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A NUMERICAL ANALYSIS OF ZEOLITE STRUCTURES ¹

II. THE VALENCE DISTRIBUTION WITHIN ZEOLITE STRUCTURES AND THE OXYGEN COORDINATION

BY

Nora ENGEL ²

ABSTRACT

For zeolites, the charge distribution within the structure is important, and in order to establish a measure of this distribution, we consider the cationic valences surrounding each oxygen atom. These are expressed by the sum of the cationic bond strengths around the O atoms with the specified coordinations, discussed in a preceding paper. New parameters expressing the relative excess or deficiency in the sum of the cationic bond strengths to oxygen compared to 2 valence units are defined. They are related to the so-called "identifiers for the coordination of O atoms", which were defined in a preceding paper, by an analysis which follows the *Baur's extended electrostatic valence rule*. A relation between cationic valences and the O coordinations is thus established for the O atoms coordinated to Al atoms or cavity cations. Following a scheme for possible charge transfer within zeolite structures, limiting conditions for a "*structural*" composition of these minerals are deduced. Thus, for structures of Si and Al-bearing zeolites, there are, at least, on average, two O atoms, whose sum of the bond strengths is below 2 valence units, which, linked to the Al atoms, form part of these O tetrahedra; there are further, per Al atom, between 1 and 4 water molecules which belong to the cavity cations polyhedra; finally, a limit between zeolites with a *low water content* and zeolites with a *high water content* is drawn in terms of the O coordinations.

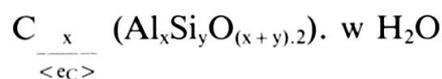
Keywords: zeolites, structural chemistry, electrostatic valence rule, oxygen coordination, classification.

1. INTRODUCTION

Structures of zeolites are characterized by water molecules stacked beside cavity cations in channels or cavities formed within a framework of oxygen tetrahedra centered, for most of these minerals, by Si or Al atoms. The water molecules either belong to the polyhedra formed around the cavity cations or are "free" in this space. In a preceding paper, for structures of zeolites with the ideal theoretical composition.

¹ The first paper of this series of three papers has been published in a preceding issue. The last paper entitled "'Structural' and chemical compositions: a discussion in relation to the classification of natural zeolites" will come out in the next issue.

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[$\langle e_C \rangle$: mean valence electron number of the cavity cations (C); $e_C = 1$ for $C = Li^{1+}, Na^{1+}, K^{1+} \dots$; $e_C = 2$ for $C = Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} \dots$], we defined as a model 6 possible coordinations for O atoms (left column of table 1). We showed that the mean number, per Al atom, of O atoms with specific coordination, the so-called “identifiers for the coordination of O atoms”, have characteristic values for each structure type. These identifiers were also expressed as a function of the mean number of coordination of cavity cations ($\langle CN_C \rangle$) and of the mean number, per cavity cation, of water molecules bound to one C atom (parameter ξ). These two parameters define the mean composition of the cavity cation polyhedra. The averages are all taken over the unit cell.

As part of a global study of zeolite structures, it is of interest to try to understand how charges or valences may be distributed within these structures. For this purpose, we compare to 2.0 valence units the Pauling’s sum of the cationic bond strengths (Pauling, 1960) calculated for each of the O coordinations specified in table 1. In this manner, a “function” is now attributed to each of the O atoms in relation to its coordination sphere. The analysis leads to specific numerical relations between the identifiers for the coordination of O atoms, which define for zeolites possible compositions of water molecules according to the aluminium content and to the mean composition of the cavity cation polyhedra.

TABLE 1.

Expected coordinations for the O atoms in zeolite structures with cavity cations (C) of valence one [$e_C = 1$] or two [$e_C = 2$] and calculation of the sum of the cationic bond strengths to these oxygen atoms (Σv).

Cations coordinated to central O atoms	Σ (bond strengths) (in valence units) and, in square parentheses, the identifiers for the coordination of O atoms	
	$e_C / \langle CN_C \rangle < 0.25$	$e_C / \langle CN_C \rangle \geq 0.25$
(Si Si)	$\Sigma v = 2.0$ [k]	$\Sigma v = 2.0$ [k]
(Si Al C C)	$\Sigma v^2 = 1.75 + 2e_C / \langle CN_C \rangle$ [l]	-----
(Si Al C)	$\Sigma v^1 = 1.75 + e_C / \langle CN_C \rangle$ [i']	$\Sigma v^2 = 1.75 + e_C / \langle CN_C \rangle$ [i'']
(Si Al)	-----	$\Sigma v^1 = 1.75$ [g]
(C H H)	$\Sigma v^3 = 2.0 + e_C / \langle CN_C \rangle$ [r]	$\Sigma v^3 = 2.0 + e_C / \langle CN_C \rangle$ [r]
(H H)	$\Sigma v = 2.0$ [s]	$\Sigma v = 2.0$ [s]

¹ $\Sigma v^1 < 2.0$ v.u. or “valence deficient” O atoms which are supposed to be “acceptor” of H atoms.

² $\Sigma v^2 \geq 2.0$ or so called “overloaded” O atoms.

³ “donor” with $\Sigma v^3 > 2.0$ v.u.

2. DEFINITIONS

As mentioned in a preceding paper, zeolite structures form an *ionic network*. For such structures, according to Brown (1981), the total valence of the cations is equal to the total valence of the anions. From the physical point of view, the valence is, for each atom of the structure, the number of electrons taking part in chemical bonding. Taking Brown's definitions (1981), we consider for our purpose that the valence is equivalent to the atomic charge. In the rest of this paper, if not otherwise specified, the valences or charges will be cationic or positive.

Pauling (1960) calculates for each bond a strength ("bond strength" also called "bond valence") equivalent to the cation valence divided by the cation coordination number ($e_{\text{cation}}/\text{CN}_{\text{cation}}$). If there is no physical evidence how charges are effectively distributed within a structure, it is possible to consider a bond valence calculation as an indication for this distribution (see an interesting comment in Brown, 1981). Bond valence has further been related to the bond length (see for instance expressions (1) and (2) in Donnay and Allmann, 1970). If one applies to the Pauling's bond strength a corrected value calculated as a function of the relative anion-cation distance measured from the structure refinement, the sum of the cationic bond strengths calculated around each of the anions should be more or less equal to the charge of the anion (for a method, see Donnay and Allmann, 1970). This "bond length distortion" is thus an *effect* of the valence distribution in a crystal structure.

The bond length distortion is the most pronounced for the (H-O) bonds. *Hydrogen atoms* are in most structures bound to 2 O atoms: the so-called oxygen "donor" for which the H-O bond is relatively shorter, and the so-called O "acceptor", for which the bond (also called "H bond") is longer (Baur, 1972). For zeolite structures, where the H atoms were not refined, one generally assumes that the O atoms "donors" of H atoms (in our case, the water oxygens) are found among the O atoms coordinated to other cations so that the (H-water oxygen) bond valences added to the (other cation-water oxygen) bond valences tend to be around 2 valence units; among the O atoms situated in the close neighbourhood of the H₂O molecules, those with a deficiency in the sum of the cationic bond strengths are possible "acceptors" for H atoms.

