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W. H. Zachariasen

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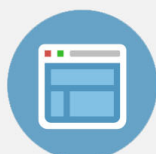
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That the diffusion of hydrogen through iron does not follow the simple relation expressed by Eq. (1), except over limited regions, is shown by Fig. 8. Here we show the log (rate) *vs.* $1/T$ for a sample of Mehl iron in the range from 925° to 300°C. Mr. W. L. Rast will shortly publish his data on these low temperature runs and discuss them in detail, in addition to discussing the anomalous behavior of hydrogen through iron below 300°. In the meantime we are indebted to Mr. Rast for allowing us to reproduce Fig. 8.

This graph also makes it clear why previous investigators only reported the range of diffusion from about 750 to 300°C. This region does correspond, to a first approximation, to Eq. (1), and if only a few points were taken it is clear that one would think that the log (rate) *vs.* $1/T$ curves should be linear. The general features of Fig. 8 have been consistently obtained for pure iron over a period of several years. These observations have been made by different observers and three different sets of apparatus.

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The Crystal Structure of Potassium Metaborate, $K_3(B_3O_6)$

W. H. ZACHARIASEN

Ryerson Physical Laboratory, University of Chicago, Chicago, Illinois

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In order to find the configuration of the metaborate group the crystal structure of potassium metaborate was determined. The crystals are rhombohedral $a_r = 7.76\text{\AA}$, $\alpha = 110^\circ 36'$ with six molecules KBO_2 . The density is 2.348. The space group is $R\bar{3}c(D_{3d}^6)$. All atoms are lying on twofold axes at positions: $\pm(u, \frac{1}{2}-u, \frac{1}{2})\cdot$. The parameters were determined by means of two-dimensional Fourier analyses:

$$\begin{array}{ll} K & u = 0.689 \pm 0.003, \quad B \quad u = 0.361 \pm 0.006, \\ O_I & 0.465 \pm 0.006, \quad O_{II} \quad 0.146 \pm 0.006. \end{array}$$

The metaborate radical is $(B_3O_6)^{-3}$, a ring of three BO_3 triangles, rather than the endless chain of BO_3 triangles found in CaB_2O_4 . The BO_3 groups are slightly distorted, the B-O distances being 1.33Å, 1.38Å and 1.38Å, the O-O distances 2.30Å, 2.38Å and 2.38Å. The nine particles of the radical lie in one plane. Potassium is surrounded by seven oxygen atoms at a distance 2.82Å.

A FEW years ago we investigated the crystal structure of calcium metaborate, $Ca(BO_2)_2$,¹ and found that it contained the metaborate groups as endless chains built up of BO_3 triangles. While our studies of the borates have convinced us of the nonexistence of radicals $(BO_2)^-$, we considered it likely that the metaborate group in some crystals occurs in a state of finite polymerization, namely as rings of BO_3 triangles. The reported symmetry and optical properties of $NaBO_2$ and KBO_2 ,² indicated that possibly such ringshaped metaborate groups might be present in these crystals, and an x-ray investigation was therefore undertaken. This article contains a discussion of the results obtained for KBO_2 .

Excellent crystals of KBO_2 were prepared by melting together K_2CO_3 and B_2O_3 in a platinum

crucible. The melt was cooled rapidly so that a crust formed on the outside. In the cavity thus produced in the interior needleshaped hexagonal crystals (up to two cm long) were found. The density was determined by the suspension method (using methylene iodide and toluol) to 2.348 ± 0.005 . The crystals are hygroscopic and were kept in minute desiccators during the x-ray exposures.

The crystals were examined by the oscillation and Laue methods. The oscillation photographs were taken with copper radiation filtered through a nickel film.

For the dimensions of the hexagonal cell we found:

$$a = 12.75 \pm 0.02\text{\AA}, \quad c = 7.33 \pm 0.04\text{\AA}.$$

However, the true unit cell is rhombohedral and has dimensions:

$$a_r = 7.76\text{\AA}, \quad \alpha = 110^\circ 36'.$$

It contains six (5.98) molecules KBO_2 .

¹ W. H. Zachariasen, Proc. Nat. Acad. **17**, 617 (1931); W. H. Zachariasen and G. E. Ziegler, Zeits. f. Krist. **83**, 354 (1932).

² S. S. Cole, S. R. Scholes, C. R. Amberg, J. Am. Ceram. Soc. **18**, 58 (1935).

