pairs of extremity of affigraphy vectors.

The approach set forth in sect. 8.2. may help understand the classes defined for  $k = 4$  diagrams by Usdansky (1987). From the affine representation of affigraphy for  $k = 4$ , it is easily shown that a single class of transposition operations in the sense of Mohr and Stout, 1980, (i.e. a geometrical transformation allowing to move from one type of diagram to another, cf. Sect. 14 on « *potential solutions* ») is not enough to define all the possible diagrams. For each type of intersection with an hyperplane, one can define a set of diagrams by rotating the two-dimensional intersecting plane around the  $n + 4$  apex polyhedron defined by the affinity points in the three dimensional space. If the intersecting plane goes inside the polyhedron one obtains the points corresponding to another polyhedron (cf. Fig. 36; if the plane is inside the polyhedron, the change of the stability of the intersecting point of the two-dimensional plane with the edges of the three-dimensional polyhedron is equivalent to change the position of the hyperplane with respect to the basic vectors, the inversion of any vector is always possible). So one only needs to rotate the plane outside the polyhedron and equivalence classes may be defined by the different possible starting polyhedra. Provided the intersecting plane is outside the polyhedron, the points of intermediate stability level do not change their stability level when the intersecting two-dimensional plane is rotated (Fig. 38); these sets define equivalence classes having such property (invariance of intermediate stability level) in agreement with the results of Usdansky (op. cit.).

The works of Provost, Lépine and Vielzeuf (1992), Lépine, Provost and Vielzeuf (1992), Guo (1980 a) treat the univariant stability sequences or rather successions for  $n + 4$  systems and are in agreement with the results presented so forth. The so called fundamental theorem of Guo (1980a) is understood in the geometrical representation of Sect. 8.1.

This theorem states that the stable line portion exists only once and is either comprised between the two stable invariant points, either semi-infinite; for the same reason, the number of stable invariant points on a line is at most equal to two. This can be generalized. A stable portion on an invariant line corresponds to *all* affinity vectors positive; this can occur but for *one* combination of the vectors. On the contrary a singly metastable portion occurs when one vector among the  $k - 1$  defining the line is negative; this may occur  $k - 1$  times. And a portion whose stability level is  $p$ , may occur for  $C_{k-1}^p$  combinations of the vectors. So the maximum number of occurrences of the  $p$ -stability level portion on a line is  $C_{k-1}^p$ . The matter is that a  $p$ -level metastable portion is graphically represented by only one type of line whereas it may be defined by  $C_{k-1}^p$  different vector associations. The above conclusion on the stable line portion holds for the highest  $(k - 1)$ -level metastable portion which may also occur once. Inspection of Fig. 34 and 40 for  $k = 5$  show that the above maximum numbers are confirmed; the actual numbers are lower than the maximum values; in the linear approximation of the paper (no curved lines nor closed loops) an univariant line in the corresponding  $k - 1$  dimensional space can encounter but a definite number of times, and lower than the upper limit, the sectors corresponding to a specific number of negative vectors. This number of times is not determined here.

#### 8.4. $n + 5$ systems

Affigraphy approach still permits to gain visual information on  $n + 5$  diagrams. In  $n + 5$  systems, the univariant lines are obtained by the intersection of four-dimensional hyperplanes with the two-dimensional (P, T) plane. The hyperplanes may be represented by affine sections in a three-dimensional space, defined by four points settling a tetrahedron. The three-dimensional space contains the univariant line, but not the two-dimensional intersecting plane. The univariant line cuts the four faces of the tetrahedron in four points. The stability of the intersecting points and of the intermediate portions of lines are determined according to similar rules as previously. Two examples are given in Fig. 39A and B; all the possible tetrahedra obtained by the intersection of four vectors in a four-dimensional space by a three-dimensional hyperplane, are not



represented here, neither all the possible ways to intersect them by lines. The synthesis of the possible univariant lines is given in Fig. 40; all the possible successions are represented. In order to find them, use may be made of the symmetries of the problem as exposed below in Sect. 8.6. The stability successions of Fig. 40 together with the list of corresponding vectors with their signs are listed in Table 3. This list of stability successions for univariant lines in  $n + 5$  systems has not yet been given in the literature.

#### 8.5. Examples of thermodynamic degeneracies for $k = 4, 5$ systems

One can use Fig. 33A to construct different examples of thermodynamic degeneracy for  $k = 4$ ; first, the (P, T) plane contains the intersection of two planes belonging to the hyperplane considered for the chemical reaction univariant line. Line  $\Delta_1$  may thus cut vector (B) and invariant points (AB) and (BC) will merge as illustrated in Fig. 41A. The corresponding invariant point will be termed (B). Next step is the merging of (B) and (A -C) when  $\Delta$  contains  $\Omega$ . In these operations, the corresponding stability changes on the univariant line are obtained by connecting the extreme portions of the non-degenerate case as given by Fig. 34. Similarly, one can use Fig. 39A to construct cases of thermodynamic degeneracy for  $k = 5$ ;  $\Delta_1$  may cross the edge (B)(D) of the tetrahedron, and points (ABD) and (BCD) will merge in (BD); subsequently  $\Delta_1$  may contain (B), and (BD) and (AB-C) will merge in (B) (Fig. 41B). Next step is the merging of (B) and (-ACD) when the line contains  $\Omega$ . This cannot be represented on the affine intersection of Fig. 39A where  $\Omega$  is lacking. All the possible stability changes for this type of degeneracy are obtained by use of Fig. 40 where 1, 2 or 3 intermediate portions are suppressed. In these cases of thermodynamic degeneracy, the notations of the points could be modified as suggested in Fig. 41C; one possibility would be to define composite invariant points gathering the underlying ordinary points. Hyperinvariant point  $\Omega$  itself gathers all the types of invariant points.

#### 8.6. Stability successions on $n + k$ system univariant lines

The previous method to determine stability successions (or « sequences ») on univariant lines may be generalized to any system for arbitrary values of  $n$  and  $k$ . As a rule, the univariant line is defined by the intersection of a  $k - 1$  dimensional hyperplane ( $k - 1$  vectors) by the (P, T) plane. The succession of points correspond to different sets of  $k - 2$  vectors among the  $k - 1$ , and reflect the intersection with other hyperplanes defined by other sets of vectors, but sharing each  $k - 2$  vectors with the whole line vector set. In order to find the possible successions, one only needs to know one of them. The other ones are obtained by use of all the symmetries concerning the relevant  $k - 1$  vectors.

Rules correlate the changes of labels for points and line portions on univariant lines; they have been partly exposed so far and it is necessary to state them exactly (Fig. 42 ). a) The label of a line portion is defined by the union of the labels of the limiting points. b) At each crossing of an invariant point, the vector of the line portion not included in the definition of the point changes its sign in the new line portion. c) As a consequence, candidates for next invariant points to a given point on a line may be proposed. They are  $k - 2$  in number, because one must subtract to the line portion vector set, any of the  $k - 1$  vectors, but not the one already subtracted in the previous point.

Let us suppose that the succession where the stability of the different invariant points increases or decreases monotonically by steps from the most stable point (stability 0) to the least stable (stability  $k - 2$ ) is always possible. As a proof, one can consider one one-dimensional line, considered as the intersection of the (P, T) plane with one reaction hyperplane; this line is supposed at first to contain the hyperinvariant point  $\Omega$  and to cross the affigraphy from the region where all the  $k - 1$  vectors of the hyperplane are positive to the opposite region where they are all negative. If now the intersecting (P, T) plane is moved a little away from  $\Omega$ , then  $k - 1$  points will appear corresponding to intersections of groups of  $k - 2$  vectors with the univariant line and the stability levels of the points will decrease by steps. The proof is complemented by the actual construction of such a succession below. The determination of a set of possible labels for this starting univariant succession may be done as follows. First choose a set of all positive letters,  $k - 2$  in number, for the first invariant point, for instance

ABCDE..MN

so that letter O is omitted from the  $k - 1$  set defining the line; then by substituting -O to any of the  $k - 2$  letters, for instance here to M, we obtain next point on the line

ABCDE N-O

and again we can now enter -M in the place of any letter for instance N giving

ABCDE -M-O

for a possible neighboring point on the line; and again till all the vectors are negative so that the requested succession with progressive decrease of point stability levels is obtained.

Starting with such succession, we can now operate all the possible symmetries of the problem. The change of the sign (or inversion) of the vectors in the starting succession one by one will lead to  $k - 1$  new successions, then the inversion of vectors two by two will lead to  $C_{k-1}^2$  new successions. And so on, the inversion of  $p$  vectors will lead to  $C_{k-1}^p$  new successions. At last the inversion of all the vectors will lead to one another succession. The total number of successions will be

$$N = C_{k-1}^0 + C_{k-1}^2 + \dots + C_{k-1}^p + \dots + C_{k-1}^{k-1}$$

where the first and last term are equal to one and refer to the first and last succession. According to the binomial Newton formula,  $N$  is equal to  $2^{k-1}$ ; this value was given through another reasoning by Lépine, Provost and Vielzeuf (1992). These authors set forth a selection « *stability rule* » that allows to extract the admissible stability successions from all the « *conceivable sequences* » (in the present sense of succession) also defined in their work; the great combinatorial number of possibilities renders the task difficult. In the present approach, the variety of the  $2^{k-1}$  successions is simply recovered by the group of symmetries of  $k - 1$  vectors in the affigraphy.

### 8.7. Determination of parageneses in affigraphy domains

So far, invariant points and univariant lines have been constructed by intersections of groups of  $k - 2$  and  $k - 1$  affigraphy vectors by two-dimensional planes. Next step is the construction of di-variant domains in the (P, T) diagrams, by the intersection of polyhedral cones, defined by  $k$  affigraphy vectors, with two-dimensional planes. The two-dimensional domains in the (P, T) diagram are defined by groups of  $k$

lines or hyperplane footprints, *each defined by a group of  $k - 1$  affigraphy vectors in the  $k$  set of the cone*. The knowledge of the  $k$  lines indicates the possible parageneses, and the position of a point in the two-dimensional diagram with respect to these  $k$  lines indicates its stability level. In order to know the stable parageneses, one needs to determine if the point of interest in the two-dimensional diagram is inside a stable, finite or semi-infinite, polygon constructed with the  $k$  lines. All the possible parageneses accessible to one point of the (P, T) diagram for different chemical compositions are determined by considering its position with respect to all the possible sets of  $k$  lines of the diagram (provided the definition of the lines in terms of absent phases is kept). The total number of possible parageneses is  $C_{n+k}^k$  but, generally, not all of them are stable together.

As a generalization of the stability successions along univariant lines, the knowing of the different stability levels of a phase basis in the different domains limited by a single set of  $k$  lines, defines what we can call a « *two-dimensional stability pattern* ». The metastable phases are obtained in the domains limited by metastable portions of the univariant lines. In order to find all the stability patterns that may be obtained for a given set of  $k$  lines, a similar method to that used to find all stability successions on univariant lines may be taken. The procedure merely lies on the systematic inversions of the affigraphy vectors defining the lines. Similarly, as an extension of the reasoning on the stability successions on univariant lines, the number of divariant domain stability patterns is  $2^k$ , because the symmetries bear on  $k$  vectors defining the different divariant domains and not  $k - 1$ .

The  $k$  lines of a given  $k$  absent phase set cone define several types of domains limited by two, three ...,  $k$  lines. These domains may be open, or semi-infinite for two lines and more, they may be closed for three lines and more, defining polygons ranging from triangles to  $k$ -apex polygons. Guo (1984) stated through a different reasoning that for a  $n + k$  multisystem the (P, T) domains may be up to  $k$ -apex polygons. The rule may be stated that for a given  $k$ -polygon,  $k$  stable invariant points at most may appear together. The total number of types of divariant domains in (P, T) diagrams for  $k \geq 2$  is  $2(k - 2) + 1 = 2k - 3$  because each

k-apex polygon is open or closed and the two-lines « *polygon* » is only open and counted once. In the case  $k = 1$  there is only an univariant line dividing the plane into two parts; the number of each type of open or closed polygon is not discussed. In the  $k$  absent phase set of lines, any two lines suffice to define the  $k$  absent phases and so the corresponding paragenesis.

Examples of stability patterns may be found in the preceding figures. For  $k = 2$ , sets of two lines must be inspected. The determination of phase associations is merely obtained by looking at the names, in terms of absent phases, of the univariant lines defining a given convex cone. For  $k = 3$ , the  $2^3 = 8$  possible patterns are given in Fig. 43. For  $k = 4$ , Fig. 44A gives the position of one point with respect to four lines. The overall « conic » domain is defined by four lines and six points limiting one closed and one open four-line domains, two closed and four open three-line domains and three open two-line domains. Fig. 44B give the sixteen possible stability patterns; the stability signatures (in terms of absent phases) of all the varieties are given only on some of the examples of the figure. When one line is crossed, the stability level of the paragenesis is changed by one, when two lines are crossed at a point, the stability changes by two.

## 9. THE SCHREINEMAKERS' RULES

### 9.1. *Historical remarks*

Affigraphy approach may be applied to the Schreinemakers rules. These govern the qualitative or topological properties of the arrangements of invariant points and univariant curves in the phase diagrams. The rules were derived by Schreinemakers (1915-1925) by a systematic exploration of the elementary algebraic relations between the compositions of phases and overall chemical systems, and the writings of the chemical reactions between the phases. Contrary to what is sometimes thought on the subject, this author did not directly consider the geometrical properties of the intersections of the free energy surfaces of the different mineralogical assemblages in the (G, P, T)

space; he rather proceeded by simple algebraic eliminations of variables between relations. No use of matrix relations was made; entropy and volumic changes were sometimes utilized to precise the statements. On several occasions, Schreinemakers stressed the duality between composition and (P, T) diagrams. However, because the dimensionality differences, this author could not go further. It is not possible to re-examine all the Schreinemakers work. We will restrict to the most important rules summarized in his review paper by Zen (1966a); we will discard the matter dealing with « *bundles* » of lines around invariant points (« *pencil theorem* » etc.), and that dealing with phases of variable composition (see some remarks in Sect. 12). Some rules are discussed in other sections of the paper, on degenerate systems (Sect. 11), stability sequences (Sect. 5, Ostwald step rule) and so on. Many other principles on the structure of phase diagrams have been stated (e.g. Zhao, 1983, Hillert 1985 etc.; see also those on  $n + 4$  systems, Sect. 8). In addition to the 1915-1925 series, other papers have been written by Schreinemakers on chemical system analysis; they will not be commented here.

### 9.2. Morey-Schreinemakers' rule

(Zen, 1966a) refers then to the reactions around an invariant point when the system is locally restricted to  $k = 2$ ; this is generally the point of view of Schreinemakers himself. Each of the reactions may be labeled by an absent phase, written between brackets; the M.S. rule states that the divariant assemblage where the two phases  $P_{i1}$  and  $P_{i2}$  are lacking, noted  $(P_{i1}, P_{i2})$ , is bounded by the curves  $(P_{i1})$  and  $(P_{i2})$ . This is clearly the case in the affigraphy where, for  $k = 2$ , the domain where phases  $P_{i1}$  and  $P_{i2}$  are lacking is the conic convex set defined by the affinity vectors  $(P_{i1})$  and  $(P_{i2})$ ; this may be generalized to the  $k$  dimensional case where the  $n$  phase ( $k$  lacking) assemblage  $(P_{i1}, \dots, P_{ik})$  is the convex cone bounded by the  $k$  affinity vectors  $(P_{i1}) \dots (P_{ik})$ , Fig. 45. The number of affigraphy vectors defining a cone may be arbitrary.

### 9.3. Overlap rule

Following the preceding rules and still for  $k = 2$  where a single invariant point is considered, the overlap rule states: if phase  $P_j$  is present in a

domain of the diagram, then the curve  $(P_j)$ , is contained (or overlapped) in the domain. At this first step, no matter whether the positive or negative part of the vector is considered. In the affigraphy framework, it is clear that the domain that contains  $P_i$  does not exclude  $P_i$  and so contains vector  $(P_i)$ ; otherwise vector  $(P_i)$  would be at the boundary of the domain. In the case  $k = 2$ , the univariant line coincides with the affinity vector and the overlap rule is demonstrated. This may be generalized for the vectors in the  $k$ -dimensional frame, Fig. 46. This result may be rendered more precise in connection with the composition of the system. In a given affigraphy domain, several co-bases are accessible depending on the overall composition; each is defined by a convex set of positive affigraphy vectors. Let a first convex set of  $k$  affigraphy vectors be considered where affigraphy vector  $(P_i)$  is not included, so that  $P_i$  is a possible phase of the domain; if however another convex set may be constructed where  $(P_i)$  is implicated, then  $P_i$  is not present for all compositions in the affigraphy domain. In order it is so, one must not be able to construct a positive convex set with  $(P_i)$  and  $k - 1$  other vectors of the starting set. This is so provided the negative part of  $(P_i)$  is inside the domain, and phase  $P_i$  is present in the domain for all possible bases. The Hillert rule discussed below results from the same property.

#### 9.4. « 180° rule »

In a two-dimensional  $(P, T)$  diagram with a single invariant point, the different univariant curves around that point are labeled by the names of the absent phases  $(P_i)$ ,  $(P_j)$  and so on. The « 180° rule » discusses the angles between neighboring lines and states that the angle of any sector where phases  $P_i$  and  $P_j$  are lacking, and bounded by curves  $(P_i)$  and  $(P_j)$  is less than 180°. This rule is a direct consequence of the convexity property of previous Morey-Schreinemakers' rule. It may be generalized in the  $k$ -dimensional framework. Let us inspect again **C** and **R** matrices. First, by convenience, let the coordinates in the chemographic matrix **C** be normed to one; i.e. the sum of the coefficients of each column is equal to one; for instance in

	A	B	C	D	E	F
A	1	0	0	$a_{AD}$	$a_{AE}$	$a_{AF}$
B	0	1	0	$a_{BD}$	$a_{BE}$	$a_{BF}$
C	0	0	1	$a_{CD}$	$a_{CE}$	$a_{CF}$

one can norm with

$$a_{AD} + a_{BD} + a_{CD} = 1$$

and the same for the other columns of **C**. For **R**, we will then have

	(A)	(B)	(C)	(D)	(E)	(F)
(D)	$-a_{AD}$	$-a_{BD}$	$-a_{CD}$	1	0	0
(E)	$-a_{AE}$	$-a_{BE}$	$-a_{CE}$	0	1	0
(F)	$-a_{AF}$	$-a_{BF}$	$-a_{CF}$	0	0	1

So

$$(A) + (B) + (C) + (D) + (E) + (F) = 0$$

and the sum of the affinity vectors is equal to zero. Thanks to coordinate changes, any hyperplane may be defined by  $k - 1$  basic affigraphy vectors. The coordinates of the  $n + k$  **R**-matrix column vectors (some to  $k - 1$  of them may belong to the above set), cannot be all of the same sign, corresponding to their being on the same side of the hyperplane, because it would violate the above relation. This is true, whatever the value of dimension  $k$ , and whatever the number of coordinates that are chosen. This gives the proof of the  $180^\circ$  rule; for  $k = 2$ , the hyperplanes and so the chemical reactions, are vectors, as ordinary affigraphy vectors are; in their disposal around the single invariant point, they cannot all be on the same side of any line, and this would give angles greater than  $180^\circ$ . As a whole, the generalized rule may be stated in the form (Fig. 47): « *the  $n + k$  vectors of the affigraphy do not have all their positive parts on the same side of any basic hyperplane* ». Several linear varieties, including hyperplanes, may be constructed on subsets of the  $n + k$  vectors, and the previous principle rules the orientation of these



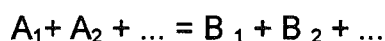
varieties with respect to the starting hyperplane. When the intersection by a two-dimensional plane is considered, the plane may be computed as contained in a set of  $k - 2$  hyperplanes; not all the  $n + k$  vectors will be on the same side of the hyperplanes, and the invariant points of the diagram cannot be all of the stable type.

### 9.5. Univariant scheme

The u. s. is another consequence of the properties of chemical reaction matrix  $\mathbf{R}$ . This rule deals with the correspondence between the arrangement of univariant curves (in the case  $k = 2$ ) labeled with absent phases and the writing of chemical reactions in the system (see also Morey and Williamson, 1918). For instance in a three component system, if reaction noted (B) is written  $A + C = D + E$ , then the curves (A) and (C) are on one side of curve (B), and curves (D) and (E) are on the other side around the invariant point. Let us suppose that the restriction of matrix  $\mathbf{R}$  to two dimensions ( $k = 2$ ) is written in the basis (A) (B)

	(A)	(B)	(C)	(D)	(E)
(A)	1	0	1	-1	-1
(B)					

where the second line is not written: reaction (B) where B is absent is given by the first line of the matrix and reads like written a few lines above. This writing expresses in the same time that the coordinates of the vectors along the first axis are such that (A) and (C) necessarily lie on the positive side and the other (C) and (D) on the negative side, so they are on both sides of the other coordinate axis (B) (Fig. 48). This result can be generalized to the disposition of the  $n + k$  vectors in the  $k$ -dimensional structure of the affigraphy: if one chemical reaction reads



where the absent phases are  $C_1, C_2, \dots, C_{k-1}$ , then vectors  $(A_1), (A_2), \dots$  lie on one side of hyperplane  $\{(C_1) (C_2) \dots (C_{k-1})\}$  and vectors  $(B_1), (B_2), \dots$

lie on the other side. By duality, a similar rule holds for the position of the phases with respect to chemography hyperplanes; these hyperplanes may be considered as « *reactions* » between absent phases, i.e. between affigraphy vectors (see Sect. 10 below).

Through appropriate generalization and definition of vectors for entropy and volume, the univariant scheme may be considered as an expression of the Le Chatelier moderation principle. The volume and entropic effect may be written in the chemical reaction itself in the form  $A_1 + A_2 + \dots + V = B_1 + B_2 + \dots + S$  where  $V$  and  $S$  are written on the side of the reaction where an increase of volume and an increase of entropy is observed (there are four possibilities depending on  $V$  and  $S$  being on the same side of reaction or each on one side). If these new components are accepted (see further discussion in App. A3), the u.s. allows to change from the point of view of the writing of the reaction to that of the position of the corresponding univariant line in the intensive ( $P$ ,  $T$ ) parameters space. In the above reaction absent volume vector, ( $V$ ), corresponding to  $P$  axis, will be on the same side of the line as vectors ( $A_1$ ), ( $A_2$ ) and so on, whereas absent entropy vector ( $S$ ), corresponding to  $-T$  axis, will be on the other side. This may be expressed by saying that, by increasing the pressure, the system moves in the direction of the absence of phases  $A_1$ ,  $A_2$  ..., i.e. in the direction where  $B_1$ ,  $B_2$  ... phases develop; the reaction proceeds in the direction where more dense phases, that « *consume* » pressure, are formed. Similar statements may be given for the entropic/temperature effect, or also to the effect of adding new amount of one phase on one side of the reaction. The Clapeyron relations are quantitative statements related to the preceding ones (see again App. A3).

#### 9.6. *Changes of phase assemblage stability level when crossing points and linear varieties; generalization of the « fundamental axiom »*

In the  $k$ -dimensional frame constructed on the  $n + k$  affinity vectors, different changes occur for the signs of the basic vectors, depending on the type of the variety that is crossed. When a path crosses the invariant hyperpoint while staying in a  $k$ -dimensional domain, all the sign of the  $k$

vectors bounding this domain change; when crossing the hyperpoint while belonging to an hyperplane, the corresponding  $k - 1$  absent phase vectors change their sign. The several possibilities to cross linear varieties of dimension  $p$  while staying in a linear variety of dimension  $q$  are indicated in Table 4. The number of affigraphy vectors that change their sign in this operation is indicated.

The cases of interest for the two-dimensional phase diagrams are: 1) the crossing of an invariant point while being along an univariant curve; in this case  $k - 2$  vectors are crossed along a variety of dimension  $k - 1$ . Then one vector changes its sign as discussed in Sect. 8. 2) The crossing of a chemical reaction ( $k - 1$  dimensional hyperplane) while being in a  $k$ -dimensional domain (= two-dimensional field of the  $(P, T)$  diagram): one vector of the  $k$  set changes its sign. Let for instance the  $k - 1$  phases of the hyperplane be  $C_1, C_2, \dots$ . The remaining  $n + 1$  absent phases will be divided into two sets; set  $A_1, A_2, \dots$  on one side of the hyperplane, and set  $B_1, B_2, \dots$  on the other side. The two sets define a chemical reaction as discussed in previous section. A  $k$  set cobasis is defined by the  $k - 1$  phases in the hyperplane to which a phase is added from the A or B group. For instance in the A group if the corresponding side is considered. When crossing the hyperplane, the A phase will change its sign and be replaced by a phase in the B set. So for instance in the  $k$ -vector set  $(C_1, C_2, \dots, A_i)$ , vector  $A_i$ , will be changed when crossing the hyperplane so that the set becomes  $(C_1, C_2, \dots, -A_i)$ . This means that there must be another positive vector, for instance  $B_j$ , that takes the place of  $A_i$  so that a full positive set is  $(C_1, C_2, \dots, B_j)$  for a new stable assemblage on the other side (the present phases are decided by complementation to the absent phases). Conversely,  $B_j$  becomes stable in the first collection and this is written as  $(C_1, C_2, \dots, -B_j)$ . On the whole there is an exchange of stability between  $A_i$  and  $B_j$ . Depending on the composition of the system, the  $k$  set may involve the different phases of the A set and they will be replaced by the different phases in the B set.

These rules are illustrated in Fig. 49 for the case of crossing the hyperpoint, (refer to Fig. 28 or 29 for the crossing of a point along an univariant line; see also figures in Sect. 8 for  $k = 4, 5$  systems) and Fig. 50 for that of crossing an hyperplane, reduced to a vector for  $k = 2$ .

