

(8) The facts can be accounted for on the view that in the formation of the polar bond, which involves a spontaneous rearrangement of the electronic systems of the atoms concerned, the bond is stabilized spontaneously by a three body collision with a free metallic electron which carries away all the reaction energy. The effect is thus a quantum phenomenon. This view gives a reasonable account of the energy distribution. It also allows of a simple interpretation of the equation $E_m + D = \text{constant}$. It is $E_m = E_c - \phi$, where E_c is the energy of the corresponding elementary chemical reaction responsible for E_m and ϕ is the work function of the metal. *This relation appears to be general and is similar to the fundamental law of photoelectricity.*

A more refined and detailed experimental investigation than has hitherto been carried out with phosgene is then given. This is followed by a discussion of the low energy part of the spectrum, the determination of the true zero on the volt scale and of E_m and its relation to E_c .

The last section confirms the equation $E_m = E_c - \phi$ for the particular case of COCl_2 .

The Structure and Formula of 12-Phosphotungstic Acid.

By J. F. KEGGIN, Ph.D.

(Communicated by W. L. Bragg, F.R.S.—Received June 14, 1933—Revised November 27, 1933.)

[PLATE 1.]

1. *Introduction.*

This acid belongs to a large class of compounds known as the heteropolyacids, of which the structures and exact formulæ have long been a subject for speculation. The heteropolyacids are compounds in which one atom of such elements as P, Si, As, B, Al, etc., is combined with a number of atoms of an element such as W or Mo, together with a relatively large number of atoms of oxygen. In addition to the elements mentioned, it has been shown that the oxides of a considerable number of other elements show a tendency to form heteropolyacids. All formulæ proposed indicate a relatively large number of atoms in the molecule, and a complex structure. In spite of the complexity of the molecule, many of these acids are quite stable, and form stable salts with practically all metals. The best known compounds of this group are the silicotungstic, silicomolybdic, phosphotungstic and phosphomolybdic acids, in which one atom of silicon or phosphorus is combined with a number of atoms

of tungsten or molybdenum. Mixed acids are also known in which a number of tungsten atoms are replaced by molybdenum atoms, or *vice versa*. The heteropolyacids are classified according to the ratio of the numbers of the two types of cations present.

Throughout the whole class of heteropolyacids, those acids which have the same cation-cation ratio tend to be isomorphous and have similar properties.

These acids have several outstanding properties; the following apply more especially to the 12-acids, though several of the other types of acids are very similar:—

- (1) They form crystals containing large amounts of water of crystallization.
- (2) They are usually very soluble in solvents containing oxygen in the molecule*—in water, ether, alcohols, alcoholic esters, ketones, aldehydes, etc., but not in such solvents as benzene which contain no combined oxygen. Ether will extract these acids from aqueous solution, forming a system of three layers, with ether on top, an aqueous layer next and at the bottom a saturated solution of the acid in ether. It has been suggested† that a loose compound of the oxonium type is formed with ether. This property is used in the preparation and purification of the heteropolyacids.
- (3) They are readily reduced‡ by common reducing agents such as nascent hydrogen, H_2SO_3 , etc.
- (4) Perhaps the most remarkable property is the ability of these acids to form insoluble precipitates, often crystalline, with many substances, which substances often have large molecules. With the alkaloids bulky precipitates are formed; the standard method of estimating nicotine makes use of this property. They have been suggested as antidotes in cases of alkaloid poisoning. Albumen, peptones, etc., also give precipitates with these acids, which are used in their separation. They give precipitates with substances containing urea, and with amino-acids form crystalline compounds.§ With basic dyes they give extremely insoluble lakes which are remarkably stable and fast to light.

The present work is concerned with 12-phosphotungstic acid.

* Scroggie, 'J. Amer. Chem. Soc.,' vol. 51, p. 1057 (1929).

† Rosenheim and Jaenicke, 'Z. anorg. Chem.,' vol. 100, p. 319 (1917).

‡ Wu, 'J. Biol. Chem.,' vol. 43, p. 189 (1920).

§ Drummond, 'Biochem. J.,' vol. 12, p. 5 (1918).

2. *Brief Review of the Literature with Reference to the Constitution of the 12-heteropolyacids.*

The heteropolyacids were first discovered by Berzelius* in 1826. Among the more important of the earlier workers on these compounds, De Marignac,† Scheibler,‡ Sprenger,§ Soboleff,|| Kehrman,¶ Parmentier,** and Copaux†† may be mentioned. Most of these workers suggest $H_3PW_{12}O_{40}$, and $H_4SiW_{12}O_{40}$ as the empirical formulæ of the anhydrous 12-phosphotungstic and 12-silicotungstic acids, as a result of dehydration experiments.

In 1908, Miolati and Pizzighelli,‡‡ and later Rosenheim and co-workers,§§ suggested $H_7[P(W_2O_7)_6]nH_2O$ and $H_8[Si(W_2O_7)_6]nH_2O$ as the formulæ of these acids, as a result of titration experiments. This type of formula is known as the Miolati-Rosenheim formula, and is now considered as the classical formula.

In 1913 W. and D. Asch||| suggested a structure for the 12-acids, in which the molecule consists of two hexite rings. This gave $H_9SiW_{12}O_{42}nH_2O$ as the formula for 12-silicotungstic acid.

Pauling,¶¶ in an attempt to explain the properties of the 12-heteropolyacids, proposed, on theoretical grounds, the first three-dimensional structural formula in which the positions of the atoms and the exact manner of co-ordination were indicated. After reviewing the literature, he decided that the 12-phospho-acids are three-basic and the 12-silico-acids are four-basic. Also that the 12-acids and their salts show a marked tendency to crystallize with cubic symmetry, which indicates a highly symmetrical molecule. The proposed molecule is a co-ordinated structure in which 12 tungsten atoms, each surrounded by an octahedron of 6 oxygen atoms, are linked in a continuous shell, by sharing oxygen atoms, round a central PO_4 or SiO_4 tetrahedral group. Each WO_6 octahedron shares three oxygen atoms with neighbouring WO_6 octahedra. In the complete acidic anion there are 18 oxygen atoms, each

* 'Pogg. Ann.,' vol. 6, p. 369 (1826).

† 'C. R. Acad. Sci. Paris,' vol. 55, p. 888 (1862).

‡ 'Z. Naturwiss. Halle,' vol. 40, p. 298 (1872).

§ 'Bull. Soc. Chim.,' vol. 36, p. 221 (1881).

|| 'Z. anorg. Chem.,' vol. 12, p. 16 (1896).

¶ 'Ber. deuts. chem. Ges.,' vol. 20, p. 1811 (1887).

** 'C. R. Acad. Sci. Paris,' vol. 92, p. 1234 (1881).

†† 'Ann. Chim. Phys.,' vol. 7, p. 118 (1906); 'Bull. Soc. Chim.,' vol. 3, p. 101 (1908).

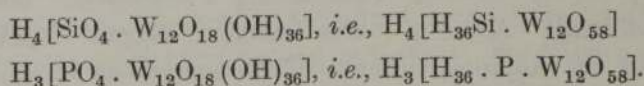
‡‡ 'J. Pract. Chem.,' vol. 77, p. 417 (1908).

§§ Rosenheim and Pinsker, 'Z. anorg. Chem.,' vol. 70, p. 73 (1911); Rosenheim and Jaenicke, 'Z. anorg. Chem.,' vol. 100, p. 304 (1917); vol. 101, p. 247 (1917).

||| "The Silicates in Chemistry and Commerce," London, vol. 15, p. 78 (1913).

¶¶ 'J. Amer. Chem. Soc.,' vol. 51, p. 2868 (1929).

shared between two tungsten atoms, thus having their charges completely satisfied. Each of the remaining 36 oxygen atoms is linked to 1 tungsten atom only, and takes up a hydrogen atom to satisfy its charge, giving 36 OH groups as an outer shell. The symmetry is of the cubic point group T_d . This gives the formulæ



Thus this type of molecule cannot exist for the dehydrated forms of the 12-acids reported, with oxygen contents less than 58.

Scroggie and Clark* attacked the problem of the structure of 12-silicotungstic acid both by chemical and X-ray methods.