The Laue photographs as well as the oscillation photographs showed the symmetry characteristic of the point group $\bar{3}m(D_{3d})$. Accordingly the following space groups come into consideration: $R3m(C_{3v}^5)$, $R3c(C_{3v}^6)$, $R32(D_3^7)$, $R\bar{3}m(D_{3d}^5)$ and $R\bar{3}c(D_{3d}^6)$. Reflections HHL (the Miller indices used throughout the article refer to the rhombohedral cell) are absent if L is odd. This fact indicates that $R3c$ or $R\bar{3}c$ is the space group.

The structure was deduced by methods of Fourier analysis. The positions of the potassium atoms were found from a two-dimensional Patterson analysis (projection plane normal to the 3-fold axis), in which the outstanding peaks must be attributed to potassium-potassium vectors. To find the positions of boron and oxygen atoms an ordinary two-dimensional analysis was next made, using the known potassium contribution to obtain the probable signs of the coefficients in the series. Finally the electron density variation was evaluated along one of the twofold axes.

The structure so obtained is as follows: Space group $R\bar{3}c$. All atoms are lying on twofold

axes at positions: $\pm(u, \frac{1}{2}-u, \frac{1}{4})^{\circ}$. The parameter values are:

	$2\pi u$	u
K	$248^{\circ} \pm 1^{\circ}$	0.689 ± 0.003
B	130 ± 2	$.361 \pm .006$
O _I	167.5 ± 2	$.465 \pm .006$
O _{II}	52.5 ± 2	$.146 \pm .006$

The observed intensities and calculated amplitudes for a number of reflections are given in Table I.

Figure 1 shows a projection of the structure on a plane normal to the 3-fold axis. Each potassium atom is surrounded by seven oxygen atoms, one O_I at a distance of 2.85Å, two O_I at 2.80Å, two O_I at 2.83Å and two O_{II} at 2.81Å. The average value, 2.82Å, agrees with the predicted value of 2.85Å for coordination number seven.³

Each boron atom is linked to three oxygen atoms forming a nearly equilateral triangle with edges 2.30Å(O_{II}-O_{II}), 2.38Å(O_I-O_{II}) and 2.38Å(O_I-O_{II}). The boron to oxygen distances are nearly equal 1.33Å(B-O_I) and 1.38Å(B-O_{II}). The same average dimensions of

³ W. H. Zachariasen, Zeits. f. Krist. 80, 137 (1931).

TABLE I. Oscillation photographs around $[111]$.¹

HKL	sin θ/λ	INT. obs.	F calc.	HKL	sin θ/λ	INT. obs.	F calc.	HKL	sin θ/λ	INT. obs.	F calc.	HKL	sin θ/λ	INT. obs.	F calc.
110	0.078	nil	1	210	0.138	vw	20	110	0.144	m	42	210	0.219	wm	51
211	.136	nil	6	212	.177	m.	71	200	.164	s	87	311	.258	nil	0
220	.157	vw	20	320	.209	wm	35	211	.182	w-	20	410	.291	wm	30
321	.208	vw	11	313	.249	wm	42	310	.213	m-	40	322	.291	wm	30
330	.235	s	70	421	.261	ms	44	222	.227	wm	34	412	.312	w-	26
422	.272	nil	6	430	.284	w.	35	312	.240	tr	4	520	.349	nil	6
431	.282	w.	28	324	.305	nil	6	411	.264	s	54	423	.349	nil	6
440	.314	w	31	414	.324	m-	35	420	.276	w-	20	513	.375	wm	48
532	.342	vw	16	531	.334	vw.	16	323	.287	w	29	621	.398	w	25
541	.359	nil	5	540	.360	nil	7	413	.307	vw	13	434	.398	w	25
550	.392	vw-	10	425	.377	nil	9	521	.327	w-	20	630	.414	vw	7
633	.408	s	89	632	.393	vw	20	334	.345	m.	58	524	.414	vw	7
642	.415	nil	4	515	.401	m	44	530	.345	w.	30	614	.442	w	20
651	.437	vw	15	641	.408	nil	6	424	.354	w-	11	731	.463	w	27
660	.463	wm	39	436	.437	vw-	6	514	.379	w.	28	535	.463	w	27
743	.477	nil	3	650	.437	w-	24	622	.387	vw-	1	740	.482	nil	0
752	.490	nil	8	526	.451	w	19	631	.395	m-	49	625	.482	nil	0
				742	.465	nil	9	435	.410	vw	5				
				616	.478	vw	10	640	.418	w-	22				
				751	.484	w	36	525	.425	vw	3				
								732	.453	vw.	20				
								615	.453	vw-	4				
								741	.466	vw.	18				
								446	.473	w	30				
								536	.479	m	44				
								750	.492	nil	8				
								626	.498	w	23				

