

Reaction	pK (25°)	pK (37.5°)	Heat evolved
$H_3PO_4 \longrightarrow H^+ + H_2PO_4^-$	2.10	2.16	+2000
$H_2PO_4^- \longrightarrow H^+ + HPO_4^{--}$	7.127	7.058	-2300

The calculated heats of ionization, which are in calories per mole, refer, of course, to the ionization at infinite dilution.

The values of pK_3 calculated are insufficiently accurate for the heat effect of the third ionization step to be calculated. Heat, however, is evolved in this ionization.

Summary

With the quinhydrone electrode measurements of the P_H values of phosphate mixtures have been made which lead to the following values for the ionization constants of phosphoric acid

$$\begin{aligned} pK_1 (25^\circ) &= 2.10, & pK_1 (37.5^\circ) &= 2.16 \\ pK_2 (25^\circ) &= 7.13, & pK_2 (37.5^\circ) &= 7.06 \end{aligned}$$

These figures are compared with those derived from other data.

From the data of Britton pK_3 at 20° is calculated to be about 12.1.

LIVERPOOL, ENGLAND

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 192]

THE PRINCIPLES DETERMINING THE STRUCTURE OF COMPLEX IONIC CRYSTALS

BY LINUS PAULING

RECEIVED SEPTEMBER 5, 1928

PUBLISHED APRIL 5, 1929

1. The Relative Stability of Alternative Structures of Ionic Crystals.—The elucidation of the factors determining the relative stability of alternative crystalline structures of a substance would be of the greatest significance in the development of the theory of the solid state. Why, for example, do some of the alkali halides crystallize with the sodium chloride structure and some with the cesium chloride structure? Why does titanium dioxide under different conditions assume the different structures of rutile, brookite and anatase? Why does aluminum fluosilicate, $Al_2SiO_4F_2$, crystallize with the structure of topaz and not with some other structure? These questions are answered formally by the statement that in each case the structure with the minimum free energy is stable. This answer, however, is not satisfying; what is desired in our atomistic and quantum theoretical era is the explanation of this minimum free energy in terms of atoms or ions and their properties.

Efforts to provide such a treatment for simple alternative structures, such as the sodium chloride and cesium chloride structures and the fluoride and rutile structures, have been made with the aid of the Born potential expression and modifications of it. Assuming that all ions repel each

other according to a high inverse power of the distance between them (the repulsive potential being proportional to r^{-n}), the equilibrium energy of a crystal is given by

$$\Phi = - \frac{z^2 e^2 A}{R} \left(1 - \frac{1}{n} \right) \quad (1)$$

in which R is the equilibrium distance between two adjacent ions in the crystal, and A is the Madelung constant characteristic of the structure. A knowledge of how R changes from structure to structure for a given substance would then allow the prediction of which structure is stable, if Equation 1 were accurate. Methods of calculating R have been suggested.¹ It is found, however, that Equation 1 is in error by at least 2% in some cases,^{1b} and this error of around 5000 cal./mole suffices to invalidate the theory in applications of this kind. An explanation of the sodium chloride-cesium chloride transition which accounts for the observed properties of the alkali halides has been reported,² but the considerations involved (including deformation phenomena) have not yet been given quantitative formulation.

The application of these methods to more complex crystals would involve the highly laborious calculation of the Madelung constant for a number of complicated ionic arrangements. Furthermore, the methods provide no way of determining the possible structures for which calculations should be made. An infinite number of possible atomic arrangements for a complicated substance such as a silicate are provided by the theory of space groups. There is desired a set of simple rules, which need not be rigorous in their derivation nor universal in their application, with the aid of which the few relatively stable structures can be identified among the multitude possible for a given substance. These rules could be used in the prediction of atomic arrangements for comparison with x-ray data. They would also provide a criterion for the probable correctness of structures suggested by but not rigorously deduced from experimental measurements. Finally, they would permit the intuitive understanding of the stability of crystals in terms of visualizable interionic interactions.

2. The Application of the Coördination Theory in the Determination of the Structures of Complex Crystals.—As a result of the recent increase in knowledge of the effective radii of various ions in crystals,³ Professor W. L. Bragg has suggested and applied a simple and useful theory leading to the selection of possible structures for certain complex crystals. His fundamental hypothesis is this: if a crystal is composed of large ions and small ions, its structure will be determined essentially by the large ions, and may approximate a close-packed arrangement of the large ions alone,

¹ (a) F. Hund, *Z. Physik*, **34**, 833 (1925); (b) Linus Pauling, *THIS JOURNAL*, **50**, 1036 (1928); *Z. Krist.*, **67**, 377 (1928).

² Linus Pauling, *ibid.*, **69**, 35 (1928).

³ Wasastjerna, *Soc. Sci. Fenn. Comm. Phys. Math.*, **38**, 1 (1923).

with the small ions tucked away in the interstices in such a way that each one is equidistant from four or six large ions. In some cases not all of the close-packed positions are occupied by ions, and an open structure results. To apply this theory one determines the unit of structure in the usual way, and finds by trial some close-packed arrangement of the large ions of known crystal radius (usually oxygen ions with a radius of 1.35–1.40 Å.) compatible with this unit. The other ions are then introduced into the possible positions in such a way as to give agreement with the observed intensities of reflection of x-rays, the large ions being also shifted somewhat from the close-packed positions if necessary. With the aid of this method Bragg and his co-workers have made a very significant attack on the important problem of the structure of silicates, involving the de-

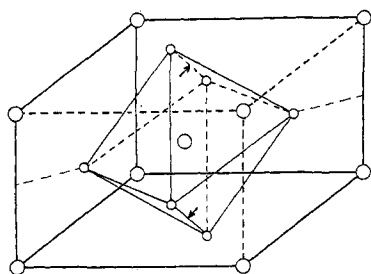


Fig. 1.—The unit of structure for rutile. Large circles represent titanium ions; small circles oxygen ions. An octahedron with a titanium ion at its center and oxygen ions at its corners is shown. The two edges marked with arrows are shared with adjoining octahedra.

termination of structures for beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$,⁴ chrysoberyl, BeAl_2O_4 ,⁵ olivine, $(\text{Mg}, \text{Fe})_2\text{SiO}_4$,⁶ chondrodite, $\text{H}_2\text{Mg}_5\text{Si}_2\text{O}_{10}$, humite, $\text{H}_2\text{Mg}_7\text{Si}_3\text{O}_{14}$, clinohumite, $\text{H}_2\text{Mg}_9\text{Si}_4\text{O}_{18}$,⁷ phenacite, Be_2SiO_4 ,⁸ etc.

