capillary used must have been sufficiently low to have necessitated measurements in the turbulent region at the pressures used.

All final data were obtained with a second platinum capillary (B) of length 75 cm. and i.d. 0.03 cm. Both ends were carefully smoothed and extreme care taken in mounting to avoid constrictions and sharp bends. The critical Re_m for this capillary at p_m = 13 to 18 cm., was found to be approximately 100 at 80° as seen from the data plotted as curve V of Fig. 3. Below $Re_m = 100$, the observed values for t_{UF_6}/t_{air} are constant to $\pm 0.5\%$ which are within the limits of experimental error at this low Reynolds number.

Values were then obtained, with this capillary, for $t_{UF_6}/t_{air} = \eta_{UF_6}/\eta_{air}$ in regions of experimentally established non-turbulent flow over a temperature range of 40 to 200° presented in Table I. The viscosity η is given in poises and both the small slip and kinetic energy corrections[10] have been applied

$$\eta_{cor.} = \eta\left(1 + \frac{4}{r}\zeta\right) - \frac{m}{8L\pi}\left(1.12 + \ln\frac{p}{p_0}\right)$$

where ξ is the path and m = flow in g./sec. The slip correction was always less than 0.5% and the kinetic energy correction less than 0.2%.

TABLE I

T	p_m	Re_l	Re_m	t_{UF_6}/t_{air}	$\eta_{UF_6} \times 10^6$
40.0	125.3	82.5	56.8	0.933	178.7
60.0	125.3	71.2	49.0	.937	189.0
80.0	132.7	99	74.3	.944	199.9
110.0	125.3	46	31.6	.955	216.1
140.0	134.9	56	38.4	.970	231.9
170.0	134.9	46	31.5	.991	248.0
200.0	134.9	40	27.4	1.004	261.1

As seen in Fig. 2, the short extrapolation of these data to 20° essentially passes through the only viscosity value available that was obtained by a method other than capillary flow. This value was determined by R. Fleischmann using the swinging disk method, and represented captured German data.[11] Further confirmation of the accuracy of these values has resulted from unpublished determinations of thermal conductivity data by the Manhattan Project, and brought to the authors' attention through personal communication.

PHILADELPHIA, PENNSYLVANIA

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[10] F. W. G. Kohlrausch, "Praktische Physik," M. Rosenberg Book Co., New York, N. Y., 1947, Vol. 1, p. 95.

[11] R. D. Present, S. A. M. Laboratories Report USAEC M-2511 (1945).

[CONTRIBUTION FROM THE GENERAL RESEARCH DIVISION, OWENS-ILLINOIS GLASS COMPANY,* AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN†]

Properties and Structures of Vitreous and Crystalline Boron Oxide[1]

BY KASIMIR FAJANS† AND STEPHEN W. BARBER*

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(1) A foundation is given for the understanding of the "anomalies" of boron-containing glasses. The consideration of the properties of boron oxide and its analogs is based on the assumption of electric forces acting between more or less strongly polarized ions with the electronic configurations O^{2-}, Be^{2+}, B^{3+}, Al^{3+}, etc. (2) A coördinative three-dimensional network, or a two-dimensional network (layer structure) are not compatible with the relatively low melting point and molar refraction of boron oxide. (3) The character of the temperature dependence of thermal expansibility, surface tension and viscosity, in the range up to 1400°, proves that, in the crystalline state and in the vitreous state below about 300°, boron oxide consists of units held together by "weak" forces and that with increasing temperature this structure changes gradually toward a "strong" one. (4) The occurrence in crystalline boron oxide of two types of forces of widely different strength follows from the fact that its heat capacity shows much larger deviations from a single Debye function than that of coördinative Al_2O_3 and BeO. The available data suggest that at very low temperatures the heat capacity of boron oxide may be due mainly to vibrations of B_4O_6 molecules held within the crystal by weak intermolecular forces. If so, boron oxide conforms to the parallelism found between the melting points of crystals consisting of symmetrical molecules and the force constants of the intermolecular vibrations.

Introduction

The current views[2] concerning the arrangement of atoms in vitreous boron oxide originated in Zachariasen's[3] general theory of the structure of oxide glasses. Warren, Krutter and Morningstar[4] interpreted the results of their X-ray diffraction study to be "in complete agreement with Zachariasen's predictions" of a "three dimensional random network" in which each boron is "at the center of a triangle of three oxygens, each oxygen bonded to two borons, with the two bonds presumably roughly diametrically opposite."

The discovery of a crystalline form of boron oxide[5] was supported by X-ray diffraction data from which, however, no structure has been derived. The view is usually held[3,2b] that the planar BO_3 groups are common to both crystal and glass, which are supposed to differ merely in the regularity of the mutual orientation of these groups.

The main characteristic of these structures for boron oxide is that they are supposed to be continuous networks. Such networks composed of planar

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[1] Presented in part at the Cleveland Meeting of the American Chemical Society on April 10, 1951, Symposium on Physical Chemistry of Glass, and before the Section of Physical and Inorganic Chemistry at the XIIth International Congress for Pure and Applied Chemistry in New York, N. Y., on September 12, 1951.

[2] (a) W. A. Weyl, *The Glass Industry*, **29**, March–Nov. 1948, especially Part II, p. 200. (b) S. Glasstone, "Textbook of Physical Chemistry," Second Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 520 ff.

[3] W. H. Zachariasen, THIS JOURNAL, **54**, 3841 (1932); fig. 1b.

[4] B. E. Warren, H. Krutter and O. Morningstar, *J. Am. Ceram. Soc.*, **19**, 202 (1936).

[5] L. McCulloch, THIS JOURNAL, **59**, 2650 (1937). See also S. S. Cole and N. W. Taylor, *J. Am. Ceram. Soc.*, **18**, 55 (1935).

BO_3 groups could be either (as mentioned above) three-dimensional or extend only in two dimensions, analogously to the layer structure of the hexagonal boron nitride. In BN both B and N atoms have the coördination number three, at a distance 1.45 Å., within common parallel planes which are 3.35 Å. apart.

It will be shown in this article that various properties of crystalline and vitreous boron oxide cannot be reconciled with a structure in which a coördinative network extends either in three or in two dimensions. However, all the facts known at present are in accord with two assumptions: (1) The crystal and the annealed glass below about 300° consist of units of molecular dimensions, probably of the compositions B_4O_6.[6] (2) Between about 300 and 1400° vitreous and liquid boron oxide change gradually from a relatively weak (molecular) structure toward a stronger one.

(1) Electronic Structure, Character of Binding and Types of Crystal Structure.—In correlating the properties and structure of B_2O_3 with each other and with those of solid BeO, BN, Al_2O_3, SiO_2 or As_2O_3, the ions Be^{2+}, B^{3+}, Al^{3+}, Si^{4+}, As^{3+}, O^{2-} and N^{3-} will be considered as representing the electronic quantum configuration of the constituent parts of these substances.

