

definite chemical compounds with hydrogen chloride. The gliadin isotherm shows three flats, corresponding to at least nine definite compounds unless one postulates a polymerization of gliadin along the second flat.

6. The equivalent weights come out 280 for arachin, 435 for casein, 330-405 for edestin, 365 for fibrin and 250 for gliadin. Since there are apparently at least nine active nitrogens per molecule of gliadin, the molecular weight of gliadin must be some multiple of 2250. The diagrams give no clue at present as to the molecular weights of the other proteins.

7. It is not safe at present to reason from the behavior of the solid proteins with hydrogen chloride to the behavior of the same proteins in presence of aqueous hydrochloric acid.

8. We are indebted to Professor R. A. Gortner of the University of Minnesota for the specimens of arachin, edestin, fibrin, gliadin, and zein.

* This work is part of the programme now being carried out at Cornell University under a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

THE STRUCTURE OF THE MICAS AND RELATED MINERALS

BY LINUS PAULING

GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY

Communicated January 16, 1930

With the aid of the general principles¹ governing the structures of complex ionic crystals I have formulated a structure for talc, pyrophyllite, the micas, and the brittle micas which is substantiated by the x-ray examination of the minerals, explains their remarkable physical properties, and leads to a general chemical formula unifying the widely varying analyses reported for different specimens. This structure is described in the following paragraphs.

The monoclinic (pseudohexagonal) unit of structure of muscovite, $\text{KSi}_3\text{Al}_3\text{O}_{10}(\text{OH},\text{F})_2$, has been reported by Mauguin² to have $a = 5.17 \text{ \AA}$, $b = 8.94 \text{ \AA}$, $c = 20.01 \text{ \AA}$, and $\beta = 96^\circ$. This unit contains 4 molecules of the above composition. We have verified this with oscillation and Laue photographs of fuchsite, a variety of muscovite; the unit found having $a = 5.19 \text{ \AA}$, $b = 8.99 \text{ \AA}$, $c = 20.14 \text{ \AA}$, and $\beta = 96^\circ$.

The dimensions of the unit in the basal plane closely approximate those for the similarly pseudohexagonal crystal hydrargillite, $\text{Al}(\text{OH})_3$, as well as of the hexagonal layers in two forms of silica, β -tridymite and β -cristobalite. The monoclinic (pseudohexagonal) unit of structure of hydrargillite³ has $a = 8.70 \text{ \AA}$, $b = 5.09 \text{ \AA}$, $c = 9.76 \text{ \AA}$, and $\beta = 85^\circ 29'$, and contains $8\text{Al}(\text{OH})_3$. The crystal is composed of layers of octahedra,