During the investigation of the structure of brookite,⁹ the orthorhombic form of titanium dioxide, a somewhat different method for predicting possible structures for ionic crystals was developed, based upon the assumption of the coordination of the anions in the crystal about the cations in such a way that each cation designates the center of a polyhedron, the corners of which are occupied by anions. This method leads for a given substance to a small number of possible simple structures, for each of which the size of the unit of structure, the space-group symmetry and the positions of all ions are fixed. In some cases, but not all, these structures correspond to close-packing of the large ions; when they do, the theory further indicates the amount and nature of the distortion from the close-packed arrangement.

The structures of rutile and anatase, the two tetragonal forms of titanium dioxide, have been determined by rigorous methods (Figs. 1 and 2). They seem at first sight to have little in common beyond the fact

⁴ W. L. Bragg and J. West, *Proc. Roy. Soc. London*, **111A**, 691 (1926).

⁵ W. L. Bragg and G. B. Brown, *ibid.*, **110A**, 84 (1926).

⁶ W. L. Bragg and G. B. Brown, *Z. Krist.*, **63**, 538 (1926).

⁷ (a) W. L. Bragg and J. West, *Proc. Roy. Soc. London*, **114A**, 450 (1927); (b) W. H. Taylor and J. West, *ibid.*, **117A**, 517 (1928).

⁸ W. L. Bragg, *ibid.*, **113A**, 642 (1927).

⁹ Linus Pauling and J. H. Sturdivant, *Z. Krist.*, **68**, 239 (1928).

that each is a coordination structure, with six oxygen atoms about each titanium atom at octahedron corners. From a certain point of view, however, they are closely similar. They are both made up of octahedra sharing edges and corners with each other; in rutile two edges of each octahedron are shared and in anatase four. In both crystals the titanium-oxygen distance is a constant, with the value 1.95–1.96 Å. The basic octahedra are only approximately regular; in each crystal they are deformed in such a way as to cause each shared edge to be shortened from 2.76 Å. (the value for regular octahedra) to 2.50 Å., the other edges being correspondingly lengthened.

As a result of these considerations the following assumptions were made: (1) Brookite is composed of octahedra, each with a titanium ion at its center and oxygen ions at its corners. (2) The octahedra share edges and corners with each other to such an extent as to give the crystals the correct stoichiometric composition. (3) The titanium-oxygen distances throughout are 1.95–1.96 Å. Shared edges of octahedra are shortened to 2.50 Å.

Two structures satisfying these requirements were built out of octahedra. The first was not the structure of brookite. The second, however, had the same space-group symmetry as brookite (V_h^{15}), and the predicted dimensions of the unit of structure agreed within 0.5% with those observed. Structure factors calculated for over fifty forms with the use of the predicted values of the nine parameters determining the atomic arrangement accounted satisfactorily for the observed intensities of reflections on rotation photographs. This extensive agreement is so striking as to permit the structure proposed for brookite (shown in Fig. 3) to be accepted with confidence.

The method was then applied in predicting the structure of the orthorhombic crystal topaz, $\text{Al}_2\text{SiO}_4\text{F}_2$.¹⁰ It was assumed that each aluminum ion is surrounded by four oxygen ions and two fluorine ions at the corners

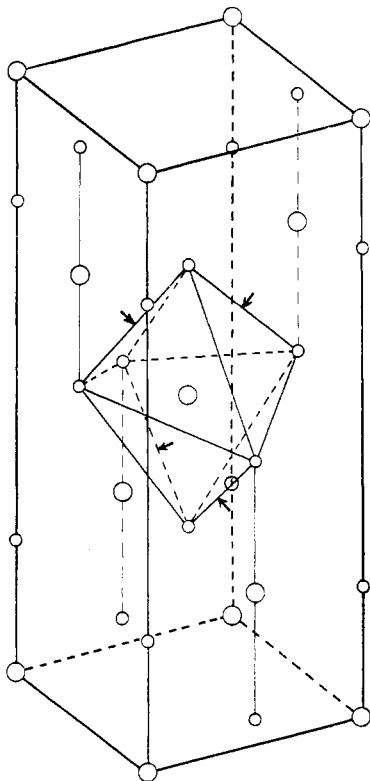


Fig. 2.—The unit of structure of anatase. The titanium octahedron shares the four edges marked with arrows with adjoining octahedra.

The method was then applied in predicting the structure of the orthorhombic crystal topaz, $\text{Al}_2\text{SiO}_4\text{F}_2$.¹⁰ It was assumed that each aluminum ion is surrounded by four oxygen ions and two fluorine ions at the corners

¹⁰ Linus Pauling, *Proc. Nat. Acad. Sci.*, **14**, 603 (1928).

of a regular octahedron, and each silicon ion by four oxygen ions at the corners of a regular tetrahedron. The length of edge of octahedron and tetrahedron was taken as 2.72 Å., corresponding to crystal radii of 1.36 Å. for both oxygen and fluorine ions. One structure was built up of these polyhedra. On studying its distribution of microscopic symmetry elements, it was found to have the space-group symmetry of V_h^{16} , which is that of topaz. Its unit of structure approximates that found experimentally, and the predicted values of the fifteen parameters determining the atomic arrangement account for the observed intensities of reflection from the pinacoids. This concordance is sufficient to make it highly probable that the correct structure of topaz has been found (Fig. 4).¹¹

3. The Principles Determining the Structure of Complex Ionic Crystals.—

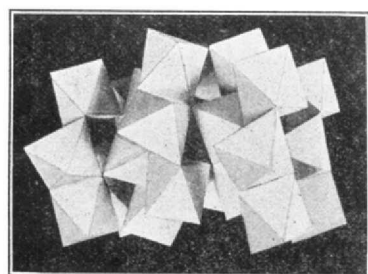


Fig. 3.—The structure of brookite.

