The Football

1. From Euclid to Soccer it is ...

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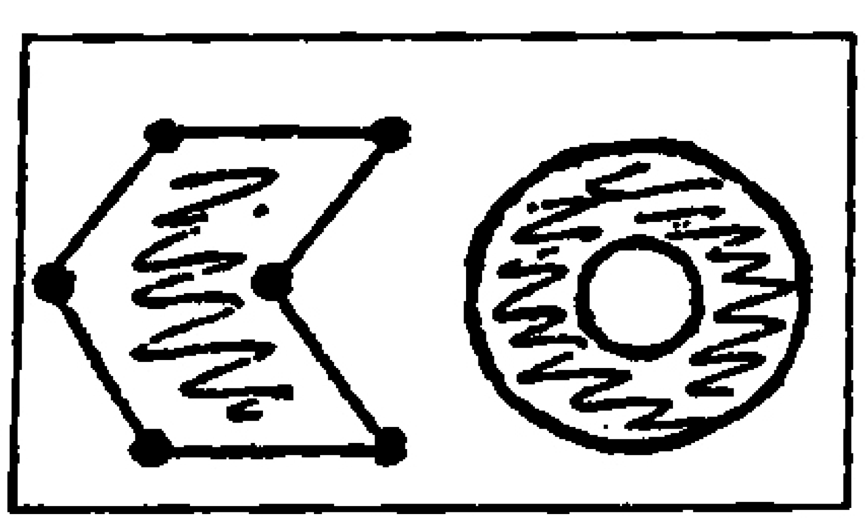
A **football** is a 3-dimensional convex polyhedron with each face a regular pentagon or a regular hexagon and with at least one hexagonal face.

This article is in two parts. In this first part, we will prove that a football exists and is unique and in the second, we identify its group of symmetries. (We will incidentally do similar things for the platonic solids to some of which the football is closely related.) I heard of this problem from Amit Roy of TIFR, Mumbai. The ideas used in the proof of the existence and uniqueness are also his. Most of the other proofs presented here can be found in Gallian (1999) and Coxeter (1948).

A *convex set* is a set $C \subseteq I\!R^3$ such that $A, B \in C \Rightarrow AB \subseteq C$. (Here AB denotes the segment joining A and B and we will study only convex subsets of $I\!R^3$.) Intersection of any family of convex sets is convex. There are plenty of examples: the empty set, a point, a line, a line segment, a plane, a half plane, a quadrant, a disc, an elliptic region, a half space (i.e., points lying on one side of a plane), a ball, a pyramid and a prism with a convex base (right or not). See V S Sunder's articles [3] for a discussion on various aspects of convexity. The five platonic solids are convex. The two figures in *Figure* 1 are not. Note that the hexagon shown in the figure is equilateral but not equiangular. By a *regular polygon* we mean a plane polygon which is both equilateral and equiangular.

Figure 1.



A *convex polyhedron* is a finite intersection of closed half-spaces. The disc and the cylinder are not convex polyhedra.

A *convex polytope* is a convex polyhedron which is bounded.

By a *regular solid* we mean a convex polyhedron such that the faces are all regular, equal polygons and the same number of faces occurs at each vertex. It was already known 2400 years ago that there are exactly five such solids, viz. the platonic solids, see *Box* 1. The Greeks associated the tetrahedron (this means a solid bounded by four faces) with fire, the cube with earth, the octahedron with air, the icosahedron with water and the dodecahedron with universe or cosmos. The study of dodecahedron was considered dangerous and restricted during some period. On the other hand, the dodecahedron was used as a toy at least 2500 years ago.

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Apparently Theaetetus "first wrote on the 'five solids' as they are called" around 380 B.C. and probably knew that there are exactly five regular solids. Around 320 BC, Aristaeus (known as 'the elder') wrote a book called *Comparison of the five regular solids.* Euclid wrote his *Elements* around 300 BC.

In the diagrams in *Box* 1, the symbol $\{p, q\}$, known as a Schlafli symbol, means that each face is a regular p-gon and that there are q faces at each vertex. Of the five regular solids, the cube and octahedron are duals of each other, the dodecahedron and the icosahedron are duals of each other and the tetrahedron is self-dual in the following sense: if we start with the cube and form a new solid by taking a new vertex at the centre of each face of the cube and joining two new vertices by an edge iff they are centres of adjacent faces of the cube, we get the octahedron. If we do the same starting from the octahedron we get back the cube; similarly for the dodecahedron and the icosahedron. (This duality is the same as that used for planar maps in graph theory.)

Incidentally, the tetrahedron, cube and octahedron are the crystal structures of sodium sulphantimoniate, sodium chloride (common salt) and chrome alum, respectively.

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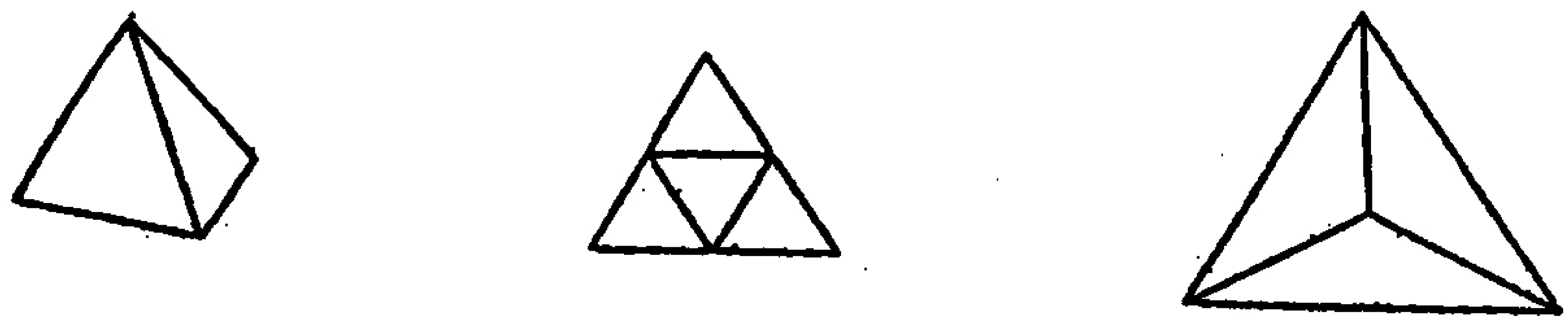
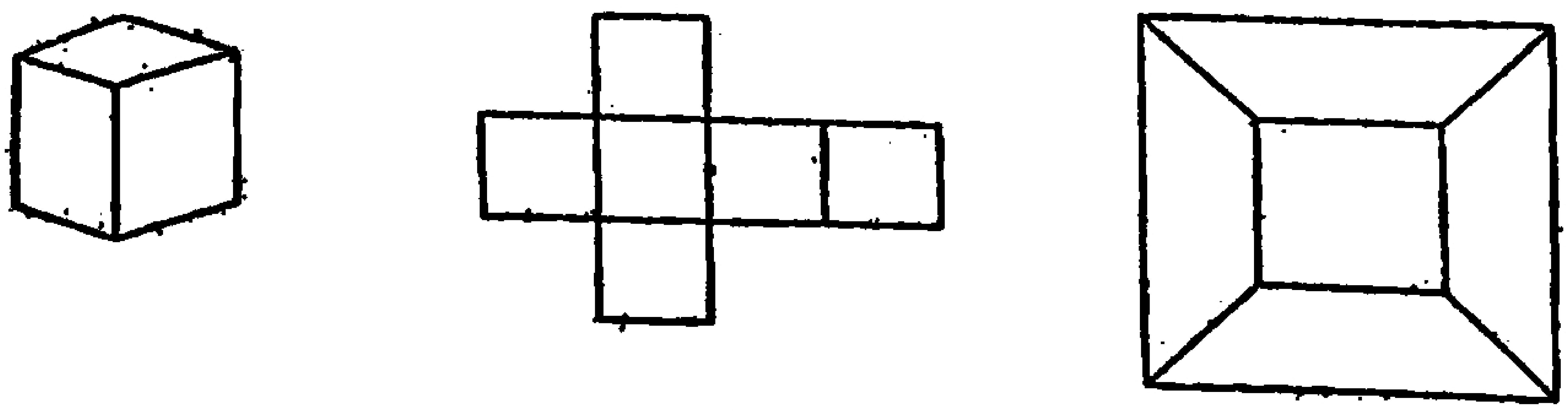
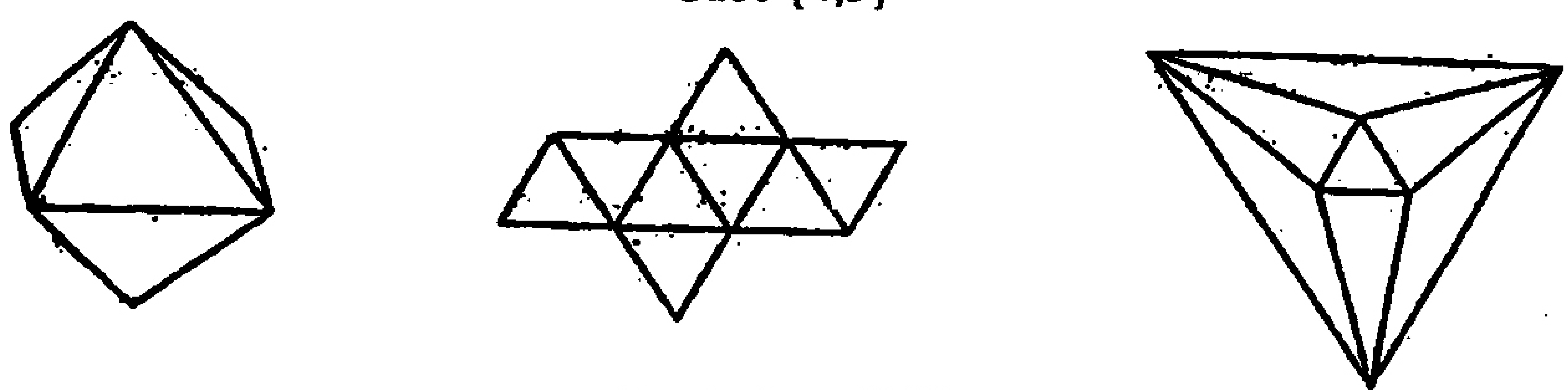
Box 1. Introduction to Geometry by H S M Coxeter, 1961.