3. THE BOND VALENCE DISTRIBUTION WITHIN ZEOLITE STRUCTURES

Within zeolite structures, each oxygen tetrahedron centered by the Al atoms presents a deficiency of one cation valence which is supplied by the valences provided by the cavity cations either through bonding with these O atoms or through H bonds (fig. 1). In this global study about valence distribution, the (cation-O) bond length

distortions are not considered at all. Consequently, for this discussion, only three kinds of O atoms are considered (fig. 1): the so-called "overloaded" O atoms; the "valence deficient" O atoms, which are possible "acceptors" for H atoms (these two kinds of O atoms form the Al-centered tetrahedra); and the water oxygens bound to the cavity cations, which are also "donor" of H atoms. As shown in table 1, the "overloaded" O atoms and the O "donors" present an excess in the cation valences (the sum of the bond strength is above 2.0 v.u., this, without taking into account any correction for the bond length distortion).

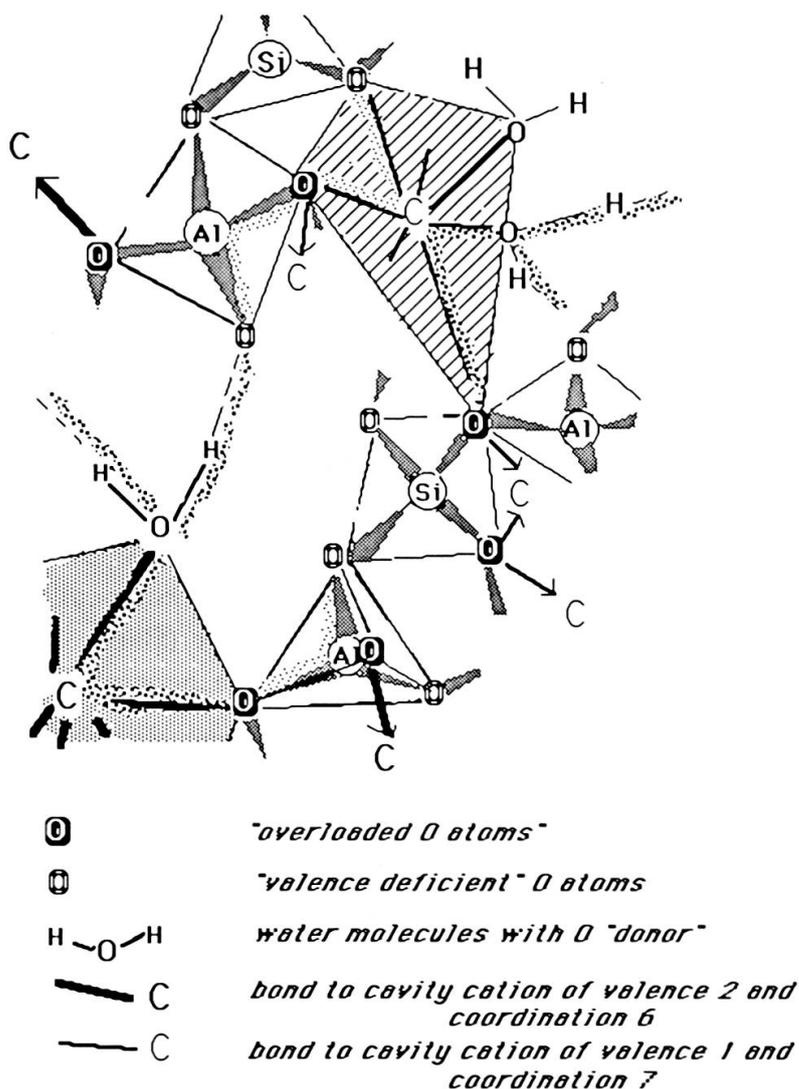


FIG. 1.

Schematic representation of part of a zeolite structure. The O atoms forming the tetrahedra are all bound to one Si atom and one Al atom and possibly to cavity cations. The possible valence transfer from an "overloaded" O atom through H bonding (hypothesis 1° in text) is sketched with heavy dots in contrast to the possible valence transfer through bonds within the tetrahedra or within the C coordination polyhedra (small dots, hypothesis 2°).

Most water molecules in zeolite structures are bound to cavity cations. The two (H-O) bonds are in this analysis considered as a path for a “cationic valence transfer” from the cavity cation to the Al centered tetrahedron oxygens (fig. 1). It may be noticed, that, for bond length distortion, the scheme of an electrostatic repulsion or attraction produced by valence transfer agrees with the bond length distortion theory relative to the bond strength variation. According to the theory and general observations on structures, the O atoms with an excess of cationic valences are supposed to be bound to the neighbouring cations with weaker (longer) bonds. This corresponds to a possible cationic valence transfer from an anion to a cation, which might produce a slight repulsion between these atoms. In this context, we postulate for the H bonds a slight attraction produced by the positive charge transfer from the hydrogen to the O “acceptor”.

In order to estimate the amount of the transferred valences, we refer first to the Pauling’s sum of the cationic bond strengths (*electrostatic valence rule*; Pauling, 1960), which we calculate for each of the O atoms with the specified coordinations given in table 1. Then, from the range of values for bond length distortion and therefore bond valence variation discussed in the literature, a possible maximal valence transfer is deduced. In this discussion, only mean values calculated over each structure are considered (their definitions were given in the appendix A of a preceding paper). These averaged values are useful, since several zeolite structures are refined with disorder on the Si/Al sites as well as partial occupation for cavity cations and water oxygens.

4. THE SUM OF THE BOND VALENCES AROUND EACH CENTRAL O ATOM AND THE IDENTIFIERS FOR THE COORDINATION OF O ATOMS

Baur (1970), observing that Pauling’s electrostatic valence rule is only approximately fulfilled for each anion surrounded by cations, established an extended rule which states that “the value of the sum of the bond strengths received by the anions is on the average equal, with changed sign, to the valences of the anions”. We shall use this statement to analyse the distribution of bond valences calculated, in the average over the structure, around the O tetrahedra centered by Al atoms.

