THE CANADIAN MINERALOGIST

Journal of the Mineralogical Association of Canada

Volume 18 May 1980 Part 2

Canadian Mineralogist
Vol. 18, pp. 153-156 (1980)

POLYHEDRAL VOLUME CALCULATIONS

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ABSTRACT

A Fortran IV computer program, POLYVOL, has been developed to calculate the volume, surface area and interedge angles for any convex polyhedron. It has checks to determine whether the polyhedron is convex and whether its surface has been correctly closed by the defined exterior faces. These two checks provide a powerful aid in assuring that the computed volume is correct. A specific application of this program is made to the cubic synthetic zeolite type *A*.

Keywords: polyhedron volume, crystal structure, zeolite type *A*.

SOMMAIRE

POLYVOL, programme rédigé en Fortran IV, permet de calculer le volume, la superficie et les angles entre arêtes d'un polyèdre convexe quelconque. Il permet de vérifier si le polyèdre est convexe et si sa surface est effectivement fermée par les faces extérieures préalablement définies; ces deux tests permettent de s'assurer que le volume calculé est exact. Nous appliquons ce programme à la zéolite synthétique cubique de type *A*.

(Traduit par la Rédaction)

Mots-clés: volume d'un polyèdre, structure cristalline, zéolite de type *A*.

INTRODUCTION

Crystal structures are composed of packed arrays of various occupied and vacant polyhedra that totally fill the space in the unit cell. The polyhedra are commonly described in terms of coordination number, bond lengths, bond angles and distortional indices (Dollase 1974). In addition to these parameters are the volume, surface area and interedge angles of the polyhedra. These polyhedral parameters are all directly related to such structural properties as cation distribution and unit-cell parameters. The value of the program POLYVOL is that it allows simple and rapid calculation of these parameters with only a minimal amount of input data. The program, written in Fortran IV, is available from the authors upon request.

Polyhedral volumes are directly applicable to the study of crystal structures, particularly of zeolites, in which the volumes of large cages often control the occlusion of molecular species within the zeolite framework.

The variation of polyhedral volumes is an important stereochemical response to changes in temperature and pressure. It should be possible to determine whether the volume decrease accompanying increasing pressure is due to compression of the filled polyhedra or to their rotation with respect to each other (Hazen & Finger 1979). A rotation should be reflected in a volume decrease of only the unfilled polyhedra within the structure.

DEFINING A POLYHEDRON

Any convex polyhedron composed of n points is uniquely defined by its v vertices. By definition, a point is a vertex if there exists a plane such that 1) the point is contained in that plane and 2) all remaining points lie to one side of that plane. Collinear and coplanar points can be identified with vector tests and then elimi-

nated from the initial array of n points if they do occur. An interior point creates a special situation, which will be discussed below.

By permuting the n points three at a time, the number R of unique triangular planes is given by $n!/3!(n-3)!$. The number T of exterior triangular faces that define the polyhedron is given by $2v-4$, as a direct consequence of Euler's theorem. Since every triangular face has three edges and each edge is shared by two faces, the number of edges is given by

$$E = 3F/2 \quad (1)$$

from Euler's theorem:

$$F = 2v-4 = T \quad (2)$$

Determining the T Exterior Faces

Each of the R triangular planes, defined by three points, can be described by two vectors $\mathbf{V}_1$ and $\mathbf{V}_2$, with one of the three points being chosen arbitrarily as an origin for the plane (Fig. 1). Identification of the exterior faces of the polyhedron requires using the cross-product vector $\mathbf{V}_3 = \mathbf{V}_1 \times \mathbf{V}_2$ (or $\mathbf{V}_2 \times \mathbf{V}_1$). The vectors $\mathbf{V}_1$ and $\mathbf{V}_2$ are crossed in the order that will direct the vector $\mathbf{V}_3$ away from the geometric centre of the polyhedron. Thus $\mathbf{V}_1$, $\mathbf{V}_2$ and $\mathbf{V}_3$ constitute a set of basis vectors for each plane R, which can be used to describe the location of all of the n points. The exterior faces are the only faces for which none of the n points can be expressed with a positive linear component of the cross-product vector $\mathbf{V}_3$, in that basis.

Each exterior face is then tested to see whether any of the remaining $n-3$ points lie in that face. If no other points lie in the face, then all three points must be vertices and the face constitutes one of the T exterior triangular faces. If, however, other points do lie in the face, then the total set of points m comprising the face is treated separately. Collinear and coplanar points are first eliminated from the set of m points, leaving j vertices to define a convex polygonal face. The face is then broken down into $j-2$ triangles with each triangle representing one of the T faces.

Computing the Volume

Each exterior triangular face T is the base of a tetrahedron whose apex can be any point P lying inside the polyhedron. P is the common apex of the T tetrahedra and also defines an origin for the polyhedron, so that the three