The charges of these ions, effective at the given internuclear distance, *e.g.*, in the B---O direction, are not $3+$---$2-$ but $p3+$---$p2-$, where the degree of polarity[7] $p < 1$ decreases with increasing strength of the deforming field of the positive ions and with increasing deformability of the negative ions. One can conclude that p decreases in the series Al---O, B---O, B---N. However, even in boron nitride the residual charges $p3+$ and $p3-$ must be large enough to account for the considerable forces binding the layers within the crystal.

Various types of structure are known for solid substances of the composition M_2O_3. In corundum each Al is surrounded by six O, three at the distance (in Å.) of 1.89 and three at 1.93. Thus, even if Al_2O_3 molecules should be indicated[8] in this structure, the deviation from an ideal three-dimensional coördinative type is not pronounced. On the other hand, the sesquioxides of phosphorus, arsenic and antimony, which form glasses, occur as dimeric molecules P_4O_6, As_4O_6 and Sb_4O_6 in the vapor state, in solutions, and in crystals. Such molecular crystals are characterized geometrically by the fact that the nearest M–O distance (*e.g.*, 2.01 for As) within the grouping M_4O_6 is shorter than that between M and O belonging to two neighboring M_4O_6 (2.78 for M equal As).

These extreme types of crystal structure will be represented by the following schemes in which n means a very large number.

Coördinative aluminum oxide: $[2Al^{3+}, 3O^{2-}]_n$. The atom ions, separated by a comma, are the largest structural units, distinguishable within a unit cell.

Molecular crystalline arsenic trioxide: $[((e^-)_2\text{-}As^{5+})_4(O^{2-})_6]_n$. Concerning the details of the electronic structure of As_4O_6 see Section 6.

The question arises whether and under what conditions boron oxide forms a three- or two-dimensional coördinative structure $[2B^{3+}, 3O^{2-}]_n$ or a molecular structure $[\{(B^{3+})_2(O^{2-})_3\}_x]_n$ and in the latter case whether x equals 1, 2, or more.

In an attempt to answer these questions various properties of boron oxide will be compared with those of typically coördinative as well as typically molecular solid substances.

(2) Molar Refraction and Melting Point.—Table I shows that the apparent molar refraction,[9] $R_{O^{2-}}$, of one O^{2-} ion (see Section 1) is smaller in crystalline boron oxide than in any crystalline form of aluminum oxide or silica and smaller in vitreous boron oxide than in vitreous silica. This means that B^{3+} exerts a stronger tightening effect on O^{2-} than does Al^{3+} or $^3/_4$ Si^{4+}. Thus the forces acting between the oppositely charged ions must be, on the average, stronger in boron oxide than in the other two oxides. Nevertheless, the melting point of crystalline boron oxide (Table I) is much lower than that of aluminum oxide or of cristobalite. This apparent contradiction can be resolved if one assumes that boron oxide consists of molecules $(B_2O_3)_x$ and that its low melting point is due to the relatively weak intermolecular forces, the low molar refraction to the relatively strong intramolecular forces.

TABLE I

APPARENT MOLAR REFRACTIONS $R_{O^{2-}}$ (IN CC.) AND MELTING POINTS (°C.)

Oxide	Form	$R_{O^{2-}}$	M.p., °C.
BeO	Crystalline	$3.25^{7,9b}$	2530
B_2O_3	Crystalline	3.38^a	450^a
	Vitreous	3.50^b	
Al_2O_3	Hexagonal	$3.48^{c,d}$	2045
	Cubic	$3.49^{e,d}$	
SiO_2	Quartz	3.54^f	
	Cristobalite	3.65^f	1713
	Vitreous	3.66^f	

The following references give the source of n_D and d values used in the calculation of $R_{O^{2-}}$. The abbreviations (B 65 etc.) are those used in *Bull. Nat. Res. Council*, No. 118 (1949), where most of the individual values are compiled. [a] F. C. Kracek, G. M. Morey and H. E. Merwin, *Am. J. Sci.*, (5) **35A**, 143 (1938). [b] P. Wulff and S. K. Majumdar, *Z. physik. Chem.*, **31B**, 319 (1936). [c] B 65. [d] M 76. [e] K 68. [f] S 76.

Two types of forces of widely differing strength occur also in layer structures; cleavage and lubricity of graphite or BN parallel to the layers are due to this factor. However, in a melt units of atomic or molecular dimensions are involved in the flow[10]; thus the strong forces *within* the layers must be weakened in order to melt a layer crystal. In fact, the melting points of graphite (3550°) and of $[B^{3+}, N^{3-}]_n$ (> 2530°) are very high. Hence, if crystalline $[2B^{3+}, 3O^{2-}]_n$ had layer structure, the strength of the interaction between the nearest ions would be intermediate between those in BN and in the three-dimensionally coördinative $[Be^{2+}, O^{2-}]_n$ (m.p. 2530°); the m.p. of boron oxide would be

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(6) S. A. Schtschukarew and R. L. Müller (*Z. physik. Chem.*, **150A**, 439 (1930)) ascribed the electric conductivity of vitreous $B_2O_3 + Na_2O$ systems between 200° and 300° to Na^+ and $B_4O_7^{2-}$ ions solvated by B_4O_6 molecules.

(7) (a) K. Fajans, *Z. Elektrochem.*, **34**, 502 (1928); (b) *Ceramic Age*, **54**, 288 (1949).

(8) "Strukturbericht," Vol. I (1931), Fig. 110, and Table on p. 212.

(9) Concerning the evaluation and variability of the apparent molar refraction of O^{2-}, see: (a) N. Bauer and K. Fajans, THIS JOURNAL **64**, 3023 (1942); (b) K. Fajans and N. J. Kreidl, *J. Am. Ceram. Soc.*, **31**, 105 (1948).

(10) J. E. Stanworth, *J. Soc. Glass Tech.*, **32**, 21 T (1948).

expected to be much higher than the experimental value 450 ± 2°.[11]

The m.p. of boron oxide is much closer to the melting points of the molecular crystals P_4O_6 (23.8°) and As_4O_6 (275°) (see Section 6) than to those of Al_2O_3, BeO, or BN. Hence the occurrence of B_4O_6 molecules in the crystal merits consideration. The presence of B_4O_6 molecules in the solutions of boron oxide in concentrated sulfuric acid is strongly indicated by molecular weight determinations.[12]

(3) **Thermal Expansion, Surface Tension and Viscosity.**—According to Section 2, the relatively low m.p. of boron oxide can be understood if, around 450°, it contains in the crystal, in the liquid, or in both states units of molecular dimensions held together by considerably weaker forces than those expected to be active between the nearest ions within a coördinative, two- or three-dimensional structure $[2B^{3+}, 3O^{2-}]_n$. The consideration of other properties confirms the presence of such relatively weak forces in the crystal and glass and reveals that in the liquid these forces become gradually strengthened with increasing temperature.

