# THE CRYSTAL STRUCTURE OF POTASSIUM DITHIONATE, $K_2S_2O_6$[1]

M. L. HUGGINS AND GLENN O. FRANK,[2] *Stanford University.*

Potassium dithionate crystallizes[3] with the symmetry of the trigonal trapezohedral class, $D^3$ ($A_3 \cdot 3A_2$), of the hexagonal system. The observed forms include $\{0001\}$, $\{10\bar{1}1\}$, $\{10\bar{1}0\}$, $\{11\bar{2}0\}$, and $\{11\bar{2}1\}$. The crystals rotate polarized light, as would be expected of crystals having this symmetry.

The crystals used in the present investigation were prepared by treatment of an aqueous solution of barium dithionate with potassium sulphate, filtering, evaporating, and recrystallizing from water solution.[4]

## THE STRUCTURE ANALYSIS

The $x$-ray analysis was made by the oscillating crystal method, a horizontal beam of $x$-rays, consisting chiefly of the K radiation of molybdenum, striking a crystal which was oscillated around a vertical axis at constant angular velocity through an angle of 20 degrees. A photographic film was placed normal to the $x$-ray beam,
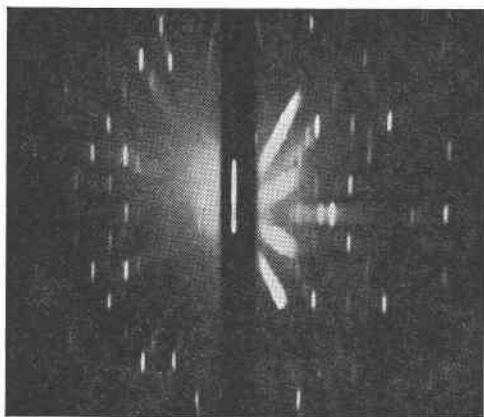


FIG. 1. Photograph taken with the crystal oscillating around the $a$ axis.

10 cm. from the crystal. One of the photographs obtained in this way is reproduced in Fig. 1.

For such a photograph the "identity distance," $J$, between two identical points within the crystal in the direction of the axis of rotation is obtainable from the wave-length $\lambda$ and the angle $\mu_n$ between the central "layer line" (that of zero order) and that of order $n$ by means of the relation[5]

$$J = \frac{n\lambda}{\sin \mu_n}.$$

In taking this photograph the axis of rotation was the $a$ axis (as assumed by Groth[3]). Other photographs were taken with the crystal rotated about the $c$ axis and about the axis $a'$, perpendicular to $c$ and making an angle of 30° with $a$. From these the following identity distances were obtained.

$$a \smallsmile 9.8\text{Å}$$
$$a' \smallsmile 17.0\text{Å} = \sqrt{3} \times 9.8\text{Å}$$
$$c \smallsmile 6.4\text{Å} = 0.65 \times 9.8\text{Å}$$

Since the identity distance in the direction of the $a$ axis is less than that in the direction of the $a'$ axis, the orientation as given by Groth gives the smallest unit cell. 9.8Å and 6.41Å are then approximately the unit distances $a$ and $c$, i.e. the lengths of the edges of the unit cell.

More accurate values, obtained from the $(h0.0)$ and $(00.l)$ spectra, by comparison with reflections from a cleavage face of calcite, are

$$a_0 = 9.82\text{Å}$$
$$c_0 = 6.36\text{Å}$$
$$a_0 : c_0 = 1 : 0.648.$$

The axial ratio so obtained is in good agreement with that $(1:0.6467)$ given by Groth.[3]

The volume of the unit cell, computed from these dimensions, equals 3.08 times the volume per "molecule," calculated from the density $(2.278 \text{ g/cc.})$,[6] the molecular weight, and Avogadro's number. There are thus six potassium, six sulfur and eighteen oxygen atoms within the unit.

