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A NUMERICAL ANALYSIS OF ZEOLITE STRUCTURES ¹

I. THE RELATION BETWEEN THE STOECHIOMETRIC COMPOSITION AND THE COORDINATION OF THE CHEMICAL CONSTITUENTS

BY

Nora ENGEL ²

ABSTRACT

In this series of three papers, a relation between the stoichiometric composition and the coordination numbers of atoms in structures of zeolites composed of cavity cations of valence one or two, Si and Al atoms centering oxygen tetrahedra and water molecules is established and discussed. Attention is concentrated on the cavity cations and their coordination polyhedra and on the number of H₂O molecules in the structure. In this paper, using a model for the coordination of the O atoms based on Pauling's electrostatic valence rules, we deduce that the number of water molecules bound to cavity cations never exceeds the number of O atoms for which the sum of the bond strengths (cation-oxygen) is less than 2, and which therefore may possibly be "acceptors" towards hydrogen atoms. In this context, examples for natural zeolites with relatively low content of water molecules are presented. The whole study may help in the general understanding of zeolite structures in relation to their chemical composition. Fields for the composition of zeolites are numerically defined, which will be discussed in the last paper in relation to the classification for natural zeolites.

Keywords: zeolites, structural chemistry, cavity cation coordination sphere, oxygen coordination.

1. INTRODUCTION

Zeolites form an important class of minerals which are characterized by a relational stoichiometric composition corresponding to typical features in their structures. They are composed mostly of Si and Al atoms, which, with a coordination of 4 O atoms in shape of tetrahedra, build a three dimensional framework. In this

¹ This is the first part of a series. Two other parts entitled "The valence distribution within zeolite structures and the oxygen coordination" and "'Structural' and chemical compositions: a discussion in relation to the classification of natural zeolites" will come out in the next issues.

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framework, cavities or channels are formed, in which other cations, the so-called cavity cations, are located as well as water molecules or even anionic complexes. From the chemical point of view, zeolites show a characteristic behaviour in that the cavity cations, whose stoichiometric composition is related to the aluminium content, may be artificially exchanged with other cations and that these minerals may be dehydrated and rehydrated. It is frequent that, in their structures, sites for cavity cations and water oxygens are only partially refined and that a disorder on the sites of the Si and Al atoms is observed. It is striking to observe the diversity of zeolite structures, whose classification is based on the geometrical ordering of the tetrahedra, and how numerous these minerals are as well. For natural zeolites only, Gottardi and Galli (1985) list more than 40 mineral species.

The purpose of this series of three papers is to define with quite simple equations the numerical relationship which may exist between the coordinations of cations and anions and their stoichiometric composition. This is made possible by referring to an uncomplicated structural model which treats the coordination of the O atoms following the *electrostatic valence rule* of Pauling (1960) and by using mean numbers, calculated over one unit cell, for the parameters describing the coordination of the cavity cations. These average numbers are relevant for a statistical distribution of these polyhedra within the structures. It is not the purpose of these papers to propose an accurate review of all the known structures of zeolites, but to present a global study for this class of minerals. It will be shown that for each species which crystallizes with a structure type, there is a defined numerical relationship among the coordinations of the O atoms in the structure. The equations developed throughout these papers may further help in the understanding of these structures. Finally, some conditions which define characteristic compositions for zeolites are shown to be relevant for the groups of the classification. For this reason, there is a hope that in future the numerical parameters defined in these papers may find several applications in particular in the field of computing and data bases.

In this first part, a numerical relationship between the coordination of atoms and the stoichiometric composition for zeolites is established in terms of a model and discussed in relation to several examples, all characterized by a relatively low content of water molecules; it will be shown that the cavity cations and the composition of the coordination polyhedron formed around them, are essential in these structures. The second part deals with valence distribution within zeolite structures and possible valence transfer through hydrogen — oxygen bonds; it leads to conditions concerning the composition of cavity cations in relation to the amount of water molecules necessary for the formation of these structures. A complete discussion of zeolites is presented in the third part in terms of the classification for natural zeolites proposed by Gottardi and Galli (1985), after we have discussed possible relationships among the coordination numbers of O atoms within their structures.

2. MAIN STRUCTURAL AND CRYSTALLOCHEMICAL FEATURES FOR ZEOLITES

From the point of view of crystal chemistry, zeolites form ionic networks which contain only bonds between anions and cations (for a definition of this term, see Brown, 1981). The second rule of Pauling (1960) or electrostatic valence rule is therefore relevant for these structures as well as calculations derived from this rule, which are frequently used to localize hydrogen atoms (i.e. Donnay and Allmann, 1970). It is now generally accepted that cation-anion bonding occurs with relatively short interatomic distances (Brown, 1981). Consequently, for these minerals, the terms "number of bonds" and "coordination number" are considered as synonymous (Brown, 1981). In zeolites, the Si and Al atoms are always bound to 4 O atoms in tetrahedra. Most of the cavity cations are found to be bound between to 6 and 8 O atoms. The H atoms were not refined in all structures, but, according to generally accepted features for the coordination of this cation (see Baur, 1972), one expects them to be bound to one O atom (the so-called "donor") and one other (the so-called "acceptor") for which the H-O distance is longer.