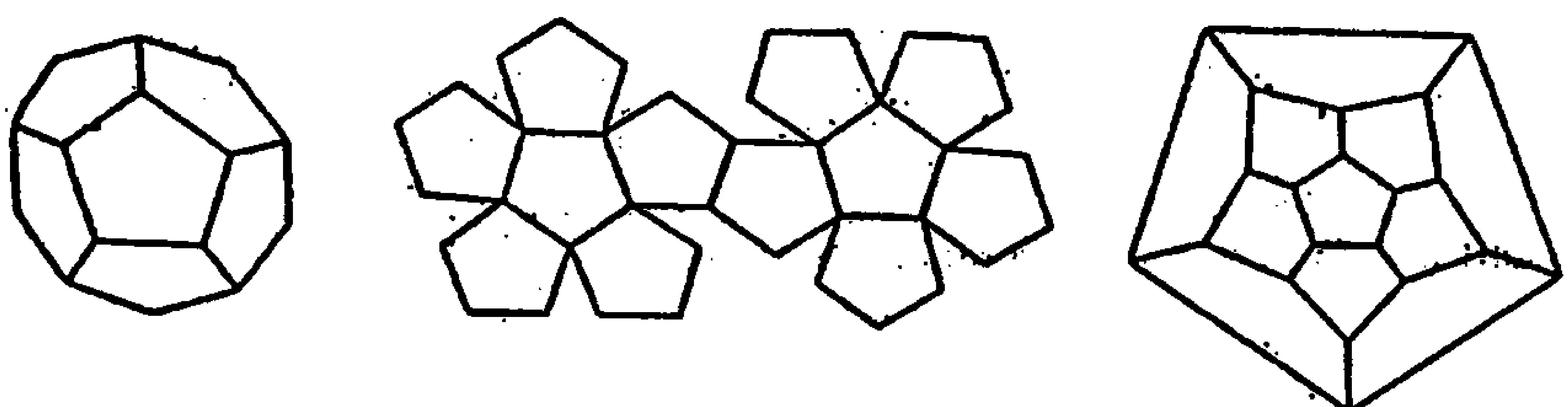
Tetrahedron {3,3}



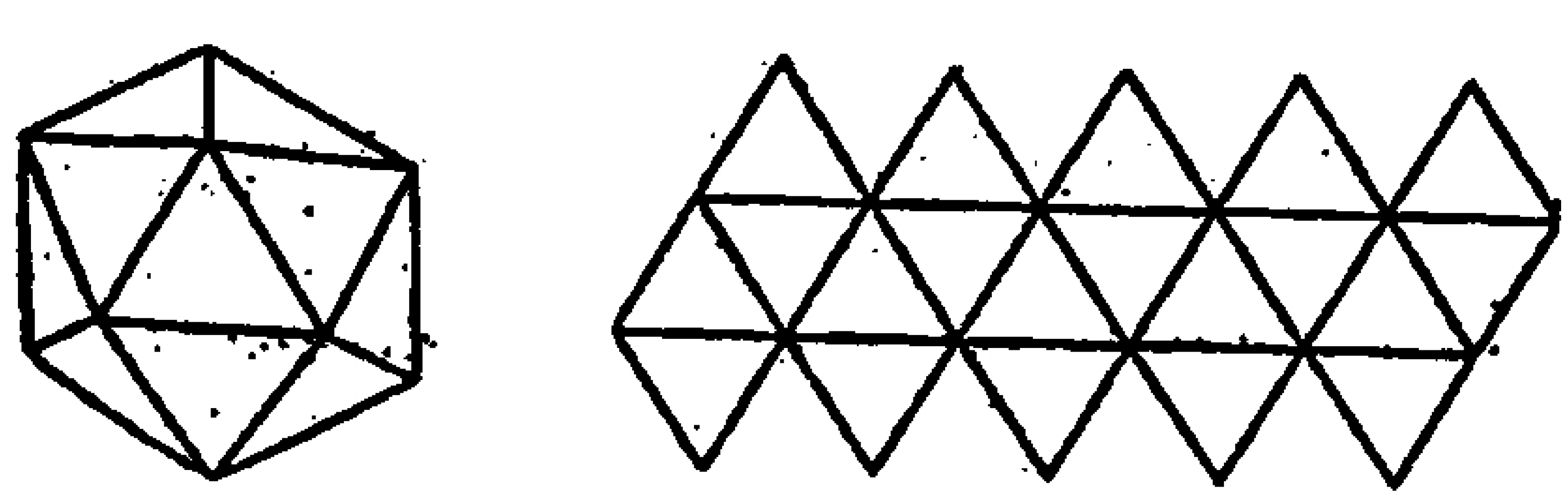
Cube {4,3}

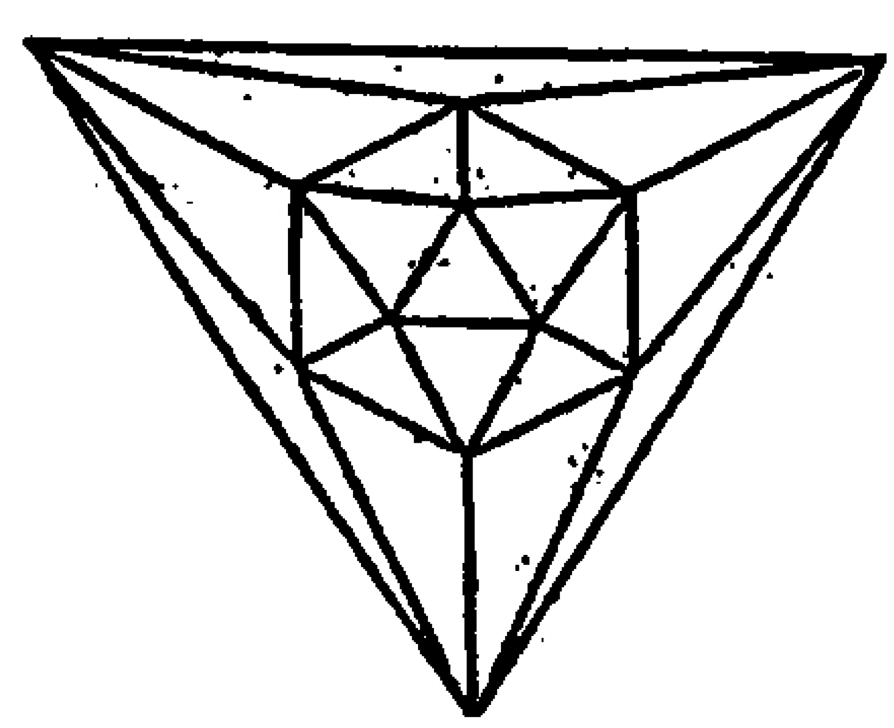


Octahedron {3,3}



Dodecahedron {5,3}





Icosahedron {3,3}

The skeletons of certain microscopic sea animals called *Circorrhegma dodecahedra* and *Circogonia icosahedra* (and some other viruses) are in the shape of a dodecahedron and an icosahedron, respectively, see Gallian (1999) and Coxeter (1948). In 1985, Robert Curl, Richard Smalley and Harold Kroto created a form of carbon by using a laser beam to vapourize graphite. The resulting molecule has 60 carbon atoms arranged in the shape of a football. Curl, Smalley and Kroto received the Nobel Prize for this discovery in 1996.

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We now show briefly how vertices, edges and faces, which we all understand intuitively, can be defined formally. An *extreme subset* of a convex set C is a convex set $D \subseteq C$ such that $C \in D, C \in AB, C \neq A, C \neq B$ and $A, B \in C \Rightarrow A, B \in D$.

Such an extreme subset is called a *vertex, edge* or *face* accordingly as it is of dimension 0, 1 or 2. The dimension of a non-empty proper subset of $\mathbb{R}^3$ is 0 if it is a singleton, 1 if it is contained in a line and is not a singleton and 2 if it is contained in a plane and is not contained in any line. Note that a cube has 8 vertices, 12 edges and 6 faces.

Recall the Krein–Milman theorem which was discussed in V S Sunder's article [3]. A simple consequence of the theorem is: *A convex polytope has finitely many vertices and is their convex hull.* Conversely, the convex hull of finitely many points is a convex polytope.

Every extreme subset of a convex polytope C is the intersection of C with a plane P such that C is contained in a half-space corresponding to P. An extreme subset of an extreme subset is an extreme subset. Each edge of C is the line segment joining two vertices of C and is on the boundary of exactly two faces. Each face of C is a convex polygon formed by some edges of C.

Since each face of a football is bounded, it can be proved that the football is bounded and, so, is a convex polytope. We omit this proof.

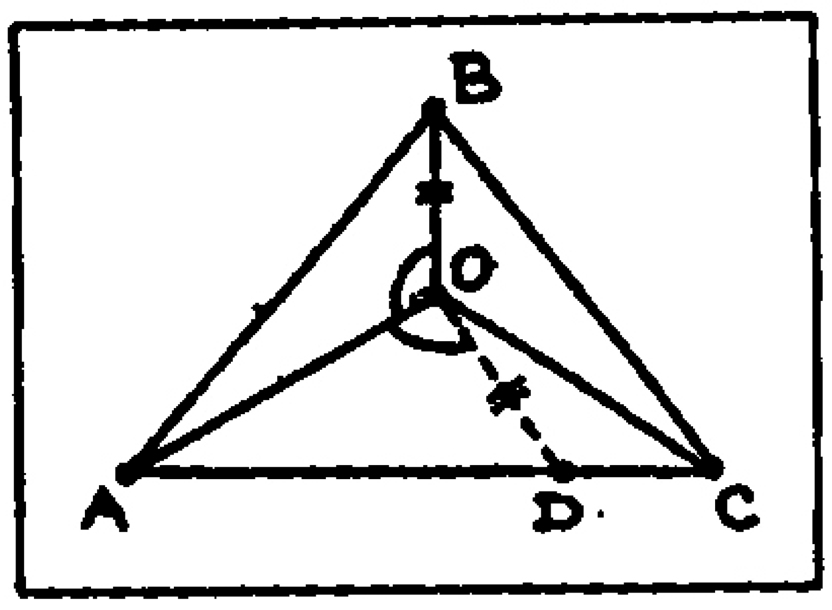


Figure 2.

From now on, we consider only convex polytopes with dimension 3. Also, whenever we talk of $\angle ABC$, we shall mean that angle which is between 0° and 180°. We prove the uniqueness of a football first assuming its existence and later prove the existence. We start with a simple result which is intuitively obvious.

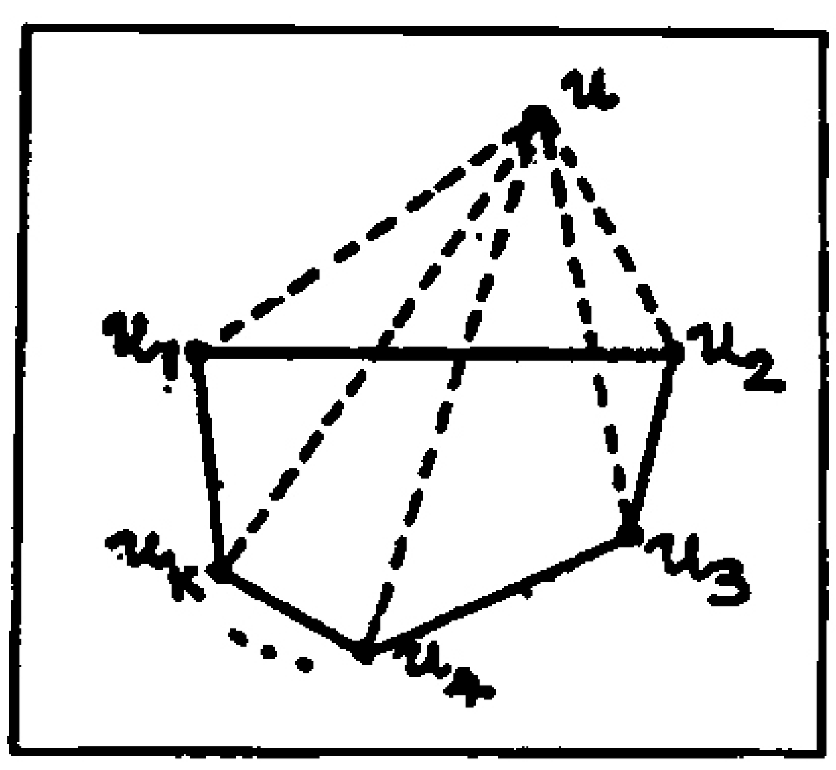
Lemma 1. There are at least 3 edges at every vertex of a convex polytope.

Lemma 2. (Euclid, XI.20) Suppose A, B, C and O are not coplanar. Then $\angle AOB + \angle BOC > \angle AOC$.

Proof: We may assume that $\angle AOC > \angle AOB$, for, otherwise the result is trivial. Let D be a point in the plane AOC such that $\angle AOD = \angle AOB$ and $OD = OB$. Refer to *Figure* 2. We may take C to lie on AD extended. Now triangles AOB and AOD are congruent, so $AB = AD$. Since $AB + BC > AC$, we get $BC > AC - AD = DC$. So comparing triangles DOC and BOC, we get $\angle BOC > \angle DOC$. So $\angle AOB + \angle BOC > \angle AOD + \angle DOC = \angle AOC$. □

Lemma 3. (Euclid, XI.21) The sum of the angles in all the faces at any vertex u of a convex polytope with dimension 3 is less than 360°.

Figure 3.



Proof: We may take the faces at u to be $u_i u u_{i+1}, i = 1, 2, \ldots, k$ where $u_1 u_2 \ldots u_k$ is a convex polygon in a plane P and $u \notin P$. See *Figure* 3. Let us call the angles of the type $u u_i u_{i-1}$ or $u u_i u_{i+1}$ *base angles*, angles of the type $u_{i-1} u_i u_{i+1}$ *polygonal angles* and angles of the type $u_i u u_{i+1}$ *vertical angles.* Using the result that the sum of the angles in a triangle equals π, we see that the sum of the base angles and the vertical angles is $k\pi$. Using the fact that the sum of the two base angles at u_i is greater than the polygonal angle at u_i, we see that the sum of all the base angles is greater than the sum of all the polygonal angles which is $(k-2)\pi$. So the sum of all the vertical angles is less than 2π. This proves the lemma. □

It may be worth noting here that the following simple 'proof' for the preceding lemma does not work always: let v be the foot of the perpendicular from u to the plane P. We may assume that v lies inside the convex polygon $u_1u_2\ldots u_k$. Then, it is perhaps natural to guess that angle u_iuu_{i+1} < angle u_ivu_{i+1} for each i, and so the lemma would follow. But, the inequality stated can be false if one of the angles vu_iu_{i+1} and $vu_{i+1}u_i$ is greater than a right angle (to get a counter-example, take angle vu_iu_{i+1} close to 180° and length uv moderately large).

At every vertex of a football, there is exactly one pentagonal face and so there are two hexagonal faces.

Next, we can single out an observation about the football.

Theorem 1. At every vertex of a football, there are exactly three faces and so three edges.

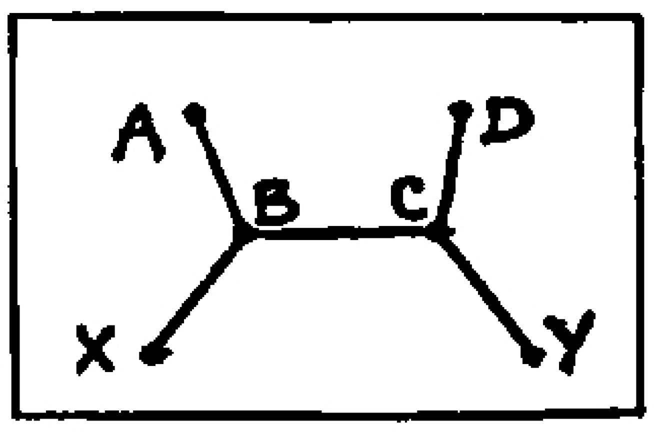
Proof: Since the angles in a regular pentagon are 108° each and the angles in a regular hexagon are 120° each, there cannot be more than three faces at any vertex by lemma 3. So the theorem follows from lemma 1. □

Lemma 4. If two regular polygons $\ldots ABCD \ldots$ and $\ldots XBCY \ldots$ in $\mathbb{R}^3$ have a common edge BC (see *Figure* 4), then $\angle ABX = \angle DCY$.

Proof: We first clarify that a regular polygon is, by definition, planar. Now triangles ABX and DCY are congruent since each is the reflection of the other in the plane P perpendicularly bisecting BC. Thus, the lemma follows. □

Here is another observation about the football.

Figure 4.



Theorem 2. At every vertex of a football, there is exactly one pentagonal face (and so there are two hexagonal faces).