The determination of the indices of the observed reflections was simplified by making projections from the photographs with a ruler

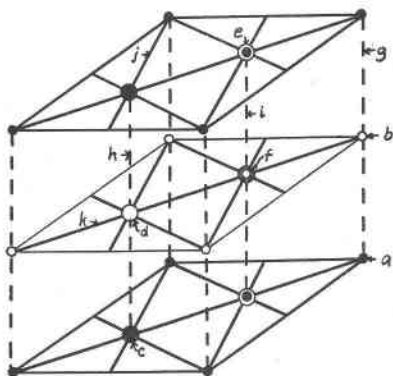[5] Polanyi, *Naturwiss.*, **9**, 337, 1921.

[6] *International Critical Tables*.

Fig. 2. The distribution of symmetry elements within the unit cell, for a structure having the symmetry of the space-group $D_3{}^1$ (from Wyckoff[9]).
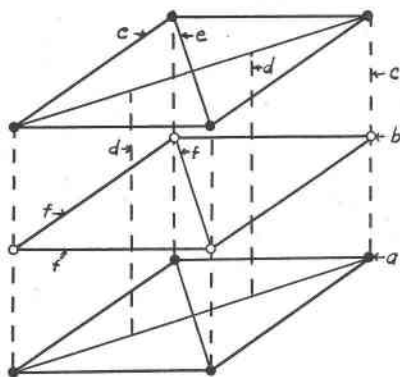


Fig. 3. The distribution of symmetry elements within the unit cell, for a structure having the symmetry of the space-group $D_3{}^2$ (from Wyckoff[9]).

devised by the senior author. The necessary data for constructing such a ruler and a description of its use will be published elsewhere.

The presence of many reflections having indices such that $(2h+k+l)/3$ is not integral proves the fundamental lattice to be the hexagonal rather than the rhombohedral.[7] This and the observation that $(00.l)$ reflections with $l/3$ not integral were obtained eliminate[8] as possibilities space-groups $D_3{}^{3-7}$ inclusive, leaving only $D_3{}^1$ and $D_3{}^2$.

[7] Schiebold, *Leipziger Abh.*, **36,** 65, 1919.

[8] Astbury and Yardley, *Phil. Trans. Roy. Soc.* (London), **A224,** 221, 1924. Wyckoff, *Zeit. Krist.*, **63,** 507, 1926.

The special distribution of symmetry elements within a unit cell of a structure isomorphous with the space-group $D_3{}^1$ is represented[9] in Fig. 2, the coördinates and symmetry of the various sets of equivalent positions being given in Table 1. Fig. 3 and Table 2 give the same for $D_3{}^2$.

TABLE 1

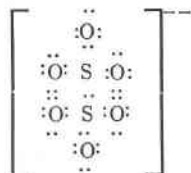**Equivalent positions for the space-group $D_3{}^1$ with the point-group symmetry for each.**

(a) $D_3$ 000   (b) $D_3$ 00½   (c) $D_3$ ⅓⅔0   (d) $D_3$ ⅓⅔½   (e) $D_3$ ⅔⅓0   (f) $D_3$ ⅔⅓½

(g) $C_3$ $00u$; $00\bar{u}$   (h) $C_3$ ⅓⅔$u$; ⅓⅔$\bar{u}$   (i) $C_3$ ⅔⅓$u$; ⅔⅓$\bar{u}$

(j) $C_2$ $u\ \bar{u}\ 0$; $2\bar{u}, \bar{u}, 0$; $u, 2u, 0$   (k) $C_2$ $u\ \bar{u}\ ½$; $2\bar{u}, \bar{u}, ½$; $u, 2u, ½$

(l) $C_1$ $xyz$; $y-x, \bar{x}, z$; $\bar{y}, x-y, z$; $x, x-y, \bar{z}$; $\bar{y}\ \bar{x}\ \bar{z}$; $y-x, y, \bar{z}$

