A series of photographs showed that the cell dimensions of potassium caproate varied continuously with temperature and no sudden change in the diffraction pattern was observed. The change in the cell dimensions is thus a measure of the coefficient of expansion of the crystal.

The only cell dimension to increase significantly was $a$, the coefficient of expansion parallel to this axis being $1\cdot75\times10^{-4}$ per °C. It is interesting that the direction of maximum expansion is normal to the plane of the molecule; this is the direction one would predict if the thermal energy supplied in heating were equally divided among vibrations about three mutually perpendicular axes, since the moment of inertia of the molecule about its long axis is very much smaller than that about the other two. The amplitude of the vibrations about this axis would thus be much larger than those about the other two, and this would tend to produce the maximum expansion in a direction normal to the plane of the molecules.

It is known from single-crystal measurement that the $A$ phase of potassium caprate crystallizes in the space group $P2_1/a$. As the photographs of all other members of the $A$ phase, with the exception of the butyrate, could be completely indexed without introducing indices $h0l$ with $h$ odd, or $0k0$ with $k$ odd, it seems certain that all these soaps also crystallize in the space group $P2_1/a$. In the butyrate, however, the 010 reflexion was observed, so that this soap must be in a different space group. Moreover, the observed and calculated densities do not agree so well as for the other soaps, and it must be realized that the photograph may be incorrectly indexed, although much patient work failed to produce a better agreement. The soaps in the $B$ phase are triclinic, $P1$ or $P\bar{1}$. The photographs of soaps in the $C$ phase were all indexed without the introduction of the indices $10l$ and 010. This slight evidence suggests $P2_1/a$ as the most probable space group for this phase as well.

I wish to acknowledge my indebtedness to Dr V. Vand for his constant advice and interest in this work.

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# The Application of Booth's Method of Steepest Descents to the Determination of the Structure of Potassium Caproate

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The crystal structure of potassium caproate has been determined from powder photographs alone by the application of the method of steepest descents. The use of the method is discussed, and the means of overcoming some of its limitations is indicated.

The unit cell and probable space group of potassium caproate have been determined in the preceding paper, which has shown the possibility of indexing powder photographs of such organic compounds of low crystal symmetry. The present paper attempts to go a stage further and to determine the complete crystal structure of such a compound from its powder photograph. The chief limitation to this is that only an incomplete set of structure factors can be obtained, since the reflexions from some planes overlap each other, and many weak reflexions, which would easily be recorded on single-crystal photographs, are lost in the high background of the powder photograph. Fourier-series methods for the refinement of atomic parameters are thus not feasible, but the method of 'steepest descents' (Booth, 1947) may be used since this does not require a complete set of structure factors. In this method a quantity $R$ is defined which measures the discrepancy between the observed and calculated structure factors. From the differentials of $R$ with respect to each of the atomic parameters it is possible to compute the required changes in each parameter in order that $R$ may be diminished as rapidly as possible. The definition of $R$,

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however, presents some difficulties, since errors in both the observed and calculated structure factors will be included. Hence if $R$ is defined as

$$R_1=\sum_{h,k,l}|F_o-F_c|,$$

the method of steepest descents will lead to the correct structure only if all observed structure factors are determined with an error of $\pm\delta F_c$, where $\delta F_o$ is independent of the magnitude of $F_o$. Similarly, if $R$ is defined as

$$R_2=\sum_{hkl}(F_o^2-F_c^2)^2,$$

the method will give the correct structure only if the intensities $I_o$ are determined with an error of $\delta I_o$, where $\delta I_o$ is again independent of the magnitude of $I_o$. Vand (1948*a*) has suggested the use of

$$R_3=\sum_{hkl}\left(\log\frac{F_c^2}{F_o^2}\right)^2;$$

this leads to the correct result if the intensities are estimated so that $\delta I_o$ is directly proportional to $I_o$. This expression has the disadvantage of becoming infinite when $F_o$ or $F_c=0$, and hence it cannot be used unless the signs of all the structure factors are known. In the present paper $R_2$ was used in the initial stages of the refinement until it seemed that no more signs were likely to change; $R_3$ was then used for the final stages. Vand (1948*a*) has shown how to avoid the calculation of the second differentials required in Booth's (1947) formula, and this method was used here.