These rules may be understood as the generalization of the « *fundamental axiom* » (Zen, 1966a) ruling the exchange in stability between two assemblages I and II when crossing an univariant curve on the (P,T) diagram: on one side assemblage I is less stable than assemblage II, and conversely on the other side of the curve assemblage II is less stable than assemblage I.

#### 9.7. « *Mirror image* » rule

In the end, each of the preceding topological rules is respected for two kinds of arrangements of the univariant curves around an invariant point in a two-dimensional plane. These two arrangements correspond to each other in a mirror (Zen, 1966a); only thermodynamic data allow to choose among those two. This may be understood in the affigraphy framework where the two-dimensional diagrams are obtained by an intersection of vectors by a two-dimensional linear variety. This plane may be contemplated from one side or the other; in other words the orientation of the two axes in this plane is not known. The two possibilities of looking at the plane or of orienting the axes in the plane lead to the two mirror images, Fig. 51A.

#### 9.8. Other rules

It is not the purpose of this paper to examine all possible « *topological* » rules pertinent to phase diagrams. In the case of the reactions around an invariant point, Hillert (1985) recalls that the number of unstable lines in a sector indicates the total number of phases that may be obtained in the sector. In affigraphy words, when the positive or negative part of a vector is overlapped in a sector, the corresponding phase cannot be taken as a boundary for a conic domain and so, depending on the composition, can be computed in the present phases (cf. overlap rule above). This is illustrated in Fig. 51B for a  $n (= 2) + 2 = 4$  phase invariant point. Sector  $\alpha$  (0 negative part) may be obtained by two possible cones (A,C) and (B,D), in addition to (A,B), and  $n + 2 - 0$  phases are possible in the sector. In sectors  $\beta_1$  and  $\beta_2$ ,  $n + 2 - 1 = n + 1$  phases are possible (1 negative part); in sector  $\gamma$  only one cone is possible (C,D) and  $n + 2 - 2 = n$  phases may be observed (2 negative parts).

Another rule discussed by Zharikov (1961) (cf. Sect. 6.2.) states that for  $k = 3$ , a (P, T) diagram contains at least one metastable point. This may easily be understood in the affigraphy frame: the lines of chemical reaction matrix **R** represent reactions; one coefficient at least per line is negative. In the affigraphy space, the vectors are not on the same side of any two-dimensional plane, and, in the section by such a plane, they cannot be cut in just one type (positive or negative) part. This precept is of the same nature for  $k = 3$  as the  $180^\circ$  rule for  $k = 2$ , and is one expression of the generalized  $180^\circ$  rule discussed above. An addition to Zharikov rule is proposed by Stout and Guo (1994); these authors state that, in the case there is one single metastable invariant point, the (missing) phase to which it corresponds is necessarily an interior phase in the chemography, i.e. it lies inside the composition domain defined by the other phases. Again, this is a consequence of the duality between chemography and affigraphy and corresponding **C** and **R** matrices. By transforming the **R** matrix back to a **C** matrix, the negative affinity vector corresponding to the metastable point will give a positive vector inside the basis of the other phases; the positive combination expresses the interiority of the point with respect to the other phases. The « *intrinsic stability rule* » of the authors (op. cit.) is another consequence of this duality.

As a conclusion to this section, Schreinemakers rules may be understood and generalized in the framework of the affigraphy. They are not by themselves a property of the (P, T) space, or of any two-dimensional space. They are more general, and are a property of the affigraphy space, which is dual to the chemography space. They are more appropriately stated in the  $k$ -dimensional framework. Thanks to the intersection procedure by a two dimensional plane, for instance a (P,T) plane, the rules have a counterpart in the two-dimensional frame.

## 10. GENERALIZATION OF COMPOSITION AND REACTION MATRICES

In the present section, some generalizations are deduced from the duality between chemography and affigraphy. In particular, on the chemography side, the case of phases with negative quantities of some of the components, or the case of systems with negative amount of some of the phases, is examined.

In the examples discussed so forth, the problems were generally initiated with composition matrix **C** showing a unit sub-matrix corresponding to a basis of the phase space; the finding of a complementary co-basis, and the construction of reaction matrix **R** was straightforward. No basis may be explicit in the starting **C** matrix when the compositions of the phases are expressed by the contents in chemical elements (not phases) a, b and c and so on. By pivoting on the phases (i.e. manipulation of the matrix as is done in linear programming, see App. 1 and 2), or, by adding the elements as new phases, a unit matrix may become apparent. This procedure was utilized in the examples discussed in Fig. 20 through 22. Similarly, no basis may be apparent in the chemical reaction matrix, for instance when it is given independently of the composition matrix. By the same procedure of pivoting, a basis may become apparent. In that case, and by analogy to the composition case, one can speak of « *absent elements* » as combinations of the absent phases appeared in the co-basis. In both cases, the elements or absent elements may be pointed on the chemography and affigraphy respectively.

In the composition matrix, some coefficients may by generalization be negative, depending on the choice of the basic phases, and of the origin of the coordinates. Mathematically, there is no problem for such a representation. Some basic phases may be non physical if they have negative amounts of some or all chemical elements. One can call « *negative phase* » that corresponding to a phase with all coefficients negative (let restrict the word « *absent* » to the affigraphy nomenclature). When only some of the coefficient are negative, words « *exchange vector* » or « *operator* » are used in the literature. A corresponding **R**

chemical reaction matrix may be constructed according to the method described in the paper. An illustration is given on an example, modified after the example studied in Fig. 3 to 5 (see also App. 2):

matrix **C**:

	A'	B	C	D	E
A'	1	0	0	-1	-2.5
B	0	1	0	4	1
C	0	0	1	1.5	1.5

where  $A' = -A$ , so that D and E have a negative co-ordinate on A'. The new **R** matrix is

	(A')	(B)	(C)	(D)	(E)
(D)	1	-4	-1.5	1	0
(E)	2.5	-1	-1.5	0	1

and when compared to the non modified **R** matrix, (A') takes the place of -(A). This is illustrated in Fig. 52. If B and C were also changed into -B and -C in the composition matrix, phases D and E would both have all their coordinates negative (as in a chemical reaction matrix), and the new chemical reaction matrix would have no negative coefficient (as in an ordinary chemical composition matrix).

By generalizing this procedure, two matrices **C** and **R** may be simply defined in duality, whatever the signs of the coefficients of the phases. In the discussion then, on one hand, the phases will be considered as present, and on the other, as absent. At this stage, the physical units used in both representations are not specified. From a physical and thermodynamic point of view, the equivalence between mass and energy would provide some justification for such practice. In that frame, chemography may be seen as an affigraphy for the affigraphy, or a diagram of present phases i.e. absent absent phases. For  $n = 3$ , the point representing a phase in the chemography is equivalent to an invariant point of the affigraphy. It is labeled by the present phase (=

absent absent phase) and the lines connecting this phase to the neighboring ones may be labeled by these last phases, similarly to the labeling of chemical reactions around an invariant point, Fig. 53. For  $n > 3$ , one cannot define invariant points in the chemography, unless a two-dimensional intersection of it is proposed, and the « *invariant points* » then correspond to sets of  $n - 2$  phases (Sect. 13.5). Corresponding hyperplanes connecting present phase points or vectors are multidimensional (not mere lines) and the labeling also involves collections of phases. In the generalized case, because of possible negative components of the phase vectors in the vectorial chemography, the vectors may not all cut the plane  $\sum x_i = 1$  used to construct the affine representation of the composition space. Similarly to what is done in the affine representation of the affigraphy or in two-dimensional phase diagrams, one may envisage to distinguish black and white points for the phases in the chemography (a white point is used if the negative part of the vector is concerned in the representation). One may also envisage to cut the chemography vectors by an hyperplane defined by  $\sum x_i = -1$  corresponding to negative closure.

The concept of reaction may itself be generalized to the chemographic space. « *Ordinary* » chemical reactions are defined by sets of  $n + 1$  chemography phases, and define hyperplanes in the affigraphy whose equations are defined by  $k - 1$  absent phases. Similarly, « *reactions* » (or « *co-reactions* ») may be defined by sets of  $k + 1$  affigraphy absent phases, allowing the writing of the equations for  $(n - 1)$ -dimensional hyperplanes limiting the different composition domains of the chemography. Pursuing the example of Fig. 53, one may say that CE line in the chemography corresponds to the « *reaction* »  $(A) = (B) + (D)$  where C and E are present (absent (C) and (E) are absent, so phases are present; Fig. 53B). The equation of the line ( $n = 3$ ), or hyperplane in the general case, in the chemography is given by appropriate row of **C** matrix, in the same way chemical reactions are given by **R** rows, following the procedure given in section 3.4. « *Backward* » Schreinemakers rules may hold for these reactions between absent phases. For instance, if one considers « *invariant point* » E of the chemography, phase A is on one side of « *co-reaction* » C, i.e. on one



side of line CE, and B and D are on the other; the corresponding equation written in terms of absent phases is thus  $(A) = (B) + (D)$ . Other rules may be derived following the same token. As usual, a reaction in the affigraphy (or P, T diagram) indicates a possible (depending on the composition) change in mineralogy one may observe by crossing the reaction and changing the intensive conditions. Conversely, a « *co-reaction* » in chemography indicates a change in mineralogy that may occur by varying the composition of the system; the change is expressed via absent phases and depends on the conditions also expressed by absent phases (Fig. 53B).

In composition space, « *exchange components* » (or « *exchange vectors* » or « *exchange operators* »; Thompson, 1982A and B; Burt, 1974, 1991) have some of their chemical composition co-ordinates negative. They are constructed by subtraction of ordinary phases. It may indeed prove convenient (in the case of solid solutions<sup>17</sup> for instance) to replace one set of phases, by an equivalent set of other phases, in same number, so that the all the original phases may be defined. For instance phases A and B may be replaced by phases A and A - B. In the vocabulary, one may distinguish the phases where no negative proportion appear (they define the so-called additive components, Thompson op. cit.) and those where negative proportions appear, called exchange vector. If several chemical substitutions are of interest, several exchange vectors may be defined from a given solid solution end-member<sup>18</sup>. As a generalization to this practice, one may define phases with no positive component at all (the corresponding exchange would be that with a vacancy). If the same chemical substitution exists in several minerals, the same exchange vector will appear several times if the corresponding phases are replaced by associations of additive and exchange components, and we are in a situation of degeneracy. Two types of reactions (exchange or net transfer) may be distinguished depending if the exchange components do appear or not. Exchange reactions may merely correspond to the degenerate equilibria of the type  $E_1 = E_2$  (where exchange components  $E_1$  and  $E_2$  have the same composition) among the degenerate exchange vectors. Depending on the values of  $n$  and  $k$  and of the number of such exchange vectors, it may appear interesting opportunities to express some reaction as combinations of exchange reactions only. Thompson, Laird and Thompson, 1982, derive some of these consequences on reaction space (the use of reaction space is a priori independent on the existence or not of exchange components, see below).

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<sup>17</sup> The description of solid solutions by such practice (see also Sect. 12 below) is straightforward. The definition of a solid solution is of thermodynamic and *not* mathematical nature: any association of phases may correspond to a solid solution between these phases taken as end-members provided that, thermodynamically, the free energy of this « *solution* » is lower than the sum of the corresponding free energies of the phases. In both cases the composition of the system will be described mathematically in the same way.

<sup>18</sup> These linear operations on the phases lead to mathematical items of the same dimension as the phases, that do not ordinarily correspond to the « *reactions* » or hyperplanes of the chemography. So the labelling of the exchange components may be done by the phases they connect to the chosen additive end-member cf. Fig. 54B, and is of different nature from the labelling of the hyperplanes of chemography.

Some remarks on the vocabulary on exchange components are necessary. In the literature on the subject, the matter is presented as of possible negative components, or of a change in the origin of the chemographic space (and a correlative change from an affine representation to a vectorial one). Actually, exchange components are often graphically represented as « *vectors* » by the authors whereas the other phases remain « *points* ». However in the calculations, exchange vectors are still on an equal footing as the other phases. All are points. If they are different from the other phases in that they have negative proportions of some of the chemical components, they may deserve a special label or name. But the words vectors or operators are misleading because they are mathematical words and lead one to think that exchange vectors have a different mathematical nature from the other phases. They are not special vectors nor operators and these words should be avoided; they may be replaced for instance by « *generalized phases* » or « *exchange phases* ». One should also make a distinction between exchange *components* and exchange *phases* in the same way chemical components and phases are characterized (each of them has negative coefficients). The practice of such components in the literature rather corresponds to exchange phases than exchange components.

So forth, we have examined the case when some of the starting phases may have their co-ordinates negative in the basis (« *negative phase composition* »). Although it is linked to the previous one, one must distinguish the case when we accept that the composition of the overall system may be built by negative proportions of some of the phases (« *negative system composition* »). In that second generalized frame metastabilities may be envisaged both in the affigraphy side and in the chemography side. The stability level of an association of (present or absent) phases is a property of the dual or supplementary association of phases with respect to the whole set. So the stability level of a present phase association is given by the number of negative vectors in the corresponding co-basis; this holds for a range of physico-chemical conditions, i.e. for a specified position in the affigraphy. By reciprocity, one can define a stability level for a co-basis, by the number of negative vectors (or phases) of the corresponding basis. By extension, when transported to a two-dimensional diagram where P and T are combinations of absent phase affinities, one is led to speak of « *unstable* » temperature or pressure. When dissociation affinity of phase  $P_j$  is such that  $A^0 < 0$ , phase j would be more stable to enter the basis, i.e. to appear in the list of the present phases. Conversely, when the quantity of phase  $P_j$  is such that  $x_j < 0$ , negative phase j, computed in the list of the present phases would be more stable to enter the co-basis,

i.e. to appear in the list of the absent phases. In the first case, metastable fields correspond to portions of space limited by one or several negative parts of affinity vectors ( $k + 1$  stability levels); in the second case, metastable fields are defined in the chemography by negative proportions of some or all of the phases in the paragenesis ( $n + 1$  stability levels). Following the preceding ways of generalization, stability sequences may be defined in chemography space for the co-bases. Figures in duality to Fig. 24 through 27 might be drawn. In the direct case, possible bases are listed for a given region of chemography, and classified according to corresponding co-bases for a given affigraphy region. In the reverse case, possible co-bases are listed for a given region of affigraphy and classified by corresponding bases for a given chemography region, according to the number of negative phases in the paragenesis. A Table in duality to Table 1 might be written. The lists of bases and of co-bases are known a priori. For each chemography region and each affigraphy region, the two lists may be examined and signs are given to each phase in the basis and each absent phase in the co-basis. On the whole, the list of corresponding bases and co-bases may be given, together with two stability indices, one for the basis and the second for the co-basis. For instance, in the case of Fig. 25, chemography region between phases A and B and affigraphy region between (A) and (D) are considered. The inspection of all the six pairs of associated bases and co-bases give the following stabilities:  $\{AB^\circ, (C)(D)^\circ\}$ ,  $\{AC^1, (-B)(D)^\circ\}$ ,  $\{AD^2, (-B)(-C)^\circ\}$ ,  $\{B-C^\circ, (A)(D)^1\}$ ,  $\{B-D^1, (A)(-C)^1\}$ ,  $\{C-D^\circ, (A)(B)^1\}$  with stability signatures (0, 0), (1, 0), (2, 0), (0, 1), (1, 1) and (0, 1) respectively. The number of negative vectors in one association gives the stability level of the other part. In this example no basis shows both phases negative because the cutting of composition space is done by the positive closure  $\sum x_i = 1$ , or equivalently because no phase is negative or has negative components at the beginning (all vector phases are in the positive two-dimensional orthant). The unstable extension of chemography « *univariant lines* » in Fig. 53A and 3 corresponds to system with negative amounts of phases. An example of such representation of stability levels for co-bases is given in Fig. 54 for a  $2 + 2$  system.

In the case a phase is replaced by the corresponding negative phase, one would expect some direct link between the change in stability signatures of bases and co-bases and the change in the signs of the phases and absent phases. Isn't a negative amount of a phase with negative co-ordinates equivalent to the positive amount? For a given system composition however, when the composition of possible phases changes, the structure of the chemography is also changed. There is a change in the algebraic composition of the system. If phase A is changed into -A, the cobases without (A) are not affected. So the bases with A do not change their stability. But the others change and the stability signatures of pairs of bases and co-bases computed for associated chemography and affigraphy regions change selectively. This may be seen in the example of Fig. 52 changed from Fig. 25.

When negative phases are considered as possible and distinct from the positive ones, e.g. -A added to A, new reactions may be written, e.g.  $A - C = D - B$  as distinct from  $A + B = C + D$ . Because the negative phases are in a situation of degeneracy with respect to the positive ones, the new chemical reactions will coincide with the ordinary ones. In that case, the univariant lines must associate different types of lettering corresponding to the different reactions for systems that may not be compatible from the composition point of view. Conversely, if negative absent phases are also considered in addition to the ordinary positive absent phases, the chemography co-reactions will be augmented by new reaction coincident with the basic ones. In that case also, different types of letterings should co-exist for the possible lines for these co-reactions (if a two-dimensional section is envisaged) because the affigraphy negative absent phases are degenerate with respect to the positive ones. In the standard cases one may choose that no negative phase is possible on the chemography, whereas negative absent phases are accepted on the affigraphy side; these express the different stability levels of phase associations in the ordinary thermodynamic sense.

If the preceding generalizations are mathematically self-coherent, it should be emphasized that the graphical representations derived from them may not fulfill all the orthodox Schreinemakers laws. Some of the laws are based on the positivity of all the coefficients of **C** matrix and on

the consequences on the **R** matrix. For example the 180° rule is not verified in the chemography for the external phases, Fig. 53A. As another example, the chemical reactions written in such approach may have all positive coefficients and thus one side only! On another hand, no thermodynamic data are directly available for components with negative coefficients such as exchange components. Affigraphy may however still be constructed, and chemical potential diagrams and so on may be drawn. By extension, two-dimensional sections of corresponding affigraphies may be obtained, simulating (P, T) diagrams for systems with components of arbitrary types. In this operation, thermodynamic data are thus ascribed to the components. If we take the example of the exchange component  $\text{FeMg}_{-1}$ , a deviation from the linear equality  $g_{\text{FeMg}_{-1}} = g_{\text{Fe}} - g_{\text{Mg}}$  will allow to shift from the position of thermodynamic degeneracy to that giving a possible diagram.

## 11. DEGENERATE SYSTEMS

The degeneracy in the chemography may correspond to a coincidence of two or more phases for  $n \geq 2$ , to the colinearity of three or more phases for  $n \geq 3$ , and, more generally, to the belonging to one hyperplane, i.e. an  $n - 1$  dimensional linear variety, of  $n$  or more phases in a  $n$ -dimensional chemical system. The non-degenerate phases are called indifferent phases. With increasing values of  $n$ , and if the value of  $k$  permits it, the several types of degeneracies for all the dimensions from 1 to  $n$  may coexist. For  $n = 1$  all the systems are degenerate. A systematic discussion of degeneracies for systems with  $n = 1, 2, 3$  and  $k \leq 3$  has been done by Zen in his papers (1966a, 1966b, 1967, Zen and Roseboom, 1972). All the types of degeneracies for arbitrary values of  $n$  and  $k$  cannot be examined here. Some principles may however be given on how a degeneracy on the chemography is transported to the affigraphy and finally to the (P,T) diagram, thanks to the correspondence between the underlying **C** and **R** matrices. This will be best explained by examining a few examples.

### 11.1. Example 1

$n = 2$ ,  $k = 2$ , Fig. 55. Matrices **C** and **R** for this system are respectively:

**C:**

	A	B	C	D
A	1	0	1	0
B	0	1	1	1

**R:**

	(A)	(B)	(C)	(D)
(C)	-1	-1	1	0
(D)	0	-1	0	1

Phases B and D coincide; as a consequence, affinity vectors (A) and (C) are colinear in opposite directions, i.e. coincide stable to metastable, by construction of the **R** matrix from the **C** matrix.

### 11.2. Example 2

$n = 2$ ,  $k = 2$ ; Fig. 56. Matrices **C** and **R** are

**C:**

	A	B	C	D
A	1	0	1	1
B	0	1	1	1

**R:**

	(A)	(B)	(C)	(D)
(C)	-1	-1	1	0
(D)	-1	-1	0	1

In this case, phases C and D coincide; on the affigraphy, (A) and (B) coincide, stable to stable.

### 11.3. Example 3

$n = 2$ ,  $k = 3$ ; Fig. 57. Matrices **C** and **R** are respectively:

**C:**

	A	B	C	D	E
A	1	1	2	1	0
E	0	0	1	2	1

**R:**

	(A)	(B)	(C)	(D)	(E)
(B)	-1	1	0	0	0
(C)	-2	0	1	0	-1
(D)	-1	0	0	1	-2

Phases A and B coincide. As a consequence, phases (C) (D) and (E) belong to the same plane, since their first coordinate on (B) is the same and equal to 0 for each of them. A similar example is discussed by a different method by Mohr and Stout (1980, p. 157) with the same conclusions.

#### 11. 4. Example 4

$n = 3$ ,  $k = 3$ , Fig. 58. Current chemical composition and reaction matrices are

C:

	A	B	C	D	E	F
A	1	0	0	0	0	1
B	0	1	0	1	1	1
C	0	0	1	0	0	1

R:

	(A)	(B)	(C)	(D)	(E)	(F)
(D)	0	-1	0	1	0	0
(E)	0	-1	0	0	1	0
(F)	-1	-1	-1	0	0	1

Phases B, D and E coincide so there are two associate degeneracies. The remaining phases (A) (C) and (F) belong to the same two planes  $(D) = 0$  and  $(E) = 0$  (two degeneracies) or other said are colinear. (A) and (C) coincide stable to stable and (F) coincide with the metastable part of (A) and (C).

#### 11.5. Example 5

$n = 3$ ,  $k = 3$ , Fig. 59

C and R matrix read respectively

	A	B	C	D	E	F
A	1	0	0	0	1	1
B	0	1	0	1	1	1
C	0	0	1	0	1	1

	(A)	(B)	(C)	(D)	(E)	(F)
(D)	0	-1	0	1	0	0
(E)	-1	-1	-1	0	1	0
(F)	-1	-1	-1	0	0	1

Two degeneracies are observed in the chemography: E and F coincide, so as B and D. In consequence (A) and (C) coincide and (A), (C), (E) and (F) are coplanar.

#### 11.6. Example 6

$n = 3$ ,  $k = 3$ , Fig. 60

Two associate degeneracies are obtained: phase D is colinear with A and C and phase E is colinear with C and B; the C and R matrices are:

	A	B	C	D	E
A	1	0	0	1	0
B	0	1	0	0	1
C	0	0	1	2	1

	(A)	(B)	(C)	(D)	(E)
(D)	-1	0	-2	1	0
(E)	0	-1	-1	0	1

In the affigraphy (Fig. 60B) (A) is colinear to (D) and in opposite direction, and (B) is colinear to (E) and in opposite direction.

On a general point of view, if there is a degeneracy on  $p$  phases in the chemography that belong to a  $p - 1$  dimensional subspace, there will be a degeneracy on the remaining  $n + k - p$  absent phase vectors of the affigraphy. These will belong to a  $(n + k - p - 1)$ -dimensional affigraphy subspace; this can be looked as a generalization, on the affigraphy, of the laws bearing on the univariant curves in two-dimensional diagrams for  $k = 2$ . For  $k = 3$  for instance, affigraphy approach allows to understand the degeneracy of reactions as a coincidence of two or more different planes as illustrated above. In degenerate systems invariant points or univariant lines may have more phase labels than ordinary ones. However, the nomenclature of invariant points and univariant lines need not special modification with respect to the non-degenerate case (contrary to the case of thermodynamic degeneracy), because the matter is simply of a *superposition* of ordinary points or lines with possible different stability levels. It seems appropriate to represent all these coincident points or lines, in the same way as for instance coincident degenerate phases are represented together in the chemography. As an example, if an additional affigraphy vector belongs to a  $k - 2$  dimensional variety of affigraphy vectors, it will be involved in the same invariant points of a  $(P, T)$  diagram as the others. Actually this invariant point represents  $k - 1$  ordinary invariant points defined by all  $k - 2$  subsets of vectors taken in the  $k - 1$  set altogether. Degenerate univariant lines may also be considered as the case when an indifferent crossing point between two different univariant lines degenerates into the same line because the two corresponding affigraphy hyperplanes coincide. In this way, it is easy to see that the different coexisting portions of degenerate univariant lines correspond to different bases, and so to systems of different chemical composition, that are generally non compatible. This is a reason to keep the coexistence of the different letterings for the line portions. If however a system of particular composition is considered, for which the degenerate univariant lines are compositionally compatible, the numbers of useful independent components and accessible phases are lowered. The number of reactions and thus of stability levels may be lowered on the univariant lines. For example, if the system composition in Fig. 57A lies in A, the sole possible reaction in the system is  $A = B$ ;



the (P, T) diagram of Fig. 57C is composed of one single line (C)(D)(E) dividing the plane in two domains.

### 11.7. Coincidence rule

This rule applies to a  $k = 2$  restriction of a system and has been illustrated in previous examples (Fig. 55 and 56 for examples 1 and 2). It states that, if the indifferent phases in the chemography are on one and same side of the variety of the degenerate phases, the corresponding degenerate reactions will be on opposite sides of the invariant point on the phase diagram, i.e. will coincide stable to metastable; conversely, if the indifferent phases are on both sides on the degenerate chemography variety, the vectors of the reaction will coincide stable to stable (see also Schreinemakers, 1915-1925, and Morey and Williamson, 1918). This rule may easily be demonstrated from the correspondence between **C** and **R** matrices or between chemography and affigraphy.