A classification for zeolites is based on the arrangement of the tetrahedra in a three dimensional framework within the structure. Accordingly, Meier (1968) considers 9 different secondary building units, from which Gottardi and Galli (1985) define a further 7 finite or infinite structural units and classify natural zeolites in 6 groups.

3. BASIC DEFINITIONS AND MODEL FOR THE COORDINATION OF THE O ATOMS

For the purpose of a numerical analysis for zeolite structures, we use the ideal theoretical chemical formula

$$\frac{C_x}{\langle e_c \rangle} (Al_x Si_y O_{(x+y) \cdot 2}) \cdot w H_2O$$

C: cavity cations of valence one [$e_c = 1$; for $C = Li^+, Na^+, K^+ \dots$] or of valence two [$e_c = 2$; for $C = Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} \dots$]; $\langle e_c \rangle$: mean valence electron number per cavity cation for all cavity cations contained in the unit cell (for a more detailed definition, see Appendix A).

For natural zeolites, it is further known that the stoichiometric composition of the Al atoms is always equal to or less than the stoichiometric composition of the Si atoms [$x \leq y$]. The ideal chemical formula of about 40 natural zeolites (Gottardi and Galli, 1985) agrees with the above theoretical formula. Some other zeolites, which

show slight discrepancies with this theoretical formula (i.e. Be or P-bearing zeolites, or those with an interrupted framework) will not be discussed in these papers.

In the structures of zeolites, the tetrahedra of O atoms coordinated to Si atoms or Al atoms, in agreement with the above theoretical formula, share all their corners with each other: the sharing coefficient is equal to 2 (see the definition given by Zoltai, 1960) or to 4 (see other definitions by Coda, 1969 or by Parthé and Engel, 1986). Further, the tetrahedra centered by the Al atoms are not expected to be connected to each other, this, in accordance with the well known *Loewenstein rule*, as well as with a structural *assumption* which concerns *the maximal diversity of cations coordinated to O atoms* and which asserts that the cations coordinated to each O atom tend to be as much of different nature as possible, provided that the sum of the bond strengths calculated around each anion is close or equal to the charge of the anion (Engel, 1986). This assumption was generally verified by Engel (1986) for the structures of the zeolites of the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$.

In zeolites, the cavity cations are bound to at least 4 O atoms or water molecules. However for most of these cations, the coordination numbers are 6, 7 or 8 and over a structure one can expect in most cases $6 \leq \langle \text{CN}_C \rangle \leq 8$ where $\langle \text{CN}_C \rangle$ is the mean coordination number of the cavity cations calculated over the unit cell (for a detailed definition, see Appendix A).

TABLE 1.

Expected coordinations for the O atoms in zeolite structures with cavity cations (C) of valence one [$e_C = 1$] or two [$e_C = 2$]

Cations coordinated to central O atoms	Σ (bond strengths) (in valence units) and, in square parentheses, the identifiers for the coordination of O atoms			
	$e_C / \langle \text{CN}_C \rangle < 0.25$ ¹		$e_C / \langle \text{CN}_C \rangle \geq 0.25$ ¹	
(Si Si)	2.0	[k]	2.0	[k]
(Si Al C C)	≥ 2.0	[l]	-----	
(Si Al C)	< 2.0	[i'] ²	≥ 2.0	[i'']
(Si Al)	-----		1.75	[g] ²
(C H H)	> 2.0	[r] ³	> 2.0	[r] ³
(H H)	2.0	[s] ³	2.0	[s] ³

¹ mean bond strength per cavity cation - O bond; for $6 \leq \langle \text{CN}_C \rangle \leq 8$ then $e_C=1$ for the left column and $e_C=2$ for the right column.