TABLE 2

**Equivalent positions for the space-group $D_3{}^2$ with the point-group symmetry for each.**

(a) $D_3$ 000   (b) $D_3$ 00½   (c) $C_3$ $00u$; $00\bar{u}$

(d) $C_3$ ⅓⅔$u$; ⅔⅓$\bar{u}$   (e) $C_2$ $uu0$; $0\bar{u}0$; $\bar{u}00$   (f) $C_2$ $uu½$; $0\ \bar{u}\ ½$; $\bar{u}\ 0\ ½$

(g) $C_1$ $xyz$; $y-x, \bar{x}, z$; $\bar{y}, x-y, z$; $y\ x\ \bar{z}$; $\bar{x}, y-x, \bar{z}$; $x-y, \bar{y}, \bar{z}$

Chemical evidence indicates that the substance contains $S_2O_6{}^{--}$ groups in which the sulfur atoms are bonded together and each sulfur is bonded also to three of the oxygens. The valence bonds (electron-pairs), according to the Lewis theory,[10] should be tetrahedrally disposed around the sulfur atoms, this arrangement being represented in two dimensions by the structural formula:

$$\left[ \begin{array}{ccc} & :\!\overset{..}{O}\!: & \\ :\!\overset{..}{O}\!: & S & :\!\overset{..}{O}\!: \\ :\!\overset{..}{O}\!: & S & :\!\overset{..}{O}\!: \\ & :\!\overset{..}{O}\!: & \end{array} \right]^{--}$$

Much evidence from various experimental fields[11] might be cited to show that such an arrangement is very probably correct. In this work we have tentatively assumed it to be so, to see whether or not such an assumption will lead to a distribution of atomic centers in agreement with our experimental data.

[9] Wyckoff, The Analytical Representation of the Results of the Theory of Space-Groups, *Carnegie Inst. Pub., No.* **318**, Washington, 2nd Edition, 1930, pp. 153, 154, 223, 224.

[10] Lewis, *Valence and the Structure of Atoms and Molecules*, Chem. Cat. Co., New York, **1923**.

[11] Cf. Huggins, *Phys. Rev.,* **27**, 286, 1926.

The S–S centerline in such a group is a three-fold symmetry axis. Since the crystal also possesses three-fold symmetry axes, we should expect the sulfur atom centers to lie on them, that is, if $D_3^1$ is the correct space-group, in positions $(g)$, $(h)$ and $(i)$. The oxygen centers would then be in three sets of positions $(l)$, with such parameters as would place them similarly around each $S_2$ group. The six potassium atoms could either be in $(l)$ also or in various combinations of the other positions. From other crystal structure data rough values of the S–S and S–O distances (2.1 and 1.5–1.6Å respectively) can be obtained. From these and the assumption that the angles between the bonds joining each sulfur atom with the four surrounding atoms are not far from 109.5° (the angle between the lines joining the corners of a regular tetrahedron with its center) were calculated approximate values for the three $u$ parameters for sulfur and the three $z$ parameters for oxygen. (Both structures in which the centers of all the negative ions are in the same plane, say $z=0$, and those in which two such ion centers are in one plane, say $z=0$, while the other is in a different plane, $z=\frac{1}{2}$, were of course considered). Then for the various alternative distributions of the K atoms structure factors were calculated for the first six orders of reflection from (00.1) planes, using the relationship[12]

$$F_{calc} = \sqrt{A^2 + B^2} \quad \text{where}$$
$$A = \sum_i F_i \cos 2\pi \, (hx_i + ky_i + lz_i)$$
$$B = \sum_i i \, F_i \sin 2\pi \, (hx_i + ky_i + lz_i).$$

The summations are taken over all the atoms $i$ in the unit cell. $F_i$ is the atomic structure factor for the $i$th atom (K, S or O). Various curves for the variation of these factors with $\sin \theta$ were tried. In no case was even fair agreement obtained with the $F_{obs}$ values (Table 3). The latter were obtained from the observed intensities, estimated by visual comparison with a scale produced by placing a film in the path of the direct beam for various known lengths of time, by means of the relation

$$F_{obs} = \sqrt{\left(\frac{\sin 2\theta}{1 + \cos^2 2\theta}\right) I_{obs}.}$$

(These $F_{obs}$ values are of course only relative. Moreover no account is taken in their calculation of any correction for absorption,

[12] Wyckoff, *The Structure of Crystals*, Chemical Catalog Co., New York, 1931, p. 95.

approximate calculations having shown that the error thereby introduced is insufficient to invalidate any of the conclusions reached. The chief effect of this neglect is to make $F_{obs}$ somewhat smaller than it should be for very strong reflections).

