obtained from the nitrogen coefficients alone. A paper will soon be forthcoming from this Laboratory dealing with the data on other gases, but for the present it appears that 273.13° is about as good a value for T_0 as can be decided upon.

In conclusion it is desired to thank Dr. Keyes for his valuable suggestions and assistance.

Summary

The value of T_0, the absolute temperature of melting ice, from the nitrogen volume and pressure expansion coefficients gives a mean value of 273.12°. The mean value obtained by using the data of other gases including the Joule-Thomson coefficient is 273.13° ± .01°.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 29]

THE CRYSTAL STRUCTURE OF POTASSIUM HYDROGEN FLUORIDE

BY RICHARD M. BOZORTH

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Introduction

Crystals of potassium hydrogen fluoride, KHF_2, were prepared by the spontaneous evaporation at room temperature of an aqueous solution of potassium fluoride and hydrofluoric acid. They are known[1] to belong to the tetragonal system and to have an axial ratio $a:c = 1:0.601$.

The X-ray data were obtained (1) from photographs of line spectra from the principal planes, using rhodium as the target, and (2) from two Laue photographs taken with the beam approximately perpendicular to the (001) planes. The methods of analysis and treatment are the same as those previously employed.[2]

The Unit of Structure

The data from the spectral photographs are given in Table I; d is the interplanar distance expressed in Ångstrom units and n the order of reflection. The wave length of the rhodium $K\alpha_1$ line was taken to be 0.6121 Å., and that of the unresolved $K\alpha$ line to be 0.614 Å.

Combining the values of d/n with the density of the crystals, determined by a suspension method to be 2.37, it was found that the data are consistent with a unit containing 1 molecule of KHF_2. Examination of the Laue photographs, however, showed that many values of $n\lambda$ calculated for this unit by means of the well-known Bragg equation were smaller

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[1] P. Groth, "Chemische Krystallographie," Engelman, Leipzig, **1906**, vol. 1, p. 312.

[2] Bozorth, THIS JOURNAL, **44**, 317 (1922); **44**, 2232 (1922). See also Wyckoff, *Am. J. Sci.*, [5] **1**, 127 (1921) and Dickinson, THIS JOURNAL, **44**, 276 (1922).

than any wave lengths that could be present at the voltage applied to the X-ray tube, which was about 53,000 volts. The smallest unit that would avoid this difficulty was found to have the dimensions 5.67 × 5.67 × 6.81 Å., so this unit was considered to be the true one. The axial ratio is therefore 1.201, and the distance between any two adjacent *hkl* planes is 5.67 $(h^2 + k^2 + 0.685\, l^2)^{-\frac{1}{2}}$ Å. The density calculated for this unit containing $4KHF_2$ is 2.35.

Table I

Data from the Spectral Photographs

Reflecting plane	Angle of reflection	Spectral line	d/n	Estimated intensities	Calculated structure factor
(001)	(5°)	α_1	(3.5)	Extremely weak	4
	10° 21′	α_1	1.703	Very strong	148
	15° 39′	α_1	1.135	Extremely weak	4
(110)	4° 23′	α	4.016	Medium strong	47
	8° 48′	α	2.007	Medium	79
	13° 19′	α	1.333	Very weak	21
	17° 50′	α	1.002	Weak	138

The Possible Arrangements

The symmetry of the Laue photographs corresponds to the point group D_{4h}; accordingly, only space groups were considered which are isomorphous with the point groups V_d, C_{4v}, D_4, and D_{4h}. Furthermore, since all the planes reflecting in the first order on the Laue photographs were found to have one index even and two indices odd, it was concluded that the underlying lattice was the body-centered one, and the space groups were considered accordingly.

It was observed (see Table I) that reflections from the (001) planes were extremely weak in the second and sixth orders, and very strong in the fourth order, while odd orders were absent. It seemed reasonable, therefore, to suppose that in the fourth order all the atoms are reflecting in phase, while in the second and sixth order the potassium atoms act in opposition to the fluorine atoms. Therefore, the arrangements were limited to those which place the fluorine atoms in planes $^1/_2 d_{(001)}$ apart, and the potassium atoms in planes midway between the fluorine atoms. There are three such arrangements[3] for the fluorine atoms, as follows.