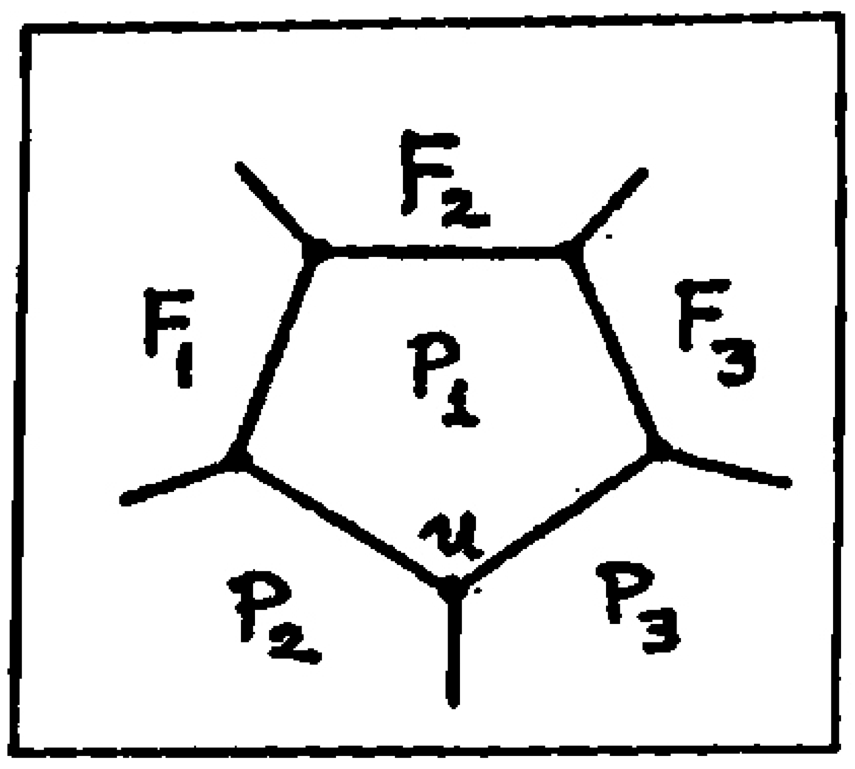


Figure 5.

Proof: Suppose that at a vertex u there are three pentagonal faces P_1, P_2 and P_3. See *Figure* 5. Then, lemma 4 applied to P_1 and P_2 gives F_1 is a pentagon. Similarly, F_2 and F_3 are pentagons. Since we can go from P_1 to any face by passing along adjacent faces, it follows that all faces are pentagons, a contradiction. (Incidentally, there is a convex polytope called dodecahedron with 12 faces all of which are regular pentagons.)

Suppose next that at a vertex u there are two pentagonal faces P_1 and P_2 and a hexagonal face H_1 (see *Figure* 6). Then, lemma 4 applied to P_1 and F_1, gives F_2 is a pentagon. This gives a contradiction to lemma 4 when applied to P_1 and F_3.

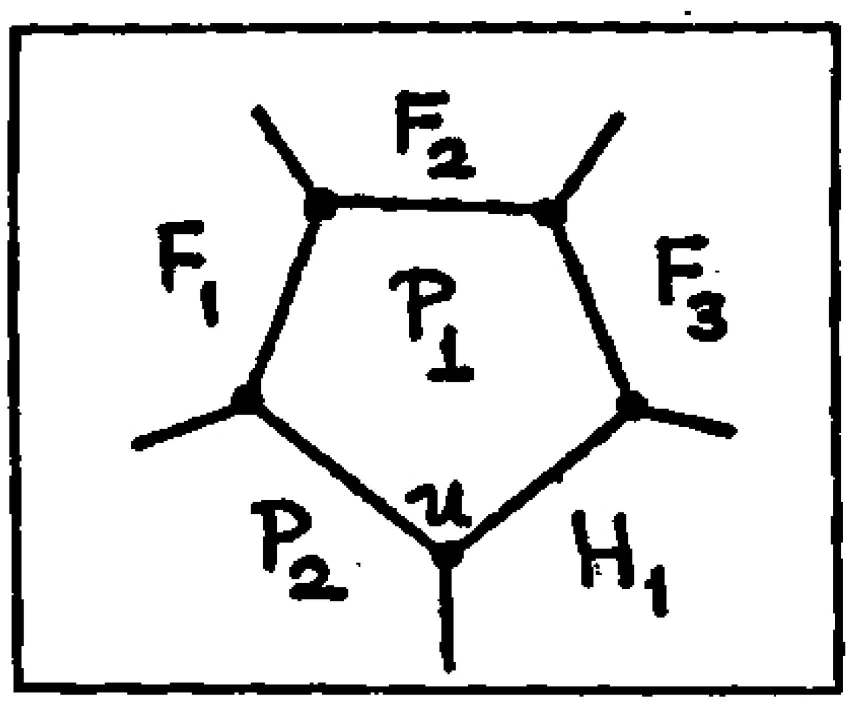


Figure 6.

Thus at any vertex there is at most one pentagonal face. By lemma 3, all the three faces at a vertex cannot be hexagonal, so the theorem follows. □

Lemma 5. Suppose $u_1u_2u_3u_4u_5$ is a regular pentagon in some plane in $\mathbb{R}^3$. Then there is a unique way in which two regular hexagons can be attached at u_1u_2 and u_2u_3 so that they have a common edge u_2v and lie above the plane of $u_1u_2\ldots u_5$. (See *Figure* 7).

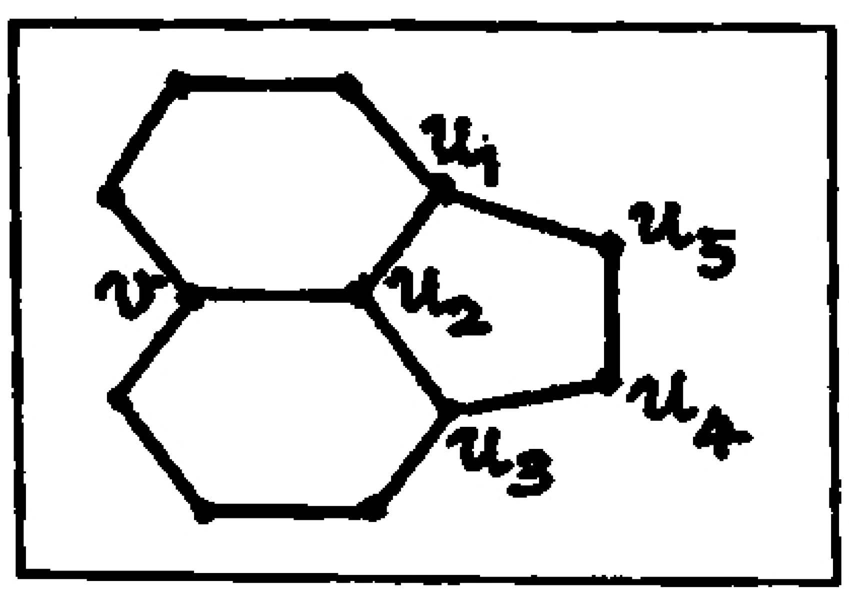
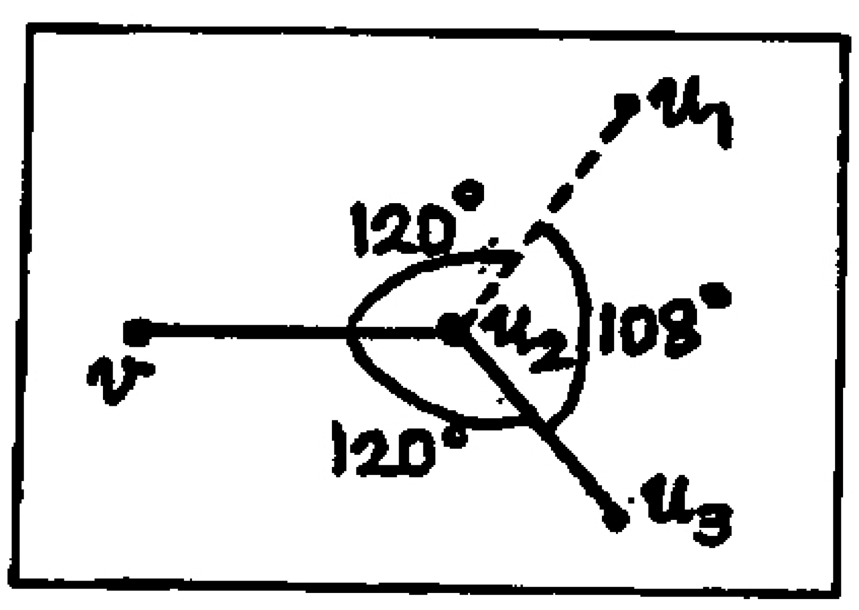


Figure 7.

Proof: Take $u_2 = (0,0,0), v = (-1,0,0)$ and $u_3 = (\alpha,\beta,0)$. Refer to *Figure* 8. Since $\angle vu_2u_3 = 120°$, we have $-\alpha = \langle v, u_3\rangle = \cos 120° = -1/2$. Here $\langle u,v\rangle$ denotes the dot product of u and v. Since $u_2u_3 = 1$, we may take $\beta = -\sqrt{3}/2$. Thus $u_3 = (1/2, -\sqrt{3}/2, 0)$.

Let $u_1 = (\gamma,\delta,\epsilon)$. Since $\angle vu_2u_1 = 120°$, we get $\gamma = 1/2$ as above. So $u_1 = (1/2,\delta,\epsilon)$ where $\delta^2+\epsilon^2 = 3/4$. Now $\angle u_1u_2u_3 = 108°$ and $\cos 108° = (1-\sqrt{5})/4$. So

Figure 8.



$$\frac{1-\sqrt{5}}{4} = \langle u_1, u_3\rangle = \frac{1}{4} - \frac{\sqrt{3}}{2}\delta.$$

Hence $\delta = \sqrt{5}/(2\sqrt{3})$ and $\epsilon = \pm 1/\sqrt{3}$. Assuming that u_1 lies above the x-y plane, we get $\epsilon = 1/\sqrt{3}$. Thus $u_1 = (1/2, \sqrt{5}/(2\sqrt{3}), 1/\sqrt{3})$. Since a regular polygon is determined by three consecutive vertices, it follows that the relative positions of the three polygons at u_2 are uniquely determined and the lemma follows. □

It is easy to write down the equations of the three planes at u_2 and so their normals at u_2. Using these, we can find the angle between the planes of the two hexagons to be $\cos^{-1}(\sqrt{5}/3) = \tan^{-1}(2/\sqrt{5}) \approx 41.81°$ and the angle between the planes of the pentagon and each of the hexagons to be $\tan^{-1}(3 - \sqrt{5}) \approx 37.38°$.

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We can now prove that there is at most one football.

Theorem 3. Given a regular pentagon P in some plane in $\mathbb{R}^3$, a football with P as a face and lying on a given side of the plane of P is unique if it exists.

Proof: The positions of the five hexagons around P are unique by the preceding lemma. Imagine attaching regular pentagons and regular hexagons (with the side same as that of P) in the order shown in *Figure* 9. At each stage, the type of face to be used is unique by theorem 2 and its position is unique since three or four consecutive vertices of a regular polygon determine the polygon. Hence the uniqueness follows. □

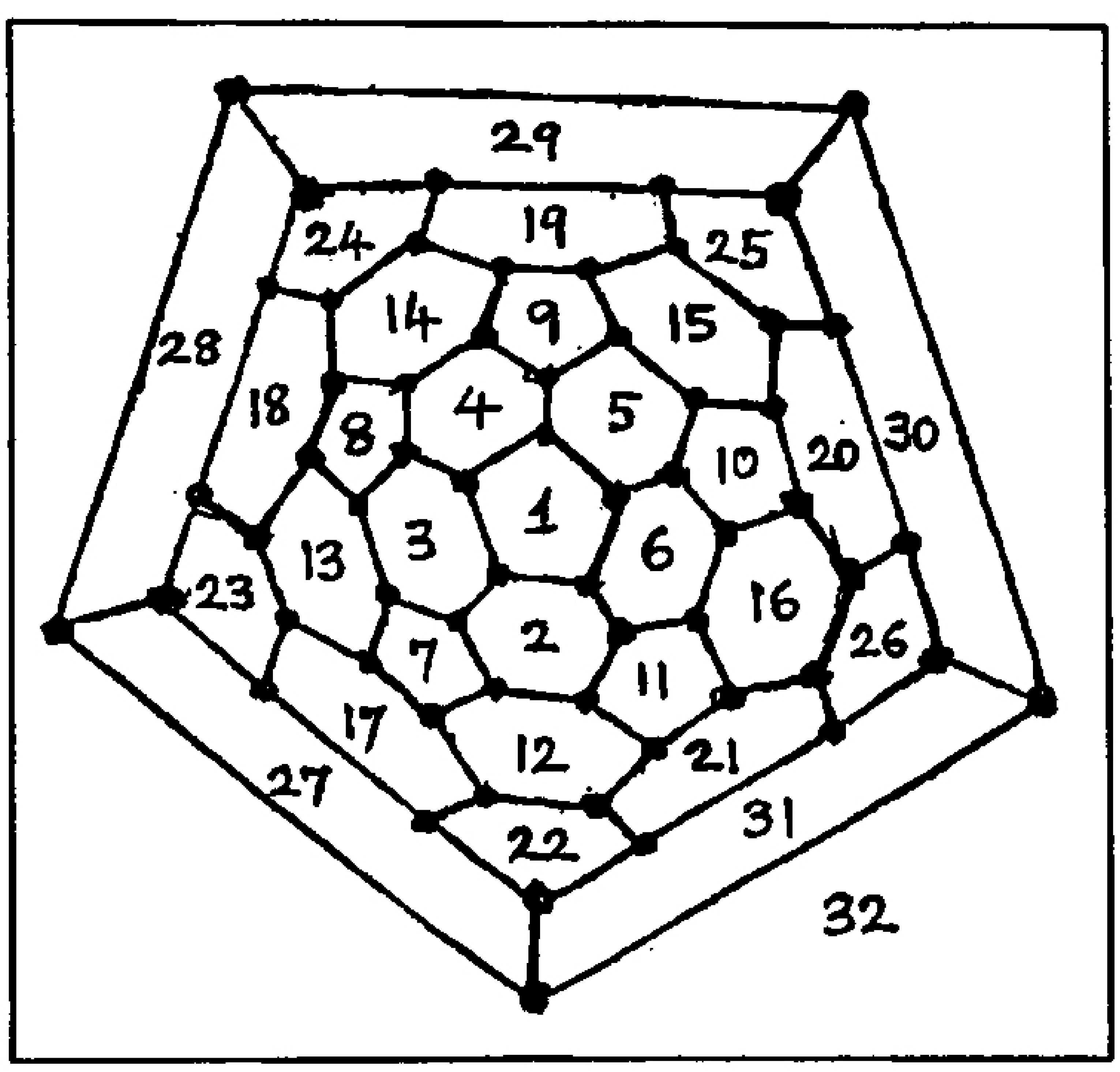


Figure 9.