The disagreement can be most simply illustrated by considering only the (00.$l$) reflections for which $l$ is even. Using the structure
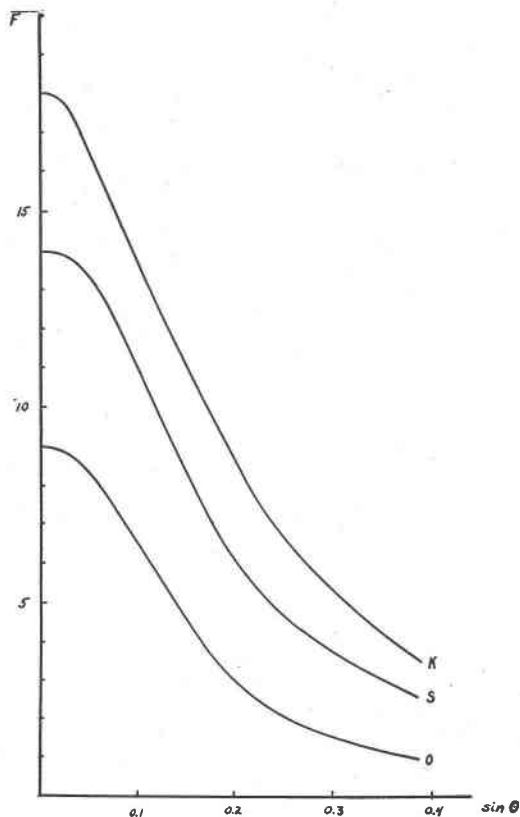


Fig. 4. Atomic $F$ curves used in this structure analysis.

factor curves given in Fig. 4, relative $F_{calc}$ values for (00.2), (00.4) and (00.6) are (neglecting the sign) 10, 12 and 4 respectively, for all arrangements except those with the K atoms in positions ($l$). In those cases the magnitude of $F_{calc}$ is (on the same scale) for all values of $Z_k$ equal to or larger than 10 for (00.2), equal to or smaller than 12 for (00.4), and equal to or less than 5 for (00.6). These are to be compared with $F_{obs}$ values of 4, 10 and 7, respectively. It is

therefore evident that $D_3{}^1$ cannot be the correct space-group, provided our assumptions are even approximately correct.

A similar procedure was followed for the space-group $D_3{}^2$. (See Fig. 4 and Table 2). Good agreement with the observed intensities of the $(00.l)$ spectra was obtained only for the case in which the $S$ atoms are in pairs on the three-fold symmetry axes, i.e. in positions (c), (d) and (d), with the centers of these pairs in layers $z=0$, $z=v$ and $z=\bar{v}$, $v$ being in the neighborhood of 0.42–0.43, and with the potassium atoms in positions (e) and (f), on two-fold symmetry axes.

Different atomic $F$ curves given in the literature were tried, the set finally adopted being reproduced in Fig. 4. $F_K$ is that calculated by West[13] for use in the analysis of $KH_2PO_4$, using a temperature factor found for KCl. We have extrapolated the curve to $F_K = 18$ (the number of electrons in the $K^+$ ion) at $\sin\theta = 0$. $F_0$ is from the corresponding curve given by West, except for a slight increase below $\sin\theta = 0.1$ in order to make $F_O = 9$ at $\sin\theta = 0$. This amounts to an assumption that one electron of each pair shared between $S$ and $O$ atoms contributes to the structure factor of each of the two atoms. Similarly the $F_S$ curve was obtained by assuming $F_S$ to be everywhere slightly greater than $F_P$ (as calculated by West) and to equal 14 at $\sin\theta = 0$. It should be noted that although these particular atomic structure factor curves were chosen in preference to others partly because they gave better agreement with the $F_{obs}$ values for the $00.l$ reflections, they were used without further change to obtain $F_{calc}$ values for many $hk.0$ reflections and gave very satisfactory agreement.