Powder photographs of potassium caproate were taken in the focusing camera described by Vand (1948*b*). The relative intensities in a camera of this type are modified from those in a conventional powder camera by additional angular-dependent factors, such as the effect of absorption in the oblique passage through the flat specimen, and by the different geometry of the camera and oblique incidence on the film. At small Bragg angles, as observed in organic crystals of relatively large unit cells, however, the corrections due to absorption and the geometry of the camera are small and the correction for oblique incidence on the film is given by Cox & Shaw (1930).

Relative intensities were estimated by eye, using several exposure times. The observed structure factors were then calculated from the formula

$$D_2I=F^2p\,\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta},$$

where $D_2$ is the Cox & Shaw factor, and the other symbols have their usual meanings.

The first trial structure was obtained from the known structure of potassium caprate (Vand, Lomer & Lang, 1949) by assuming the same structure for the ionic layer and the same values for the angles of tilt of the chains. The resulting calculated structure factors showed this to be near the correct structure. The atomic parameters were then refined as described above. In the course of the calculation it was noticed that the correction to the $y$ co-ordinates of certain atoms was always zero. Mathematical investigation shows that in this space group ($P2_1/a$) the correction for the $y$ co-ordinate of atoms lying near a glide plane will always be zero unless some reflexions of the type ($hkl$) with $h$ odd are included. The $y$ co-ordinates of these atoms had thus to be adjusted by trial-and-error methods. At the end of the computation it was noticed that the calculated structure factor was larger than the observed, for planes of small Bragg angles, and vice versa for large Bragg angles. An empirical correction was applied; this was determined as a function of the reciprocal spacing by plotting $\log F_c/F_o$ against $n/d$ and calculating the regression line of $\log F_c/F_o$ on $n/d$. The application of this correction made a great improvement in the agreement between observed and calculated $F$'s. The magnitude of the correction (a factor of two for the highest Bragg angles observed) suggests that the error is due to a systematic error in intensity estimation rather than to a factor peculiar to the focusing camera.

The results of the Booth calculations are summarized in Table 1.

The atomic co-ordinates are given in Table 2, and diagrams of the structure in Figs. 1, 2 and 3.

A comparison of the observed and calculated reciprocal spacings and structure factors is given in Table 3. (When two reflexions overlap on the powder photograph, the effective calculated structure factor for the combined reflexion is reported as plus or minus

Table 1. *Results of Booth calculations*

| | No. of reflexions used | Initial value of $R$ | Final value of $R$ |
|---|---|---|---|
| 1st approximation using $R_2$ | 23 | $27\cdot4\times10^8$ | $22\cdot6\times10^8$ |
| 2nd approximation using $R_2$ | 33 | $24\cdot8\times10^8$ | $21\cdot2\times10^8$ |
| 3rd approximation using $R_2$ | 33 | $21\cdot2\times10^8$ | $20\cdot5\times10^8$ |
| 4th approximation using $R_3$ | 33 | 3·93 | 3·33 |
| 5th approximation using $R_3$ | 33 | 3·33 | 2·99 |
| 6th approximation ($y$ co-ordinates by trial and error) | 33 | 2·99 | 2·03 |
| 7th approximation ($y$ co-ordinates by trial and error) | 33 | 2·03 | 2·00 |
| 8th approximation (observed $F$ scale factor corrected) | 33 | 2·00 | 1·42 |
| 9th approximation using $R_3$ | 33 | 1·42 | 1·36 |
| 10th approximation (observed $F$ systematic error correction) | 33 | 1·36 | 0·56 |

the square root of the sum of the squares of the individual calculated structure factors.)

Table 2. *Atomic co-ordinates*

| Atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| K | 0·2126 | 0·2500 | 0·0463 |
| $O_1$ | 0·9615 | 0·9668 | 0·0815 |
| $O_2$ | 0·9615 | 0·5332 | 0·0815 |
| $C_1$ | 0·9656 | 0·7429 | 0·0963 |
| $C_2$ | 0·9827 | 0·7757 | 0·1814 |
| $C_3$ | 0·9911 | 0·5554 | 0·2153 |
| $C_4$ | 0·0064 | 0·5924 | 0·2979 |
| $C_5$ | 0·0144 | 0·3673 | 0·3283 |
| $C_6$ | 0·0304 | 0·4039 | 0·4148 |

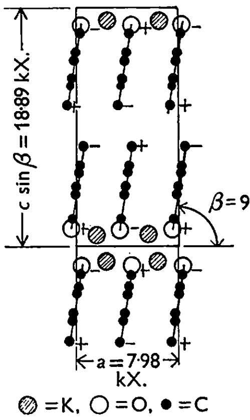

Fig. 1.