² O atoms deficient in positive valences and therefore possible "acceptors" for hydrogen atoms

³ "donor"

In order to establish a relation between the coordination numbers of cations and their stoichiometric composition, it is useful to set up a model relative to the coordinations of the O atoms. In table 1, are given the cations expected to be coordinated to O atoms in these structures as well as an estimation for the sum of the cationic bond strengths around each central O atom. There are 2 groups of O coordinations depending on the mean bond strength of the cavity cation — O atom bond, calculated over the unit cell ($e_c / \langle CN_c \rangle$, for a detailed definition, see Appendix A). The assumption relative to the maximal diversity of cations coordinated to O atoms is implicitly included there. Thus, as shown by the void in the right column of table 1 (O atoms coordinated to a cavity cation with a mean bond strength superior or equal to 0.25 valence units), coordination by 4 cations (Si Al C C) should be avoided, the sum of the cationic bond strength of such a coordination being more than 2.25 v.u. Similarly, for zeolite structures with cavity cations with a mean bond strength inferior to 0.25 v.u., a coordination only to one Si and one Al atoms should be avoided. In practice, for structures of exclusively Ca-bearing zeolites with a relatively low content of water molecules, only the coordinations for O atoms in the column for $e_c / \langle CN_c \rangle \geq 0.25$ (table 1) have been observed (Engel, 1986).

In table 1, the letters shown within square brackets symbolise the mean number of O atoms, per Al atom, having the coordination indicated in the left column. The averages are taken over the unit cell. These so-called *identifiers for the coordination of O atoms*, are used to establish a numerical relationship between cation coordination numbers and the chemical composition for zeolites.

4. THE IDENTIFIERS FOR THE COORDINATION OF O ATOMS AND THE CHEMICAL COMPOSITION

It is well known, that within a structure with an ionic network, the total number, calculated over the unit cell, of bonds starting from the cations is equal to the total number of bonds starting from the anions. The relationship between the chemical composition of cations and the identifiers for the coordination of O atoms (as defined in table 1) are deduced from this principle.

The *number of Si atoms* in a zeolite is at least equal to the number of Al atoms (x). The stoichiometric composition for Si atoms (y) will therefore be

$$y = x + y^+$$

y^+ : number of the Si atoms in excess compared to the number of the Al atoms.
 y^+ is also related to k , or the mean number, per Al atom, of O atoms surrounded by (Si Si) (table 1), and the total number of apices of the tetrahedra centered by the

Si atoms in excess divided by 2 (two apices for one O atom surrounded by (Si Si)) is equal to k :

$$k = 4 \cdot y^+ / (2 \cdot x)$$

Inserting $y^+ = y - x$ in this expression, we obtain

$$k = 2 \cdot (y/x - 1) \quad (1)$$

or inversely:

$$y/x = k/2 + 1$$

$k \geq 0$ or $y \geq x$ as defined in section 3.

Further, if $4x$ is the total number, over one structure, of apices of the tetrahedra formed by the O atoms bound to the Al atoms then

$$x \cdot (l + i + g) = 4 \cdot x \quad (2)$$

for which $i = i' + i''$, mean number of O atoms, per Al atom, coordinated to (C Al Si) with any value of $e_c / \langle CN_C \rangle$.

The *stoichiometric composition for cavity cations* is equal to $x / \langle e_c \rangle$ (see theoretical formula above and appendix A). The total number of the apices of the O polyhedra shaped around the C atoms is thus $\langle CN_C \rangle \cdot x / \langle e_c \rangle$ and:

$$x \cdot (2l + i + r) = \langle CN_C \rangle \cdot x / \langle e_c \rangle \quad (3)$$

For *water molecules*, it is obvious that $w/x = r + s$ (4)

r : mean number, per Al atom, of O atoms bound to (C H H)

s : mean number, per Al atom, of "free" water molecules whose O atoms are linked to 2 hydrogen atoms only.

5. THE IDENTIFIERS FOR THE COORDINATION OF O ATOMS IN RELATION TO THE COMPOSITION OF THE CAVITY CATION COORDINATION POLYHEDRON

In order to define the possible stoichiometric compositions for zeolites, it is of special interest to discuss numerical relations among the identifiers for the coordination of O atoms. Since the number of the cavity cations contained in the structures of zeolites is numerically related to the Al content [composition of cavity cations = $x/\langle e_c \rangle$], the number of O atoms linked to Al atoms or cavity cations [l, i, g and r in table 1] may all be related to the numbers of O atoms and water molecules, which belong to the coordination polyhedron of the cavity cation.

Let us first define a parameter V which expresses the number of water molecules bound to cavity cations per O atom which are deficient in the cationic valences and therefore, in the structure, are possible "acceptor" of H atoms. Using the identifiers for the coordination of O atoms (table 1), we write

$$V = \frac{r}{i' + g} \quad (5)$$

Inserting the equations (2) and (3) in order to eliminate l and considering as before that $i' + i'' = i$, we obtain:

$$V = \frac{r}{8 - \langle CN_C \rangle / \langle e_c \rangle + r - (i'' + g)} \quad (5')$$

V is thus expressed in relation to identifiers for the coordination of O atoms, as well as to the mean coordination number of the cavity cations and to $1/\langle e_c \rangle$ which is the mean stoichiometric composition of the cavity cations per Al atom ($x/(x \cdot \langle e_c \rangle)$); $\langle e_c \rangle / \langle CN_C \rangle$ also expresses the mean bond strength of the cavity cation — O atom bond.

