simplex $P_0 = 5$, $P_1 = 10$, $P_2 = 10$, $P_3 = 5$.

From Eq. 2.17 the analogous formula for a honeycomb (space filling by n-dimensional polytopes)can be derived[1]:

$$\sum_{i=0}^{n} (-1)^i P_i = 0 \qquad \text{(A2.18)}$$

Where now the numbers should be interpreted as *relative* numbers of figures of the appropriate dimensionality. For a plane tessellation Eq. A2.18 gives the result: $V - E + F = 0$ which we have used many times. We use the analogous expression for three-dimensional honeycombs in Appendix 3.

A2.7 References

One of the best introductions to elementary n-dimensional geometry is still *An Introduction to the Geometry of n Dimensions* by D. M. Y. Sommerville (Dover, New York, 1958). The definitive work on regular polytopes in n-dimensions is *Regular Polytopes* by H. S. M. Coxeter [third edition, Dover, New York, 1973] and on polytopes in general *Convex Polytopes* by B. Grünbaum [Interscience, New York, 1967]. Four-dimensional lattices are described fully by H. Wondratschek *et al.*, *Acta Crystallogr.* A**27**, 523 (1971) and an account of the four-dimensional space groups is in *Crystallographic Groups of Four-Dimensional Space* by H. Brown *et al.* [Wiley, New York, 1978]. A good introduction to four-dimensional crystallographic point groups and symmetry operations has been given by E. J. W. Whittaker [*An Atlas of Hyperstereograms of the Four-Dimensional Crystal Classes*, Clarendon Press, Oxford, 1985]. The four-dimensional hyperlayer groups (i.e. the symmetry groups of four-dimensional objects with translations in three dimensions) are described in *Colored Symmetry* by A. V. Shubnikov and N. V. Belov [Pergammon Press, Oxford, 1964]. For a wild ride into many-dimensional space (but with some excellent introductory material) *Sphere Packings, Lattices and Groups* [Springer-Verlag (1988)] by J. H. Conway and N. J. A. Sloan is highly recommended (this book also includes an enormous bibliography). There have been many recent examples of higher-dimensional crystallography applied to real world problems a good starting point is T. Janssen, *Acta Crystallogr.* A**42**, 261-271 (1986). Applications to quasicrystals will be found in the review by W. Steurer, *Zeits. Kristallogr.* **190**, 179 (1990). Two commonly used notations for point symmetry operations in four dimensions are those of C. Hermann [*Acta Crystallogr.* **2**, 139-145 (1949)] and A. C. Hurley [*Proc. Cambridge Philos. Soc.* **47**, 650-661 (1951)].

[1]For Eqs. A2.17 and A2.18, see the Coxeter reference cited in the next section.

APPENDIX 3

THE TOPOLOGY OF POLYHEDRA, NETS AND MINIMAL SURFACES

A3.1 Introduction

Topological aspects of crystal chemistry are attracting increasing attention. One reason for the interest is that zeolite catalysts are of major economic importance and their properties are intimately related to structural features such as the size of the pores and cages. These in turn are related to topological properties such as the connectivity and the sizes and numbers of rings in the net of the framework atoms. This Appendix describes some topological aspects of structures, particularly of 3- and 4-connected nets and infinite polyhedra. It will be seen that the subject poses some interesting and challenging unsolved problems.

A3.2 Finite polyhedra

Normally a polyhedron is thought of as a simple convex object topologically equivalent to a sphere: thus if the faces were deformable, it could be "blown up" so that it became a sphere in the same way as a truncated icosahedron (5.6^2) becomes a soccer ball. A finite polyhedron of this sort is topologically equivalent to a tiling of the surface of a sphere. The well-known Euler equation for the number of faces (F), edges (E), and vertices (V) of such a tiling is $F - E + V = 2$

A torus (an object shaped like a doughnut or the inner tube of a tire) has a hole through it, and is topologically different from a sphere. For a tiling of a torus, $F - E + V = 0$. This is the same as for a tiling of the plane (see § 5.6.11).

What about surfaces with more than one hole in them? A teacup with one handle is topologically the same as a torus and contains one hole. A soup bowl with two handles has two holes and is thus topologically distinct. The number of holes in a surface (H) is related to the *Euler-Poincaré characteristic* χ of a surface by:[1]

$$\chi = 2 - 2H \qquad \text{A3.1}$$

and for a surface with characteristic χ:

$$V - E + F = \chi \qquad \text{A3.2}$$

Thus the torus (and the infinite plane) have $\chi = 0$ and a simple closed surface (such as that of a sphere) has $\chi = 2$ ($H = 0$).

[1]See H. S. M. Coxeter, *Introduction to Geometry* (Book List). A simple proof of Eq. A3.2 is given by R. Courant & H. Robbins, *What is Mathematics?* [4th Ed. Oxford (1947)].

A simple example of a polyhedron with $\chi = 0$ can be obtained from a ring of eight cubes fused together as shown on the left in Fig. A3.1. There are 32 faces, 64 edges and 32 vertices. Note that there are eight vertices of the sort 4^3, sixteen 4^4 and eight 4^5.

Also shown in the figure is a polyhedron made by fusing together 20 cubes. It has five[1] holes ($\chi = -8$) and 72 faces, 64 vertices and 144 edges, so $V - E + F = -8$ confirming the formula above.

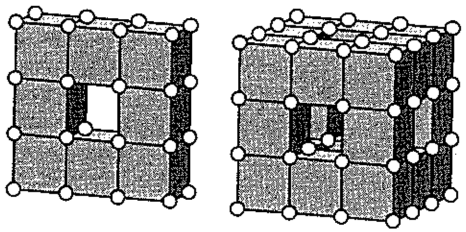

Fig. A3.1. Polyhedra with holes.

A3.3 Infinite polyhedra

An obvious next step is to repeat the above process to make an infinite polyhedron with connecting holes. Consider a cubic unit cell with side 2 containing a cube of side 1 centered at 1/2,1/2,1/2 and fused to unit cubes centered at the face centers (0,1/2,1/2)κ. Repetition of the unit cell will produce a solid figure with 8 vertices, 12 faces, and 24 edges per unit cell. The empty space left behind will be exactly the same: empty cubes at 0,0,0 and at (0,0,1/2)κ (the same coordinates as before but displaced by 1/2,1/2,1/2). The structure shown on the right in Fig. A3.1 is an element of the infinite structure; it may be seen that square holes emerge through each face of the unit cell. As holes emerging from opposite faces are equivalent (really the same hole) the number of holes per unit cell is 6/2 = 3.