Recalling the identifiers for the coordination of O atoms (latin letters in the expression below) and the model defined precedently (see table 1), we express Baur’s statement in the following way:

$$\frac{k \cdot \Sigma v + (g + i') \cdot \Sigma v^1 + (l + i'') \cdot \Sigma v^2 + r \cdot \Sigma v^3 + s \cdot \Sigma v}{k + g + i' + i'' + l + r + s} = 2.0 \text{ (valence units)} \quad (1)$$

The sum of the bond strengths (Σv) around the O atoms are shown without bond length correction in table 1 as a function of the cavity cation mean bond strength ($e_c / \langle CN_C \rangle$; for a definition see appendix A of a preceding paper). As defined in table 1, there are two groups for the O coordinations according to the value for $e_c / \langle CN_C \rangle$. The “valence deficient” O are in the left group ($e_c / \langle CN_C \rangle < 0.25$ v.u.) identified by i' and in the right group ($e_c / \langle CN_C \rangle \geq 0.25$ v.u.) by g , whereas the “overloaded” O atoms are identified by l or by i'' respectively.

Considering only the terms for which the sum of the bond strengths given by the cations to the O atoms is different from 2.0 v.u., we write:

$$\frac{(g + i') \cdot \Sigma v^1 + (l + i'') \cdot \Sigma v^2 + r \cdot \Sigma v^3}{g + i' + i'' + l + r} = 2.0 \text{ valence units} \quad (2)$$

For the structures built exclusively of cavity cations of one or other of the two cases cited in table 1, we insert the numerical definitions for Σv^1 , Σv^2 and Σv^3 into (2) and solve expression (2) (for a detailed calculation, see appendix A). For structures containing exclusively cavity cations with $e_c / \langle CN_C \rangle < 0.25$ v.u.:

$$\frac{l}{i'} = \frac{(0.25 - (V + 1) \cdot e_c / \langle CN_C \rangle)}{(-0.25 + 2 \cdot e_c / \langle CN_C \rangle)} \quad (3')$$

and for structures containing exclusively cavity cations with $e_c / \langle CN_C \rangle \geq 0.25$ v.u.:

$$\frac{i''}{g} = \frac{(0.25 - V \cdot e_c / \langle CN_C \rangle)}{(-0.25 + e_c / \langle CN_C \rangle)} \quad (3'')$$

where V : parameter expressing the number of water molecules bound to cavity cation per “valence deficient” O atom, which are possible “acceptor” of H atoms [$V = r / (g + i')$, equ. (5) in a preceding paper].

The expressions (3) show the relationship between the mean numbers of the “overloaded” O atoms [i'' or l] and the “valence deficient” O atoms [g or i'] per aluminium atom. This ratio is related to the amount of valences expressed by the mean bond strength of (cavity cation — O atom) bonds. In fact, the denominator of the right hand side of the equations (3) (called *parameter B* here below) expresses the mean excess of valence ($\Sigma v^2 - 2.0$ v.u.) which is available on each i'' or l O atoms for the valence deficient (< 2.0 v.u.) g or i' O atoms. Whereas the numerator of this term is a measure of the mean valence that each of the i' or g O atoms should receive from the “overloaded” O atoms (*parameter A* below). In a structure containing both kinds of cavity cations (of valence one as well as of valence two), the total numbers of “valence deficient” O atoms and of the “overloaded” O atoms

are equal to $(i' + g)$ and to $(l + i'')$ respectively. The equations (3) may therefore be expressed generally as

$$\frac{(l + i'')}{(i' + g)} = \frac{A}{B}$$

relation between the "overloaded" O and the "valence deficient" O atoms

Now, according to the model for the O coordination (table 1), the mean excess of valence of the C-coordinated water oxygens is equal to $\Sigma v^3 - 2.0 = e_C / \langle CN_C \rangle$.

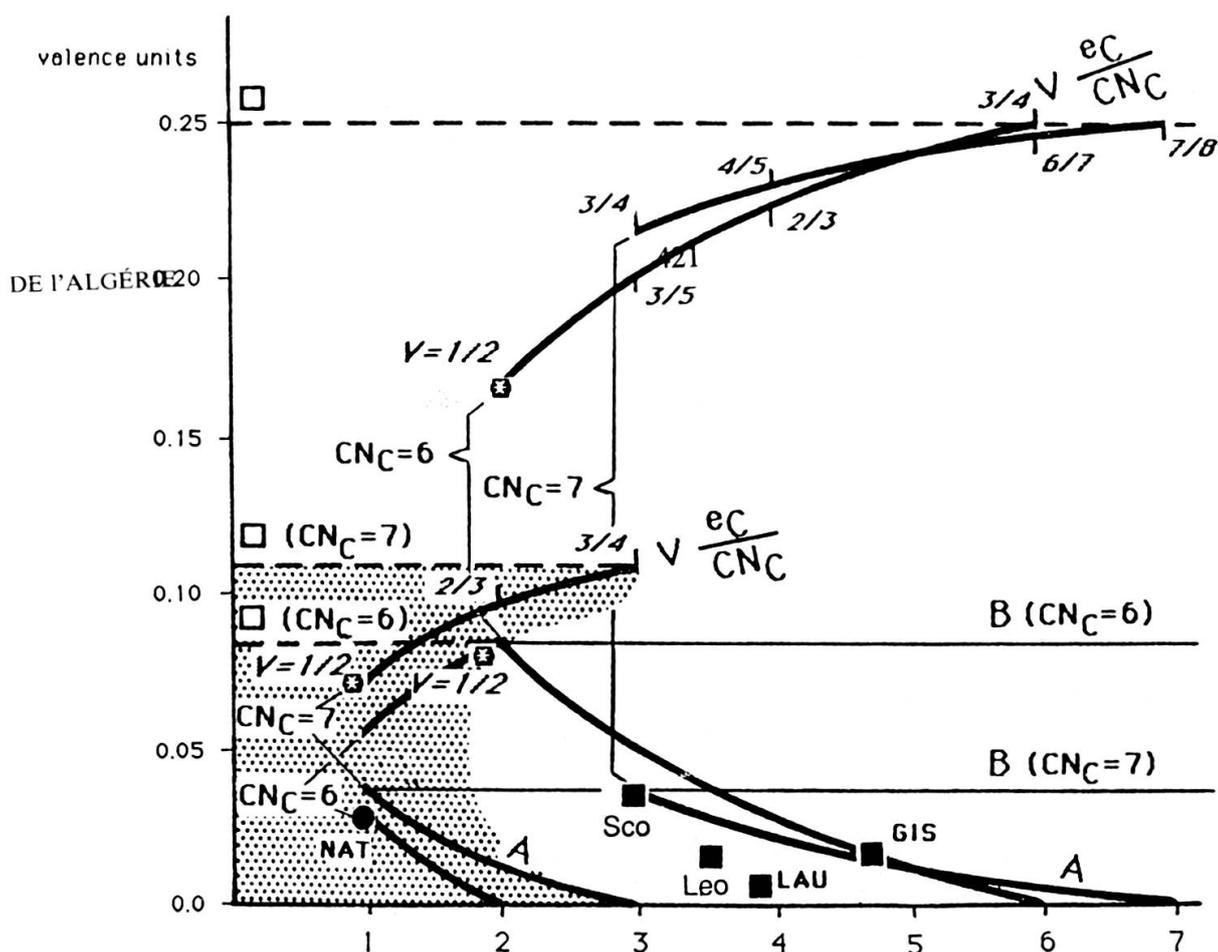


FIG. 2.