The acid dried at 100° C. was examined by X-rays using the powder method. They obtained lines corresponding to a body-centred cube of edge = 12·16 Å. By density measurements they found that the unit cell contained two molecules. No attempt was made to work out the positions of the atoms, or to get further details from this photograph. Their work showed that 12-silicotungstic acid is 4-basic. The acid dried at 100° C. they represent by $4H_2O \cdot SiO_2 \cdot 12WO_3 \cdot 4H_2O$, i.e., $H_{16} \cdot SiW_{12}O_{46}$.

This form of the acid they found to be very persistent, and very strong dehydrating conditions were necessary to remove more water. They succeeded in dehydrating to $2H_2O \cdot SiO_2 \cdot 12WO_3$, i.e., $H_4SiW_{12}O_{40}$, and found that this apparently was the anhydrous acid, as the removal of any further oxygen caused the acid to change its physical and chemical properties completely, indicating a breakdown of the molecule. From these results they proposed a molecule for 12-silicotungstic acid which gave the formula of 12-silicotungstic acid as $H_4[H_{12}SiW_{12}O_{46}]$.

M. and E. Kahane† studied the dehydration of 12-phosphotungstic acid and came to the conclusion that the dehydrated acid has a formula of the type $H_nP \cdot W_{12}O_{40}$. As the classical Rosenheim-Miolati formula and also Pauling's proposed formula have more than 40 oxygen atoms in the molecule, they consider these formulæ incompatible with their results for dehydrated forms of the acid, and further, consider it unlikely that there should be a different molecule for more highly hydrated forms of the acid.

A large number of hydrates of the 12-acids and their salts have been described by many workers. Representing the 12-acids by the typical formula

* 'Proc. Nat. Acad. Sci. Wash.', vol. 15, p. 1 (1929).

† 'Bull. Soc. Chim.', vol. 49, p. 557 (1931).

$H_xRM_{12}O_n$, including water of crystallization to avoid confusion, hydrates have been described where $n = 40, 44, 46, 58, 58\frac{1}{2}, 61, 62, 65, 68, 69, 69\frac{1}{2}, 70, 70\frac{1}{2}$.

In addition to the normal 12-acids which have been discussed, so-called iso-12-acids have been reported in the cases of 12-silicotungstic and 12-borotungstic acid. The cation-cation ratio is reported to be still 1-12, but the properties of these iso-12-acids differ from those of the normal 12-acids; the iso-acids and their salts crystallize in more complex forms with different amounts of water of crystallization, etc. Iso-12-silicotungstic acid was first reported by De Marignac,* who also prepared its salts. Copaux† and Rosenheim‡ have also studied these iso-12-acids. The iso-12-acids are thought to be isomeric forms of the normal 12-acids. The literature, however, is not very definite concerning these iso-acids. Rosenheim, in his proposed formula, attempts to account for their existence by assigning different properties to different atomic positions in his molecule, whilst Pauling suggests that they may be explained by assuming condensation of two molecules of the normal 12-acid to form the molecule of the iso-12-acid, which would then contain 24 tungsten atoms and 2 silicon or boron atoms.

3. Discussion of Literature.

The literature concerning the 12-heteropolyacids is very large, and much confusion exists owing to uncertainty as to the correct formula of the molecule. Many formulæ have been suggested which differ widely. The classical chemical formula attributes a basicity of 7 to the 12-phospho-acids and a basicity of 8 to the 12-silico-acids, but the experimental evidence for this is not conclusive. Only in very rare cases have salts been reported in which this number of hydrogen atoms have been replaced, *e.g.*, some Ag and guanidine salts, and even for these salts it is more normal to have only 3 and 4 hydrogens replaced instead of 7 and 8 respectively. The salts in which 7 and 8 hydrogens are replaced are only prepared with difficulty. The electrometric evidence supporting these high basicities again cannot be considered conclusive. Practically all salts reported support the formulæ which treat with 12-phospho-acids as 3-basic and the 12-silico-acids as 4-basic, and modern workers tend to consider these basicities as correct. Also the reactions of the 12-acids indicate a structure of MO_6 octahedra rather than one of MO_4 tetrahedra. For example,

* 'Ann. Chim. Phys.,' vol. 3, p. 5 (1864).

† 'Ann. Chim. Phys.,' vol. 17, p. 217 (1909).

‡ Rosenheim and Jaenicke, 'Z. anorg. Chem.,' vol. 101, p. 235 (1917).

the MoO_4 group is not usually highly coloured, whereas 12-phosphomolybdic acid is of a bright orange colour, which colour is a characteristic of the MoO_6 group. Again, the fact that these acids are very susceptible to reduction would seem to suggest MO_6 groups rather than MO_4 groups.

References to hydrates are meaningless unless the formula used for the acid is given. Some workers tend to treat different hydrates of the same type of acid as distinct acids, describe them as coming out of the same solution together, with differing crystalline forms, and from these differing crystals prepare salts which they declare to differ according to the hydrate of the acid used. Some of these statements are due possibly to the use of impure heteropolyacids; great care must be taken in preparing the 12-acids to ensure that no 9-acid is present. Throughout all the published work, however, there appears to be general agreement that the hydrate of the 12-acids which crystallizes out of saturated aqueous solution at room temperature is of the type $\text{H}_x\text{RM}_{12}\text{O}_{70}$, though some workers suggest $\text{H}_x\text{RM}_{12}\text{O}_{69}$, and also that when salts of these acids are dehydrated, the lowest form of the anion is $\text{RM}_{12}\text{O}_{40}$; removal of more oxygen results in a complete change of properties. There is also much evidence that when 12-acid is dehydrated the lowest form is $\text{H}_n\text{RM}_{12}\text{O}_{40}$. In fact several formulæ have been proposed which are based on these facts, the molecule being represented as $\text{H}_n\text{RM}_{12}\text{O}_{40}$.

4. *The Results of the Present Work.*

*A General Account of the Structure of the Molecule of 12-phosphotungstic Acid, with its Formula, as found by X-ray Analysis.**—The derivation of this structure is given in a later section of this paper. The molecule of 12-phosphotungstic acid has the formula $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$. The phosphorus atom is at the centre of a group of 4 oxygen atoms arranged with their centres at the corners of a regular tetrahedron as in fig. 1. Each tungsten atom is approximately at the centre of a group of 6 oxygen atoms, the centres of which are at the corners of a distorted octahedron, as in fig. 2.

The complete acidic anion $\text{PW}_{12}\text{O}_{40}^{-3}$ is a co-ordinated structure of point group symmetry T_d , consisting of a central PO_4 tetrahedron, surrounded by 12 WO_6 octahedra as a shell, linked together by shared oxygen atoms. The 12 WO_6 octahedra are arranged in four groups. Each group consists of 3 WO_6 octahedra round a trigonal axis, so that the co-ordinates of the 3 tungsten atoms are of the type $(a . a . b)$ $(a . b . a)$ $(b . a . a)$, with two co-ordinates

* See also 'Nature,' vol. 131, p. 908 (June 24, 1933).

equal, referred to the rectangular axes of cubic symmetry, with origin at the centre of the central phosphorus atom. Fig. 3 shows the arrangement for one group of 3 WO_6 octahedra relative to the PO_4 tetrahedron. Considering first only this one group of three octahedra, there is 1 oxygen atom shared in

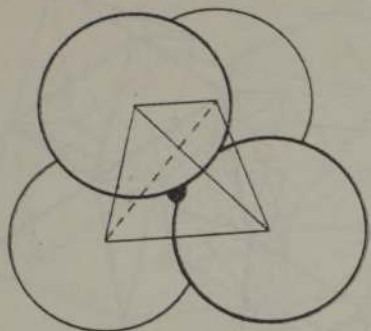


FIG. 1.—Four oxygen atoms arranged with centres at the corner of a tetrahedron, with a phosphorus atom at the centre.