(1) $u,\frac{1}{2}+u,0;\ \bar{u},\frac{1}{2}-u,0;\ \frac{1}{2}-u,u,0;\ \frac{1}{2}+u,\bar{u},0;\ \frac{1}{2}+u,u,\frac{1}{2};\ \frac{1}{2}-u,\bar{u},\frac{1}{2};\ u,\frac{1}{2}-u,\frac{1}{2};\ \bar{u},\frac{1}{2}+u,\frac{1}{2}.$
(2) $u00;\ \bar{u}00;\ 0u0;\ 0\bar{u}0;\ \frac{1}{2}+u,\frac{1}{2},\frac{1}{2};\ \frac{1}{2}-u,\frac{1}{2},\frac{1}{2};\ \frac{1}{2},\frac{1}{2}+u,\frac{1}{2};\ \frac{1}{2},\frac{1}{2}-u,\frac{1}{2}.$
(3) $uu0;\ \bar{u}\bar{u}0;\ u\bar{u}0;\ \bar{u}u0;\ \frac{1}{2}+u,\frac{1}{2}+u,\frac{1}{2};\ \frac{1}{2}-u,\frac{1}{2}-u,\frac{1}{2};\ \frac{1}{2}+u,\frac{1}{2}-u,\frac{1}{2};\ \frac{1}{2}-u,\frac{1}{2}+u,\frac{1}{2}.$

There are two such ways of placing the potassium atoms with respect to the fluorine atoms, namely,

(1) $0\ 0\ ^1/_4,\ 0\ 0\ ^3/_4,\ ^1/_2\ ^1/_2\ ^1/_4,\ ^1/_2\ ^1/_2\ ^3/_4.$
(2) $0\ ^1/_2\ ^1/_4,\ 0\ ^1/_2\ ^3/_4,\ ^1/_2\ 0\ ^1/_4,\ ^1/_2\ 0\ ^3/_4.$

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[3] Wyckoff, "The Analytical Expression of the Results of the Theory of Space Groups," *Carnegie Inst. Pub.*, **318** (1922).

Determination of the Structure

The six ways of arranging the potassium and fluorine atoms were investigated for all values of the parameter *u;* and it was shown on the basis of qualitative comparisons of intensities of Laue spots that the only arrangement consistent with the data is the combination of (1) for potassium with (1) for fluorine. The intensity data chiefly used in arriving at this conclusion are: $(2\bar{5}1) > (\bar{4}31)$, $(\bar{5}\bar{6}1) > (\bar{7}01)$, $(\bar{5}\bar{6}1) > (\bar{2}\bar{7}1)$, $(\bar{9}\bar{2}3) > (\bar{7}01)$, $(\bar{9}\bar{2}3) > (3\bar{8}3)$, $(7\bar{3}4) > (\bar{7}32)$, $(5\bar{7}4) > (\bar{5}\bar{7}2)$. The value of the parameter *u* in the correct arrangement was determined from these and other intensity comparisons to be 0.14, with an estimated maximum error of 0.01. The data from one Laue photograph are given in Table II. The reflections are in the second order when a 2 is prefixed to the indices of the reflecting plane; otherwise they are in the first order. The last columns in both tables give the structure factor calculated for the correct arrangement when *u* is 0.14.