Let us consider an  $n + 2$  system (or the corresponding restriction of a  $n + k$  system) composed of the phases A, B, ..., M, X, Y; let the basis be the  $n$ -phase set B, C, ..., X. Let us consider the case of degeneracy where the  $n$  phases A, B, C, ..., M belong to the same hyperplane and have the same coordinate 0 on X. The two indifferent remaining phases X and Y have a non zero coordinate on X, 1 and  $a$  for X and Y respectively. If  $a$  is positive, indifferent phases X and Y are on the same side of the degenerate phase hyperplane; if  $a$  is negative the indifferent phases are on opposite sides of the hyperplane. This is summarized by matrix **C**:

	A	B	C	M	X	Y
B	$A_B$	1	0	0	0	$Y_B$
M	$A_M$	0		1	0	$Y_M$
X	0	0	0	0	1	$a$

The corresponding **R** matrix is easily constructed:

	A	B	C	...	M	X	Y
A	1	$-A_B$	$-A_C$		$-A_M$	0	0
Y	0	$-Y_B$	$-Y_C$		$-Y_M$	-a	1

One can easily see that if parameter  $a$  is positive the two vectors (X) and (Y) are now on opposite direction around the invariant point, that is to say coincide stable to metastable, whereas if  $a$  is negative (X) and (Y) coincide stable to stable.

The generalization of this rule for  $k > 2$  is interested in the orientation of the indifferent phase affinity vectors in their subspace of the affigraphy. Because of the degeneracy, they are at least one more than the dimension of their subspace  $q$ , i.e.  $q + 1$  in number. If  $q$  of them define the basis in the subspace, the  $q + 1^{\text{st}}$  left phase may have a variable position with respect to this basis, i.e. zero to  $q$  coordinates negative. This position is dependent on the position of the degenerate phases with respect to the indifferent ones in the chemography, and is transported from **C** to **R** matrix.

Take as an example the case  $k = 3$ , Fig. 57A, where indifferent phases C, D, E are on the same side of the degenerate phases A and B; vectors (C), (D) and (E) in Fig. 57B belong to the same plane and no angle between them is greater than  $180^\circ$ . On a two-dimensional intersection, the orientation of the invariant points (C), (D), (E) on the corresponding univariant line is the alternate orientation stable - metastable - stable or metastable - stable - metastable (black - white - black or white - black - white). On the contrary, the reader may check that in this example if the indifferent phases were located on both sides of the degenerate phases, the corresponding co-planar affigraphy vectors would be oriented in a different way: the third vector would be in the positive sector defined by the two first ones and, in the (P, T) intersection the invariant points would be all stable (black) or unstable (white).

## 12. AFFIGRAPHY AND (P,T) DIAGRAMS IN THE CASE WITH SOLUTION

If the phases possess solid solution, the obtention of possible (P,T) diagrams by the affigraphy method is no longer easily practicable, since the (P,T) planes depend on composition parameters, as it may be demonstrated. However the affigraphy may still be constructed and provide some local and global structural informations. All the problems relevant to solutions are not studied. Three methods are presented.

### 12.1 Parametrization of the solid-solution vectors

The case of one phase with solid solution only will be considered; the case with several phases having solution may easily be treated by

appropriate extension. In the phase composition matrix **C**, the solid solution may be parametrized between  $s$  end-members, so  $s$  coordinates of one column vector depend on  $s - 1$  parameters. After constructing matrix **R** of chemical reactions,  $s$  affinity vectors will depend on  $s - 1$  variable parameters for one and the same of their coordinates. The affigraphy will show what is similar to solid solution for  $s$  affinity vectors; these « solutions » have the particularity not to be independent. As an example, a simple  $3 + 2$  system is described by the following **C** composition matrix

	A	B	C	D	E
A	1	0	0	$1+a$	1
B	0	1	0	$2-a$	1
C	0	0	1	3	1

where the two first components of D phase composition may vary when parameter  $a$  is varied between 0 and 1. The corresponding chemography is represented in Fig. 61A. The correlated matrix **R** of chemical reactions is

	(A)	(B)	(C)	(D)	(E)
(D)	$-1-a$	$a-2$	-3	1	0
(E)	-1	-1	-1	0	1

and the corresponding affigraphy is represented in Fig. 61B; two vectors (A) and (B) have one variable coordinate on (D) axis. Their projection on (E) axis is fixed. All the chemical reactions in the affigraphy that exclude phases A and B, that is to say that contain vectors (A) and (B), will thus be variable. In the general  $k$ -dimensional case, some hyperplanes of the affigraphy will thus be variable when there is solid solution. These results are independent of any thermodynamic data.

The operation of intersection of affigraphy by (P, T) planes is more complex task. The free energies of the phases are now dependent on composition parameters by laws of the type

$$g^j = ag^{j1}(P,T) + (1-a)g^{j0}(P,T) + RTf(a)$$

for a solid solution in phase  $P_j$ , with two end-members 0 and 1, and with composition parameter  $a$ ;  $f(0) = f(1) = 0$ .  $g^{j0}$  and  $g^{j1}$  may be linearized in T and P as done before, but due to the new internal composition parameter  $a$ , also present in the additional factor  $RTf(a)$ , the planes cutting the affigraphy will be parametrized by  $a$ . By analogy with the cutting of the affigraphy by two-dimensional (P, T) planes, one can say here that the total affinity belongs to a three-dimensional variety that can be parametrized by (P, T, a); this variety is not linear since the development of the  $g(P, T, a)$  has terms in  $aP$ ,  $aT$  and so on. It is convex since the  $g$ 's are convex, and mathematical programming methods may still be utilized (Dantzig, Johnson and White, 1958). Intersection for  $a = \text{constant}$  may be computed yielding ordinary (P, T) diagrams. All the successive intersections may be projected on the same (P, T) plane; families of straight lines will correspond to the reactions involving solid solutions, or the univariant lines will be variable on the solid solution composition as already known. These families may define envelopes (Sect. 12.3), corresponding to the successive stable equilibria of neighboring reactions for progressively variable  $a$  parameter. The invariant point  $\Omega$  in Fig. 61B actually represents a continuous collection of invariant points when the composition parameter  $a$  is varied; it represents the local relations resulting from the intersection of five reactions for given values of the parameter, for the two of them (A) and (B) that are variable on the parameter.

### 12.2 Representation of end-members

It is also possible to represent the solid solution by distinct end members, together with the definition of the linear variety depicting the possible compositions between these end-members. In the preceding

example, D may be represented by the two end-members  $D_0$  (for  $a = 0$ ) and  $D_1$  (for  $a = 1$ ) in a composition matrix as

	A	B	C	$D_0$	$D_1$	E
A	1	0	0	1	2	1
B	0	1	0	2	1	1
C	0	0	1	3	3	1

The corresponding affigraphy is constructed after the reaction matrix

	(A)	(B)	(C)	( $D_0$ )	( $D_1$ )	(E)
( $D_0$ )	-1	-2	-3	1	0	0
( $D_1$ )	-2	-1	-3	0	1	0
(E)	-1	-1	-1	0	0	1

In this approach, the affigraphy vectors may be seen as variable between ( $D_0$ ) and ( $D_1$ ) when  $a$  is varied from 0 to 1; this variation will be linear and thus the linear variety constructed on ( $D_0$ ) and ( $D_1$ ) will be obtained. In this representation, the (P, T) plane will apparently be independent of the intermediate compositions, provided the thermodynamic data for the end-members are known, and a (P, T) diagram seems to be at reach with a single intersection; but it is not so, since any intermediate composition will need a specific (P, T) plane depending on the composition parameter; this would increase the dimension of affigraphy. The method may provide a first approximation to the diagram with uncomplete variation of the composition solution. Chemography and affigraphy corresponding to this second method are illustrated in Fig. 62A and B. In Fig. 62C, projection has been made in the  $D_0$ ,  $D_1$  plane. The representations in Fig. 61B (first method, variable vectors) and 62B and C (second method, representation of end members) do not give exactly the same relations. The invariant point on Fig. 61B allows to represent the intersections between all reactions ( $A_i$ ) and ( $B_j$ ). The two collections ( $A_i$ ) and ( $B_j$ ) may separately define enveloppes as will be indicated below. The coincidence of ( $A_{1/2}$ ) and ( $B_{1/2}$ ) defines a singular line (Sect. 12.4). On the contrary in Fig. 62, only

one reaction is variable; the relations between neighboring reactions on the *same* continuous reaction may be more easily seen. The correspondence between the two methods may be retrieved by coordinate changes. Vectors (A) and (B) may be taken as defining the basis in Fig. 61B, in which case vector (D) will be variable as in Fig. 62B and C since the variable coordinate of (A) and (B) is the one on the (D) axis; vector (C) is not concerned since phase D has a constant composition in component C, nor (E) is concerned for it is not involved in the representation bases

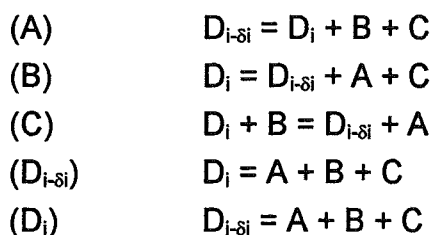
Another method for discussing the diagrams with solid solution is that of using exchange components; it is equivalent to the method of end-members but with possible negative coordinates in phase space.

### 12.3. *Pseudocompounds*

As a third method, the composition of the solid solution phase may be approximated by a finite set of phases of differing compositions (or pseudocompounds, Connolly and Kerrick, 1987), along the variation of the solid solution. This is an extension of the previous method. The number of the phases may be increased when one wants to be closer to the solution. Basically, this procedure increases the number  $k$ . For each pseudocompound, one can compute the possible chemical reactions in the system. When  $k$  increases, the number of reactions also increases, together with the number of invariant points and stability levels of all types of possible phase associations. When  $k$  goes to infinity the complete solution is obtained; in that case the number of reactions, points and of stability levels is also infinite. Envelopes may be defined as gathering neighboring stable invariant points and replace the infinite collections of reactions by one single curve.

In order to understand the relations between individual reactions and envelopes, it is convenient to consider first the case of a finite set of pseudocompounds and then discuss what happens when this number goes to infinity. Let again consider the example of Fig. 62A where solution parameter is  $a$  for phase D; different pseudocompounds  $D_i$ ,  $D_{i+\delta i}$ ,  $D_{i+2\delta i}$  ... are considered when composition parameter equals  $i$ ,  $i + \delta i$ ,  $i + 2\delta i$ ... The limit of the solution will be obtained when  $\delta i$  goes to zero. Let

us restrict to the five reactions (A), (B), (C), ( $D_{i-\delta i}$ ), ( $D_i$ ) at the invariant point  $P_{i-\delta i, i}$  for a 3 + 2 system. The different reactions read:



The coefficients are not computed. The reaction ( $D_i$ ) is also called  $R_i$ , and the reactions (A), (B) and (C)  $R'_{i-\delta i, i}$ ,  $R''_{i-\delta i, i}$  and  $R'''_{i-\delta i, i}$ . The writing of reactions  $R'$ ,  $R''$  and  $R'''$  may be obtained when that of adjacent reactions  $R$ 's are known. The five reactions are represented in Fig. 62D. At invariant point  $P_{i-\delta i, i}$  neighboring reaction  $R_i$  and  $R_{i-\delta i}$  meet corresponding to neighboring compositions of the pseudocompound. The set of additional reactions (A), (B and (C) meet at the invariant point and respect the Schreinemakers laws. When the difference between the neighboring compositions goes to zero (when the number of pseudocompounds is increased)  $\delta i$  goes to zero; the line portions joining the  $P_{i, j}$  (where  $i$  goes to  $j$ ) in the figure diminish their size and define the seached envelope. Reactions  $R'$ ,  $R''$  and  $R'''$  vanish because the coefficients of phases A, B and C go to zero; these reactions reduce to the tautology  $D_i = D_i$ . In this operation the envelope may thus be understood as an infinite collection of stable invariant points (Fig. 62E); each represents the point of contact of individual reactions  $R_i$  with the envelope. Paradoxically, at the limit, the invariant points concern only one reaction whereas several would be expected to fulfill Schreinemakers laws. The paradox that other reactions are lacking at these « *invariant points* » is solved by the above conclusion that other reactions vanish. Each individual reaction  $R_i$  is tangent to the envelope and, away from it, changes its stability degree an infinite number of times. The metastable invariant points such as all the  $P_{i, j}$  (with  $i \neq j$ ) in Fig. 62D define an infinite number of points and stability levels. This infinite number of stability levels cannot be represented and in Fig. 62E the lining of the reaction tangent to the envelope is unique; but it is continuously changing its stability. Contrary to an ordinary reaction the

envelope has an additional degree of freedom in the variation of the composition of the solution phase along it; the choice has been done to keep only one stability degree (e.g. most stable: it is equivalent to say that two different compositions of the solid solution cannot be associated) contrary to an ordinary reaction which by itself does not take care of the stability levels and contains all possible stability degrees. The reaction defining the envelope is unique. The mathematical equation of the envelope is obtained by derivating the chemical equation with respect to the solution parameter, this is equivalent to finding the intersection of two neighboring reactions. Each reaction for each specific composition is represented by a straight line; the envelope is a curve obtained by joining the adjacent stable portions as represented in Fig. 62E and going to the limit when the size of the portions goes to zero. If we restrict the word reaction to the writing with specific coefficients, the continuous reaction is not ordinary but generalized reaction. In the literature on the subject, the envelope for one continuous reaction is sometimes represented by a straight line and the individual reactions by curved lines; this representation does not fit the straight line hypothesis for individual reactions (cf. Sect. 12.4). Similarly to what is done for the stable invariant portions and points, one may also join the portions of lower stability levels and there is thus an infinity of envelopes with differing stability levels. The complete application to solid solution phases needs to consider the generalization of the affigraphy approach for  $k \rightarrow \infty$  and Hilbert spaces.

#### *12.4. Singular lines and singular points*

The structure of diagrams involving phases with solid solution and the variation of composition along reactions involving solution is studied by such authors as Rumble (1974), Hensen (1987), Guiraud, Holland and Powell, (1990) among many others. The singular point analysis of Abart, Connolly and Trommsdorff. (1992) may be understood in the affigraphy frame. In the case of solid solutions, degenerate reactions may obtain for some specific compositions of the solid solution. The specific hyperplanes related to two such degenerate reactions locally coincide; this corresponds to the situation of so-called singular lines in the two-



dimensional diagrams. In the general case when entropy and volume data for the phases are considered as slowly variable, the singular lines, which correspond to reactions among fixed composition phases are best represented by straight lines, as said above. This is in general conformity with the « *straight line analog* » hypothesis of the literature; the singular (straight) lines are in tangency with the reactions with variable composition phases. These last reactions are represented by curves, obtained by enveloping families of straight lines (Sect. 12.3). This is not the choice of Abart, Connolly and Trommsdorff (op. cit.), nor of other authors treating this matter, where singular curves are not straight lines, while reactions with solution phases are; this last representation is problematic. The laws ruling the structure of invariant points, singular points, reactions and singular curves may be understood by considering the structure of the corresponding vectors and hyperplanes of the affigraphy. Let us consider the previous example where the solution is parametrated (Sect. 12.1, Fig. 61). The degenerate reaction reads  $E + C = D_{1/2}$  for  $a = 1/2$  where phases A and B are absent; this reaction is degenerate from  $E + C = D + A$  (for  $a \leq 1/2$ ) and  $E + C = D + B$  (for  $a \geq 1/2$ ). The other possible continuous reactions are not considered here; they fall out of the composition range of the solid solution. In the affigraphy, vectors  $(A_{1/2})$  and  $(B_{1/2})$  are colinear and with the same direction (A and B are on opposite sides of line  $ED_{1/2}C$  of the chemography). The line  $(A_{1/2}) = (B_{1/2})$  represents in the same time the singular curve and the singular points. The curve for the continuous reaction is not visible because no (P, T) plane is considered. In Fig. 62 these degeneracies are not visible: because of the representation, there is only one variable reaction at the invariant point whereas there are two in the Fig. 61 representation.

Another example can be considered; let **C** matrix be:

	A	B	C	D
A	1	0	2 - a	1
B	0	1	a	2

In association with **R** matrix:

	(A)	(B)	(C)	(D)
(C)	$a - 2$	$-a$	1	0
(D)	-1	-2	0	1

The second method of representing solid solution corresponds to **C** written as :

	A	B	$C_0$	$C_1$	D
A	1	0	2	1	1
B	0	1	0	1	2

and **R** is

	(A)	(B)	( $C_0$ )	( $C_1$ )	(D)
( $C_0$ )	-2	0	1	0	0
( $C_1$ )	-1	-1	0	1	0
(D)	-1	-2	0	0	1

and the corresponding chemography and affigraphies are given in Fig. 63 A, B and C. In this example the degenerate reaction reads  $(A) = (C)$  when composition parameter  $a = 0$ . It corresponds to absent phases B and D: in Fig. 63B affigraphy vectors (B) and (D) are colinear for  $a = 0$ ; the degenerate reaction is common to the reactions  $A + B = C$  (D absent) and  $A + D = C$  (B absent). The degeneracy is also visible in the second representation (Fig. 63C) where  $C_0$  is coincident with A; the three vectors (B) ( $C_1$ ) and (D) are coplanar. One may cut the structure of Fig. 63C by a two-dimensional plane and obtain Fig. 63D. The set of the lines connecting (D) and (B) to the points of ( $C_0$ )( $C_1$ ) have the line (D)(B)( $C_1$ ) in common; it represents the singular line, whereas points (B) and (D) represent the singular points.

The stability levels of singular lines needs be discussed. By itself, a singular line has the same meaning as any other reaction in a  $k$ -infinite dimensional system; it thus has an infinity of stability levels. In addition, it corresponds to a situation of degeneracy in the composition of the phases of the system, and the line is common to two reaction systems; two straight lines, each tangent to a curve, coincide in a singular line. In this operation each of the lines still has an infinite number of

stability degree; it may also be viewed as the degeneracy of an indifferent crossing point (section 6.4.) into a line: in general the two lines can have less than  $n$  phases in common, the two coincident lines are not compatible from a composition point of view and the infinite stability levels of the lines must be considered separately. In the literature on singular lines (e.g. Schreinemakers, 1915-1925, Connolly and Trommsdorff, 1991, Abart, Connolly and Trommsdorff, 1992) the number of stability levels of singular lines is not in agreement with the announced number  $k$ . For instance the last authors indicate three stability levels for the singular line, but  $k$  is announced to be two and there should be only two stability levels.

Actually, finite portions of the singular line can be stable only for a specific composition of the system, as a part of a « *pseudosection* » (Sect. 6.5.). For instance if the composition of the system lies in  $D_{1/2}$  in Fig. 62A, the accessible reaction is  $D_1 + D_0 = E + C$ ; or if the system is in  $C_0$  (Fig. 63A), the only accessible reaction is  $A = C_0$ . In that case the whole singular line is stable; it is the only reaction of the diagram that divides (P, T) plane into two parts. In summary, the association of a singular line for a specific system composition and the rest of the diagram for all compositions may be misleading.

Another application of the affigraphy approach to problems with solution may consider the case where a new component is added in limited amount to a system. One wishes to know how the invariant points and univariant lines are marginally modified. In the case where solution is possible, some of the coefficients of the composition matrix will have lower values than in the case without solution; it is not needed to add new components (and new lines in the matrix); the consequences of the variation of the coefficients in the composition matrix on the variation of the reaction matrix may easily be computed. Without changing the (P, T) intersection, the movement of the intersecting points and lines will thus be visible. The sense of variation of the solution composition along a given reaction may similarly be found by considering the relations of the different composition vectors around the running invariant points; for example, Fig. 62C, the continuous reaction curve will be tangent to vectors  $D_0$  and  $D_1$  as represented in Fig. 62E. We conclude that the solution composition increases from right to left on the reaction curve.

### 13. DIFFERENT TYPES OF PHASE DIAGRAMS

It is not in the scope of the paper to discuss all the possible types of phase diagrams. In the following, some types of diagrams are briefly reviewed in relation with the concepts developed so far.

### 13.1. Four basic types of phase diagrams

Two basic types of thermodynamic variables, namely concentrations and potentials have been recognized (e.g. Connolly, 1990). Two basic types of diagrams are associated to these variables. The chemography is associated to the chemical concentrations (or mole numbers);  $n + k$  phases are located as points (or vectors) in an  $n - 1$  (or  $n$ ) dimensional space, read as the  $n + k$  column vectors of matrix  $\mathbf{C}$ . For each value of  $P$  and  $T$ , a chemical potential picture may be associated to chemography; in the  $n$ -dimensional space of the potentials  $\underline{\mu}$  of the chemical components, each of the  $n + k$  phases is represented by one hyperplane whose equation is  $\underline{\mu} \cdot \mathbf{C} = \mathbf{g}$ . Each column of  $\mathbf{C}$  gives one hyperplane, and vector  $\mathbf{g}$  is known because  $P$  and  $T$  are chosen; the system is restricted to the inequality  $\underline{\mu} \cdot \mathbf{C} \leq \mathbf{g}$  and only parts of the hyperplanes are taken; a convex polyhedron is defined; this limits a saturation chemical potential hypersurface (the word « *surface* » or « *hypersurface* » is used by extension to name the convex set defined by hyperplane portions in preceding equation). These classical chemography and chemical potential representations are in geometric duality: points or vectors of the chemography are replaced by hyperplanes in the chemical potential diagram. Another type of diagram may be constructed with chemical potential variables; we will name it chemical potential *grid* (see below) in order to distinguish it from the chemical potential saturation surface.

In the preceding sections, a new duality has been discussed; in what was named combinatorial duality, a phase or collection of absent phases is considered in the place of another set of present phases, in complement to the whole set of the phases; the correspondence between chemography and affigraphy involves that type of complementarity. Chemical reactions or hyperplanes in the affigraphy are defined by collections of absent phases. The so-called unitary absent phase vectors are given by the  $n + k$  columns of matrix  $\mathbf{R}$ ; they may be represented in the  $k$ -dimensional space of affinities, called the affigraphy;  $k$  is supplementary to  $n$  with respect to  $n + k$ .

At this stage, the number of listed diagrams amounts to three: chemography, chemical potential diagrams and affigraphy. Because of

the above double, both geometric and combinatorial, duality, the two basic types of variables actually give rise to four basic types of diagrams. The fourth type of diagram is in geometric duality with affigraphy and combinatorial duality with the chemical potential diagram. For this diagram the columns of matrix  $R$  are expected to give equations of hyperplanes. Such diagram is described in the literature, although its matrix structure has not been considered: « *reaction space* » (e.g. Prigogine and Defay, 1946; Thompson, 1982b), whose axes are the progresses  $\xi_f$  of  $k$  independent reactions in a  $k$ -dimensional space. The hyperplanes are given by the equations  $\xi^T \cdot R = -x_0^T$  defined by the columns of matrix  $R$ ;  $x_0$  are the initial quantities of the  $n + k$  phases; a limiting polyhedron bounding reaction space is defined because  $\xi^T R \geq -x_0^T$ . Because of  $x = x_0 + \xi = x_0 + R^T \cdot \xi$ , relation  $\xi^T \cdot R = -x_0^T$  corresponds to  $x = 0$  and the hyperplanes refer to absent or completely consumed phases. Reaction space is also considered in Ferry (1983), Fisher (1989), Spear (1988) and Thompson, Laird and Thompson (1982); Chen (1994) discusses the use of reaction progress for an experimental open system where the quantity of total pervasive water is taken into account in the calculation. In Thompson (1982b) the chemical reaction considered are not the basic phase dissociation reactions examined in the present paper but other independent reactions; this is equivalent representation through coordinate changes.

It is useful to use  $n + k$  dimensional spaces to precise the geometrical connections between all these representations (Fig. 64). Vector  $x$  with  $n + k$  components may be represented in an  $n + k$  dimensional space (Fig. 64A); it defines the modal space (e.g. Thompson, 1991) where the quantities of all the possible phases are represented. Variety  $V$  defined by  $C \cdot x = C \cdot x_0 = \underline{c}$  is the intersection of  $n$  hyperplanes in an  $n + k$  dimensional space; it is  $k$ -dimensional; it is parallel to the variety  $V_0$ ,  $C \cdot \xi = 0$  containing the origin.  $V$  and  $V_0$  define the null space or reaction space; the admissible parts of this subspaces are limited by  $x \geq 0$  or by  $\xi \geq -x_0$  with  $\xi = x - x_0$ . Point  $x_0$  is chosen as the origin in  $V$ . Limits of reaction space are obtained by the intersection of  $V$  and the basic coordinates hyperplanes of the modal space, or of  $V_0$  with hyperplanes of equations  $\xi = -x_0$ ;  $k$  independent reaction advances may be chosen as a

Reaction space is supplementary to the  $n$ -dimensional composition space  $W$  (chemography) with respect to the whole  $(n + k)$ -dimensional composition diagram; with the appropriate definition of a scalar product, the two spaces may be defined as orthogonal. The origin on  $W$  is  $x_0$ . The variety parallel to  $W$  and containing the origin  $O$  is  $W_0$ . The projection of the  $n + k$  unitary vectors of the whole  $n + k$  space onto  $W_0$  and parallel to  $V$  or  $V_0$  yields the chemography. The projection  $\underline{c}$  of  $x$  on  $W_0$  is ruled by  $C \cdot x = \underline{c}$ . The unitary vectors in  $n + k$  space are projected along the column vectors of  $C$  representing phases in the chemography. The projection of vector  $x$  onto the chemography is  $c$  constant; vector  $\underline{c}$  is also the intersection of  $W_0$  with  $V$ .