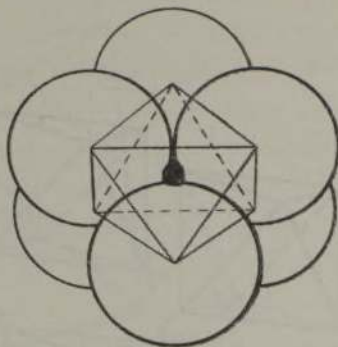


FIG. 2.—Six oxygen atoms arranged with centres at the corners of an octahedron, with a tungsten atom at the centre.

common between the 3 WO_6 octahedra and the central PO_4 tetrahedron, and each octahedron shares two other oxygen atoms, one with each of the two neighbouring octahedra. Thus each octahedron has two edges shared, one

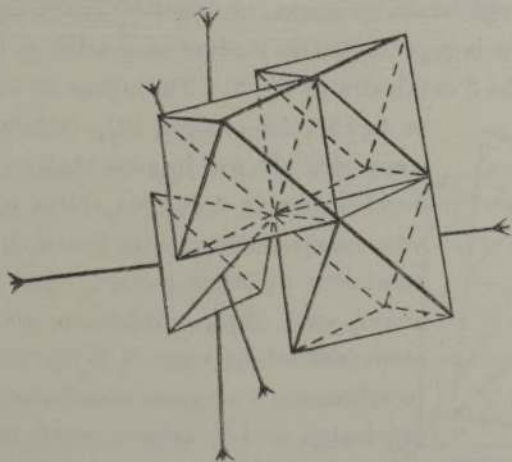


FIG. 3.—The arrangement of one group of three WO_6 octahedra relative to the central PO_4 tetrahedron.

with each of the two neighbouring octahedra. Fig. 4 shows this arrangement exploded outwards for simplicity. The arrows indicate the corners which coincide when in their correct positions as shown in fig. 3.

Four such groups of 3 WO_6 octahedra are arranged round the central PO_4 tetrahedron in tetrahedral symmetry, so that each oxygen atom of the PO_4 tetrahedron is now an oxygen atom already shared between 3 WO_6 octahedra. Fig. 5 shows the arrangement with two groups of 3 WO_6 octahedra. For a

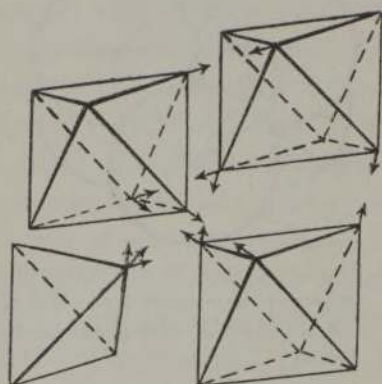


FIG. 4.—Exploded diagram of the arrangement shown in fig. 3.

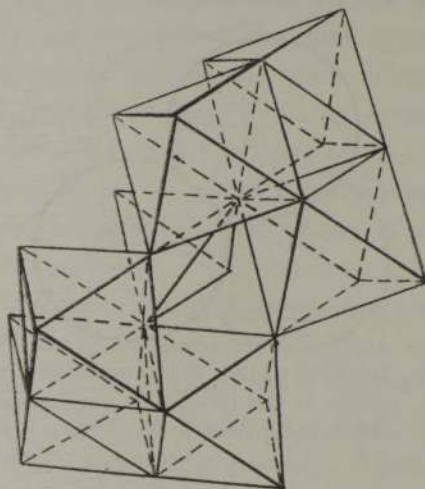


FIG. 5.—The arrangement of two groups of 3 WO_6 octahedra relative to the central PO_4 tetrahedron.

diagram of the complete acidic anion, in order to avoid confusion, each group of 3 WO_6 octahedra is represented in outline as a solid as in fig. 6, which is a representation of the 3 octahedra in fig. 3. The complete acidic anion is shown

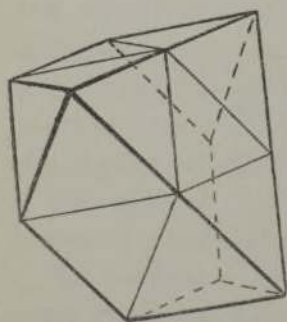


FIG. 6.—Simplified representation of the 3 WO_6 octahedra shown in fig. 3.

in fig. 7, the central PO_4 tetrahedron being shown complete. It will be seen that each WO_6 octahedron, besides sharing 2 oxygen atoms with octahedra in its own group of three, also shares 2 oxygen atoms with octahedra in other groups. In the complete acidic anion, each WO_6 octahedron consists of 1 oxygen atom shared between 3 WO_6 octahedra and 1 PO_4 tetrahedron, 4 oxygen atoms shared between 2 WO_6 octahedra, and 1 oxygen atom unshared with other polyhedra. Also, two edges of each WO_6 octahedron are shared with edges of two other octahedra.

This anion has the formula $\text{PW}_{12}\text{O}_{40}^{-3}$. Hence the molecule of 12-phosphotungstic acid has the formula $\text{H}_3\text{PW}_{12}\text{O}_{40}$. This might be written $\text{H}_3[\text{PO}_4(\text{WO}_3)_{12}]$, to indicate a central PO_4 tetrahedral group surrounded by 12 WO_6 octahedra, each of which is WO_3 in effect. But perhaps

the best form of expression is $H_3[P \cdot (W_3O_{10})_4]$, to indicate a modified PO_4^{-3} tetrahedral group, in which each of the 4 oxygen atoms has been replaced by

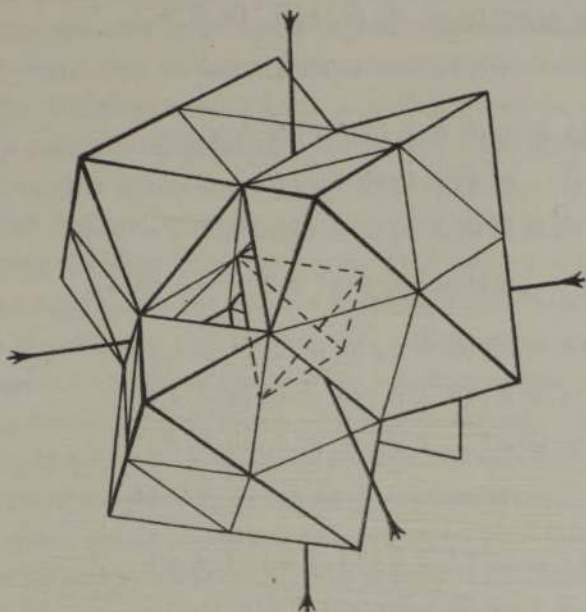


FIG. 7.—The complete anion $PW_{12}O_{40}$.

a $W_3O_{10}^{-2}$ group, each $W_3O_{10}^{-2}$ group consisting of 3 WO_6 octahedra sharing oxygen atoms with other octahedra. This formula agrees with the mass of chemical evidence.

Co-ordinates of Atoms, and Interatomic Distances.—The oxygen atoms fall into four groups, which will be called O_1 , O_2 , O_3 and O_4 . The positions of these types of oxygen atoms are indicated in fig. 8, which represents the left-hand octahedron in fig. 3. The O_1 oxygen atoms are shared between 3 WO_6 octahedra and 1 PO_4 tetrahedron. The O_2 oxygen atoms are shared between 2 WO_6 octahedra. The O_3 oxygen atoms are also shared between 2 WO_6 octahedra. The O_4 oxygen atoms are unshared with other polyhedra. The O_1 - O_3 edges are shared between 2 WO_6 octahedra.

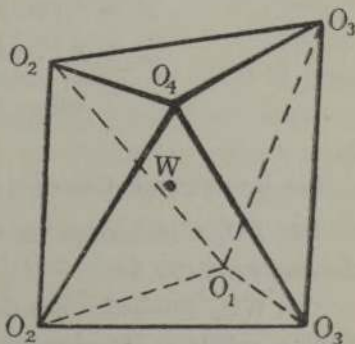


FIG. 8.—The left-hand octahedron in fig. 3, showing the position of the four types of oxygen atoms.

The atoms are referred to the rectangular axes of cubic symmetry, with origin at the centre of the central phosphorus atom.

The co-ordinates of the atoms are :—

1 P atom at (0, 0, 0)

4 O₁ atoms at (*a a, a*) (*a, ā, ā*) (*ā, a, ā*) (*ā, ā, a*)

where *a* = 0.99 Å.

