

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 10.]

THE CRYSTAL STRUCTURE OF POTASSIUM CYANIDE.

By RICHARD M. BOZORTH.¹

Received December 22, 1921.

I. Introduction.

The purpose of this research was to study by means of X-rays the crystal structure of potassium cyanide, hoping thereby to throw some light on the similarity in properties between this substance and the alkali halides. The crystallographic information is very meagre, nothing having been found in the literature except the statement² that the salt crystallizes from the melt in cubes and from an aqueous solution in octahedra.

This research was carried out in part with the aid of a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington, for which I wish to express my indebtedness. I also wish to express my thanks to Dr. R. G. Dickinson, under whose immediate direction the work was carried out.

II. Preparation of the Crystals and the Methods of Measurement.

The crystals used in this research were prepared by two methods. Slow evaporation of a saturated aqueous solution in a desiccator yielded crystals with (111) faces large enough for good spectrometer measurements. Cubes large enough for Laue photographs were formed by placing a layer of alcohol over the saturated aqueous solution and allowing diffusion to take place. After several days crystals formed on the sides of the container.

Observation under a polarizing microscope showed optical isotropy, confirming the fact that the crystal has cubic symmetry. A good cubic cleavage was found, but no cleavage was observed parallel to (111) or (110) planes.

Most of the X-ray data were obtained from Laue photographs and from photographs of line spectra from single faces. The apparatus used and the treatment of the spectral photographs were the same as those employed by Dickinson.³ The angles and relative intensities of two reflections from the (111) face were measured on the X-ray spectrometer.⁴

III. The Spectral Measurements and the Unit of Structure.

The values of the angles of reflection for different planes are given in the second column of Table I. The number of molecules per unit of structure and the dimensions of the unit were derived from these data. To

¹ Du Pont Fellow in Chemistry.

² P. Groth, "Chemische Krystallographie," Leipsic, 1906, vol. 1, p. 203.

³ Dickinson, THIS JOURNAL, **44**, 276 (1922).

⁴ Dickinson and Goodhue, *ibid.*, **43**, 2046 (1921).

find the number m of molecules in the unit of structure, the following well-known equation was employed.

$$\frac{n^3}{m} = \frac{8 \sin^3 \theta \cdot M}{\lambda^3 \rho N} \quad (1)$$

In this equation n denotes the order of reflection, θ the angle of reflection from a (100) plane, M the molecular weight of the substance, λ the wavelength of the X-rays, ρ the density of the substance (1.52), and N the Avagadro number.

The length d_{100} of the unit cube, on the basis that $m = 4$, was calculated by the equation

$$n\lambda = \frac{2 d_{100} \sin \theta}{\sqrt{h^2 + k^2 + l^2}} \quad (2)$$

The values so calculated in 10^{-8} centimeters are given in the sixth column of Table I.

TABLE I
THE SPECTRAL MEASUREMENTS

Crystal Face	Angle of Reflection	Order of Reflection	Spectral Line	Wave-length	Length of Unit Cube	Intensity of Reflection
(100)	5° 23'	2	<i>Rh</i> α	0.614	6.54	Strong
	10° 51'	4	α	0.614	6.52	Medium
	16° 23'	6	α	0.614	6.53	Weak
	4° 47'	2	β	0.545	6.54	
	4° 40'	2	γ	0.534	6.56	
(110)	7° 39'	2	α	0.614	6.52	Strong
	15° 22'	4	α	0.614	6.55	Weak
	6° 42'	2	β	0.545	6.60	
	6° 35'	2	γ	0.534	6.59	
(111)	5° 24'	1	Mo α	0.710	6.53	100:153
	10° 51'	2	α			
			(Mean)		6.55	

The value of d_{100} calculated directly from the density under the assumption that there are 4 molecules in the unit is 6.55×10^{-8} cm. This is equal to the mean of the above values. This value was used for calculations of the wavelengths from the Laue photographs.

IV. The Laue Photographs.

Laue photographs were taken with the beam of X-rays approximately perpendicular to the (100) face, and also with the beam approximately perpendicular to the (111) face. Gnomonic projections were made from the photographs, and the analysis carried out according to the method described by Wyckoff.⁵ A gnomonic projection of an unsymmetrical photograph taken with the beam making an angle of 4° with the perpendicular to the (111) face, showing the 3-fold axis of symmetry, is repro-

⁵ Wyckoff, *Am. J. Sci.*, 50, 318 (1920).

duced in Fig. 1. The area of each spot is proportional to the intensity estimated directly from the plate.