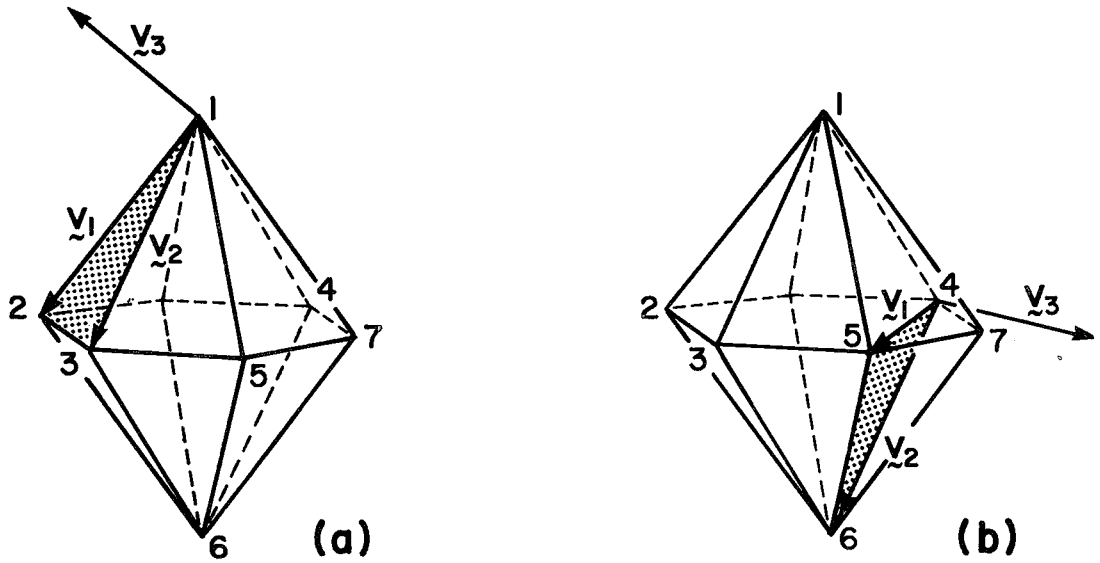

FIG. 1. (a) The vertices, 1, 2 and 3 define one of the polyhedron's R triangular planes. To determine whether this is an exterior face, the vectors $\mathbf{V}_1$ and $\mathbf{V}_2$ are crossed in the order that directs their cross-product vector $\mathbf{V}_3$ away from the geometric centre of the polyhedron. This plane is an exterior triangular face because all the remaining n points possess a negative $\mathbf{V}_3$ component. (b) For the plane defined by the vertices 4, 5 and 6, vertex number 7 has a positive $\mathbf{V}_3$ component and is therefore not an exterior triangular face.

vertices that define the face become the end points of three vectors denoted **A**, **B** and **C**, which outline a tetrahedron. The volume of the tetrahedron is one-sixth of the volume of the parallelepiped defined by the same three vectors and is given by $\frac{1}{6}$ $|\mathbf{A} \cdot \mathbf{B} \times \mathbf{C}|$. Summing the T tetrahedral volume elements gives the total volume of the polyhedron.

Concavity

One possible problem, here referred to as concavity, results if one or more of the n points is positioned inside the convex polyhedron formed by the v vertices. Some of the faces then indent the polyhedron's exterior. POLYVOL computes the volume of the convex polyhedron, however, resulting in the generation of an incorrect number of tetrahedra. The point(s) that causes the concave arrangement of exterior faces can be identified, since it is not eliminated as being collinear or coplanar and does not occur as one of the polyhedron's vertices.

For some concave polyhedra, it is necessary to correct for the re-entrant volume, which is calculated in a similar manner and subtracted from the volume calculated assuming convexity. If the problem is more complex than this, it is then necessary to divide the large concave polyhedron into smaller convex segments and sum their respective volumes.

An additional test sums the cross-product vectors (with magnitudes proportional to the areas of their respective faces) of the T exterior faces. If the polyhedron's surface has been correctly closed, this results in a zero vector. A scalar sum of the cross-product vector magnitudes is equal to twice the total surface area of the polyhedron.

Polyhedral Volumes in a Zeolite

The synthetic zeolite type *A* was first described by Reed & Breck (1956) as a cubic aluminosilicate framework structure with space group $Pm3m$ and a cell edge of 12.32 Å. The sodium analogue of this structure has the formula $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27H_2O$ and contains two large cavities, each of which is capable of occluding water. The smaller, 36-coordinated β cage is located at each corner of the primitive cell, whereas the larger, 72-coordinated α cage occupies the centre of the unit cell (Breck 1974).

Water molecules have a minimum kinetic diameter of 2.65 Å (Hirschfelder *et al.* 1954), so that they pass easily into the α cage through an 8-membered oxygen ring, with an aperture of 4.2 Å. For water to occupy the smaller β cage, it must pass through a 6-membered oxygen ring with an aperture of 2.2 Å and displace the sodium atoms that occupy the centres of these rings. It has been suggested that this requires dipole–cation interaction (Breck 1974).

The sodium type-*A* structure was found to hold 27 water molecules, which is equivalent to an occlusion volume of 833 Å^3 (Reed & Breck 1956). Reed & Breck estimated the volume of each cavity by inscribing the largest possible sphere within that cavity, giving calculated volumes of 775 Å^3 for the α cage and 157 Å^3 for the β cage. To account for the 833 Å^3 of occluded water, they reasoned that the water must fill both cavities. The water molecules are thought to adopt a pentagonal dodecahedral arrangement inside the α cage and to be bonded to the framework oxygens in the β cage (Gramlich & Meier 1971). This is inconsistent with n.m.r. data, which show the water to be present as an isolated liquid phase inside the α cage (Breck 1974).

The volume of the α cage, as computed by POLYVOL, is 1310 Å^3. The actual void volume of this cavity is less, because the coordinating atoms are actually spheres of finite volume. The volume taken up by these atoms, calculated by POLYVOL using the appropriate radii from Shannon & Prewitt (1969), was found to be 266 Å^3. This results in a net volume for the α cage of 1044 Å^3, which is large enough to hold the 833 Å^3 of adsorbed water.

In summary, the volume data indicate that water may occupy only the α cage and does not enter the β cage. This eliminates the need for dipole–cation interaction and is also consistent with the n.m.r. data.

Acknowledgements

The authors are grateful to Professors M. Boisen and G.V. Gibbs for helpful discussion, and the National Science Foundation for financial support through grant DES75–14912. Dr. C.D. Feustel is acknowledged for suggestions involving the manipulation of Euler's theorem. The comments of the anonymous reviewers were much appreciated.

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Received June 1979, revised manuscript accepted November 1979.