12 O₂ atoms at (*b̄, b, c*) (*b̄, b̄, c̄*) (*b, b, c̄*) (*b, b̄, c*)

(*b̄, c, b*) (*b̄, c̄, b̄*) (*b, c, b̄*) (*b, c̄, b*)

(*c̄, b, b*) (*c̄, b̄, b̄*) (*c, b, b̄*) (*c, b̄, b*)

where *b* = 0.97 Å.; *c* = 2.84 Å.

12 O₃ atoms at (*d, d, e*) (*d, d̄, ē*) (*d̄, d, ē*) (*d̄, d̄, e*)

(*d, e, d*) (*d, ē, d̄*) (*d̄, e, d̄*) (*d̄, ē, d*)

(*e, d, d*) (*e, d̄, d̄*) (*ē, d, d̄*) (*ē, d̄, d*)

where *d* = 1.49 Å.; *e* = 3.54 Å.

12 O₄ atoms at (*f̄, g, g*) (*f̄, ḡ, ḡ*) (*f, g, ḡ*) (*f, ḡ, g*)

(*ḡ, f, g*) (*ḡ, f̄, ḡ*) (*g, f, ḡ*) (*g, f̄, g*)

(*ḡ, g, f*) (*ḡ, ḡ, f̄*) (*g, g, f̄*) (*g, ḡ, f*)

where *f* = 0.1 Å.; *g* = 3.79 Å.

12 W atoms at (*h, k, k*) (*h, k̄, k̄*) (*h̄, k, k̄*) (*h̄, k̄, k*)

(*k, h, k*) (*k, h̄, k̄*) (*k̄, h, k̄*) (*k̄, h̄, k*)

(*k, k, h*) (*k, k̄, h̄*) (*k̄, k, h̄*) (*k̄, k̄, h*)

where *h* = 0.07 Å.; *k* = 2.495 Å.

The interatomic distances are as follows :—

The PO₄ tetrahedron in the centre is undistorted. All edges (O₁–O₁ distances) are 2.80 Å.

The WO₆ octahedra are distorted. The shared edges (O₁–O₃ distances) are 2.65 Å. The O₁–O₂ distances are 2.70 Å. The O₃–O₃ distances are 2.90 Å.

The O₂–O₂ distances are 2.65 Å. The O₃–O₂ distances are 2.61 Å. The O₂–O₄ distances are 3.10 Å. The O₄–O₃ distances are 2.80 Å.

The tungsten atom is 2.34 Å. distant from the O₁ oxygen atom, 1.85 Å. distant from the O₂ and O₄ oxygen atoms and 2.0 Å. distant from O₃ oxygen atoms.

5. Discussion of this Structure.

From a consideration of the forces acting in this structure, these distances and the distortions are seen to be quite logical. The average crystal radii of the P, W, and O atoms may be taken as equal to 0.34 Å., 0.62 Å., and 1.35 Å. respectively. The tungsten atoms have a major effect in determining the structure, and the positions of the oxygen atoms will be to a large extent governed by them. The tungsten atoms repel each other, and tend to distribute themselves in the most uniform manner possible where their potential energy is lowest. Neglecting the very small displacement (0.07 Å.) of these atoms from the ideal positions, the reasons for which will be dealt with later, in this structure this distribution is realized; the 12 tungsten atoms are arranged on a sphere with the most uniform distribution possible, each tungsten atom being equidistant (3.53 Å.) from four neighbouring tungsten atoms. They may also be regarded as being at the centres of the edges of a regular octahedron, or at the centres of the edges of a cube. The oxygen atoms then form distorted octahedra round these tungsten atoms in such a manner as to give this distribution for minimum potential energy of the tungsten atoms most closely. The edge of a PO_4 tetrahedron is normally about 2.6 Å. In this case the edge is lengthened to 2.8 Å, as 3 tungsten atoms act in opposition to the central phosphorus atom and tend to pull the oxygen atoms of the PO_4 group outwards. The tungsten atoms are not at the centres of the octahedra. Mutual repulsion tends to make the sphere on which they lie be of as large a radius as possible, and in this structure this effect is considerable. Hence the distance of the tungsten atoms from the inner O_1 oxygen atoms is relatively large (2.34 Å.) as compared with their distances from the other oxygen atoms. Also, in order to reach positions of minimum potential energy, the tungsten atoms are displaced from the centres of the octahedra so as to be nearer the O_2 oxygen atoms (1.85 Å. distant) than the O_3 oxygen atoms (2.0 Å. distant). In agreement with this displacement, the O_3 - O_3 distances are lengthened to 2.90 Å. and the O_2 - O_2 distances and the shared edges, (O_1 - O_3 distances) are shortened to 2.65 Å.

The formula $\text{H}_3\text{PW}_{12}\text{O}_{40}$ agrees with the large mass of evidence already mentioned, which gives this formula for the anhydrous acid.

This structure has some remarkable features. It appears that some of the principles determining the structure of complex ionic crystals as formulated by Pauling* are not strictly obeyed. Each of the 4 oxygen atoms of the type O_1

* 'J. Amer. Chem. Soc.,' vol. 51, p. 1010 (1929).

which form a tetrahedron round the central phosphorus atom, is shared between 1 phosphorus and 3 tungsten atoms. According to Pauling's "electrostatic valence principle," where the electrostatic valence bonds of the cation act in a roughly symmetrical manner and are neutralized by the immediate neighbouring anions, this implies that each O_1 oxygen atom has a force of $+4\frac{1}{4}$ acting upon it, if the phosphorus atom has charge of $+5$ and the tungsten atom a charge of $+6$. Again, there is an outer shell of 12 O_4 oxygen atoms, each of which is directly connected with only 1 tungsten atom. According to the above principle each of these oxygen atoms has a force of only $+1$ acting upon it. This structure may be considered in two ways. (A) If the bonds of the cations act in a roughly symmetrical manner, then this complex anion has a region of large positive potential at its centre, surrounded by a region of negative potential as a shell, which, by action through a distance across intervening atoms, gives a total charge of -3 , or (B) the electrostatic valence bonds of the cations do not necessarily act in a symmetrical manner, the directions of their action being determined by the positions of the unsatisfied anions.

The properties to be expected from this structure agree well with the known properties of 12-phosphotungstic acid.

This acidic anion would be expected to be stable, as the tungsten atoms are practically in positions of minimum potential energy, and the whole structure is compact and tightly bound together.

These acidic anions are complete structural units in themselves, and when packed together in a crystal are not strongly linked to each other, and should thus be relatively easy to separate. Thus the acid would be expected to be highly soluble.

Also any crystalline structure formed by the packing together of these anions would be expected to contain a relatively large amount of water of crystallization. For these anions are large, roughly spherical units, and, when arranged even in close packing, will still leave a considerable volume of unoccupied space. Water of crystallization will tend to pack in these spaces so as to make the whole structure more homogeneous, and as oxygen atoms are very small compared with these acidic anions, there is always room for a relatively large amount of water.

This anion also explains why numerous hydrates are formed by the acid. As the atoms are arranged in a fairly uniform manner, and the charge is small for such a large group of atoms, this anion may be considered as a large, practically spherical, unit, with a fairly uniform charge distribution over its

surface. Such a unit has no strong directional forces which would tend to make one type of packing more probable than any other arrangement. Thus it is to be expected that quite a number of arrangements would exist. Also, as these units are so uniform in shape and charge distribution, they will tend to pack in simple arrangements, which explains the tendency for the hydrates to be cubic, despite the complexity of the anion.

The tungsten atom, by reason of its small size, may be surrounded by a tetrahedron of oxygen atoms, as well as by an octahedron, as in this structure. Thus the reduction of the present arrangement should not be difficult.

The marked tendency of these acids to combine with large organic molecules to form insoluble precipitates is possibly connected with the large, shell-like region of negative potential surrounding the anion.

The basicity of three for this structure agrees with that found by most chemical workers. Also the oxygen content of the molecule—40 atoms of oxygen—agrees exactly with the results obtained for the anhydrous acid by many workers on the dehydration of the acid and its salts.

