841. *The Molar Volume of Co-ordinated Boron Trifluoride.*

By N. N. Greenwood and R. L. Martin.

An examination of the densities of 26 molten complexes leads to an apparent molar volume for co-ordinated boron trifluoride which is appreciably smaller than the molar volume of either the free liquid or solid boron trifluoride. Complex formation also appears to reduce the effective molar volume of the donor molecule. An empirical rule is given for estimating the densities of liquid co-ordination compounds when experimental values are not available. Less regularity is observed in the data on solid co-ordination compounds.

The relationship between molar volume and molecular composition is well known and there is now an extensive literature on the subject (see, *e.g.*, Mellor, " A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. I, Longmans Green and Co., London, 1922; Hückel, " Structural Chemistry of Inorganic Compounds," Elsevier Publ. Co. Inc., 1950; Partington " An Advanced Treatise on Physical Chemistry," Vol. II, Longmans Green and Co., London, 1951). In seeking to develop such relations, many authors have stressed the importance of structural as well as constitutive influences, and appropriate volume increments have been assigned to many structural groups or configurations. In co-ordination chemistry most attention has been concentrated on the apparent molar volume of water or ammonia in solid salt hydrates or ammoniates and in aquo- and ammino-complexes. These results, however, are frequently difficult to interpret because of the influence of crystal structure (see Parry, *Chem. Reviews*, 1950, **46**, 507).

Many boron trifluoride co-ordination compounds can be obtained in the liquid state, where the effects of crystal structure do not intervene. The compounds therefore afford a convenient means of studying the effect of donor–acceptor bonding on molar volume (see Laubengayer and Finlay, *J. Amer. Chem. Soc.*, 1943, **65**, 884). By subtracting the molar volume of the donor from that of the complex, one obtains the apparent molar volume of co-ordinated boron trifluoride :

$$\Delta V_M = V_M(\text{complex}) - V_M(\text{donor}) = V_M(\text{co-ordinated } BF_3)$$

The results are summarized in Table 1, from which it is evident that an approximately constant value of 27·8 cm.^{3} is obtained from all complexes on which reliable information is available. This value is appreciably smaller than the molar volume of liquid boron trifluoride, which is $\sim$39 cm.^{3} at the m. p. and $\sim$43 cm.^{3} at the b. p.; the molar volume of solid boron trifluoride is $\sim$35 cm.^{3} (see Booth and D. R. Martin, " Boron Trifluoride and its Derivatives," John Wiley and Sons, Inc., N.Y., 1949, pp. 18—19, for references). It would seem that donor–acceptor bond formation reduces the volume requirements of boron trifluoride by as much as 10 cm.^{3}, the contraction arising mainly from the decrease in the distance of closest approach of unlike molecules as a result of the new chemical bond.

The molar volumes of the complexes were calculated for 20°, as most of the available density data refer to this temperature. The b. p. is not a suitable comparison temperature as all the complexes are thermolabile.

A further regularity may be noted in Table 1, *viz.*, that the apparent molar volume of boron trifluoride in a 1 : 1 complex is always greater than that in the corresponding 1 : 2 complex. Four examples of this are the complexes with water, methanol, ethanol, and acetic acid. It has been suggested (Greenwood and R. L. Martin, *Quart. Reviews*, in the press) that the second donor molecule in the di-complex forms a bond with the ionizable proton of the 1 : 1 complex to give an oxonium ion :

TABLE 1. *Molar volumes at* 20°.

	Complex[a]		Donor moiety[b]		
Compound	*d*	V_M	*d*	V_M	ΔV_M
BF_3,H_2O	1·7850	48·1	0·9982	18·1	30·0
$BF_3,2H_2O$	1·6320	63·6	0·9982	36·1	27·5
BF_3,H_3PO_4	1·932	85·8	1·834[g]	53·4[g]	32·4
BF_3,Me_2O	1·241	91·8	0·6606[h]	60·7[h]	31·1
BF_3,MeOEt[c]	1·176	108·8	0·6986[i]	86·0[i]	22·8
BF_3,Et_2O	1·128	125·8	0·7135	103·9	21·9
BF_3,MeOH	1·4081	70·9	0·7914	40·5	30·4
BF_3,2MeOH	1·2120	108·8	0·7914	81·0	27·8
BF_3,EtOH	1·353	84·2	0·7893	58·4	25·8
BF_3,2EtOH	1·1638	137·5	0·7893	116·7	20·8
BF_3,2Pr^{n}OH	1·0561	178·0	0·8035	149·6	28·4
BF_3,2Bu^{n}OH	1·0442	206·9	0·8096	183·1	23·8
$BF_3,2CH_2Cl{\cdot}CH_2{\cdot}OH$	1·4009	163·4	1·2020	134·0	29·4
$BF_3,2H{\cdot}CO_2H$	1·5145	105·6	1·2201	75·5	30·1
$BF_3,Me{\cdot}CO_2H$	1·4958[d]	85·5[d]	1·0492	57·2	28·3
$BF_3,2Me{\cdot}CO_2H$	1·3421	140·0	1·0492	114·5	25·5
$BF_3,2Et{\cdot}CO_2H$	1·2283	175·8	0·9933	149·2	26·6
$BF_3,2Pr^n{\cdot}CO_2H$	1·1506	212·1	0·9578	184·0	28·1
$BF_3,H{\cdot}CO_2Me$	1·424[d]	89·8[d]	0·9742	61·6	28·2
$BF_3,H{\cdot}CO_2Et$	1·322	107·4	0·9226	80·3	27·1
$BF_3,Me{\cdot}CO_2Me$	1·301[e]	109·1[e]	0·9335	79·4	29·7
$BF_3,Me{\cdot}CO_2Et$	1·251[d]	124·6[d]	0·9006	97·8	26·8
$BF_3,Me{\cdot}CO_2Pr^n$	1·1999	141·6	0·8866	115·0	26·6
$BF_3,Me{\cdot}CO_2Bu^n$	1·1554	159·2	0·8814	131·8	27·4
$BF_3,(MeC_6H_4)_3PO_4$	1·264	345·0	1·183[j]	311·4[j]	33·6
$BF_3,Me{\cdot}CO{\cdot}NMePh$	1·269[f]	171·0[f]	1·074[k]	138·9[k]	32·1
				Mean	27·8