The success of the coordination method in predicting structures for brookite and topaz has led to the proposal of a set of principles governing the structure of a rather extensive class of complex ionic crystals.

The crystals considered are to contain only small cations, with relatively large electric charges, that is, usually trivalent and tetravalent cations, with crystal radii not over about 0.8 Å. All anions are large (over 1.35 Å.) and univalent or divalent. Furthermore, they should not be too

highly deformable. The most important anions satisfying this restriction are the oxygen ion and the fluorine ion, with crystal radii 1.35–1.40 Å.¹²

This physical differentiation of the anions and cations under discussion in regard to size and charge finds expression throughout this paper. Markedly different roles are attributed anions and cations in the construction of a crystal; as a result a pronounced distinction between them has been made in the formulation of the structural principles.

Throughout our discussion the crystals will be referred to as composed of ions. This does not signify that the chemical bonds in the crystal are necessarily ionic in the sense of the quantum mechanics; they should not, however, be of the extreme non-polar or shared electron pair type.¹³ Thus compounds of copper¹⁴ and many other eighteen-shell atoms cannot be

¹¹ Professor W. L. Bragg has written the author that the same ideal structure has been found by J. West (paper to be published in the *Proceedings of the Royal Society*).

¹² The crystal radii used in this paper are those of Pauling, *THIS JOURNAL*, **49**, 765 (1927).

¹³ (a) F. London, *Z. Physik*, **46**, 455 (1928); (b) L. Pauling, *Proc. Nat. Acad. Sci.*, **14**, 359 (1928).

¹⁴ Such as $K_2CuCl_4 \cdot 2H_2O$, whose structure has been determined by S. B. Hendricks and R. G. Dickinson, *THIS JOURNAL*, **49**, 2149 (1927).

treated in this way. Shared electron pair bonds are also present in complexes containing large atoms with a coordination number of four, such as the molybdate ion, $[\text{MoO}_4]^{--}$, the arsenate ion, $[\text{AsO}_4]^{--}$, etc.

The principles described in the following six sections have been deduced in part from the empirical study of known crystal structures and in part from considerations of stability involving the crystal energy.

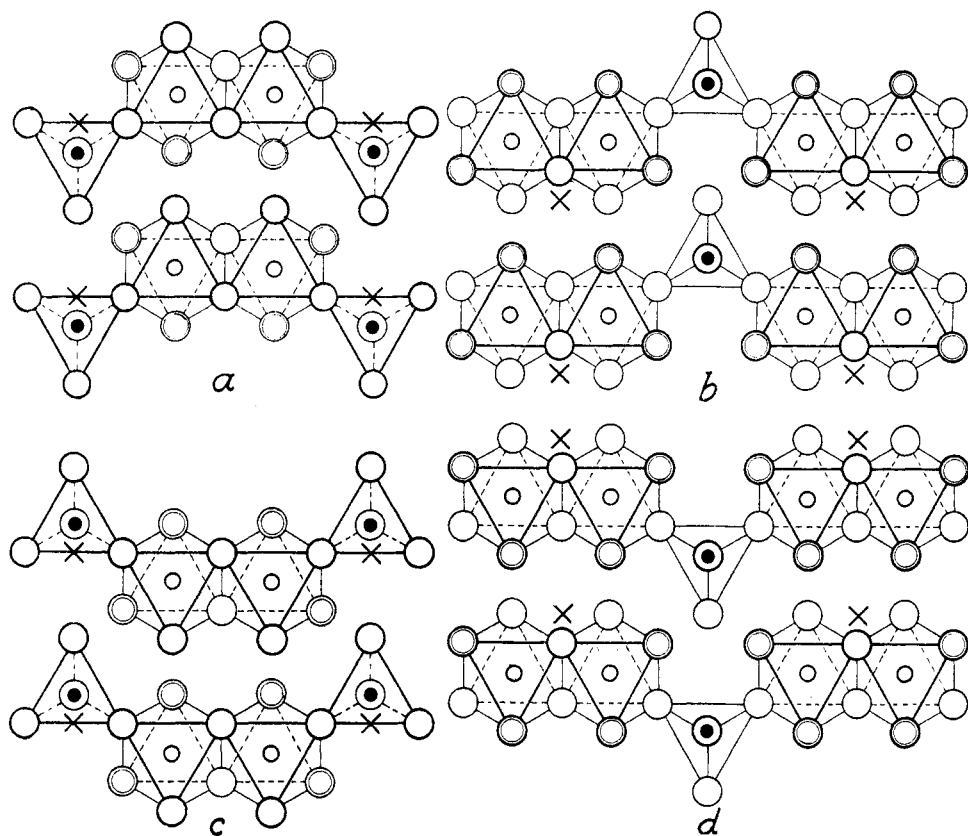


Fig. 4.—The structure of topaz. The layers are to be superposed in the order *abcd*, with *d* uppermost. The crosses are the traces of the corners of the unit of structure in the plane of the paper. Large circles represent oxygen, large double circles fluorine, small open circles aluminum, and small solid circles silicon ions.

4. The Nature of the Coordinated Polyhedra.—I. A coordinated polyhedron of anions is formed about each cation, the cation-anion distance being determined by the radius sum and the coordination number of the cation by the radius ratio.