6. Experimental.

The preparation of the acid used in this work was that described by Wu.* It was found that if no HCl was added during the last ether extraction, the product was pure 12-phosphotungstic acid, though the omission of HCl reduces the yield.

The colourless octahedra which crystallize from aqueous solutions at room temperatures are extremely unstable, and commence to lose water and to break down to a white powder immediately on drying. Thus, though by taking precautions against loss of water an apparently good photograph of this hydrate was obtained, this photograph was not used in this work owing to the uncertainty introduced by the instability of the crystal. The structure of this hydrate, however, has since been determined.

Dehydration of the Acid.—In order to obtain a more definite photograph, a more stable hydrate was sought. It was assumed that the hydrate which crystallizes out of saturated aqueous solution at room temperature in colourless octahedra was of empirical formula either $H_xPW_{12}O_{70}$ or $H_xPW_{12}O_{69}$. This was the only assumption made as regards the formula, and losses of water on dehydration were calculated on the first formula. Whether H_7 or H_3 is

* 'J. Biol. Chem.,' vol. 43, p. 189 (1920).

taken as the basicity is immaterial, owing to the large molecular weight of the acidic anion.

In order to find the loss in weight, it was necessary to weigh this unstable hydrate. To do this with as little error as possible, large crystals were grown, of dimensions of the order of 1 cm. These crystals were taken out of the solution, dried quickly with filter paper, put in a closely stoppered bottle and weighed immediately. By using large crystals, surface action had a relatively small effect and it was found possible to repeat results quite accurately.

This unstable hydrate was allowed to reach constant weight in the open at about 70% RH. 15.6 mols. of water were lost. An X-ray photograph of this product showed a mixture with no distinct lines.

Drying over CaCl_2 at atmospheric pressure and room temperature was next tried. The acid reached constant weight with a loss of 22.5 mols. of water. On standing in the open this product took up only 0.5 mols. of water, which was probably due to surface adsorption, and indicated that this product is fairly stable. This gave a photograph with sharp lines. On drying over P_2O_5 *in vacuo*, the weight was practically constant with a loss of 23.5 H_2O . On prolonged drying, however, over a period of several days, the weight continued to fall very slowly, until after about a week, 24 mols. of water were lost. After this period the acid commenced to turn brown on the surface, indicating that disintegration of the molecule had commenced. For losses of water ranging from 22.5 mols. to 23.5 mols. the product gave identical sharp lines but after losses of more than 23.5 mols. of water the lines commenced to broaden, and after a loss of 24 mols. of water the lines were distinctly blurred, which indicates the beginning of a change in the crystal structure. There is a definite structure in this range, but the number of molecules of water present is not definitely fixed by the above results. The water content of this hydrate will be considered later.

X-ray Technique.—The X-ray photographs were taken by the powder method in a camera of the modified Debye-Scherrer type as described by Bradley and Jay.* The specimen to be photographed is in the form of a powder rod. Owing to the chemical activity of this acid, and its variable water content, the normal method of preparing the powder rod, by fixing the powder to a hair with adhesive, was not used. In order to avoid the possibility of change, the powder was packed into a fine capillary of Lindemann glass, which was sealed, mounted in the camera and used as a specimen. This glass

* 'Proc. Phys. Soc.,' vol. 44, p. 563 (1932).

has a low absorption for X-rays, being composed of lithium and beryllium borates.

The observed intensities of reflection were obtained by measuring the blackening of the powder photograph by means of a Cambridge microphotometer designed by Dobson.* The figures for blackening were then converted into intensity values by means of a calibration curve for the emulsion used, in which exposure is plotted against blackening. The intensity measurements were then plotted against distance along the film, and an integrated value of the intensity of each line was obtained by determining the area under the curve and above the base line of general blackening.

The structure investigated in this work was that of the dehydrated 12-phosphotungstic acid discussed before, which gave sharp lines. The acid actually photographed was the product obtained by dehydrating the octahedral crystals over P_2O_5 *in vacuo*, with a loss in weight corresponding to loss of 23.5 mols. of water.

CuK_{α} radiation was used. A typical powder photograph of this hydrate is shown in Plate 1.

7. Determination of the Lattice.

The values of Σh^2 for the lines were found to be all even numbers, except for two very faint lines, corresponding apparently to $\Sigma h^2 = 33$ and 41. These two lines were neglected at first, as it was thought that they were due to slight impurity. An arrangement of lines where Σh^2 corresponds to consecutive even numbers is a characteristic of the body-centred cubic arrangement. Also, as lines where $\Sigma h^2 = 28, 60, 92$, etc., which are theoretically impossible, were missing from the photograph, it was assumed, at first, that this structure was a body-centred cubic arrangement. It was found later that this was not quite the true arrangement. The effect of the modification necessary, is, however, extremely small. This will be considered later. The value of "a," the length of the edge of the unit cube, was now calculated for each line. The results are given in Table I.

The usual practice of comparing the observed $\sin^2\theta$ with the calculated $\sin^2\theta$ is unnecessary here.

By plotting these values of "a" against $\cos^2\theta$, and extrapolating to $\cos^2\theta = 0$,† the true value of the edge of the unit cube was found to be 12.141 ± 0.005 A.

* 'Proc. Roy. Soc.,' A, vol. 104, p. 248 (1923).

† 'Proc. Phys. Soc.,' vol. 44, p. 562 (1932).

The density of this hydrate was determined by the displacement of benzene, using a density bottle, and was found to be 5.6. The density calculated for two molecules of $H_xPW_{12}O_{46}$ in a cube of side 12.14 Å. is 5.55. This agrees well with the experimental value. For a body-centred cubic arrangement, this implies that there is an anion at each corner of the unit cube and one at the centre, all anions being equivalent for this symmetry.

Table I.

Σh^2 .	"a" in Å.	Σh^2 .	"a" in Å.	Σh^2 .	"a" in Å.
2	11.665	60	—	118	—
4	11.827	62	12.113	120	—
6	11.891	64	—	122	12.139
8	11.937	66	12.115	124	—
10	11.955	68	12.118	126	12.141
12	11.981	70	12.122	128	—
14	12.004	72	12.122	130	—
16	12.007	74	12.121	132	12.147
18	12.027	76	—	134	12.145
20	12.035	78	12.124	136	—
22	12.040	80	—	138	12.147
24	—	82	12.125	140	—
26	12.052	84	—	142	12.144
28	—	86	12.129	144	—
30	12.069	88	—	146	—
32	12.080	90	12.130	148	—
34	12.079	92	—	150	12.147
36	12.078	94	12.127	152	12.143
38	12.075	96	—		
40	12.083	98	12.130		
42	12.083	100	12.129		
44	12.085	102	12.129		
46	—	104	—		
48	12.093	106	12.134		
50	12.101	108	—		
52	12.106	110	12.132		
54	12.099	112	—		
56	12.101	114	—		
58	12.111	116	12.135		

The above, together with the observed intensity values, were all the data available, as no single crystal data could be obtained.

The problem was now to locate the atoms in the structure by use of the above data.

8. Location of the Tungsten Atoms.

As the scattering power of a tungsten atom for X-rays is much greater than that of either an oxygen or a phosphorus atom, it was possible to locate the 12 tungsten atoms quite accurately, by neglecting all other types of atoms at first, and considering the agreement between the observed intensities and the

intensities calculated for the 12 tungsten atoms only. It was assumed that there were 12 tungsten atoms in each molecule of the acid, and that the anions were arranged in body-centred cubic packing.

The simplest way to arrange groups of 12 tungsten atoms to agree with body-centred cubic symmetry, is to arrange them in the manner already given in the section describing the structure of the anion, each group of 12 tungsten atoms having point group symmetry T_d . In this arrangement the positions of the atoms are defined by only two variables, and it is thus possible to represent atomic positions on a graph. When such groups of atoms are arranged with body-centred packing, the space group is T_d^3 . From a consideration of the observed intensities it was possible to impose very rough limits for the calculated intensities which would be consistent with those observed on the film. In this way curves defining areas of possible atomic positions could be drawn on a graph for each reflection. This was done for a large number of reflections until only a small area of possible positions for the tungsten atoms was left.