(a) **The cubic expansion coefficient,** α, is represented in Fig. 1 as a function of temperature. For comparable structures the thermal expansion coefficient can in general be expected[13] to increase with decreasing strength of the forces involved and thus for a given substance with increasing temperature. At 25° the value of α (in 10^{-4} degree^{-1}) for crystalline boron oxide (0.3) is[14] about twice as large as that[15] for coördinative Al_2O_3 (0.17); at 440° the ratio is 1.91:0.23 = 9. These data show that the structural units, the distance between which increases in the expansion, are held by weaker forces in crystalline boron oxide than in Al_2O_3. The value of α for vitreous boron oxide which, at 200°, is 1.4 times larger than that for the crystalline form, increases[14] in the softening range between 200 and 290° approximately 19-fold. It is also seen in Fig. 1 that the α *vs.* t curve of boron oxide glass is roughly parallel to that of glucose glass, which is certainly molecular; the displacement of the two curves (on the average by about 220°) is of the order of magnitude of the difference in m.p. (304°).

It is most remarkable that the value of α of liquid boron oxide[16] decreases 9-fold between 500° (4.0) and 1300° (0.43) and becomes at the latter temperature about equal to the value of vitreous boron oxide at 25°, although the absolute volume is 1.25 times larger at 1300 than at 25°. This behavior leads to the conclusion that vitreous boron oxide begins to change its structure somewhere between 300 and 500° (no measurements of α are known in this interval) from a "weaker" toward a "stronger" one.

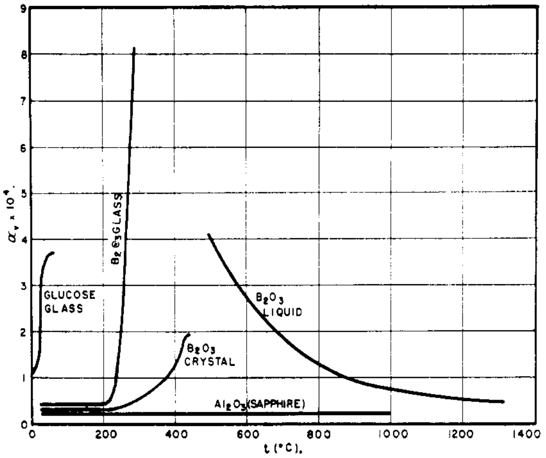

Fig. 1.—Volume expansion coefficients *vs.* temperature.

(b) **Surface tension** of vitreous and liquid boron oxide changes between 300 and 1400° according to eq. (1).[17]

$$\gamma = 58.2 + 0.0354\,(t - 300°)\ \text{dynes/cm.} \qquad (1)$$

Therefore γ has the very unusual positive temperature coefficient. Both properties, $d\gamma/dt > 0$ (above 300°) and $d\alpha/dt < 0$ are closely related and can be explained by a structural change which causes a strengthening of the forces involved when temperature is raised.

The lowest measured value of γ (in dynes/cm.) at 300° (58.2) is one-tenth as large as that (580) of liquid Al_2O_3 at 2050°, just above the m.p. On the other hand, the value 58.2 lies about half-way between 36.6 for molecular liquid P_4O_6 at 34.3° and 76.4 for H_2O at −5°. This shows that the strength of the forces involved at 300° is of the order of magnitude of "weak" intermolecular forces.

One can expect that at any temperature in the equilibrium between the "weak" and the "strong" structures the surface of the liquid is enriched with respect to the weak structure which lowers the surface tension. This must be partly responsible for the fact that even the highest value 97.1, obtained for boron oxide at 1400° is only $^1/_6$ that of Al_2O_3 at 2050°.

(c) **Viscosity** data (Fig. 2) become understandable on the basis of the above conclusions. Between 220° and about 370° the log η *vs.* $1/T$ plot[18] is linear as expected when the activation energy for flow remains constant. At higher temperatures, where according to Fig. 1 and eq. (1) the "weak" structure changes gradually toward the "strong" one, the experimental log η values become increasingly larger than those obtained by the dotted extrapolation of the straight line. For instance, at 727° the actual value is 2.7, the extrapolated −0.8, *i.e.*, the viscosity is 3000 times larger than expected for the "weak" structure.

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[11] F. C. Kracek, G. M. Morey and H. E. Merwin, *Am. J. Sci.*, [5] **35A**, 143 (1938).

[12] E. Beckmann, *Z. physik. Chem.*, **53**, 129 (1905). No decision has been reached whether B_4O_6 molecules are present in dioxane which we found to dissolve vitreous boron oxide slowly on heating. The determination of the boiling point elevation of these solutions, performed for us by Dr. Lev Akobjanoff at the University of Michigan in 1949, showed that they contain less than two boron atoms per one dissolved molecule, *i.e.*, that a partial dissociation of B_2O_3 must have taken place.

[13] M. Born in E. Grüneisen, "Handbuch der Physik," Vol. X, 1926, p. 40.

[14] J. J. Donoghue and D. Hubbard, *Natl. Bur. Standards, J. Res.*, **27**, 371 (1941).

[15] J. B. Austin, *J. Am. Ceram. Soc.*, **14**, 795 (1931).

[16] (a) M. P. Volarovich, *Acta Physicochimica (U.S.S.R.)*, **2**, 695 (1935); (b) A. A. Leonteva, *J. Phys. Chem. (U.S.S.R.)*, **17**, 264 (1943).

[17] (a) L. Shartsis and A. W. Smock, *J. Am. Ceram. Soc.*, **30**, 130 (1947); (b) according to these authors and S. Spinner, *ibid.*, **31**, 23 (1948), $d\gamma/dt$ is positive also for PbO.

[18] B. V. Rabinowich, *J. Phys. Chem. (U.S.S.R.)*, **16**, 23 (1942).

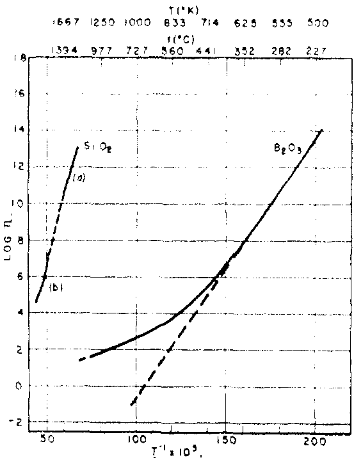

Fig. 2.—Logarithms of viscosity (η in poises) *vs.* reciprocal temperature.

The comparison (Fig. 2) of boron oxide with vitreous silica is also significant. For the latter[19] log η = 13.0 at 1260°. Extrapolation of the boron oxide curve[20] over a 160° range gives at that temperature log η = 1.4, *i.e.*, the viscosity of boron oxide is smaller than that of silica by a factor of $10^{-11.6}$, although the interionic forces are, according to the $R_{O^{2-}}$-values of Table I, on the average stronger in boron oxide. The difference in viscosity would be still much larger if one could extrapolate the SiO_2 line to the region of the "weak" structure, *e.g.*, to the m.p. of boron oxide which is 1263° lower than that of cristobalite. If one recalls that the m.p. of BN is at least 800° higher than that of silica it becomes obvious that the relatively high fluidity of boron oxide, as compared with SiO_2 and BN, is completely incompatible with the assumption that at low temperatures it may have a coördinative structure, either in three or in two directions.