It is interesting to consider this figure as an infinite periodic polyhedron with $\chi < 0$. The numbers of vertices, edges, faces and holes per repeat unit are expressed as lower case letters (v, e, f and h respectively), we then have with $x = 2 - 2h$:

$$v - e + f = 2 - 2h = x \qquad \text{A3.3}$$

This formula applied to the infinite polyhedron constructed from fused cubes gives $8 - 24 + 12 = 2 - 2 \times 3 = -4$. Note that each vertex is 4^6. This polyhedron is an example of a *skew polyhedron.*[2] The edges and vertices form a 6-connected net.

[1] Counting holes can be tricky. Start with a cube and make a hole between two opposite faces (one hole). Make a hole through a third face to join the first hole (the total is now two holes). Repeat for the fourth, fifth and sixth faces (three more holes for a total of five).

[2] H. S. M. Coxeter, *Proc. Lond. Math. Soc.* **43**, 33 (1937).

The polyhedron and the complementary empty space have the same connectivity. In this case the connectivity of the network of face-sharing cubes is just that of the primitive cubic lattice (six) and h is one half this connectivity. As discussed particularly by Wells (reference in § A3.9) it is often simpler to consider the connectivity of the polyhedron than to count holes. In some cases (those in which the polyhedron in question and its complementary polyhedron are topologically identical) care must be exercised in deciding the repeat unit and the connectivity, and we now give some examples which also illustrate how to count vertices, edges and faces.

For a polyhedron with just one kind of vertex, once the number of vertices in the repeat unit is identified, counting edges and faces is easy. The number of edges is just one-half the number of vertices times the connectivity (i.e. $2v$ if four polygons meet at a vertex). To count faces note that each n-gon is shared by n faces, so that if there are (for example) v vertices of the type $n_1.n_2.n_3.n_4$, the number of faces is $v/n_1 + v/n_2 + v/n_3 + v/n_4$.

An infinite polyhedron can be obtained from the sodalite net (§ 7.3.10) by considering one-half the polyhedra of a space filling by truncated octahedra. Again the filled and empty space regions are identical. The cubic unit cell contains a truncated octahedron at 0,0,0 and it is fused together with its neighbors by sharing square faces, and has the same connectivity ($6 = 2h$) as the first infinite polyhedron. The reader should confirm that $v = 12$, $f = 8$ (the hexagonal faces) and $e = 24$, so that again $v - e + f = -4$ for a unit cell including three holes. This structure is also a regular (skew) polyhedron, in this case 6^4.

In § 7.4.1 (p. 323) we described the two complementary Archimedean polyhedra $4^2.6^2$ of the Linde A structure. In this structure the number of vertices in the repeat unit (unit cell) is $v = 24$. Accordingly $e = 48$ and $f = 20$. The connectivity is again six ($h = 3$ and $x = -4$) as can be seen readily from Fig. 7.38 (p. 324) and again $v - e + f = x$.

Consider next the infinite polyhedron $4^3.6$ corresponding to the zeolite rho net (Fig. 7.39, p. 325). The body-centered cubic cell has again three holes and contains 48 vertices. Note that in considering this structure as an infinite polyhedron we consider points at the origin as *inside* the polyhedron and points at 1/2,1/2,1/2 as *outside* so in *this* sense the unit cell is primitive (so care must be taken in deciding what is the repeat unit). Thus the net of the tunnels is again the 6-connected simple cubic array and $h = 3$, $x = -4$.

We also described the same set of points as the polyhedron 4.8.4.8 which was shown (Fig. 7.39) as a packing of octagonal prisms; the structure is now connected as the 8-coordinated body-centered cubic array so in this case $h = 4$ and $x = -6$ for the primitive unit as shown in Fig. A3.2. The number of vertices in the primitive unit is 24 so the number of edges is 48, the number of faces is 18 and $v - e + f = 24 - 48 + 18 = -6 = x$.

Fig. A3.2. Left: a repeat unit of **bcc**. Right: the repeat unit of the diamond structure; each bond (except the one in the center) traverses a face of the primitive unit cell.

The infinite polyhedron corresponding to the faujasite net (Fig. 7.41, p. 326) is another $4^3.6$. There are 192 vertices in the face-centered cell, or 48 in the primitive cell. The network of tunnels in the faujasite structure has a diamond connectivity so now a hole enters (and leaves) through each face of the primitive cell (see Fig. A3.2) so there are now three holes per *primitive* cell. Enumeration shows that for the primitive cell $v = 48$, $e = 96$ and $f = 44$. Again $v - e + f = -4$ as expected for $h = 3$.

So far we have considered infinite polyhedra with four polygons meeting at each vertex. In § 7.2 (Fig. 7.7) we described two nets 6.8^2. The one we called 6.8^2P is a tiling of a surface with primitive cubic connectivity ($h = 3$, $x = -4$). The repeat unit contains 48 vertices (eight hexagons) and as the net is 3-connected the number of edges is $48 \times 3/2 = 72$ and $f = 48/6 + 48/4 = 20$. Note that the repeat unit is taken as the body-centered cell; this because, just as for the polyhedron $4^3.6$ (zeolite rho) discussed above, the complementary polyhedron is the same as the original polyhedron.

The other polyhedron 6.8^2 (also shown in Fig. 7.7) called 6.8^2D also requires some care, again because the complementary polyhedron is the same. The repeat unit contains 24 vertices. The net of the structure (the surface being tiled) is that of diamond but now the unit cell contains just one "diamond" unit and the connectivity is 4 ($h = 2$, $x = -2$) (contrast the discussion of the faujasite structure above). The number of edges is $24 \times 3/2 = 36$ and the number of faces is $24/6 + 24 \times 2/8 = 10$ and $v - e + f = 24 - 36 + 10 = -2 = x$ as expected.