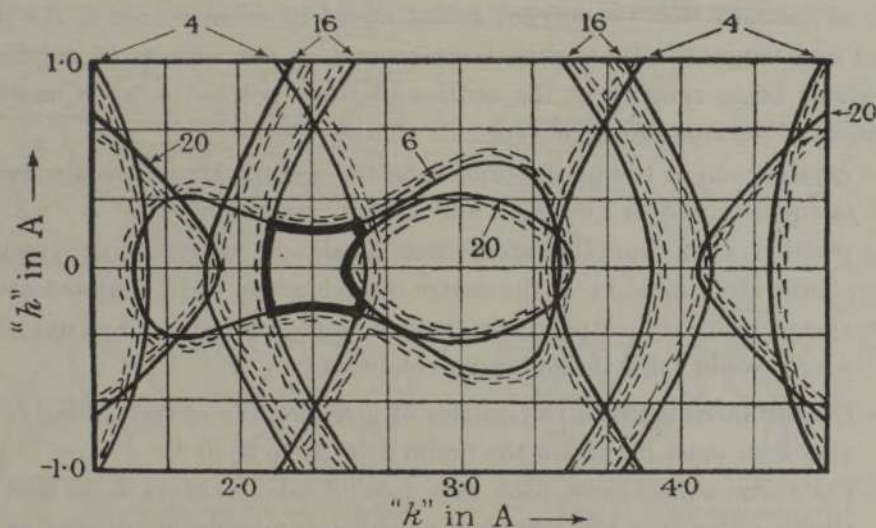


FIG. 9.—Curves locating the final small area of possible positions for the tungsten atoms. The final area is heavily outlined.

Fig. 9 shows the location of the final area of possibility. This area is shown heavily outlined, and the reflections used for this location are shown. The areas on the shaded sides of the curves are areas of forbidden co-ordinates for the tungsten atoms. The area left gives possible co-ordinates for the tungsten atoms between the limits $k = 2.155 \text{ \AA} \rightarrow 2.51 \text{ \AA}$, $h = 0.185 \text{ \AA} \rightarrow 0 \rightarrow -0.185 \text{ \AA}$. Thus the possible variation of h or k is not more than about 0.36 \AA . The location is

surprisingly definite, even though the limits of possible intensities imposed were quite rough, owing to the large allowances made for the possible effect of atoms other than tungsten. In spite of this, a sufficient number of sensitive lines, for which the intensity varies very rapidly for small changes in the atomic co-ordinates, were found to give this small final area of possibility. A similar method was used by W. L. Bragg and Warren* in work on the silicates. The mean location is $h = 0$, $k = 2.33$ A.

To get a still more accurate location of the tungsten atoms, the intensities of many lines were now worked out for sets of co-ordinates in this area, still considering only the tungsten atoms. By considering the best general agreement between observed and calculated intensities, it appeared that the most probable co-ordinates for the tungsten atoms are $h = 0$, $k = 2.495$ A. The general agreement for these co-ordinates is reasonably good for all lines.

9. *The Structure of Co-ordinated Oxygen Polyhedra agreeing with these Tungsten Co-ordinates.*

It was assumed that the oxygen atoms would be arranged round the phosphorus and tungsten atoms with their centres at the corners of polyhedra, the cations being roughly at the centres of these polyhedra, as is usual for structures of the complex ionic type.

The crystal radii of the phosphorus, tungsten and oxygen atoms are usually taken as equal to 0.34 A., 0.62 A., and 1.35 A. respectively.

The positions of the tungsten atoms were fixed, and to agree with symmetry a phosphorus atom must be at the centre of each group of 12 tungsten atoms. An arrangement of oxygen polyhedra around these fixed atoms had now to be found which would fulfil the following conditions:—

- (1) The distances between the centres of neighbouring oxygen atoms in the structure must be within the limits 2.50 A. to 3.10 A.
- (2) The acidic anions must pack in a cube of side = 12.14 A. so that the distances between the centres of neighbouring atoms in adjacent anions are of the correct dimensions. There must be two anions in each cube.
- (3) The number of hydrogen atoms necessary to give a neutral structure, *i.e.*, the basicity of the acid, must be reasonable, preferably 3 or 7 to agree with the bulk of chemical evidence.
- (4) The stability of the acid suggests that the polyhedra should be well linked together by sharing oxygen atoms.

* 'Z. Kristallog.' vol. 69, p. 168 (1928).

Many arrangements were tried with various types of polyhedra, but the conditions imposed were found to be very stringent, and condition 1 alone eliminated decisively all arrangements other than the anion which was found to be correct and which has been described. This structure was found to fulfil all the other conditions, and gave the formula of the molecule as $H_3PW_{12}O_{40}$. It is interesting to note that in none of the structures tried was a basicity of 7 indicated for this acid.

10. *The Arrangement of these Anions in the Structure of the Hydrate Investigated.*

The symmetry of this anion is essentially tetrahedral, and in considering the orientation of the anions it is convenient to refer to the orientation of the central PO_4 tetrahedron. The O_2 oxygen atoms are above a base, and the O_3 oxygen atoms are above an apex of this central tetrahedron.

The structure which has been described for the anion of 12-phosphotungstic acid is very symmetrical. At first it was thought that the anions were packed

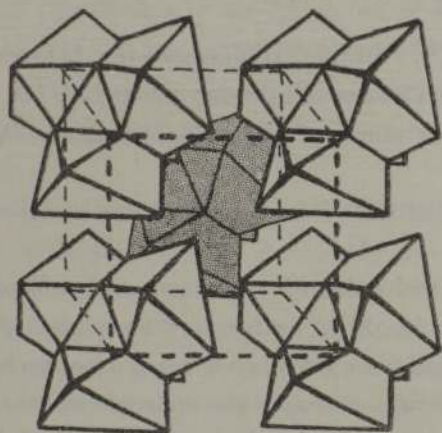


FIG. 10.—True body-centred arrangement (T_d^3).

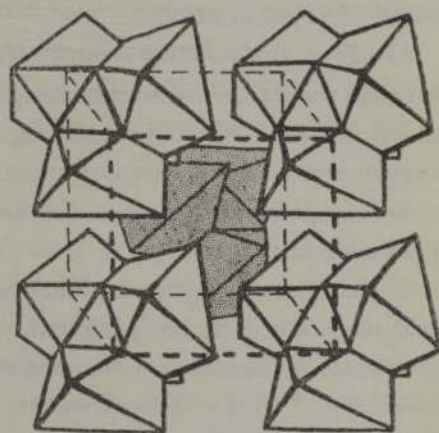


FIG. 11.—Arrangement O_h^4 .

in a body-centred cubic arrangement, as all the lines on the powder photograph indicated this type of packing, with the exception of two very faint lines corresponding to $\Sigma h^2 = 33$ and 41, which were at first neglected as being due to impurity. In this arrangement the orientation of all anions is identical, the anions being arranged base to apex right through the structure. This arrangement is shown in fig. 10. The space group for this arrangement is T_d^3 , and no reflections for which Σh^2 is odd are possible.

On further consideration, it was realized, however, that an arrangement where the anions were base to base and nose to nose in the structure would differ only slightly from the true body-centred arrangement. This arrangement is shown in fig. 11. The space group here is O_h^4 , and the only difference between this packing and the previous body-centred packing is that the anion in the centre of the cube is inverted. Thus, if the tungsten co-ordinates are actually $h = 0$, $k = 2.495$ A., there will be no change at all in the arrangement of the tungsten atoms, and as the oxygen arrangement is also fairly symmetrical, the change in the oxygen lattice will not be great. Thus it is to be expected that the photographs for these two types of arrangement would be very similar.

For the O_h^4 arrangement, lines where Σh^2 is odd are possible, but only oxygen atoms contribute to these reflections if $h = 0$ for the tungsten atoms. Hence these lines will be very weak.

The intensities of reflection for both arrangements were calculated, and compared with the observed intensities, in order to decide which arrangement is correct. An attempt was also made to find positions for the molecules of water of crystallization.