The effect of slightly varying the parameters $z$ and $v$ independently was also tried, the values finally adopted as most probable being $z = 0.23$ and $v = 0.43$. The structure factors calculated on this basis are compared with the "observed" values in Table 3.

TABLE 3

Comparison of relative values of $F_{obs}$ and $F_{calc}$ (on the basis of the final structure) for $(00.l)$ reflections.

|  | (00.1) | (00.2) | (00.3) | (00.4) | (00.5) | (00.6) |
|---|---|---|---|---|---|---|
| $F_{obs}$ | 3 | 4 | 2 | 10 | 6 | 7 |
| $F_{calc}$ | 3.2 | 4.1 | 2.3 | 10.0 | 3.8 | 5.3 |

The approximate values for the $z$ coordinates of the oxygen

---

[13] West, *Zeit. Krist.*, 74, 306. 1930.

atoms are 0.20, 0.23, 0.34, 0.66, 0.77 and 0.80. They are thus in rather widely separated layers, with each layer containing atoms in three separate levels. By analogy with the known structures of silicates, sulfates and other oxygen compounds, one might expect approximate close-packing within each layer, the oxygens in the three different levels being disposed roughly as are those in three adjacent levels in a cubic close-packed structure. This leads to the approximate arrangement shown in Figure 5. The potassium centers might be expected to be between the oxygen layers, in such a way that each is surrounded by six oxygen centers and is as far as possible from other potassium atoms.
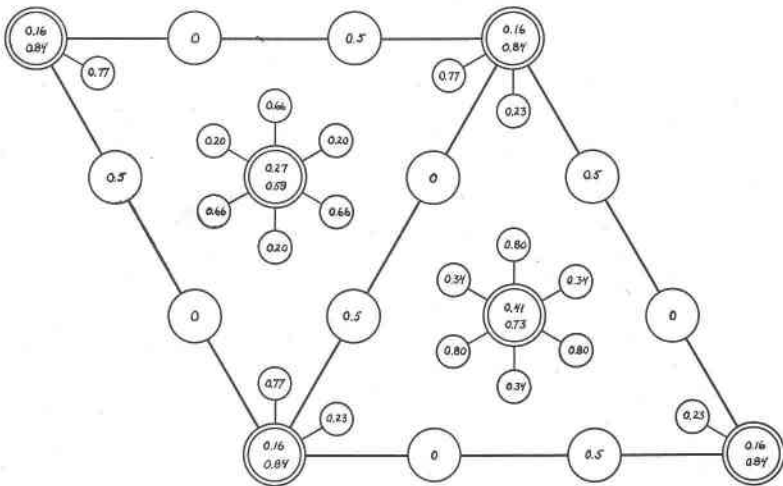


Fig. 5. The approximate arrangement within the unit cell, projected on (00.*l*). Small circles represent oxygen atoms, large single circles potassium atoms, and large double circles pairs of sulfur atoms. The *z* coördinates are shown within the circles.