Other infinite polyhedra with just one kind of vertex have also been described. In Chapter 6 on the right of Fig. 6.73 (p. 276) an infinite polyhedron $3.4^2.3.4^2$ was illustrated. The reader may wish to verify that for this structure $x = -4$, $v = 12$, $e = 36$, and $f = 20$ and that again $f - e + v = x$.

In § 6.8.5 we also mentioned (p. 277) the polyhedron $3^3.4^3$ made from rhombicuboctahedra and octahedra sharing faces (not illustrated). The net of the surface being tiled is eight connected (as in **bcc**) so $h = 4$.

Examples of infinite polyhedra with five faces meeting at a vertex were described in § 7.9. These are: 3.4^4 and $3^3.6^2$ (Fig. 7.75, p. 357) and a second 3.4^4 (Fig. 7.74, p. 356); all have $h = 3$ (for the primitive cell in the last two cases).

A polyhedron 3^7 was described in § 6.8.6 (Fig. 6.78, p. 280). Again $h = 3$ for the primitive cell which contains 24 vertices, 84 edges (7-connected) and 56 faces. This polyhedron was derived from the packing corresponding to the **Al** vertices in $\mathbf{WAl_{12}}$. The reader might verify that in the latter structure nine triangles meet at every vertex and they tile a surface with the connectivity corresponding to **bcc** ($h = 4$) and can therefore be considered as an infinite polyhedron 3^9. It should be clear that many of the sphere packings of Chapter 6 can also be described as infinite polyhedra. As examples we leave the reader to verify that the **pyrochlore** packing (p. 236) and that of the atoms on the snub cubes in $\mathbf{NaZn_{13}}$ (p. 273) are both polyhedra 3^8.[1] These polyhedra are included in Table A3.1.

An interesting (and equivalent) way of considering the above polyhedra is in terms of the sums of angles of the polygons meeting at a vertex. The interior angle at the vertex of a regular N-gon is $\alpha = \pi(1 - 2/N)$. Now for a polyhedron the angular defect at each vertex k is defined as $\delta_k = 2\pi$ minus the sum of the angles α. Thus consider a vertex common to an n_1-gon, n_2-gon, ..., n_i-gon:

$$\delta_k = 2\pi[1 - \sum_i (\tfrac{1}{2} - \tfrac{1}{n_i})] \qquad \text{A3.4}$$

This formula defines δ_k for any vertex even if the individual polygons are not regular; all that matters is the n_i, the number of edges of the polygons. With δ_k so defined an alternative way of writing equation A3.3 is:

$$\sum_k \delta_k = 2\pi x \qquad \text{A3.5}$$

Thus for a finite convex polyhedron ($x = 2$) we have Descartes' formula for the sum over the k vertices:

$$\sum_k \delta_k = 4\pi \qquad \text{A3.6}$$

For a plane tiling (net) with $x = 0$:

$$\sum_k \delta_k = 0 \qquad \text{A3.7}$$

For infinite polyhedra with a topology characterized by h, the sum over the v vertices in the primitive unit gives:

$$\sum_k \delta_k = 4\pi(1 - h) \qquad \text{A3.8}$$

These formulas hold for all polyhedra of the types indicated even if there are many kinds of vertex and irregular polygons. They are quite useful for determining the numbers of different kinds of vertex that can be combined in a polyhedron (or a plane net).

To eliminate the factors of π we define $\Delta = \delta/4\pi$, then for a polyhedron with one kind of vertex, the number of vertices in the repeat unit for a given connectivity are $v = (1 - h)/\Delta$. Table A3.1 below lists some of the infinite polyhedra we have mentioned above. It may be verified by referral to the crystallographic data given in the text that indeed v is given correctly.

Yet another useful form of Eq. A3.3 can be obtained for infinite polyhedra with all vertices with the same connectivity r (the number of polygons meeting at a point). Let there be f_i polygons with i sides per repeat unit so that $\Sigma f_i = f$. The number of edges is $e = rv/2$ and, as each polygon contributes i/r vertices, $v = \Sigma i f_i / r$. Substituting these expressions in

[1] The second of these requires some care. The primitive repeat unit is a pair of (opposite hand) snub cubes. The ten (so far) unshared square faces of this unit are each shared with other pairs so $h = 10/2 = 5$.

Eq. A3.3:

$$\sum_i [2r + (2-r)if_i] = 2rx \qquad \text{A3.9}$$

With the special cases:

$r = 3$ (three-connected) $\quad \Sigma(6-i)f_i = 6x \qquad$ A3.9a
$r = 4$ (four-connected) $\quad \Sigma(4-i)f_i = 4x \qquad$ A3.9b

As polygons with faces all having r sides are dual to polyhedra with r-connected vertices, the number p_n of n-connected vertices of polyhedra made of r-gons is:

$$\sum_n [2r + (2-r)np_n] = 2rx \qquad \text{A3.10a}$$

In particular for simplicial polyhedra (all faces triangles), $r = 3$ and:

$$\Sigma(6-n) = 6x \qquad \text{A.3.10b}$$

Table A3.1. Data for some infinite polyhedra (see text for symbols). Notice that a vertex symbol can refer to more than one polyhedron.

polyhedron	name or comment	page	$-1/\Delta$	h	$v = (h-1)(-1/\Delta)$
6.8^2	6.8^2 *D*	296	24	2	24
6.8^2	6.8^2 *P*	296	24	3	48
$4^3.6$	rho, faujasite	324, 326	24	3	48
$4^2.6^2$	Linde A	323	12	3	24
4.6.4.6	analcime	376	12	3	24
6^4	regular	405	6	3	12
4^6	regular	404	4	3	8
$4^3.8$	rho, W^*8	325, 327	16	4	48
4.8.4.8	Fig. 7.39	325	8	4	24
$3^3.6^2$	Fig. 7.75	357	12	3	24
3.4^4	Figs. 7.74 and 7.75	356, 357	12	3	24
$3.4.6^2.4$	part of UB_{12} packing	356	6	3	12
$3.4^2.3.4^2$	Fig. 6.73 (right)	276	6	3	12
$3^3.4^3$	not illustrated	277	8	4	24
3^7	Fig. 6.78	280	12	3	24
3^8	pyrochlore	236	6	3	12
3^8	$NaZn_{13}$	273	6	5	24
3^9	WAl_{12}	257	4	4	12

Note that a 4-connected net has six angles at a vertex and only four of these are considered when we consider the structure as a 4-connected infinite polyhedron. As the omitted angles are an opposite pair, there can be as many as three different descriptions of a given structure as an infinite polyhedron. Thus the net A·B·C·D·E·F could be described as polyhedra A.C.B.D, C.E.D.F or A.E.B.F.[1]

A3.4 Space filling by polyhedra: nets and ring sizes

Instead of considering infinite polyhedra (tilings of surfaces with holes), we could consider the patterns arising from the vertices of a space *filling* (or tiling) by finite polyhedra. Let there be P polyhedra, F faces, E edges and V vertices. Euler's equation becomes now (see Eq. A2.18):

$$P - F + E - V = 0 \qquad \text{A3.11}$$

We will discuss infinite patterns with p, f, e and v polyhedra, faces, edges and vertices respectively per repeat unit. We start by verifying Eq. A3.11 for some simple cases.