TABLE II

DATA FROM ONE OF THE LAUE PHOTOGRAPHS

Reflecting plane	Interplanar distance $\div n$	Wave length of X-rays	Intensity of spot	Calculated structure factor	Reflecting plane	Interplanar distance $\div n$	Wave length of X-rays	Intensity of spot	Calculated structure factor
$(\bar{3}10)$	1.79	0.34	2.5	116	(714)	0.73	0.43	0.1	30
$(\bar{1}41)$	1.35	.35	0.2	20	(554)	.73	.41	.2	69
$2(\bar{2}\bar{1}0)$	1.27	.41	2.5	89	$(\bar{7}32)$	.73	.43	.05	13
$(\bar{4}31)$	1.12	.47	0.07	13	$2(232)$	.72	.40	.05	40
$(\bar{5}\bar{1}0)$	1.11	.33	0.6	90	$(\bar{5}\bar{6}1)$	.72	.39	.02	58
$(5\bar{1}2)$	1.06	.44	1.3	62	$2(0\bar{4}1)$	.70	.43	.05	24
$(2\bar{5}1)$	1.04	.42	0.8	67	$(\bar{5}63)$	.69	.43	.05	58
$(\bar{5}\bar{3}0)$	0.97	.32	0.1	56	$(7\bar{3}4)$	.69	.45	.4	139
$(5\bar{3}2)$	0.94	.41	1.0	96	$(\bar{7}43)$	.67	.48	.00	3
$(1\bar{6}1)$	0.92	.40	0.1	47	$2(\bar{3}\bar{3}1)$	.66	.47	.05	55
$2(\bar{1}31)$	0.89	.36	0.3	83	$(\bar{5}\bar{7}2)$	.65	.45	.05	54
(613)	0.86	.42	0.1	47	$2(\bar{1}42)$	.64	.40	.02	66
$(\bar{3}\bar{6}1)$	0.84	.46	0.05	29	$(3\bar{8}3)$	.64	.42	.00	24
$(\bar{7}01)$	0.80	.40	0.00	0	$2(\bar{4}\bar{2}1)$	.62	.43	.1	125
$(\bar{5}52)$	0.78	.39	0.3	83	$(5\bar{7}4)$	.62	.46	.1	98
$(1\bar{7}2)$	0.78	.49	0.8	122	$(\bar{9}\bar{1}2)$	.62	.39	.05	73
$(\bar{2}\bar{7}1)$	0.77	.39	0.00	9	$(\bar{9}\bar{2}3)$	.59	.48	.02	71

For the comparison of intensities, planes may be divided into two classes: (1) those having the last index odd and reflecting in the first order; (2) all other planes. This classification is such that the intensities of the reflections from planes of Class 1 depend only on the reflecting power of the fluorine atoms, while those from Class 2 planes depend on both kinds of atoms. Intensities were calculated in the usual manner, assuming the reflecting powers of the atoms to be proportional to their atomic numbers; however, when only qualitative comparisons are made involving planes of the same class, the validity of comparing calculated intensities with observation is dependent only on the assumption that the reflecting power of the potassium atom is approximately as great as or greater than twice the reflecting power of the fluorine atom.

Discussion of the Structure

The structure is represented diagrammatically in Fig. 1. It may be regarded as an ammonium chloride arrangement of potassium atoms and fluorine dumb-bells. The arrangement may be derived from any of the space groups D_{4h}^{18}, V_d^{10}, and D_4^9. For the hydrogen atoms the only positions consistent with the symmetry are (1) $00u$; $00\bar{u}$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + u$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} - u$; (2) $0\,\frac{1}{2}\,0$, $\frac{1}{2}\,0\,0$, $\frac{1}{2}\,0\,\frac{1}{2}$, $0\,\frac{1}{2}\,\frac{1}{2}$; (3) $0\,\frac{1}{2}\,\frac{1}{4}$, $0\,\frac{1}{2}\,\frac{3}{4}$, $\frac{1}{2}\,0\,\frac{1}{4}$, $\frac{1}{2}\,0\,\frac{3}{4}$. Of these the first may be discarded; for, if the hypothesis of constant atomic radii is even approximately correct, there is not room for the hydrogen atoms between potassium atoms that are 3.41 Å. apart.