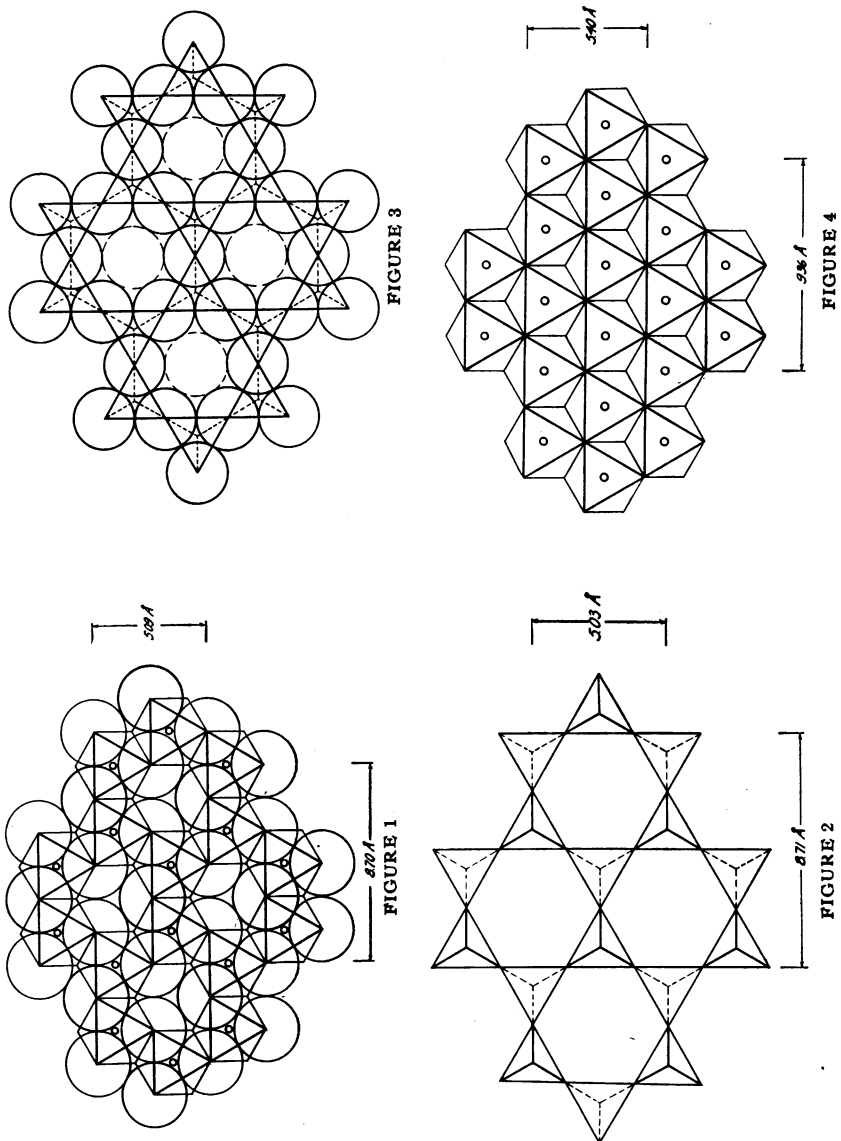


Fig. 1. A hydrargillite layer of octahedra. The light circles indicate oxygen ions, the heavier ones hydroxyl or fluorine ions in mica.

Fig. 2. A tetrahedral layer from β -cristobalite or β -tridymite. A silicon ion is located at the center of each tetrahedron, and an oxygen ion at each corner.

Fig. 3. A tetrahedral layer in which all the tetrahedra point in the same direction.

Fig. 4. A complete layer of octahedra (brucite layer).

each consisting of 6 OH^- ions grouped about an Al^{+3} ion, with each octahedron sharing three edges as shown in figure 1. The electrostatic valence rule is satisfied; each OH^- ion is held by two bonds of strength $s = 1/2$. These layers are superimposed, sharing no octahedral elements with one another.

In β -tridymite and β -cristobalite⁴ there are present the hexagonal layers of silicon tetrahedra shown in figure 2. Their dimensions, $a = 5.03 \text{ \AA}$ and $b = 8.71 \text{ \AA}$, agree closely with those of the hydrargillite layers and of mica. Another type of tetrahedral layer with the same dimensions can be obtained by pointing all the tetrahedra in the same direction (figure 3). The oxygen ions forming the bases of the tetrahedra have their valences satisfied: the strength s of a silicon bond is 1, and each O^- is held by two such bonds, giving $\Sigma s = 2$. But the oxygen ions at the unshared tetrahedral corners have $\Sigma s = 1$ only; it is hence necessary that they be held by further bonds. Now the relative positions of these tetrahedron corners are such that the tetrahedral layer can be imposed on the hydrargillite layer with the tetrahedron corners coincident with two-thirds of the shared octahedron corners; namely, those indicated in figure 1 by the large light circles. These positions are occupied by oxygen ions, which have $\Sigma s = 1 + 1/2 + 1/2 = 2$. The remaining positions, indicated by heavy circles, have $\Sigma s = 1/2 + 1/2 = 1$, and are occupied by hydroxide or fluoride ions. A similar tetrahedral layer is attached to the other side of the hydrargillite layer.

The resultant layer, with a total thickness of about 10 \AA , is electrically neutral. A crystal built up by the superposition of such layers would have the composition $\text{Si}_4\text{Al}_2\text{O}_{10}(\text{OH})_2$. It is very probable that the mineral pyrophyllite, with this composition, has this structure.