In closest sphere packing there are two tetrahedra and one octahedron ($p = 3$) per vertex ($v = 1$). Each vertex is connected to 12 others, so (per vertex) $e = 6$. The octahedron has 8 faces and each of the tetrahedra has 4 faces, but as each face is shared with another the total number of faces is $f = (8 + 2 \times 4)/2 = 8$. In this case $p - f + e - v = 3 - 8 + 6 - 1 = 0$.

The body centered cubic structure divides space into six tetrahedra per atom so for $v = 1$, $p = 6, f = 6 \times 4/2 = 12$. To count edges we note that the edges of the tetrahedra are half cube body diagonals and cube edge lengths, so we consider the vertices as coordinated to the 8 nearest neighbors and the 6 next-nearest neighbors; accordingly $e = (8 + 6)/2 = 7$. Again $p - f + e - v = 0$.

Many intermetallic structures ("topologically close packed") are made up of a packing of tetrahedra (sharing faces) only. For these $f = 2p$ and so $p = e - v$. If further there are N_n vertices that are n-coordinated, then e is half the sum of nN_n, i.e.

$$p = \sum_n nN_n / 2 - v \qquad \text{A3.12}$$

We now apply this formula to the **β-W** structure of A_3B (§ 6.6.4) in which A is 14-coordinated and B is 12-coordinated. Per unit A_3B, $p = (3 \times 14 + 12)/2 - 4 = 23$.

Note that if we divide Eq. A3.12 on both sides by p we get the result that the number of tetrahedra per vertex is half the average coordination number minus one:

$$p/v = \sum_n nN_n / 2v - 1 \qquad \text{A3.12a}$$

An example of a 4-connected net derived from a polyhedral packing is that of sodalite (see Fig. 7.30, p. 316). Per primitive cell: $p = 1$, $v = 6$, $e = 12$ and $f = 7$ (half the number

[1] Note also that we group the angles by opposite pairs when determining the long Schläfli symbol for a 4-connected net; but, in accord with established usage, give the sizes of rings contained in angles in *cyclic* order when describing a polyhedron.

of faces of a truncated octahedron). Again $p - f + e - v = 0$. We use below the fact that there are 3 square faces and 4 hexagonal faces in the primitive cell.

For a 4-connected net $e = 2v$ and Eq. A3.11 becomes:

$$f - p = v \qquad \text{A3.13}$$

Let f_n be the number of n-faces per repeat unit ($f_4 = 3$ and $f_6 = 4$ for sodalite) then as each vertex is shared with 6 faces (a 4-connected net has six angles), the number of vertices is:

$$v = \Sigma n f_n / 6 \qquad \text{A3.14}$$

The average ring size is $\langle n \rangle = \Sigma n f_n / f$ so that from Eqs. A3.12-14:

$$\langle n \rangle = 6 - 6p/f \qquad \text{A3.15}$$

It should be verified that for the sodalite net $p/f = 1/7$ and $\langle n \rangle = 36/7$.

The derivation of Eq. A3.15 shows that we only count the shortest rings at each angle (corresponding to polyhedron faces) and not the larger rings inside the polyhedra (for example the 12-rings around the truncated octahedra in the sodalite structure).

A number of nets derived from a space filling by polyhedra were described in Chapter 7. (See the exercises § 7.12.5 for $HL4_2$). Some of those with just one kind of vertex are listed in Table A3.2 below. r is the density expressed as the number of vertices per unit volume (for unit edge length). Clearly there is not a strong correlation between average ring size and density. Generally the larger the *range* of ring size the smaller the density. The nets of § 7.6 (clathrate hydrates etc.) with 4-, 5- and 6- rings all have r about 0.57. This suggests that the geometric mean ring size should be considered.[1] This is shown in the last column of the table as $\{n\}$ and clearly correlates better with r than does $\langle n \rangle$.

Be sure to distinguish the two different descriptions of a structure (such as **rho**) as an infinite polyhedron ($4^3.6$) and as a four-connected net (4·4·4·6·8·8). Nets that can be described as polyhedron packings have no subscripts in the long Schläfli symbol.

Other 4-connected nets based on polyhedron packings were described in § 7.6. For the packings of 14-hedra, the average ring size is the same as for **sodalite** ($\langle n \rangle = 5.142$). For the packings of dodecahedra and larger polyhedra corresponding to the nets of the hydrates the average ring size is given in Appendix 4 (§ A4.5) and ranges from 5.06 to 5.11. The average ring size in all known zeolite structures (including those with more than one kind of vertex) that are derived from polyhedron packings falls in the narrow range $144/29 = 4.966 \le \langle n \rangle \le 36/7 = 5.142$. We conjecture that for any 4-connected net realizable with edges of equal length, and derived from packings of finite polyhedra, the average ring size is in the range $9/2 = 4.5 \le \langle n \rangle \le 36/7 = 5.14$.[2]

[1]Remember to count rings *per vertex*. An n-ring at a vertex is $1/n$ of an n-ring per vertex as an n-ring belongs to n vertices.

[2]The restriction to *finite* polyhedra is necessary. A net like **MAPO-39** (Fig. 7.17, p. 306) is composed of finite and infinite (in one-dimension) polyhedra and the average ring size is $16/3 = 5.33$.