[a] For refs. see Greenwood and R. L. Martin (*loc. cit.*). [b] Timmermans, "Physicochemical Constants of Pure Organic Compounds," Elsevier Publ. Co. Inc., N.Y., 1950, except for data on water, phosphoric acid, and tolyl phosphate. [c] Data refer to 25°. [d] Supercooled liquid. [e] Hypothetical value for supercooled liquid; data extrapolated below 65°. [f] As for (*e*); extrapolated below 114°. [g] At 18° (International Critical Tables). [h] At 5 atm. [i] At 1·6 atm. [j] At 25° (Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., N.Y., 1950). [k] By extrapolation from the results of Turner and Merry, *J.*, 1910, **97**, 2069.

$$BF_3 + H_2O \longrightarrow BF_3,H_2O \rightleftharpoons H^+BF_3{\cdot}OH^- \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$H^+BF_3{\cdot}OH^- + H_2O \longrightarrow H_3O^+BF_3{\cdot}OH^- \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This second process, like the first, may also be expected to occur with a reduction in volume. The apparent molar volume of the second donor molecule may be estimated by subtracting the molar volume of the mono-complex from that of the di-complex. The results are given in Table 2; the final column represents the decrease in volume occurring on oxonium-ion formation. It is clear that the change in effective volume of the donor is considerably less than the change calculated for boron trifluoride as acceptor (~10 cm.^{3}).

TABLE 2. *Apparent molar volume of the second donor molecule.*

Donor	$V_M(1:2) - V_M(1:1)$	V_M (donor)	Δ, cm.^{3}	Donor	$V_M(1:2) - V_M(1:1)$	V_M (donor)	Δ, cm.^{3}
H_2O	15·5	18·1	−2·6	EtOH	53·3	58·4	−3·1
MeOH	37·9	40·5	−2·6	$Me{\cdot}CO_2H$	54·5	57·2	−2·7

If this interpretation is correct, then the apparent molar volume of boron trifluoride would more correctly be estimated from 1 : 1 complexes alone, the value derived from 1 : 2 complexes being consistently lower because of the formation of a second donor–acceptor bond. The data in Table 1 show a fairly large scatter, but it may be significant that the mean apparent molar volume of boron trifluoride in the sixteen 1 : 1 complexes listed is 28·4 cm.^{3} as compared with 26·8 cm.^{3} in the ten 1 : 2 complexes.

The approximate constancy of the molar volume change which occurs during complex formation may be used to estimate the density of a co-ordination compound of boron trifluoride when experimental values are not available :

$$d_4^{20}(\text{complex}) = M(\text{complex})/\{V_M(\text{donor}) + 28\}$$

where M(complex) refers to the molecular weight. The relation may also be used to check density values suspected of error, and it suggests that some of the values in Table 1 may require revision. In the same way the density of boron trifluoride–phenol (not listed in Table 1) has been given as 1·244 (Topchiev and Paushkin, *Chem. Progress, U.S.S.R.*, 1947, **16**, 644; Paushkin, *J. Appl. Chem., U.S.S.R.*, 1948, **21**, 1199); this leads to a molar volume of 130·1 cm.^{3}, and an apparent molar volume for boron trifluoride of 42·3 cm.^{3}. In view of the absence of experimental data in the Russian reviews cited, the density may well refer to boron trifluoride–diphenol, as this leads to an apparent molar volume of 30·2 cm.^{3}, which is much closer to the values given in Table 1.

Less regularity is observed among the molar volumes of solid boron trifluoride co-ordination compounds. Here, the inaccuracy of the density data and the influence of crystal structure vitiate a detailed analysis, and for this reason the results will not be tabulated. The mean value of the apparent molar volume of boron trifluoride in ten of its solid complexes for which sufficient data are available is 25·4 cm.^{3}. In view of the large deviations from the mean for some complexes, it is not certain that this value is significantly smaller than that obtained from liquid complexes.

This paper is published by permission of the Director, Atomic Energy Research Establishment, Harwell, Didcot, Berkshire.

DEPARTMENT OF CHEMISTRY, THE UNIVERSITY, NOTTINGHAM.
UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[*Received, August 7th*, 1953.]