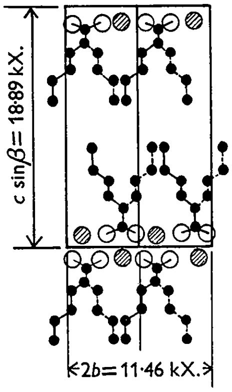

Fig. 2.

Fig. 1. Projection along $b$ axis. Positive and negative signs denote atoms above and below the plane of the paper respectively.

Fig. 2. Projection along $a$ axis. Molecules represented by full lines are $\frac{1}{2}a$ above those represented by broken lines. Key as for Fig. 1.

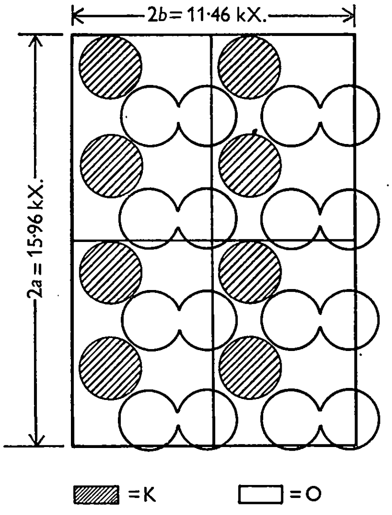

Fig. 3. Structure of ionic layer.

Each individual bond length in the hydrocarbon chain was calculated and the mean was determined. The C–C bond is 1·53 ± 0·04 kX.; the mean distance between alternate carbon atoms is 2·45 ± 0·03 kX.; and the bond angle is 106° ± 2·5° (the errors are standard deviations of the means). These values are almost certainly not significantly different from those commonly accepted, namely, 1·54 kX., 2·52 kX. and 109° 30′, although the distance 2·45 kX. between alternate carbon atoms is appreciably lower than the value of 2·61 kX. obtained for the same distance in potassium caprate. However, as only some thirty reflexions were used in the present determination it would be dangerous to draw any conclusions from the difference.

Table 3. *Comparison of $F_c$ and $F_o$*

| ($hkl$) | $n/d$ (kX.$^{-1}$)<br>Calc. | $n/d$ (kX.$^{-1}$)<br>Obs. | $F_c$ | $F_o$ |
|---|---|---|---|---|
| 001 | 0·0529 | 0·0528 | +109 | 130 |
| 002 | 0·1058 | 0·1052 | +24 | 27 |
| 003 | 0·1588 | 0·1596 | +48 | 39 |
| 004 | — | — | −21 | < 26 |
| 005 | — | — | −29 | < 29 |
| 011 | 0·1823 | 0·1825 | +21 | 37 |
| 012 | 0·2046 | 0·2036 | +43 | 41 |
| 013 | 0·2359 | 0·2361 | −58 | 64 |
| 015 | 0·3170 | 0·3177 | ±76 | 34 |
| 006 | 0·3176 | | | |
| 110 | 0·2148 | 0·22 | — | Diffuse |
| 111 | 0·2222 | | | |
| $11\bar{1}$ | 0·2202 | | | |
| 200 | 0·2512 | 0·2512 | +152 | 136 |
| 201 | — | — | −17 | < 30 |
| 202 | 0·2757 | 0·2745 | ±72 | 77 |
| 014 | 0·2743 | | | |
| 204 | — | — | −60 | < 34 |
| $20\bar{1}$ | — | — | −30 | < 30 |
| $20\bar{2}$ | 0·2694 | 0·2694 | −117 | 152 |
| $20\bar{3}$ | — | — | −30 | < 30 |
| 210 | 0·3054 | 0·3047 | ±63 | 127 |
| 203 | 0·3019 | | | |
| 211 | 0·3086 | 0·3096 | ±85 | 133 |
| $21\bar{1}$ | 0·3114 | | | |
| $21\bar{2}$ | 0·3206 | 0·3202 | ±152 | 120 |
| $20\bar{4}$ | 0·3227 | | | |
| 212 | 0·3259 | | | |
| $21\bar{3}$ | 0·3406 | 0·3423 | −39 | 32 |
| 020 | 0·3488 | 0·3492 | ±27 | 47 |
| 213 | 0·3476 | | | |
| 021 | 0·3528 | 0·3535 | −44 | 57 |
| 400 | 0·5024 | 0·5023 | ±179 | 142 |
| 401 | — | | | |
| 402 | — | — | +16 | < 40 |
| $40\bar{1}$ | — | — | +16 | < 40 |
| $40\bar{2}$ | 0·5130 | 0·5126 | −92 | 95 |