Table A3.2. Average $\langle n \rangle$, and geometric meanring size $\{n\}$, and density r of some polyhedron packings.

net	symbol	$\langle n \rangle$	r	$\{n\}$
W^*4	3·8·3·12·3·12	144/31 = 4.645	0.197	3.945
W^*8	4·4·4·8·4·12	144/29 = 4.966	0.302	4.636
Linde *A*	4·6·4·6·4·8	144/29 = 4.966	0.428	4.806
faujasite	4·4·4·6·6·12	36/7 = 5.142	0.380	4.858
$HL4_2$	3·4·6·8·6·8	36/7 = 5.142	0.395	4.799
rho	4·4·4·6·8·8	36/7 = 5.142	0.426	4.917
ZK5	4·4·4·8·6·8	36/7 = 5.142	0.448	4.917
sodalite	4·4·6·6·6·6	36/7 = 5.142	0.530	5.043

In § 7.6 we mentioned the similarity between bubble packings and the hydrate structures. Experimental studies of froths of approximately equal-volume bubbles show that some of the bubble faces have four sides and that the average number of edges per face is 5.14.[1] It has been calculated[2] that for a *random* froth (i.e. with a random distribution of edge lengths) the average ring size is $6/(1 + 35/24\pi^2) = 5.23$.

Many of the 4-connected nets of interest in crystal chemistry have more than one ring of a given size at an angle. (**Diamond** has two 6-rings at each angle). They cannot be considered as packings of polyhedra with three edges meeting at each vertex and for this reason the above analysis does not apply directly to them. However we saw in § 5.1.10 (Fig. 5.16, p. 148) that **diamond** could be considered as a packing of hexagonal tetrahedra (containing divalent vertices) to produce a structure with 2 faces common to each angle (12 common to each vertex). Let there be μ faces meeting at a vertex in a 4-connected net derived from a space filling by polyhedra, then instead of A3.15 (which applies for $\mu = 6$):

$$\langle n \rangle = \mu(1 - p/f) \qquad \text{A3.16}$$

In the case of **diamond** $\mu = 12$, and for tetrahedra sharing faces $p/f = 1/2$, so Eq. A3.16 gives $\langle n \rangle = 6$ as is indeed the case.

Note that for **quartz**, which has Schläfli symbol $6{\cdot}6{\cdot}6_2{\cdot}6_2{\cdot}8_7{\cdot}8_7$, $\mu = 20$ and $\langle n \rangle = 80/11$. If we were to consider that net as derived from a packing of polyhedra, Eq. A3.16 shows that $p/f = 7/11$; so some, at least, of the "polyhedra" have less than four faces.

A3.5 Coordination sequences and topological density

In Chapter 7 the number n_k of kth topological neighbors of a vertex of a net was defined. The sequence of numbers n_k is called the coordination sequence. A measure of the local topological density is defined as ρ_k which is the sum of all the topological neighbors in the first k shells divided by k^3.

[1]For illustrations of bubble shapes see E. B. Matzke, *Amer. J. Botany* **33**, 58 (1946).
[2]J. L. Meijering, *Philips Res. Rep.* **8**, 270 (1953).

$$\rho_k = \sum_{i=1}^{k} n_i / k^3$$

A3.17

As n_k is often given by a quadratic in k, $n_k = ak^2 + bk + c$ (see Chapter 7 for examples), the limit of ρ as $k \rightarrow \infty$ is the global topological density $\rho_\infty = a/3$. For uninodal 4-connected nets ρ_∞ seems to be a rational number between 1/3 and 2 and correlates well with the geometrical density.[1]

A3.6 Enumerating and identifying nets

It is difficult to enumerate nets in a systematic and comprehensive way. The problem can be considered purely topological, or it could be required that the nets be *realizable*. A realizable net is defined to be one that can be made in Euclidean space with equal edges and all shortest distances between vertices corresponding to edges. The problem then becomes one of enumerating sphere packings. But note that some zeolite nets have as many as a dozen topologically-distinct vertices.

The topology of a realizable net is very simply specified. Each vertex must be connected to others either in the same unit cell or one of the 26 contiguous ones (i.e. the 6 sharing a cell face, the 12 sharing a cell edge and the 8 sharing a cell corner). Fig A3.3 shows the repeat unit of **diamond** (compare Fig. A3.2). The vertices in the primitive cell are labeled "1" and "2" and are connected to each other; each "1" is also connected to a "2" in a neighboring cell related by a primitive lattice translation in the x, y or z direction, and similarly for each "2." We could code this information in what we call a *connectivity table* as follows:

1	2 [000]	2 [100]	2 [010]	2 [001]
2	1 [000]	1 [$\bar{1}$00]	1 [0$\bar{1}$0]	1 [00$\bar{1}$]

Note that the second line is redundant in the sense that it follows immediately from the first. In general for an n-connected net with v vertices in the repeat unit, we need only specify the connectivity of the $nv/2$ edges in the repeat unit. In what follows we omit redundancies in the connectivity tables.

The regular Y^* (**SrSi$_2$**) net has four vertices in the primitive cell and the connectivity is also shown in Fig. A3.3. The connectivity table is:

1	2 [000]	3 [000]	4 [000]
2		3 [100]	4 [010]
3			4 [001]

[1]For more on coordination sequences for 4-connected nets see M. O'Keeffe, *Zeits. Kristallogr.* **196**, 21 (1991) and M. O'Keeffe & S. T. Hyde, *Zeits. Kristallogr.* , 1996).

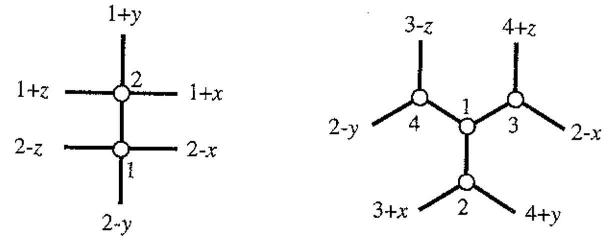

Fig. A3.3. The connectivity of **diamond** (left) and Y^* (**SrSi$_2$**) nets (right).