The smallest value of $n\lambda$ for any plane, as calculated from Equation 2, was found to be 0.24×10^{-8} cm.; consequently it was deemed safe to consider any values of $n\lambda$ between this value and 0.48×10^{-8} cm. to be pure first-order reflections. The forms giving reflections in the first order were: (311), (331), (531), (533), (551), (711), (731), (553), (731), (751), (753). Those appearing in the second order, but not in the first, were: (221), (320), (321).

All of the spots from planes reflecting in the first order on Laue photographs had comparative intensities such that the planes with the greater

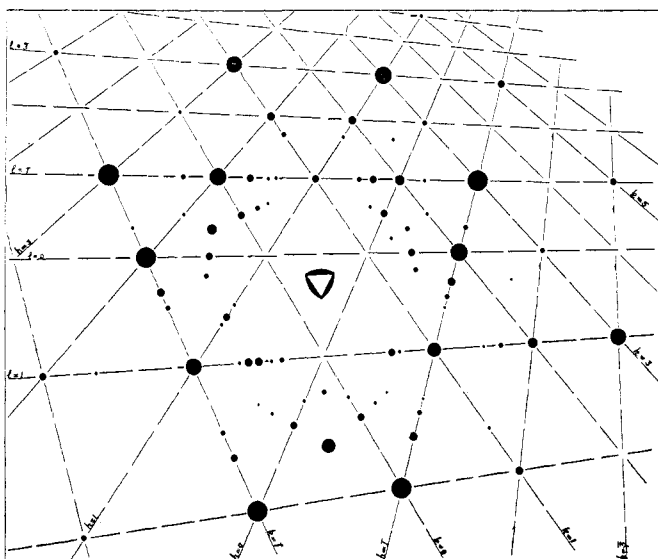


Fig. 1.

interplanar distance always had the greater intensity when reflecting with the same wavelength. Also, spots produced by second-order (221) planes could not be distinguished in intensity from those produced by first-order (531) planes; and second-order (321) reflections could not be distinguished in intensity from first order (731) reflections.

It was possible to obtain one additional piece of information from a powder photograph. From this it was clear that the second-order (100) reflection was more intense than the first-order (111) reflection.

V. Interpretation of the Data.

The relative intensities of reflection of various orders shown in Table I are characteristic of crystals with the sodium chloride structure having

the halogen appreciably, but not too greatly, different in weight from the metal. Thus there is a rapid decline of intensity with increasing order for the planes (100) and (110), and a weaker reflection of the first order from (111) than of the second order. The facts shown by the powder photograph that the second order reflection from (100) was stronger than the first order from (111) in spite of the smaller value of d/n in the former case is also in agreement with a sodium chloride structure. In view of these facts and of the close resemblance between potassium cyanide and the alkali halides, the attempt has been made to satisfy the requirements of the remaining X-ray data on the assumption that the potassium atoms are located in the same way as the metal atoms in sodium chloride, and that the carbon and nitrogen atoms are near the corresponding halogen position. This assumption, whose approximate validity is clear from the above X-ray considerations, simplifies the treatment of the possible structures given below, which would otherwise contain three parameters to be determined.

Magnesium oxide is a crystal having the sodium chloride structure; and the application of the theory of space groups to this substance has been treated in detail by Wyckoff.⁶ All the possible positions for the atoms of potassium cyanide are included in the possibilities given by Wyckoff for magnesium oxide. There are two possible arrangements for a substance having 4 molecules in the unit and 3 atoms in the molecule. These are,

- (a) K at : (u, u, u) (u, \bar{u}, \bar{u}) (\bar{u}, u, \bar{u}) (\bar{u}, \bar{u}, u)
 C at : (v, v, v) (v, \bar{v}, \bar{v}) (\bar{v}, v, \bar{v}) (\bar{v}, \bar{v}, v)
 N at : (w, w, w) (w, \bar{w}, \bar{w}) (\bar{w}, w, \bar{w}) (\bar{w}, \bar{w}, w)
- (b) K at : (u, u, u) $(\frac{1}{2} + u, \frac{1}{2} - u, \bar{u})$ $(\frac{1}{2} - u, \bar{u}, \frac{1}{2} + u)$ $(\bar{u}, \frac{1}{2} + u, \frac{1}{2} - u)$
 C at : (v, v, v) $(\frac{1}{2} + v, \frac{1}{2} - v, \bar{v})$ $(\frac{1}{2} - v, \bar{v}, \frac{1}{2} + v)$ $(\bar{v}, \frac{1}{2} + v, \frac{1}{2} - v)$
 N at : (w, \bar{w}, w) $(\frac{1}{2} + w, \frac{1}{2} - w, \bar{w})$ $(\frac{1}{2} - w, \bar{w}, \frac{1}{2} + w)$ $(\bar{w}, \frac{1}{2} + w, \frac{1}{2} - w)$.