The Booth method of steepest descents does indeed provide a method of refining atomic parameters when only an incomplete set of structure factors is available, but it has a number of serious limitations, some of which apply even when a complete set of structure factors is available. The difficulty in finding a suitable definition for $R$ is great; it would be largely overcome if observed structure factors were measured much more accurately than is general practice at the present time. Secondly, the rate of convergence is small and much computation is required to obtain an accurate answer. The rate of convergence is probably small because the minimum in $R$ space is not spherically symmetrical, so that the steepest descent is not necessarily in the direction of the minimum. Qurashi (1949) has shown that suitable transformations exist by which the shape of the $R$ function may be made spherically symmetrical near the minimum, and this is reported to improve the rate of convergence.

The difficulty experienced in refining the $y$ coordinates of atoms near glide planes is inherent in the absence of recorded reflexions of the type $(hkl)$ with $h$ odd, and this difficulty would be experienced in Fourier methods as well as in the steepest-descent method.

If accurate observed structure factors were available, together with a suitable transformation to render the minimum in $R$ space spherically symmetrical, then there seems to be no reason why results given by Booth's method of steepest descents should not be of comparable accuracy with those from Fourier methods, even though a complete set of structure factors is not available. In any case it is possible to obtain at least a good approximation to the true crystal structure from a powder photograph only, as is shown by the work in this paper.

I wish to express my thanks to Dr V. Vand for his advice and encouragement in this work, and to Misses B. Edkins and M. Old for help in the computations.

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# Crystal Chemical Studies of the 5*f*-Series of Elements. XV. The Crystal Structure of Plutonium Sesquicarbide

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$Pu_2C_3$ is cubic with eight molecules per unit cell and $a = 8{\cdot}129 \pm 0{\cdot}001$ Å. The calculated density is $\rho = 12{\cdot}70$ g.cm.$^{-3}$ The space group is $I\bar{4}3d$–$T_d^6$. The plutonium atoms are in 16-fold positions with $x = 0{\cdot}050 \pm 0{\cdot}003$. A reasonable structure is obtained with the carbon atoms in 24-fold positions with $y = 0{\cdot}280$.

Each plutonium atom is bonded to nine carbon atoms, three being at a distance of 2·48 Å, three at 2·51 Å, and three at 2·84 Å. The shortest Pu–Pu distance is 3·35 Å. The carbon atoms are bonded together by covalent bonds to form $C_2$ groups.

The first identification of plutonium carbide was reported in 1944. Dr E. F. Westrum submitted for X-ray diffraction study a micro preparation which he had obtained by lithium reduction of plutonium trifluoride in a graphite crucible. The diffraction study showed the presence of three phases in the sample.

One of these phases corresponded exactly to the compound PuO, which had been encountered in earlier work. The second phase had the sodium-chloride type of structure with $a = 4{\cdot}910 \pm 0{\cdot}005$ kX. and was identified as PuC.

The third phase was cubic with a body-centered translation group and $a = 8{\cdot}11 \pm 0{\cdot}01$ kX. On the basis of volume considerations the compound was tentatively identified as $Pu_2C_3$ with eight molecules per unit cell and a calculated density of $\rho = 12{\cdot}70$ g.cm.$^{-3}$. The space group was given as $I\bar{4}3d$.

The corresponding carbide of uranium was not known at the time these results for plutonium sesquicarbide were obtained. Recently the existence of $U_2C_3$ has been reported (Mallett, Gerds & Vaughan, 1950), and some crystal-structure information given. It is clear from the reported results that $U_2C_3$ is isostructural with $Pu_2C_3$. The authors have, however, overlooked the earlier work on the plutonium compound.

It is the purpose of the present paper to describe the crystal-structure determination of $Pu_2C_3$ in some detail. In the preliminary account of the investigation the identification of $Pu_2C_3$ was given as tentative in character. The uncertainty of the identification was later removed,* and the identity is, of course, further confirmed by the recent identification of the isostructural uranium compound.

## Determination of the crystal structure

Table 1 gives the X-ray diffraction data for $Pu_2C_3$ as obtained with Cu $K$ radiation filtered through nickel

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* $Pu_2C_3$ has also been observed at Los Alamos according to a private communication by A. Coffinberry and F. Ellinger.