Brucite, $\text{Mg}(\text{OH})_2$, is built of complete octahedral layers such as that shown in figure 4, with dimensions not much greater than those of a hydrargillite layer, and with the octahedron corners in the same positions. A neutral layer containing tetrahedra and octahedra closely similar to that described above can be made with this complete octahedral layer in place of the hydrargillite layer; the electrostatic valence rule will be again satisfied, O^- having $\Sigma s = 1 + 1/3 + 1/3 + 1/3 = 2$ and OH^- having $\Sigma s = 1/3 + 1/3 + 1/3 = 1$. These layers probably occur in talc, $\text{Si}_4\text{Mg}_3\text{O}_{10}(\text{OH})_2$, which is reported to be monoclinic, pseudo-hexagonal, and morphologically similar to mica.

By replacing one-fourth of the silicon ions in a pyrophyllite layer by aluminum ions, which can have the coordination number 4 as well as 6, the layers become negatively charged. To regain neutrality further positive ions must be introduced, such as K^+ or Na^+ . There is room for these ions between the layers, in the pockets formed by six oxygen ions on the top of one layer and six on the bottom of the layer above. The

composition of such a crystal is $K \cdot Si_3Al \cdot Al_2O_{10}(OH, F)_2$, which is the formula generally assigned to muscovite. A similar treatment of talc gives $KSi_3AlMg_3O_{10}(OH, F)_2$, which is biotite.

Pyrophyllite, talc, muscovite, and biotite have the following sequence of atom-planes along the pseudo-hexagonal axes:

Pyrophyllite		Talc	
6O ⁻		6O ⁻	
4 Si ⁺⁴		4 Si ⁺⁴	
4O ⁻ + 2OH ⁻		4O ⁻ + 2OH ⁻	
4Al ⁺³		6Mg ⁺²	
4O ⁻ + 2OH ⁻		4O ⁻ + 2OH ⁻	
4Si ⁺⁴		4Si ⁺⁴	
6O ⁻		6O ⁻	
Muscovite		Biotite	
z_2 6O ⁻	} Charge -2	6O ⁻	} Charge -2
u 3Si ⁺⁴ + Al ⁺³		3Si ⁺⁴ + Al ⁺³	
z_1 4O ⁻ + 2(OH ⁻ , F ⁻)		4O ⁻ + 2(OH ⁻ , F ⁻)	
Origin 4Al ⁺³		6Mg ⁺²	
4O ⁻ + 2(OH ⁻ , F ⁻)		4O ⁻ + 2(OH ⁻ , F ⁻)	
3Si ⁺⁴ + Al ⁺³		3Si ⁺⁴ + Al ⁺³	
6O ⁻		6O ⁻	
2K ⁺		2K ⁺	
6O ⁻		6O ⁻	
3Si ⁺⁴ , etc.		3Si ⁺⁴ , etc.	

The verification of the suggested structures by the comparison of the observed and calculated intensities of reflection of x-rays has been begun. So far the calculations have been carried out for 18 even orders of re-

TABLE 1
ATOMIC A-VALUES

d/n =	10	5	2.5	1.0	0.75	0.60Å
A_o =	30	21	10	2.0	0.8	0.25
A_{Al} =	49	28	17	5.2	3.0	1.7
A_{Si} =	53	30	18	6.0	3.7	2.1
A_K =	72	45	24	7.8	5.0	3.2

flection from (001). The observed intensities given in table 2 were obtained by the visual comparison of four photographs from fuchsite, identical except for varying exposure times of 15, 90, 300, and 960 minutes. The calculated intensities were obtained from the formula

$$I = \text{constant} \cdot A^2,$$

$$\text{with } A = \sum_n A_n e^{2\pi i (hx_n + ky + lz_n)}, \quad (1)$$

the summation being taken over all the atoms in the unit. Values of the atomic amplitude functions⁵ used are given in table 1. Assuming the group of atoms such as $4O^- + 2(OH^-, F^-)$ to depend on a single parameter, only three parameters are involved, z_1 , u , and z_2 . Giving the hydrargillite layer the thickness found for it in hydrargillite, and assuming the tetrahedra to be regular and 2.60 Å on an edge as in silicates in general, the parameter values $z_1 = 0.055$, $z_2 = 0.165$, and $u = 0.137$ were predicted.