(4) **Heat Capacity.**—The above qualitative comparison of various properties of boron oxide with those of analogous substances strongly suggests that at low temperatures it may have a molecular structure. The following consideration and semi-quantitative treatment of the heat capacity of crystalline boron oxide confirm the conclusion that the structure of crystalline boron oxide cannot be analogous to that of the three-dimensionally coördinative Al_2O_3 and show that if boron oxide is of the molecular type the molecules may have the composition B_4O_6 but not B_2O_3.

(a) **Comparison of the Heat Capacities of B_2O_3 and Al_2O_3.**—Figure 3(a) gives C_p *vs.* T curves for $^1/_5$ B_2O_3 and $^1/_5$ Al_2O_3 in the whole available temperature range. It is remarkable that at about 325°K. vitreous boron oxide has a somewhat smaller heat capacity than the crystalline form. At 1300°K., where the curves for solid $^1/_5$ Al_2O_3 and liquid $^1/_5$ B_2O_3 cross, C_p equals about $3R$, the classical limiting value per one gram-atom expected for C_v of a crystal. In the region below 300°K., reproduced on a larger scale in Fig. 3(b), the crystalline oxides of boron and aluminum are compared using older measurements[21] down to 50°K. and more recent ones[22] down to about 18°K.

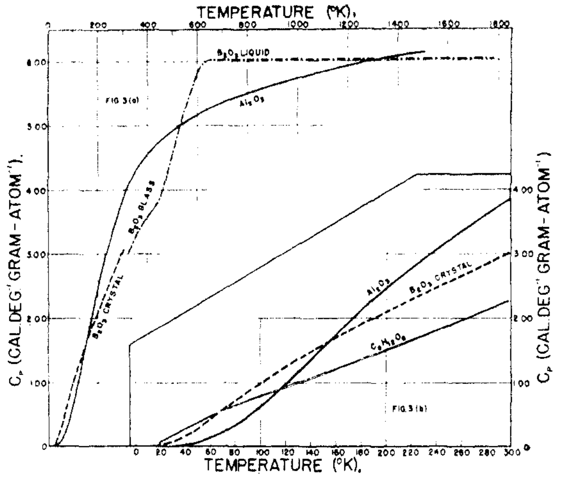

Fig. 3.—Heat capacity per gram-atom *vs.* temperature.

If the two crystalline oxides had the same type of coördinative structure[3] below 300°K., one would expect the following relations between their C_p *vs.* T curves.

The forces between B^{3+} and O^{2-} are stronger than those between Al^{3+} and O^{2-} (see Section 1) and the mass of B is smaller than that of Al. The frequency of vibration, ν, and the characteristic temperature, θ, are related to the force constant (*f.c.*) by eq. (2) in which h and k have the usual

$$\theta = \frac{h}{k}\nu = \frac{h}{k} \times \frac{1}{2\pi}\sqrt{\frac{f.c.}{\mu}} \qquad (2)$$

meaning, and μ is the reduced mass. It follows that θ should be larger for B_2O_3. Hence, for analogous structures, the heat capacity of which would follow the same function $C_v = f(\theta/T)$, the whole C_v or C_p *vs.* T curve for B_2O_3 should lie below that for Al_2O_3. Instead it is seen in Fig. 1 that, at the lowest temperatures, the values (in cal. deg.$^{-1}$ gram-atom^{-1}) for $^1/_5$ B_2O_3 are much higher than those for $^1/_5$ Al_2O_3; *e.g.*, at 25°K. they are 0.20 and 0.04, respectively. The two curves cross at 157°K. where C_p = 1.66. At the highest comparable temperature of 300°K., the value for the crystalline state given by Kerr, Johnston, *et al.*, is considerably lower for $^1/_5$ B_2O_3 (3.027) than that for $^1/_5$ Al_2O_3 (3.838). In order to relate this complex behavior to a probable structure of boron oxide the C *vs.* T curve for the coördinative Al_2O_3 will be analyzed first.

(b) **Temperature Dependence of the Heat Capacity of Al_2O_3.**—A single Debye function (D-F) with a constant θ value has often been applied not only to monoatomic solid elementary substances but also to simple compounds with coördinative structures, including Al_2O_3.[23] At sufficiently low temperatures the D-F assumes the form of the limiting law (3).

$$C_v = 464.4\,(T/\theta_D)^3 \text{ cal. deg.}^{-1} \text{ g.-atom}^{-1}, \quad \text{when } T < \sim 0.08\,\theta \qquad (3)$$

The constant 464.4 applies when $3R$ is taken as the limit of C_v at high temperatures, *i.e.* in the case of coördinative structures this constant applies to one gram-atom, in the case of molecular structures to each, the translational vibration and rotational oscillation (see Section 4,d,β). In order to calculate the entropy of Al_2O_3, Kerr, Johnston and Hallett[22b] used in the T^3 region θ = 571°, applying eq. (3) to one mole of Al_2O_3.

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[19] M. P. Volarovich and A. A. Leonteva, *J. Soc. Glass Tech.*, **20**, 139 (1936).

[20] K. Arndt (1908), *cf.* "I.C.T.," Vol. VII, p. 212.

[21] (a) G. S. Parks and K. K. Kelley, *J. Phys. Chem.*, **30**, 47 (1926), for natural sapphire; (b) K. K. Kelley, THIS JOURNAL, **63**, 1137 (1941), for B_2O_3.

[22] (a) E. C. Kerr, H. N. Hersh and H. L. Johnston, *ibid.*, **72**, 4738 (1950), for B_2O_3; (b) E. C. Kerr, H. L. Johnston and N. C. Hallett, *ibid.*, **72**, 4740 (1950), for synthetic sapphire.

[23] F. Seitz, "The Modern Theory of Solids," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Fig. 3 p. 109.

A critical review of experimental data revealed[24] that a single D-F does not apply exactly in a broad temperature range even to the simplest solids.[25] Since θ is not a constant independent of T, it became customary to derive the *apparent* value θ_D which fits the function $C_v = D(\theta/T)$ for the given experimental values of C_v and T.

