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Summary

Quantitative measurements on the adsorption

of phosphate ion by powdered enamel, dentine and bone have been made. From varying concentrations of radioactive phosphorus as sodium acid phosphate in ethylene glycol, the tissues adsorb phosphate according to the Freundlich adsorption isotherm. The adsorptive power of dentine and bone are about the same and seven times greater than that of enamel.

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A Redetermination of the Fluorine-Fluorine Distance in Potassium Bifluoride

BY L. HELMHOLZ AND M. T. ROGERS

Introduction

In an electron diffraction investigation of gaseous hydrogen fluoride, Bauer, Beach and Simons¹ obtained the value $2.55 \pm 0.03 \text{ \AA}$. for the F-H-F distance and confirmed the existence of polymers $(\text{HF})_n$. The reported values for the F-H-F distance in crystals are:

$$\begin{aligned} \text{NH}_4\text{HF}_2 &= 2.37 \pm 0.1 \text{ \AA}.^2 \\ \text{NaHF}_2 &= 2.50 \pm 0.2 \text{ \AA}.^3 \\ \text{KHF}_2 &= 2.25 \pm 0.2 \text{ \AA}.^4 \end{aligned}$$

The assumption that the mean value 2.25 \AA . reported for potassium bifluoride is correct leads to the conclusion that the F-H-F bond is weakened and the distance correspondingly increased when additional hydrogen bonds are formed as in $(\text{HF})_n$. Also the distance is not accurately enough known to judge whether the two additional hydrogen bonds from fluorine to nitrogen in ammonium bifluoride cause a lengthening of the F-H-F distance over that in alkali bifluorides. In view of the large limits of error ascribed to the F-H-F distance, a redetermination of the parameter in potassium bifluoride has been carried out in order to test this conclusion.

In this work the value $2.26 \pm 0.01 \text{ \AA}$. has been found for the F-H-F distance in close agreement with the mean value reported by Bozorth.⁴

Experimental

Potassium hydrogen fluoride crystallizes in the tetragonal system forming plates with $\{001\}$ de-

veloped and sides parallel to $\{110\}$. The structure was determined by Bozorth,⁴ who gives it the space group D_{4h}^{18} , four molecules in the unit cell, with the atoms in the following positions

$$4\text{H in } 0\frac{1}{2}0; \frac{1}{2}00; \frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}\frac{1}{2}$$

$$4\text{K in } 00\frac{1}{2}; 00\frac{1}{2}; \frac{1}{2}\frac{1}{2}\frac{1}{2}; \frac{1}{2}\frac{1}{2}\frac{1}{2}$$

$$8\text{F in } u, \frac{1}{2} + u, 0; \bar{u}, \frac{1}{2} - u, 0; \frac{1}{2} - u, u, 0; \frac{1}{2} + u, \bar{u}, 0;$$

$$\frac{1}{2} + u, u, \frac{1}{2}; \frac{1}{2} - u, \bar{u}, \frac{1}{2}; u, \frac{1}{2} - u, \frac{1}{2}; \bar{u}, \frac{1}{2} + u, \frac{1}{2}$$

$$a = 5.67 \text{ \AA}. \quad c = 6.81 \text{ \AA}. \quad u = 0.14 + 0.01 \text{ F-H-F} = 2.25 \pm 0.02 \text{ \AA}.$$

Symmetric and asymmetric Laue photographs were taken with the beam normal to (001) . The parameter was narrowed down to a small range by the use of qualitative Laue data.

Theoretical curves for the dependence of intensity on the parameter u were calculated from the equation

$$I = C \left| S \right|^2 e^{-3.0(\sin \theta / \lambda)^2}$$

using f values from the Pauling-Sherman tables.

Comparing observed intensity ratios with the theoretical curves of Fig. 1, the upper and lower limits shown in Table I were placed on the value