The True Body-centred Arrangement (T_d^3).—In this arrangement the distance between the centres of neighbouring oxygen atoms of adjacent anions is 2.7 A., which is reasonable. Here the O_3 oxygen atoms of one anion touch the O_4 oxygen atoms of the adjacent anion.

It is impossible to pack six molecules of water* in this structure to agree with symmetry.

A possible arrangement giving seven molecules of water per molecule of acid may, however, be suggested. A molecule of water may be placed at the centre of each face of the unit cube—at $bo\bar{o}$, $o\bar{b}o$, $o\bar{o}b$, $\bar{b}oo$, $o\bar{b}\bar{o}$, $o\bar{o}\bar{b}$, where $b = 6.07$ A. This gives three molecules of water per molecule of acid. The centres of water molecules in such positions are 3.2 A. from the centres of neighbouring oxygen atoms in the cube face, and 3.3 A. from the centres of neighbouring oxygen atoms in a direction perpendicular to the cube face. These water molecules have thus considerable freedom of motion. The other four molecules of water might be arranged between the acidic anions, on the trigonal axes of the cube, in tetrahedral symmetry, in positions aaa , $a\bar{a}\bar{a}$, $\bar{a}a\bar{a}$, $\bar{a}\bar{a}a$, where $a = 3.28$ A. Here, however, the centre of each water molecule is only

* The term "water molecule" is used here in a general sense to indicate those oxygen atoms which could be removed as water without affecting the chemical properties of the acid. No attempt is made to define the positions of the hydrogen atoms.

2.57 A. distant from the centres of six neighbouring oxygen atoms. The distance is somewhat small.

The Arrangement O_h^4 .—In this arrangement, where the two adjacent anions are base to base the oxygen atoms of the anion do not touch, being about 3.5 A. apart. There is, however, just room for a molecule of water in the hollow left here between the anions, which would hold them apart. The water— O_2 oxygen distance is 2.9 A. The positions of these four water molecules are $\bar{a}\bar{a}\bar{a}$, $\bar{a}aa$, $a\bar{a}\bar{a}$, $aa\bar{a}$, where $a = 3.03$ A. This arrangement contributes two molecules of water per molecule of acid. Where the two adjacent anions are apex to apex, the O_3 oxygen atoms of one anion touch the O_4 oxygen atoms of the neighbouring anion, the distance between their centres being 2.85 A. There is no room for a molecule of water between the anions here.

Three more water molecules may be placed, as before, at the centres of the faces of the unit cube. This gives, in all, five molecules of water per molecule of acid for this arrangement.

11. Comparison of the Intensities of Reflection Calculated for these two arrangements with those observed on the Photograph.

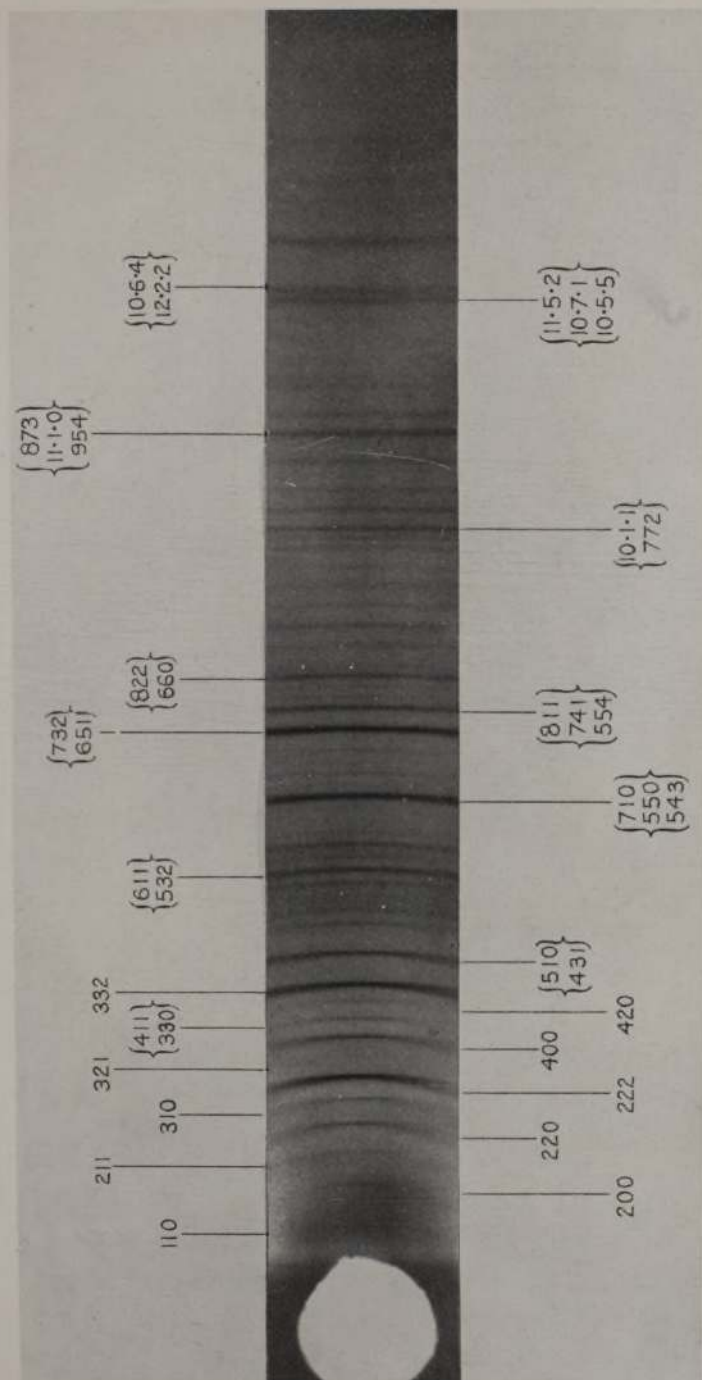
The intensities of reflection for these two arrangements were now calculated and compared with the observed intensities. The results are given in Table II.

For the O_h^4 arrangement, the tungsten atoms were first considered to have co-ordinates $h = 0$, $k = 2.495$ A. With such co-ordinates the tungsten atoms do not contribute to reflections where Σh^2 is odd. It was found that, though lines 33 and 41 were the strongest of the odd lines, they were not quite strong enough to account for the observed intensities. It was found, however, that if the tungsten atoms were shifted a very small distance (0.07 A.) to have co-ordinates $h = 0.07$ A., $k = 2.495$ A., so that these atoms began to contribute to the odd lines, the effect was greatest on lines 33 and 41, and gave calculated values which agreed with the observed intensities.

The third column in Table II gives the calculated intensities of reflection when the tungsten atoms only are considered. The values for lines where Σh^2 is odd refer only to the O_h^4 arrangement, as for the T_d^3 arrangement the values for these reflections are zero. As the calculated intensities for tungsten atoms only, for reflections where Σh^2 is even, are practically identical for the two arrangements, the values given in this column for these reflections refer to both arrangements.

Table II.