In order to test how well the D-F applies to Al_2O_3, the experimental C_p values of Kerr, Johnston and Hallett for $^1/_5$ Al_2O_3 were reduced to C_v using the relation (4), according to reference (24), p. 209.

$$C_p - C_v = AC_p^2T = 8.4 \times 10^{-6}\, C_p^2T \qquad (4)$$

The value 8.4×10^{-6} cal.$^{-1}$ g.-atom given for the constant A was obtained by applying eq. (4) and the thermodynamic relation (5) to the known data for V,[26] α[15] and β[27] at 25°, at which temperature C_p = 3.818 cal. deg.$^{-1}$ g.-atom^{-1} and

$$\begin{aligned} C_p - C_v = TV\alpha^2/\beta &= 298 \text{ deg.} \times 5.63 \text{ cc. g.-atom}^{-1} \\ &(1.75 \times 10^{-5} \text{ deg.}^{-1})^2/3.4 \times 10^{-7} \text{ atm.}^{-1} \\ &= 3.65 \times 10^{-2} \text{ cal. deg.}^{-1} \text{ g.-atom}^{-1} \qquad (5) \end{aligned}$$

The $C_p - C_v$ correction calculated in this way is negligibly small at low temperatures and increases between 100 and 294.85°K. from 0.0003 to 0.03 cal. deg.$^{-1}$ per $^1/_5$ Al_2O_3. Using the resulting C_v values, the apparent θ_D values were calculated and the latter plotted *vs.* T (Fig. 4) as the smoothed curve C_v ($^1/_5$ Al_2O_3). Between 20 and 30°K., θ_D does not change in a systematic manner and has an average value $\theta_D = 991.5 \pm 8.5°$. Thus, the T^3 law can be considered valid here (see Fig. 5), although only up to $T = 0.03\ \theta_D$ instead of $0.08\ \theta_D$ as expected by the D-F. At higher temperatures, θ_D first decreases to a minimum, 888° at 86°K., *i.e.*, by 11.6% of the minimum value, and then increases to 950° at 234°K., *i.e.*, by 7%. Between 234 and 295°K., θ_D remains practically constant and has an average value of 949.0 ± 1.5°, which is lower than that at 20°K.

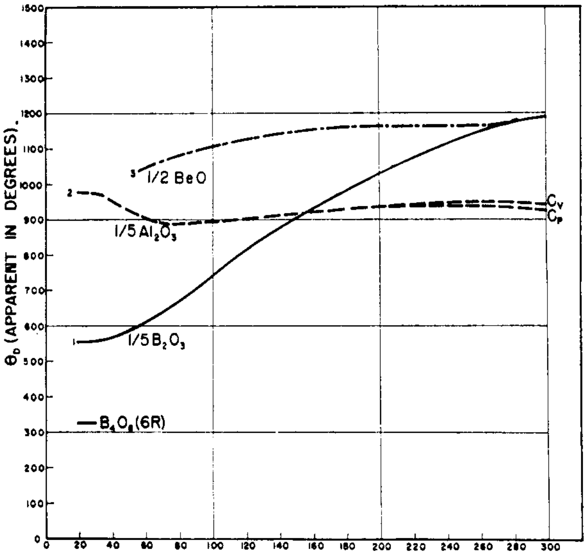

Fig. 4.—Apparent characteristic Debye temperatures *vs.* temperature.

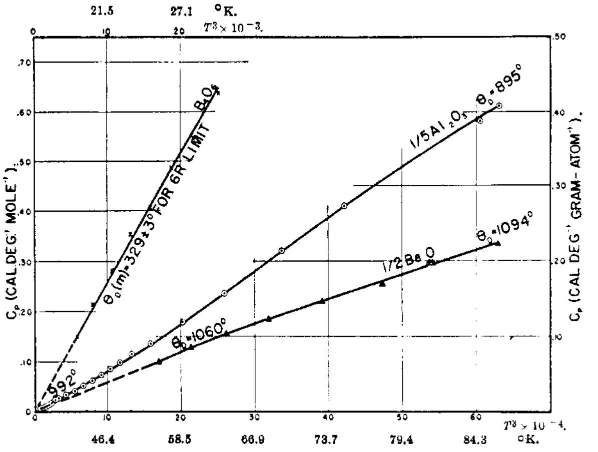

Fig. 5.—Heat capacity *vs.* T^3.

A minimum in the θ_D *vs.* T curve was expected theoretically[25] and has been found for KCl, NaCl and LiF. However, the region of the T^3 law has not been reached for any of these three substances although the measurements have been extended[28] for KCl down to 4°K. = 0.017 θ_D.

(c) Dependence of θ_D on T and Electronic Structure of Cations.—In spite of these deviations from the general D-F, inspection of the available experimental material, in the temperature range below 300°K., showed that in coördinative structures, which can be formulated as consisting of noble gas type ions, the variation of the apparent θ_D values does not exceed 25%. In the case of LiF the change amounts[29] to 24% between 18°K. and the minimum value, 607°, at 75°K. and to 6.8% between 75 and 273°K.

The restriction of the above statement to noble gas type ions is due to the finding by one of us (K. F.) and J. H. La Rochelle (unpublished evaluation of literature data) that large variations of θ_D with temperature occur in structures of non-molecular type when they contain non-noble gas type cations. This is the case for Cu_2O, CuI, AgCl, AgBr, AgI, HgO, TlCl, PbO and PbI_2. One example may serve as illustration: for AgI the values[30] of θ_D increase from 94.5 to 160°, *i.e.*, by 69% in the small interval 15–59°K. and decreases then with increasing temperature, assuming *e.g.* the value 107 at 117°K. Above 150°K. the heat capacity exceeds the classical value and the D-F cannot be applied.

In view of this influence of the electronic configuration of the cation, it is important to state that the different character of the dependence of C_p on T for boron and aluminum oxide is not due merely to the fact that B^{3+} has a helium-like, Al^{3+} a neon-like configuration. Although Li^+ and H^- are both of the helium type, solid LiH shows[31] a practically constant θ_D (average = 824 ± 9°) between 74 and 293°K.

More closely analogous to B_2O_3 and Al_2O_3 in chemical respects is BeO = $Be^{2+}O^{2-}$, with Be^{2+} also of helium type. For the calculation of θ_D, the C_p values[32] for $^1/_2$ BeO (be-

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[24] A. Eucken, Energie and Wärmeinhalt, "Handbuch der Experimental-physik," Vol. VIII/1, Akademische Verlagsgesellschaft. Leipzig, 1929, p. 244ff.

[25] For the theoretical justification for this behavior, see M. Blackman, *Proc. Roy. Soc.* (*London*), **148A**, 365 (1935).

[26] Density = 2.619 g./cc. E. Kordes, *Z. Krist.*, **91**, 193 (1935).

[27] P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **68**, 27 (1933).

[28] (a) W. H. Keesom and C. W. Clark, *Physica*, **2**, 698 (1935); (b) M. Iona, *Phys. Rev.*, **60**, 822 (1941).

[29] K. Clusius, *Z. Naturforschung*, **1**, 79 (1946).

[30] Calculated from C_p (corrected to C_v) as measured by: (a) W. Nernst and F. Schwers, *Sitzungsber. preuss. Akad. Wiss.*, 355 (1914); (b) K. S. Pitzer, THIS JOURNAL, **63**, 516 (1941).

[31] P. Günther, *Ann. Physik*, **63**, 476 (1920).