TABLE I
PARAMETER DETERMINATION FOR POTASSIUM BIFLUORIDE
USING INTENSITIES OF LAUE REFLECTIONS

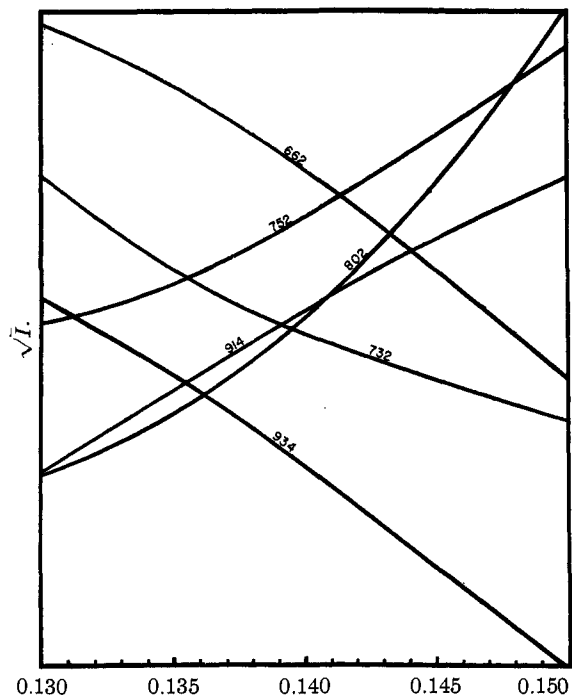
Reflecting planes	$\frac{\sin \theta}{\lambda}$	λ	Observed intensity ratio	Parameter
(802)	0.720	0.349	(802) < (732)	$u > 0.1393$
(732)	.687	.350		
(662)	.762	.333	(752) > (662)	$u < .1413$
(752)	.773	.328		
(914)	.851	.361	(194) > (732)	$u > .1390$
(732)	.687	.367		
(864)	.924	.406	(864) > (934)	$u > .1381$
(934)	.884	.408		

(1) S. H. Bauer, J. Y. Beach and J. H. Simons, *THIS JOURNAL*, **61**, 19 (1939).

(2) L. Pauling, *Z. Krist.*, **85**, 380 (1933).

(3) C. Anderson and O. Hassel, *Z. physik. Chem.*, **123**, 151 (1926).

(4) R. M. Bozorth, *THIS JOURNAL*, **45**, 2128 (1923).



802-732 →.
 ← 752-662.
 194-732 →.
 864-934 →.
 u →.

Fig. 1.

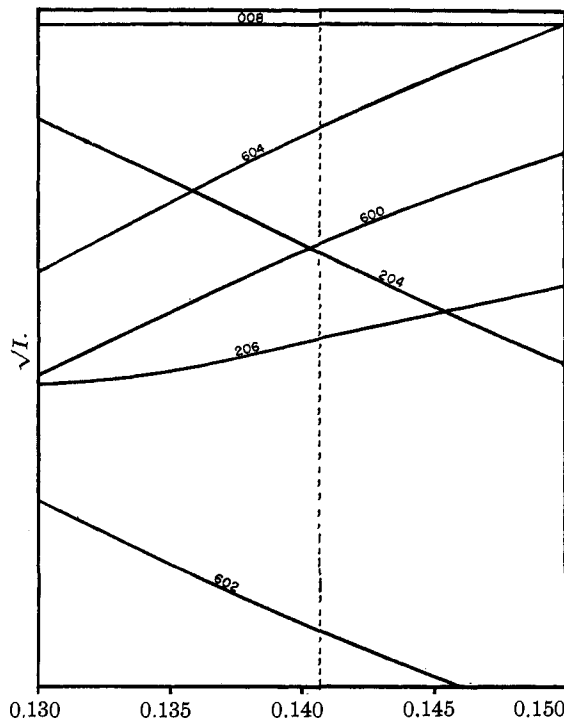


Fig. 2.

of u . This gives $0.1394 \leq u \leq 0.1413$ and $2.235 \leq \text{F-H-F distance} \leq 2.265 \text{ \AA}$.

A more exact value of the parameter was then found by visually comparing intensities of reflections on oscillation photographs. Theoretical curves for the dependence of intensity on parameter were drawn (Fig. 2) using

$$I = \text{Const.} \frac{1 + \cos^2 2\theta}{\sin^2 2\theta} \left| S \right|^2 e^{-3.0(\sin \theta/\lambda)^2}$$

From a visual estimate of the ratio of the intensities of two reflections, estimates of the parameter value probably good to $\pm 5\%$ were made using the theoretical curves. Comparisons were made between reflections in the same layer line and not too widely separated values of $\sin \theta$. The mean value for the twenty-seven independent estimates made was weighted by multiplying each value by the angle between the intensity curves for the planes involved. The weighted mean for the parameter u is 0.1408, the average deviation is 0.0015 and the most probable deviation is $0.0015/27^{1/2}$ or 0.0003. The value $u = 0.1408 \pm 0.0003$ corresponds to the distance F-H-F = $2.258 \pm 0.005 \text{ \AA}$. This is in good agreement with the