Let us consider now the  $n + k$  space of the affinities  $A^\Phi$  of all the phases; the origin is  $\Omega$  (Fig. 64B). In a similar manner to what is done on the modal space,  $n$ -dimensional variety  $RA^T = \underline{a}^T$  is considered where  $k$  independent affinities  $\underline{a}$  are « mathematically » fixed; physically it corresponds in fine to the choice of both parameters  $P$  and  $T$ . It is  $V'$  (dim.  $n$ ), parallel to  $V'_0$   $RA^T = 0$ . The supplementary orthogonal variety to  $V'$  and containing  $A_0$  is called  $W'$  (dim.  $k$ ).  $A_0$  is the initial affinity vector for the values of affinities at the beginning of the equilibrium process.  $W'_0$  is parallel to  $W$  and contains origin  $\Omega$ . Because of the properties of  $C$  and  $R$  matrices, variety  $R \cdot y = \text{constant}$  and  $C \cdot y = \text{constant}$  are perpendicular. The admissible field of the  $n + k$  dimensional affinity space is limited by  $A \geq 0$  or equivalently  $\mu = \underline{\mu} \cdot C \leq g$  bounding the subspace  $V'$  and this defines chemical potential saturation space. Affigraphy is obtained by projecting the  $n + k$  unitary affinity vectors of total affinity space onto  $W'_0$  subspace parallel to  $V'$ . The unit vectors in the  $n + k$  affinity space are projected along the column vectors of  $R$  representing absent phases of affigraphy.

As a synthesis, the structural aspects alone may be considered without taking into account the values of the coordinates. Chemography may be considered as the projection of the apex of an  $n + k$  dimensional hypercube and its radiating unit vectors (edges) onto an  $n$ -dimensional variety, whereas affigraphy is the projection of such an apex onto an orthogonal  $k$ -dimensional variety. Reaction space results from the

intersection of the positive orthant of the  $n + k$  dimensional space with a  $k$ -dimensional variety, whereas chemical potential hypersurface results from the intersection with an  $n$ -dimensional variety. Chemical potential hypersurface corresponds to reaction space. For each initial composition in modal space, one reaction space is constructed containing the initial condition point; chemography is perpendicular. Similarly, in total affinity space, chemical potential saturation hypersurface is perpendicular to affigraphy and contain the « *initial affinity* »  $A_0$  (for a generalized given set of  $P$  and  $T$ ). In order to construct reaction space, one needs to know the initial concentrations  $x_{0i}$  which are in mathematical correspondence with the  $A_0^i$  of the phases in the affinity diagram.

Total composition space may be interpreted in terms of disequilibrium: a given chemical system is constructed by the mixture of  $n + k$  phases before they react to reach thermodynamical equilibrium. The total affinity space may be interpreted in a similar way thanks to some generalization; the  $n + k$  phases are mixed together at different temperatures and pressures so that their energies are not in thermodynamical coherence; their chemical potential are also supposed to be fixed independently. Remind that in the present approach at equilibrium  $k$  independent affinities are fixed (and eventually two of them will have a physical correspondence with  $P$  and  $T$ ).

It is convenient to represent the relationships between the four basic types of diagrams in Table 5 where the two types of duality define four cells. The different phase diagrams and corresponding variables may also be considered embodied in different algebraic problems discussed in Appendix 4 and summarized in Table 6; chemography and affigraphy are associated together in one type of problem where the global composition of the system (vector  $\underline{c}$ , dim.  $n$ ) and the free energies of the phases (vector  $\underline{g}$ , dim.  $n + k$ ;  $P$  and  $T$  are given) are known. Similarly, chemical potential diagram and reaction space appear together as complementary diagrams when the problem is set in a different way; in this case  $k$  affinities are known (vector  $\underline{a}$ , dim.  $k$ ) so is the complete initial composition (vector  $\underline{x}_0$ , dim.  $n + k$ ).

At last, the preceding projection and intersection operations allow the definition of other « *residual* » diagrams: basic vectors of the  $(n + k)$ -dimensional composition space may be projected onto  $V$  (the projected vectors are perpendicular to the reaction space hyperplanes) and basic  $(n + k)$ -dimensional affinity vectors may be projected onto  $V'$  (projected vectors are perpendicular to the chemical potential hyperplanes); conversely, space  $W'$  may be intersected with the basic  $(n + k)$ -dimensional basic affinity hyperplanes, yielding a complementary chemical potential surface, and variety  $W$  may be intersected with the basic  $(n + k)$ -dimensional basic composition hyperplanes, yielding a complementary reaction space (Table 7).

As was shown by Korzhinskii (1959), the line connecting two phases in a two-dimensional composition diagram is perpendicular to the line that separates the two same phases in the corresponding two-dimensional chemical potential saturation diagram. This property may be understood more generally in higher-dimensional representations. Let us consider an  $n$ -dimensional space where we represent in the same time the concentrations and the potentials. Each of the  $n + k$  phase vectors given by the columns of the composition matrix is perpendicular to the hyperplane of the same phase in potential representation. The hyperplane  $H_0$  that contains  $n - 1$  phase vectors  $B, C$  and so on will simulate a joint in the chemography connecting phases  $B, C$  and so on; it will be perpendicular to all the potential hyperplanes  $H_B, H_C, \dots$  for each of the phases and so also to the intersecting of any number of these hyperplanes. If they are  $n - 1$  in number, the intersection of potential hyperplanes will be a vector. This vector will be perpendicular to the hyperplane  $H_0$ . In the case  $n = 3$ , in the orthogonal affine representation, the variety connecting two phases in the chemography will be a line; it will be perpendicular to the intersection of the two potential planes for the corresponding two phases.

This may also be seen at the level of the equations of the varieties. In the two-dimensional composition diagram of Fig. 6, the equation of the line connecting phases  $B$  and  $C$  in base  $A, B, C$  is  $A = 0$  (this equation is a restriction of the complete equation given by one line of matrix  $C$  in the  $(n + k)$ -dimensional composition  $x$  space). In the chemical potential saturation diagram, the line that separates phases  $B$  and  $C$  corresponds to the equation  $B = C$ ; phase  $A$  is absent (so are other phases...) and the equation of this reaction read in matrix  $R$  shows a null coefficient for phase  $A$ . The two lines are perpendicular.

## 13.2. Examples

### Example 1

The foregoing  $(n + k)$ -dimensional diagrams can be represented for  $3 = 1 + 2$  or  $3 = 2 + 1$  systems; let us discuss completely the case  $n = 1, k = 2$  already discussed in part. The modal space is represented in Fig.



65A; so as variety  $V$  containing initial composition  $x_0$ , and variety  $W$  orthogonal to  $V$  at  $x_0$ . The equation of  $V$  is taken here  $C \cdot x = \underline{c} = 1$  where  $C$  is

	A	B	C
A	1	1	1

with  $x_0$  arbitrarily chosen equal to  $(.6, .1, .3)^T$ . Due to the choice of basis in  $C$  matrix, the global composition of the system is expressed in terms of  $A$  phase. The whole modal space is splitted into the two orthogonal supplementary spaces of reaction space and chemography represented in Fig. 65B and C. The boundaries of reaction space  $V$  are the three planes of basic coordinates; these represent the disappearance of phases  $A$ ,  $B$  and  $C$ , portrayed by lines (A), (B) and (C); in  $V$ ,  $\xi = x - x_0$  for  $B$  and  $C$  is considered as new co-ordinates. The chemography is here reduced to one point, where the three unitary vectors  $A$ ,  $B$  and  $C$  are projected together with the overall composition  $\underline{c}$ .

The affinity space is represented in Fig. 65D. When phase  $B$  is present (and phases  $A$  and  $C$  are absent), total affinity vector lies in plane  $B$  and its position may be variable between (A) and (C) vectors. When phases  $B$  and  $C$  are present together, the affinity vector is along vector (A). And so on for the other domains. Variety  $V'$  is given by  $RA^T = RA_0^T = \underline{a}^T$  where  $R$  is

	(A)	(B)	(C)
(B)	-1	1	0
(C)	-1	0	1

and  $\underline{a}$  is  $(0, -.2)$ .  $W'$  is perpendicular to  $V'$  in arbitrarily chosen  $A_0$   $(.5, .3, .2)$ . The affigraphy is represented in Fig. 65E and the intersection of  $V'$  with the constraints  $A \geq 0$  gives the chemical potential saturation space in Fig. 65F.

In Fig. 65G the affinity vectors are represented in the reaction space. They represent the admissible thermodynamic movement of the system when one specific assemblage is considered. Let us examine how the free energy  $G$  may be increased while the

system remains at a given point of the modal space of Fig. 65A. The gradient  $\mu$  is represented with respect to the current point  $g$  so that  $g - \mu = A$  is represented;  $A$  is equivalently recovered by  $A = \partial G / \partial \xi$  where  $\xi$  is the pertinent variable in reaction space. The gradients are also projected in a  $k$  dimensional space, such as in Fig. 65E. If the point stays in the plane of Fig. 65A where the three phases A, B and C co-exist, the gradient must be perpendicular to the plane if the three-phase assemblage is to be preserved; this defines one point in the projection of Fig. 65E. If the point stays along a line where two phases are present, the movement must be perpendicular to the line; this defines one vector in the projection. At last, when the point coincides with one phase, the projected admissible movement is restricted to an angular sector, limited by the vectors corresponding to the pairs of phases that include the current phase. The admissible directions are given by the vectors of  $R$  matrix. This is another way to find back the affigraphy from the modal space.

### Example 2

Let us consider now the case  $n = 2$ ,  $k = 1$  (Fig. 66 A through F, with same captions and operations as in Fig. 65). The matrices are not given. The orientation of the planes and lines of interest are different from the preceding case and lead to the different diagrams shown in the figures. The affigraphy is limited to one point; it is the superposition of the three affinity vectors, two positive and one negative parts are concerned; in the section two points are represented as black, and one as white. In Fig. 65 and 66 the total affinity vector  $\underline{a}$  may be located outside the potential saturation surface, or its co-ordinate in one basic affinity is negative although the corresponding phase is absent. This merely results from the choice of basic vectors for the matrices; similarly, the system may be represented in chemography by negative co-ordinates of the basic phases although in that case it will be physically defined by *positive* amounts of *other* phases.

For each pair of  $P$  and  $T$  values, a change may be defined from the affinity variable to the chemical potential variable inside the corresponding  $n$ -dimensional chemical potential surface, taking into account a mere change in the origin defined by  $A = g(P, T) - \mu$ . Prior to the cutting by  $(P, T)$  planes, each point of the affigraphy has definite values for the  $k$  affinities of the basic reactions chosen for the representation; thanks to basis changes, the affinities of all the reactions can be computed. For a given composition of the system, a single basis is obtained in each domain of the affinity diagram, and the values of affinities are determined univocally. Provided a change of the coordinates is operated,  $P$  and  $T$  themselves may be considered as two affinities among the  $k$  of the affigraphy space. From a vectorial point of view they should not be added to the list of the intensive variables but rather be considered as combinations of some of them. The knowing of  $P$  and  $T$  also allows to know the values of the chemical potentials at each point of the  $(P, T)$  diagram thanks to the relations  $\mu = g(P, T) - A$ . So the  $(P, T)$  diagram may be tabulated in affinities and/or chemical potentials for any given composition of the system.

### 13.3. Combinations of the basic type diagrams

The four basic types of diagrams or spaces may be combined in several ways (Tables 5 and 6; corresponding algebraic problems are discussed in Appendix 4). Horizontal combination I associates chemography and chemical potential diagram that both have the dimension  $n$ ; some of the chemical elements may be specified by their quantity as in the chemography,  $i$  in number, and the others by their chemical potential at equilibrium,  $m$  in number; the mixed type diagram ( $\underline{\mu}$ ,  $\underline{c}$ ) is obtained; the dimension of the diagram remains equal to  $n$ . Such diagrams are examined by Korzhinskii (1959; see also Meunier and Velde, 1986). To construct them, the values of  $P$  and  $T$  must be specified so that the  $g$ 's are known. Horizontal combination II is parallel to the preceding one in Table 5; it is associated to it in the sense affigraphy is associated to chemography. It defines a new type of diagram where affinities and advances of reactions are associated in a  $k$ -dimensional diagram; combination II is in combinatorial duality with combination I. The initial composition  $\mathbf{x}_0$  must be specified.

Other combinations of diagrams at different horizontal levels along the vertical axis of Table 5 may be defined; the combinations cannot be of the above exchange type because of the change in the dimension; so  $(n + k)$ -dimensional diagrams are constructed. *Combination III*: chemical potential diagram and reaction space may be associated in an  $(n + k)$ -dimensional diagram where vector  $\underline{\mu}$  (dim.  $n$ ) and  $\underline{\xi}$  (dim.  $k$ ) are represented as a single vector (the  $2(n + k)$  components of vectors  $\underline{g}$  and  $\mathbf{x}_0$  must be known). *Combination IV*: similarly the association of chemography and affigraphy may be envisaged, where composition and affinity are represented in the same diagram. Starting with these two types of combinations, other diagrams with lower dimensionality may be constructed by appropriate projections or intersections with (linear) varieties. Other types of  $(n + k)$ -dimensional diagrams may be defined such as modal space (total  $\mathbf{x}$  is represented; this is equivalent to total  $\underline{\xi}$  with a shift in the origin; or also equivalent to representing  $\underline{x}$  (dim.  $n$ ) +  $\underline{\xi}$  (dim.  $k$ )); one can imagine other combinations depending on the origins chosen for the spaces, for instance combination  $\underline{x} + \underline{\mu}$  equivalent to combination IV.

Vectors  $\mathbf{x}$  and  $\underline{\mu}$  may be both represented in the same  $2(n + k)$  diagram like position and velocity in mechanics. The diagrams with higher dimension than  $n$  or  $k$  may be used to represent out of equilibrium situations and evolutions which cannot be pictured on the projected diagrams such as chemography and affigraphy.

### 13.4. Affinity - composition diagrams

In above combination number IV, an  $(n + k)$ -dimensional space is constructed by the addition of chemography (dim.  $n$ ) and affigraphy (dim.  $k$ ). The limits of the chemography regions are open out in the  $(n + k)$ -dimensional space parallel to the  $k$ -dimensional affigraphy subspace. Similarly, the limits between affigraphy domains are extended parallel to the  $n$ -dimensional chemography subspace. Cells in the  $(n + k)$ -dimensional space are defined. Several types of linear varieties of dimension  $p + q$  may intersect the  $n + k$  dimensional structure;  $p$  is the dimension of the restriction of the variety to the  $n$ -dimensional subspace, and  $q$  to the  $k$ -dimensional subspace. Intersection by a  $(1 + 2)$ -dimensional variety will simulate  $(x, P, T)$  or  $(x, A^1, A^2)$  diagrams, intersection by a  $(1 + 1)$ -dimensional variety will simulate  $(x, A^1)$  or  $(x, \mu^1)$  or  $(x, T)$  diagrams and so on. This procedure may equivalently be understood as the operation of two separate intersections of chemography and affigraphy hyperplanes by one univariant line. Each intersection gives rise to a number of invariant points corresponding to the intersection of the line with the chemography or affigraphy hyperplanes. So invariant points along the composition axis correspond each to  $n - 1$  or (concentration representation)  $n - 2$  phases, and along the temperature (or any combination of affinities) axis to  $k - 1$  absent phases. These points correspond in the same time to reactions (change of mineralogy due to change of conditions) along the composition axis and to co-reactions (change of mineralogy due to change of chemistry) along the temperature axis. The stability level of the reactions and co-reactions is given once, by the intersection operation of affigraphy and chemography defining the two co-ordinate axes. The intersection by a monodimensional line of affine chemography and of affigraphy give rise to  $n - 2$  stability levels for the invariant points of the horizontal axis and  $k - 1$  stability levels for the invariant points of the vertical axis. So there are a priori  $(n - 2)(k - 1)$  stability levels for the « *invariant points* » of the whole affinity-composition diagram. By expanding in the two-dimensional diagram the limits defined by the points, cells are defined. If two neighbouring vertical or horizontal cells have the same bases (and thus cobases), it is not useful to represent the reaction or co-reaction limit between them; so the lines will stop at the previous neighboring intersection point. Taking into account the possible interruption of lines

the number of different points in the diagram then amounts to  $6(n - 2)(k - 1)$ .

The list of all the bases and all corresponding cobases may be written for each cell together with the stability signatures. Each base is followed by the associated cobase, between brackets; the number of negative vectors in the base or cobase give the stability level of the cobase or base. The full understanding of co-reactions needs to adopt the generalized case when negative amounts of phases may obtain in composition space. When comparing the list of signed bases and co-bases in two neighbouring cells, reactions and coreactions are evidenced. A reaction induces an exchange in the stability of two bases; a co-reaction induces the exchange of stability of two co-bases. If we decide that negative amounts of phases are forbidden, only stable co-bases will be envisaged and co-reactions do not appear. Degeneracies may occur when the one-dimensional axes intersect chemography and affigraphy along degenerate hyperplanes or intersections of hyperplanes. Several varieties will coincide at the same point; this will give rise to several types of lines, that will coincide, for the cell limits in the two-dimensional diagram. Depending on the composition or temperature range, one type of line may or may not be valid. This problem will not be discussed here on a general standpoint.

The simplest example that can be represented in the three dimensional space is the case of a  $2 + 2$  system, where composition is counted for one dimension (affine representation). The association of chemography and affigraphy is given in Fig. 67. The  $2 + 2$  dimensional cells are represented. For an overall composition located for instance between phases C and D, the possible bases are AC, AB, CD and BD, associated to cobases (B)(D), (C)(D), (A)(B) and (A)(C) respectively. By cutting the structure by a two- dimensional plane (one dimension for affigraphy, + one dimension for chemography) parallel to the chemography, planar diagrams are arrived at. They may simulate the structure of the system at P or T fixed. Two examples are given; intersecting planes  $P_1$  and  $P_2$  are shown in Fig. 68A. The two diagrams of Fig. 68B and C are obtained. In Fig. 68B, phases A and B are the only stable phases for all compositions. The limits between the different cells are kept however

because metastable associations differ. As announced above when metastable associations of neighbouring cells are the same, the corresponding limiting line is not represented. The list of signed bases and cobases helps discuss the meaning of reactions and co-reactions. As an example, one may easily write the list of bases and cobases with their stability levels in cell 1 of Fig. 68B :  $\{AB^0, (CD)^0\}$ ,  $\{AC^1, (-BD)^0\}$ ,  $\{AD^2, (-B-C)^0\}$ ,  $\{-BC^1, (-AD)^1\}$ ,  $\{-BD^2, (-A-C)^1\}$ ,  $\{-CD^1, (-AB)^1\}$ . In cell 4, it is  $\{AB^0, (CD)^0\}$ ,  $\{AC^1, (-BD)^0\}$ ,  $\{-AD^2, (-B-C)^1\}$ ,  $\{-BC^1, (-AD)^1\}$ ,  $\{BD^2, (-A-C)^0\}$ ,  $\{CD^1, (-AB)^0\}$ . In Fig. 68B the co-reaction called « D » (D present) limiting cells 1 and 4 governs the exchange between cobases  $(-B-C)^1$ ,  $(-A-C)^0$ ,  $(-AB)^0$  in 1 and  $(-B-C)^0$ ,  $(-A-C)^1$ ,  $(-AB)^1$  in 4.

Fig. 68C corresponds to intersection with plane  $P_2$ ; phase association is variable depending on the composition range and depending on the magnitude of the intensive parameter along the vertical axis. The domains are separated in several sub-domains corresponding to several stability sequences as in Fig. 68B.

This type of approach pictures the connection between all the  $(\mu, x)$  diagrams of a given system when the temperature is varied. The stability sequences for all sub-regions of the diagram are understood in the same frame. Intersections of the  $(n + k)$ -dimensional space by varieties that are not parallel to the chemography may also be envisaged, simulating variations of the potentials with the composition (which is the case when there is solid solution). The projection of the complete  $n + k$  dimensional structure along several directions may also be envisaged.

#### *Diagrams with solidus and liquidus curves for solutions*

The depiction of temperature composition diagrams with solid solutions may also be envisaged by use of pseudocompounds in the sense of Sect. 12; number  $k$  increases, co-reactions are more difficult to write as they involve more and more absent phases. The representation with pseudocompounds helps understand the structure of the diagram when  $k$  goes to infinity and then simulates the complete solution. Composition-temperature diagrams with liquidus and solidus for a solid solution are of that type, Fig. 69. The composition is restricted to  $n = 2$  and the solid solution is described by a finite set of pseudocompounds  $h, i, j, k$  and so

on. Each of the pseudocompounds is degenerate into two phases, the liquid and the solid, e.g.  $i^l$  and  $i^s$  for compound  $i$ . Different cells are represented in the figure. Temperature is quantified in the vertical axis because of the different possible reactions. In that approach, all the cells are two-phase domains. This is not the case for that type of diagram in the literature where usually two types of domains, one-phase (solid or liquid) and two-phase (solid + liquid) domains are considered. Here we see that the domains usually considered as one-phase (solid or liquid) may be considered on an equal footing as the other two-phase solid + liquid parts. They merely represent the stable association of two infinitely neighbouring compositions for liquid or solid, whereas an infinity of other more metastable associations could be considered in the same time. In the ordinarily called two-phase region the stable associations gather phases more distant in the composition axis. One phase is liquid on one side and solid on the other side. For example, in the cell between  $j$  and  $k$  of the  $(i^s + m^l)^0$  domain (Fig. 69) the association of  $i^s + m^l$  is more stable than any combination of two solids or two liquids or a solid and a liquid with indices lower or equal to  $j$  and greater or equal to  $k$ . Similarly in the liquid cell  $(m^l + n^l)^0$ , this association is more stable than any other association of liquid or solid pseudocompounds different from that one. In the limit, when  $k$  goes to infinity and the number of pseudocompounds increases, the staired curve of the diagram becomes an oblique line. This is a limit of horizontal and vertical line segments; it is a composite line representing in the same time a reaction (change of temperature) and a co-reaction (change of composition).

### *13.5. Applications to the study of metamorphic and metasomatic assemblages. Chemical potential grids*

Depending on the problems, changes may be operated in matrices **C** and **R**, in correspondence with geometric transformations in the chemography and affigraphy. It may be convenient to view these operations as changing the status of some components, in the sense of Korzhinskii (1959) (see also Rumble, 1982). In matrix **C**, the total number

of lines corresponding to independent chemical components is  $n$ . This number may be divided into two subgroups  $i$  and  $m$ ;  $i$  refers to the number of inert components whose quantity is maintained constant, and  $m$  refers to the number of mobile components for which no conservation constraint holds; in that last case, constraints may be written that bear on chemical potentials or affinities imposed by an external template. The representation of the chemical composition of the system in the inert frame may be obtained by the use of the reduced matrix  $\mathbf{C}^*$  obtained by suppressing the  $m$  lines of the mobiles elements. The corresponding geometric operation is a projection of the chemography onto the inert component subspace and parallel to the mobile component axes. These last elements will necessarily be computed as increasing the  $k$  dimensions of affigraphy. This is because  $n + k = i + m + k = i + k'$ , and the decrease from  $n$  to  $i$  implies an increase from  $k$  to  $k'$  where  $k' = m + k$ .  $\mathbf{R}$  matrix may be constructed on reduced  $\mathbf{C}^*$  matrix; it will have  $k' = m + k$  lines and  $n + k$  columns. We can similarly suppress  $k$  lines in matrix  $\mathbf{R}$ , when it is constructed on the reduced  $\mathbf{C}^*$  matrix; the geometric operation is a projection of the affigraphy onto the mobile component subspace, parallel to the  $k$  inert components; the remaining affigraphy concerns the  $m$  mobiles elements. These operations allow to construct several types of diagrams. The projections of the chemography from one phase as defined in Thompson (1982a) are similar operations (the corresponding phase is present in all mineral associations). One can also define a projection of affigraphy from one absent phase (the corresponding phase will be absent in all mineral associations considered). The several types of phase diagrams depicted in previous sections can also be viewed as concerning different status of the components. The affinities are considered for the mobile components, and the reaction advances for the inert components.

In the study of metamorphic assemblages, it is often convenient to consider parts of the whole chemical system where one of the phases and/or one of the chemical components is suppressed; the use of corresponding modified affigraphy as just discussed may help to quickly visualize the effect of these operations on the thermodynamic phase diagrams.

The study of metasomatic assemblages may benefit from the affigraphy approach. By itself the concept of dissociation affinity  $A = g(P, T) - \mu$  combines the possible effect of the variation of physical parameters  $P$  and  $T$  in a closed system (first term  $g(P, T)$ ) and



the possible variations in the chemical potentials of elements or phases in an open system (second term  $\mu$ ). One may thus combine the effect of the variation of physical and chemical parameters in a single representation. In a metasomatic zoning (e.g. Fonteilles, 1980, Guy, 1988, 1993), it is in effect more appropriate to infer that the metasomatic fluid in the extreme zones is close to the saturation with a mineral or a group of minerals, as given by the value of the affinities, than to specify pressure, temperature and chemical potentials separately. Physical conditions may change during the formation of metasomatic assemblages, but the system may still be constrained by the presence of some specific minerals. The path followed by the system along the zoning pattern may then be easily visualized in an affinity diagram; parts of it obtained by projection, or intersections if some additional hypotheses are taken as valid, may also be used. Metasomatism in a temperature gradient is easily represented by this way; this is also a manner to depict chemical and thermal diffusion together. In these representations, both stable and metastable zoning patterns may be given. The degrees of freedom of such zoned systems is bracketed by the « *phase rule generalized to systems of zones* » (Guy, 1988).