It is, in this context, convenient to define a parameter more explicit than r (the mean number of O atoms, per Al atom, linked to one cavity cation and to two hydrogen atoms). We define ξ as the mean number (per cavity cation) of H_2O molecules bound to C atoms. This average number, calculated over each unit cell, is relevant for the cavity cation coordination polyhedron. Thus

$$r = \xi \cdot 1/\langle e_c \rangle \quad (6)$$

or inversely ξ is equal to the parameter $r \cdot x$ divided by the stoichiometric number of the C atoms. The fraction of the mean polyhedron shaped around the cavity cations which is built of water molecules will then be easily expressed by $\xi/\langle CN_C \rangle$ and substituting into (6), we obtain:

$$\xi / \langle \text{CN}_C \rangle = r \cdot \langle e_C \rangle / \langle \text{CN}_C \rangle \quad (7)$$

The fraction of the mean coordination number per cavity cation which is built of water molecules may thus be estimated from the chemical formula, if in the zeolite, all water molecules are bound to one C atom [$w/x=r$ in equation (4)]. It is equal to the number of water molecules per Al atom times the mean bond strength of the C atom — O atom bonds. Expression (7) is represented graphically and illustrated in fig. 1 with examples of zeolites with a relatively low content of water molecules.

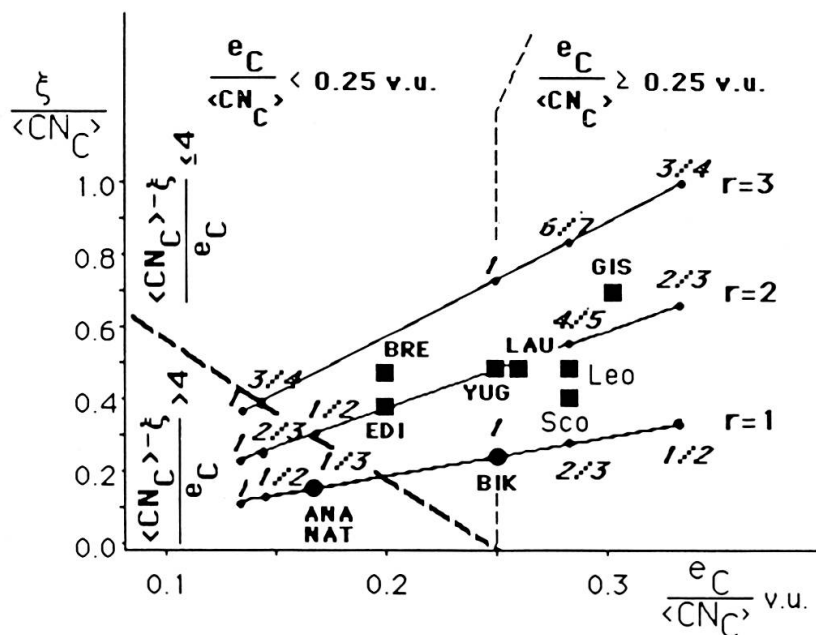


FIG. 1.

Relations within the cavity cation mean coordination polyhedron. Mean bond strength ($e_C / \langle \text{CN}_C \rangle$) versus the fraction of the polyhedron built of water molecules as defined in text ($\xi / \langle \text{CN}_C \rangle$, equation (7)). r : mean number, per Al atom, of water molecules bound to one cavity cation; values given in *italics* are for the parameter V (see text). The examples are for zeolites with relatively low content of water molecules and with cavity cations either of valence one only (black circles) or of valence two only (black squares) (codes are given according to the recommendations of the International Zeolite Association).

A complete list for these structures is given in the last paper of this series. For the structures with cavity cations of valence one only, the content of H_2O molecules per C atom is much less ($\xi / \langle \text{CN}_C \rangle < 0.3$) than for structures with cavity cations of valence two. The value for the parameter V is also slightly lower for the former than for the latter (fig. 1). In fact, as demonstrated in appendix B, the parameter V may also be expressed as a function of ξ . But first, we may insert ξ calculated from (6) into (5'):

$$V = \frac{\xi}{8 \langle e_C \rangle - \langle \text{CN}_C \rangle + \xi - (i'' + g) \cdot \langle e_C \rangle} \quad (8)$$

The solutions for this equation may be written in the following way (see results in appendix B):

$$V = \frac{\xi}{\text{constant} - \langle \text{CN}_C \rangle + \xi} \quad (9)$$

for which $\text{constant} = 8\langle e_C \rangle - (i'' + g)\langle e_C \rangle$

and for values of $\langle e_C \rangle$ and $\langle \text{CN}_C \rangle$ corresponding to structures of natural zeolites with a relatively low content of water molecules:

constant = 4 $\langle \text{CN}_C \rangle = 4$ and $e_C = 1$ bikitaïte

constant = 8 $6 \leq \langle \text{CN}_C \rangle \leq 8$ $1 \leq \langle e_C \rangle \leq 2$ natrolite, scolecite, thomsonite etc.

