XXVI. A quantitative X-ray Analysis of the Structure of Potassium Dihydrogen Phosphate (KH_2PO_4).

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(With 9 figures.)

I. Introduction.

Following upon a preliminary examination of the dihydrogen phosphates of potassium and ammonium by O. Hassel[1]) the structure of KH_2PO_4 has been examined in detail by S. B. Hendricks[2]). Laue, rotation and powder photographs were employed in this last investigation, and, in the case of the rotation photographs, a correction was applied to the intensities of the registered photographic spots to allow for the different degree of absorption of the incident radiation due to the varied orientation of the reflecting planes.

Of the atoms composing the crystal, the potassium and phosphorus atoms are fixed by symmetry whilst the positions of the hydrogen atoms must to some extent remain speculative. The oxygen atoms are in the general position and, being all equivalent, require the evaluation of three parameters only. The structure is therefore a very simple one.

In his treatment of the problem, Hendricks virtually assumes a PO_4 group by supposing the $P—O$ distance to be less than 1.95 Å. His assumption with regard to the relative scattering powers of the constituent elements practically reduces to an assumption that the atoms scatter proportionately to their atomic number.

His conclusions are rather challenging. He insists on the PO_4 group possessing a very definite sphenoidal rather than regular tetrahedral shape and considers the structure as evidence that the shape of the PO_4 group is not independent of the ionic surroundings. He also considers it impossible for an oxygen atom to be equidistant from its two potassium neighbours. Some idea of the general shape and dimensions of the group of four oxygen atoms about each phosphorus atom and

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1) Z. Elektrochem. **31**, 523, 1925.

2) Am. J. Sci. **14**, 269, 1927.

of eight oxygens about each potassium atom may be gathered from a study of Fig. 8 in conjunction with Table VI. The bracketed pairs of letters in Table VI refer to distances in Fig. 8.

The present investigation was undertaken for two reasons. First, because of the interest of Hendricks' conclusions with regard to the geometrical configuration in the structure, and second because it was thought that the crystal would offer an interesting example of the use of direct quantitative X-ray analysis. The development of this type of analysis has advanced rapidly during recent years, and now appears to have reached a stage when a more accurate determination of parameters in the more interesting simple structures can be attempted with some confidence. This paper is the first of a proposed series of such attempts.

The following treatment which is based on experimental work with the ionisation spectrometer and some photometric measurements of powder photographs makes no initial assumptions other than the generally accepted formal relations between the intensity of reflexion of X-rays from crystal planes and certain known factors affecting their intensity.

II. Crystallographic Details.

The crystals were kindly prepared for me by Mr. H. E. Buckley. They are referred to by him in a recent paper[1]).

The measurements made on the crystal with the ionisation spectrometer and by the powder method lead to a unit cell and space group in agreement with those given previously by Hassel[2]) and by Hendricks[3]).

The unit cell is body-centred tetragonal with sides $a = b = 7.43$ Å, $c = 6.97$ Å and contains four molecules of KH_2PO_4.

The Space Group is V_d^{12}. For the symmetry elements of this group reference should be made to the usual sources. Some of these elements are indicated in Fig. 1 which may be regarded as a key diagram to the paper showing the way in which a typical atom in the general position (angular coordinates θ_1, θ_2, θ_3[4])) is repeated throughout the unit cell. Hendricks, following Wyckoff, takes the origin of coordinates on the tetragonal axis halfway between the two points where it is intersected by screw axes parallel to (001). For simplicity of comparison we shall adopt the same origin although a displacement to a point $\pm (0\,\frac{1}{4}\,\frac{1}{8})$ possesses advantages.

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[1]) In press (Z. Krist.). [2]) Z. Elektrochem. **31**, 523, 1925.

[3]) Am. J. Sci. **14**, 269, 1927.

[4]) $\theta_1 = 2\pi x/a$; $\theta_2 = 2\pi y/b$; $\theta_3 = 2\pi z/c$. In the text these coordinates are expressed in degrees.