Calculations on the basis of such an arrangement showed fair agreement with the "observed" (*hk*.0) structure factors, but not good enough. Keeping the distance of each oxygen from the nearest $S_2$ axis equal to about 1.45–1.65Å and assuming all the K–O distances to be approximately equal to each other, however, resulted in parameters (obtained by a combined graphical and analytical method) which gave much better agreement with experiment. Our "most probable" values, obtained in this way, are listed in Table 4 and a comparison of the $F_{obs}$ and $F_{calc}$ values for the *hk*.0 reflections appearing on one of our films is given in Table 5. Con-

## TABLE 4

### Parameter values for $K_2S_2O_6$.

S in (c) with $u_s = .16_0$      K in (e) with $u_k = .30_0$
(d) with $u_s' = .59_0$      (f) with $u_k' = .62_5$
(d) with $u_s'' = .27_0$

O in (g) with $x, y, z = .16_5, .11_0, .23_0$
(g) with $x'y'z' = .61_5, .17_0, .34_0$
(g) with $x''y''z'' = .50_5, .21_0, .80_0$

## TABLE 5

Indices of $(hk.0)$ reflections from a crystal oscillated about the $a'$ axis, with $F_{obs}$ (above the indices) and $F_{calc}$ (below the indices).

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | | | 13 | |
| | | | | | | $(07.0)$ | |
| | | | 14 | | 52 | 8 | |
| | | | $(\bar{1}5.0)$ | | $(06.0)$ | | |
| | | 39 | 6 | 11 | 55 | 17 | |
| | | $(\bar{1}4.0)$ | | $(05.0)$ | | $(16.0)$ | |
| | 21 | 34 | 0 | 12 | 22 | 26 | |
| | $(\bar{1}3.0)$ | | $(04.0)$ | | $(15.0)$ | | |
| 85 | 19 | 72 | 3 | 14 | 26 | 34 | |
| $(\bar{1}2.0)$ | | $(03.0)$ | | $(14.0)$ | | $(25.0)$ | |
| 75 | 9 | 92 | 30 | 6 | 15 | 29 | |
| | $(02.0)$ | | $(13.0)$ | | $(24.0)$ | | |
| 0 | 10 | 13 | 34 | 28 | 12 | 0 | |
| $(01.0)$ | | $(12.0)$ | | $(23.0)$ | | $(34.0)$ | |
| 3 | 54 | 19 | 9 | 19 | 37 | 7 | 26 |
| | $(11.0)$ | | $(22.0)$ | | $(33.0)$ | | $(44.0)$ |
| 0 | 75 | 13 | 9 | 28 | 67 | 0 | 25 |
| $(10.0)$ | | $(21.0)$ | | $(32.0)$ | | $(43.0)$ | |
| 3 | 9 | 19 | 30 | 19 | 15 | 7 | |
| | $(20.0)$ | | $(31.0)$ | | $(42.0)$ | | |
| 85 | 10 | 72 | 34 | 14 | 12 | 34 | |
| $(2\bar{1}.0)$ | | $(30.0)$ | | $(41.0)$ | | $(52.0)$ | |
| 75 | 21 | 92 | 0 | 6 | 22 | 29 | |
| | $(3\bar{1}.0)$ | | $(40.0)$ | | $(51.0)$ | | |
| 26 | 19 | 39 | 3 | 11 | 26 | 17 | |
| $(3\bar{2}.0)$ | | $(4\bar{1}.0)$ | | $(50.0)$ | | $(61.0)$ | |
| 19 | 17 | 34 | 14 | 12 | 52 | 26 | |
| | $(4\bar{2}.0)$ | | $(5\bar{1}.0)$ | | $(60.0)$ | | |
| 56 | 9 | 34 | 6 | 22 | 55 | 13 | |
| $(4\bar{3}.0)$ | | $(5\bar{2}.0)$ | | $(6\bar{1}.0)$ | | $(70.0)$ | |
| 34 | 43 | 19 | 22 | 26 | 17 | 8 | |
| | $(5\bar{3}.0)$ | | $(6\bar{2}.0)$ | | $(71.0)$ | | |
| | 19 | 68 | 12 | 42 | 26 | 19 | |
| | | $(6\bar{3}.0)$ | | $(7\bar{2}.0)$ | | $(8\bar{1}.0)$ | |
| | | 67 | | 29 | | 20 | |