Thus the value for the *constant* is always superior or equal to the value for $\langle \text{CN}_C \rangle$ so that the parameter *V* is always smaller than or equal to 1 (compare equation (9)):

$$V \leq 1 \quad (10)$$

This means that the number of O atoms coordinated in such a way that the sum of the cationic bond strengths is less than 2.0 v.u. (which are therefore most possibly O atoms “acceptors” towards H atoms) is, in our case, always equal to or greater than the number of H₂O molecules belonging to coordination polyhedra of the cavity cations.

Putting the conditions $V \leq 1$ into equation (5'), we deduce that for $(i'' + g) \geq 0$ (i.e. the value for the mean bond strength for polyhedra formed around the C atoms is greater than zero):

$$8 - \langle \text{CN}_C \rangle / \langle e_C \rangle \geq 0 \quad \text{or} \quad \langle e_C \rangle / \langle \text{CN}_C \rangle \geq 0.125 \text{ v.u.} \quad (11)$$

This defines the *minimal value for the mean bond strength for cavity cations*, according to the model given in table 1.

The identifiers *g*, *i*, *l* and *r* may also be expressed in relation to the mean coordination number for the cavity cations ($\langle \text{CN}_C \rangle$), the parameter ξ and the mean valence electron number for cavity cations ($\langle e_C \rangle$). For this purpose, *r* is replaced in equations (2), (3) and (4) by the definition of ξ (equation (6)) and these equations are solved in function of the stoichiometric composition for the cavity cations ($x / \langle e_C \rangle$) (see table 2). The limits for the expected coordination for the O atoms are now expressed in terms of $[(\langle \text{CN}_C \rangle - \xi) / e_C]$ instead of the mean bond strength of the cavity cation-O atom bond (table 1). As shown in fig. 1 and 2, the two limits

TABLE 2.

Identifiers for the coordination of O atoms expressed as a function of ξ [mean number (per cavity cation) of H_2O molecules linked to one C atom] and $\langle CN_C \rangle$ [mean coordination number of cavity cations]

Cations coordinated to central O atoms	identifiers for the coordination of O atoms	
	$[\langle CN_C \rangle - \xi] / e_C > 4$	$[\langle CN_C \rangle - \xi] / e_C \leq 4$
(Si Si)	$(k = 2 \cdot (y/x - 1))^{1/2}$	
(Si Al C C)	$l = [\langle CN_C \rangle - \xi] / e_C - 4$	-----
(Si Al C)	$i' = 8 - [\langle CN_C \rangle - \xi] / e_C$	$i'' = [\langle CN_C \rangle - \xi] / e_C$
(Si Al)	-----	$g = 4 - [\langle CN_C \rangle - \xi] / e_C$
(C H H)	$r = \xi / e_C$	$r = \xi / e_C$
(H H)	no relation with ξ	

¹ see equation (1)

do not coincide. For zeolites with cavity cations of valence two and a coordination number greater than 8 (i.e. brewsterite, edingtonite), the coordinations of the O atoms occur according to the right columns of tables 1 and 2, but the O atoms coordinated to (C Al Si) have a cationic bond strength inferior to 0.25 v.u so that identifier i' is used instead of i'' . The value for V is for this case calculated as the number of water molecules bound to C atoms divided by 4. For zeolites containing cavity cations with valence one such as natrolite, analcime and also thomsonite, mesolite and gonnardite, equations (6), (7) as well as the relation between (5) and (9) should be revised, since the H_2O molecules may be bound to more than one cavity cation (see following papers).

The equations shown in table 2 are represented in the graph of figure 2. It allows us to estimate possible values for the identifiers for the coordination of O atoms, starting from the composition of water molecules and cavity cations. Examples are for natural zeolites with either cavity cations of valence one or cavity cations of valence two only and with relatively low content of water molecules. Notice that, for the zeolites with cavity cations whose coordination number is greater than 8 and which are situated in the middle dotted field, as discussed above, the identifier i'' should be replaced by i' . From these examples (fig. 2), one can conclude that each mineral species needs specific values for the identifiers for the coordination of O atoms. Thus, the cavity cation and the composition of its coordination polyhedra are essential for the definition of a structure type.

In figures 1 and 2, one notices further that, for these minerals, the value for r rarely exceeds 2 water molecules per Al atom, so that, generally, in zeolites with relatively low content of H_2O molecules, less than half of the cavity cation mean polyhedron is formed by H_2O molecules. A more precise limit between the high or low content of water molecules in zeolites structures will be drawn in the following paper in relation to an analysis of the valence distribution within zeolite structures.