*Chemical potential grids* are distinct from the potential saturation diagrams. They are obtained when one is interested to discuss the role of the chemical potential of two mobile elements, the other elements being inert. Temperature and pressure are fixed and their role on phase assemblages is not taken into consideration. The composition of the system is depicted in matrix **C**, where the first *i* lines refer to inert components and the two last lines to the mobile components here called D and E; for simplicity in the following, the components are directly computed as phases and named equally by *components* or *phases*. An affigraphy is constructed from the restriction of **C** to inert components. The affinities of the reactions in the affigraphy write, for instance for phase M,

$$A^{(M)} = g^M(P, T) - \mu^M = g^M(P, T) - \sum_{j=1}^{n-2} c_j^M g^j(P, T) - c_D^M \mu^D - c_E^M \mu^E$$

where the sommation is done on the  $n - 2$  phases of the chemography basis restricted to the inert elements (phases); in the representation basis the  $\mu$ 's are equal to the  $g$ 's. The two additional terms refer to mobile elements (phases) D and E. Coefficient  $c_j^M$  is the content of phase *j* in one mole of phase M, read in composition matrix. P and T are now fixed. K independent relations as such may be written. The elimination of  $\mu^D$  and  $\mu^E$  among the *k* affinities gives a two-dimensional plane for the chemical potential grid. This corresponds to an *intersection of the affigraphy, constructed on inert elements only, by a two dimensional plane*; this is similar to the obtention of (P, T) diagrams. The co-ordinates

of the origin of such grids are  $g^M(P, T) - \sum_{j=1}^{n-2} c_j^M g^j(P, T)$  for the  $k$  independent absent phases; the two basic vectors of the potential grid are the vectors  $c_D^j$  and  $c_E^j$  for the  $k$  phases  $j$  for the co-ordinates on D and on E. Inside the different domains of the chemical potential grid, one may represent the composition of the phases and of the system in the inert frame, for instance by triangles for three inert components; depending on the values of the potentials, different phase assemblages may obtain. Such grids are used in the metasomatic literature (e.g. Salim, 1993; Salemink, 1987 a and b, Van Marcke, 1983).

One can also combine the chemical potential of a component and P or T to construct a  $(\mu, P)$  or  $(\mu, T)$  grid by the same method. The parameters that are fixed are involved in the computation of the origin of the diagram and the « *mobile* » ones are extracted and define the vectors of the intersecting two-dimensional plane. Three-dimensional representations may also be constructed for  $(\mu, \mu, \mu)$  diagrams or  $(\mu, \mu, T)$  or  $(\mu, P, T)$  or  $(P_1, P_2, T)$  -two different pressures, lithostatic and hydrostatic for example are considered- and so on: the affigraphy restricted to the inert components is intersected by a three-dimensional volume. If  $k = 3$ , the diagram will have one invariant point with  $n + 3$  phases in the three dimensional space. If  $k = 4$  the intersection by a three-dimensional volume will give rise to  $n + 4$  invariant points with each  $n + 3$  phases and so on.

*Inert component grids.* The previous method may be used to construct dual type grids of a new kind. We have considered so forth the case of two (or even three) mobile components, the others being inert. Conversely, two elements may be considered as inert, and the others mobile. Phase assemblages were represented in inert frame as dependent on the potentials of mobile components. Conversely, one may want to represent the phase assemblages obtained for a given range of potentials of mobile elements A, B ... when the inert elements are varied. The content  $x_i$  for  $n$  basic phases in chemography is given by

$$x_i = x_{0i} + \xi_i = x_{0i} + \sum_{j=1}^{k-2} r_{ij}^j \xi_j + r_{iA}^A \xi_A + r_{iB}^B \xi_B$$

where  $x_{0i}$  is the initial content in  $i$ ,  $\xi_j$  is the advance of reaction  $j$ . The summation is taken only on  $k - 2$  independent chemical reactions corresponding each to a mobile component; the two reactions corresponding to the inert elements A and B are extracted. The coefficients  $r_{ij}^j$  are the coefficient of phase  $i$  in reaction  $j$ . The chemical reaction matrix  $R$  is constructed (and so the corresponding chemography) on the mobile elements; the two inert elements A and B are involved in two additional lines of the matrix. In the composition representation basis chosen, the  $x$ 's in the co-basis are taken zero and the corresponding  $\xi_j$  are equal to  $-x_{0j}$ . The above relation may be written for the  $n$  phases in the basis. By eliminating  $\xi_A$  and  $\xi_B$  between the  $n$  relations, a two-dimensional plane is obtained. The searched two-dimensional diagram has its origin defined by  $x_{0i} + \sum r_{ij}^j \xi_j = x_{0i} - \sum r_{ij}^j x_{0j}$  and the basic vectors of the  $(\xi_A, \xi_B)$  plane are given by the  $n$  co-ordinates  $r_{iA}^A$  and  $r_{iB}^B$  for the  $n$  basic phases  $i$ . Equivalently, the representation may be done in  $(x_A, x_B)$  plane where  $x_A = -\xi_A$  and  $x_B = -\xi_B$  are the contents in inert components, the unit vectors are then  $-r_{iA}^A$  and  $-r_{iB}^B$ . Such diagrams are obtained by *intersecting the chemography constructed on mobile components by a two-dimensional plane*. The interest of such diagram is when the number of non inert components is higher than two or three. Otherwise the searched phase assemblages may be read on the ordinary chemography, with adding the information on the affinities in the different domains such as in Fig. 8A. In the more general case when there are at least four components, the intersecting of the chemography by a two-dimensional plane will provide diagrams of special type. The invariant points will have  $n - 2$  phases; the reactions corresponding to change in the global chemical composition of the system, the co-reactions, will have  $n - 1$  phases. These reactions are different from the ordinary reactions. Inside the composition domains in inert frame, one may represent the phase assemblages obtained for different ranges in the values of the potentials of the mobile elements.

The interest of such diagrams may be found again in the study of metasomatic rocks. Instead of studying the influence of the potential

conditions on the mineralogy, for a given composition in inert elements, one may study the influence of the inert composition on the mineralogy for a given range in potentials. In a given geographic field, several starting materials may co-exist, because of heterogeneities in the rocks, enclaves and so on; at a given locality within an open system, all materials may suffer the same intensive conditions defined by potentials of mobile elements and thus give rise to different assemblages. This situation may be depicted by the previously defined (inert, inert) diagram. This point of view is dual to the study of different zones developed on the same starting material when intensive conditions are varied. When using the potential grid, the potentials of two phases are fixed, and their quantities are supposed to adjust themselves; the other quantities are fixed, the corresponding potentials adjust. In the dual representation, the quantities of two inert components are fixed, their potentials follow; the other potentials are fixed, the quantities of corresponding phases adjust. The dual equivalent of the pseudo-sections is here « *co-pseudo-section* » for a given set of potentials for the mobile elements.

Other types of chemical potential grids may be obtained by intermediate projections or intersections (by  $\mu^i = \text{constant} = g^i$  for instance) of the (modified) affigraphy, in the same way several composition diagrams may be obtained from a complete chemography; the intersection of affigraphy by different hyperplanes may be used to predict the influence of intensive parameter on the structure of phase diagrams; Powell & Sandiford (1988; see also Hensen, 1986) study the influence of  $a_{O_2}$  on the topology of (P, T) phase diagrams; the effect can be understood by cutting the affigraphy at variable  $a_{O_2}$  values before cutting by (P, T) or  $(\mu, \mu)$  planes, showing how the structure of the resulting (P, T) diagram effectively depends on  $a_{O_2}$ . The links discussed so forth between different diagrams show why the chemical potential diagrams may have the same structure as (P, T) diagrams as noted by several authors (e.g. Burt, 1972).

### 13. 6. (G, P, T) space

The relations between reactions in (P, T) diagrams has often been studied for one component systems as reflecting the relations between Gibbs Free Energy planes in (G, P, T) space. This is so-called Gibbs method (Gibbs, 1876, 1878). When the system possesses several components, the method is no longer directly practicable because the

free energies of the phase associations are variable with the composition of the system and the proportions of the phases. Families of planes may be defined by all the possible linear combinations of the  $g$ 's of the individual phases of the system, when the complete range of chemical composition of the system is explored. The correspondence between the two approaches,  $(G, P, T)$  space and affigraphy, is based on the fact that in the  $(G, P, T)$  space, the projections onto the  $(P, T)$  plane, of the intersections of the composition dependent  $G$  surfaces, are invariant. Let us prove this statement.

Along each univariant line in  $(P, T)$  space,  $n + 1$  phases are stable. So there are  $C_{n+1}^n = n + 1$  possible  $n$ -phase associations in contact with one another along the line. For a given composition of the system, all these associations have the same  $g$ . The  $n$  relations thus hold:

$$g_1 = g_2$$

$$g_2 = g_3$$

...

$$g_n = g_{n+1}$$

where these  $g$ 's are written for all the possible phase associations (and *not* for the individual phases); this is understood in a general sense where the associations may have negative proportions of some of the phases. Each association may be defined by  $n - 1$  composition parameters; provided one representation basis is chosen, several linear combinations of the same parameters may be used for all the associations. Because of the dependence of the type  $g(P, T)$  for the individual phases, the preceding relations connect the  $n - 1$  composition parameters to  $P$  and  $T$ . By eliminating the  $n - 1$  parameters among the  $n$  relations, one obtains one single relation  $f(P, T) = 0$  independent of the composition. This is the equation of the univariant line in the  $(P, T)$  space. This ends the proof.

In the affigraphy approach, relations are immediately found that are independent of the composition of the system, and the use of affigraphy is thus more convenient than that of  $(G, P, T)$  space when the system has more components than one. The Gibbs method is restricted to composition fixed systems. Thanks to the higher dimensional affigraphy

space, positions of the affigraphy hyperplanes reflect those of families of G planes of the (G, P, T) space.

#### 14. POTENTIAL SOLUTIONS. FROM QUALITATIVE TO QUANTITATIVE CONSTRUCTION OF PHASE DIAGRAMS

The mathematical similarity between the chemography structures and the affigraphy ones was demonstrated in the last section. The number of possible affigraphies is the number of imaginable projections of one hypercube apex onto a k-dimensional variety of equation  $\mathbf{C} \cdot \mathbf{A}^T = \text{const.}$ ; the number of possible chemographies is the number of projections of the apex onto a n-dimensional variety perpendicular to the preceding one, of equation  $\mathbf{R} \cdot \mathbf{x} = \text{const.}$  The projection operations yielding chemography and affigraphy are thus symmetrical, so are the intersection operations yielding reaction space and chemical potential saturation space. The correlation between the symmetry properties of the different spaces may be discussed through the preceding geometrical operations. The boundaries of reaction space and chemical potential saturation space are perpendicular to the conic varieties of chemography and affigraphy (geometric duality). If one restricts to the stable assemblages of present or absent phases, the different spaces are bounded by  $\mathbf{x} \geq 0$  and  $\mathbf{A} \geq 0$ . As a whole, a (P, T) diagram results from two operations; first a projection of the apex of a (n + k) - dimensional hypercube onto a k-dimensional variety, second an intersection by a two-dimensional plane. Chemography results from the projection of the hypercube apex onto an n-dimensional variety, then, in order to have concentrations in affine representation, by the intersection by the hyperplane  $\Sigma x = 1$ .

##### 14.1 Potential solutions

For a given chemical system, several structures (or « *topologies* ») of (P, T) phase diagrams are a priori conceivable, depending on the nature of data available. Each of the structures will be called a « *solution* » and we will distinguish between « *combinatorially possible* », « *mathematically possible* » and « *potential* », solutions (Table 8). The

thorough discussion on the numbering and enumeration of the solutions needs the use of matroid theory and will be given elsewhere; only the structure of corresponding problems is presented here. « *Combinatorially possible solutions* » are those that would be possible from a mere combinatorial point of view, for a given number of components and phases, with no information on the composition of the phases, nor on the complete thermodynamic and so mathematical structure of the problem. In order to predict this number, let  $n + k$  vectors be disposed around one point in a  $k$ -dimensional space;  $\alpha_j$  designates one such arrangement, that may be called by extension a « *combinatorially possible (c.p.) affigraphy* ». Each such affigraphy will be intersected by a two dimensional plane; this is the way to obtain the right number of invariant points, univariant lines and so on, together with their combinatorial definition. The intersection will be called a combinatorially possible solution; let  $\theta_{ij}$  be the c. p. solution number  $i$  for c.p. affigraphy  $\alpha_j$ . So the total number of such solutions will be  $\Theta = \sum_{i,j} \theta_{ij}$ . One can also define total number of c.p. affigraphies  $\alpha$ , and the number of c.p. solutions for a given affigraphy  $j$ ,  $\Theta_j = \sum_i \theta_{ij}$ .

Actually, the mathematical structure of the thermodynamic problem allows a first reduction of this number; affigraphy obtention was described as a projection operation. Let  $\delta_j$  be one possible way to project the apex and related edges of one  $(n + k)$ -dimensional hypercube onto a  $k$ -dimensional variety; this will yield a « *mathematically possible affigraphy* ». A « *mathematically possible (m.p.) solution* » will be a way to intersect one mathematically possible affigraphy by a two dimensional plane when the composition parameters are still unknown ( $n$  and  $k$  only are given). Let  $\pi_{ij}$  be way number  $i$  to cut affigraphy  $\delta_j$ . The total number of mathematically possible solutions is  $\Pi = \sum_{i,j} \pi_{ij}$  for all chemographic arrangements. We have  $\Pi < \Theta$ , since the number of combinatorially possible affigraphies contains many degenerate situations not allowed by the projection operation of the apex in the mathematically possible occurrences, such as for instance the case where all  $n + k$  vectors are colinear. The orientation of the  $k$ -dimensional linear variety with respect

to the hypercube apex is not completely arbitrary, even when composition is unknown, nor that of the orthogonal  $n$ -dimensional variety, yielding the projected chemography; it depends on the general structure of  $\mathbf{C}$  and  $\mathbf{R}$  matrices. For instance, the apical vectors are all projected in the positive orthant for the chemography, whereas, in the affigraphy, some are in the positive orthant, but others in the negative or partly negative orthants. The particular orientation of the  $k$ -dimensional variety may reduce number  $\Pi$  in a way we will not debate. If generalized  $\mathbf{C}$  and  $\mathbf{R}$  matrices are considered, in the sense of Sect. 10, then number  $\Pi$  is that gained by the general approach, and the obtaining of affigraphy and chemography are purely on the same level.

When the composition of the phases is known thanks to their  $\mathbf{C}$  composition matrix, there is one single affigraphy that will be called  $\delta_0$ . We can distinguish  $\delta_0^*$  when generalized compositions, i.e. with negative proportions, are admitted. As defined in the literature, « *potential solutions* » are mathematically admissible solutions for phase diagrams, when the compositions of the phases are known, but not their thermodynamic data. The *Fundamental Theorem* (Sect. 6) easily allows to discuss their number. The number of potential solutions is that of the possible manners to cut the affigraphy by two-dimensional linear varieties. Let  $\pi_{i0}$  way number  $i$  to cut affigraphy  $\delta_0$ . The total number of potential solutions for affigraphy 0 will be  $\Pi_0 = \sum_i \pi_{i0}$ .

By itself, the obtention of potentials solutions is already a reduction in the number of diagrams that would be possible for a given number of phases not knowing their composition. The gain obtained by using the thermodynamic-algebraic approach is in the proportion  $\Pi_0 / \Pi$ ; when only the combinatorial aspects are considered the balance is  $\Pi_0 / \Theta$ . Numbers  $\Pi$  and  $\Theta$  are functions of  $n$  and  $k$ ; number  $\Pi_0$  is also function of the particular disposition 0 of the affinity vectors in correspondence to the chemography of the system. « *Isoclinal variant* »  $v_{i0}$  number  $i$  of potential solution number  $i$  for composition 0 may also be distinguished (Provost, Lépine and Vielzeuf, 1992), when the molar volumes and entropies of the phases are known; at last unique « *physical diagram* » is  $\gamma_0$  when all the information on free energies are available. Discussion of



the number of chemographic arrangements and potential solutions may be found in Usdansky and White (1983), Fujii (1977), Mohr and Stout (1980) among others.

The next step in the discussion on potential solutions is to find one of them. In the case  $k = 3$ , the use of so-called polyhedra and closed nets allows to find some or all. By appropriate transformations of one solution, others may be found. Mohr and Stout (1980) discussed the number and obtaining of potential solutions in the case  $k = 3$ . The different potential solutions may be connected by an operation called transposition. This operation may be understood in the present frame as related to the change of the position of the (P,T) two-dimensional plane with respect to the affigraphy. When the plane parallelizes one vector of the affigraphy, the corresponding intersection yielding one invariant point shifts from one side of the diagram to the opposite and changes its stability. The different cases of Fig. 30 illustrate these changes in the position of the cutting plane. This is valid for exterior invariant points. In the context of the  $k = 3$  affigraphy, the transposition may be monitored by an angle by which the plane is defined with respect to affigraphy.

The obtaining of potential solutions by the above method is however valid only for  $k = 3$  systems. The definition of this procedure is not systematic; outside the present approach, there is so far no general way to exhibit a potential solution. The important here is that *the affigraphy approach and Fundamental Theorem easily allow one to exhibit potential solutions for arbitrary values of  $n$  and  $k$* ; the intersection of the affigraphy by any two-dimensional variety gives one. When  $k$  is arbitrary, generalizations of the transposition operations may be proposed for three dimensional sub-sets of the affigraphy.

The last step is to select one potential solution by use of paragenetic information. From the observation of natural phase assemblages, four types of qualitative information may in principle be obtained:

- 1) a paragenetic information telling that a specific group of phases may co-exist; in affigraphy language, this may refer to a  $k$ -dimensional domain of the affigraphy; depending on the number of phases in the paragenesis, which may be lower than  $n$ , singular situations may be

envisaged (indifferent crossing situations); the collection of absent phases may be pointed in an hyperpolyhedron (Sect. 7).

2) a reaction information according to which a specific group of phases react together and may co-exist along univariant lines or at invariant points; in the general case, this refers to  $(k - 1)$ - or  $(k - 2)$ -dimensional varieties of the affigraphy.

3) an information on incompatible phases where collections of up to  $n$  phases are not encountered together; this also corresponds to a  $k$ -dimensional domain of the affigraphy but a metastable one. Some of the defining vectors will be negative; the number and names of negative vectors can be decided only when the metastable association can be compared with other possible associations, including that of type 1); it may not be easy to decide whether such assemblage belongs to type 1) or 3); this is also a function of the composition of the system.

4) some associations may never be encountered neither stable nor metastable. If any, the corresponding points in affigraphy are rejected at infinite.

These four types of information may tentatively be pointed on the affigraphy through the complementary sets of phases: then, the intersecting  $(P, T)$  plane will be chosen in the affigraphy so as to contain the possible paragenetic or reactional association, including the metastable association, but to avoid the variety of the absent associations (it will be parallel to the corresponding variety); if the information is sufficient, a plane for the  $(P, T)$  section of the affigraphy may be constructed and provides a possible phase diagram. In principle three points are needed to define a two-dimensional plane; but more than three qualitative pieces of information are needed; for instance for a paragenesis the representing point will be in a sector limited by  $k$  vectors, or for a reactional association in one hyperplane; but the exact location is unknown. The number of qualitative pieces of information to define the qualitative localization of a two-dimensional plane in a  $k$ -dimensional space will be discussed in the paper of matroid theory. The illustration of the method is unambiguous for  $k = 3$ ; the polyhedron of a  $1 + 3$  system is given in Fig. 11D and the corresponding two-dimensional sections in Fig. 30. One could imagine that phases A, B and D may

coexist, so that the searched two - dimensional (P, T) plane will cut vector (C); if phases A, B and C never co-exist, the two dimensional-plane will not cut the positive part of (D); this will be the case of Fig. 30A or 30B; if phases D, B, C coexist, we are in the case of Fig. 30A; in Fig. 30B, A and B are never together, nor A, B and D: in that case (P, T) is parallel to (C).

As suggested in the literature (e.g. Guo, 1984), a way to define and select appropriate potential solutions for systems with large  $n$  and  $k$  values is to construct them by steps by progressive increase of  $n$  and  $k$  numbers from more simple diagrams corresponding to already known subsystems. The complete diagram will result from combining the sub-diagrams. We can distinguish simple cases. When  $n$  is increased to  $n + 1$  ( $\Delta n = +1$ ) while  $k$  remains constant ( $\Delta k = 0$ ), one vector will be added to the affigraphy and this will add new invariant points and reactions; the additional number of invariant points will be  $\Delta i$  ( $\Delta n = +1$ ,  $\Delta k = 0$ ) =  $(n+k)! / (n+3)!(k-3)!$ ; for  $k = 3$  one invariant point is added, for  $k = 4$   $\Delta i = n + 4$  and the same number of invariant point as the number of starting phases is added. The location of the (P, T) plane is unchanged and, apparently the composition of the new phase suffices to locate the new invariant points. If, in the  $\Delta n = +1$  increase, the new independent component is not present in the older phases but only in the new phase, the new affigraphy vector will be the null vector  $(0, 0, \dots)^T$ . This is generally the case when an independent component is but contained in a single phase. Then the corresponding affigraphy vector is reduced to  $\Omega$  and the corresponding phase is present everywhere.

When  $k$  is increased to  $k + 1$  with  $n$  constant, this is an unfolding of the new affigraphy with respect to the former one, i.e. its immersing inside a higher dimensional space. The location of the intersecting two-dimensional variety is in a situation of thermodynamic degeneracy in the first case with respect to the second. One can compute that  $\Delta i$  ( $\Delta n = 0$ ,  $\Delta k = +1$ ) =  $(n+k)! / (n+1)!(k-1)!$ . For  $n = 1$  and  $k = 2$ ,  $\Delta i = n + 2 = 3$  and one shifts from one invariant point to 4. A new look at Fig. 30A compared to Fig. 30E illustrates this situation, where the roles of phases A and D must be exchanged. The first position of the (P, T) plane (Fig. 30E) contains  $\Omega$  and is perpendicular to one basic affinity vector; this vector corresponds to phase A not involved in the system. Then the (P, T) plane is raised away from  $\Omega$ . The three univariant lines (B), (C) and (D) are developed in (AB), (AC) and (AD); so invariant point  $\Omega$  corresponding at first to the presence (or absence) of three phases B, C and D must split into four points where each of the four phases of the system is absent. Univariant lines of type (BC), (BD) and (CD) must also appear.

Other  $\Delta i$  ( $\Delta n$ ,  $\Delta k$ ) may be computed; one may also solve the equation  $\Delta i(\Delta n, \Delta k) = 0$  for associated values of  $\Delta n$  and  $\Delta k$ . Natural observational data may help to define a potential diagram in which an additional invariant point will be located when  $n$  is increased, or to define how a thermodynamic degeneracy will be unfolded when  $k$  is increased from a known diagram. The general case  $\Delta n > 0$ ,  $\Delta k > 0$  will combine the above cases.

The dual networks of O'Hanley (1987) already discussed by Roseboom and Zen (1982), Kujawa, Dunning and Eugster (1965) are also used to exhibit potential solutions but only in the case of unary systems (in these papers the duality is understood in a restricted meaning with respect to the present paper).

At last, the reciprocal or inverse problem may also be studied where the phase relations of the chemography are inferred from the phase relations at different P and T values in the thermodynamic diagram and associated affigraphy. If a complete

affigraphy is known, a chemography may be constructed by duality. Numbers  $n$  and  $k$  may be determined by the observation of the different phase assemblages in the system. The problem is to construct an affigraphy from a two-dimensional  $(P, T)$  section. The method may be to try placing a two dimensional plane inside a  $k$  dimensional space; by connecting the origin  $\Omega$  of the  $k$ -dimensional space to the different reactions and points of the section, hyperplanes and vectors may be defined and thus an affigraphy may be proposed; the matter is to find a location of  $\Omega$  compatible with the definitions of the varieties, otherwise another attempt must be done; the solution is not unique. The  $n_1 = 3k$  coordinates of the origin and basic vectors of  $(P, T)$  plane in affigraphy are sought. The coordinates of the invariant points in the  $(P, T)$  diagram are supposed to be known, their number is  $n_2 = 2 \cdot C_{n+k}^{n+2}$ . One must have  $n_2 > n_1$  and apparently, enough pieces of information are available.

#### 14.2 Quantitative construction of $(P, T)$ diagrams

The quantitative construction of a  $(P, T)$  diagram for an  $(n + k)$ -phase multisystem may be operated by the affigraphy approach when the linearization hypothesis of the  $g$  functions is taken for granted. The following algebraic procedure may be taken. Let  $M$  be a point of the affigraphy described by the vectorial relation

$$\Omega M = x_1 A^1 + \dots + x_k A^k$$

where the  $x_i$  are the coordinates along  $k$  unit basic affinity vectors  $A^i$  and  $\Omega$  is the origin of the affigraphy space<sup>19</sup>. If  $M$  also belongs to a two-dimensional  $(P, T)$  diagram, its coordinates in the corresponding plane,  $\alpha_1$  and  $\alpha_2$ , (they represent  $P$  and  $T$ ), verify

$$OM = \alpha_1 V^1 + \alpha_2 V^2$$

where  $O$  is the origin on the  $(P, T)$  plane and  $V^1$  and  $V^2$  are the basic unit vectors of the  $(P, T)$  plane<sup>20</sup>. The correspondence between the coordinates in both systems is given by the  $k$  equations in vectorial form

$$OM = \Omega M - \Omega O$$

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<sup>19</sup> The variables  $x$  in this section have not the phase composition meaning of the rest of the paper. Affinity vectors  $A^{(i)}$  are written  $A^i$  for simplicity.

<sup>20</sup> The  $(P, T)$  plane can equivalently be defined by a set of  $k - 2$  hyperplanes, see below.

If M is an invariant point, it belongs to a subset of  $k - 2$  vectors  $A^1 \dots A^{k-2}$  taken in the whole  $n + k$  set of affigraphy vectors, and the preceding equations may be solved for the  $k$  unknowns  $x_1 \dots x_{k-2}$ ,  $\alpha_1$ ,  $\alpha_2$ , provided vectors  $A^i$  and  $V^i$  and O point are known. The names of the indices in the collection  $x_1$  to  $x_{k-2}$  give the name of the invariant point and the signs of the coordinates give the stability level of the point. For an arbitrary point  $(\alpha_1, \alpha_2)$  in the diagram, one can also compute its coordinate on the  $k$  basic affinity vectors by a backward reading of the preceding relation  $\Omega M = OM + \Omega O$  and so define the corresponding paragenesis; by changing the bases in the affigraphy, other sets of  $k$  vectors may be chosen; the new coordinates  $x$  on the new basis will indicate another possible paragenesis and the  $C_{n+k}^k$  possible bases may be explored in this way. One may restrict to the positive coordinates for the stable bases.