The amplitude expression is

$$A = 2A_{Al} + (-1)^{l/2} A_K + (3A_{Si} + A_{Al}) \cos 2\pi lu + 6A_O(\cos 2\pi lz_1 + \cos 2\pi lz_2), \quad (2)$$

with l having even values from 2 to 36. It was found that the values of A^2 were in general agreement with the observed intensities for the predicted parameter values. Slightly better agreement was obtained by reducing u to 0.135. The calculated intensities (the constant in equation 1 being given the arbitrary value 0.015) are included in table 2, and represented graphically together with the observed intensities in figure 5. The general agreement is striking, and lends strong support to the suggested structure.

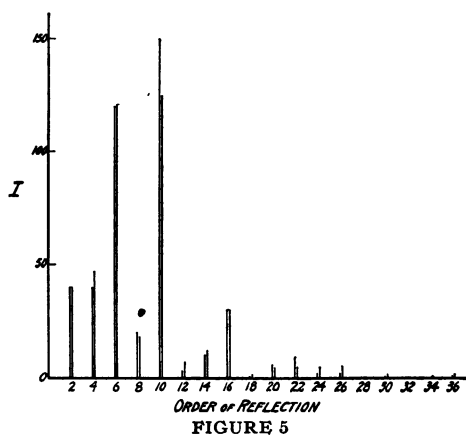


FIGURE 5
Comparison of the observed and calculated intensities of reflection of x-rays from (001) of fuchsite, in the 2nd to 36th order. In each pair of vertical lines that on the left shows the observed intensity, that on the right the calculated intensity.

TABLE 2

OBSERVED AND CALCULATED INTENSITIES OF REFLECTION FROM (001) OF FUCHSITE

ORDER OF REFLECTION	2	4	6	8	10	12	14	16	18
Observed intensity	40	40	120	20	150	3	10	30	0.5
Calculated intensity	40	47	121	18	124	7	12	30	1.4
ORDER OF REFLECTION	20	22	24	26	28	30	32	34	36
Observed intensity	6	9	2	2	0	0.8	0.1	0	1
Calculated intensity	4.3	4.5	4.8	5.2	0.0	1.6	0.2	0.6	1.7

The mica structure provides an interesting variation of the types of close-packing observed for large ions in crystals. The two central layers of O^- , OH^- , and F^- ions form close-packed planes with three spheres in a hexagonal unit of edge 5.2 Å, at positions 00 , $1/3^2/3$, and $2/3^1/3$ relative

to axes 120° apart. The outer layers, however, consist of oxygen ions occupying three of the four positions of a close-packed plane with four spheres in the same unit of edge 5.2 \AA , at positions such as 00 , $0^{1/2}$, and $^{1/2}0$. The insertion of a fourth sphere at $^{1/2}^{1/2}$, indicated by the dotted circles in figure 3, would complete this layer. Such a large variability in the effective dimensions of the large ions introduces some ambiguity in structure determinations involving the deduction of the type of close-packing from the size of the unit of structure.

The structure leads to a general formula for the micas: namely, $KX_nY_4O_{10}(OH,F)_2$, with $2 \leq n \leq 3$, in which X represents cations of coordination number 6 (Al^{+3} , Mg^+ , Fe^{++} , Fe^{+3} , Mn^{++} , Mn^{+3} , Ti^{+4} , Li^+ , etc.) and Y cations of coordination number 4 (Si^{+4} , Al^{+3} , etc.). The subscript n can have any value between 2 (hydrargillite layer) and 3 (complete octahedral layer). K^+ can be partially replaced by Na^+ and possibly to some extent by Ca^{++} . This formula represents satisfactorily the numerous recently published mica analyses almost without exception.⁶ The distribution of the various ions X and Y must be such as to give general agreement with the electrostatic valence rule.