In the case of crystals containing highly charged cations the most important terms in the expression for the crystal energy are those representing

the interaction of each cation and the adjacent anions. The next terms in importance are those representing the mutual interaction of the anions. The negative Coulomb energy causes each cation to attract to itself a number of anions, which approach to the distance at which the Coulomb attraction is balanced by the characteristic cation-anion repulsive forces. This distance is given with some accuracy by the sum of the crystal radii of cation and anion.¹²

If too many anions are grouped about one cation, the anion-anion repulsion becomes strong enough to prevent the anions from approaching this closely to the cation. The resultant increase in Coulomb energy causes such a structure to be unstable when the anion-cation distance is increased to a value only slightly greater than the radius sum. Approximate lower limits of the radius ratio (the ratio of cation radius to anion radius) leading to a stable structure with given coordination number can accordingly be calculated purely geometrically.^{15,12} The minimum radius ratios for tetrahedra, octahedra and cubes are given in Table I.

TABLE I
RADIUS RATIOS AND COÖRDINATION NUMBERS

Polyhedron	Coördination number	Minimum radius ratio
Tetrahedron	4	$\sqrt{3}/\sqrt{2} - 1 = 0.225$
Octahedron	6	$\sqrt{2} - 1 = 0.414$
Cube	8	$\sqrt{3} - 1 = 0.732$

Since the repulsive forces are determined by the true sizes of ions, and not their crystal radii, the radius ratios to be used in this connection are the ratios of the univalent cation radii to univalent anion radii.¹² Values of this ratio for small ions are given in Table II, together with predicted and observed coordination numbers, the agreement between which is excellent.

TABLE II
COÖRDINATION NUMBERS FOR IONS IN OXIDES

Ion	Radius ratio	Predicted coördination number	Observed coördination number	Strength of electrostatic bonds
B ⁺⁺⁺	0.20	3 or 4	3 or 4	1 or $\frac{3}{4}$
Be ⁺⁺	.25	4	4	$\frac{1}{2}$
Li ⁺	.34	4	4	$\frac{1}{4}$
Si ⁺⁺⁺⁺	.37	4	4	1
Al ⁺⁺⁺	.41	4 or 6	6	$\frac{3}{4}$ or $\frac{1}{2}$
Mg ⁺⁺	.47	6	6	$\frac{1}{3}$
Ti ⁺⁺⁺⁺	.55	6	6	$\frac{2}{3}$
Sc ⁺⁺⁺	.60	6	6	$\frac{1}{2}$
Mo ⁺⁺⁺⁺⁺	.53	6	6	1
Nb ⁺⁺⁺⁺⁺	.57	6	6	$\frac{5}{6}$
Zr ⁺⁺⁺⁺	.62	6	6 or 8	$\frac{2}{3}$ or $\frac{1}{2}$

¹⁵ Such calculations were first made and substantiated by comparison with observed structures in some cases by V. M. Goldschmidt, "Geochemische Verteilungsgesetze der Elemente," Oslo, 1927.

The radius ratio for B^{+3} is only a little less than the lower limit for tetrahedra. The usual coordination number for boron with oxygen is 3 (in the borate ion, $[BO_3]^{-3}$). It is four, however, in the 12-tungstoborate ion,¹⁶ in which a stabilizing influence is exerted by the tungsten octahedra.

So far as I know, Al^{+3} has the coordination number 6 in all of its compounds with oxygen the structures of which have been determined. The coordination number 4 would also be expected for it, however; it is probable that it forms tetrahedra in some of its compounds, as, for example, γ -alumina, the cubic form of Al_2O_3 , and the feldspars, in which there occurs replacement of Na^+ and Si^{+4} by Ca^{++} and Al^{+3} . This possibility is further discussed in Section 11.

Zr^{+4} has the coordination number 8 in zircon. The polyhedron of oxygen ions about it is, however, not a cube. It is on account of the ease with which these polyhedra are distorted that large cations, with coordination numbers greater than six, are not included in the field of application of the suggested principles. Octahedra and tetrahedra retain their approximate shapes even under the action of strong distorting forces, and, moreover, rules have been formulated governing the distortion that they do undergo (Section 9).

5. The Number of Polyhedra with a Common Corner. The Electrostatic Valence Principle.—The number of polyhedra with a common corner can be determined by the use of an extended conception of electrostatic valence. Let ze be the electric charge of a cation and ν its coordination number. Then the *strength of the electrostatic valence bond* going to each corner of the polyhedron of anions about it is defined as

$$s = \frac{z}{\nu} \quad (2)$$

Let $-ze$ be the charge of the anion located at a corner shared among several polyhedra. We now postulate the following *electrostatic valence principle: II. In a stable coordination structure the electric charge of each anion tends to compensate the strength of the electrostatic valence bonds reaching to it from the cations at the centers of the polyhedra of which it forms a corner; that is, for each anion*

$$\zeta = \sum_i \frac{z_i}{\nu_i} = \sum_i s_i \quad (3)$$

In justification of this principle it may be pointed out that it places the anions with large negative charges in positions of large positive potentials; for the bond strength of a cation gives approximately its contribution to the total positive potential at the polyhedron corner (the factor $1/\nu$ accounting for the larger cation-anion distance and the greater number of adjacent anions in the case of cations with larger coordination number),

¹⁶ Pauling, unpublished material.

and the application of the principle requires that the sum of these potentials be large in case the valence of the anion is large.