Related problems are that of determining O,  $V^1$  and  $V^2$  when the set of hyperplane equations  $A(P, T)$  is known. If  $k$  equations of the type  $A^i = a^i P + b^i T + c^i$  are known, equations  $P = 0$  and  $T = 0$  will give the coordinates of the origin O; equation  $P = 0$  in the  $k$  equations give, by elimination of  $T$ ,  $k - 1$  equations defining unit vector  $V^1$  and the same for  $T = 0$  defining vector  $V^2$  (see also Appendix 3). This procedure is a new way for determining (P, T) diagrams when (averaged) thermodynamic data are known.  $3k$  data are needed to determine O,  $V^1$  and  $V^2$ ; if one knows the linear relations of the type  $g^i = a^i P + b^i T + c^i$ , there are at first sight  $3(n + k)$  pieces of information. Actually, they are not independent since there are  $k$  independent reactions whose affinities give  $3k$  linear relations in P and T. Many other algorithms to construct phase diagrams are found in the literature, such as by Usdansky (1989), Vielzeuf and Boivin (1984), Connolly and Kerrick (1987), Cheng and Greenwood (1990).

If all the parameters allowing a quantitative construction of the diagram are not known, the method described may still allow to predict possible structures of  $n + k$  diagrams for arbitrary values of  $n$  and  $k$ , taking the  $3k$  lacking data as parameters. Part of the data may be known; in that case the diagrams may be parametrized by the lacking numbers, and trials may be done by « *reasonable* » values for these unknown parameters; the knowledge of natural compatibilities or incompatibilities may help

then to restrict the choice of the diagram. This gives an alternative semi-quantitative method for the above search of potential solutions<sup>21</sup>.

When one wants to construct a  $(\mu, \mu)$  grid, the orientation of the two vectors  $V^1$  and  $V^2$  is known; the preceding approach may be readily used, the different possible types of diagrams are dependent on the O position which is a function of thermodynamical parameters. This is the same for the isoclinal variants of (P, T) diagrams in the case where only the molar volumes and entropies of the phases are known, but not the complete free energies; the orientation of the two-dimensional intersecting plane is then known, so are the slopes of the univariant lines; isoclinal variants may then be readily constructed and parametrated on the position of the origin, dependent on k unknown independent free energy parameters. The volumic and entropic data are generally better known than the free energies and so this method may provide a quick way to draw candidates for (P, T) diagrams.

## 15. CONCLUSIONS

### 15.1. *The meaning of chemical affinity*

A unique algebraic framework allows to bring together the different concepts of chemical component, chemical reaction, chemical content, affinity, and the properties of stability, metastability and so on. What is called « *affigraphy* », constructed on the column vectors of chemical reaction matrix, is the foundation of this frame. The algebraic duality between chemography and affigraphy is general and does not depend on the linearity of the G « *cost function* ». The important is the linearity of the transformations to change the bases of the system. Through this duality, one is able to give an algebraic definition of affinity, as the « *pricing vector* » of the mathematical programming problem. This may be defined for a large class of problems and constraints and is largely independent of its thermodynamic definition. A dual representation of the

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<sup>21</sup> Preliminary Pacal computer program has been written to solve the problem discussed in the present section (Scheberova, 1994).

chemography may be derived with the sole composition of the phases. The coordinates of the affigraphy are dual to the chemical content axes of the chemography; the affinity axes express the unity to measure absent phases. Absent phases are involved in the sense they are the possible end or target of an evolution; the preliminary inventory of all the system in the matrix **C** is thus compulsory. At this step a « *mathematical thermodynamics* » with  $k$  parameters may be defined; it is known from physics that two parameters only are independent,  $T$  and  $P$  related in fine to energy and momentum. When the quantities of the chemical component are added,  $n + 2$  parameters define the system. In Appendix 3, the reciprocal and generalized point of view is exposed where a temperature is ascribed to the points of affigraphy space. Relations  $T = \sum_i A_i^0$  for temperature as a function of the basic affinities may be written. « *Partial temperatures* » are computed dependent on the thermodynamic parameters of the system.

Affinity naturally appears as an algebraic tool to monitor the state of a thermodynamic system. In order to understand the physical meaning of affinity, it is needed from thermodynamics to know that a scalar function  $G$  exists, that it is an additive function of the corresponding  $g$  functions of the phases, and that this function has a minimum at equilibrium. Affigraphy concept gives a thermodynamic meaning to the use of absent phases to designate the reactions. It is not merely a matter of being more practical (for  $k > n$  the collection of absent phases is longer than that of the present ones) but is connected to the duality between the bases and co-bases. The vectorial orientation of the univariant lines allowing the distinction of the stable and metastable parts is understood in the same frame by the sign of chemical affinities. Historical remarks on the concept of affinity may be found in Goupil (1991). In the exposed frame,  $P$  and  $T$  may be seen as mere combinations of affinities, and temperature and pressure scales be expressed in energetic units. The « *affinity tables* » of the old chemists in the eighteenth century were first attempts to class compounds according to the preference for reacting with one of them (e.g. Goupil, 1991); it can easily be demonstrated that this ordering is equivalent to finding stability sequences in the sense of the present paper. Oxydo-reduction, electronegativity scales and so on

may be understood in the same way. The different arrangements are connected to each other inside the algebraic frame and depend on the conditions in P and T. The historical meaning of affinity intends to express the tendency phases have to react together. The longer the distance between phase associations in the affigraphy (or the more numerous the hyperplanes between them), the greater the tendency they have to react together.

### *15.2 Further research*

So forth, conservation of chemical components has been written at fixed T and P, in which case use was made of the Gibbs Free Energy function G. Problems may be considered where the volume, the total energy, the entropy etc. is conserved, in which case other types of functions and of variables will be relevant. For each type of problem, sets of diagrams analogous to the A-, B-, C- and D- type diagrams of Table 5 above and their combinations may be drawn. Corresponding two-dimensional phase diagrams may also be derived by proper intersections of the composition or affinity spaces by two-dimensional varieties. For some particular systems, more than two physical parameters, or others than P and T, could be considered e.g. three or more for osmotic systems, for systems dependent on magnetic field (supraconductors) and so on. Similarly, for rock systems suffering pressure induced dissolution, two pressures (solid and fluid) or more may be defined (Albee, 1965); the Gibbs free energies of some phases may depend on one of these pressures or the other (or both); a phase may also be counted twice at different pressures depending on its location in the rock; by extension of the methods of the present paper, it is easy to obtain the structure of phase diagrams where the phase associations depend on such appropriate generalized parameters.

In summary, we believe affigraphy concept may help discuss structural aspects in all types of phase diagrams. The applications of the approach are many; only the general frame has been given. Knowing the  $n + k$  vectors of the affigraphy one is able to predict the organization of the  $C_{n+k}^{n+1}$  univariant lines of the chemical reactions of the system. In order to derive the possible (P,T) diagrams, one must infer that linear relations



between  $g$  and  $P$  and  $T$  are obtained. New types of diagrams may be defined. The resolution of all the exposed problems may be automated with computers; the different structures that one may expect for the phase diagrams of a given system can thus be displayed (partial attempts are found in Pla, 1991 and Scheberova, 1994). The knowledge of natural compatibilities or incompatibilities may help to restrict the number of solutions.

To end this paper, it should be stressed that, in the discussions so far, the magnitude of the compositional or thermodynamic parameters studied do not matter as such; the important are qualitative parameters such as the position of a phase with respect to other phases in the composition space, the list of phases in a paragenesis, the side on which a phase appears in a reaction, the stability level of an association and so on. These different parameters may simply be described by sets of signs  $+$  or  $-$ , or sets of  $1$  or  $0$  for the presence or absence of a character. Refinements of the qualitative structure described in this paper will find in Matroid theory a suitable abstract frame, lying on a generalization of linear algebra and of the linear dependency.

This work was initiated by discussions with J.M. Pla, mathematician, whom I sincerely thank here. The problems that may appear in the mathematical formulations are my sole responsibility, however. Thanks are also addressed to M. A. Lallemand for his careful work on the drawings, MM. W. Bienia, J. Salemink, D. Garcia, F. Gruy, M. Guiraud for valuable discussions, M. Fontelles for providing copies of the original Schreinemakers papers and L. Raimbault for translating Zharikov paper from Russian. Pascal computer programs written by J.M. Pla and K. Scheberova may be obtained on request. Many directions for research have not been exploited due to lack of time; propositions for collaborative work on application and development of the concepts in the paper will be examined with attention.

## REFERENCES

- Abart R., Connolly J.A.D. and Trommsdorff V. (1992) Singular point analysis: construction of Schreinemaker's projections for systems with a binary solution, *American Journal of Science*, 292, 778-805.
- Albee A.L. (1965) A petrogenetic grid for the Fe-Mg silicates of pelitic schists, *American Journal of Science*, 263, 512-536.
- Baracs J. (1987) A timely update of descriptive geometry, in: *Raisonnement géométrique assisté par ordinateur*, Cours INRIA, 1, 1, 173-185.
- Burt D.M. (1972) Mineralogy and geochemistry of Ca-Fe-Si skarn deposits, Unpubl. Ph. D. thesis, Harvard Univ., Cambridge, Mass., USA, 445 p.
- Burt D.M. (1974) Concepts of acidity and basicity in petrology - The exchange operator approach, *Geological Society of America Abstracts with Programs*, 674-676.
- Burt D.M. (1991) Vectors, components and minerals, *American Mineralogist*, 76, 1033-1038.
- Ceolin R., Agafonov V., Toscani S. and Dugue J. (1991) Polymorphisme: représentation p-T du trimorphisme, 17<sup>e</sup> Journées d'Etudes sur les Equilibres Entre Phases, Société Française de Chimie ed., 13-15.
- Chen T. (1994) Evolution de la perméabilité d'agrégats de sels sous contrainte liée à des circulations de fluides (dissolution / colmatage / déformation), thèse Doct. Université de Grenoble 167 p.
- Cheng W. and Greenwood H.J. (1990) Topological construction of nets in ternary (n + 3)-phase multisystems, with application to  $\text{Al}_2\text{O}_3$  -  $\text{SiO}_2$  -  $\text{H}_2\text{O}$  and  $\text{MgO}$  -  $\text{SiO}_2$  -  $\text{H}_2\text{O}$ , *Canadian Mineralogist*, 28, 305-320.

Connolly J.A. (1990) Multivariate phase diagrams: an algorithm based on generalized thermodynamics, *American Journal of Science*, 290, 666-718.

Connolly J.A.D. and Kerrick D.M. (1987) An algorithm and computer program for calculating composition phase diagrams, *Calphad*, 11, 1, 1-55.

Connolly J.A.D. and Trommsdorff V. (1991) Petrogenetic grids for metacarbonate rocks: pressure-temperature phase-diagram projection for mixed-volatile systems, *Contribution to Mineralogy and Petrology*, 108, 93-105.

Dantzig G., Johnson S. and White W. (1958) A linear programming approach to the chemical equilibrium problem, *Management Science*, 38-43.

Day H.W. (1972) Geometrical analysis of phase equilibria in ternary systems of six phases, *American Journal of Science*, 272, 711-734.

Ferry J.M. (1982) editor, Characterization of metamorphism through mineral equilibria, *Reviews in Mineralogy*, vol. 10, Mineralogical Society of America, 397 p.

Ferry J.M. (1983) Applications of the reaction progress variable in metamorphic petrology, *Journal of Petrology*, 24, 4, 343-376.

Fisher G.W. (1989) Matrix analysis of metamorphic mineral assemblages and reactions, *Contribution to Mineralogy and Petrology*, 102, 69-77.

Fisher G.W. (1993) An improved method for algebraic analysis of metamorphic mineral assemblages, *American Mineralogist*, 78, 1257-1261.

Fonteilles M. (1980) Les mécanismes de la métasomatose, *Bulletin de Minéralogie*, 101, 166-194.

Fujii T. (1977) The configuration of the univariant curves and their metastable extensions around an invariant point on P-T diagram, *Journal of Geology*, 85, 571-589.

Gordon T.M. (1973) Determination of internally consistent thermodynamic data from equilibrium experiments, *Journal of Geology*, 81, 199-208.

Goupil M. (1991) Du flou au clair? Histoire de l'affinité chimique, Editions du C.T.H.S., Paris, 348 p.

Gibbs J.W. (1876, 1878) On the equilibrium of heterogeneous substances, *Transactions of the Connecticut Academy* 3, 108-248 and 343-524; reprinted, 1961, *The scientific papers of J.W. Gibbs*, 1, Dover Publications, New York, 55-371.

Greenwood H.J. (1967) The N-dimensional tie-line problem, *Geochimimica et Cosmochimica Acta*, 31, 465-490.

Guiraud M. Holland T. and Powell R. (1990) Calculated mineral equilibria in the greenschist-blueschist-eclogite facies in  $\text{Na}_2\text{O}$ - $\text{FeO}$ - $\text{MgO}$ - $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ - $\text{H}_2\text{O}$ . Methods, results and geological applications, *Contribution to Mineralogy and Petrology*, 104, 85-98.

Guo Q. (1980a) Topological structures in multisystems of  $n + 4$  phases, *Scientia Sinica*, XXIII, 1, 88-99.

Guo Q. (1980b) Closed-net-diagrams of binary six-phase ( $n + 4$ ) multisystems, *Scientia Sinica*, XXIII, 3, 346-356.

Guo Q. (1980c) Complete systems of closed nets for unary five-phase ( $n + 4$ ) multisystems and their application to concrete configurations of phase diagrams, *Scientia Sinica*, XXIII, 8, 1039-1045.

Guo Q. (1981) A further study on closed-nets-diagrams of binary six-phase ( $n + 4$ ) multisystems, *Scientia Sinica*, XXIV, 5, 678-683.

Guo Q. and Cai C. (1982) Some properties of closed-net-diagrams of  $n + k$  ( $k \geq 3$ ) phase multisystems, *Scientia Sinica*, XXV, 7, 756-764.

Guo Q. (1984) Topological relations in multisystems of more than  $n + 3$  phases, *Journal of Metamorphic Geology*, 2, 267-295.

Guy B. (1988) Contribution à l'étude des skarns de Costabonne (Pyrénées Orientales, France) et à la théorie de la zonation métasomatique, Thèse Doctorat d'Etat, Université Paris VI, Mémoire des Sciences de la Terre de l'Université Pierre et Marie Curie n° 88-29, 3 tomes, 928 p.

Guy B. (1993) Mathematical revision of Korzhinskii's theory of infiltration metasomatic zoning, *European Journal of Mineralogy*, 5, 317-339.

Guy B. and Pla J.M. (1986) Thermodynamique chimique et matroïdes, Rapport final A.T.P. C.N.R.S. n°950010, Annexe 8, Ecole des Mines de Saint-Etienne.

Guy B. and Pla J.M. (1992) Structure des diagrammes de phases: l'apport de la programmation linéaire, première approche, 18<sup>e</sup> Journées d'Etude des Equilibres entre Phases, Chatenay Malabry, B. Legendre, Y. Feutelais et G. Morgant éditeurs, Université Paris Sud et Société Française de Chimie, p. 140.

Guy B. and Pla J.M., Studies of phase diagrams: the contribution of matroid theory, in preparation.

Hensen B.J. (1971) Theoretical phase relations involving cordierite and garnet in the system  $\text{MgO} - \text{FeO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ , *Contribution to Mineralogy and Petrology*, 33, 191-214.

Hensen B.J. (1986) Theoretical phase relations involving cordierite and garnet revisited: the influence of oxygen fugacity on the stability of sapphirine and spinel in the system Mg-Fe-Al-Si-O, *Contribution to Mineralogy and Petrology* 92, 362-367.

Hensen B.J. (1987) P-T grids for silica undersaturated granulites in the systems MAS (n + 4) and FMAS (n + 3) - tools for the derivation of P-T paths in metamorphism, *Journal of Metamorphic Geology*, 5, 255-271.

Hillert M. (1985) Principles of phase diagrams, *International Metals Reviews*, 30, 2, 45-67.

Jeter M. W. (1986) Mathematical programming, an introduction to optimization, Marcel Dekker, Inc., New York and Basel, 342 p.

Korzhinskii D.S. (1959) Physico-chemical basis of the analysis of the paragenesis of minerals (English translation), New York, Consultants Bureau Inc., 142 p.

Kujawa F.B., Dunning C.A. and Eugster H.P. (1965) The determination of stable unary phase diagrams through the use of dual networks, *American Journal of Science*, 263, 429-444.

Kujawa F.B. and Eugster H.P. (1966) Stability sequences and stability levels in unary systems, *American Journal of Science*, 264, 620-642.

Laffitte P. (1961) Généralisation des représentations des équilibres paragénetiques sur un plan (P, T) et multisystèmes, (translated by L. Raimbault, original in Russian), in: Physico-chemical problems of the formation of rocks and ores, in D.S. Korzhinskii commemorative: I, Moscow, Akademic Press Nauk SSSR, v.1, 78-80.

Lépine L., Provost A. and Vielzeuf D. (1992) Séquences de stabilité des lignes univariantes dans les systèmes à (C + N) phases, *Comptes Rendus à l'Académie des Sciences*, Paris, 314, II, 1463-1468.

Meunier A. and Velde B. (1986) Construction of potential-composition and potential-potential phase diagrams for solid solution-type phases: graphical considerations (a graphical method based on Korzhinskii's equipotential theory), *Bulletin de Minéralogie*, 109, 657-666.

Mohr R.E. and Stout J.H. (1980) Multisystem nets for systems of  $n + 3$  phases, *American Journal of Science*, 280, 143-172.

Monge G. (1800) *Géométrie descriptive*.

Morey G.W. and Williamson E.D. (1918) Pressure-temperature curves in univariant systems, *American Chemical Society Journal*, 40, 59-84.

O'Hanley D. (1987) The construction of phase diagrams by means of dual networks, *Canadian Mineralogist*, 25, 105-119.

Ostwald W. (1902) *Lehrbuch der allgemeinen Chemie*, Leipzig, Verlag von Wilhelm Engelmann, 2, 2, 1188 p.

Pla J.M. (1980) *Cours de programmation linéaire*, Ecole Nationale Supérieure des Mines de Saint-Etienne, 170 p.

Pla J.M. (1989a) *Mariages, structures en barres et pétrogenèse des roches métamorphiques (les matroïdes et leurs applications)*, Ecole des Mines de Saint-Etienne, 50 p.

Pla J.M. (1989b) « *LINEAR* », a Pascal program for manipulation of matrices and linear programming problems, Ecole des Mines de Saint-Etienne.

Pla J.M. (1990) « *MATROIDO* », a Pascal program for manipulation of oriented matroids, Ecole des Mines de Saint-Etienne.

Pla J.M. (1991) « *POLYANI* », a Pascal program for manipulation and geometric representation of polyhedra and polytopes (dimension  $\leq 6$ ), Ecole des Mines de Saint-Etienne.

Powell R. and Sandiford M. (1988) Sapphirine and spinel phase relationships in the system  $\text{FeO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{TiO}_2 - \text{O}_2$   
Contribution to Mineralogy and Petrology, 98, 64-71.

Prigogine I. and Defay R. (1946) Thermodynamique chimique conformément aux méthodes de Gibbs et de Donder, tome II, Dunod, Paris, 430 p.

Prince A. (1963) The application of topology to phase diagrams, Metallurgical reviews, 8, 30, 213-276.

Provost A., Lépine L. and Vielzeuf D. (1992) Diagrammes T-P des systèmes à (C + N) phases: nombre de variantes isoclines, construction des grilles à (C + 4) phases, Comptes Rendus à l'Académie des Sciences, Paris, 315, II, 1349-1356.

Roseboom E.H. and Zen E-an (1982) Unary and binary multisystems; topologic classification of phase diagrams and relation to Euler's theorem on polyhedra, American Journal of Science, 282, 286-310.

Rumble D. (1974) Gibbs phase rule and its application in geochemistry, Journal of Washington Academy of Sciences, 64, 3, 199-208.

Rumble D. (1982) The role of perfectly mobile components in metamorphism, Annual Review of Earth and Planetary Sciences, 10, 221-233.

Salemink J. (1987a) A practical guide for the graphical construction of topologically correct phase diagrams, Ecole Nat. Sup. des Mines de Saint-Etienne, unpub., 42 p.

Salemink J. (1987b) A program for the calculation and graphical representation of various types of (c + 3) phase diagrams, Ecole Nat. Sup. des Mines de Saint-Etienne, unpub., 40 p.



Salim J. (1993) Géologie, pétrologie et géochimie des skarns à scheelite de la mine de Brejui, Currais Novos, Région du Serido, N.E. du Brésil, thèse Doct. Univ. Cath. Louvain, 272 p.

Scheberova K. (1994) HEDGEHOG, a Pascal program to determine two dimensional phase diagrams by two-dimensional intersection of  $n + k$  vectors in  $k$  dimensional space, Ecole des Mines de Saint-Etienne, Département Géochimie.

Schreinemakers P. (1915-1925) In-, mono- and divariant equilibria, Proceedings of the Koninklijke Akademie van Wetenschappen te Amsterdam (I to XXIX). The first and last paper of the series are:

I. (1915/1916), 18, 116-126, (Introduction, General properties, Unary systems, Binary systems).

XXIX. (1925), 28, 252-261 (Influence of one or more new substances on an equilibrium in which a phase reaction may occur, Influence of one or more substances under constant pressure, in which a phase reaction may occur).

Smith W.R. and Missen R.W. (1982) Chemical reaction equilibrium analysis, J. Wiley and sons, New York, 364 p.

Spear F.S. (1988) The Gibbs method and Duhem's theorem: the quantitative relationships among  $P$ ,  $T$ , chemical potential, phase composition and reaction progress in igneous and metamorphic systems, Contribution to Mineralogy and Petrology, 99, 249-256.

Stout J.H. (1990) Phase chemographies in quaternary systems of seven phases, I: the five convex polytopes, American Journal of Science, 290, 719-738.

Stout J.H. and Guo Q. (1994) Phase diagram topology and the intrinsic stability rule, American Journal of Science, 294, 337-360.

Thompson J.B. (1982a) Composition space: an algebraic and geometric approach, in Ferry J.M. editor, Characterization of metamorphism

through mineral equilibria, *Reviews in Mineralogy*, vol. 10, Mineralogical Society of America, 1-31.

Thompson J.B. (1982b) Reaction space: an algebraic and geometric approach, in Ferry J.M. editor, *Characterization of metamorphism through mineral equilibria*, *Reviews in Mineralogy*, vol. 10, Mineralogical Society of America, 33-52.

Thompson J.B. (1991) Modal space: applications to ultramafic and mafic rocks, *Canadian Mineralogist*, 29, 615-632.

Thompson J.B., Laird J. and Thompson A.B. (1982) Reactions in amphibolite, greenschist and blueschist, *Journal of Petrology*, 23, 1, 1-27.

Usdansky S.I. and White D.E. (1983) Invariant point configurations - A combinatorial approach, *Mathematical Geology*, 15, 5, 607-615.

Usdansky S.I. (1987) Some topological and combinatorial properties of  $c$  component  $(c + 4)$ -phase multisystem nets, *Mathematical Geology*, 19, 8, 793-805.

Usdansky S.I. (1989) A simplified combinatorial algorithm for construction of straight-line multisystem nets for  $c$ -component,  $(c + 3)$ -phase multisystems - theory and application, *American Journal of Science*, 289, 1117-1133.

VanMarcke G. (1983) *Pétrologie et géochimie des skarnoïdes du site tungstifère de Costabonne (Pyrénées Orientales)*, thèse Université Catholique de Louvain, 293 p.

Vielzeuf D. and Boivin P. (1984) An algorithm for the construction of petrogenetic grids: application to some equilibria in granulitic paragneisses, *American Journal of Science*, 284, 760-791.

White W.B., Johnson S.M. and Dantzig G.B. (1958) Chemical equilibrium in complex mixtures, *The Journal of Chemical Physics*, 28, 5, 751-755.

Zen E-An (1966a) Construction of pressure-temperature diagrams for multicomponent systems after the method of Schreinemakers, a geometric approach, *Geological Survey Bulletin* n° 1225, 56 p.

Zen E-An (1966b) Some topological relationships in multisystems of  $n + 3$  phases, I. General theory; unary and binary systems, *American Journal of Science*, 264, 401-427.

Zen E-An (1967) Some topological relationships in multisystems of  $n + 3$  phases, II. Unary and binary metastable sequences, *American Journal of Science*, 265, 871-897.

Zen E-An and Roseboom E. H. Jr. (1972) Some topological relationships in multisystems of  $n + 3$  phases III. Ternary systems, *American Journal of Science*, 272, 677-710.

Zhao M. (1983) The theorem of corresponding relation between neighbouring phase regions and their boundaries in phase diagrams, *Calphad*, 7, 3, 185-199.

Zharikov V.A. (1961) Problems of the general theory of multisystem equilibrium diagrams; I. Univariant ( $n = - 1$ ) multisystems, (in Russian), in: *Physico-chemical problems of the formation of rocks and ores*, in D.S. Korzhinskii commemorative: I, Moscow, Akademic Press Nauk SSSR, v.1, 56-77.