The parameters expressing the relative excesses or deficiencies in the sum of the cationic bond strengths relative to 2 valence units are shown in function of the mean number (per cavity cation) of H₂O molecules bound to one C atom (ξ). A and $V \frac{e_C}{CN_C}$ (heavy lines), \square (dashed lines) and B (fine lines) are drawn for structures with cavity cation of coordination number 6 or 7 either with $e_C = 1$ (dark field) or with $e_C = 2$ (clear field). Values for the parameter V are shown in italics on the curves $V \frac{e_C}{CN_C}$. The parameter A is calculated for specific examples of zeolites (codes according to IZA recommendations).

Thus, the mean excess of valence that each of the “valence deficient” O atoms is supposed to receive from the C-coordinated water molecules, is equal to $V \cdot e_c / \langle CN_C \rangle$. Finally, this mean valence received from the O “donors” added to A is equal to the valence deficiency of these O “acceptors” (we call here \square):

$$\square = A + V \cdot e_c / \langle CN_C \rangle \quad (4)$$

With the definition for A [see upper terms of (3') and (3'')], this expression becomes, for structures containing exclusively cavity cations with $e_c / \langle CN_C \rangle < 0.25$ v.u.:

$$\square = 0.25 - e_c / \langle CN_C \rangle \quad (4')$$

and for structures containing exclusively cavity cations with $e_c / \langle CN_C \rangle \geq 0.25$ v.u.:

$$\square = 0.25 \quad (4'')$$

Expressions (4') and (4'') are also equal to the expressions for Σv^1 (table 1) subtracted from 2.0 v.u.

A , B , \square and $V \cdot e_c / \langle CN_C \rangle$ are shown in figure 2 as functions of the mean number, per cavity cation, of H₂O molecules bound to one C atom (parameter ξ ; see equation (6) in a preceding paper) for $e_c / \langle CN_C \rangle = .167$, $e_c / \langle CN_C \rangle = .143$, $e_c / \langle CN_C \rangle = .333$ and $e_c / \langle CN_C \rangle = .286$. It may be recalled that the parameter V was related to ξ and $\langle CN_C \rangle$ by equation (9) in a preceding paper [here: $V = \xi / (8 - \langle CN_C \rangle + \xi)$]. In fig. 2, one notices that, since \square is a constant for given values of $e_c / \langle CN_C \rangle$, A decreases proportionally to the increase of $V \cdot e_c / \langle CN_C \rangle$ (equ. (4)).

With the help of examples of zeolite structures with a relatively low content of water molecules, we establish from fig. 2 that the excess of valences of the “overloaded” O (B) should always be greater than or equal to the valence that the “valence deficient” O atoms are supposed to receive from these O atoms (A),

$$B \geq A \quad (5)$$

Further, the relation between the excesses of valences supposed to be transferred ($e_c / \langle CN_C \rangle$ and B) compared to the deficiency of valence of the O atoms “acceptors” for H atoms (\square) is:

$$e_c / \langle CN_C \rangle \geq \square \geq B$$

As shown in fig. 3 with the clear fields, this relation is only valid for specific values for $e_c / \langle CN_C \rangle$. Zeolites are not expected to be built with cations with coordina-

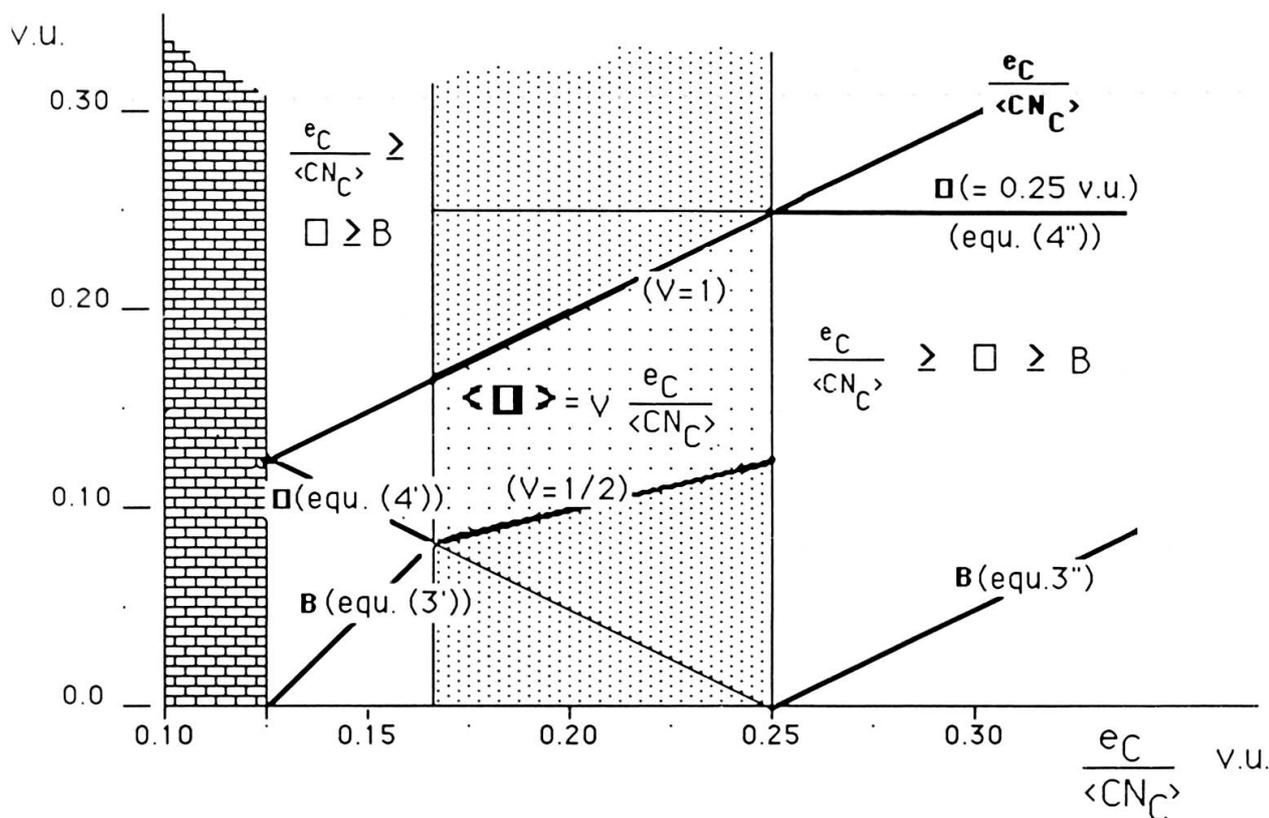


FIG. 3.