¹ The scale of intensities is: s, s-, ms, m., m, m-, wm, w., w, w-, vw., vw, vw-, vvw, tr. The f curves of James and Brindley were used in the calculations. All reflections up to $\sin \theta/\lambda = 0.63$ were measured. This table includes only reflections for which $H+K+L \leq 3$ up to $\sin \theta/\lambda = 0.50$. The amplitudes have been calculated using the parameter values 247.5° , 127.5° , 165° , 52.5° which are slightly different from the correct ones.

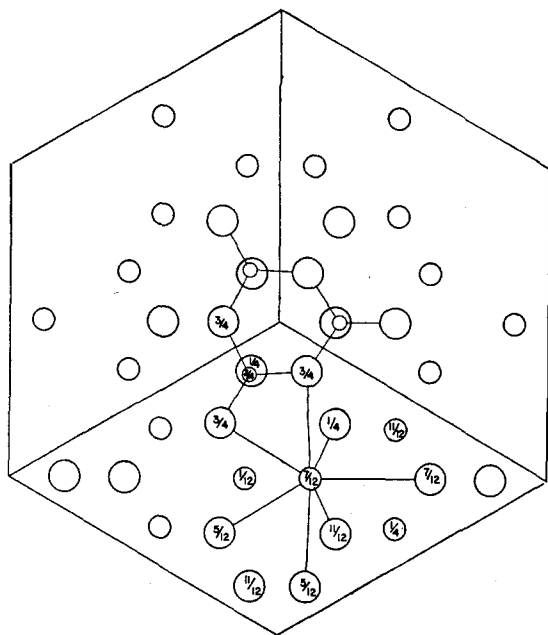


FIG. 1. A projection of the structure on a plane normal to the threefold axis. Only some of the atoms are shown; the remaining ones may be located by symmetry considerations. Large circles represent oxygen atoms, medium sized circles potassium and small circles boron atoms. Attached numbers give heights of atoms above plane of projection, expressed as fractions of cell diagonal (7.33 Å). The figure is bounded by the projected rhombohedral edges.

the BO_3 configuration have previously been found in other crystals.⁴ An oxygen atom of the first kind (O_I) is thus linked to one boron and five potassium atoms, while an oxygen atom of the second kind is linked to two boron and two potassium atoms. The total bond strengths are 1.71 and 2.29, respectively. The angle between the two bonds $\text{B}-\text{O}_{II}$ is $126\frac{1}{2}^\circ$ at the oxygen atom and $113\frac{1}{2}^\circ$ at the boron atom.

Three BO_3 triangles are linked together by shared corners to form radicals $(\text{B}_3\text{O}_6)^{-3}$, the structure of which is shown in Fig. 2. All the nine atoms of the radical lie in the same plane, normal to the threefold axis. The observed strong negative birefringence ($\omega=1.526$, $\alpha=1.450$, Cole, Scholes, Amberg, reference 2) is thus simply accounted for.

The structure of the $(\text{B}_3\text{O}_6)^{-3}$ radical may be interpreted either in terms of ionic bonds or in terms of covalent bonds. Using the concept of

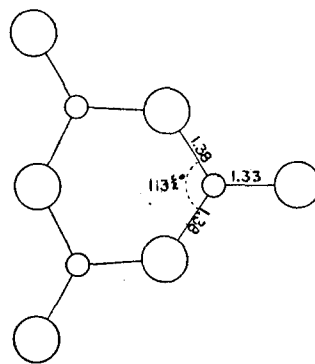
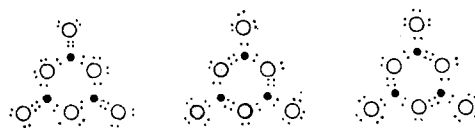


FIG. 2. The structure of the $(\text{B}_3\text{O}_6)^{-3}$ radical. Boron to oxygen distances are given in Å.

covalent binding there would be resonance between the following three electronic structures:



The observed interatomic distances show, however, that the first of these three electronic structures is somewhat more important. The deformation within the BO_3 triangles may, on the other hand, equally well be explained by the repulsion between boron ions in the ionic interpretation.