[32] K. K. Kelley, THIS JOURNAL, **61**, 1217 (1939). For a purely empirical representation of the data for one mole of BeO a combination of a Debye function (θ = 855°) and an Einstein function (θ = 1170°) has been used by the author.

tween 55.5 and 292.4°K.) were used without correcting to C_v since the compressibility is not known. Between 64 and 292°K. the resulting θ_D values show an increase from 1062 to 1178°, *i.e.*, by 11%. This behavior is closely analogous to that of $^1/_5$ Al_2O_3 above the temperature of the minimum of the θ_D *vs.* T curve. In Fig. 4, in which for comparison, θ_D values calculated from uncorrected C_p values are given also for $^1/_5$ Al_2O_3, the whole $^1/_2$ BeO curve lies above both $^1/_5$ Al_2O_3 curves. Around 250°K., where the curves for both substances are nearly parallel, θ_D of $^1/_2$ BeO is 1160°, that of $^1/_5$ Al_2O_3 is 950°. This conforms to eq. (2) since, according to the lower $R_{O^{2-}}$ and higher m.p. of BeO (see Table I), the interionic forces in BeO are stronger than in Al_2O_3, and the mass of Be is smaller than that of Al. The coördination number (4) of the ions in the wurtzite structure of BeO (average distance 1.65 Å.) also differs from that in Al_2O_3 (6 and 4, average distance 1.91). Nevertheless, the temperature dependence of the heat capacity of both BeO and Al_2O_3 is in accord with the behavior known for other coördinative structures which can be derived from ions of noble gas type.

(d) Temperature Dependence of the Heat Capacity of Boron Oxide

(α) Presence of Two Kinds of Forces.—In order to arrive at a semi-quantitative interpretation of the crossing in Fig. 3 of the C_p *vs.* T curves for $^1/_5$ B_2O_3 and $^1/_5$ Al_2O_3, the apparent θ_D values for crystalline boron oxide, calculated from the C_p values of Kerr, Hersh and Johnston[22a] with $3R$ as limit for $^1/_5$ B_2O_3, are plotted in Fig. 4, curve 1. The compressibility is not known, hence no correction to C_v was attempted. It is seen that these θ_D values increase between 18 and 296°K. from 555 to 1185°, *i.e.*, by more than 100%, which would be quite unusual for a three-dimensionally coördinative structure derived from the noble gas type ions B^{3+} and O^{2-}. It is obvious that at least two widely different θ values have to be applied to crystalline boron oxide.[33] According to eq. (2) the θ values which are larger than those for Al_2O_3 can be correlated qualitatively with the vibrations of the ions B^{3+} and O^{2-} against each other. However, the small θ, which accounts for the main part of the heat capacity at low temperatures, must be due to weaker forces or a larger vibrating mass or to both factors. This agrees qualitatively with the assumption, suggested by the molar refraction and m.p., that solid boron oxide consists of $(B_2O_3)_x$ molecules with relatively weak intermolecular and strong intramolecular forces.

Two types of forces occur also in the layer structures considered in Sections 2 and 3. No information (below 400°) is available concerning the heat capacity for BN, which is the closest chemical analog to B_2O_3 among the representatives of such structures. However, since it was concluded in Sections 2 and 3 that a layer structure is highly improbable for boron oxide below its m.p., the peculiarities[34] of the heat capacity of layer structures do not need to be considered here.

(β) Heat Capacity of Molecular Structures.—The quantitative treatment of the temperature dependence of the heat capacity is naturally still more complex for molecular solids than for coördinative ones. Nevertheless, it has been found in numerous cases[35] that at sufficiently low temperatures the heat capacity follows approximately a D-F with such low θ values that they can be due only to modes of motion of the whole molecule within the crystal.

These modes are of two types, each involving potential and kinetic energy: translational vibration (t.v.) in three directions of space (limiting value $3R$) and torsional vibration which will be called here rotational oscillation (r.o.) about three axes (limiting value also $3R$ for non-linear molecules). In general, one would expect[35b] the frequency of t.v. to be lower than that of r.o. While the t.v. of a molecule can be expected to follow a D-F with an approximation comparable with that of monoatomic solids, little can be predicted concerning the temperature dependence of the heat capacity due to the r.o. The available data show that for molecules, like simple hydrogen compounds,[35a] the D-F applies at low temperatures with a limiting value $3R$. This means that here the r.o. does not contribute appreciably to the heat capacity C_m due to the motion of the molecule. For larger molecules the limit $6R$ gives in general a better fit at low temperatures. For instance in the case of benzene, two D-F's with a common $\theta_D = 150°$, considered as average of θ_D for both, the t.v. and the r.o. of the molecule within the crystal, apply satisfactorily[36] up to 50°K., *i.e.*, here $C_{exp} = C_m = 2D(150/T)$. Above 50°K., C_{exp} minus C_m has positive values which were represented by Planck–Einstein functions (E-F) corresponding to the 30 intramolecular modes of vibration, each with the limiting value R. The shares of C_m and C_{int} (internal) at a few selected temperatures are given in Table II.

TABLE II

INTER- AND INTRAMOLECULAR HEAT CAPACITY (CAL. DEG.$^{-1}$ MOLE^{-1}) OF BENZENE,[36] GLUCOSE[37] AND BORON OXIDE[22a]

T, °K.	C_p	C_v	$C_m(6R)$	C_{int}	$\frac{100C_{int}}{(3n-6)R}$
	(1)	C_6H_6	θ_m 150°	M.p. 5°	
4	0.018	0.018	0.018	0.001	0
60	9.23	8.92	8.90	.02	0
100	12.02	11.21	10.68	.53	.89
200	20.06	16.53	11.56	4.97	8.35
270	29.03	21.20	11.72	9.48	15.9
	(2)	$C_6H_{12}O_6$	θ_m 147°	M.p. 146°	
20	2.11	2.11[a]	2.06	0.05	0
40	6.89	6.89	6.60	0.29	.22
50	9.28	9.28	8.05	1.23	.93
100	18.79	18.75	10.73	8.02	6.12
200	35.76	35.44	11.60	23.84	18.2
300	54.84	53.71	11.78	41.93	32.0
	(3)	B_4O_6	θ_m 329°	M.p. 450°	
18	0.149		0.150	0	0
31.6	0.847		0.804	.043	0
50	2.852		2.62	.23	0.48
100	9.974		7.34	2.63	5.55
200	21.00		10.44	10.56	22.2
275	27.87		11.10	16.77	35.2
300	30.27		11.22	19.05	40.0

[a] The experimental C_p values for glucose were corrected to C_v values by Mr. J. H. La Rochelle in the way explained in Section 4a for Al_2O_3. At 25°, $\alpha = 0.8 \times 10^{-4}$ deg.$^{-1}$ (G. S. Parks, H. M. Huffman and F. R. Cattior, *J. Phys. Chem.*, **32**, 1366 (1928)); $\beta = 5.216 \times 10^{-6}$ atm.$^{-1}$ (P. W. Bridgman, *Proc. Amer. Acad. Arts Sci.*, **76**, 20 (1945)).