The excess of valences of the "overloaded" O atoms (B) and the water molecules ($e_C / \langle CN_C \rangle$) compared to the valence deficiency of the O atoms which are possible "acceptors" for H atoms (\square). The middle dotted field concerns zeolites with $e_C = 2$ and $\langle CN_C \rangle > 8$ (possibly also with $e_C = 1$ and $\langle CN_C \rangle \leq 6$) in which structures the Al-coordinated O atoms are all "valence deficient". The function B is there ignored, whereas both functions for \square (4') and (4'') are represented. The average of these two functions ($\langle \square \rangle$), as calculated in text, is included within the coarse dotted field.

tion numbers such that $e_C / \langle CN_C \rangle$ is inferior to 0.125 v.u. as the parameter V would exceed 1.0 (see (10) and (11) in a preceding paper). Further, on the left limits of the clear fields, $B = 0$ means that there is on average no excess of valence coming from the "overloaded" i' or l O atoms whose sum of cationic bond strengths is now equal to 2.0 v.u.; thus for structures with cavity cations with $CN_C = 8$ (possibly also $CN_C = 4$) and valence one or valence two, $B = 0$, $A = 0$ and only the water molecules bound to cavity cations will be concerned by equation (2).

Up to now, we have made a difference between zeolites whose cavity cation polyhedra have a higher or a lower mean bond strength than 0.25 v.u. (table 1). This limit has to be redefined and we will consider from now on the structures with cavity cations whose mean bond strength is inferior to $1/6$ v.u., the structures with cavity cations with $e_C / \langle CN_C \rangle \geq 0.25$ v.u., these two groups being relevant for the model for the oxygen coordination (as defined in table 1), as well as a third group of structures characterized with cavity cations such that $1/6 \leq e_C / \langle CN_C \rangle < 0.25$

v.u. (middle dotted field in fig. 3). This concerns structures for which the cavity cations of valence two are characterized by a high coordination number such as Ba- or Sr-bearing zeolites (i.e. edingtonite, brewsterite) or structures with $e_c = 1$ and a low coordination number ($\langle CN_C \rangle \leq 6$). As discussed in a preceding paper, within these structures, the O atoms forming the Al-centered tetrahedra are all valence deficient supposed to be "acceptor" ($g + i' = 4$, $V = r/4$) to that B and A are not considered. In the middle field on fig. 3, both functions \square [(4') and (4'')] are drawn. The mean value for the valence deficiency of the O "acceptors" is expressed as a function of the fraction of the mean cavity cation polyhedron built of water molecules ($\xi / \langle CN_C \rangle$, see appendix B):

$$\langle \square \rangle = \frac{1}{4} \xi / \langle CN_C \rangle \quad \text{mean valence deficiency of O "acceptors"}$$

and

$$\langle \square \rangle = V \cdot e_c / \langle CN_C \rangle \quad \text{for } 0.167 \leq e_c / \langle CN_C \rangle < 0.25$$

Values for this term fall within the coarse dotted field in fig. 3.

5. LIMITING CONDITIONS FOR ZEOLITE STRUCTURES DEDUCED FROM CHARGE TRANSFERS

In section 3, we noticed that the bond length distortion is an effect of the valence distribution and that it may be related to a possible charge transfer. Charge transfer between the "overloaded" O atoms and the "valence deficient" O atoms may occur either directly through the Al-centered tetrahedra, possibly also through the cavity cation polyhedra if $e_c = 1$ (hypothesis 2° in the sketch of fig. 1) or through the cavity cation — O bonds and then added to the excess of valences of the O "donor" through the H bonds (fig. 1; hypothesis 1°).

Considering the maximal case for which all the excesses of valences are transferred through H bonds (hypothesis 1°), we calculate the total transferred excess of valence. Since this amount of valence should be inferior to the missing valence of the "valence deficient" O atoms (\square , equation (4), $A \leq B$ and $V \leq 1$), we write the following relations:

for structures containing exclusively cavity cations with a mean bond strength inferior to 0.1667 v.u.

$$\frac{e_c}{2 \cdot \langle CN_C \rangle} + \frac{1}{2 \cdot r} \cdot B \leq 0.25 - \frac{e_c}{\langle CN_C \rangle} \quad (6')$$

for structures containing exclusively cavity cations with a mean bond strength superior or equal to 0.25 v.u.

$$\frac{e_c}{2 \cdot \langle \text{CN}_c \rangle} + \frac{i''}{2 \cdot r} \cdot B \leq 0.25 \quad (6'')$$

The first term of the left handside of (6) represents the mean excess of valence (per H atom) of the water molecules linked to a cavity cation; the second term, the mean excess of valence of the “overloaded” i'' or l O atoms (B) per H bond. From equations (3), we know that $l \cdot B = i' \cdot A$ or $i'' \cdot B = g \cdot A$ respectively and from the definition of V , we may write that $l \cdot B/r = A/V$ or $i'' \cdot B/r = A/V$. The equations (6) then become:

$$\frac{e_c}{2 \cdot \langle \text{CN}_c \rangle} + \frac{(0.25 - (V+1) \cdot e_c / \langle \text{CN}_c \rangle)}{2V} \leq 0.25 - \frac{e_c}{\langle \text{CN}_c \rangle}$$

and:

$$\frac{e_c}{2 \cdot \langle \text{CN}_c \rangle} + \frac{(0.25 - V \cdot e_c / \langle \text{CN}_c \rangle)}{2V} \leq 0.25$$

Solving these two equations for V , we find that $V \geq 0.5$ or $V_{min} = 0.5$ in both cases.

It is striking to observe that for structures of zeolites with cavity cations characterized by $e_c / \langle \text{CN}_c \rangle \leq 0.167$ v.u., the theoretically allowed number of H_2O molecules (see in fig. 2: $V = 1/2$ for $\xi = 2$) is sometimes superior to the observed value. Whereas for a structure with cavity cations characterized by a mean bond strength equal to 0.1428 v.u. ($\langle \text{CN}_c \rangle = 7$ for $e_c = 1$), 1 H_2O (in the average per C atom) is allowed and corresponds to the value of $V = 1/2$. In structures with such cavity cation coordinations (analcime, natrolite and some structures with “mixed” cavity cations; see below or a following paper), water oxygens may be bound to 2 cavity cations, which is a different coordination from the ones given in table 1.

Since we know that the parameter V does not exceed 1 (equation (10) in a preceding paper), we write for its limiting values:

$$\boxed{1/2 \leq V \leq 1} \quad (7)$$

The parameter V , which was defined in a preceding paper from the identifiers for the coordination of O atoms according to the expected O coordinations (table 1), is also relevant for the number of H bonds per “valence deficient” O atom which are possible “acceptor” of these H bonds. Thus, in zeolite structures, provided that all H atoms are bound to one “valence deficient” O atom and one O “donor”, there should be on average between 1 ($V = 1/2$) and 2 ($V = 1$) H atoms bound to these O “acceptors”. V is further a measure of the mean charge transfer from each O “donor” to the O “acceptors”. If $V = 1$, the whole charge is “accepted”, whereas for $V = 1/2$, only half of this charge is taken by the “valence deficient” O atoms.