## SYMBOLS

- $\underline{a}$  row vector (dim.  $k$ ); for specified  $P$  and  $T$ , values of the  $k$  basic independent phase dissociation affinities in the system. It is also the constant projection of the total  $(n + k)$ -dimensional affinity  $\underline{A}$  onto affigraphy (in mathematical correspondence with projected global composition onto chemography). We have  $\underline{R}\underline{A}^T = \underline{a}^T$ . The value of  $\underline{a}$  is dependent on the chosen affinity co-basis,  $\underline{M} - \underline{l}_0$ , used to construct chemical reaction matrix  $\underline{R}$ ; ( $\underline{l}_0$  refers to a chosen representation basis for composition space).
- $\underline{A}$  row vector (dim.  $n + k$ ): values of the affinities of all the elementary phase dissociation reactions. Vector  $\underline{A}$  may be restricted to the  $k$  dimensional projected vector  $\underline{a}$ .
- $\underline{A}^i$  or  $\underline{A}^{(j)}$  affinity of the dissociation of phase  $P_j$  in a specified phase basis; the dissociation reaction reads  $P_j = \sum C_j^i P_i$  where  $P_i$  is basic phase  $i$  ( $i = 1 \dots n$ ), then  $\underline{A}^i = g^j - \sum c_j^i g^i$  or  $\underline{A}^i = g^j - \mu^j = -(\mu^j - g^j)$ ; the  $g$ 's are the molar Gibbs free energies and the  $\mu$ 's are the chemical potentials of the phases. The unit used to measure the affinity is the same as for free energy  $G$  or  $g^j$ .
- $\langle \underline{A}^f \rangle$   $f^{\text{th}}$  unit affinity vector such that its  $j^{\text{th}}$  co-ordinate  $\langle \underline{A}^f \rangle_j = g^j - \mu^j = 1$  for  $j = f$  and  $0$  otherwise. Unit vectors may be defined by brackets  $\langle \rangle$  for the different vectors of interest; when there is no confusion, the brackets are omitted.
- $\underline{B}$  restriction of matrix  $\underline{C}'$  (see below) to the columns that do not belong to the basis.
- $\underline{c}$  column vector (dim.  $n$ ): quantities, in number of moles, of the chemical components in the system expressed in a specified phase composition basis.
- $c_i$  quantity of independent component  $i$ , or independent phase  $i$  in the system ( $i = 1, \dots, n$ ).
- $\underline{C}$  matrix of the chemical compositions ( $n$  rows,  $n + k$  columns).
- $c_i^j$  number of moles of chemical component or phase  $i$  in one mole of phase  $j$  ( $i = 1, \dots, n$ ;  $j = 1, \dots, n + k$ ).
- $\underline{C}^l$  restriction of  $\underline{C}$  to a set of independent columns defining a basis of the phase space; indices belong to set  $l$ . In general  $\underline{C}^l$  is a  $n \times n$  matrix; in the new basis  $l$ ,  $\underline{C}$  becomes  $\underline{C}' = (\underline{C}^l)^{-1} \cdot \underline{C} = (\underline{U}_n, (\underline{C}^l)^{-1} \cdot \underline{C} \underline{M}^{-l}) = (\underline{U}, \underline{B})$ ;  $\underline{M}$  is the set of all column indices and  $\underline{U}$  a unit matrix. In the paper  $\underline{C}$  is often of the form  $\underline{C}'$ , and  $\underline{C}$  and  $\underline{C}'$  are not distinguished; in that case the basis used to describe  $\underline{C}$  is called  $\underline{l}_0$ ; this method is used to change the bases in the general case.
- $\underline{C}_m^n$  number of possible arrangements of  $n$  objects chosen among  $m$ ; it equals  $m! / n!(m-n)!$ ; it may also be written  $\binom{m}{n}$ ;  $\underline{C}_m^n = \underline{C}_m^{m-n}$ .
- $\underline{g}$  row vector (dim.  $n + k$ ): Gibbs molar free energies of the phases.
- $g^j$  Gibbs molar free energy of phase  $j$  ( $j = 1, \dots, n + k$ ); the unit for  $g$  is not specified (joules for instance).
- $G = \underline{g}\underline{x} = \sum_{j=1}^{n+k} g^j x_j$  Gibbs free energy of the total system; also called cost or objective function.
- $l$  set of phase indices defining a basis of the phase space.
- $\underline{l}_0$  particular basis chosen for the representation of the phases in the chemography.
- $k$  difference between the total number of possible species or phases ( $n + k$ ) and the number of independent chemical components ( $n$ ).

- M in matrix  $C$ , set of (column) indices of all the phases
- M-l set of indices of the phases that do not belong to the basis; the set M-  $l_0$  is a natural representation basis (or « co-basis ») for the affinities in the affigraphy
- n number of independent chemical components
- $n_{ic}$  number of indifferent crossing points per univariant line
- $P_j$  phase j (with no solution in general); phase vectors in composition space and phases may be designated by the same upper case letters A, B, C and so on. Total number of phases is  $n + k$
- ( $P_j$ ) between brackets: absent phase  $P_j$ ; on the affigraphy symbol ( $P_j$ ) may be attributed to the « unitary absent phase » equivalent to unit affigraphy vectors  $\langle A^j \rangle$
- (P) the primal linear programming problem
- ( $P^*$ ) the dual programming problem
- P pressure
- R a matrix of chemical reactions (k lines,  $n + k$  columns);
- $r_f^j$  coefficient of phase j in reaction f. In the text R is written in correspondence with matrix  $C'$  after a unit matrix corresponding to base  $I = l_0$  has been exhibited in C. R verifies  $C'R^T = 0$  where  $R^T$  is the transposed of R; the coefficients  $r_f^f(l)$ , i.e. for base I, behave like the homogeneous solutions  $r(f)$
- $r(f)^T = y^{(f)}$  column vector (dim.  $n + k$ ): homogeneous solutions of the primal programming problem. Columns of  $R^T$  are homogeneous solutions; when a basis I is chosen  $y^{(f)}_j(l) = r_f^j$ ; f is the index for the homogeneous solution (corresponds to reaction f) and j is the index for its components. Following relations are verified:  $y^{(f)}_f(l) = 1$ ,  $y^{(f)}_l(l) = -(Cl)^{-1}C(l)$  and  $y^{(l)}_{M-l-f(l)} = 0$ , where f belongs to M-l.  $r(f)$  may also be noted  $r_f$  where a point stands for the mute indices
- $s^j$  molar entropy of phase j
- T temperature
- T the primal simplex tableau
- U unit matrix;  $U_n$  unit matrix of rank n
- $u^j$  internal energy of phase j
- $v^j$  molar volume of phase j
- V linear variety  $C.x = \underline{c}$
- $V'$  linear variety  $R.A^T = R.A_0^T = \underline{a}^T$
- $V_0$  linear variety  $C.x = 0$
- $V'_0$  linear variety  $R.A^T = 0$
- W linear variety  $R.x = R.x_0$
- $W'$  linear variety  $C.A^T = C.A_0^T$
- $W_0$  linear variety  $R.x = 0$
- $W'_0$  linear variety defined by  $C.A^T = 0$
- $T^*$  the dual simplex tableau
- x column vector (dim.  $n + k$ ): quantity (number of moles) of the phases in the system; x is restricted to the projected n dimensional vector in basis  $l_0$  of matrix C through  $Cx = \underline{c}$
- $x^*$  value of x at equilibrium (« optimum »)
- $x_j$  quantity of phase j in the system ( $j = 1, \dots, n + k$ )
- $x^l(l)$  when a basis I is chosen the principal unknowns are the components of x on the basis and are written  $x^l(l)$ ; the non principal unknowns  $x^{M-l}(l)$  are the other components of x
- $x_0$  variable associated to the economic function  $G$ :  $x_0 = \underline{g}x$
- $x_0$  is also the initial quantity of the phases in a given problem (no confusion is possible)

**Y** matrix of homogeneous solutions corresponding to representation basis  $l_0$  in **C**. In general **R** and **Y** are identified.

$\Theta$  number of combinatorially possible solutions

$\underline{\mu}$  row vector (dim.  $n + k$ ): chemical potential of the phases

$\mu^j$  chemical potential of phase  $j$  ( $j = 1, \dots, n + k$ )

$\underline{\mu}$  row vector (dim.  $n$ ): chemical potential of the chemical components or basic phases, that may be expressed in an  $n$ -dimensional phase basis

$\underline{\mu}^i$  chemical potential of component or basic phase  $i$  ( $i = 1, \dots, n$ ); we have  $\underline{\mu} = \underline{\mu} \mathbf{C}$

$\xi_j$  column vector; advance of reaction  $j$ ; following the notation on affinities should also be written  $\xi_{(j)}$

$\Pi$  number of mathematically possible solutions

$\Pi_0$  number of potential solutions for composition 0

The complete list of symbols for different types of affigraphies and of potential solutions for phase diagrams, depending on the information available, is given in Table 8.

$\chi_i$  chemical component  $i$ ; chemical components may be designated by lower case letters  $a, b, c$  and so on; the total number of independent chemical components is  $n$

### Principal vector and matrix relations

Vectors and matrices are noted in bold letters, scalars in normal letters, so as the points on the diagrams. When there is no ambiguity bold lettering may be omitted.  $-\mathbf{A}$  designates the negative part of vector **A** and  $(-\mathbf{B})$  the negative part of vector (**B**).

Elements (vectors, points and so on) are usually noted between brackets in the affigraphy, and with no brackets in the chemography. When there is no ambiguity, a group of absent phases in the affigraphy may be noted (A, B, C) rather than  $\{(A), (B), (C)\}$ .

When sum index is not indicated, the sum is done on the repeated index at different levels

Through the action of **C** and **R** matrices,  $n + k$  dimensional vectors may be projected onto lower  $n$ - or  $k$ -dimensional vectors; these may be underlined in order to avoid confusion. Projection relations are

$$\begin{aligned}\mathbf{C} \cdot \mathbf{x} &= \mathbf{C} \cdot \mathbf{x}_0 = \underline{\mathbf{c}} \\ \mathbf{R} \cdot \mathbf{A}^T &= \mathbf{R} \cdot \mathbf{A}_0^T = \underline{\mathbf{a}}^T \\ \underline{\mu} \cdot \mathbf{C} &= \underline{\mu} \\ \underline{\xi}^T \mathbf{R} &= \underline{\xi}^T\end{aligned}$$

The dimensionality of the projected vectors is more usually  $n$  for  $\mathbf{x}$  and  $\underline{\mu}$ , and  $k$  for  $\underline{\xi}$  and  $\mathbf{A}$ .

Other relations:  $\underline{\mu} \cdot \mathbf{C} \leq \underline{\mathbf{g}}$ ,  $\underline{\xi}^T \mathbf{R} \geq -\mathbf{x}_0^T$ ,  $\mathbf{C} \cdot \mathbf{R}^T = 0$ , and  $\mathbf{A} \cdot \mathbf{x} = 0$  (complementarity relations).

If  $c_i^j$  is a coefficient of matrix **C**,  $c_{(i)}^j = c_i^j$  is the line vector of line index  $i$  and  $c_i^{(j)} = c_i^j$  is the column vector of column index  $j$ , where the points replace the different co-ordinates of the vector. Points and brackets may be omitted.

## APPENDICES

### APPENDIX A1: SOME RESULTS OF MATHEMATICAL PROGRAMMING

#### *A1.1. Principal and non-principal unknowns, homogeneous solutions; the general solution*

Equation  $\mathbf{C} \cdot \mathbf{x} = \underline{\mathbf{c}}$  can be described by the following tableau; column  $\underline{\mathbf{c}}$  is written besides matrix  $\mathbf{C}$ :

$\mathbf{C}$	$\underline{\mathbf{c}}$
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If  $\mathbf{D}$  is a non-singular  $(n, n)$  matrix, mathematical programming theory shows that the solution of  $\mathbf{C} \cdot \mathbf{x} = \underline{\mathbf{c}}$  and of  $\mathbf{D} \cdot \mathbf{C} \cdot \mathbf{x} = \mathbf{D} \cdot \underline{\mathbf{c}}$  are the same; the corresponding systems of equations are equivalent. Let consider a set  $I$  of independent column vectors of  $\mathbf{C}$  defining non singular  $(n, n)$  matrix  $\mathbf{C}^I$ . The remaining matrix is called  $\mathbf{C}^{M-I}$ ;  $M$  is the set of all column indices:

$\mathbf{C}^I$	$\mathbf{C}^{M-I}$	$\underline{\mathbf{c}}$
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Let us choose for matrix  $\mathbf{D}$  the inverse of  $\mathbf{C}^I$ :  $\mathbf{D} = (\mathbf{C}^I)^{-1}$ . The multiplication is represented as:

	$C^I$	$C^{M-I}$	$\underline{c}$
$(C^I)^{-1}$	$U_n$	$(C^I)^{-1}C$	$(C^I)^{-1}\underline{c}$
	$U_n$	$B$	$(C^I)^{-1}\underline{c}$

A unit  $(n, n)$  matrix called  $U_n$  appears. The remaining matrix  $(C^I)^{-1}C$  is called  $B$ ;  $C$  has been written for  $C^{M-I}$ . « *Principal unknowns* »  $x^I(I)$  are the co-ordinates of  $x$  on the basis; « *non principal unknowns* » are the other co-ordinates  $x^{M-I}(I)$ . The last tableau suggests a possible solution of the starting problem. One may choose for  $x^I(I)$  the values of the second member  $(C^I)^{-1}\underline{c}$  and for  $x^{M-I}(I)$  the value  $x^{M-I}(I) = 0$ . This solution will be called a *basic solution*; the optimal solution generally belongs to the set of the basic solutions. Different bases may be envisaged for other sets  $I$  of independent column vectors of  $C$ ; the corresponding solutions may be derived by the operations described above through the action of the corresponding  $C^I$  matrices.

The solutions of  $C.x = 0$  will be called the homogeneous solutions and called  $y$ ; so  $C.y = 0$ . It is useful to consider the « *fundamental homogeneous solutions* » corresponding to a given basis. Let us start then with  $C' = (U_n, B)$  (in the case a unit matrix is present in  $C$  from the beginning, the notation of  $C^I$  and  $U_n$ , and of  $C^{M-I}$  and  $B$  are equivalent);  $k$  is the cardinal, i.e. the number of elements of the  $M - I$  set:  $k = n + k - n$ .



Let us add a unit matrix  $U_k$  below matrix  $-B$  to build what we call matrix  $Y^T$ , (superscript  $T$  indicates the transposition of a matrix):

$$Y^T = \begin{array}{c|c|c} \begin{array}{c} \text{M - I} \\ \hline \begin{array}{c} -B \\ \\ U_k \end{array} \end{array} & \begin{array}{c} I \\ \\ M - I \end{array} & \begin{array}{c} f \\ M - I - f \end{array} \end{array} \quad \begin{array}{c} y^{(f)} \\ \hline \begin{array}{c} -(C^I)^{-1}C \\ 0 \\ 1 \\ 0 \end{array} \end{array}$$

So  $Y = (-B^T, U_k)$ ;  $Y$  is a matrix of chemical reactions (see below). One checks that  $C^I \cdot Y^T = (U, B) \cdot (-B, U)^T = 0$ ; the columns of  $Y^T$  verify  $C \cdot y = 0$  and are homogeneous solutions. The set of the  $k$  fundamental homogeneous solutions define matrix  $Y$ ; its generic element is  $y_j^f$ . The fundamental homogeneous solutions  $y^{(f)}$  may be named according to the index  $f$  of the corresponding row of matrix  $U_k$  where  $y_f^{(f)}(I) = 1$ . The other components of  $y^{(f)}$  are  $y_i^{(f)}(I) = (C^I)^{-1} \cdot C^f$  and  $y_{M-I-f}^{(f)}(I) = 0$ .

A specified basis is defined by  $n$  phases; the formula of each of the  $k$  remaining phases may be written in that basis and thus define  $k$  chemical reactions. The chemical reactions may be defined in matrix  $R$  ( $k$  rows,  $n + k$  columns) where the coefficient  $r_j^f$  is the number of moles of phase  $j$  that participates in reaction  $f$ . We will identify here  $r_j^f$  and  $y_j^f$  (or  $R$  and  $Y^T$ ) although the definition of  $r_j^f$  is more general than that of  $y_j^f$ ;  $y_j^f$  is defined after a basis has been chosen. When matrices are written with corresponding unit sub-matrices, relation  $C \cdot R^T = 0$  hold.

#### Convex sets

A convex combination is a linear combination where the factors are positive and their sum equal to one; this is the case for  $x$  as a combination of the phases and when concentrations are considered. In the case of a conic combination, the requirement is simply that the coefficients of the combination are positive. Theory shows that the

general feasible solution of  $\mathbf{C} \cdot \mathbf{x} = \underline{\mathbf{c}}$  is a convex combination of the basic solutions to which can be added a conic convex combination of the corresponding fundamental homogeneous solutions. In the combination, the factors of the homogeneous solutions, corresponding to reactions, are the advance  $\xi_f$  of the reactions.

Korzhinskii (1959) proposed a method with determinants to balance chemical reactions once the composition of the phases is known and to write all the reactions once a basis of  $k$  of them is known; this is equivalent to basis changes and algebraic manipulations in the  $k$ -dimensional space of reactions. Other ways to write reactions are given in Fisher (1989, 1993).

#### A1.2. The dual programming problem

Program (P) is equivalent to (P\*): find row vector  $\underline{\mu}$  of  $n$  components such that:

$$\begin{aligned} \text{Max } \underline{\mu} \cdot \underline{\mathbf{c}} &= \text{Max } \sum \underline{\mu}_i \mathbf{c}_i \\ (\underline{\mu}) \\ \underline{\mu} \cdot \mathbf{C} &\leq \mathbf{g} \end{aligned}$$

where  $(\underline{\mu})$  means that the sign of  $\underline{\mu}$  is unconstrained. (P\*) is a linear programming problem in canonical form called the « *dual programming problem* ». There is a duality between the constraints of the primal problem and the variables of the dual problem. One speaks of dual feasibility when the last condition  $\underline{\mu} \mathbf{C} \leq \mathbf{g}$  is verified. This condition does not involve the initial composition  $\underline{\mathbf{c}}$ . The  $\underline{\mu}$  may be interpreted as the chemical potentials of the chemical components. The interpretation appears clearly at optimum where

$$\underline{\mu} \cdot \underline{\mathbf{c}} = \mathbf{g} \cdot \mathbf{x} = G$$

According to this last equation, the partial derivatives with respect to the quantities  $\underline{\mathbf{c}}$ , of the total energy  $G$ , are

$$\partial G / \partial \underline{c} = \underline{\mu}$$

This is the definition of the chemical potentials. In (P\*) the solution is approached by lower values (search of a maximum) and in (P), the solution is approached by higher values (search of a minimum). Through

$$\mu = \underline{\mu} \cdot \underline{C}$$

we can also define the chemical potentials of the phases,  $\mu^j$  ( $j = 1, \dots, n + k$ ), in row vector  $\underline{\mu}$ . If optimum is verified for basis I for which  $x^I(I) = (C^I)^{-1} \underline{c}(I)$  and  $x^{M-I}(I) = 0$ , the chemical potentials of the phases  $\mu^I(I)$  are  $\underline{g}^I (C^I)^{-1} \underline{C}$  (they are equal to  $g^I$  for the phases in the basis).

#### A1.3. The primal simplex tableau

The objective function may be considered as defining a new variable  $x_0$  =  $-\underline{g} \cdot \underline{x}$ ; one must then add the constraint  $x_0 + \underline{g} \cdot \underline{x} = 0$ ; in the primal problem, one has to maximise  $x_0$ . All the information on the constraints and the economic function is gathered in the following simplex tableau T:

1	<b>g</b>	0
0	<b>C</b>	<b><u>c</u></b>

The first column has been added and corresponds to variable  $x_0$ . It will be omitted in the following. Following the same notation as above,  $\underline{g}^I$  is the restriction of  $\underline{g}$  to the basis I. Similarly one can consider the matrix

<b><u>g</u><sup>I</sup></b>
<b><u>C</u><sup>I</sup></b>



and one multiplies tableau T by its inverse according to

$\mathbf{g}^I$	$\mathbf{g}^{M-I}$	0
$\mathbf{C}^I$	$\mathbf{C}^{M-I}$	$\underline{\mathbf{c}}$

$-\mathbf{g}^I(\mathbf{C}^I)^{-1}$
$(\mathbf{C}^I)^{-1}$

0	$\mathbf{g} - \mathbf{g}^I(\mathbf{C}^I)^{-1}\mathbf{C}$	$-\mathbf{g}^I(\mathbf{C}^I)^{-1}\underline{\mathbf{c}}$
$\mathbf{U}_n$	$(\mathbf{C}^I)^{-1}\mathbf{C}$	$(\mathbf{C}^I)^{-1}\underline{\mathbf{c}}$

The quantities  $\mathbf{g} - \mathbf{g}^I(\mathbf{C}^I)^{-1}\mathbf{C}$  are the affinities of the dissociation of the phases that do not belong to the basis I; the chemical reaction are expressed in terms of the phases in the basis. When including the first n quantities of the additional line that are equal to zero, the total affinity row vector may also be expressed as  $\mathbf{A} = \mathbf{g} - \underline{\mu}\mathbf{C}$ , equal to  $\mathbf{g} - \mu$  where the chemical potential appear.  $\mathbf{A}$  is called the reduced cost of the cost, or objective, function. The factors  $\mathbf{g}^I(\mathbf{C}^I)^{-1}$  are the Lagrange multipliers; they define the so-called pricing vector, here noted  $\underline{\mu}$ . In summary the simplex tableau T may be written as

0	$\underline{\mathbf{a}}$	$-\mathbf{g}^I(\mathbf{C}^I)^{-1}\underline{\mathbf{c}}$
$\mathbf{U}_n$	$\mathbf{B}$	$(\mathbf{C}^I)^{-1}\underline{\mathbf{c}}$

when the system is in one basis;  $\underline{\mathbf{a}}$  is the k-dimensional affinity when optimum basis is I. Optimum solution is one basic solution that verifies, in the same time, two groups of conditions read on the simplex tableau; the first group expresses the so-called primal feasibility and reads

$$x_j \geq 0 \text{ for } j \text{ in the set } I$$

The values of the  $x_j$  in the basis are given by the rightmost column of the simplex tableau,  $\mathbf{x} = (\mathbf{C}^I)^{-1}\underline{\mathbf{c}}$ ; and

$$x_j = 0 \text{ for } j \text{ in the set } M - I.$$

The second group of conditions expresses dual feasibility and reads

$$A^j \geq 0 \text{ for } j \text{ in the set } M - I$$

and

$$A^j = 0 \text{ for } j \text{ in the set } I$$

These conditions are given by the additional upper line of the simplex tableau. The affinities  $\underline{\mathbf{a}}$  are ruled by the matrix of chemical reactions in  $\underline{\mathbf{a}} = \mathbf{g}(\mathbf{U}_k, -(\mathbf{C}^I)^{-1}\mathbf{C}) = \mathbf{g}.\mathbf{R}^T$ .

Thanks to the preceding results (P) and (P\*) are shown to be equivalent to:

Find  $\mathbf{x}$  (column,  $n + k$ ) and  $\underline{\mu}$  (row,  $k$ ) such that

$$\mathbf{C}.\mathbf{x} = \underline{\mathbf{c}}$$

$$\mathbf{x} \geq 0$$

$$\underline{\mu}\mathbf{C} \leq \mathbf{g}$$

$$(\mathbf{g} - \underline{\mu}\mathbf{C}).\mathbf{x} = 0$$

$$(\underline{\mu})$$

where no extremum condition is required (( $\underline{\mu}$ ) expresses that the sign of  $\mu$  is unconstrained). The last two relations may equivalently be expressed in terms of total affinity  $\mathbf{A}$  by  $\mathbf{A} \geq 0$  and  $\mathbf{A}.\mathbf{x} = 0$ . Is it a complementary slackness or linear complementarity problem.

#### A1.4. Parametrisation of the simplex tableau

The  $n + k$  molar free energies  $g^j$  of the phases are supposed to be unknowns. The preceding results may be parametrated. Let us first choose a representation basis  $l_0$  to compute the phase compositions and to construct the reaction matrix; in matrix  $R$  the corresponding representation co-basis will be  $M-l_0$ . Representation basis  $l_0$  must be distinguished from the other possible bases among which the particular optimal basis will be. Among the  $n + k$  affinities defined above,  $k$  are independent. One can thus decompose line 0 for the cost function into  $k$  linearly independent lines; the coefficients of the cost function will be obtained by different possible linear combination of these lines. The factors of the combination will be the  $k$  affinities  $\underline{A} = \underline{a} = \underline{g} - \underline{\mu}$  corresponding to the choice of the co-basis  $M - l_0$  and taken as parameters. They are

$$\underline{a} = \underline{g} - \underline{\mu} = \underline{g} - \underline{g}^l_0 (\underline{C}^l_0)^{-1} \underline{C}^{M-l_0}$$

The underlined values correspond to the projected  $k$  dimensional values with indices belonging to set  $M - l$ . In the same manner, the initial composition  $\underline{c}$ , which is also supposed to be unknown, may be decomposed into  $n$  independent columns. We will suppose that we start with the simplicial table corresponding to basis  $l_0$

0	<u>a</u>	0
$U_n$	B	<u>c</u>

where the first  $n$  components apply to the chemography representation basis and the  $k$  remaining apply to the other phases.

The parametrization is then represented by the following tableau; two matrices have been added: the first is composed of a unit matrix  $U_k$  and of a zero matrix for the parametrization of the  $k$ -dimensional affinity; the second is a unit matrix  $U_n$  for the parametrization of the total chemical

composition (this matrix  $U_n$  already appears in the starting tableau; for clarity, we add it to the right hand side of the tableau).

0 $U_k$		
$U_n$	$B$	$U_n$

All the chemographic bases can be systematically explored. For each of them, two groups of conditions are expressed that the basis is an optimum basis. For this, by means of pivoting, algebraic combinations of the  $x_i$  define the corresponding admissible chemography regions; combinations of the  $A^i$  define admissible relations among the affinities for the phases that do not belong to corresponding chemographic basis. For instance, after a first algebraic operation, suppose another chemographic basis is obtained and the new integrated tableau is

$G$		
$B''$	$B'$	$E$

We will call  $F$  the square restriction of matrix  $G$ , to the  $k$  columns of the phases that do not belong to the current chosen basis (these  $k$  columns define the co-basis);  $F$  is not composed of neighbouring columns.