In the case of crystalline glucose (m.p. 146°), for which the difference between the strength of inter-

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(33) The above conclusion is in accord with the equation used by Kelley[21b] between 51 and 298°K. It consists of one D-F ($\theta_1 = 311°$) and three Einstein functions ($\theta_2 = 480°$, $\theta_3 = \theta_4 = 1086°$), but does not apply satisfactorily to the new data[22a] at lower temperatures.

(34) (a) V. V. Tarasow, *Zhur. Fiz. Khim.* (*Russian*), **24**, 111 (1950); (b) W. De Sorbo and W. W. Tyler, *Bull. Am. Physic. Soc.*, June 14, 1951, p. 14.

(35) See *e.g.* (a) A. Eucken and E. Karwat, *Z. physik. Chem.*, **112**, 467 (1924); (b) R. C. Lord, *J. Chem. Phys.*, **9**, 693 (1941).

(36) R. C. Lord, Jr., J. E. Ahlberg and D. H. Andrews, *ibid.*, **5**, 649 (1937).

and intramolecular forces is smaller than for benzene (m.p. 5°), Simon[37] found it simplest to apply only D-F's with θ values (and number of D-F's) 120° (1), 310° (3), and 1700°(20). A re-examination of these data has shown that, between 20 and 40°K. the experimental points are represented very satisfactorily by two D-F's with a common $\theta_D = 147°$ but not by one D-F. Therefore it appears justifiable to consider 147° as average for t.v. and r.o. of the glucose molecule, to apply $C_m = 2D(147/T)$ above 40°K. and to assign the difference

$$C_{exp} - C_m = C_{int} \qquad (6)$$

to the 66 internal modes of vibration. The shares of C_m and C_{int} are listed in Table II.

In view of the uncertainty whether E-F's or D-F's are appropriate for the treatment of the "internal" vibrations of such complex molecules held together within the solid by considerable intermolecular forces, the following semi-quantitative discussion of the heat capacity of boron oxide will be limited to the question whether it can be resolved into C_m and C_{int}.

(γ) **Low- and High-Frequency Vibrations of Boron Oxide.**—For boron oxide between 18 and 29°K., log C_p shows a linear dependence on log T with a slope of 3.00 ± 0.10. In this region of the T^3 law (see Fig. 5) the value $\theta_D = 555°$ would result if boron oxide had coördinative structure, *i.e.*, a limiting value $3R$ for $^1/_5$ B_2O_3. The value 555° is, however, much too low as compared with 991° found for the coördinative Al_2O_3 (see Section 4b). In the case of a molecular structure of boron oxide and a limiting value $6R$ for t.v. and r.o., the characteristic temperature depends on whether the molecules have the composition B_2O_3 or B_4O_6, namely, $\theta(B_2O_3) = 415°$ and $\theta(B_4O_6) = 329°$. The latter value is identical with that used by Kerr, Hersh and Johnston,[22a] who applied eq. (3) assigning the $3R$ limit to one mole B_2O_3.

In order to test these two alternatives of molecular structure, eq. (6) was applied above 30°K. in the forms 6(a) and 6(b)

$$C_{int}^{B_2O_3} = C_{exp}^{B_2O_3} - 2D\left(\frac{415}{T}\right) \quad (6a);$$

$$C_{int}^{B_4O_6} = C_{exp}^{B_4O_6} - 2D\left(\frac{329}{T}\right) \quad (6b)$$

For $C_{int}^{B_2O_3}$ negative values result between 30 and 150°K., and therefore the assumption of B_2O_3 molecules, with a $6R$ limit, is not in accord with the experimental heat capacity data.[37a] However, $C_{int}^{B_4O_6}$ (in cal. deg.$^{-1}$ mole^{-1}) shows in Table II a regular rise between 31.6°K. (0.04) and 300°K. (19.05). At the latter temperature the heat capacity of the intermolecular modes reaches nearly the limiting value ($6R$) for B_4O_6 (11.22), $C_6H_{12}O_6$ (11.78) and C_6H_6 (11.72 at 270°K.), while the internal heat capacity acquires the following fractions of the limiting values: 0.40 for B_4O_6, 0.32 for glucose, 0.16 for benzene (at 270°K.). The corresponding fraction for $^1/_5$ Al_2O_3 at 300°K. is 0.63. As shown in Fig. 3b, the C_p *vs.* T curve for glucose crosses that for boron oxide at 65°K., that for alumina at 115°K.

Summarizing the results of Section 4, one can say that the heat capacity of the coördinative aluminum oxide is reproduced approximately by one D-F with an average value $\theta_D = 950°$. In the case of boron oxide, vibrations of B_4O_6 molecules with $\theta_D = 329°$ contribute the main part in the lower temperature range while in the higher temperature range intramolecular vibrations become of increasing importance. An approximate estimation of some of the internal frequencies is possible on the basis of infrared measurements[38] on well annealed boron oxide glass which revealed two strong peaks at 710 and 1270 cm.$^{-1}$ corresponding to θ values of 1020 and 1830°. They are both above the value 950° for Al_2O_3, as expected in Section 4a.

(5) **Force Constant and Melting Point.**—In order to test whether the value $\theta_D = 329°$ derived for B_4O_6 molecules agrees with other properties of boron oxide, it was examined (unpublished) whether for analogous molecular structures a relation exists between the m.p. and the f.c. of the t.v. derived from the low temperature θ values. The f.c. was calculated from eq. (1) applied in the following form in which M is the molecular weight

$$\text{f.c. (dynes cm.}^{-1}) = 2.85 \times 10^{-2}\theta_D^2 M \qquad (1a)$$

In evaluating θ_D, the limit $3R$ was used for the monoatomic molecules[39] vibrating in crystalline Ne (64°), A (80°), Kr (63°), Xe (53°), and for the simple hydrogen-containing molecules H_2(91°), HCl (125°), HBr (85°), H_2S (36°) and H_3N (215°). However, the limit $6R$ was applied to the larger molecules $C(CH_3)_4$ (107°),[40] C_6H_6 (150°), $C_6H_{12}O_6$ (147°), B_4O_6 (329°).

Figure 6, in which log m.p. is plotted *vs.* log f.c., shows that for the noble gases the f.c. increases regularly with the m.p. Helium is not included but it is in accord with the parallelism, since its m.p. (1.13°K. at the lowest observed pressure of 25.3 atm.) and its f.c. (154 dynes/cm., calculated from

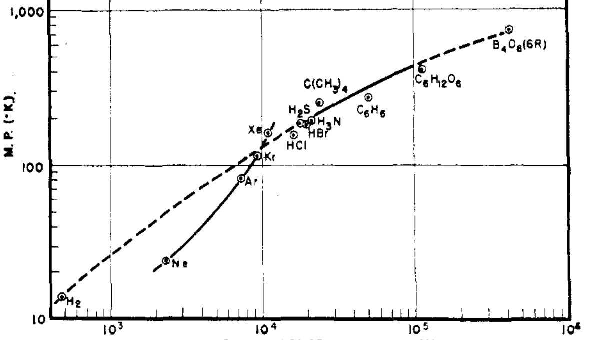

Fig. 6.—Melting points *vs.* force constants of intermolecular vibrations.