The minimal value for V has to be revised for zeolites containing cavity cations with mean bond strengths greater than or equal to 0.25 v.u. Since the valence deficiency (\square) is a constant equal to 0.25 v.u., if one considers the hydrogen atom-O “acceptor” bond strength as a measure for the valence transfer, then its expected maximal value should be equal to 0.25 v.u. This value is high compared to values given in the literature (i.e. Brown, 1981). It is therefore to expect that, on average over such a structure, there should be more than one (H — “valence deficient” O atoms) bond. In the context of this analysis, expression (6) has to be rewritten: for structures containing only cavity cations with $e_c / \langle CN_C \rangle \geq 0.25$ v.u.

$$\frac{e_c}{2 \cdot \langle CN_C \rangle} + \frac{i''}{2 \cdot r} \cdot B \leq \text{max. valence of the H bond}$$

For a reasonable maximal value of 0.20 v.u., one finds that $V_{\min} = 0.625$.

In the beginning of this section, we postulated that the transfer of valence from the “overloaded” O atoms occurs through the cavity cation-O polyhedra and then through H bonds (hypothesis 1° in fig. 1). For this scheme, we calculate now the possible valence which, through each H bond, may be transferred from the “overloaded” O atoms beside the excess of valences from the O “donors” ($\{e_c / \langle CN_C \rangle\}$). A comparison of this value with the excess of valences of the “overloaded” O atoms (B) allows to estimate the amount of the valence transferred through each cavity cation — O “donor” bond. Thus, calculating the deficiency of valences (\square) per H bond:

$$\text{mean deficiency of valence per H bond} = \frac{\langle \square \rangle \cdot (i' + g)}{2 \cdot r}$$

As $V = r / (i' + g)$:

$$\text{mean deficiency of valence per H bond} = \frac{\langle \square \rangle}{2 \cdot V}$$

or calculated per H₂O bound to one cavity cation:

$$\text{mean deficiency of valence per H}_2\text{O} = \langle \square \rangle / V$$

The excess of valence from the “overloaded” O atoms, which could be transferred through H bonds is then:

$$\text{excess of valence} = \frac{\langle \square \rangle}{V} - \{e_c / \langle CN_C \rangle\}$$

$\{e_c / \langle CN_C \rangle\}$: mean excess of valence of C-coordinated water oxygens.

Now, if this value is superior to B , then the (cavity cation-O “donor”) bond valence should be relatively high:

$$\frac{\langle \square \rangle}{V} - \{e_c / \langle CN_C \rangle\} \geq B$$

Developing this expression with the equations (4) and comparing the result to the valence definition of A (numerator of equ. (3') and (3'')), we find:

$$\boxed{A/B \leq V} \quad (8)$$

This expression shows that the amount of positive charge which, according to the above scheme, is transferred from the "overloaded" O atoms within the cavity cation polyhedron through the cavity cation-O "donor" bond is estimated to be important. An effect of this is a short interatomic distance for this bond, which might be observed in zeolites with a low water content (see below).

Calculations have been carried out in this section in order to determine the possible amount of charge transfer within zeolite structures, in particular through the H bonds. Although this analysis has to be considered with caution, since there is up to now no physical evidence of how charges are effectively distributed within zeolite structures, its result (equations (7) and (8)) is significant for a "structural" composition of zeolites.

6. "STRUCTURAL" COMPOSITION OF ZEOLITES

In table 2, the specific relations between the identifiers for the coordination of O atoms are deduced from the relations we established between the parameters A , B and V . Only the O coordinated to the Al atoms or cavity cations expressed with the corresponding identifiers (see table 1) are considered.

The relation among the identifiers for the O atoms coordinated with an excess of valences defines the zeolites with a low water content from those with a high water content. The ratio

$$r / (i'' + 1)$$

is equal to the parameter V [$V = r/(i' + g)$] divided by the expressions (3) [$(i'' + 1)/(i' + g) = A/B$]:

$$\boxed{\frac{r}{i'' + 1} = V \cdot \frac{B}{A}} \quad (9)$$

Thus, for instance, if $r \geq (i'' + 1)$ then, as a consequence:

$$V \geq A/B \quad (\text{see equation (8)})$$

In this case the number of the water molecules is superior to the number of the "overloaded" O atoms.