It is not to be anticipated that Equation 3 will be rigorously satisfied by all crystals. It should, however, be always satisfied approximately. As a matter of fact, almost all crystals which have been investigated conform to the principle. Equation 3 is necessarily true for all crystals the anions of which are crystallographically equivalent, such as corundum, Al_2O_3 ,¹⁷ rutile, anatase, spinel, MgAl_2O_4 , garnet, $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$,¹⁸ cryolithionite, $\text{Na}_3\text{Li}_3\text{Al}_2\text{F}_{12}$,¹⁹ etc. It is also satisfied by topaz; each oxygen ion, common to one silicon and two aluminum ions, has $\Sigma s_i = 2$ (see Table II for a list of values of s), while each fluorine ion, attached to two aluminum ions only, has $\Sigma s_i = 1$. Similarly in beryl some oxygen ions are shared between two silicon ions, and some between one silicon, one beryllium and one aluminum ion; in each case $\Sigma s_i = 2$. In chondrodite, $\text{H}_2\text{Mg}_5\text{Si}_2\text{O}_{10}$, humite, $\text{H}_2\text{Mg}_7\text{Si}_3\text{O}_{14}$, and clinohumite, $\text{H}_2\text{Mg}_9\text{Si}_4\text{O}_{18}$, there are oxygen ions common to one silicon tetrahedron and three magnesium octahedra ($\Sigma s_i = 2$), and OH^- groups common to three magnesium octahedra ($\Sigma s_i = 1$). This list of examples could be largely extended.

6. The Sharing of Edges and Faces.—The electrostatic valence principle indicates the number of polyhedra with a common corner but makes no prediction as to the number of corners common to two polyhedra; that is, whether they share one corner only, two corners defining an edge, or three or more corners defining a face. In rutile, brookite and anatase, for example, each oxygen ion is common to three titanium octahedra (and hence has $\Sigma s_i = 2$, satisfying Equation 3); but the number of edges shared by one octahedron with adjoining octahedra is two in rutile, three in brookite and four in anatase. In corundum on the other hand, each aluminum octahedron shares one face and three edges with other octahedra. The reason for this difference is contained in the following rule. *III. The presence of shared edges, and particularly of shared faces, in a coordinated structure decreases its stability; this effect is large for cations with large valence and small coordination number, and is especially large in case the radius ratio approaches the lower limit of stability of the polyhedron.*

This decrease in stability arises from the cation-cation Coulomb terms. The sharing of an edge between two regular tetrahedra brings the cations at their centers to a distance from each other only 0.58 times that obtaining in case the tetrahedra share a corner only; and the sharing of a face decreases this distance to 0.33 times its original value (Fig. 5). The corresponding positive Coulomb terms cause a large increase in the crystal energy and decrease in the stability of the structure, especially for highly

¹⁷ Linus Pauling and S. B. Hendricks, *THIS JOURNAL*, **47**, 781 (1925).

¹⁸ G. Menzer, *Z. Krist.*, **63**, 157 (1926).

¹⁹ G. Menzer, *ibid.*, **66**, 457 (1927).

charged cations. The effect is not so large for regular octahedra, amounting to a decrease in the cation-cation distance to the fractional value 0.71 for a shared edge and 0.58 for a shared face.

These calculated decreases are valid only in case the change in structure is not compensated by deformation of the polyhedra. Some compensating deformation will always occur; the rules governing deformation (Section 9) show that it will be small in case the radius ratio approaches the lower limit of stability for the polyhedron, and will increase with the radius ratio.

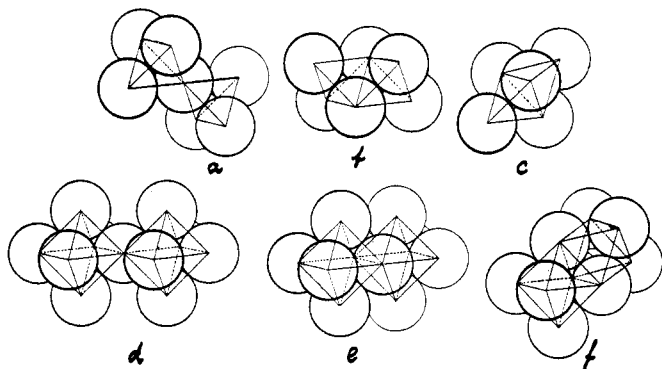


Fig. 5.—*a*, *b* and *c* show two tetrahedra of oxygen ions with a corner, an edge and a face in common; *d*, *e* and *f* show two octahedra of oxygen ions with a corner, an edge and a face in common.

In agreement with expectation, silicon tetrahedra tend to share only corners with other polyhedra when this is possible (as in topaz, $\text{Al}_2\text{SiO}_4\text{F}_2$, etc.), titanium octahedra share only corners and edges, while aluminum octahedra, when constrained by the stoichiometrical formula of the substance, will share faces in some cases, as in corundum, Al_2O_3 . The effect of large radius ratio in diminishing the instability due to an increase in the number of shared edges is shown by the approximate equality in free energy of rutile, brookite and anatase, with two, three and four shared edges, respectively. As a matter of fact, the order of stability is just that of the number of shared edges, rutile being the most stable,²⁰ in agreement with expectation. Many other dioxides also crystallize with the rutile structure but no other is known with the brookite or anatase structure.

The effect of small valence and large coördination number is further shown by the observation that silicon tetrahedra, which share corners only with aluminum octahedra, share edges with magnesium octahedra (in olivine, chondrodite, humite, clinohumite) and with zirconium polyhedra with coördination number eight (in zircon).

7. The Nature of Contiguous Polyhedra.—IV. *In a crystal con-*

²⁰ C. Doelter, "Handbuch der Mineralchemie," Theodor Steinkopff, Dresden, 1918, Vol. III, Part 1, p. 15.

taining different cations those with large valence and small coördination number tend not to share polyhedron elements with each other. This rule follows directly from the fact that cations with high electric charges tend to be as far apart from each other as possible, in order to reduce their contribution to the Coulomb energy of the crystal.

The rule requires that in silicates the silicon tetrahedra share no elements with each other if the oxygen-silicon ratio is equal to or greater than four (topaz, zircon, olivine, orthosilicates in general). If stoichiometrically necessary, corners will be shared between silicon tetrahedra, but not edges or faces. In the various forms of silicon dioxide all four corners of each tetrahedron are shared with adjoining tetrahedra. In diorthosilicates the Si_2O_7 group is formed of two tetrahedra sharing a corner. The metasilicates should not contain groups of two tetrahedra with a common edge, but rather chains or rings, each tetrahedron sharing two corners (as in beryl, with a ring of six tetrahedra, stable because of the approximation of the tetrahedral angle to 120°). Other silicates are no doubt similar. It is of interest that the electrostatic valence principle requires that corners shared between two silicon tetrahedra be not shared also with other polyhedra; this is true for beryl.