The clintonites or brittle micas have a similar structure, the layers having twice the electrical charge of those in mica, and being held together by calcium ions instead of potassium ions. The correspondingly stronger forces bring the layers closer together, the separation of adjacent layers being $9.5\text{--}9.6 \text{ \AA}$ in place of the value $9.9\text{--}10.1 \text{ \AA}$ for the micas. The general formula $CaX_nY_4O_{10}(OH, F)_2$, with $2 \leq n \leq 3$, holds for these minerals.

The physical properties of talc, pyrophyllite, the micas, and the brittle micas are in agreement with the suggested structure. To tear apart one of the pseudohexagonal layers it is necessary to break the strong Si-O, Al-O, etc., bonds; as a consequence these individual layers are tough. But they can be easily separated from one another, giving rise to the pronounced basal cleavage shown by all these minerals. In talc and pyrophyllite the layers are electrically neutral, and are held together only by stray electrical forces. These crystals are accordingly very soft, feeling soapy to the touch as do graphite crystals. To separate the layers in mica it is necessary to break the bonds of the univalent potassium ions, so that the micas are not so soft, thin plates being sufficiently elastic to straighten out after being bent. Separation of layers in the brittle micas involves breaking bonds of bivalent calcium ions; these minerals are hence harder, and brittle instead of elastic, but still show perfect basal cleavage. The sequence of hardness is significant; on the Mohs scale it is: talc and pyrophyllite, 1-2; the micas, 2-3; the brittle micas, $3^{1/2}$ -6.

I wish to acknowledge the assistance of Mr. J. Sherman in the preparation and analysis of the x-ray photographs.

A further account of the x-ray investigation of these minerals and a comparison of the suggested general formulas with the reported chemical analyses will be published in the *Zeitschrift für Kristallographie*.

¹ Linus Pauling, "Sommerfeld Festschrift," S. Hirzel, Leipzig, 1928, p. 11; *J. Am. Chem. Soc.*, **51**, 1010 (1929).

² Ch. Mauguin, *Comp. Rend.*, **185**, 288 (1927).

³ The determination of the structure of hydrargillite will be reported in a paper to be published in the *Zeits. für Krist.*

⁴ For known crystal structures reference may be made to the Strukturbericht of P. P. Ewald and C. Hermann in current numbers of *Zeits. für Krist.*

⁵ The atomic amplitude functions take account of the atomic F -factor, the temperature factor, the Lorentz factor, and the polarization factor.

⁶ Mauguin showed that for various micas the unit of structure uniformly contains the number of atoms $O + F$ given by the above formula.

THE DECOMPOSITION OF NITROGEN PENTOXIDE AT LOW PRESSURES

BY HANS-JOACHIM SCHUMACHER* AND GERHARD SPRENGER

LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY, AND TECHNISCHE HOCHSCHULE, DANZIG-LANGFUER

Communicated December 20, 1929

Introduction.—Nitrogen pentoxide¹ and nitrylchloride^{2,3} are the only known inorganic compounds which decompose unimolecularly. Because of their simple molecular structure these two compounds should be well adapted to give direction to the theory of unimolecular reactions. For this reason the kinetics of these reactions have been investigated with the utmost care.

In spite of these studies the velocity of the decomposition of nitrogen pentoxide, at least at low pressures, is still in dispute.⁴ For the most part the explanation of the discordant results is to be found in the experimental difficulties involved in working at low pressures with a chemically active substance such as N_2O_5 . However, the behavior at low pressures is of special interest.

As is well known, the present theory requires that every unimolecular reaction should become bimolecular at a certain pressure. This change is indicated by a falling off in the value of the unimolecular constant. The pressure at which this occurs for different compounds is greatly influenced by the number of degrees of freedom of the molecule.

Recently it has been shown, in the accurate work of Ramsperger, Nordberg and Tolman,⁵ that for pressures down to 0.2 mm. Hg the velocity