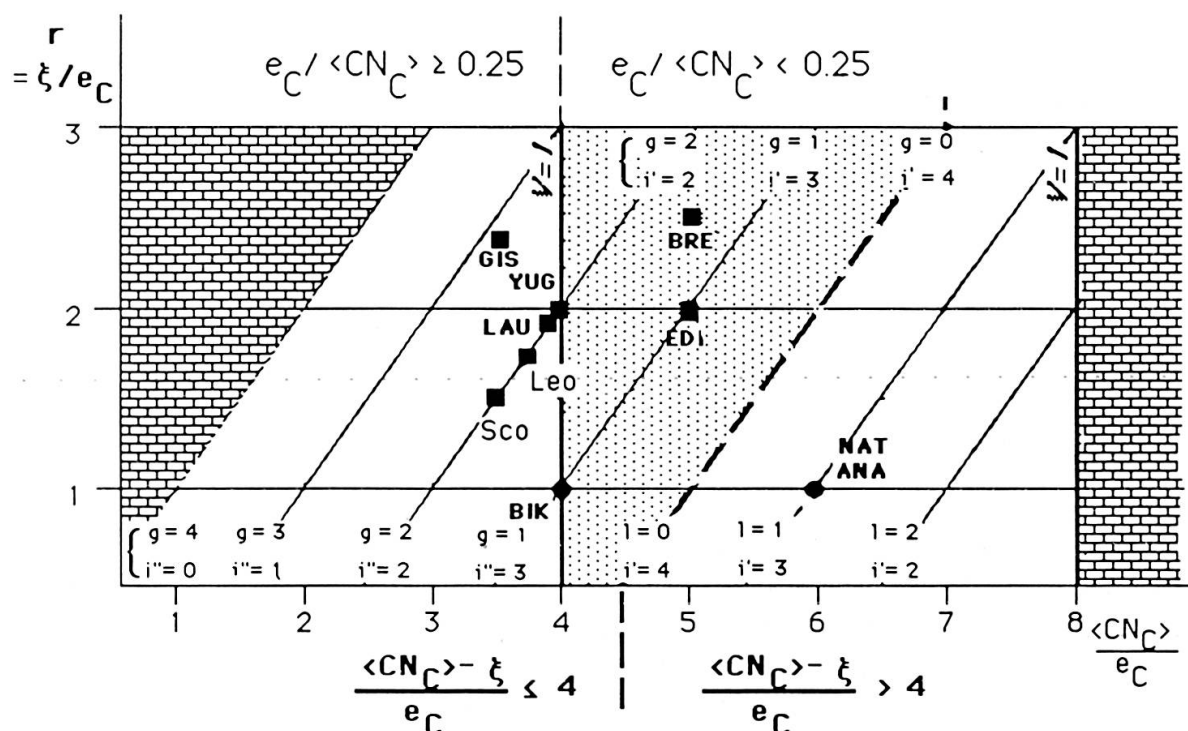


FIG. 2.

Identifiers for the coordination of O atoms expressed as a function of the mean composition of the cavity cation coordination polyhedron ($\langle CN_C \rangle$ and ξ) (oblique lines). $e_C/\langle CN_C \rangle$: cavity cation mean bond strength. ξ/e_C is equal to the mean number, per Al atom, of water molecules bound to one cavity cation (r). The clear fields are delimited on one side by maximal values for the numbers of O which are valence deficient relative to the number of Al atoms ($g=4$) and on the other side by $e_C/\langle CN_C \rangle = 0.125$ corresponding to $V = 1$. The examples are for zeolites with relatively low content of water molecules and with cavity cations either of valence one only (black squares) or of valence two only (black circles) (codes are given according to the recommendations of the International Zeolite Association).

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N° 2.720-0.85. After the completion of this study, Prof. W. M. Meier, Institute of Crystallography and Petrography, ETH, Zürich, drew our attention on the new Atlas of Zeolite Structure Types. Our definition of a structure type differs in that it includes, in theory, the cavity cations and water molecules. However, in figs 1 and 2 the structure type codes are used as given in the Atlas. 16 secondary building units are now considered instead of 9 given previously.

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APPENDIX

A. DEFINITION OF AVERAGE NUMBERS AND THE CALCULATION
OF THE STOICHIOMETRIC COMPOSITION OF THE CAVITY CATIONS AS A FUNCTION
OF THE ALUMINIUM CONTENT

The average numbers, which are used throughout this paper, all being calculated over a unit cell, are formulated as follows.