In the calcium metaborate structure which we examined some years ago, the metaborate group does not occur in the form of a radical as in KBO_2 ; but rather as an infinite chain of BO_3 triangles. All the atoms of one such chain were found to lie approximately in one plane. (This is probably due to the resonating double bond.) We must emphasize the important result that in both calcium- and potassium-metaborate polymerization of the metaborate group has taken place rather than a reduction in the coordination number from three to two. Recently Rud Nielsen and Ward⁵ have claimed that aqueous solutions of NaBO_2 contain radicals $(\text{BO}_2)^-$ built like CO_2 . We consider this result highly improbable. It is quite possible that the $(\text{B}_3\text{O}_6)^{-3}$ radicals would break up when NaBO_2 enters into solution; but even if this be the case, one cannot expect radicals $(\text{BO}_2)^-$. In the presence of the oxygen atoms of the water molecules boron would certainly tend to be surrounded by as many

⁴ For example: 1.35 Å in $\text{Be}_2\text{BO}_3\text{OH}$, W. H. Zachariasen, *Zeits. f. Krist.* **76**, 289 (1931); 1.36 Å in $\text{Ca}(\text{BO}_2)_2$, reference 1.

⁵ J. Rud Nielsen and N. E. Ward, *J. Chem. Phys.* **5**, 201 (1937).

oxygen atoms as is sterically possible, i.e. boron would either be in a triangular or a tetrahedral configuration of oxygen atoms (respectively hydroxyl groups).

It may be of interest to point out the analogy which exists between metaborates and meta-silicates (to a certain extent between borates and silicates in general). The metasilicates too show

polymerization to retain the proper coordination number of four for silicon. The diopside chain corresponds to the (BO_2) chains of CaB_2O_4 , while the three-membered ring of benitoite, $\text{BaTiSi}_3\text{O}_9$, corresponds to the $(\text{B}_3\text{O}_6)^{-3}$ radical of KBO_2 . It is probable that some borates contain radicals $(\text{B}_4\text{O}_8)^{-4}$ analogous to the four rings of SiO_4 tetrahedra occurring in some silicates.

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Bimolecular Association Reactions

LOUIS S. KASSEL

Universal Oil Products Company, Riverside, Illinois

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The recent classical treatment of the rates of bimolecular association reactions proposed by Kimball is extended, and found to involve an essentially different dependence of reaction probability on vibrational energy initially present in the natural coordinates as kinetic energy from that present as potential energy. Since this difference can scarcely have any quantum-mechanical analog, it is concluded that a classical treatment cannot be satisfactory.

A PURELY classical calculation of the mean life of molecules formed by a bimolecular association reaction has recently been proposed by Kimball.¹ This treatment takes as the criterion for dissociation to have occurred the possession of a critical energy, D , by some natural coordinate of the molecule. The initial conditions chosen as corresponding to the formation of the molecule are potential energy $D + kT$ and kinetic energy zero for the natural coordinate involved in the dissociation, and both kinetic and potential energy zero for all other natural coordinates. The amplitudes of the motions in the various normal coordinates are thereby determined. The probability of dissociation per vibration of some suitable normal coordinate is then taken as the probability that the dissociable natural coordinate will have potential energy at least D when the kinetic energy of the chosen normal coordinate is zero.

There can be little doubt that some modification of this treatment is needed to take account of energy initially present in the other natural coordinates. We shall first consider a direct extension of Kimball's treatment.

Let the transformation from natural coordi-

nates, y , to normal coordinates, x , be

$$y_i = \sum_{k=1}^n a_{ik} x_k, \quad (1)$$

$$\text{where } |a_{ik}| = \begin{vmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ a_{n1} & a_{n2} & \cdots & a_{nn} \end{vmatrix} = 1. \quad (2)$$

Then the transformation from normal to natural coordinates is

$$x_i = \sum_{k=1}^n A_{ki} y_k, \quad (3)$$

where A_{ki} is the minor of $|a_{ik}|$ associated with a_{ki} . The following relations are then fulfilled.

$$\begin{aligned} \sum_{i=1}^n a_{ki} A_{ki} &= 1, \\ \sum_{k=1}^n a_{ki} A_{ki} &= 1, \\ \sum_{i=1}^n a_{mi} A_{ki} &= 0 \text{ when } k \neq m, \\ \sum_{k=1}^n a_{km} A_{ki} &= 0 \text{ when } i \neq m. \end{aligned} \quad (4)$$

¹ G. E. Kimball, J. Chem. Phys. 5, 310 (1937).