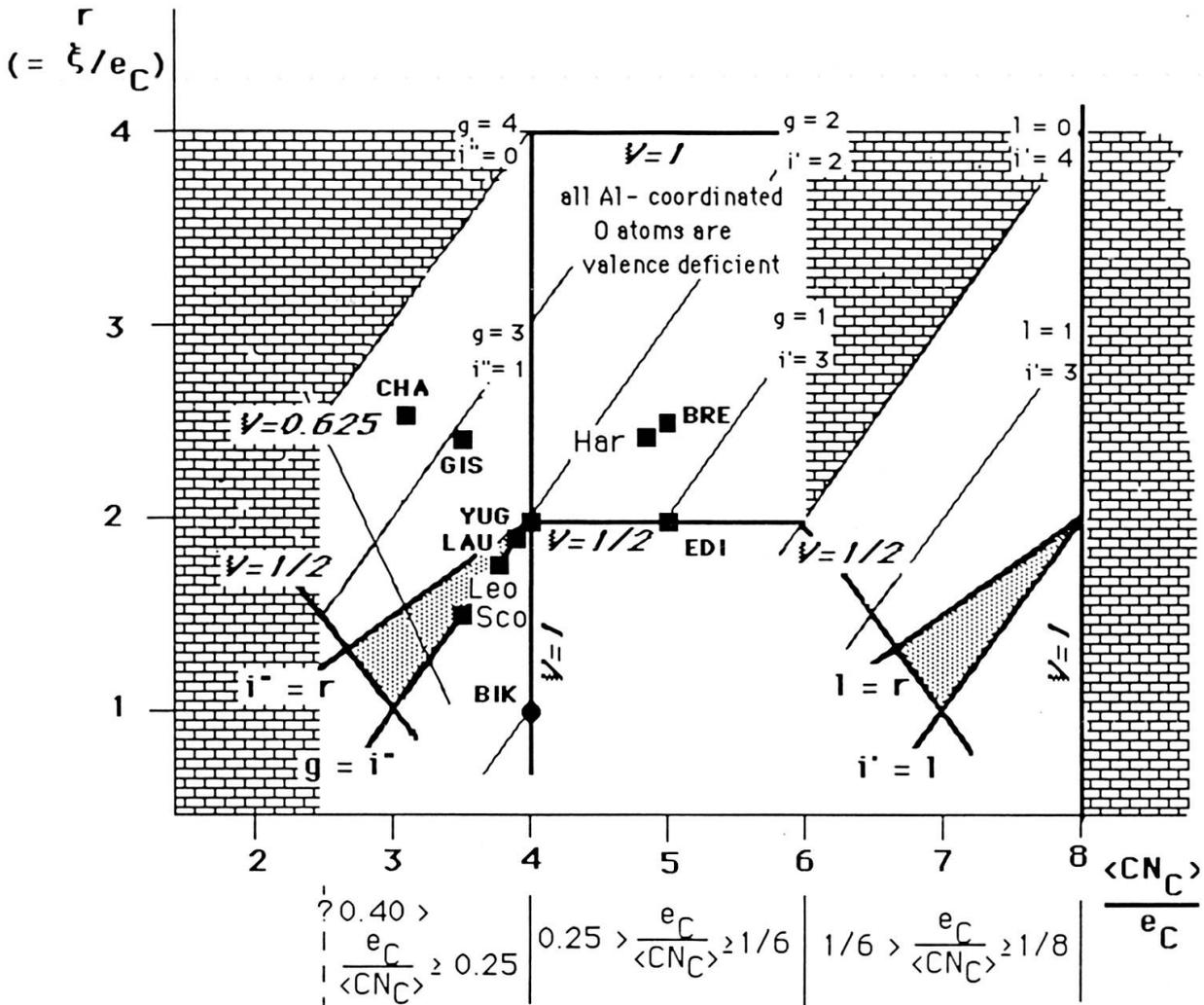


FIG. 4.

Possible compositions for zeolite structures expressed in terms of coordination with the identifiers for the coordination of O atoms (g, i', i'', l and r) and in relation to the mean composition of the cavity cation coordination polyhedra ($\langle CN_C \rangle$ and ξ). Minimal conditions for zeolite structures are given by $V=1/2$ and by either $g=i''$ or $i'=1$. The dotted fields are for zeolites with a low water content ($i'' \geq r, l \geq r$ respectively). Examples are for zeolites either with cavity cations of valence one only (black circles) or with cavity cations of valence two only (black squares) (codes are given according to the recommendations of the IZA).

of valence one only or cavity cations of valence two only. A complete list for these structures will be given in a following paper. For zeolite structures with cavity cations coordination number equal to 8 (possibly also 4), for which $A=0$ and $B=0$ and therefore equations (8) and (9) are not valid, the limiting conditions in terms of coordinations are however fulfilled (fig. 4). One notices one only exception to these fields: bikitaite ($Li_2(A_2Si_4O_{12}) \cdot 2H_2O$) whose Li atoms surrounded by 3 O atoms and 1 water molecule present a mean bond strength of 0.25 v.u. and thus on average around each Al-centered tetrahedron, 3 O are surrounded by (Li Al Si) with the sum

of the bond strengths equal to 2.0 v.u. and one O atom is coordinated to (Si Al); for this structure, $V=1$ but ξ is below the limitation given by $g \geq i''$ (see table 2).

For structures containing cavity cations of valence one as well as of valence two whose cavity cations are coordinated to 6, 7 or 8 O atoms, i.e. mesolite, thomsonite and gonnardite, and for the "series" analcime-wairakite, these calculations may be made by addition of the identifiers for the coordination of O atoms. However, as shown with white triangles in the diagram of fig. 5, most of these zeolite structures

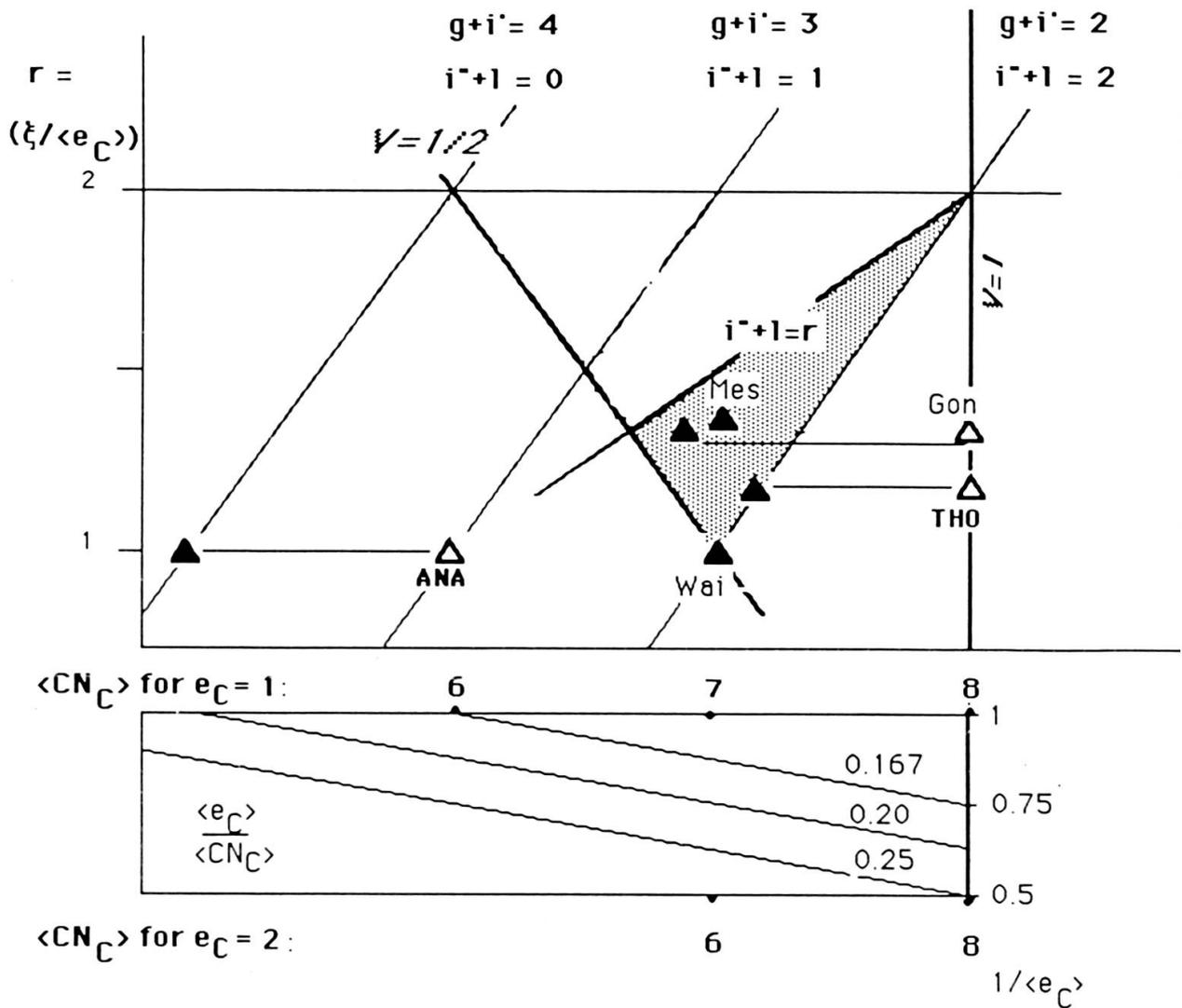


FIG. 5.