Consider a structure whose unit cell is built of m' cavity cations with a defined valence electron number of $e_{C'}$, m'' cavity cations of $e_{C''}$... m^n cavity cations of e_{C^n} , then the mean valence electron number per cavity cation is defined as:

$$\langle e_C \rangle = \frac{m' \cdot e_{C'} + m'' \cdot e_{C''} + \dots + m^n \cdot e_{C^n}}{m' + m'' + \dots + m^n}$$

For a structure with, in one unit cell, m' cavity cations characterized by a coordination number of $CN_{C'}$, m'' cavity cations of $CN_{C''}$... and m^n cavity cations of CN_{C^n} , the mean coordination number per cavity cation is defined as:

$$\langle CN_C \rangle = \frac{m' \cdot CN_{C'} + m'' \cdot CN_{C''} + \dots + m^n \cdot CN_{C^n}}{m' + m'' + \dots + m^n}$$

For the same structure, the mean bond strength per cavity cation — O atom bond is:

$$\langle e_C / CN_C \rangle = \frac{\frac{e_{C'}}{CN_{C'}} \cdot CN_{C'} \cdot m' + \frac{e_{C''}}{CN_{C''}} \cdot CN_{C''} \cdot m'' + \dots + \frac{e_{C^n}}{CN_{C^n}} \cdot CN_{C^n} \cdot m^n}{CN_{C'} \cdot m' + CN_{C''} \cdot m'' + \dots + CN_{C^n} \cdot m^n}$$

Using the definitions for $\langle e_C \rangle$ and $\langle CN_C \rangle$ and developing this equation, we find that

$$\langle e_C / CN_C \rangle = \langle e_C \rangle / \langle CN_C \rangle$$

In the structures of zeolites, the stoichiometric number for cavity cations (m) is related to the stoichiometric number of Al atoms. For x = the number of Al atoms in the structure, for m^1 = the number of C atoms, with $e_C = 1$ and m^2 = the total number of cavity cations, with $e_C = 2$, we find that:

$$x = m^1 \cdot e_{C1} + m^2 \cdot e_{C2} = m^1 \cdot 1 + m^2 \cdot 2$$

As $m = m^1 + m^2$ then

$$x/m = (m^1 \cdot 1 + m^2 \cdot 2) / (m^1 + m^2)$$

The right hand side of this equation is equivalent to the definition for $\langle e_C \rangle$ (see above) and therefore:

$$x/m = \langle e_C \rangle \quad (A1)$$

Thus the ratio of the stoichiometric compositions of the Al atoms and respectively cavity cations is equal to the mean valence electron number of the cavity cations per cavity cation, or $m = x/\langle e_C \rangle$ as formulated in the theoretical chemical formula in section 3.

Using the above definition, we also find that:

$$x/m = (m^1 + m^2)/m + m^2/m$$

$$\text{in which we insert (A1) and} \quad \langle e_C \rangle = 1 + m^2/m \quad (A2)$$

so that the fraction of cavity cations of valence two (m^2/m) is equal to the decimal part of the mean valence number of cavity cations per cavity cation. Further, the fraction of cavity cations of valence one (m^1/m) is calculated with the above definitions:

$$m^1/m = 2 - \langle e_C \rangle \quad (A3)$$

Example: Heulandite

The refinement of the structure of Heulandite with space group C 2/m (Alberti, 1972), revealed 4.64 cavity cations distributed between two sites, whose occupancy is given as 66.4% Ca atoms, 23.4% Na atoms, 8.0% K atoms, 1.1% Ba atoms, 0.9% Sr atoms and 0.2% Mg atoms. Accordingly, the mean valence electron number per cavity cation is:

$$\langle e_C \rangle = \frac{66.4 \cdot 2 + 23.4 \cdot 1 + 8 \cdot 1 + 1.1 \cdot 2 + 0.9 \cdot 2 + 0.2 \cdot 2}{100.0} = 1.69 \text{ v.u.}$$

In the same structure, on the partly occupied sites for the T atoms, 8.2 aluminium atoms were found. Taking this number into account and applying formula (A1), one calculates 4.87 cavity cations contained in the structure.

The same calculation carried out from the chemical formula (Passaglia and Gittoni, cit. in Alberti, 1972)



gives $\langle e_C \rangle = 1.74 \text{ v.u}$ when using $m = 5.38$ and $\chi = 9.36$ in equation (A1).