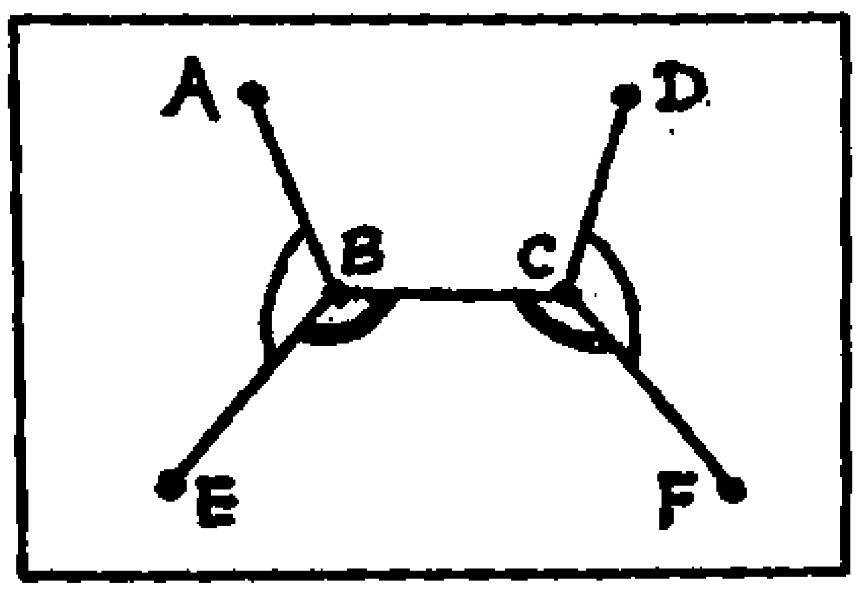


Figure 10.

Here is a result which provides the key to actually assembling the football thereby proving its existence.

Lemma 6. Let $\ldots ABCD \ldots$ be a regular polygon. Let BE and CF be such that $\angle ABE = \angle DCF$ and $\angle EBC = \angle FCB$ (see *Figure* 10). If E and F are both on the same side of the plane of $ABCD$, then E, B, C and F are coplanar.

Proof. We may take $B = (-1/2, 0, 0), C = (1/2, 0, 0)$ and $D = (a, b, 0)$. Then clearly $A = (-a, b, 0)$. Now let $F = (\alpha, \beta, \gamma)$ and $E = (\delta, \epsilon, \phi)$. We may also suppose that $BE = CF = BC$. Then

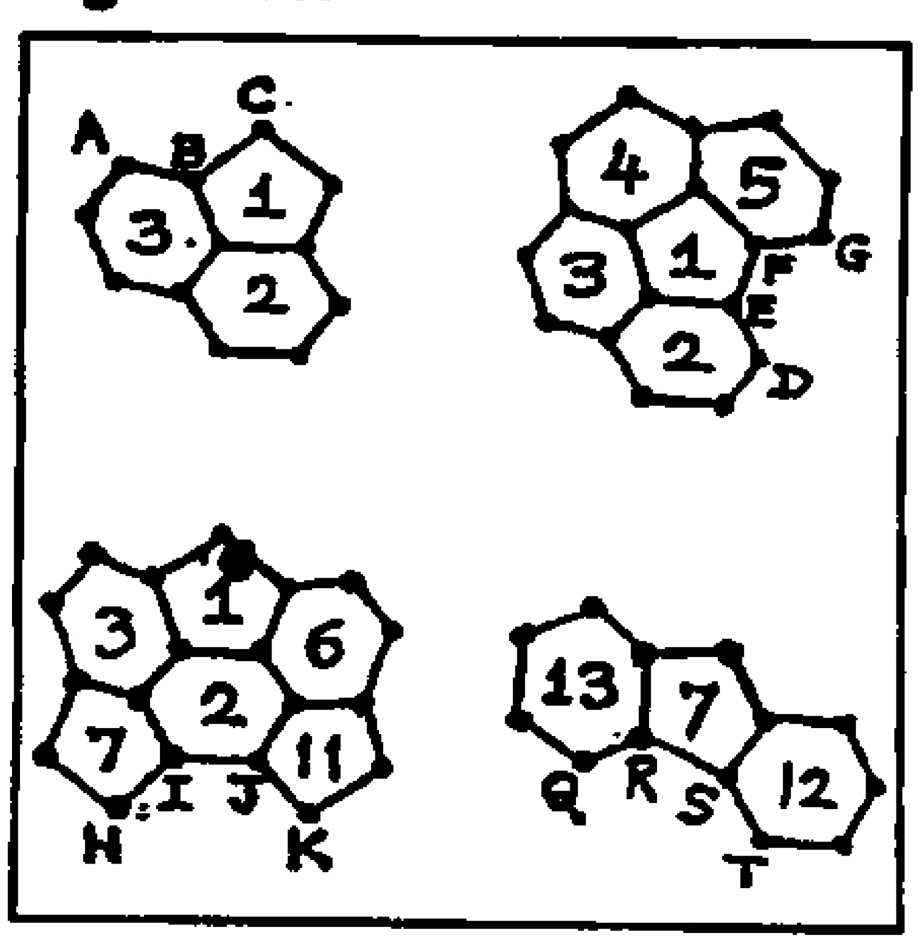
$$\cos \angle EBC = \langle (\delta + \frac{1}{2}, \epsilon, \phi), (1, 0, 0) \rangle = \delta + \frac{1}{2}$$

and $\cos \angle FCB = -(\alpha - \frac{1}{2})$. So $\delta = -\alpha$. Now $\cos \angle ABE = \cos \angle DCF$ gives $b\epsilon = b\beta$ and so $\epsilon = \beta$. Now $BE^2 = CF^2$ gives $\phi^2 = \gamma^2$. Since γ and ϕ have the same sign, they are equal. Thus $E = (-\alpha, \beta, \gamma)$ and E, B, C and F lie on the plane $\gamma y - \beta z = 0$. □

The footballs we see are not supposed to be footballs as defined here because nobody wants to play football with a solid with sharp edges and corners.

We now prove that a football exists. Why, one may wonder, because all of us have seen footballs. Well, there is a problem here. Firstly, the footballs we see are not supposed to be footballs as defined here because nobody wants to play football with a solid with sharp edges and corners. (The edges of the football we see are geodesics and the faces are spherical regions.) Secondly it is possible that a football as defined here does not exist and the footballs we see are only approximations.

Figure 11.



Theorem 4. The football referred to in theorem 3 exists.

Proof: We show that the football can be assembled as shown in *Figure* 9 used in the proof of theorem 3. Refer also to *Figure* 11. We start with faces 1, 2 and 3. This is possible by lemma 5. By lemma 4, $\angle ABC = 120°$, so we can attach face 4 at ABC. Similarly we can attach face 5 also. Then by lemma 6, D, E, F and G are coplanar, so face 6 can be fitted there. Then clearly faces 7 and through 11 can be fitted. Then, again by lemma 6, H, I, J and K are coplanar, so face 12 can be fitted there. Next we can fit faces 13 through 16. Now Q, R, S and T are coplanar, so face 17 can be fitted there. Proceeding thus we fit faces 18-21, then 22-26, then 27-31 and finally face 32. This proves that the football can be assembled and so exists. □

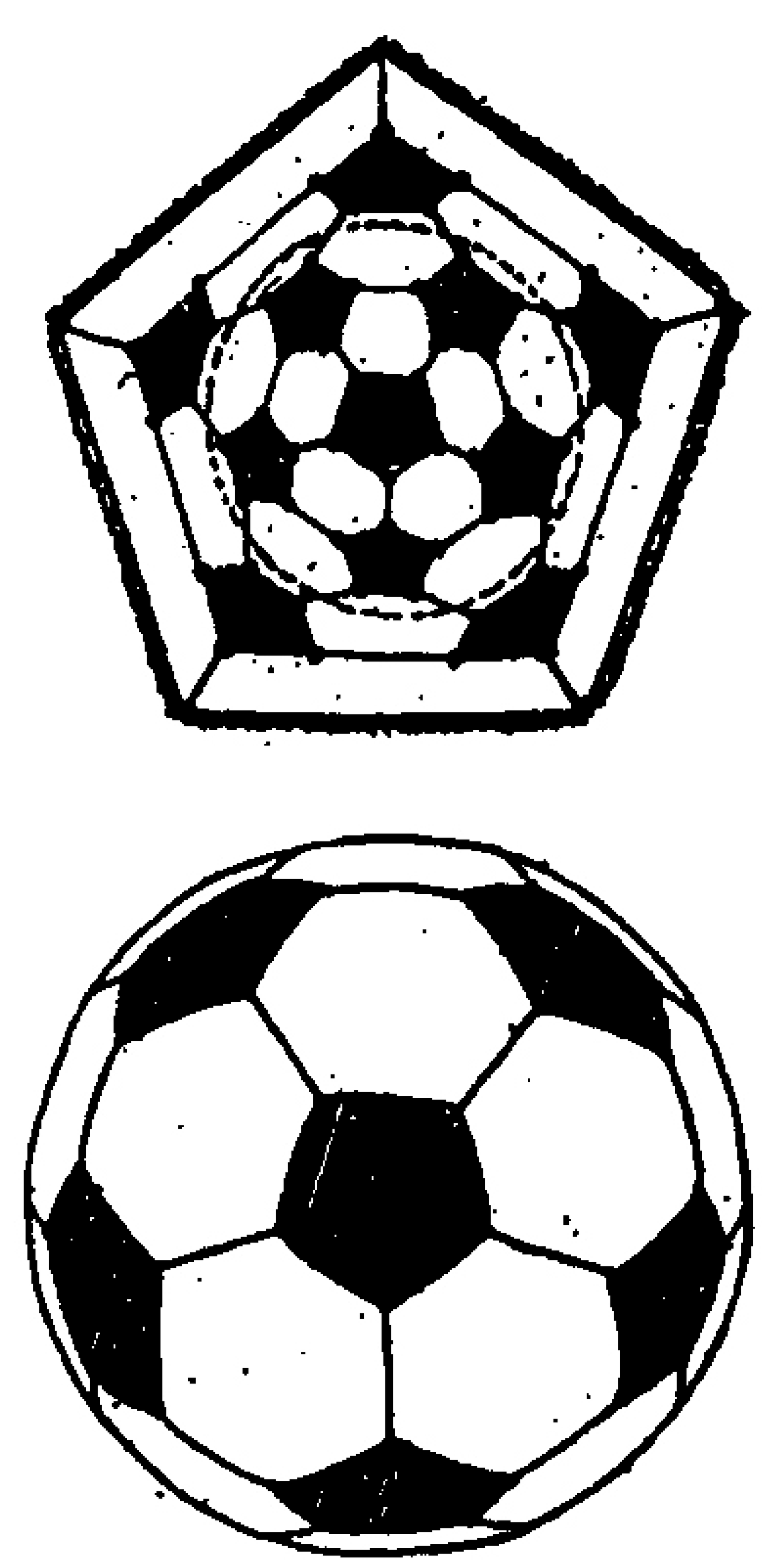
We next see how symmetric the football is. We start by showing that the vertices lie on a sphere. Note that the following analogue in two dimensions is false: the vertices of a convex polygon with all sides equal lie on a circle. The polygon shown in *Figure* 12 is far from equi-angular and can be perturbed further.

Theorem 5. The normals to any three mutually adjacent faces of a football are concurrent at a point O which is the centre of a sphere on which the vertices lie.

Proof: By the normal to a face we mean the line passing through its centre and perpendicular to its plane. Refer to *Figure* 13. Let AB be the common edge between two faces and C and D the centres of the two faces. Then it is easy to see that the plane perpendicularly bisecting AB will contain the normals to the two faces. So these normals are coplanar. Since the faces are not parallel, these normals intersect at, say, O. Since O lies on the normal to face ABF, we have $OA = OB = OF$. Since O lies on the normal to face ABG, $OB = OG$. Thus $OF = OB = OG$. So O lies on the planes perpendicularly bisecting BF and BG. Hence O lies on the normal to the face FBG. Thus the normals to the three faces are concurrent at O and $OA = OB = OF = OG$. By proceeding through adjacent faces, we can see that O lies on the normal to every face. This proves the theorem. □

It will be an interesting exercise to determine the radius of the sphere on which the vertices of the football lie,

Box 2.