8. The Rule of Parsimony.—V. *The number of essentially different kinds of constituents in a crystal tends to be small.* First, the electrostatic bonds satisfied by all chemically similar anions should be the same if possible (topaz, all oxygen ions common to two aluminum octahedra and one silicon tetrahedron, all fluorine ions common to two aluminum octahedra). This does not require the anions to be crystallographically equivalent (in topaz the oxygen ions are crystallographically of three kinds, in brookite of two kinds); crystallographic non-equivalence does not imply essential difference from the standpoint of the coördination theory. Often the preceding rules do not permit all anions to be alike, as, for example, in the case of silicates with an oxygen-silicon ratio greater than four, in which the four orthosilicate oxygens are necessarily different from the others. In these cases the number of different kinds of anions will, however, be small.

Second, the polyhedra circumscribed about all chemically identical cations should, if possible, be chemically similar, and similar in their contiguous environment, that is, in the nature of the sharing of corners, edges and faces with other polyhedra. For example, each aluminum octahedron in topaz has as corners four oxygen and two fluorine ions, and each shares two edges with other octahedra and four corners with silicon tetrahedra. The titanium octahedron in rutile shares two edges, in brookite three and in anatase four, but no structure is known in which these different octahedra occur together. The polyhedra which are similar in these respects may or may not be crystallographically equivalent, for they

may differ in their remote environment. Thus the contiguously similar tetrahedra of silicon atoms about carbon atoms in carborundum are crystallographically of several kinds (five in carborundum I).

9. Distortion of the Polyhedra.—The above rules suffice to indicate the nature of the structure of a given crystal, so that a structure can be composed of regular polyhedra in accordance with them, and its space-group symmetry and approximate dimensions compared with those found by x-ray analysis. In this way a structure can be identified as giving approximately the correct atomic arrangement (as was done for brookite and for topaz); but the actual atomic arrangement may differ considerably from this "ideal" arrangement corresponding to regular polyhedra, as a resultant of distortion of the polyhedra. The investigation of the agreement between observed intensities of x-ray reflections and structure factors calculated for all atomic arrangements involving small displacements from the ideal arrangement would be extremely laborious. It is accordingly desirable to be able to predict with some accuracy the nature and the amount of the distortion to be expected for a given structure.

In not too complicated cases this can be done theoretically by finding the minimum in the crystal energy with respect to variations in the parameters determining the structure, with the use of a theoretical expression for the interionic repulsion potential. Such calculations have been carried out for rutile and anatase,²¹ leading to the result that in each case the shared edges of the titanium octahedra are shortened to the length 2.50 Å., other edges being compensatorily lengthened. This distortion is actually found experimentally for these crystals. It was accordingly assumed to hold for brookite also, and the atomic arrangement derived in this way was shown to be in complete agreement with the observed intensities of x-ray reflection.

In general it is not possible to make such calculations on account of the excessive labor involved. It can be seen, however, that the cation-cation repulsion will shorten shared edges and the edges of shared faces, and reasonably confident application may be made of the following rule. Polyhedra of oxygen ions about trivalent and tetravalent cations are distorted in such a way as to shorten shared edges and the edges bounding shared faces to a length of about 2.50 Å. Edges bounding shared faces have been observed to be shortened to 2.50 Å. in corundum, Al_2O_3 , and to 2.55 Å. in hematite, Fe_2O_3 , in agreement with the foregoing rule.

It is furthermore to be anticipated that the cation-cation repulsion will operate in some cases to displace the cations from the centers of their coördinated polyhedra. This action will be large only in case the radius ratio approaches the lower limit for stability, so that the size of the polyhedron is partially determined by the characteristic anion-anion repulsive

²¹ Linus Pauling, *Z. Krist.*, **67**, 377 (1928).

forces (the distribution of closely neighboring cations must, of course, be one-sided in addition). Hematite and corundum provide an example of this effect. In these crystals each octahedron shares a face with another octahedron. Now in an iron octahedron, with radius ratio about 0.48, the repulsive forces principally effective in determining the interionic distances are those between iron and oxygen ions. The Coulomb repulsion of the two iron ions accordingly can produce only a small displacement of these ions from the octahedron centers; the iron ions in hematite are observed to be 2.06 Å. from the oxygen ions defining the shared face and 1.99 Å. from the other oxygen ions. In an aluminum octahedron, on the other hand, with radius ratio 0.41, the characteristic repulsive forces between oxygen ions as well as those between oxygen and aluminum ions are operative; as a result of this "double repulsion"¹² the distance from the center of the octahedron to a corner is somewhat greater than the sum of the crystal radii of aluminum and oxygen. The aluminum ions are correspondingly mobile and the aluminum-aluminum Coulomb repulsion is to be expected to cause a large displacement in their positions. This is observed; the two aluminum-oxygen distances in corundum are 1.99 Å. and 1.85 Å.