In the structure of Heulandite, each of the 2 sites occupied by cavity cations appears 4 times in the unit cell. The first one (C1) is 70% occupied and is coordinated to 2 O atoms and 5 H₂O, two of the water molecules showing an occupancy of 75%. The coordination number for this cation will therefore be equal on average to 6.5. The site for C2 is 46% occupied and this cation has a coordination number of 8, 3 O atoms and 5 H₂O molecules. The mean coordination number per cavity cation is calculated as:

$$\langle \text{CN}_C \rangle = \frac{4 \cdot 0.7 \cdot 6.5 + 4 \cdot 0.46 \cdot 8}{4 \cdot 0.7 + 4 \cdot 0.46} = 7.10$$

For the values calculated from the structure refinement, one finds for the mean bond strength:

$$\langle e_C \rangle / \langle CN_C \rangle = 1.69/7.10 = 0.238 \text{ v.u.}$$

or according to the value for $\langle e_C \rangle$ calculated from the chemical formula:

$$\langle e_C \rangle / \langle CN_C \rangle = 1.74/7.10 = 0.245 \text{ v.u.}$$

B. RELATION BETWEEN THE STOICHIOMETRIC COMPOSITION OF ZEOLITES AND THE IDENTIFIERS FOR THE COORDINATION OF O ATOMS IN THE CALCULATION OF THE PARAMETER V

We define a structure with some cavity cations whose polyhedra are on average (calculated over each polyhedron) characterized by a mean bond strength of less than 0.25 v.u. and with the remaining cavity cations whose polyhedra are characterized by a mean bond strength equal or superior to 0.25 v.u.

The definition for V as given from equation (8) states:

$$V = \frac{\xi}{8\langle e_C \rangle - \langle CN_C \rangle + \xi - (i'' + g) \cdot \langle e_C \rangle}$$

In this structure, the number of O atoms surrounded by (C Al Si) for $e_C / \langle CN_C \rangle \geq 0.25$ v.u. (i'') and by (Si Al) (g) gives the Al content (so called x'') which is theoretically associated in the structure with cavity cations whose polyhedra are characterized by $e_C / \langle CN_C \rangle \geq 0.25$ or the fraction of this number written x''/x . We write then for equation (2):

$$(i'' + g) = 4 \cdot x''/x$$

Inserting this expression into the above definition, we find:

$$V = \frac{\xi}{8\langle e_C \rangle - \langle CN_C \rangle + \xi - 4 \cdot x'' \langle e_C \rangle / x}$$

In this structure, there will be $x^2 \cdot q^2$ Al atoms related to $m^2 \cdot q^2$ cavity cations of valence two and with coordination polyhedra with $e_C / \langle CN_C \rangle \geq 0.25$, and respectively $x^1 \cdot q^1$ Al atoms related to $m^1 \cdot q^1$ cavity cations of valence one and with coordination polyhedra with $e_C / \langle CN_C \rangle \geq 0.25$ where q^1, q^2 are respectively the fractions of cavity cations with valence one or with valence two having coordination polyhedra with $e_C / \langle CN_C \rangle \geq 0.25$ v.u. And:

$$x'' = x^2 \cdot q^2 + x^1 \cdot q^1$$

If x^2 is the number of the Al atoms theoretically in the structure with cavity cations of valence $e_C = 2$ then

$$m^2 = x^2/2$$

in an analogous way: $m^1 = x^1$

$$\text{and } x = x^1 + x^2$$

With these two equations in addition to (A2) and (A3), the equation for x'' becomes:

$$x'' = 2 m \cdot q^2 \cdot (\langle e_C \rangle - 1) + m \cdot q^1 \cdot (2 - \langle e_C \rangle)$$

If ' K ' is the fraction of the number of cavity cations whose polyhedra are characterized by a mean bond strength superior or equal to 0.25 v.u. (' K ' = $q^2 (\langle e_C \rangle - 1) + q^1 (2 - \langle e_C \rangle)$), the above equation becomes:

$$x'' = ('K' + (\langle e_C \rangle - 1) \cdot q^2) \cdot m$$

Inserting this expression for x'' as well as equation (A1), we write for the preceding equation for V :

$$V = \frac{\xi}{8\langle e_C \rangle - \langle CN_C \rangle + \xi - (4'K' + 4(\langle e_C \rangle - 1) \cdot q^2)} \quad (B1)$$

RESULTS

(B1) is solved for two cases:

1° For $q^2=0$ and ' K ' = 1: $e_C=1$ and $\langle CN_C \rangle = 4$

$$V = \frac{\xi}{4 - \langle CN_C \rangle + \xi}$$

2° For $q^2=1$ and ' K ' = $\langle e_C \rangle - 1$: $1 \leq \langle e_C \rangle \leq 2$ and $6 \leq \langle CN_C \rangle \leq 8$

$$V = \frac{\xi}{8 - \langle CN_C \rangle + \xi}$$

This is a special case for V when the cavity cation is coordinated in the average to 6 up to 8 0 atoms, insofar for most zeolites.

A third case for which $q^2=0$ and ' K ' = 0: $\langle e_C \rangle = 2$ and $8 \leq \langle CN_C \rangle < 16$, is discussed in the text.

All natural zeolites fall into one of these three cases.