Matrices **E** and **F** give the following equations expressing the basis is optimum:

$$\begin{aligned} \mathbf{E} \cdot \underline{\mathbf{x}} &\geq 0 \\ \underline{\mathbf{A}} \cdot \mathbf{F} &\geq 0 \quad \text{or} \quad \mathbf{F}^T \cdot \underline{\mathbf{A}}^T \geq 0 \end{aligned}$$

$\underline{\mathbf{x}}$  and  $\underline{\mathbf{A}}$  describe two spaces of parameters, respectively n- and k-dimensional, in the starting representation basis and co-basis respectively. Matrix **F** is read in columns ( $\underline{\mathbf{A}}$  is a row vector) and matrix **E** is read in lines ( $\underline{\mathbf{x}}$  is a column vector). In other words, one starts with n- and k- dimensional vector restrictions  $\underline{\mathbf{x}}$  and  $\underline{\mathbf{A}}$  in the representation basis and co-basis respectively; the combinations of  $\underline{\mathbf{x}}$  and  $\underline{\mathbf{A}}$  obtained by means of **F** and **E** give the values in the new basis.

The same method may be used to predict the domains of metastable associations; one to k of the constraints bearing on the affinities can be negative instead of positive (k + 1 stability levels). For one metastable basis

$$\mathbf{E} \cdot \underline{\mathbf{x}} \geq 0$$

with, for some of the  $\underline{\mathbf{A}}$ ,

$$\underline{\mathbf{A}} \cdot \mathbf{F} \leq 0 \quad \text{or} \quad \mathbf{F}^T \cdot \underline{\mathbf{A}}^T \leq 0,$$

instead of  $\underline{\mathbf{A}} \cdot \mathbf{F} \geq 0$  or  $\mathbf{F}^T \cdot \underline{\mathbf{A}}^T \geq 0$ . The procedure is illustrated on an example in Appendix 2. It can be automated (program « *LINEAR* », Pla, 1989b).

Matrix **F** behaves like corresponding square part of  $-\mathbf{R}^T$  where **R** is chemical composition matrix; had we written  $-\mathbf{U}_k$  instead of  $\mathbf{U}_k$  above **B** in the starting tableau, the whole **R** matrix would have been perceptible.



## APPENDIX A2: PROPERTIES OF CHEMOGRAPHY, AFFIGRAPHY AND MATRICES

### A2.1. Properties of lines of **C** matrix.

For each chemography basis one can compute the limits of the corresponding domains in the chemography. *The consideration of these limits is useful to the general understanding of the paper.* Let us discuss the example of Fig. 2 of the main text. Six phases A, B, C, D, E, F are considered whose chemography was given in Fig. 2; the composition of the phases is expressed, for instance in the basis (A, B, C) by the following **C** composition-matrix:

A	B	C	D	E	F
1	0	0	0.4	0.4	0.2
0	1	0	0.2	0.4	0.4
0	0	1	0.4	0.2	0.4

Column vectors for phases A, B and C are unit vectors since {A, B, C} is chosen as the basis; D, E and F are represented by their coordinates in this basis; vectorial relations of the following type are thus verified:

$$\mathbf{A} = 1.\mathbf{A} + 0.\mathbf{B} + 0.\mathbf{C}$$

$$\mathbf{D} = .4.\mathbf{A} + .2.\mathbf{B} + .4.\mathbf{C}$$

and so on; the phases are represented by vectors or, more usually by points (affine representation) in the chemography. *The equations of the lines (or hyperplanes) connecting the points of the chemography are given by the lines of the matrix as in a chemical matrix (read in lines);* in the general case hyperplanes i.e.  $n - 1$  dimensional varieties connect sets of  $n - 1$  phase vectors. The equation of line BC is

$$A = 0$$

where this time A designates the first coordinate of any vector in the {A, B, C} basis. Such relation represents the compositions of the system where A is absent and B and C are present; actually D, E and F are also absent but they do not appear in the restriction of the equation in the A, B, C basis; the complete equation given by the first line of the matrix would be:

$$1.A + .4.D + .4.E + .2.F = 0$$

In other words, the equation is projected onto the (A, B, C) basis in A = 0. In the same basis, the equations of lines AC and of AB are B = 0 and C = 0 respectively, as given by the two next lines of matrix C. If one wants to know the equation of the other hyperplanes (here lines) of the chemography, a change of basis is necessary; for example, by pivoting to make the new basis ABF appear, matrix C is transformed in the following

	A	B	C	D	E	F
A	1	0	-0.5	0.2	0.3	0
B	0	1	-1	-0.2	0.2	0
F	0	0	2.5	1	0.5	1

This new matrix gives the composition of the phases in basis ABF and also gives the equations of the lines AB, BF and FA: the first line of the matrix gives the equation of BF for which B and F are present and A, C, D and E absent; in the starting representation basis (A, B, C) this equation reads:

$$1.A - .5.C = 0$$

This is a valid projection in the sense of Sect. 3.4 from an  $n + k$  dimensional composition space onto  $n$ -dimensional chemography; the useless co-ordinates are forgotten. The second line of the matrix gives the equation of AF, for which A and F are present and B, C, D, E absent:

$$B - C = 0$$

And similarly for AB, (A and B present, C, D, E, F absent):

$$2.5.C = 0 \text{ or } C = 0$$

#### A2.2. Link between lines and columns of *R* matrix

The organization of the vectors and hyperplanes defining the structure of affigraphy is given by *R* matrix in the same way as vectors (or points) and hyperplanes are organized in chemography by consideration of *C* matrix. Depending on the cases, equations of varieties contain phases that may or may not directly correspond to the present or absent phases in the geometrical varieties themselves. Let us study an example. A corresponding *R* reaction matrix to matrix *C* discussed in section 3.1. is the following

	(A)	(B)	(C)	(D)	(E)	(F)
(D)	-0.4	-0.2	-0.	1	0	0
(E)	-0.4	-0.4	-0.	0	1	0
(F)	-0.2	-0.4	-0.	0	0	1

The corresponding affigraphy was represented in Fig. 3. The three lines of the *R* matrix give the writing of three independent chemical reactions between the phases, or, geometrically, hyperplanes, as usual. In the co-basis of affinities  $A^{(D)}$ ,  $A^{(E)}$ ,  $A^{(F)}$  or more simply (D), (E), (F) the equation of the plane containing vectors  $A^{(E)}$  and  $A^{(F)}$  (or E and F absent, noted as (E), (F), and A, B, C, D present) is given by the first line of the matrix:

$$-.4.A^{(A)} -.2.A^{(B)} -.4.A^{(C)} + 1.A^{(D)} = 0$$

restricted to  $A^{(D)} = 0$  in the (D), (E), (F) space (D present) corresponding to reaction

$$-.4A -.2B -.4C + 1D = 0$$

Accordingly, the two other lines of the matrix give the equations of:

$$A^{(E)} = 0 \text{ (E present as well as A, B, C; D and F absent)}$$

$$A^{(F)} = 0 \text{ (F present, D and E absent)}$$

In composition **C** matrix, the zeroes of the lines gave the names of the phases present in the corresponding hyperplanes; conversely in **R** matrix, the zeroes give the absent phases. In a similar way to what obtained in **C** matrix, the columns of the **R** matrix give the intersections of the hyperplanes defining the chemical reactions -in the present example the planes are taken two by two- and define the basic affinity vectors; for instance, in the basis  $A^{(D)}$ ,  $A^{(E)}$ ,  $A^{(F)}$  the vectorial relations hold:

$$A^{(D)} = 1.A^{(D)} + 0.A^{(E)} + 0.A^{(F)}$$

(fourth column of reaction matrix) or

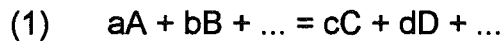
$$A^{(A)} = -.4.A^{(D)} - .4.A^{(E)} - .2.A^{(F)}$$

(first column). The plane containing vectors  $A^{(E)}$  and  $A^{(F)}$  represents the reaction where E and F are absent. After having chosen as independent affinities (D), (E) and (F) these three affinity vectors must simultaneously be combined in the proportion given above to have affinity vector (A). For the equations of the other planes one must change the basis and, by pivoting on **R** matrix, we have, for instance for basis (D), (E) and (C):

	(A)	(B)	(C)	(D)	(E)	(F)
(D)	-0.	0.2	0	1	0	-1
(E)	-0.	-0.	0	0	1	-0.5
(C)	0.5	1	1	0	0	-2.5

Plane (C), (E) or ABDF ( A, B, D, F present; C and E absent) is given by  $A^{(D)} = A^{(F)}$  or more simply  $(D) = (F)$  (first line of matrix); we also have  $A^{(E)} = .5.A^{(F)}$  for (C)(D) plane (A, B, E, F present) containing both vectors  $A^{(C)}$  and  $A^{(D)}$ .

Another way to understand the above relations is as follows. A chemical reaction may be written as



where  $n + 1$  phases are present; at equilibrium the following relation is verified:

$$(2) \quad ag^A + bg^B + \dots = cg^C + dg^D + \dots$$

where the  $g$ 's depend on  $P$  and  $T$ ; the dependence is univariant and allows to define a relation  $f(P, T) = 0$ . When written in terms of chemical potentials relation (2) gives

$$(3) \quad a\mu^A + b\mu^B + \dots = c\mu^C + d\mu^D + \dots$$

among  $n + 1$  chemical potentials; (3) is valid whatever the presence or absence of the phases. By an extension of thermodynamic equilibrium, we will consider in (3) to have  $n$  degrees of freedom and not 2 and will allow  $n$  potentials to vary independently; the phases are considered as virtually in equilibrium even if not present, i.e. even if the  $\mu^j$  are strictly lower than the  $g^j$ . Relation (2) is a particular case of (3). By combining (2) and (3) one obtains

$$(4) \quad aA^A + bA^B + \dots = cA^C + dA^D + \dots$$

where the affinities are  $A = g - \mu$ . In (4)  $A^A$  stands for  $A^{(A)}$ . Like (3), relation (4) is an extended condition verified for all the phases in « *equilibrium* ». Under this meaning, (4) gives the equations of the reactions in the affigraphy. If all the phases are present (4) is a tautology since all the  $A$  are equal to zero.

### A2.3. An example of systematic investigation of the corresponding regions of chemography and affigraphy

The determination of the corresponding regions (optimum bases / optimum co-bases) of the chemography and the affigraphy may be done by direct inspection of the convex and conic convex domains in the figures; this is possible for values of  $n$  and  $k$  not exceeding 4. For greater values, it is necessary to have a general method. This has been exposed in Appendix A1.4. Here, the method is presented on a simple example. The chemography of a  $3 + 2$  system was represented in Fig. 6 and the corresponding composition matrix is

	A	B	C	D	E
A	1	0	0	1	2.5
B	0	1	0	4	1
C	0	0	1	1.5	1.5

The parametrization of the cost function and of the overall composition of the system is operated by adding two matrices as indicated in previous Appendix:

	A	B	C	D	E			
(D)	0	0	0	1	0			
(E)	0	0	0	0	1	A	B	C
A	1	0	0	1	2.5	1	0	0
B	0	1	0	4	1	0	1	0
C	0	0	1	1.5	1.5	0	0	1
	*	*	*					

The three stars indicate the phases in the starting basis. Starting basis ABC is optimum when:

$$A \geq 0, B \geq 0, C \geq 0 \text{ and}$$

$$(D) \geq 0 \text{ and } (E) \geq 0$$

which are the expression of the general relations  $\mathbf{E} \cdot \mathbf{x} \geq 0$  and  $\mathbf{A} \cdot \mathbf{F} \geq 0$  in this particular case. The relations are thus provided by the additional side composition matrix and upper affinity matrix respectively. Above relations define permitted regions in the associated spaces of the chemography (A, B, C parameters) and of the affigraphy ((D) (E) parameters) as represented in Fig. 7A. The  $C_3^3 = 10$  bases in the system are: ABC, ABD, ABE, ACD, ACE, ADE, BCD, BCE, BDE, CDE; they can be enumerated automatically (Program « MATROIDO », Pla, 1990). By appropriate pivoting, a new tableau is computed for basis ABD:

	A	B	C	D	E			
(D)	0	0	-0.67	0	-1			
(E)	0	0	0	0	1	A	B	C
A	1	0	-0.67	0	1.5	1	0	-0.67
B	0	1	-2.67	0	-3	0	1	-2.67
D	0	0	0.67	1	1	0	0	0.67
	*	*		*				

Equations of the searched limits in chemography are given automatically by

$$A - 0.67C \geq 0$$

$$B - 2.67C \geq 0$$

$$C \geq 0$$

corresponding to the hatched region in Fig. 7B for basis ABD; limits in affigraphy are

$$-0.67(D) \geq 0 \text{ or } (D) \leq 0$$

$$-(D) + (E) \geq 0 \text{ or } (E) \geq (D)$$

corresponding to the hatched affigraphy region in Fig. 7B for cobasis (C)(E). As noticed above, matrix  $\mathbf{F}$  is then composed of the two non

neighbouring columns (C) and (E) of the co-basis; rows of E and columns of F are used. As an additional example, basis BCD gives the tableau:

	A	B	C	D	E			
(D)	-1	0	0	0	-2.5			
(E)	0	0	0	0	1	A	B	C
D	1	0	0	1	2.5	1	0	0
B	-4	1	0	0	-9	-4	1	0
C	-1.5	0	1	0	-2.25	-1.5	0	1
		*	*	*				

the corresponding regions are respectively

$$A \geq 0$$

$$-4A + B \geq 0$$

$$-1.5A + C \geq 0$$

for the chemography and

$$-(D) \geq 0 \text{ or } (D) \leq 0$$

$$-2.5(D) + (E) \geq 0$$

for the affigraphy (Fig. 7G). The complete set of bases can be explored in this way. All the corresponding regions of the chemography and the affigraphy were represented in Fig. 7A through J. A synthesis was given in Fig. 8A and 8B. The procedure described may be used to draw the restriction of the affigraphy for a chemical system with specified composition for which a limited number of chemography bases is considered: only a limited number of co-bases will exist in the affigraphy; transported in the (P, T) diagrams, this will give so-called pseudo-sections (e.g. Guiraud, Holland and Powell, 1990).



### APPENDIX A3: CO-ORDINATES OF THE ORIGINS OF (P, T) DIAGRAM AND AFFIGRAPHY IN THE DIFFERENT SYSTEMS

$\Omega$  is the origin of k-dimensional affigraphy and O the origin of two-dimensional (P, T) plane; k phases have been chosen to define the affigraphy co-basis. Let us first calculate the co-ordinates of O in the affigraphy. The k affinities of a point in affigraphy are given by

$$\begin{aligned} A^i &= g^i - \mu^i = g^i(P, T) - \sum_{j=1}^n c_j^i g^j(P, T) \\ &= (u^i + Pv^i - Ts^i) - \sum_{j=1}^n c_j^i (u^j + Pv^j - Ts^j) \\ &= u^i - \sum_{j=1}^n c_j^i u^j + (v^i - \sum_{j=1}^n c_j^i v^j)P - (s^i - \sum_{j=1}^n c_j^i s^j)T \end{aligned}$$

where the  $u^i$ ,  $v^i$  and  $s^i$  are the molar internal energy, volume and entropy of phase i, and the coefficients  $c_j^i$  are given by the composition matrix **C** for a chosen n-phase basis. The origin O is defined by  $P = T = 0$ . The above relations give the co-ordinates of O in the affigraphy system:

$$A^i = u^i - \sum_{j=1}^n c_j^i u^j$$

The pressure axis is given by  $T = 0$ , so by:

$$A^i = u^i - \sum_{j=1}^n c_j^i u^j + (v^i - \sum_{j=1}^n c_j^i v^j)P$$

The k co-ordinates depend on one parameter, P. By eliminating P among the k equations, k - 1 equations among the  $A^i$ , or k - 1 hyperplanes, are obtained and this defines one basic vector **P**. By subtracting the origin contribution in the last equation, **P** vector is parallel to the vector whose co-ordinates are:

$$P^i = v^i - \sum_{j=1}^n c_j^i v^j$$

This vector may be normalized to one, defining vector  $\langle \mathbf{P} \rangle$ . Similarly, the temperature axis is given by  $P = 0$ , so by:

$$A^i = u^i - \sum_{j=1}^n c_j u^j - (s^i - \sum_{j=1}^n c_j s^j) T$$

By eliminating  $T$  among the  $k$  equations,  $k - 1$  hyperplanes are obtained and this defines one basic vector  $T$ . By subtracting the co-ordinates of the origin, it is parallel to the vector whose coordinates are

$$T^i = -(s^i - \sum_{j=1}^n c_j s^j)$$

This vector may also be normed to one in vector  $\langle T \rangle$ .

Reciprocally, the affigraphy origin and basic affinity vectors may be projected onto the  $(P, T)$  plane. The co-ordinates  $P_\Omega$  and  $T_\Omega$  of the affigraphy origin are the scalar products of  $O\Omega = -\Omega O$  with  $\langle P \rangle$  and  $\langle T \rangle$ . Similarly, the basic vectors  $\langle A^i \rangle$  may be projected onto  $(P, T)$  plane by use of scalar products with basic vectors  $\langle P \rangle$  and  $\langle T \rangle$ . Some particular interest may be found to assigning a temperature and a pressure to any point in the affigraphy frame by projecting the current point onto the  $(P, T)$  plane. The hyperplane containing an affigraphy point of co-ordinates  $A^i$  and perpendicular to vector  $\langle P \rangle$  has the equation:

$$OM \cdot \langle P \rangle = P$$

$$(O\Omega + \Omega M) \cdot \langle P \rangle = P$$

$$(-\Omega O + A) \cdot \langle P \rangle = P$$

or

$$P - P_\Omega = A \cdot \langle P \rangle = \sum_{i=1}^k A^i \cdot \langle P \rangle^i$$

and a « *unit affinity pressure content* » may be defined; it is given by the co-ordinates of vector  $\langle P \rangle$ . Similarly, temperature  $T$  may verify an equation of the type:

$$T - T_\Omega = \sum_{i=1}^k A^i \cdot \langle T \rangle^i$$

and a « *unit affinity temperature content* » may be defined. It is given by the co-ordinates of vector  $\langle T \rangle$ . The above relations may be defined for each choice of co-basis, i.e. for a set of  $k$  absent phases.

Vectors  $\langle P \rangle$  and  $\langle T \rangle$  may be added as new columns to the reaction matrix and represented in the basis of the  $k$  unit affinity vectors;  $R$  matrix will then be  $k \times (n + k + 2)$ . By writing a composition matrix  $C$  from the new reaction matrix  $R$ , one gets a  $(n + 2) \times (n + k + 2)$  matrix. In affinity space, vectors are defined by the absence of a phase. It is natural to define  $\langle P \rangle$  and  $\langle T \rangle$  vectors as « *absent volume* » and « *- absent entropy* » « *phases* ». In the new composition matrix, a new  $n + 2$  dimensional basis will be composed of  $n$  phases plus two « *phases* » representing « *pure volume* » and « *pure entropy* », pure in the sense these volume and entropy are not associated to matter. Notice conversely that the basic phases have no volume nor entropy. The remaining  $k$  phases will be defined by their composition and also now by their volume and entropy. Actually, the corresponding volumes (or entropies) are not their own volume (or entropy) but that corresponding to the reactions that synthesise them from the basic phases. It gathers all volumic (entropic) data from all the phases.

In another approach, vectors  $\langle P \rangle$  and  $\langle T \rangle$  may be chosen as part of the co-basis of the  $k$ -dimensional space; there will be  $n + 2$  remaining phases. In the new composition matrix, volume and entropy will be outside the basis and will be defined by their  $n + 2$  components along the basic phases,  $n + 2$  in number.

Vectors  $\langle P \rangle$  and  $\langle T \rangle$  in affigraphy may also *replace* two affinity vectors either among the unit vectors of the co-basis either among the remaining  $n$  vectors. Two phases will be omitted. Similarly, composition matrices will be written and in that case  $n$ -dimensional (not  $n + 2$ ) composition spaces will be defined. In that case, volume and entropy will be represented by the phases themselves.

By changing the origin of temperature and pressure scales, one could choose  $T_\Omega = P_\Omega = 0$ ; in that case all affinities are zero with  $P$  and  $T$ . In

the generalized composition space (composition + volume + entropy), the volume and entropy of a system are zero when the composition variables  $x$ 's are also zero. Conversely, the origin for  $V$  and  $S$  could differ from the origin of composition variables; in that case,  $(V, S)$  diagrams could be drawn by a similar method as for  $(P, T)$  diagrams, by cutting the structure given by the composition vectors by two-dimensional plane.

In affinity coordinates, the orientation of hyperplanes with respect to the basic affinity vectors are merely function of the stoichiometric coefficients. If a two-dimensional restricted co-basis  $\{A^{(0)}, A^{(0)}\}$  is chosen, the orientation of a univariant line (corresponding to one hyperplane) will also be a function of the composition coefficients. Generalization of Clapeyron relations may thus be written. If now vectors  $\langle P \rangle$  and  $\langle T \rangle$  are added to the vectors in the affinity space, the orientation of the hyperplanes with respect to them will give the ordinary Clapeyron relations; they will involve the volume and entropy variations of the corresponding reaction as may be read in the generalized reaction matrix where  $\langle P \rangle$  and  $\langle T \rangle$  are treated on a equal footing as other (absent) phases.

#### APPENDIX A4: ALGEBRAIC PROBLEMS ASSOCIATED TO SEVERAL TYPES OF PHASE DIAGRAMS

The different sets of variables and corresponding phase diagrams are embodied in different algebraic problems (Table 6). The equations of the regions of chemography directly appear in problem (P) defined in Sect. 2 of the main text; here (P) will be called  $(P_1)$ . The equations of the hyperplanes of the chemical potential diagram appear in the dual formulation  $(P_1^*)$  of  $(P_1)$ , see Appendix A1. Similarly affigraphy and reaction space, and corresponding variables  $A$  and  $\xi$ , respectively appear in two another problems  $(P_2)$  and its dual  $(P_2^*)$ . In  $(P_2)$  one must find row vector  $A$  ( $n + k$ ) fulfilling

$$\begin{aligned} \text{Min } A \cdot x_0 \\ R \cdot A^T &= \underline{a}^T \end{aligned}$$

$$\mathbf{A} \geq 0$$

where column vector  $\mathbf{x}_0$  ( $n + k$ ) is fixed. For a specified choice of  $\mathbf{P}$  and  $\mathbf{T}$ , the  $n + k$  values of the  $g$ 's are known,  $k$  of them are independent, allowing the assigning of  $k$  independent chemical affinities in constant vector  $\underline{\mathbf{a}}^T$ ; from there appears the structure of affigraphy. In dual problem ( $P_2^*$ ) one looks for  $\underline{\xi}$  ( $k$ ) such that

$$\begin{aligned} &\text{Max } \underline{\mathbf{a}} \cdot \underline{\xi} \\ &\underline{\xi}^T \cdot \mathbf{R} \geq -\mathbf{x}_0^T \\ &(\xi) \end{aligned}$$

$(\xi)$  means that no sign constraint holds;  $\mathbf{A} = \mathbf{g} - \mu$  is supposed to be known for  $k$  components like in ( $P_2$ ); similarly,  $\mathbf{x}_0$  is given. The last problem gives the structure of reaction space. For ( $P_2$ ) and ( $P_2^*$ ) exclusion relations hold:

$$\mathbf{A} \cdot (\mathbf{x}_0 + \mathbf{R}^T \cdot \underline{\xi}) = 0$$

which is the same as

$$(\mathbf{g} - \mu) \cdot \mathbf{x} = 0$$

for the first group of problems. Similarly to what was done for ( $P_1$ ) and ( $P_1^*$ ), ( $P_2$ ) and ( $P_2^*$ ) may be combined in the following problem with no extremum condition: find  $\mathbf{A}$  and  $\underline{\xi}$  such that

$$\begin{aligned} &\mathbf{R}\mathbf{A}^T = \underline{\mathbf{a}}^T \\ &\mathbf{A} \geq 0 \\ &\underline{\xi}^T \cdot \mathbf{R} \geq -\mathbf{x}_0^T \\ &\mathbf{A} \cdot (\mathbf{x}_0 + \mathbf{R}^T \cdot \underline{\xi}) = 0 \\ &(\xi) \end{aligned}$$

The relations between the different problems ( $P_1$ ), ( $P_1^*$ ), ( $P_2$ ) and ( $P_2^*$ ) may be described in terms of the status of the components. In ( $P_1$ )  $n$  constraints on  $n$  inert phases are given first (by the  $c$ 's); the  $n + k$

specified values for the  $g$ 's at  $T$  and  $P$  refer to  $k$  independent conditions on the mobile phases (the use of phases is equivalent here to that of components that are represented by phases in the bases). Both constraints are needed to completely characterize the state of equilibrium. ( $P_2$ ) is associated to the case where the role of the previous constraints is exchanged in the matrices;  $k$  constraints on affinities for mobile phases are given first (by the  $a$ 's);  $n + k$  values are specified for the initial composition, from which  $n$  are independent (Table 6 in the main text).

Combined type diagram  $(\mu, x)$  is in correspondence with the mathematical programming problem written in Appendix 1; at given  $P$  and  $T$ ,  $m$  « *mobile* » and  $i$  « *inert* » phases are defined ( $m$   $g^j$ 's and  $i$   $c_i$ 's are given); one must find  $x$  and  $\mu$  such that

$$\begin{aligned} Cx &= c \\ x &\geq 0 \\ \underline{\mu}C &\leq g \\ (g - \underline{\mu}C)x &= 0 \\ (\underline{\mu}) \end{aligned}$$

the dimensions of vectors  $x$  and  $\underline{\mu}$  and of matrix  $C$  are  $i$ ,  $m$  and  $(i, i + m)$  respectively. The dimensions of the matrices operating on  $x$  and on  $\underline{\mu}$  may be changed to simulate various cases of inert and mobile components; the different boundaries between domains in  $(x, \mu)$  space may be projected onto lower-dimensional spaces. The different problems discussed in the present Appendix may also be derived by means of Legendre transform (Connolly, 1990).