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(37) F. Simon, *Ann. Physik*, **68**, 241 (1922); reproduced in Fig. 3b.

(37a) According to J. Biscoe and B. E. Warren, *J. Am. Ceram. Soc.*, **21**, 287 (1938), "the existence of discrete B_4O_6 molecules in the glass is definitely ruled out" by their X-ray work.

(38) Performed for Owens-Illinois Glass Company by H. L. McMahon and I. Simon of Arthur D. Little, Inc., Cambridge, Mass.

(39) K. Clusius, *Z. physik. Chem.*, **31B**, 459 (1936).

(40) J. G. Aston and G. H. Messerly, THIS JOURNAL, **58**, 2354 (1936).

$\theta = 37°$ at 1.2°K.) have both by far the smallest values.

A similar parallelism applies in Fig. 6 to the other molecular crystals and the values for B_4O_6, m.p. 723°K. and f.c. = 4.29×10^5 dynes cm.$^{-1}$ fit into the extrapolated curve as well as can be expected for this rough empirical relation between m.p. and f.c. of intermolecular vibrations.

It should be stated that this parallelism may not apply to molecules of low symmetry because their force field within the crystal is far from being uniform. In fact, while the symmetrical neopentane (m.p. 256°K.) compares satisfactorily in Fig. 6 with the simple hydrogen compounds and with the cyclic benzene and glucose, *n*-pentane ($\theta = 134°$, m.p. 143.5°K.) and isopentane ($\theta = 122.5°$, m.p. 113.4°K.) do not.

(6) Structure and Force Field of the B_4O_6 Molecule.—The presence of B_4O_6 molecules is very probable[12] in solutions in concentrated sulfuric acid; assuming their occurrence in crystalline and vitreous boron oxide the behavior of these substances discussed in Sections 2–5 can be well understood.

As to the geometry of a B_4O_6 molecule, one can expect it to be in some respects analogous to, in others different from the known structure of M_4O_6 where M is P, As or Sb. In these three molecules the M's occupy the corners of a tetrahedron and the six O's are near the middle of its edges. According to the quantum configurations indicated in Section 1, the three O^{2-} nearest to each $P^{3+} = (P^{5+})3^2$ or $As^{3+} = (As^{5+})4^2$ will repel the most easily polarizable outermost two-electron shell with the quantum numbers 3 or 4, respectively. Hence, *e.g.*, in P_4O_6, the quantum configuration of the surroundings of each P can be formulated as $(e^-)_2P^{5+}(O^{2-})_3$ in analogy[41,7b] to the configuration $(O^{2-})'P^{5+}(O^{2-})_3$ which in P_4O_{10} has the shape of an irregular tetrahedron.

In a vapor molecule with the electronic configuration $(B^{3+})_4(O^{2-})_6$, the cores B^{3+} can be considered to be spherically symmetrical. Thus in a geometrical structure similar to that of the other M_4O_6 molecules, the electronic configuration around each B is $(O^{2-})B^{3+}(O^{2-})_2$ and the angle OBO can be expected to approach 120°. This is in agreement with the X-ray study by Warren, Krutter and Morningstar[4] on vitreous boron oxide, the main result of which was the evidence for triangular coördination within BO_3 groups.[42] However, it is felt that a new diffraction study is needed in order to test directly the structure of crystalline boron oxide.

In the free B_4O_6 molecule each B^{3+} has only 3 adjacent O^{2-}, while higher coördination numbers are known for Be^{2+} (4) and have been reported[37a] for B^{3+} (up to 3.9) in alkali borate glasses. Therefore, a direct interaction between a B^{3+} of one molecule and an O^{2-} of an adjacent molecule is possible in $[(B^{3+})_4(O^{2-})_6]_n$ while in solid $[((e^-)_2P^{5+})_4(O^{2-})_6]_n$ each P^{5+} is surrounded by four negative groups within a single molecule. This difference in the force field of the molecule may cause the higher m.p. (see Section 2) and be one of the factors accounting for the much smaller volatility of boron oxide as compared with P_4O_6 or P_4O_{10}. Depending on whether the vapor molecule has the composition B_2O_3 or B_4O_6 the vapor pressure of the liquid is given[43] as 7.7×10^{-4} mm. or 4.15×10^{-4} mm. at 1058°. As to the other factor, one can presume that at temperatures at which a condensed phase held together by "weak" forces between B_4O_6 molecules could be expected to have an appreciable vapor pressure, it is already partly transformed (see Section 3) into the "strong" structure. In the case of the two crystalline modifications of phosphorus pentoxide, the one consisting of P_4O_{10} molecules[44a] has the vapor pressure 222.5 mm.[45] at 401° while for the coördinative modification,[44b] stable above 500°, the vapor pressure extrapolated to 401° is only 2.3 mm.

Another spectacular example is elementary gallium. Its very low m.p. (30°) must be related to its crystal structure, in which the presence of Ga_2 molecules is shown by the relatively small internuclear distance between two nearest atoms.[46] Nevertheless the vapor pressure of liquid gallium is[47] only 6×10^{-4} mm. at 940°.

These analogies in the behavior of boron oxide, phosphorus pentoxide and gallium can be understood when the weak structures stable at lower temperatures consist of units of molecular dimensions and are transformed at higher temperatures into stronger structures approaching more nearly the ideal coördinative type. However, the existence of some other structures which would behave in many respects as anticipated for a crystal or glass consisting of B_4O_6 molecules is not considered to be unequivocally excluded.

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ANN ARBOR, MICHIGAN
TOLEDO, OHIO

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(41) K. Fajans, *J. Chem. Phys.*, **10**, 759 (1942).

(42) Professor B. E. Warren, to whom we communicated the above conclusions expressed the opinion that his X-ray results cannot distinguish between a triangular random network and the B_4O_6 molecules. He also kindly informed us that "the samples of vitreous B_2O_3 used in our X-ray work were fine rods about 0.5–1.0 mm. diameter drawn out directly from the melt. There was no annealing and they represent a moderate quench from the melt." According to the conclusions of the present paper the material obtained in this way can be expected to have partly the high temperature structure, partly the low temperature (molecular) structure.

(43) R. Speiser, S. Naiditch and H. L. Johnston, THIS JOURNAL **72**, 2578 (1950).

(44) (a) H. C. J. de Decker and C. H. MacGillavry, *Rec. trav. chim.*, **60**, 153 (1941); (b) de Decker, *ibid.*, **60**, 413 (1941).

(45) A. Smits and H. W. Deinum, *Proc. Acad. Sci. Amsterdam*, **33**, 514, 619 (1930).

(46) A. J. Bradley, *Z. Kristall.*, **A91**, 302 (1935).

(47) P. Harteck, *Z. physik. Chem.*, **134**, 8 (1928).