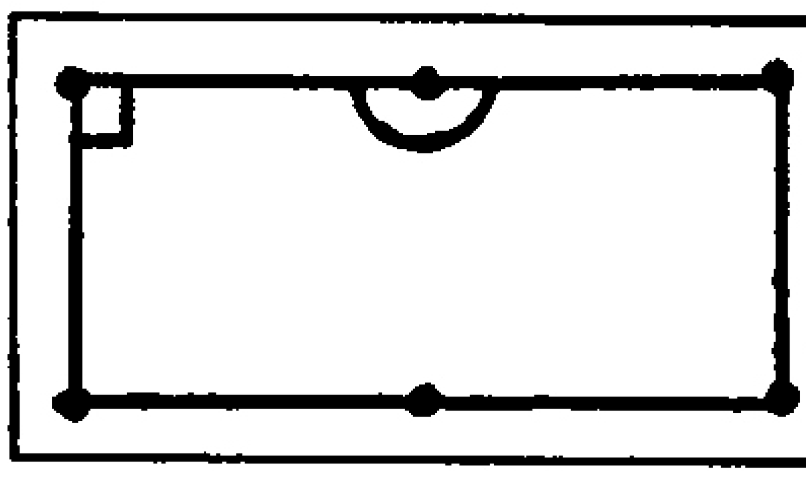
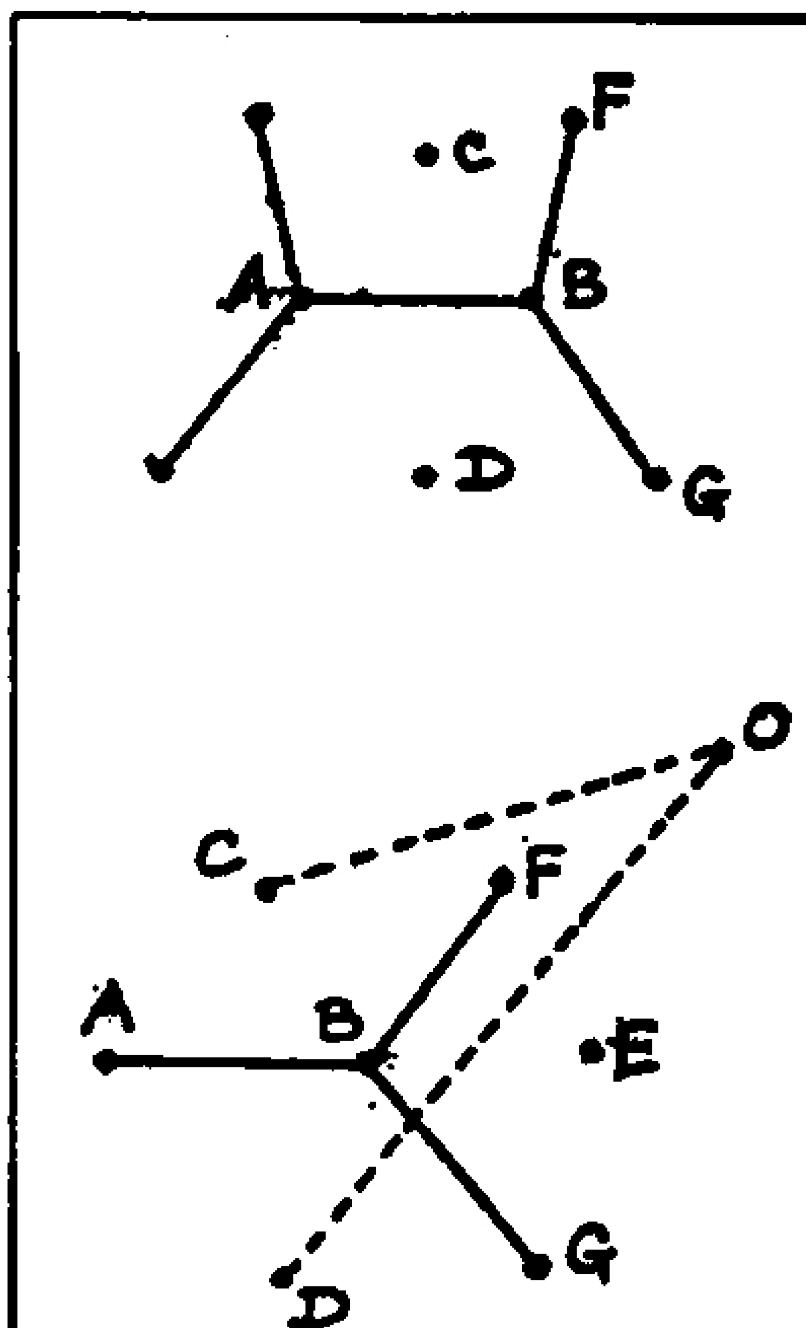


Figure 12.

Figure 13.



given the length of an edge.

We now determine the numbers of vertices, edges and faces on the football. This will be needed later in part II where we determine its group of symmetries. Though these numbers can be counted from a drawing of the football, we will use a bit of graph theory to find these (partly explaining my interest in the topic).

The numbers of vertices, edges and faces on the football can be counted from a drawing of the football but a bit of graph theory can be used too to find these.

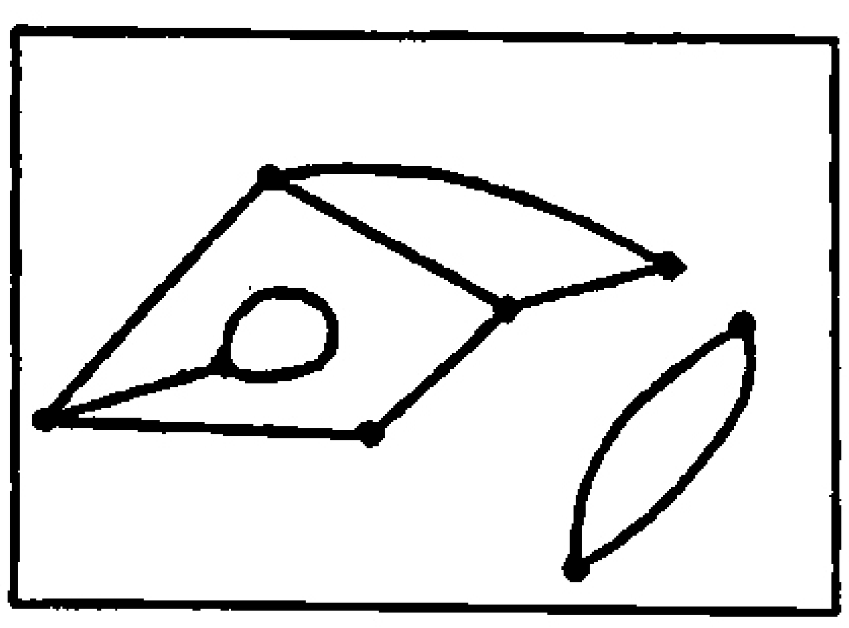
A (finite) *graph* G consists of a finite non-empty set V whose elements are called vertices and a finite collection E of unordered pairs (called edges) of elements of V. A *plane graph* is a graph whose vertices are points in the plane and whose edges are arcs joining the vertices, no two of these arcs meeting each other except at the ends. A *face* of a plane graph G is a maximal connected region of the plane left when the vertices and edges of G are removed. It is easy to see that the vertex set of a graph G can be partitioned into its *components* such that we can go from every vertex in a component to every other vertex in the same component and to no vertex in any other component by travelling along edges (see *Figure* 14). We now prove a slight generalisation of a well-known formula so that we can use induction conveniently.

Lemma 7. (Euler's formula): For any plane graph G,

$$\nu - \epsilon + \gamma = 1 + p$$

where ν is the number of vertices, ϵ is the number of edges, γ is the number of faces (including the unbounded face) and p is the number of components.

Figure 14.



Proof: We prove the result by induction on ϵ. If $\epsilon = 0$, then $\gamma = 1$ and $p = \nu$, so the result follows. So assume the result for plane graphs with less than ϵ edges and let G have ϵ edges. If an edge belongs to a 'cycle', then by deleting this edge, we get a plane graph with ν vertices, $\epsilon - 1$ edges, $\gamma - 1$ faces and p components, so by induction hypothesis, we are done. If an edge uv does not belong to any cycle, then by deleting this edge, we get a plane graph with ν vertices, $\epsilon - 1$ edges, γ faces and $p + 1$ components, so by induction hypothesis, we are again done. □

Euler's polyhedral formula can be used to show that there are only five regular solids.

Theorem 6. A football has 60 vertices, 90 edges and 32 faces of which 12 are pentagons and 20 are hexagons.

Proof: Any football can be represented by its *Schlegel diagram* which is what the football (assumed to be transparent except for the edges) appears like when seen from a position just outside the centre of one face. This is like stereographic projection from the top (assumed to be not a vertex and not lying on any edge) of the sphere on which the vertices of the football lie, onto a horizontal plane below the sphere. The Schlegel diagram is a plane graph G, vertices, edges and faces of the football corresponding naturally to those of G, the face of the football nearest to the viewer corresponding to the unbounded face. Note that G has only one component, so Euler's formula reduces to $\nu - \epsilon + \gamma = 2$. By theorem 1, there are exactly three edges at every vertex and every edge is incident with exactly two vertices. Thus $2\epsilon = 3\nu$. Since every vertex is incident with exactly one pentagon and each pentagon is incident with exactly 5 vertices, it follows that the number of pentagons is $\nu/5$. Since every vertex is incident with exactly two hexagons and each hexagon is incident with exactly 6 vertices, it follows that the number of hexagons is $\nu/3$. Substituting these in Euler's formula we get

$$\nu - \frac{3\nu}{2} + \frac{\nu}{5} + \frac{\nu}{3} = 2,$$

so, $\nu = 60$. Now the theorem follows easily. □

Finally, we show how Euler's polyhedral formula can be used to show that there are only five regular solids. In a plane graph, a k-cycle refers to a sequence of edges of the type $v_1v_2, v_2v_3, \ldots, v_{k-1}v_k, v_kv_1$ where the vertices $v_1, v_2, \ldots, v_k$ are all distinct and $k \geq 1$.

Lemma 8. If each face of a connected plane graph G is a p-cycle for a fixed $p \geq 3$ and if there are $q \geq 3$ edges at every vertex of G, then $(p,q) = (3,3), (3,4), (3,5), (4,3)$ or $(5,3)$.

Proof: We first note that every edge joins two distinct vertices since if there is a self-loop, the face just inside it cannot be a p-cycle with $p \geq 3$. So, as in the proof of theorem 6, we get $q\nu = 2\epsilon = p\gamma$. Now, by Euler's formula, $\nu - \epsilon + \gamma = 2$. So

$$\frac{\nu}{\frac{1}{q}} = \frac{\epsilon}{\frac{1}{2}} = \frac{\gamma}{\frac{1}{p}} = \frac{\nu - \epsilon + \gamma}{\frac{1}{q} - \frac{1}{2} + \frac{1}{p}} = \frac{2}{\frac{1}{q} - \frac{1}{2} + \frac{1}{p}} = \frac{4pq}{2p - pq + 2q}$$

So $2p - pq + 2q > 0$ or $(p-2)(q-2) < 4$. It follows easily that $p \leq 5$. Moreover, if $p = 3$, then q can take only the values 3, 4 and 5. If $p = 4$ or 5, then q can take only the value 3. □

Lemma 9. (Euclid's Comment at the end of Book XIII): The Schlafli symbol of any regular solid (i.e., a 3-dimensional polytope with each face a regular p-gon and with exactly q faces at each vertex) is (3,3), (3,4), (3,5), (4,3) or (5,3).

Proof: We will give two proofs of this result, the first using Euler's formula. The Schlegel diagram of any regular solid with Schlafli symbol (p,q) is a plane graph G satisfying the hypothesis of lemma 8, so (p,q) can take only one of the five values mentioned in that lemma. This proves lemma 9.

We now give a second proof, essentially due to Euclid, which is applicable only to regular solids and which does not use Euler's formula. Since each angle in a regular p-gon is $(1-2/p)\pi$ and there are q such faces at any vertex, it follows from lemma 3 that $q(1-2/p)\pi < 2\pi$ which, on simplification, becomes exactly $2p - pq + 2q > 0$. Now the conclusion follows as in lemma 8. □

Now, if there is a regular solid with Schlafli symbol (p,q), then (p,q) can take only the five values stated in the preceding lemma. Using the equalities displayed in the proof of lemma 8 (or by direct counting), it is easy to find the numbers of vertices, edges and faces in each of the above five cases. Finally it can be shown, as for a football, that a regular solid with Schlafli symbol any one of the five referred to above, is unique. This shows that the platonic solids are the only 'regular solids' as stated by Euclid at the end of Book XIII.

Incidentally, a plane *tessellation* is a covering of the plane with nonoverlapping (except for the edges between) polygons. A tessellation is a *regular tessellation* if the polygons are all regular p-gons for some p. If a regular plane tessellation exists with p-gons and if there are q such polygons at *some* vertex, then we have $q(1 - 2/p)\pi = 2\pi$, so $(p-2)(q-2) = 4$. It follows that $(p,q) = (3,6), (4,4)$ or $(6,3)$. Each of these is actually possible as the tessellations in *Figure* 15 show. (Note that, now, p determines q and the same number of polygons occurs at every vertex; this was not assumed in the definition).

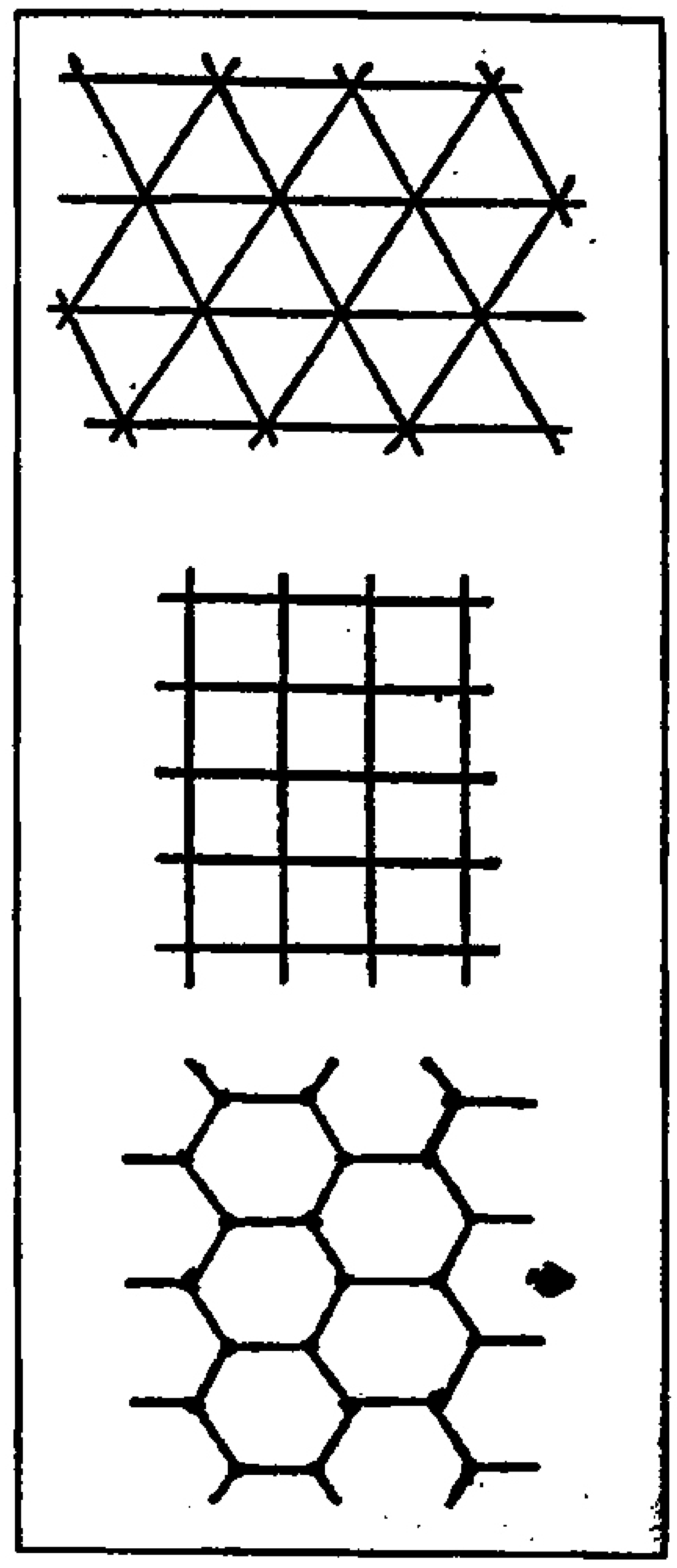


Figure 15.