sidering the facts that the intensities were only roughly determined, that no correction for absorption was made and that the atomic structure factors are not accurately known, the agreement is remarkably good. We therefore believe these parameter values to be not far from the correct ones.
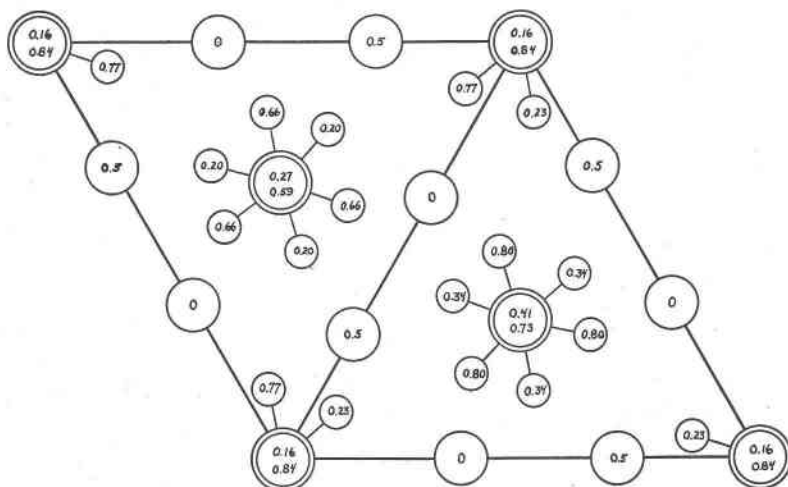


FIG. 6. The same as Figure 5, but with more exact parameter values (Table 4).

## DISCUSSION OF THE STRUCTURE

The structure so obtained is diagramatically represented in Fig. 6. It may be considered as an assemblage of $K^+$ and $S_2O_6^{--}$ ions, the latter having the structure predicted by the Lewis theory, these ions being distributed so as to satisfy as well as possible the following forces: (1) the attraction between positive $K^+$ ions and negative $S_2O_6^{--}$ ions (especially the O atoms in the latter); (2) the mutual repulsion between oxygen atoms, producing an approximately close-packed arrangement of their centers; and (3) the repulsion between like ions, causing each kind, considered separately, also to be distributed in an approximately close-packed manner.

From the parameter values given in Table 4 the following have been calculated:

Each sulfur is tetrahedrally surrounded by one other sulfur at a distance of $2.0_6$Å and three oxygens each at a distance of $1.5_0$Å.

Each potassium is surrounded by six oxygen atoms at corners of a distorted octahedron, at distances of $2.7_7$–$2.8_2$Å.

Each oxygen is at a distance of $1.5_0$Å from one sulfur and $2.7_7$–$2.8_2$Å from two potassium atoms.

These distances are in excellent agreement with corresponding distances in other compounds. The S-S distance in pyrite ($FeS_2$) has been determined[14] as 2.09Å. The S-O distance in various sulfates has been found[15] to be 1.5–1.6Å. The K-O distance has been given as 2.79–2.81Å in $KH_2PO$,[16] as 2.72–2.95Å in $KAl(SO_4)_4$,[17] and as 2.73–3.12Å in $KClO_3$.[18] In the $K_2SO_4$ structure 10 oxygen atoms are found[19] at distances of 2.71–3.15Å from a potassium center, with an eleventh at 3.50Å.

## Rubidium Dithionate

Sufficient data were also obtained from $Rb_2S_2O_6$ crystals to show that it has the same type of structure as the potassium salt, as would be expected from the crystallographic data.[20] From the distances between layer lines the unit distances $a_0$ and $c_0$ were determined as about 10.0Å and 6.3Å respectively, in agreement with the density, which we roughly determined as 3.00 g./cc., and the axial ratio ($a:c = 1:0.6307$) as given by Groth, if there are three "molecules" per unit.

Although we have made no attempt to determine accurately the parameters a comparison (Table 6) of the observed intensities with values of $F^2$ calculated on the assumption that the parameters are the same as for $K_2S_2O_6$ (Table 4) shows quite good agreement. We therefore conclude that the true parameters are not very different in the two cases.