The arrangement (a) has tetrahedral symmetry, while (b) has tetartohedral symmetry. The first can be made to approximate the sodium chloride structure by giving u the value 0.25, and v and w values on either side of 0.75. The second can be made to approximate the sodium chloride structure by giving u the value zero and v and w values on either side of 0.50. Since the reflecting powers of carbon and nitrogen are probably about the same, these two arrangements are indistinguishable by the present methods of analysis, provided the atoms are in the positions indicated above. There is, moreover, a holohedral arrangement (Wyckoff's (j)), having 32 molecules in a unit (the d_{100} for which is 13.10×10^{-8} cm.), derivable from the space group O_h^5 ; but this would also be indistinguishable from these. It suffices, therefore, to consider only the first arrangement.

For the intensity, I , of reflection of a given wavelength from any plane

⁶ Wyckoff, *Am. J. Sci.*, **1**, 138 (1921).

It will be seen that the values of $\sqrt{A^2 + B^2}$ calculated for $u = 0.25$, $v = 0.70$, $w = 0.80$, correspond satisfactorily with the observations. The only exception is that the calculated value for (711) is (104/76) or 1.4 times that calculated for (551), while the observed intensities of the (711) and (551) spots were the same as nearly as could be determined.

The intensities obtained from spectrometer measurements and from reflection photographs are in good agreement with the calculated values. The relative intensities of the spectra from a simple face can be estimated by assuming the normal decline to be 100:20:7. Values of the intensities so calculated are compared with the observations in Table III.

TABLE III
CALCULATED AND OBSERVED INTENSITIES

Plane	Relative Intensities Calculated for			Observed Intensities
	$u = 0.25$ $v = 0.70$ $w = 0.80$	$u = 0.25$ $v = 0.65$ $w = 0.85$	$u = 0.25$ $v = 0.75$ $w = 0.75$	
(100)	100:10:3	100:2:1	100:20:7	Rapid decline for the three orders
(110)	100:11	100:17	100:20	First order much stronger
(111)	100:218	100:51	100:570	100:153

VI. Representation of the Crystal Structure.

Figure 2 represents $1/8$ of the unit of structure, with the atoms placed in accordance with the values of the parameters, $u = 0.25$, $v = 0.70$, $w = 0.80$. The potassium atoms are represented by the larger circles, and the carbon and nitrogen atoms by the smaller ones. These latter atoms are equidistant from the corners of the cube not occupied by potassium atoms. Since the measurements do not serve to distinguish between the carbon and nitrogen atoms, both of these kinds of atoms are represented by the same sized circle. Table IV gives the distances between the centers of the atoms, together with the sum of the corresponding Bragg radii,⁷ both in 10^{-8} centimeters.

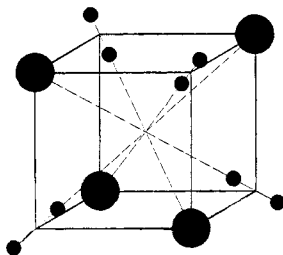


Fig. 2.

TABLE IV
DISTANCES BETWEEN THE ATOMS

	Distance	Sum of Bragg Radii
Carbon to nitrogen.....	1.15	1.4
Potassium to carbon.....	3.0	2.8
Potassium to nitrogen.....	3.0	2.7

⁷ Bragg, *Phil. Mag.*, **40**, 180 (1920).

It will be seen that the values of $\sqrt{A^2 + B^2}$ calculated for $u = 0.25$, $v = 0.70$, $w = 0.80$, correspond satisfactorily with the observations. The only exception is that the calculated value for (711) is (104/76) or 1.4 times that calculated for (551), while the observed intensities of the (711) and (551) spots were the same as nearly as could be determined.