"Structural" composition for zeolites with mixed cavity cations. The oblique lines give the mean composition of the Al-centered tetrahedra or the mean numbers of the valence deficient O atoms ($g+i'$) and of the "overloaded" O atoms ($i''+l$) in relation to the mean composition of the cavity cation polyhedra (ξ and $\langle CN_C \rangle$). Values for the mean number of water molecules per Al atoms (r) are functions of the mean bond strength for cavity cations ($\langle e_C \rangle / \langle CN_C \rangle$) as indicated with the oblique lines in the graph at the bottom. Examples are for zeolites with a low water content. White triangles: calculated values according to r and $\langle e_C \rangle / \langle CN_C \rangle$. Black triangles: calculated values from the structure refinements for ($i''+l$) and ($g+i'$). (Codes according to the recommendations of the IZA).

do not fall within the limits discussed above, and it is to be expected that the distribution of the cavity cation — oxygen atom bonds may not occur according to the expected O coordinations that this calculation is based on. In fact some water molecules are bound to 2 cavity cations so that their coordination polyhedra are enlarged as well as being joined together and the valence supposed to be transferred from these water molecules to the “valence deficient” O atoms is increased as well. The black triangles in fig. 5 show the relationship for $(g + i')$ and $(i'' + 1)$ O atoms as calculated from the refinements (mesolite: Artioli *et al.*, 1986; thomsonite: Pluth *et al.*, 1985; gonnardite: Mazzi *et al.*, 1986; analcime: Ferraris *et al.*, 1972; wairakite: Takeuchi *et al.*, 1979).

Only few structures with a *high water content* and with either cavity cations of valence one only or cavity cations of valence two only, where water molecules are all bound to cavity cations, are reported in fig. 4. For this group of structures, a disorder on water oxygen sites as well as on the cavity cation sites is often observed. Furthermore, the silicon content is high. A global analysis for this group of structures is presented in a following paper in relation to an analysis of the O coordination numbers.

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APPENDIX

A. THE CALCULATION OF THE RELATIONSHIP BETWEEN THE NUMBERS OF THE "OVERLOADED" O ATOMS AND THE O "ACCEPTORS"

Starting from equation (2) which states:

$$\frac{(g+i') \cdot \Sigma v^1 + (l+i'') \cdot \Sigma v^2 + r \cdot \Sigma v^3}{g + i' + i'' + l + r} = 2.0 \text{ v.u.}$$

and inserting the expressions for Σv^1 , Σv^2 and Σv^3 (table 1) in it, we obtain:

if $e_c / \langle \text{CN}_C \rangle < 0.25$ v.u. only:

$$(-0.25 + e_c / \langle \text{CN}_C \rangle) \cdot i' + (-0.25 + 2 \cdot e_c / \langle \text{CN}_C \rangle) \cdot l + e_c / \langle \text{CN}_C \rangle \cdot r = 0$$

if $e_c / \langle \text{CN}_C \rangle \geq 0.25$ v.u. only:

$$(-0.25) \cdot g + (-0.25 + e_c / \langle \text{CN}_C \rangle) \cdot i'' + e_c / \langle \text{CN}_C \rangle \cdot r = 0$$

Using the definition of the parameter V [$V = r / (g + i')$], we replace $e_c / \langle \text{CN}_C \rangle \cdot r$ either by $e_c / \langle \text{CN}_C \rangle \cdot V \cdot (i')$ or by $e_c / \langle \text{CN}_C \rangle \cdot V \cdot (g)$ in the above equations and find for each of them:

if $e_c / \langle \text{CN}_C \rangle < 0.25$ v.u. only:

$$(-0.25 + (V + 1) e_c / \langle \text{CN}_C \rangle) \cdot i' + (-0.25 + 2 \cdot e_c / \langle \text{CN}_C \rangle) \cdot l = 0$$

if $e_c / \langle \text{CN}_C \rangle \geq 0.25$ v.u. only:

$$(-0.25 + V \cdot e_c / \langle \text{CN}_C \rangle) \cdot g + (-0.25 + e_c / \langle \text{CN}_C \rangle) \cdot l = 0$$

and finally, we obtain for structures with exclusively cavity cations with $e_c / \langle \text{CN}_C \rangle < 0.25$ v.u.:

$$\frac{l}{i'} = \frac{(-0.25 - (V + 1) \cdot e_c / \langle \text{CN}_C \rangle)}{(-0.25 + 2 \cdot e_c / \langle \text{CN}_C \rangle)} \quad (3')$$

and for structures with exclusively cavity cations with $e_C / \langle CN_C \rangle \geq 0.25$ v.u.:

$$\frac{i''}{g} = \frac{(0.25 - V \cdot e_C / \langle CN_C \rangle)}{(-0.25 + e_C / \langle CN_C \rangle)} \quad (3'')$$

B. THE CALCULATION OF THE VALENCE DEFICIENCY OF O "ACCEPTORS" FOR STRUCTURES WITH $1/6 \leq e_C / \langle CN_C \rangle < 0.25$

These structures are characterized by two kinds of "valence deficient" O atoms: i' O atoms surrounded by (C Al Si) and g O atoms by (Si Al). According to the equations (4), the valence deficiency is:

$$\begin{aligned} \square i' &= 0.25 - e_C / \langle CN_C \rangle \\ \square g &= 0.25 \end{aligned}$$

Since $g + i' = 4$ ($l=0$ and $i''=0$ in equ. (3), preceding paper), the mean valence deficiency is equal to:

$$\langle \square \rangle = \frac{0.25 \cdot g + (0.25 - e_C / \langle CN_C \rangle) \cdot i'}{4}$$

g and i' may be expressed as a function of $\langle CN_C \rangle$ and ξ (table 2 in a preceding paper):

$$g = 4 - [\langle CN_C \rangle - \xi] / e_C$$

$$i' = [\langle CN_C \rangle - \xi] / e_C$$

Inserting these equations into the above equation and developing this term, we find:

$$\langle \square \rangle = \xi / (4 \cdot \langle CN_C \rangle)$$

Since for these structures $V = r/4$ and as $\xi = r \cdot e_C$ (equ.(6), preceding paper) we consider $\xi = 4 \cdot V \cdot e_C$ and

$$\langle \square \rangle = V \cdot e_C / \langle CN_C \rangle$$