We mention in passing that a beehive looks quite like a 3-dimensional convex polytope with every face a regular hexagon and with three faces meeting at every vertex. However, this cannot really be, since the sum of the angles at any vertex will then be 360° and the polytope has to be planar by lemma 3. Thus the polytope with the stated properties does not exist and a beehive is only a clever approximation. This shows the need for proving the existence of a football.

We end the first part here. In the next part, we shall identify the group of symmetries of a football. That will also contain a discussion on the groups of symmetries of some other objects in 3-space.

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Chemical Research of Sir Prafulla Chandra Rây

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Sreebrata Goswami is a Reader at the Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta. His major research interests include synthesis of coordination compounds with special reference to metal promoted chemical transformation of coordinated organic ligands and electronic structure of compounds of redox non-innocent ligands.

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Prafulla Chandra Rây was the pathfinder and originator of chemical research in modern India. He was introduced to research by Alexander Crum Brown, a notable chemist and teacher at Edinburgh University. His doctoral work was on the chemistry of double sulphates. He received the D.Sc. degree of Edinburgh University in 1887. A year later he returned to India and in 1889 started his career as a junior professor in Presidency College, Calcutta. He was then twenty-eight. His research activities flourished in the laboratories of the college even though the facilities were inadequate. He moved to the College of Science of Calcutta University as the first Palit Professor of Chemistry in the year 1916 and the work of his school continued there with renewed vigour.

Prafulla Chandra was a synthetic chemist specially of inorganic compounds. But he also made outstanding contributions to the chemistry of thio-organic compounds. He and his students prepared many new interesting families of compounds and examined their physical properties to the extent possible at that time. He first became well known for his work on the inorganic and organic nitrites. Among metals, he had a very special fascination for mercury probably because of its importance in Ayurvedic medicines in which he was very interested. He published about two hundred original papers. The majority of his contributions until 1924 (the year when the *Journal of the Indian Chemical Society* was born) were published in the *Journal of Chemical Society* (London).

It is convenient to discuss Prafulla Chandra's research contributions under a few broad categories highlighted in *Box* 1.

In the following sections we shall present a few selections from his many-sided experimental findings. His celebrated historical research culminating in the creation of *History of Hindu Chemistry* has not been elaborated in this article.

Box 1. Categories of Research Contributions

(i) Metal nitrites with special reference to mercurous nitrite
(ii) Ammonium nitrite and related compounds
(iii) Chemistry of sulphur compounds
(iv) Coordination compounds

Mercurous Nitrite and Related Compounds

In 1895 Prafulla Chandra reported the first synthesis of the hitherto unknown mercurous nitrite, $Hg_2(NO_2)_2$. This event was described by him in his autobiography as "the discovery of mercurous nitrite opened a new chapter in my life". It is relevant to mention here that stable mercury(I) complexes are sparse in literature, even today, owing to the instability of mercury(I) towards disproportionation to mercury(II) and metallic mercury in solution. Moreover, the nitrite ion is not very stable and can undergo facile decomposition. The compound, $Hg_2(NO_2)_2$ is thus a fascinating example of a stable substance composed of two relatively unstable ions.

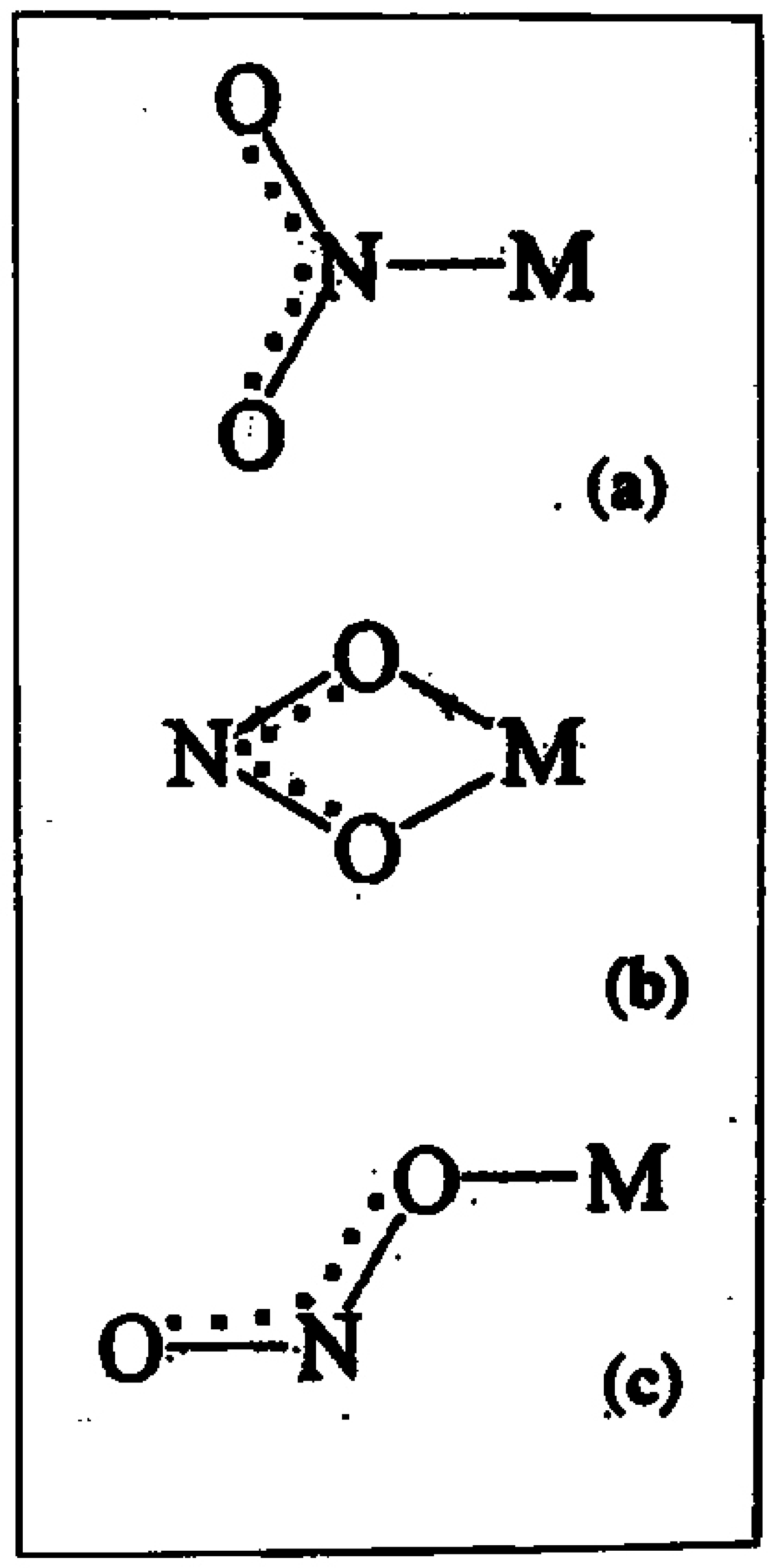
The preparation of $Hg_2(NO_2)_2$ was an accidental discovery. He wanted to prepare water soluble mercurous nitrate as an intermediate for the synthesis of calomel, Hg_2Cl_2. Accordingly, dilute aqueous nitric acid (1:4) was reacted with excess mercury. To his surprise this resulted in the formation of yellow crystalline $Hg_2(NO_2)_2$.

$$Hg\,(\text{excess}) + HNO_3\,(\text{dilute}) \longrightarrow Hg_2(NO_2)_2 \qquad (1)$$

This result was first published in the *Journal of Asiatic Society of Bengal* which was immediately noticed by *Nature*. This was the beginning of a series of thorough investigations which resulted in many significant publications on this nitrite and its derivatives.

It is now known that the nitrite ion can bind to a metal ion in three different fashions (*Figure* 1) and there have been numerous structural investigations in many laboratories around the world to sort out the coordination modes. As mercury (*Figure* 1a) is a soft cation, the nitrite ions in $Hg_2(NO_2)_2$ are likely to be linked to mercury (*Figure* 1a), which exist as a dimer due to metal-metal bonding, through the soft nitrogen centers forming a linear N-

Figure 1. Coordination modes of NO_2^- to metal.



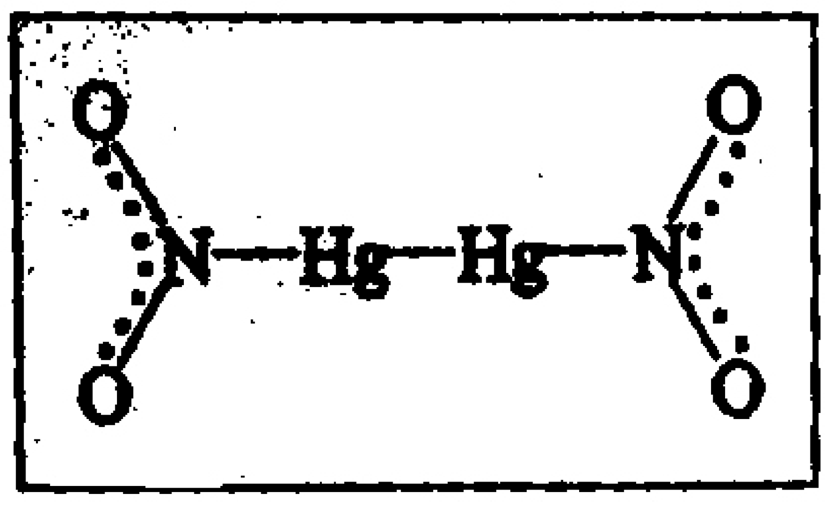


Figure 2. Structure of $Hg_2(NO_2)_2$.

Hg-Hg-N chain (*Figure* 2). It was not possible to make such a proposal in Prafulla Chandra's time because structural principles were in their infancy. A direct experimental proof of the structure of the above nitrite is still awaited.

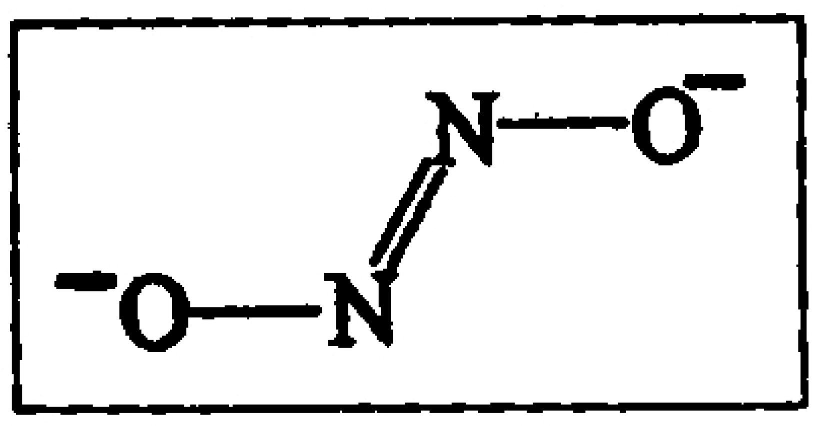
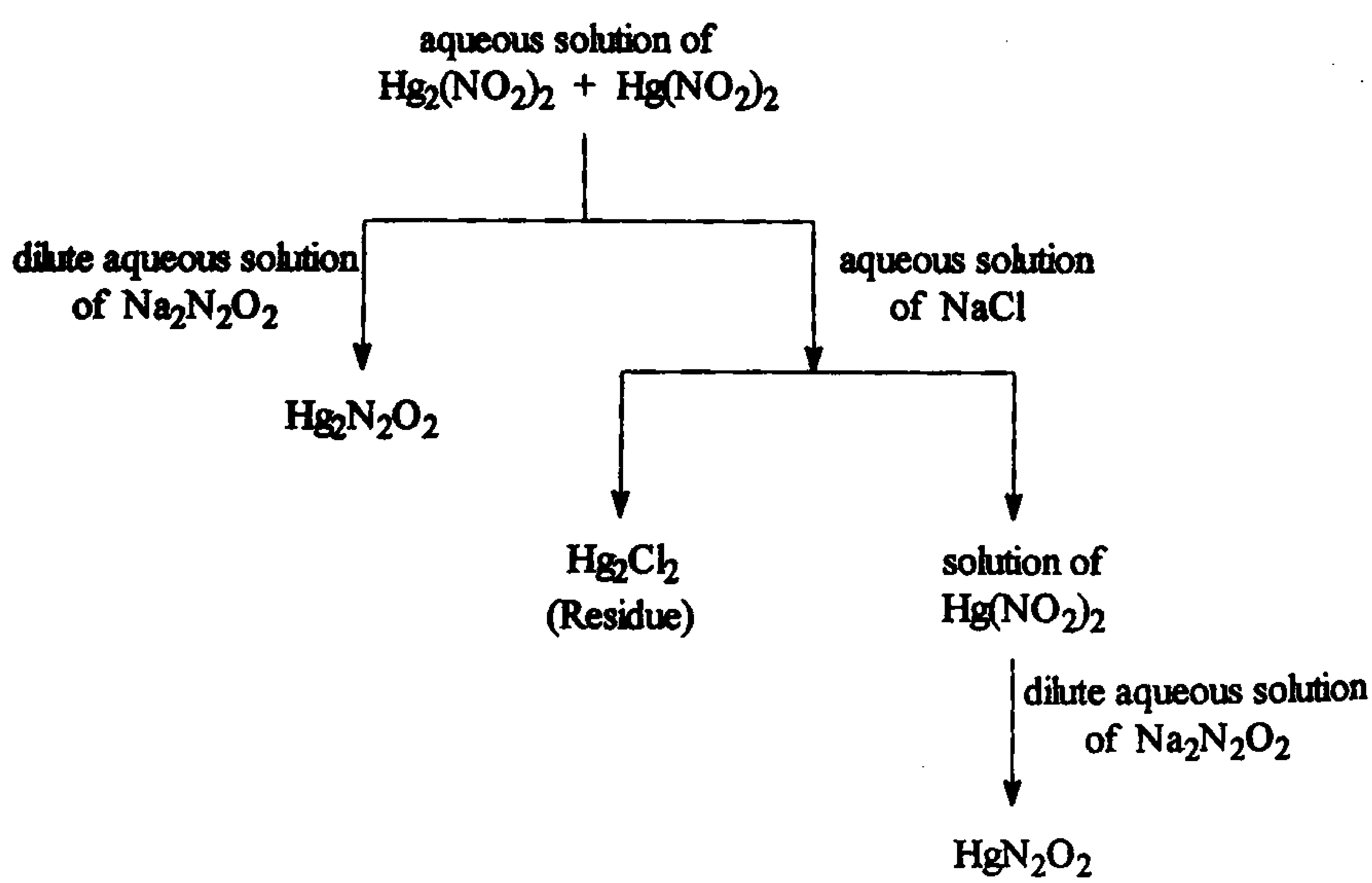