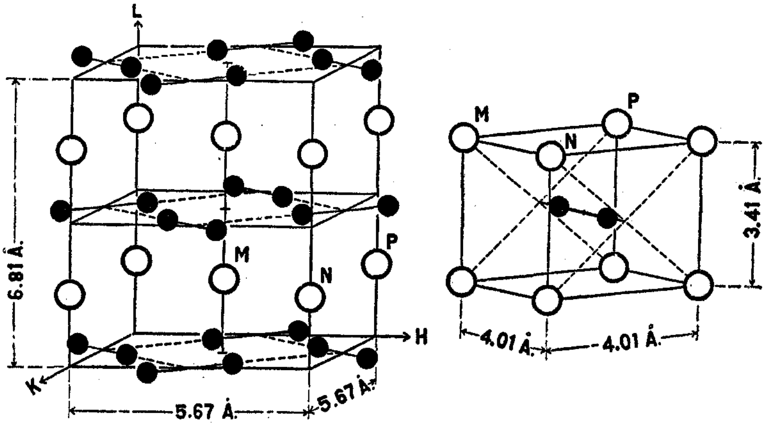

Fig. 1.—The arrangement of the atoms in KHF_2. The potassium atoms are represented by the larger circles and the fluorine atoms by the smaller ones. The larger tetragonal prism represents a complete unit of structure containing 4 KHF_2. The smaller prism contains one KHF_2 and is related to the larger in the way indicated by the letters M, N and P; it shows how the structure is similar to that of ammonium chloride, the K atoms corresponding to N atoms and the F dumb-bell corresponding to Cl atoms

The second arrangement places each hydrogen atom between 2 fluorine atoms that are 2.24 Å. apart, and forms what may be considered an HF_2^- ion. If the radius[4] 0.62 Å. be assigned to the fluorine atom, the radius of the hydrogen atom in this position is 0.50 Å. The third possible position for hydrogen leaves the fluorine atoms much farther apart than the radius usually ascribed to them permits, but permits the same unusually large distances between adjacent negative atoms observed in cadmium iodide,[5] stannic iodide,[6] and molybdenum disulfide.[7]

The distances in Ångstrom units between the atoms are given in Table

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[4] Wyckoff, *Proc. Nat. Acad. Sci.*, **9**, 33 (1923).

[5] Ref. 2, p. 2232.

[6] Dickinson, THIS JOURNAL, **45**, 958 (1923).

[7] Dickinson and Pauling, *ibid.*, **45**, 1466 (1923).

III, where they are compared with the corresponding distances in potassium fluoride.[8]

TABLE III

THE DISTANCES BETWEEN THE ATOMS

	K and F	K and K	F and F
In KHF_2	2.77	3.41 4.01	2.25
In KF	2.68	3.79	...

Summary

The positions of the potassium and fluorine atoms in tetragonal potassium hydrogen fluoride, KHF_2, have been determined by means of X-rays. The dimensions of the unit are 5.67 × 5.67 × 6.81 Å. The structure may be described as an ammonium chloride arrangement of potassium atoms and fluorine dumb-bells, the two atoms of each dumb-bell lying in a plane perpendicular to the tetragonal axis. For the hydrogen atoms there are two possible positions, one of which is in the middle of the dumb-bell, forming an HF_2^- ion. The distances in Ångstrom units between the atoms are summarized in Table III.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM SANDERS CHEMICAL LABORATORY, VASSAR COLLEGE]

THE STABILITY OF SODIUM THIOSULFATE SOLUTIONS

BY MARTIN KILPATRICK, JR., AND MARY L. KILPATRICK

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The present investigation was undertaken as a critical study of the stability of 0.01 N sodium thiosulfate under the conditions of its use as a standard solution in an analytical laboratory. It was also hoped that the investigation might throw some light on the mechanism of the decomposition.

Topf[1] in 1887 proved that the carbon dioxide of the air could not account for the deterioration, and concluded that it was to be attributed to direct oxidation: $Na_2S_2O_3 + O \longrightarrow Na_2SO_4 + S$. He also noticed that the fall in normality was greater in summer than in winter. Kolthoff[2] made an extensive study of the behavior of 0.1 N and 0.01 N sodium thiosulfate solutions under various conditions and in the presence of a great number of substances. He found that sunlight hastened the decomposition; that 0.01 N solutions decomposed much more rapidly than 0.1 N; that small amounts of mercuric iodide greatly retarded the decomposition, as did small amounts of alkaline substances; that salts of the heavy metals

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[8] Wyckoff, *J. Washington Acad. Sci.*, **12,** 251 (1922).

[1] Topf, *Z. anal. Chem.*, **26,** 137 (1887).

[2] Kolthoff, *Pharm. Weekblad,* **56,** 878 (1919); *Z. anal. Chem.*, **60,** 344 (1921).