The nature and approximate amount of the distortion to be expected in other cases can be similarly estimated; an example will be given in a later paper.¹⁶

10. The Close-Packing of Large Ions.—In piling together polyhedra in the attempt to predict a possible structure for a crystal with the aid of the principles described above, the recognition from the observed dimensions of the unit of structure that the atomic arrangement is probably based on a close-packed arrangement of the anions is often of very considerable assistance, for it indicates the probable orientation of the polyhedra, which can then be grouped together to form the completed structure. This was done in the determination of the structure of topaz and contributed considerably to the ease of solution of the problem. The approximation of the dimensions of the unit of structure of topaz to those of a close-packed structure does not, however, suffice to determine the positions of the anions, for there are two types of close-packing, simple hexagonal and double hexagonal,²² which have these dimensions. This ambiguity

²² An infinity of equally close-packed arrangements of spheres can be made from the close-packed layers A, with a sphere at $X = 0$, $Y = 0$ (X , Y and Z being hexagonal coordinates), B, with a sphere at $X = 1/3$, $Y = 2/3$, and C, with a sphere at $X = 2/3$, $Y = 1/3$. For simple hexagonal close-packing these layers are superposed in the order ABABAB..., for cubic close-packing in the order ABCABC... for double hexagonal close-packing in the order ABACABAC..., and so on, with ever-increasing complexity. In only the first two are the spheres crystallographically equivalent, and only these two have been generally recognized in the past; this restriction is, however, undesirable from the standpoint of the coordination theory.

was no serious obstacle in the prediction of the structure by the coördination method; the octahedra and tetrahedra were suitably piled together and the resultant arrangement of oxygen and fluorine ions was found to be double hexagonal close-packing.

Brookite is also based upon a double hexagonal close-packed arrangement of the oxygen ions. The dimensions of the unit of structure differ so much on account of distortion from those for the ideal arrangement, however, that the existence of close-packing was recognized only after the structure had been determined.

It may be pointed out that in some structures easily derivable with the coördination theory, such as the rutile structure, the anion arrangement approximates no type of close-packing whatever.

11. Applications of the Theory.—As an illustration of the application of the foregoing principles some predictions may be made regarding the structure of cyanite, andalusite and sillimanite, the three forms of Al_2SiO_5 . From the rule of parsimony we expect all aluminum octahedra to be similar and all silicon tetrahedra to be similar. Let the number of octahedra one corner of which is formed by the i^{th} oxygen ion be α_i ; then the stoichiometrical oxygen-aluminum ratio, 5:2, requires that

$$\sum_i \frac{1}{\alpha_i} = \frac{5}{2} \quad (4)$$

in which the sum is taken over the six oxygen ions forming one octahedron. Four out of five oxygen ions, in accordance with Rule IV, will be distinguished through being attached to silicon ions; this fact is expressed by the equation

$$\sum_i' \frac{1}{\alpha_i} = 2 \quad (5)$$

in which the prime signifies that the sum is to be taken over these oxygen ions only. Let us now assume that the oxygen ions are of only two kinds with respect to their values of α , those attached to silicon ions, n_1 in number, forming one class, and those not attached to silicon ions, n_2 in number, forming the other class. Equations 4 and 5 then become

$$\left. \begin{aligned} \frac{n_1}{\alpha_1} + \frac{n_2}{\alpha_2} &= 5/2 \\ \frac{n_1}{\alpha_1} &= 2 \end{aligned} \right\} \text{ with } n_1 + n_2 = 6 \quad (6)$$

The only solution of these equations involving integers is $n_1 = 4$, $\alpha_1 = 2$, $n_2 = 2$, $\alpha_2 = 4$. Thus about each aluminum ion there will be four oxygen ions common to two aluminum octahedra and one silicon tetrahedron, and two oxygen ions common to four octahedra.²³ For both kinds of oxy-

²³ It is possible that the aluminum octahedra may be of more than one kind. In this case average values of the sums would have to be used in Equations 4 and 5, and the equations would no longer possess a single solution.

gen ions $\Sigma s_i = 2$, so that the principle of electrostatic valence, which was not used in the derivation of Equation 6, is satisfied.

This result, while limiting considerably the number of possible structures for these crystals, by no means determines their structures. Further information is provided by Rule III, from which it is to be expected that the silicon tetrahedra share only corners with aluminum octahedra, and the octahedra share only corners and edges (and possibly one face) with each other.

These predictions are not incompatible with Professor Bragg's assignment of a cubic close-packed arrangement of oxygen ions to cyanite.^{7a} They are, however, in pronounced disagreement with the complete atomic arrangement proposed by Taylor and Jackson,²⁴ whose suggested structure conflicts with most of our principles. Their structure is far from parsimonious, with four essentially different kinds of octahedra and two of tetrahedra. Each silicon tetrahedron shares a face with an octahedron, contrary to Rule III. The electrostatic valence principle is not even approximately satisfied; one oxygen ion, common to four aluminum octahedra and one silicon tetrahedron, has $\Sigma s_i = 3$, while another, common to two octahedra only, has $\Sigma s_i = 1$. For these reasons the atomic arrangement seems highly improbable.

The coördination theory and the principles governing coördinated structures provide the foundation for an interpretation of the structure of the complex silicates and other complex ionic crystals which may ultimately lead to the understanding of the nature and the explanation of the properties of these interesting substances. This will be achieved completely only after the investigation of the structures of many crystals with x-rays. To illustrate the clarification introduced by the new conception the following by no means exhaustive examples are discussed.

Let us consider first the silicates of divalent cations with coördination Number 6, and hence with electrostatic bond strength $s = 1/3$. An oxygen ion forming one corner of a silicon tetrahedron would have $\Sigma s_i = 2$ if it also formed a corner of three R^{++} octahedra; if it were not attached to a silicon ion, it would have to form a corner of six R^{++} octahedra to satisfy the electrostatic valence principle. But six octahedra can share a corner only by combining in the way given by the sodium chloride structure, and this arrangement, involving the sharing of many edges, is expected not to be stable as a part of the structure of a complex silicate.²⁵ Accordingly, we conclude that no oxygen ions not attached to silicon occur in these silicates; that is, the oxygen-silicon ratio cannot be greater than

²⁴ W. H. Taylor and W. W. Jackson, *Proc. Roy. Soc. London*, **119A**, 132 (1928).

²⁵ The instability of the sodium chloride structure for oxides is shown by the heat of the reactions $\text{CaO} + \text{H}_2\text{O} = \text{Ca(OH)}_2 + 15,500 \text{ cal.}$ and $\text{MgO} + \text{H}_2\text{O} = \text{Mg(OH)}_2 + 9000 \text{ cal.}$

4:1. The silicates which will occur are orthosilicates, $R^{++}_2SiO_4$, metasilicates, $R^{++}SiO_3$, etc. This is verified by observation; no basic silicates of such cations are known, although many normal silicates such as forsterite Mg_2SiO_4 , etc., exist.