Σh^2 .	hkl .	Calculated intensities 12 tungsten atoms only for both arrangements.	Calculated intensities for T_d^3 arrangement.		Calculated intensities for O_h^4 arrangement.	Observed intensities.
			For $PW_{12}O_{40}$.	For $PW_{12}O_{40} \cdot 7H_2O$.	For $PW_{12}O_{40} \cdot 5H_2O$.	
1	100	—	—	—	—	—
2	110	28	46	43	43	43.5
3	111	0.4	—	—	0.6	Absent
4	200	12	13.5	14.5	12.5	12
5	210	—	—	—	—	—
6	211	12	11.5	13	13	12
7	—	—	—	—	—	—
8	220	32.5	42.5	29	32.5	34.5
9	{300 221}	0.3	—	—	0.2	Absent
10	310	28	24	26	26	26.5
11	311	0.2	—	—	0.7	Absent
12	222	87	99	97	101	112
13	320	—	—	—	—	—
14	321	3.5	4	3.2	3	4.1
15	—	—	—	—	—	—
16	400	40	37.5	44.5	42.5	45.5
17	{410 322}	0.01	—	—	0.2	Absent
18	{330 411}	22	18.5	18	18.5	21.5
19	331	0.5	—	—	0.7	Absent
20	420	22.5	17	18	16	13
21	421	0	—	—	0.07	Absent
22	332	116	111	108	109	101
23	—	—	—	—	—	—
24	422	0.02	1	3.1	2	?
25	{500 430}	—	—	—	—	—
26	{510 431 511}	82	62.5	62.5	62	55.5
27	{333}	1.0	—	—	1.6	?
28	—	—	—	—	—	—
29	{520 432}	0.2	—	—	1.1	?
30	521	34.5	17	18.5	18.5	16
31	—	—	—	—	—	—
32	440	15	14	18	16.5	14
33	{441 522}	1.2	—	—	1.8	Just visible
34	{530 433}	6.1	6.3	7.8	6	5.9
35	531	0.5	—	—	0.35	Absent
36	{600 442}	15.5	16.5	17	16	16.5
37	610	—	—	—	—	—
38	{611 532}	39	45	46.5	46	45
39	—	—	—	—	—	—
40	620	14.5	15	10.5	11.5	14



X-Ray powder photograph of 12-phosphotungstic acid over P_2O_5 in *vacuo*. $HgPW_{12}O_{40} \cdot 5H_2O \cdot CuK_{\alpha}$ radiation.
Cubic $a = 12.14 \text{ \AA}$.

Table II—(continued).

Σh^2 .	<i>hkl</i> .	Calculated intensities 12 tungsten atoms only for both arrangements.	Calculated intensities for T_d^3 arrangement.		Calculated intensities for O_h^4 arrangement.	Observed intensities.
			For $PW_{12}O_{40}$.	For $PW_{12}O_{40} \cdot 7H_2O$.	For $PW_{12}O_{40} \cdot 5H_2O$.	
41	{621 540 443}	2·8	—	—	4·15	4
42	541	27	29	27·5	27·5	29
43	533	0·06	—	—	0·35	Absent
44	622	5·6	6·4	6·2	6·8	7·2
45	{630 542}	0·25	—	—	0·5	Absent
46	631	2·4	1·6	1·9	1·9	?
47	—	—	—	—	—	—
48	444	1·9	4	5·2	4·7	5·2
49	{700 632}	0·1	—	—	0·2	Absent
50	{710 550 543}	98·5	111	112	111	105
51	{551 711}	1	—	—	0·8	Absent
52	640	5·6	9·1	8·9	9·6	8·3
53	{720 641 721}	0·2	—	—	0·8	Absent
54	{633 552}	12·5	14	14	14	11
55	—	—	—	—	—	—
56	642	5	6·7	4	4·3	5·8
57	{722 544}	0·26	—	—	0·6	Absent
58	730	13·5	10	10·5	10·4	10
59	{731 553}	0·45	—	—	0·6	Absent
60	—	—	—	—	—	—
61	{650 643}	0·1	—	—	0·3	Absent
62	{732 651}	117	120	116	118	130
63	—	—	—	—	—	—
64	800	0·16	0·1	0·01	0·2	Absent
65	{810 740 652}	0·35	—	—	1·8	?
66	{811 741 554}	47·5	51	51	51	58
67	733	0·04	—	—	0·2	Absent
68	{820 644}	11	12·2	12·5	12	12·8
69	{821 742}	0·4	—	—	0·95	Absent
70	653	11	11·9	12·2	12·4	12·1
71	—	—	—	—	—	—
72	{822 660}	33	41	46	45	43

All intensities are reduced to the same scale to make comparison simpler. A temperature factor $e^{-B \sin^2 \theta}$ was applied to the calculated values, where $B = 2.0$. In calculating these intensities the usual corrections were made for θ and absorption.

No correction was made for the possible effect of motion of the three water molecules in the faces of the cube. Motion would tend to decrease the effect of these molecules on the intensity.

12. Discussion of Results.

Considering the intensities calculated for the tungsten atoms only, for the lines where Σh^2 is even the agreement with the observed intensities is quite good. This applies to both arrangements. For the odd lines given by the O_h^4 arrangement, the agreement for tungsten atoms only is also reasonable. When the oxygen atoms are included, however, the agreement is much better, for both arrangements. From a consideration of the agreement for the even lines only, it is difficult to decide which arrangement is better, as the differences are very small, though the O_h^4 arrangement would appear to be slightly better.

For the odd lines, however, which are given only by the O_h^4 arrangement, the agreement is also good. In the numerical scale used here to represent intensity values, where strong lines have values in the region of 100, the lower limit of visibility is in the region 1 to 2. Thus line 33 is just visible, and line 41 is distinctly visible. From the calculations it appears that lines 27, 29 and 65 of the odd lines might also be visible, and when looked for could just be detected, though normally they would not be noticed. All the other odd lines were invisible.

This agreement of the odd lines, in addition to a slightly better agreement for the even lines for the arrangement O_h^4 , appears to prove decisively that the anions are arranged in this manner, and not in the body-centred cubic arrangement T_d^3 .

This agreement for the odd lines provides a very sensitive check on the correctness of the proposed structure. For, with 45 oxygen atoms present, it is highly probable that any error in their location would give calculated values for the intensity of some odd reflections which would be well above 2 on this scale, as the effect of the oxygen atoms can be quite large. This is well shown in the various intensity values calculated for lines 2, 26 and 30 in the table.

Thus there are only five molecules of water per molecule of acid in this partially dehydrated acid. This is of particular interest, as later work on the structure of the so-called 30 hydrate of this acid indicates that the octahedral crystals contain only 29 molecules of water per molecule of acid. Most workers have described a loss of 24 molecules of water per molecule of acid when the octahedral crystals are dehydrated to the stable hydrate investigated here. In the present work sharp lines were not obtained for losses of water of more than 23.5 molecules per molecule of acid, but it is highly probable that a certain amount of moisture is adsorbed on the surface of the fine powder. This water, though not actually in the structure, would tend to decrease the loss in weight. Thus a water content of $5\text{H}_2\text{O}$ for this hydrate may be said to agree with experimental results.

The author wishes to thank Professor W. L. Bragg, F.R.S., for his stimulating interest in the work, which was carried out in the Physical Laboratories of the University of Manchester; also Dr. A. J. Bradley for his helpful discussion.

13. *Summary.*

The structure of the molecule of 12-phosphotungstic acid has been found by X-ray analysis, using the powder method. The formula of the acid is $\text{H}_3[\text{P} \cdot (\text{W}_3\text{O}_{10})_4] \cdot n\text{H}_2\text{O}$. The anion consists of a central PO_4 tetrahedral group surrounded by 12 WO_6 octahedral groups as a shell, linked together by shared oxygen atoms. The symmetry is T_d . The positions of the atoms are given. This structure has some unusual features. In the partially dehydrated acid investigated, which contains five molecules of water per molecule of acid, these acidic anions pack together with cubic symmetry, the edge of the unit cube being $12.14_1 \pm 0.005 \text{ \AA}$. : symmetry O_h^4 . There are two molecules of acid in the unit cube. This formula agrees with the bulk of chemical evidence.

The structure was worked out rigorously from experimental results. The method used is described. From the observed intensities of reflection the positions of the heavy tungsten atoms were found, in this first stage the effect of all other types of atoms being neglected. A graphical method was used. This preliminary location of the tungsten atoms was surprisingly definite.

A structure of co-ordinated oxygen polyhedra was then found which would give these tungsten positions and also fulfil all other conditions. The com-

parison of observed intensities and those calculated for the complete acid anion is given. The agreement is good and proves the correctness of the structure.

A brief summary of the properties of the 12-heteropoly acids, and the more important papers in the literature relating to their constitution, is given and discussed.

The structure found in the present work is described.

This structure is discussed and its bearing on the properties of the acid is considered.

The preparation of pure 12-phosphotungstic acid is given and its dehydration described.

The experimental X-ray technique is described briefly.

The method of locating the tungsten atoms is described and the conditions to be fulfilled by the structure are given. Two types of arrangement of these anions in the unit cube were found to be possible. These are discussed.

The problem of the positions of the molecules of water of crystallization for both types of arrangement is discussed.

The comparison of observed and calculated intensities is given, and discussed.