Figure 3. Structure of hyponitrite anion $(N_2O_2)^{2-}$.

Subsequently, Prafulla Chandra became interested in the chemistry of hyponitrites. Structure of the hyponitrite anion $(N_2O_2)^{2-}$ is shown in *Figure* 3. The hyponitrites were prepared by reacting the corresponding nitrite with aqueous solution of sodium hyponitrite, $Na_2N_2O_2$. The reaction of mercury with nitric acid was used to prepare a solution containing a mixture of mercurous nitrite ($Hg_2(NO_2)_2$) and mercuric nitrite ($Hg(NO_2)_2$). From this mixture, he isolated the corresponding hyponitrites in the pure form by following the scheme shown in *Box* 2. A simpler procedure for the direct synthesis of mercuric hyponitrite from mercuric nitrite was invented later using KCN as the reducing agent. The hyponitrites of mercury were found to be thermally more stable than the corresponding nitrites and nitrates.

Box 2. Preparation of $Hg_2N_2O_2$ and HgN_2O_2



Prafulla Chandra also synthesised numerous nitrites of alkali, alkaline earth and coinage metals as well as double nitrites such as those containing both mercury and alkaline earth metals. Thermal decomposition of the compounds was thoroughly investigated. Other physicochemical properties such as relative stability, molecular volume and molecular conductivity were studied. Contrary to the view held earlier, Prafulla Chandra established beyond doubt that nitrites were stable substances.

Contrary to the view held earlier, Prafulla Chandra established beyond doubt that nitrites were stable substances.

Ammonium Nitrite and Alkylammonium Nitrites

One of the very notable contributions of Prafulla Chandra in the field of nitrite chemistry was the synthesis of ammonium nitrite in pure form via double displacement between ammonium chloride and silver nitrite, (2).

$$NH_4Cl + AgNO_2 \longrightarrow NH_4NO_2 + AgCl \qquad (2)$$

Ammonium nitrite, so formed, was sublimed at 32-33°C under reduced pressure to afford crystalline colourless needles. It had all along been believed that ammonium nitrite undergoes fast thermal decomposition yielding N_2 and H_2O.

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O \qquad (3)$$

Prafulla Chandra established that this reaction is far less facile than thought. He carried out a series of experiments to show that pure ammonium nitrite is indeed stable and it can be sublimed without decomposition even at 60°C. The stability of this salt in its vapour state was firmly established by vapour density measurements. He presented the results in a meeting of the Chemical Society in London and the scientific audience including William Ramsay was greatly impressed. *Nature* (August 15, 1912) immediately highlighted the successful preparation of 'ammonium nitrite in tangible form' and the determination of the vapour density of 'this very fugitive salt'. The details of these experiments were published in the *Journal of Chemical Society*, London in the same year.

His success with ammonium nitrite prompted Prafulla Chandra to develop the chemistry of alkylammonium nitrites. He prepared a family of such compounds by double displacement of alkylamine hydrochlorides and silver nitrite.

$$RNH_3Cl + AgNO_2 \longrightarrow RNH_3NO_2 + AgCl \qquad (4)$$

in cold aqueous solution. The relative stability of these compounds were studied and compared. He then proceeded to work on mercury alkyl- and mercury alkylaryl-ammonium nitrites.

Organic Sulphur Compounds

In the College of Science, Prafulla Chandra made major contributions to the chemistry of organic sulphur compounds. He synthesised new compounds and studied their interactions with the salts of mercury. Moreover, ligating properties of some of these thio-compounds were investigated. Long-chain sulphur species, sulphur-containing condensed heterocycles and thioketones are some of the systems that he synthesised. For example, as a by-product of the synthesis of 1,4-dithian (*Figure* 4) from dithioethylene glycol and ethylene bromide, he isolated the long chain compound, $BrC_2H_4(SC_2H_4)_{48}Br$ (5), which was 'the first instance of a crystalline organic sulphur compound of such high molecular weight as 3068'.

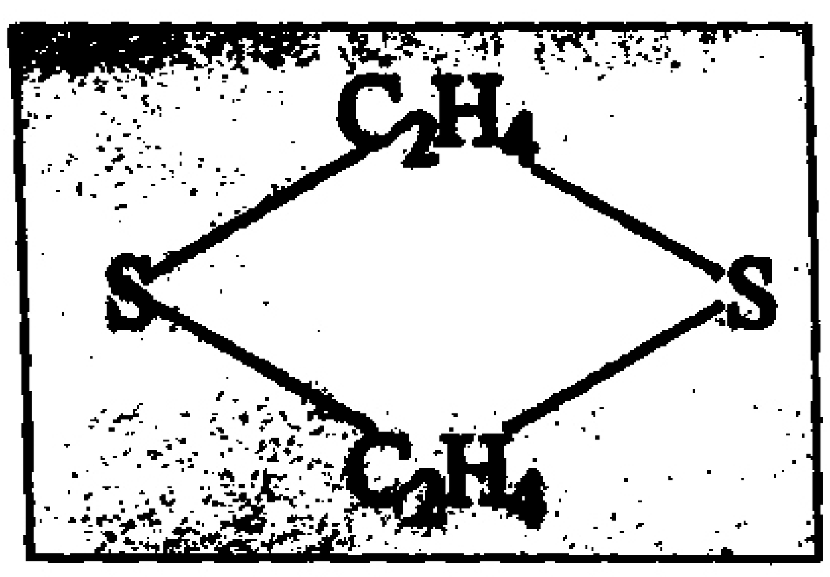
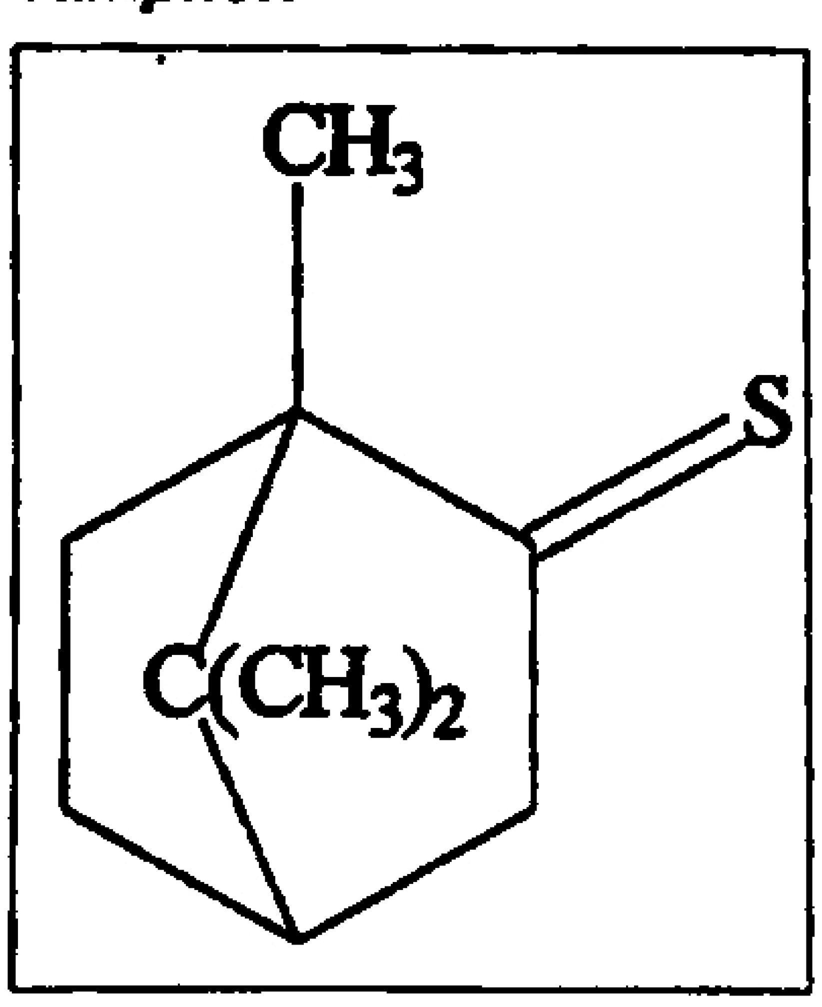


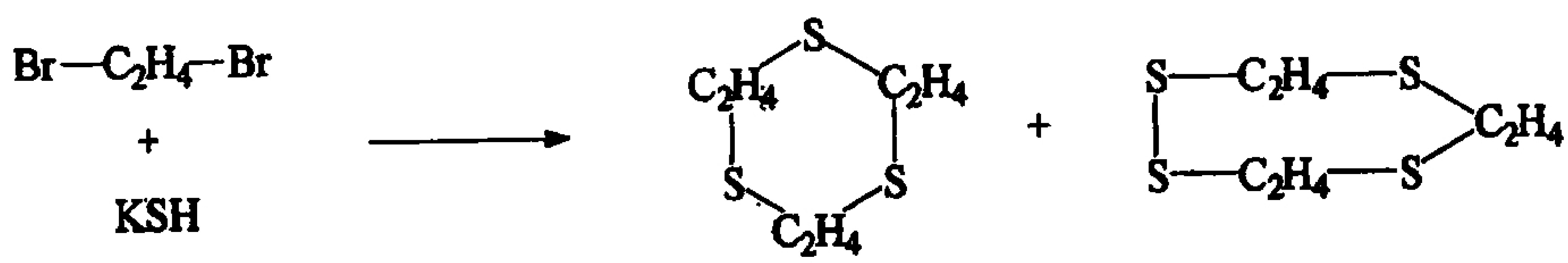
Figure 4. Structure of 1,4-dithian.

$$Br\text{-}C_2H_4\text{-}Br + NaS\text{-}C_2H_4\text{-}SNa + Br\text{-}C_2H_4\text{-}Br + \ldots + NaS\text{-}C_2H_4\text{-}SNa + Br\text{-}C_2H_4\text{-}Br \rightarrow BrC_2H_4(SC_2H_4)_nBr + nNaBr \qquad (5)$$

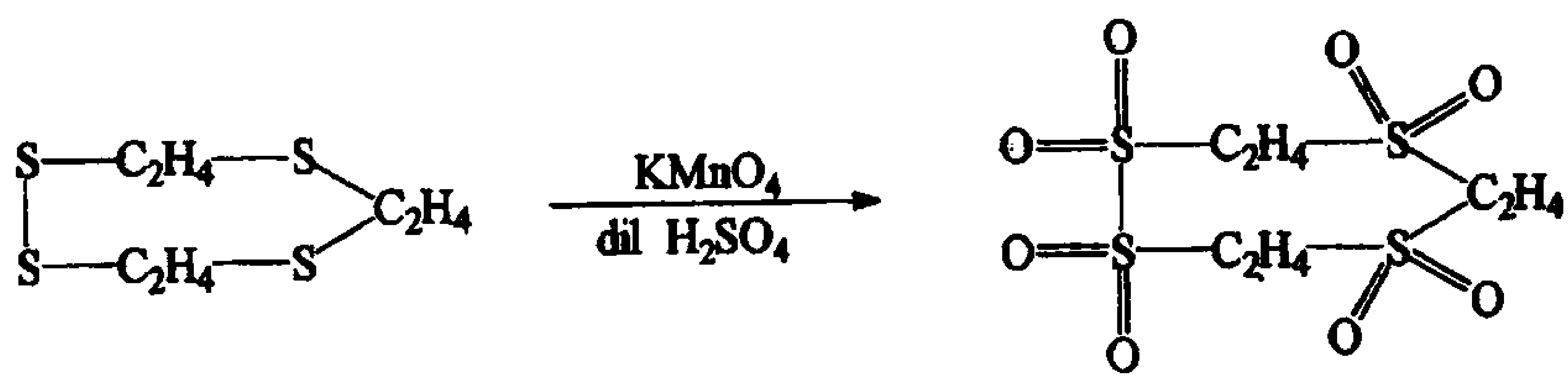
He also worked on the synthesis of condensed heterocyclic systems. Of these, the synthesis of triethylene tri- and tetrasulphides from simple reactions of ethylene dibromide and alcoholic KSH (6) are noteworthy. Potassium permanganate oxidation of the tetrasulphide to the corresponding sulphone compound (7) was also examined. A brief report of his work on the synthesis of thiocamphor and other cyclic thioketones was published in *Nature* in 1934. Thiocamphor (*Figure* 5) was synthesized in a good yield by the simultaneous action of dry H_2S and dry HCl gas at 0°C on a solution of camphor in absolute

Figure 5. Structure of thiocamphor.