A univalent anion (F^- , OH^-) may be shared among three R^{++} octahedra alone, so that compounds may occur in which these anions are present in addition to the SiO_4 groups. Such compounds are known: $Mg_3SiO_4(F, OH)_2$, prolectite, $Mg_3(SiO_4)_2(F, OH)_2$, chondrodite, etc.

Compounds of simple structure according to the coördination theory are those in which the number of essentially different kinds of anions is small. In a simple orthosilicate containing aluminum and a divalent cation each oxygen ion would form the corner of a silicon tetrahedron ($s = 1$), an aluminum octahedron ($s = 1/2$), and one or two R^{++} polyhedra (one tetrahedron or two polyhedra with $\nu = 8$). The composition of the substance would then be given by the formula $R^{++}_3Al_2Si_3O_{12}$. Similarly, in simple metasilicates there would occur such oxygen ions in addition to those common to two silicon tetrahedra; the corresponding formula is $R^{++}_3Al_2Si_6O_{18}$. This result is in striking agreement with observation. The most important double orthosilicates of divalent and trivalent metals are the garnets: $Ca_3Al_2Si_3O_{12}$, grossular, $Ca_3Cr_2Si_3O_{12}$, uvarovite, $Ca_3Fe_2Si_3O_{12}$, topazolite, etc., and the only double metasilicate is beryl, $Be_3Al_2Si_6O_{18}$.

The radius ratio of potassium ion and oxygen ion is 0.76, so that the coördination number to be expected for potassium ion in silicates is 8, the corresponding electrostatic bond strength being $1/8$. In potassium aluminum silicates containing aluminum octahedra the electrostatic valence principle would require at least four potassium polyhedra to have a common corner together with a silicon tetrahedron and an aluminum octahedron; this is not spatially possible. It is accordingly highly probable that in these compounds, the structure of none of which has yet been satisfactorily investigated with x-rays, the aluminum ions have a coördination number of 4. There could then occur oxygen ions with $\Sigma s_i = 2$ common to a silicon tetrahedron, an aluminum tetrahedron and two potassium polyhedra. The potassium-aluminum ratio would then be 1:1. In a large number of silicates, in particular the important feldspars, this ratio is observed: $KAlSiO_4$, phakelinite, $KAlSi_2O_6$, leucite, $KAlSi_3O_8$, potassium feldspar (microcline, orthoclase), $(K, Na)_8Al_8Si_9O_{34}$, nepheline, etc. In other silicates containing more than this amount of aluminum, such as muscovite, $H_2KAl_3Si_3O_{12}$, etc., it is probable that the excess aluminum ions usually have the coördination Number 6.

Other alkali ions (except lithium) also probably have the coördination Number 8 as a rule, and should similarly have a tendency to a 1:1 ratio with aluminum; this is shown in $NaAlSi_3O_8$, albite, $H_2Na_2Al_2Si_3O_{12}$, natrolite, $H_2Cs_4Al_4Si_9O_{27}$, pollucite, etc.

In spodumene, $\text{LiAlSi}_2\text{O}_6$ and petalite, $\text{LiAlSi}_4\text{O}_{10}$, it is possible that oxygen ions (with $\Sigma s_i = 2$) are common to a silicon tetrahedron, an aluminum tetrahedron and a lithium tetrahedron (the radius ratio for lithium ion is 0.33).

No aluminum silicates of alkali metals are known in which the $\text{Al}^{+3}:\text{R}^{+1}$ ratio is less than 1:1.

Summary

A set of principles governing the structure of complex ionic crystals, based upon the assumption of a coordinated arrangement of anions about each cation at the corners of an approximately regular polyhedron, is formulated with the aid of considerations based upon the crystal energy. Included in the set is a new electrostatic principle which is of wide application and considerable power.

It is shown that the known structures of many complex crystals, in particular the complex silicates, satisfy the requirements of these principles.

As an illustration of the application of the principles in the prediction of structures with the coordination theory, some properties of the structures of the three forms of Al_2SiO_5 , cyanite, andalusite and sillimanite, are predicted.

It is further shown that the theory requires that no stable basic silicates of divalent metals exist, and that in aluminum silicates of alkali metals there should be at least one aluminum ion for every alkali ion.

The structures of aluminum silicates of divalent metals which are simplest from the coordination standpoint are shown to correspond to the formulas $\text{R}_3^{++}\text{Al}_2\text{Si}_3\text{O}_{12}$ and $\text{R}_3^{++}\text{Al}_2\text{Si}_6\text{O}_{18}$, which include the most important minerals of this class, the garnets and beryl.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

SOLUBILITY IN THE GASEOUS PHASE, ESPECIALLY IN THE SYSTEM: $\text{NH}_3(\text{l})$ - $\text{NH}_3(\text{g})$, $\text{H}_2(\text{g})$, $\text{N}_2(\text{g})$

BY H. L. CUPPLES

RECEIVED SEPTEMBER 7, 1928

PUBLISHED APRIL 5, 1929

A number of investigators have found that a solubility effect may be shown within a gaseous phase, especially under circumstances in which the density of the gaseous phase is relatively high. Pollitzer and Strebel¹ were perhaps the first to mention this phenomenon.

The two-phase system $\text{NH}_3(\text{l})$ - $\text{NH}_3(\text{g})$, $\text{H}_2(\text{g})$, $\text{N}_2(\text{g})$ in which the H_2 and N_2 were maintained at the constant mole ratio of $3\text{H}_2:\text{N}_2$ has been experimentally investigated by Larson and Black.² Concentrations

¹ Pollitzer and Strebel, *Z. physik. Chem.*, **110**, 785 (1924).

² Larson and Black, *THIS JOURNAL*, **47**, 1015 (1925).