In these calculations we used an atomic $F$ curve for Rb obtained from the Cs curve calculated from Thomas' model[21] by the method given by Bragg and West.[22]

[14] Ewald and Friedrich, *Ann. Physik*, **44**, 1183, 1914.

[15] James and Wood, *Proc. Roy. Soc.*, **A109**, 598, 1925.
Bradley, *Phil. Mag.*, **49**, 1225, 1925.
Dickson and Binks, *Phil. Mag.*, **2**, 114, 1926.
Taylor and Boyer, *Mem. Proc. Manchester, Lit. Phil. Soc.*, **72**, 125, 1928.
Ogg, *Phil. Mag.*, **5**, 354, 1928.
Vegard and Maurstad, *Zeit. Krist.*, **69**, 519, 1929.

[16] West, *Ref. 13*.

[17] Vegard and Maurstad, *Ref. 15*.

[18] Zachariasen, *Zeit. Krist.*, **71**, 501, 1929.

[19] Ogg, *Ref. 15*.

[20] *Ref. 3*.

[21] Thomas, *Proc. Cambridge Phil. Soc.*, **23**, 542, 1927.

[22] W. L. Bragg and J. West, *Zeit. Krist.*, **69**, 118, 1928.

We have also made a study of the structure of $CaS_2O_6 \cdot 4H_2O$, the results of which will be published in another communication.

## SUMMARY

1. The unit cell of $K_2S_2O_6$ has the dimensions $a_0 = 9.82$Å and $c_0 = 6.36$Å.

2. The space-group is $D_3^2$.

3. The distribution of atoms within the unit is as given in Tables 2 and 4 and pictured in Fig. 7.

4. $Rb_2S_2O_6$ has the same type of structure, with $a_0 = 10.0$Å and $c_0 = 6.3$Å and with approximately the same values for the 14 parameters defining the atomic positions.

### TABLE 7

**Comparison of observed intensities with $F^2_{calc}$ for $hk.0$ and $00.l$ reflections from $Rb_2S_2O_6$.**

Intensity scale: s = strong, ms = medium strong, m = medium, mf = mediumfaint, f = faint, 0 = no observed reflection, although crystal was in the proper position for reflection. A blank indicates no reflection observed, but crystal may not have been in the proper position for reflection.

| $hk.l$ | Observed Intensity | | | Relative $F^2_{calc}$ | $hk.l$ | Intensity Film 4 | Relative $F^2_{calc}$ |
|---|---|---|---|---|---|---|---|
| | Film 1 | Film 2 | Film 3 | | | | |
| | Left | | | | | | |
| 10.0 | 0 | 0 | 0 | 0 | 00.1 | 0 | 1 |
| 20.0 | 0 | 0 | 0 | 1 | 00.2 | mf | 34 |
| 30.0 | s | s | s | 100 | 00.3 | 0 | 1 |
| 40.0 | 0 | 0 | 0 | 0 | 00.4 | m | 100 |
| 50.0 | f | 0 | 0 | 4 | 00.5 | 0 | 2 |
| 60.0 | m | ms | m | 33 | | | |
| 70.0 | 0 | 0 | 0 | 3 | | | |
| | Right | | | | | | |
| 11.0 | 0 | 0 | 0 | 13 | | | |
| 22.0 | 0 | f | 0 | 7 | | | |
| 33.0 | ms | ms | m | 49 | | | |
| 44.0 | 0 | 0 | 0 | 0 | | | |
| 21.0 | mf | m | | 5 | | | |
| 31.0 | m | ms | | 13 | | | |
| 41.0 | | 0 | | 4 | | | |
| 51.0 | | m | mf | 13 | | | |
| 32.0 | mf | m | f | 5 | | | |
| 42.0 | mf | m | mf | 12 | | | |
| 52.0 | f | | | 1 | | | |
| 43.0 | f | | | 3 | | | |