Triethylene tri-sulphide   Triethylene tetra-sulphide   (6)



tetra-sulphide   sulphone compound   (7)

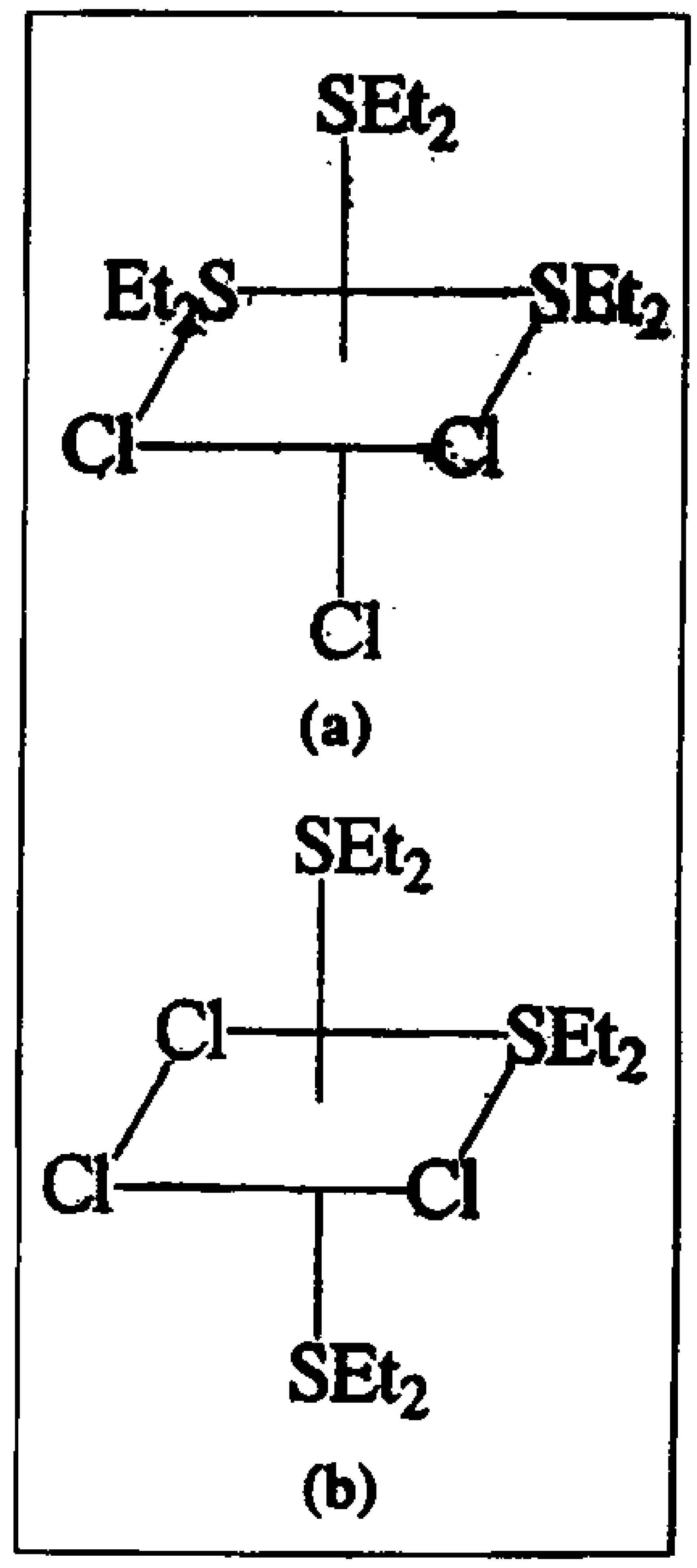
alcohol. This method was extended later to synthesize cyclic thioketones containing different ring systems.

Coordination Compounds

Prafulla Chandra made extensive contributions to the coordination chemistry of the heavier transition metal ions like platinum, iridium and gold. Particularly noteworthy are his studies on organic sulphides such as methyl sulphide, ethyl sulphide, diethyl sulphide and diethyl disulphide as ligands. Complexes of different types were isolated and their compositions were deduced based on elemental analysis and molar conductance.

From the reaction of diethyl sulphide with iridium tetrachloride he isolated two isomers of composition $IrCl_3.3Et_2S$, one orange and another red. The orange compound is now known to have the pseudooctahedral meridional geometry (*Figure* 6a) and not the facial geometry (*Figure* 6b) assigned by Prafulla Chandra. This work indeed represents the isolation of the first mixed halide octahedral thioether compound of the generic type $MX_3(R_2S)_3$ which now has rich chemistry (M=Ir(III), Rh(III), Os(III) and Ru(III); X = Cl, Br, I) representing the efforts of many later workers in different countries. The first seed was

Figure 6. a) Pseudooctahedral meridional geometry and b) facial geometry.



By the interaction of chloroplatinic acid with thio-organic compounds, numerous platinum complexes were synthesised by Prafulla Chandra and different oxidation states were assigned to the metal ion.

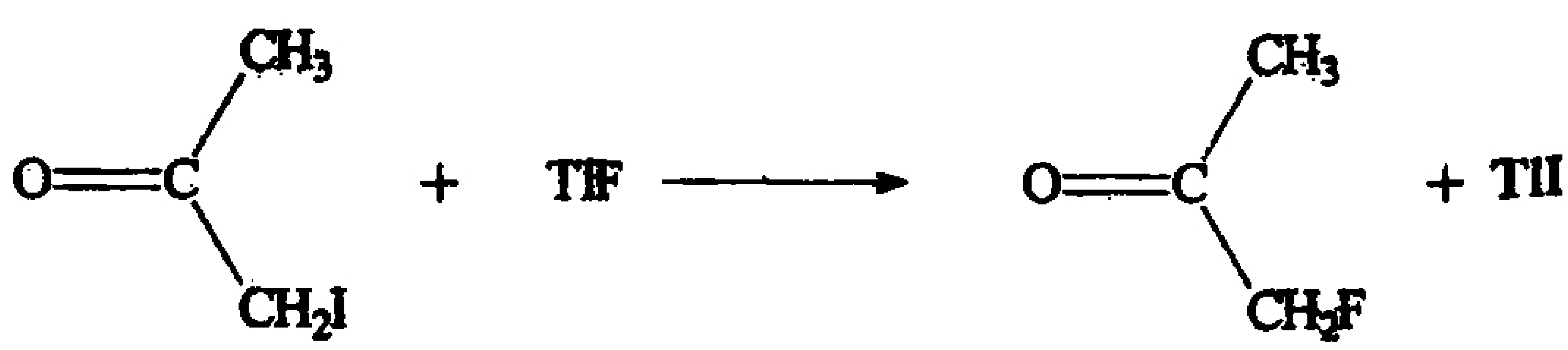
however sown by Prafulla Chandra. The red isomer of $IrCl_3.3Et_2S$ was shown by later workers to be a salt of type $[IrCl_2(Et_2S)_4]^+[IrCl_4(Et_2S)_2]^-$.

By the interaction of chloroplatinic acid with thio-organic compounds, numerous platinum complexes were synthesised by Prafulla Chandra and different oxidation states were assigned to the metal ion. Similar studies were carried out on gold compounds. However, the proposed structures and the oxidation states of such species deserve further scrutiny.

Other Activities

In Presidency College, Prafulla Chandra began his research activities by chemical examination of certain fats and oils like ghee, butter and mustard oil, used as cooking media in India. The purpose was to create standards and identify the adulteration of foodstuffs in metropolitan cities of India. He published a long report on this work in the *Journal of the Asiatic Society of Bengal* in 1894.

Much later in the College of Science, he developed certain methods for facile fluorination of organic compounds using thallous fluoride as the fluorinating agent. For example, one-pot synthesis of monofluoroacetone from the reaction of monoiodoacetone and anhydrous thallous fluoride (8) was successfully achieved in a high yield. He also isolated methyl fluoroformate and fluroacetals using the same principle of halide substitution.



(8)

Conclusion

The above account reveals the versatility of Prafulla Chandra's research activities. Most importantly, he initiated chemical research in modern India and was successful in developing the first research school of chemistry that in time spread far and wide. In his obituary notice, *Nature* (July 15, 1944) wrote "it was by the enthusiasm for research with which he inspired his students that he will best be remembered".

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A Tailor-made Integral Matrix

An $n \times n$ integral matrix with n given integers as its eigenvalues is trivially obtained by considering a diagonal matrix with these diagonal entries. If one is also given n non-zero integral vectors, how can one make up a matrix which has integer entries and which has these vectors as its eigenvectors? Here is a simple way. First, note that if $\mathbf{a}, \mathbf{b} \in \mathbf{Z}^n$ are integer vectors considered as columns, and if $\mathbf{a}^t\mathbf{b} \neq -1$, then the matrix $I + \mathbf{a}\mathbf{b}^t$ is invertible; it has the inverse $I - s\mathbf{a}\mathbf{b}^t$ where $s = \frac{1}{1+\mathbf{b}^t\mathbf{a}}$. Further, $\mathbf{a}$ and $\mathbf{b}$ may be so chosen that $\mathbf{b}^t\mathbf{a} = 0$ because this only means that $(I + \mathbf{a}\mathbf{b}^t)^{-1} = I - \mathbf{a}\mathbf{b}^t$. If we are given n integers and n non-zero integral vectors $\mathbf{a}, \mathbf{b}$ satisfying $\mathbf{b}^t\mathbf{a} = 0$, let us form the diagonal matrix A with the given integers as its diagonal entries and let us consider the matrix $B = (I + \mathbf{a}\mathbf{b}^t)A(I + \mathbf{a}\mathbf{b}^t)^{-1}$. We see that B is actually an integral matrix. Moreover, the eigenvalues of B are exactly those of A and the columns of $I + \mathbf{a}\mathbf{b}^t$ are eigenvectors of B.

Kanakku Puly

Acharya Prafulla Chandra at the College of Science

Gurunath Mukherjee

Gurunath Mukherjee is Sir Rashbehary Ghose Professor of Chemistry of Calcutta University. His major research interest is in metal-ligand complexation equilibria of relevance to biological systems.

Dream of Life

The College of Science of Calcutta University was founded in March 1914, by Vice-Chancellor Sir Asutosh Mookherjee. For this, a piece of land at 92 Upper Circular Road (now Acharya Prafulla Chandra Road) was donated by Sir Taraknath Palit, who together with Sir Rashbehary Ghose and the Raja of Khaira Estate provided funds for construction of buildings and creation of several faculty positions. Anticipating these developments, Sir Asutosh had already invited Prafulla Chandra in 1912 to be *'The first University Professor of Chemistry'*.

Prafulla Chandra, then a Professor of Chemistry in Presidency College, received the invitation letter in London where he was attending the Congress of the Universities of the Empire as a delegate. He wrote back, *"I look upon the proposed College of Science as the realization of the dream of my life and it will be a source of gratification to me to join it ..."*. Prafulla Chandra retired from Presidency College in 1916 and joined the College of Science as the first Sir Taraknath Palit Professor of Chemistry in the same year. He was fifty five.

Research School

He had already created history while working in Presidency College – by his teaching, his research, his industrial activities and by his remarkable book, *'History of Hindu Chemistry'*. His activities progressed unabated and in fact, got augmented after he arrived at the College of Science. He was already recognised as the originator of chemical research in India and he then proceeded with renewed vigour to work in new areas especially on the chemistry and coordination chemistry of sulphur compounds and noble metals as elaborated in another article in this issue.

Prafulla Chandra's research school flourished more than ever before with the likes of N R Dhar, J C Ghosh, P K Bose, J N Mukherjee, P Rây, P B Sarkar and H K Sen. One of his young research associates, now 90, Nripendra Nath Ghosh, who retired from the College of Science in 1975, recalls with great nostalgia the first synthesis and characterisation of the two isomeric forms of $IrCl_3.3Et_2S$. At that time funds for research equipment were not easy to come by and this had both a negative and a positive effect on research work especially for those in the physical chemistry area. Prafulla Chandra has described how this actually helped J C Ghosh to proceed with his seminal work on conductivity. *'Deprived of the use of apparatus he shut himself up in his room in the College of Science .... He tabulated the enormous data on conductivity and by a sort of happy sagacious intuition arrived at the equations...'.*

Prafulla Chandra himself was publishing most of his works in the *Journal of the Chemical Society,* London. It was increasingly felt by him and his associates that time has come to start a chemical society in India with a journal as its organ.

Indian Chemical Society

It has hitherto been the custom to publish research papers in the chemistry journals in England, Germany and America. Prafulla Chandra himself was publishing most of his works in the *Journal of the Chemical Society*, London. It was increasingly felt by him and his associates that time has come to start a chemical society in India with a journal as its organ. The idea was discussed in 1919 by S S Bhatnagar (a grandpupil of Prafulla Chandra), J N Mukherjee and J C Ghosh, then working at the University College Chemical Laboratory, London. They felt that an Indian Chemical Society should be established with Prafulla Chandra as the President.

The Society was finally established in 1924 with a generous donation from Prafulla Chandra who also agreed to be the President for the first two terms. The London Chemical Society sent this telegram, *"Hearty congratulations and warm wishes to the newly formed Indian Chemical Society"*. The *Journal of the Indian*