The connectivity table of the **quartz** net is:

1	2 [000]	2 [100]	3 [000]	3 [010]
2			3 [011]	3 [$\bar{1}$01]

It should be noted that the topology of the net is completely specified by the connectivity table and all topological properties such as numbers of rings and coordination sequences may be obtained from it. Unfortunately as both the numbering of the vertices ($v!$ possibilities) and the labeling of directions are arbitrary, there are many apparently different connectivity tables that can describe the same net. A further difficulty in crystal structures is that frequently the crystallographic unit cell is larger than the topological repeat unit. In practice coordination sequences combined with Schläfli symbols (both of which are readily found by computer from the connectivity table) serve to identify a net with some reliability.

This method of describing nets allows ready generalization to higher dimensions (see references § A3.9). An example of the many interesting unsolved problems in this area is that of identifying the regular n-dimensional m-connected nets ($3 \leq m \leq n + 1$) corresponding to the three-dimensional nets Y^* ($n = 3$, $m = 3$) and **diamond** ($n = 3$, $m = 4$).

A3.7 Curvature and periodic minimal surfaces

There is currently great interest in periodic minimal surfaces (see § A3.9 for references) in a variety of contexts. We touch on some aspects of relevance to crystal structure here, starting with some elementary definitions and a discussion of *curvature*—a concept that has not entered into our discussion so far as we have been considering discrete, rather than continuous, structures.[1]

The curvature at a point P on a two-dimensional curve can be defined informally as follows (see Fig. A3.4). Draw a circle through P and two neighboring points P_1 and P_2 on

[1]We are content simply to state results that are derived in standard mathematics texts. Two excellent books (see Book List) are *Introduction to Geometry* by H. S. M. Coxeter and *Geometry and the Imagination* by D. Hilbert & S. Cohn-Vossen. We have borrowed heavily from the latter for this section.

either side of P and on the curve (three points define a circle). As P_1 and P_2 approach closer and closer to P we will obtain a limiting circle with radius r. r is called the radius of curvature at P and its reciprocal $k = 1/r$ is called the curvature. It should be clear that the curvature of a straight line is zero and that the curvature of a circle is constant.

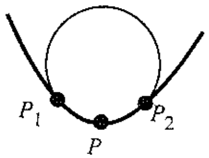

Fig. A3.4. Defining the curvature at a point on a curve (see text).

Now consider a three-dimensional surface such as an ellipsoid (Fig. A3.5) or a hill top. We can find two plane sections through the surface such that the lines of intersection are (a) of maximum curvature, k_1 and (b) of minimum curvature, k_2. These are known as the *principal curvatures*. Their product $K = k_1k_2$ is known as the *Gaussian curvature*. We adopt the convention that as the centers of curvature are "inside" the surface, the curvatures are considered positive.[1]

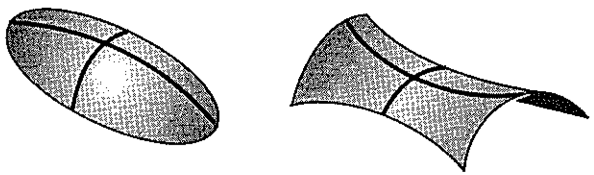

Fig. A3.5. Left: illustrating a point of positive Gaussian curvature and the directions of principal curvatures (heavy lines; the point in question is the intersection of these two lines). Right: similarly illustrating a point of negative Gaussian curvature.

An important property of the Gaussian curvature of a surface is that it remains invariant under bending; bending in this context referring to a deformation in which distances and angles on the surface remain invariant.[2]

The *mean curvature*, $H = (k_1 + k_2)/2$. A sphere has constant mean curvature and constant Gaussian curvature and is the only closed surface with these properties. The

[1]It may happen at a point on a surface that the curvature is the same in all directions, so that the principal directions are indeterminate. Such a point is called an *umbilical point*. All points on a sphere or a plane are of this type. More generally there are isolated umbilical points on a surface (there are four on an ellipsoid). If one of the principle curvatures is zero at a point, the point is referred to as *parabolic*.

[2]Thus imagine a plane sheet of paper (with zero Gaussian curvature) being rolled up into a cylinder, the minimum curvature (in a direction parallel to the axis of the cylinder) remains zero; so too does the Gaussian curvature. The maximum curvature becomes equal to the reciprocal of the radius of the cylinder

sphere is also the solid with smallest total mean curvature for a given surface area; the total mean curvature being the mean curvature integrated over the surface.

We turn now to a hyperbolic surface (or a mountain pass or a saddle) as shown schematically in Fig. A3.5 (right). The two directions along which the principal curvatures are measured are indicated. The centers of the circles defining the radii of curvature are now on opposite sides of the surface so we adopt the convention that now one of the curvatures is negative. At such a point on such a surface the Gaussian curvature is negative and the mean curvature may be positive, negative *or zero*.

A *minimal* surface is one for which the principal curvatures are everywhere equal in magnitude but opposite in sign; i.e. the mean curvature is everywhere zero. A film of soap solution formed inside an arbitrarily-shaped loop of wire forms a bounded minimal surface.

The *integral curvature* of a surface is the integral of the Gaussian curvature over the surface. A remarkable result (the Gauss-Bonnet theorem) is that this surface integral is simply related to the characteristic of the surface (discussed in § A3.2):[1]

$$\int_S K \cdot d\sigma = 2\pi\chi \qquad \text{A3.18}$$

Thus the Gaussian curvature of a sphere ($\chi = 2$) is $1/r^2$ and the integral over the surface (area $= 4\pi r^2$) $= 4\pi$.

A *geodesic* line connecting two points on a surface represents the shortest line *on the surface* joining the two points.

The surfaces of infinite polyhedra are (faceted) infinite surfaces, and some, at least, are closely related to periodic minimal surfaces.

The cuprite (Cu_2O) structure can be described as two interpenetrating nets. Imagine the nets to be replaced by hollow tubes of elastic material and then that the tubes were inflated equally until they met at a surface. The surface (clearly periodic) divides space into two halves. It also has negative integral curvature and (less obviously) zero mean curvature, and is an example of a periodic minimal surface. As the topology of the labyrinth of each set of tunnels (inflated tubes) is the same as that of the diamond net, this is usually called the D surface.[2] The symmetry of the surface is the same as that of cuprite ($Pn\bar{3}m$).