The intensities obtained from spectrometer measurements and from reflection photographs are in good agreement with the calculated values. The relative intensities of the spectra from a simple face can be estimated by assuming the normal decline to be 100:20:7. Values of the intensities so calculated are compared with the observations in Table III.

TABLE III
CALCULATED AND OBSERVED INTENSITIES

Plane	Relative Intensities Calculated for			Observed Intensities
	$u = 0.25$ $v = 0.70$ $w = 0.80$	$u = 0.25$ $v = 0.65$ $w = 0.85$	$u = 0.25$ $v = 0.75$ $w = 0.75$	
(100)	100:10:3	100:2:1	100:20:7	Rapid decline for the three orders
(110)	100:11	100:17	100:20	First order much stronger
(111)	100:218	100:51	100:570	100:153

VI. Representation of the Crystal Structure.

Figure 2 represents $1/8$ of the unit of structure, with the atoms placed in accordance with the values of the parameters, $u = 0.25$, $v = 0.70$, $w = 0.80$. The potassium atoms are represented by the larger circles, and the carbon and nitrogen atoms by the smaller ones. These latter atoms are equidistant from the corners of the cube not occupied by potassium atoms. Since the measurements do not serve to distinguish between the carbon and nitrogen atoms, both of these kinds of atoms are represented by the same sized circle. Table IV gives the distances between the centers of the atoms, together with the sum of the corresponding Bragg radii,⁷ both in 10^{-8} centimeters.

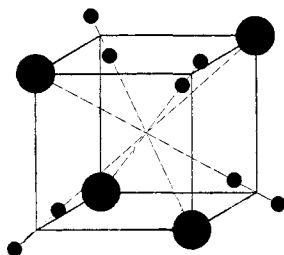


Fig. 2.

TABLE IV
DISTANCES BETWEEN THE ATOMS

	Distance	Sum of Bragg Radii
Carbon to nitrogen.....	1.15	1.4
Potassium to carbon.....	3.0	2.8
Potassium to nitrogen.....	3.0	2.7

⁷ Bragg, *Phil. Mag.*, 40, 180 (1920).

Langmuir has suggested⁸ that in the cyanide radical the carbon and nitrogen atoms possess in common an outer shell of electrons. If in accordance with this hypothesis the cyanide radical be regarded as a single atom for crystal structure purposes, potassium cyanide can be given the holohedral sodium chloride structure with four molecules in the unit; but if this be done, the values of $\sqrt{A^2 + B^2}$ for (711) and (320) will, on the same assumptions used previously, be 24 and 128, respectively, and this would make the intensity of the (320) reflection $(128/24)^2$ or 28 times as strong as that of the (711) reflection. This great discrepancy might be overcome by assuming the reflecting power of the cyanide radical to drop off much more rapidly than that of the potassium atom with decreasing values of d/n ; but there seems to be little present justification for such an assumption.

VII. Summary.

The crystal structure of potassium cyanide has been studied with X-rays making use of the Laue photographic method, the spectrometric method, and the powder method. The X-ray data show conclusively that the structure of this substance approximates the sodium chloride structure. Consequently, the potassium atoms were placed at the sodium atom positions and the carbon and nitrogen atoms near the chlorine atom positions. The positions of carbon and nitrogen atoms which give the best agreement with the data place these atoms 1.15×10^{-8} cm. apart, equidistant from the position of the chlorine atom. The structure is represented in Fig. 2.

PASADENA, CALIFORNIA.

NOTES.

Correlation of Atomic Structure and Spectra.—In the July number of THIS JOURNAL there is a very interesting article by Bury¹ on a modification of the Lewis-Langmuir hypothesis of atomic structure. The sole change in this modification is that the fourth of Langmuir's postulates is altered to read as follows.

"The maximum number of electrons in each shell or layer is proportional to the area of its surface; thus, successive layers can contain 2, 8, 18 and 32 electrons. Groups of 8 and 18 electrons in a layer are stable even when that layer can contain a larger number of electrons. The maximum number of electrons in the outer layer of an atom is 8: more than 8 electrons can exist in a shell only when there is an accumulation of electrons in an outer layer. During the change of an inner layer from a stable group of 8 to one of 18, or from 18 to 32, there occurs a transition series of elements which can have more than one structure."

The only physical substantiation of this hypothesis which Bury stresses

⁸ Langmuir, THIS JOURNAL, 41, 905 (1919).

¹ C. R. Bury, *ibid.*, 43, 1602 (1921).