TABLE II

PARAMETER DETERMINATION FOR POTASSIUM BIFLUORIDE USING INTENSITIES OF OSCILLATION REFLECTIONS

No.	(hkl)	Angle between F curves	Intensity ratio	Parameter
1	(400) (006)	22.5	0.5	0.1432
2	(600) (204)	55	1.10	.1417
3	(204) (206)	35	1.25	.1408
4	(008) (604)	20	1.20	.1423
5	(602) (604)	6	0.20	.1409
6	(026) (024)	24	0.91	.1410
7	(026) (422)	20	1.3	.1400
8	(321) (125)	27	1.1	.1420
9	(224) (024)	24	1.25	.1408
10	(323) (523)	20.5	0.83	.1417
11	(600) (206)	15	1.25	.1408
12	(512) (215)	16	1.33	.1416
13	(420) (024)	30	1.1	.1368
14	(424) (024)	24.5	0.91	.1420
15	(521) (323)	23	.74	.1411
16	(321) (226)	22	.57	.1423
17	(321) (422)	13	.67	.1396
18	(125) (323)	19	1.75	.1390
19	(424) (321)	31	2.3	.1419
20	(026) (321)	31	2	.1400
21	(611) (411)	37	1.75	.1370
22	(611) (413)	32	2	.1402
23	(316) (411)	31	3.3	.1389
24	(510) (514)	34	0.91	.1418
25	(512) (514)	24	0.74	.1442
26	(510) (215)	20	2	.1445
27	(413) (316)	23	0.22	.1422

Laue data, and, considering both, the value of the F-H-F distance may be given as 2.26 Å. with a probable error of not more than 0.01 Å.

Discussion

In going from the HF_2^- ion in crystalline potassium bifluoride to the $(\text{HF})_n$ polymers in gaseous hydrogen fluoride there is a lengthening of 0.29 ± 0.06 Å. in the F-H-F distance. This shows that formation of additional hydrogen bonds lengthens the F-H-F distance. While the value 2.37 ± 0.1 Å. for the F-H-F distance in ammonium bifluoride leaves some doubt as to a lengthening, it is strongly indicated that the formation of two additional N-H . . . F bonds causes a weak-

ening of the F-H-F bond and a probable lengthening of about 0.1 Å. The theoretical value calculated by Pauling⁵ for this distance is 2.32 Å. with a symmetrical linear configuration for F-H-F.

Summary

A redetermination of the parameter in potassium bifluoride has been carried out using Laue and oscillation photographs. The value $u = 0.1408 \pm 0.003$ leads to the fluorine-fluorine distance 2.26 ± 0.01 Å. in $\{\text{F-H-F}\}^-$. A comparison is made with other reported values.

(5) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 277.

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Silver and Mercurous Iodide Electrodes

BY WARREN C. VOSBURGH, PAUL F. DERR, GERALD R. COOPER AND ROGER G. BATES¹

The silver and mercurous iodide electrodes have both been shown to be reproducible under favorable conditions,² and it seemed desirable to attempt a direct comparison of the two. This was found surprisingly difficult, and the result can be considered only approximate. Some of the observations made in the course of the study are of value, however.

Silver Iodide Electrode.—All of the silver iodide electrodes were prepared by the thermal method; some from silver oxide and iodate^{2a} and some from oxide and iodide.^{2b} In the preparation of some, the platinum wire was electroplated with silver before application of the paste, but this was found unnecessary and was omitted in the later electrodes.

Silver iodide electrodes agreed within 0.02 mv. when compared in the same vessel with oxygen-free potassium iodide solution (about 0.02 *m*) as the electrolyte. The agreement was better on the second day than on the first, and continued good indefinitely. The agreement was not as good when the electrolyte was saturated with lead iodide or when 0.01 *m* cadmium iodide was used as the electrolyte. When air was admitted to a cell consisting of two silver iodide electrodes

in the same vessel, it caused disagreement of the electrodes.³ A trace of mercurous iodide also caused disagreement.

Mercurous Iodide Electrodes.—While the mercurous iodide electrode is highly reproducible when the electrolyte is a saturated cadmium iodide solution,^{2c,d} it was found much less reproducible when the electrolyte was a potassium iodide solution. Two mercurous iodide electrode systems in a single H-vessel prepared with nitrogen-vacuum technique gave a cell with an electromotive force anywhere from zero to well over a millivolt in spite of considerable care to avoid errors. When one electrode had a thick (1 to 2 cm.) layer of mercurous iodide paste covering the mercury and the other a thin (0.5 cm.) layer, the thick-layer electrode was always positive, and the electromotive force varied from 0.3 mv. to nearly 2 mv. in different cells and at different times. When both layers of mercurous iodide were thin, the electromotive force varied from zero to 0.3 mv. When the electrolyte was a 0.01 or 0.02 *m* cadmium iodide solution, the effect of thick and thin layers was not as pronounced. Solid lead iodide at both electrodes, with a potassium iodide electrolyte, reduced the effect of thick and thin layers, also.

(1) Sterling Fellow at Yale University, 1937-39.

(2) (a) Owen, *THIS JOURNAL*, **57**, 1526 (1935); (b) Bates, *ibid.*, **60**, 2984 (1938); (c) Vosburgh, *ibid.*, **50**, 2391 (1928); (d) Bates and Vosburgh, *ibid.*, **59**, 1584 (1937).

(3) (a) Smith and Taylor, *Rozsniki Chem.*, **18**, 762 (1938); (b) Taylor and Smith, *J. Research Natl. Bur. Standards*, **22**, 307 (1939).