A second minimal surface can be derived from two interpenetrating tubes with a six-connected simple cubic topology (Fig. A3.6). Again the surface separating the two sets of equally inflated tubes (in contact) is a periodic minimal surface, this time designated P. The symmetry is $Im\bar{3}m$. An alternative way to generate this surface is to arrange red and blue balloons as in **CsCl**; the P surface will *separate* the red and blue balloons after they are all equally inflated. Red balloons will touch red and blue will touch blue also; but the P surface corresponds to the boundary between red and blue. An approximation to the P

[1]An interesting property of a convex closed surface (such as an ellipsoid) is that it can not be bent (in the sense used above). Recall that a convex polyhedron is rigid (§ 5.6.3). When a football is deformed by kicking, the surface must be *stretched* as well as bent. Those who haven't tested it will be astonished by the rigidity of a plastic globe. Or, for that matter, of a ping pong ball.

[2]In the older literature this is also called the F surface.

surface can be obtained by packing truncated octahedra to fill space as illustrated in Fig. 7.30 (p. 316). The hexagonal faces approximate the minimal surface.

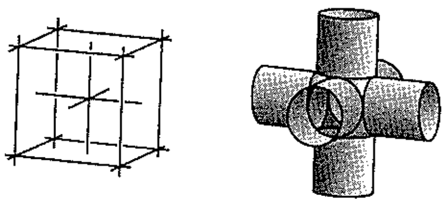

Fig A3.6. Left: part of two interpenetrating network of rods with cubic symmetry. Right: part of one set of rods shown partly "blown up" to form intersecting tubes.

A third minimal surface that is often discussed is known as Schoen's gyroid. The thought experiment suggested to the reader is now to inflate the two sets of cylinders in the intergrowth packing **γ-Si** (§ 6.7.3). The surface separating the two sets of equally inflated cylinders (no longer cylinders when "blown up") is the gyroid. The symmetry is $Ia\bar{3}d$; because of this, the surface is particularly difficult to illustrate satisfactorily. The references in § A3.9 may be consulted for help.

Much of the interest in crystal chemistry arises from the fact that some structures can be considered as tilings of periodic minimal surfaces. A good example of a 4- connected tiling of the *P* surface by hexagons and squares is provided by the net of the zeolite rho structure (see Fig. 7.39, p. 325—if the framework shown in the figure is mentally replaced by a curved surface one gets an idea of the appearance of the *P* surface). An example of a 3-connected tiling of the same surface by a hexagons and octagons is the 6.8.8 net of Fig. 7.7 (p. 297). A similar tiling of the *D* surface is the 6.8.8 net also shown in Fig. 7.7. The surface of the faujasite structure (Fig. 7.41, p. 326) is topologically the same as the *D* surface. Perhaps the most striking example is provided by the framework of the zeolite analcime (Exercise 7.12.6) which can be described as a tiling of the gyroid. This last structure is listed as an infinite polyhedron in Table A3.1.

A3.8 Some conjectures about numbers and sizes of rings

The following observations (in this and the next paragraph) apply *only* to uninodal 4-connected nets and the statements should be construed as conjectures. It is possible that proving (or disproving!) them could lead to better constraints on the numbers and sizes of rings in 4-connected nets in general. For convenience the shortest ring at an angle is referred to as a SR. For 4-connected nets at least one of the SR's is a 6-ring or larger. For nets realizable with equal length edges corresponding to shortest distances between vertices at least one of the SR's is a 6-circuit or smaller. (Our "dense" net of § 7.5.1 contains only 7-rings but cannot be realized with shortest distances only corresponding to equal length edges). The largest SR is a 20-ring and the largest ring is a 24-ring.

In a net containing 5-rings there is always exactly one 5-ring per vertex.[1] In nets containing 10-rings, the total number of such rings meeting at a vertex is always a multiple of 5, and in a net containing 7-rings or 14-rings, the total number of such rings meeting at a vertex is always a multiple of 7. Uninodal 4-connected nets containing 11-, 13-, 15-, 17-, 19-, 22- or 23-rings have not been described.

Although the number of rings meeting at a vertex must be finite, the number can be quite large. Here for entertainment, and to test ring-counting skills of computer programs, are coordinates for a uninodal 4-connected net (Schläfli symbol $4 \cdot 6_2 \cdot 4 \cdot 6_3 \cdot 6 \cdot 18_{1422}$) with two 4-rings, six 6-rings and 3615 18-rings meeting at each vertex (1422 of the 18-rings are the shortest rings contained in one of the angles):

$R\bar{3}c$, $a = 6.700$, $c = 1.881$, $r = 0.984$
vertices in 36 *f*: (*x*,*y*,*z* etc.), $x = 0.029$, $y = 0.445$, $z = 0.0$

In § A3.6 we mentioned that it might be interesting to examine nets in *n*-dimensions. n+1-connected nets [with $n(n + 1)/2$ angles at each of the vertices] that are generalizations of **diamond** and **sodalite** have been described by M. O'Keeffe, *Acta Crystallogr.* A**47**, 748 (1991). The generalizations of diamond are all regular nets with vertex symbols $(6_{n-1})^{n(n+1)/2}$; that paper may be consulted for coordinates. Some connectivity tables are given below for other simple *n*-dimensional *m*-connected nets. The challenge is to derive coordinates for uniform edge lengths and to derive the systematics of the connection between ring size and dimensionality and connectivity. Note that $3 \le m \le n+1$. Is there a regular net for every *n* and *m*? How many?

The connectivity table for a regular 3-connected 4-dimensional net $12_4 \cdot 12_4 \cdot 12_4$ is:

1	2 [0000]	4 [0000]	6 [0000]
2		3 [0000]	5 [0000]
3		4 [1000]	6 [0100]
4			5 [0010]
5			6 [0001]

This net, which also has fourteen 14-rings meeting at each angle (3 per vertex), might be compared with the 3-dimensional regular net (Y^*) $10_5 \cdot 10_5 \cdot 10_5$ (p. 295).

A very simple uniform (but not regular) 4-connected, 4-dimensional net with vertex symbol $8_6 \cdot 8_6 \cdot 8_7 \cdot 8_7 \cdot 8_7 \cdot 8_7$ has connectivity table:

1	2 [0000]	2 [1000]	3 [0100]	3 [0010]
2			3 [0000]	3 [0001]

A regular 4-connected 6-dimensional net, $10_{10} \cdot 10_{10} \cdot 10_{10} \cdot 10_{10} \cdot 10_{10} \cdot 10_{10}$, is:

[1]This means five 5-rings (each of which belongs to five vertices) meet at each vertex and the net cannot be composed entirely of 5-rings (even though the *average* ring size may be 5). In the nets of § 7.6, which have more than one kind of vertex there is more than one 5-ring per vertex; for example the type II hydrate net has 18/17 5-rings per vertex.

1	2 [000000]	3 [000000]	4 [000000]	5 [000000]
2		3 [100000]	4 [010000]	5 [001000]
3			4 [000100]	5 [000010]
4				5 [000001]

A3.9 References

There is a large literature on the topology of nets and polyhedra. Some references were given in § 7.11.10. The classic references are A. F. Wells' works: *Three-dimensional Nets and Polyhedra* [Wiley, New York (1977)] and *Further Studies of Three-Dimensional Nets* [American Crystallographic Association Monograph No. 8 (1979)].

The number and sizes of rings in 4-connected nets has been discussed by C. S. Marians & L. W. Hobbs, *J. Non-Crystalline Solids* **124**, 242 (1990); L. Stixrude & M. S. T. Bukowinski, *Amer. Mineral.* **75**, 1159 (1990); K. Goetzke & H.-J. Klien, *J. Non-Crystalline Solids* **127**, 215 (1991); M. O'Keeffe, *Zeits. Kristallogr.* **196**, 21 (1991). On the density of three-dimensional nets and its relationship to ring size, see S. T. Hyde, *Acta Crystallogr.* A**50**, 753 (1994).

The topological characterization of linkages of polyhedra has also given rise to quite a large literature. Some recent papers include E. Parthé, *Zeits. Kristallogr.* **189**, 101 (1989); E. Parthé & B. Chabot, *Acta Crystallogr.* B**46**, 7 (1990); N. Engel, *Acta Crystallogr.* B**47**, 217 (1991).

A topological topic, which we don't discuss, but which is nevertheless of considerable interest, is that of *percolation* in nets. A good introduction to this topic is D. Stauffer, *Introduction to Percolation Theory* [Taylor & Francis (1985)].

For applications of topology to molecular chemistry see *Chemical Applications of Topology and Graph Theory* [R. B. King (ed.) Elsevier, Amsterdam (1983)], and *Graph Theory and Topology in Chemistry* [R. B. King & D. Rouvray, (eds.) Elsevier, Amsterdam (1987)].

The literature on periodic minimal surfaces is rapidly expanding. A good introduction is *Crystalline frameworks as hyperbolic films* by S. T. Hyde [in *Defects and Processes in the Solid State: Geoscience Applications*, J. N. Boland & J. D. Fitz Gerald (eds.), Elsevier, (1993)]. Other references (which should be consulted for illustrations) that emphasize crystal-chemical applications are: S. T. Hyde & S. Andersson, *Zeits. Kristallogr.* **174**, 225 and 237 (1986); H. G. von Schnering & R. Nesper, *Angew. Chem. (Int. Ed.)* **26**, 1059 (1987), S. Andersson, S. T. Hyde, K. Larsson & S. Lidin, *Chem. Rev.* **88**, 221 (1988); W. Fischer & E. Koch, *Acta Crystallogr.* A**45**, 726 (1989). E. Koch & W. Fischer, *Acta Crystallogr.* A**46**, 33 (1990). The last two references describes a number of surfaces. A number of applications to chemistry, physics and biology are described in a collection of papers in *J. Phys.* C7 (1990).

APPENDIX 4

LARGE POLYHEDRA

A4.1 Introduction

In Chapter 5 we discussed some polyhedra with emphasis mainly on those polyhedra with a small number of vertices that commonly occur as coordination figures. Here we discuss some larger polyhedra (with more than 20 vertices) that are of increasing interest in several areas of chemistry and biochemistry.[1] First we review some basic material.

Simple polyhedra are those for which three edges meet at every vertex; clearly for V vertices there are $3V/2$ edges, so the number of vertices is even. *Simplicial* polyhedra have only triangular faces. It should be obvious that they are the duals of simple polyhedra.

Polyhedra with F faces, all of which are either m-gons or $(m+1)$-gons, where $m = [6 - 12/F]$,[2] are sometimes called *medial*. Their duals are simplicial polyhedra with m- and $(m+1)$-connected vertices. For $m \leq 4$ these latter are topologically equivalent to the deltahedra of § 5.1.6 (i.e. they, and only they, can be realized with equilateral triangles as faces). The interest in this appendix is mainly with the case of simple medial polyhedra with $m = 5$, i.e. those simple polyhedra with pentagon and hexagon faces (and their duals). For convenience we refer to these polyhedra as 5-6 polyhedra in what follows. In general, polyhedra cannot be realized with all faces as plane regular polygons although they are often "almost" regular polygons.[3]

Non-crystallographic symmetries are commonly encountered; as well as icosahedral symmetry, 5-fold and $\overline{10}$ and $\overline{12}$ axes often occur. Now the (probably more familiar) Schoenflies symmetry symbols are more appropriately used. Commonly encountered non-crystallographic symmetries in Hermann-Mauguin notation are $D_{6d} = \overline{12}m2$, $D_{5h} = \overline{10}m2$ and $D_{5d} = \overline{5}m$. We use the number of vertices to identify the polyhedron as this is generally more useful in chemistry (i.e. it is the number of atoms making up the polyhedron); the notation V_N refers to a polyhedron with N vertices.

A4.2 5-6 Polyhedra

For 5-6 polyhedra there are exactly 12 pentagon faces and for V vertices there are $E =$

[1]See *e.g.* T. G. Schmaltz *et al.*, *J. Amer. Chem. Soc.* **110**, 1113 (1988) for chemical applications and D. L. D. Caspar & A. Klug, *Cold Spring Harbor Symp. Quant. Biol.* **27**, 1 (1962) for biological applications.

[2]Here brackets indicate rounding down to the nearest integer.

[3]The dodecahedron and the truncated icosahedron are the only 5-6 polyhedra that can be constructed from regular plane polygons. See V. A. Zalgaller, *Convex Polyhedra with Regular Faces* [Consultants Bureau, New York (1969)].